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Ana Carolina Mendez Ecoscia, Nida Sheibat-Othman, Timothy Frederick Llewellyn Mckenna. Reaction engineering of the emulsion homopolymerization of vinylidene fluoride: Progress and challenges. Canadian Journal of Chemical Engineering, 2018, 97 (1), pp.207-216. 10.1002/cjce.23308. hal-02361626

**HAL Id: hal-02361626**

**<https://hal.science/hal-02361626>**

Submitted on 12 Nov 2020

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# **Reaction Engineering of Vinylidene Fluoride Homopolymerization: Progress and Challenges**

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## **ABSTRACT**

The emulsion polymerization of vinylidene fluoride (VDF) is used to produce a range of commercially important products. Despite this, the current review article will show that very little is known about the kinetics of polymerization, particle nucleation, and role of chain transfer reactions. This is at least in part due to the extreme conditions needed for the polymerization, which can significantly limit the number of academic laboratories able to do such reactions.

## **INTRODUCTION**

The market share for fluoropolymers in industrial applications is growing in view of their versatility and unique properties. Such polymers exhibit low cohesive energy thanks to the low intermolecular and intramolecular interaction. Additionally, they show high thermal stability, chemical and oxidative resistance, and other valuable electrical properties. In particular, poly-vinylidene fluoride (PVDF) is widely employed in industries that demand high performance thermoplastic materials, including architectural coatings, in the chemical industry for fittings, valves and pumps, and in the wire and cable industry as insulation material.<sup>[1,2,3]</sup> This increased demand also means that it would be useful for commercial producers to be able to better understand, and to be able to model processes with confidence if they are to successfully develop new products, and trouble shoot or scale-up existing products. While this can often be a

challenge for many processes, it is particularly difficult for vinylidene fluoride (VDF) production for reasons that we will discuss below.

PVDF is synthesized commercially via free-radical suspension or emulsion polymerization.<sup>[4]</sup> The properties of the polymers produced in emulsion and suspension processes can be different, so the choice of the mode of polymerization and the “ingredients” depend on the area of application. Some of the typical characteristics of emulsion and suspension products are compared in Table 1. As can be seen here, the products from the two are quite different (giving yet more credence to the adage: Polymers are product by process). In this paper, we will focus on VDF emulsion polymerization processes, and summarize what is available in the open and patent literature concerning how PVDF is made, and what is understood about the kinetics, particle formation and related issues.

*Table 1. Comparison of the characteristics of PVDF polymer produced by emulsion and suspension*

<b>Characteristics</b>	<b>Emulsion polymerization</b>	<b>Suspension polymerization</b>
Molecular Weight Distribution <sup>[4]</sup>	Relatively broad to moderately narrow.	Relatively narrow.
Crystallinity <sup>[4]</sup>	Lower (head-to-head defects).	Higher (head-to tail defects).
Melting point <sup>[4]</sup>	Lower.	Higher.
Rheology behaviour <sup>[4]</sup>	Less Newtonian – Viscoelastic.	More Newtonian.
Particle size <sup>[4]</sup>	≤ 0,4 μm	> 50 μm
Stress resistance at high temperature <sup>[4]</sup>	More resistant	Less resistant
Solubility <sup>[4]</sup>	Soluble after heating: DMF, NMP, DMSO	Soluble in polar solvents: DMF, NMP, DMSO.
Kinetics <sup>[5]</sup>	High polymerization rate and high molecular weight could be simultaneously obtained.	Rate of polymerization inversely proportional to molecular weight.

Emulsion polymerization is a common industrial process to produce latex for products such as paints, coats and other film forming materials, as well as for making polymer particles that are sold in powder form. The heterogeneous nature of the conventional emulsion polymerization process can render it quite complex, since it is necessary to master stochastically-controlled kinetics, the stability of nano-scale colloids, as well as heat and mass transfer phenomena in multiple phases. <sup>[6]</sup> These quantities depend on

several interacting parameters (e.g. temperatures, concentrations, shear rates, etc.) that can vary not just from process to process, but also within a given polymerization reactor. The three-phase nature of the reaction medium (liquid, solid supercritical), and the fact that the monomer is significantly less dense than the other 2 phases means that mass transfer, mixing and monomer partitioning can have a significant impact on the particle formation and growth processes. It is not unreasonable to suppose that particle nucleation can take place as in other emulsion polymerization processes: oligoradicals generated in the aqueous phase by water-soluble initiators can either provoke micellar nucleation if the surfactant concentration permits, or will precipitate out of solution and coagulate with other chains to make particles via homogeneous/coagulative nucleation. However, it is possible that the quantity of monomer available in the aqueous phase, and therefore in the polymer particles can depend strongly on the pressure and the conditions of agitation in the reactor.

Despite a growing commercial interest in PVDF, very few experimental (or modelling) studies on this topic are available in the open literature to help understand the important process-related aspects. There are probably practical reasons for this, not the least of which is that the low reactivity of VDF in emulsion polymerization requires high pressures (30-120 bars depending on the process) to achieve commercially viable production rates. In addition, and as mentioned above, the three-phase nature of the reaction means that one needs to pay attention to mass transfer limitations of the reaction rate.

In this article, we will present a succinct review of what is known in the field of VDF emulsion homopolymerization, and present the state of the art in terms of progress that has been made in terms of the reaction engineering challenges of the emulsion homopolymerization of VDF. More information about the recent developments and applications of the VDF based polymers can be found elsewhere. <sup>[7,8]</sup> [57], [58]. This information will be used to design a pilot scale reactor for this purpose. Before continuing, it is assumed that the reader is familiar with the basic theory and terminology of common to discussions of conventional emulsion polymerization.

## **VDF POLYMERIZATION: LITERATURE REVIEW**

## Literature Review: Patents

US 2,435,537<sup>[9]</sup> is one of the first patents to disclose vinylidene fluoride as a polymerizable compound. Varieties of initiators were proposed to polymerize VDF, including combinations of inorganic peroxides or peroxy compounds with reducing agents, as well as organic peroxides. Relatively low yields were obtained, even at pressures of several hundred bars and temperatures up to 250 °C. The reaction conditions were also more reminiscent of a high-pressure ethylene polymerization process than conventional emulsion polymerizations. Polymers obtained from organic peroxide initiators apparently showed a better thermal stability than those obtained with persulphate initiators. In addition, a later patent reveals that although redox systems such as a persulfate initiator, sodium hydrogen sulfite and ferrous sulphate can be used to rapidly polymerize VDF under reasonable conditions (pressures less than 200 bars, and temperatures between 60-150°C), the iron residues pose significant problems in terms of coloration (a particularly important end user requirement for most PVDF applications), so they cannot be used commercially. <sup>[10]</sup>

Later inventions focused on yield enhancements. For example in US 3,012,021<sup>[11]</sup> and 3,193,539-A<sup>[12]</sup> di-tertiary-butyl peroxide (DTBP), was found to promote high productivity at temperatures of 120 °C to 130 °C, under reaction pressures from 20 bar to 70 bar. In 3,012,021 the inventors used DTBP in conjunction with alkene epoxides (e.g. ethylene oxide or propylene oxide), but while the continuous phase of the reactor was water, there was no mention made of surfactant so the question arises as to whether this can be considered as an emulsion polymerization. In 3,193,539<sup>[12]</sup> the authors found that the use of fluorochlorinated, or perfluorocarboxylic acids significantly improved the reproducibility of their experiments without posing problems with respect to yield. As such this is certainly one of the first patents to describe an emulsion polymerisation process for VDF. The authors also observed that even though di-tertiary-butyl peroxide is mainly water soluble, and that most of the polymer will be formed there, VDF could also be polymerized in the vapour phase.

In US 3,245,971 <sup>[13]</sup> the authors proposed other kinds of organic peroxides initiators (viz. disuccinic acid peroxide), that, in the presence of iron and a water-soluble ionizable fluorinated surfactant, lead to the production of a thermally stable polymer.

Unfortunately, the required reaction time was more than 20 hours. In US 3,714,137<sup>[14]</sup>, the inventors point out that the disadvantage of this type of initiator is that it is not particularly soluble in the water phase, so leads to the formation of agglomerates of PVDF. In addition, the authors of US 3,475,396<sup>[15]</sup> pointed out that temperatures of well over 100°C are necessary with these initiators, and that the product of initiator decomposition under such conditions could provoke significant problems of corrosion. They disclosed an aqueous polymerization process was disclosed relying on diisopropyl peroxydicarbonate as the free radical initiator. They claimed that the interaction between this initiator, fluorinated surfactants (e.g. perfluorinated surfactant, especially sodium perfluorooctanoate) and the chain transfer agent (peroxy alkenes) led to faster reaction times (0.5 to 6 hours) and good yields at moderate pressures. The inventors found that better yields and improved polymer properties (notably thermal stability) were obtained with perfluorinated surfactants, especially sodium perfluorooctanoate. Amounts from 3 to 5 percent by weight of VDF were preferable; this percentage can be reduced to 0.5 % to 3 %, if 0.005 % to 1 % of chain transfer agents (CTA) are included in the recipe (to note that all percentages are referred to the weight of monomer). This may suggest that the chain transfer agent serves as a co-stabilizer to a certain extent since when the surfactant was added alone, the polymer product was in the form of latex or dispersion of size from 0.05 to 0.5µm. On the other hand, when CTA was incorporated they recovered a narrow dispersion.

Other initiators, e.g. peroxidisulphates, used in surfactant-free systems in combination with a CTA such as ethyl acetate have also proposed for use in semi-batch systems.<sup>[16]</sup>

Generally speaking, by this time researchers had figured out that the use of fluorinated (or perfluorinated) surfactants was important for PVDF, as other traditional surfactants were far more temperature sensitive and had a tendency to decompose at the temperatures required to process PVDF, and thus pose colour-related (and other) problems. For example, based on the tests carried out by the inventors of US 4,025,709<sup>[17]</sup>, the polymer obtained with salts of perhalogenated carboxylic acids formed a colored product with cavities upon heating. As is the case in all commercial emulsion polymerization processes, producers strive to use the lowest amount of surfactant possible, typically less than 0.1% by weight of water in PVDF formulations.<sup>[18]</sup> In addition to discussing different initiator systems, US 3,245,971<sup>[13]</sup> also teaches the use

of a water soluble chain transfer agent (CTA) for this purpose. As mentioned above, some patents discuss surfactant-free emulsion polymerisations with 1-2 weight percent (with respect to monomer) ethyl acetate as a CTA.<sup>[16]</sup> Obviously the patents do not discuss the reason for the need for less surfactant, which could possibly be related to a reduction of the interfacial energy if the water phase contains a certain level of organic compounds, or to the fact that higher levels of CTA in the water phase promote the formation of water soluble oligomers which can help stabilise the emulsion particles.

Furthermore, US 4,025,709<sup>[17]</sup> disclosed a polymerization process for VDF in presence of potassium persulphate as initiator (0.005 %wt - 0.5 %wt based on weight of monomer), sodium acetate as buffer, and as an emulsifying agent a water-soluble salt of formula  $R_f-C_2H_4SO_3-M$ . Here  $R_f$  is referred to the perfluorinated radical and  $M$  is an alkali metal or ammonium. Additionally, to improve the latex quality and to avoid reactor fouling a mineral oil or paraffin can be added. Here, the preferable operating pressure is 100 bar and the temperature was adjusted between 80 °C and 85 °C. The resulting polymer had high molecular weight, limiting its molding capabilities, so the inventors added a chain transfer agent (sodium acetate) to the formulation.

A chain transfer agent should have a labile hydrogen or halogen atom, for instance ketones and esters with 3 to 8 carbons atoms were proposed as efficient agents. In EP0387938-B1<sup>[19]</sup> the inventors disclosed the use of alkyl acetates as chain transfer agent, with ethyl acetate being preferred. The amount of CTA varies between 0.5 %wt to 3 %wt based on monomer weight. <sup>[17,19]</sup> Later, in US 4,569,978<sup>[20]</sup> proposed trichlorofluoromethane (CFC) as a CTA. In a similar vein, the authors of 5,473,030<sup>[21]</sup> proposed using 1,1,1-trifluoro-2,2-dichloroethane. These CTA could solve the discoloration problem that can take place at temperatures over 280 °C, due to the presence of the polar end group on the molecular chain. But, since they are ozone-depleting materials, their use was later banned. More recent inventions propose the use of C3-C5 hydrocarbons <sup>[22,23]</sup> the hydrocarbons are comparable in terms of efficiency with the CFC in that they are able to provide highly temperature resistance to the polymer, but can eventually slow down the polymerization rate. In particular, some patents recommended feeding the chain transfer agent continuously in discrete amounts during the polymerization, as feeding the entire amount of chain transfer agent at the beginning of the polymerization inhibited the polymerization process (and was thought

to have a negative influence on some mechanical properties of the polymer).[24] A variety of chain transfer agents have also been cited in the patent literature, including acetone[25], ethane,[22] pentane[26], or even trichlorofluoromethane[20] – which apparently improves high temperature stability and reduces discoloration (However, with the evolution of environmental regulations and awareness of problems related to ozone depletion, most halogenated CTA are to be avoided).[27] CTAs such as isopropanol or ethyl acetate[16] seem to reduce yellowing, and appear to be widely cited in many PVDF-related patents.

It also appears to be a wide spread practice to add a liquid (at the reaction temperature) mineral oil or a paraffin to the polymerization order to inhibit the coagulation of the polymer and hinder the adhesion to the reactor walls.[13,20,24,28,29]

Focusing on the reactors, it is difficult to find descriptions of reactors for the polymerisation of VDF in the patent literature. Two patents[25,28] refer to the use of a “horizontal stainless steel autoclave equipped with a paddle agitator”, but say very little else. A US Patent application[30] also cites the use of “preferably horizontal” reactor. In addition, the reactor described in this patent is a 7.6L pilot plant, rather than a production unit. In US4569978, the authors state that they too use a “horizontal polymerizer” (same company so we imagine the agitator is similar) for the EP of VDF, stating that “The use of a horizontal polymerizer is preferred as it has less tendency to cause agitation induced coagulation during polymerization.” (presumably because of the very low levels of surfactant that are preferred in these reactions.). On the other hand, in US 5473030, Ausimont refers to the use of a vertical polymerizer (again a lab scale unit, this time with a volume of 10L), and to a horizontal reactor (7.5L).[21] Solvay Solexis also refers to a horizontal unit, but gives essentially no detail about the reactor.[31]

To summarize rapidly, the patent literature is of very little help in understanding how the emulsion polymerization of VDF is carried out industrially. One can get a perception of the range of temperatures (60-150°C) and pressures (30-200 bars) that are typically used. We have purposely not discussed the range of comonomers used in different formulations, as these are clearly used to modify final properties, but have considered other parameters. Essentially all the patents considered cite the use of a paraffin or wax to compliment the surfactant used in the process to improve latex stability (obviously,

no explanation as to why is available). Generally, these appear to be simple long chain, saturated hydrocarbons that are commercially available from several suppliers. Most processes seem to rely on the use of fluorinated surfactants, apparently for reasons of compatibility and resistance to discoloration during post reactor treatments at high temperatures. Of course, these compounds can pose many environmental challenges, so are used at very low levels (this will also be a quality constraint in many cases as well). This implies that stabilization of the latex during the reaction, and during later transfer operations in a plant can be a significant challenge. On a related point, a large number of patents (too numerous to cite in their entirety, including references [20,32,33,34]) mention briefly that a wax is added along with the surfactant to help with the stabilization. It is known from other free radical systems, e.g. the suspension polymerization of vinyl chloride<sup>[35,36]</sup>, the use of (halogenated) paraffins is thought to help latex stability and reduce deposits on the reactor wall. Other patents, e.g. reference cite the use of waxes as antifouling agents in PVDF emulsion systems. <sup>[30,37]</sup> Yet another patent cites the use of paraffin oils as emulsifiers in the emulsion polymerization of vinyl chloride <sup>[38]</sup>. And yet other patents suggest that this helps to disperse the gaseous/supercritical component. <sup>[27]</sup> As we will see below, there are no studies on the use of waxes or paraffins in the open literature, and the different patents cited above do not allow us to draw any conclusions on the eventual importance of this type of (omnipresent) compound.

Finally, a range of initiators are cited, without one system appearing to be favored over others. The main concerns appear to be (logically) the control of the molecular weight distribution and problems related to discoloration. Finally, in terms of the reactor systems, very little information is available. Those patents that give any information, simply state that the reactor can be a vertical or horizontal autoclave. No information is given (or patented) in terms of the agitators that are used, the presence or absence of baffles, nor even of the aspect ratios of the reactors themselves.

### **Literature Review: Open literature**

In the paragraphs that follow, we will summarize the advances in understanding the kinetics of VDF that have been reported in the open literature (c.f. Table 2). Most of the

open literature in this field was published well after the defining patents mentioned above, however very little academic work has been done on understanding the emulsion polymerization of this monomer. In fact, we will see that a great part of the investigation concerns the polymerization of VDF in supercritical CO<sub>2</sub> (scCO<sub>2</sub>) in recent years as this approach has gained popularity for a number of reaction (and separation) processes. We will include a brief discussion of the scCO<sub>2</sub> processes to complement the meager information on standard emulsion homopolymerization processes. Even, if there are obvious differences between the polymerization of VDF in scCO<sub>2</sub> and VDF in water, these studies can help us to understand the free radical mechanism and parameters that intervene in the VDF polymerization and some conclusion might be extrapolated to our reaction system.

Table 2. Characteristics of the kinetic models for vinylidene fluoride polymerization.

Ref	System	Condition	Remarks
Charpentier et al. 2000 <sup>[39]</sup>	Continuous mode VDF in scCO <sub>2</sub> .	Precipitation T= 65 - 85 °C / P= 210 - 305 bar	<p><i>Modeling of polymerization rate:</i></p> <ul style="list-style-type: none"> <li>- Homogeneous chain growth model considering termination by combination and/or disproportionation, and by the inhibitor.</li> <li>- <math>R_p \propto [I]^{0.5}[M]^1</math>.</li> <li>- Reactor behaves as an ideal CSTR.</li> <li>- Good agreement with the experimental rate.</li> </ul>
Saraf et al. 2002 <sup>[40]</sup>	Continuous mode VDF in scCO <sub>2</sub> .	Precipitation T= 65 - 85 °C / P= 210 - 305 bar	<p><i>Impact of reaction condition on MWD:</i></p> <ul style="list-style-type: none"> <li>- MWD broadens and bimodality appears at high monomer concentration <math>[M]_{in} = 0.8 - 1.5</math> M.</li> <li>- MWD independent of the stirring rate (N= 1300 -2700 rpm).</li> <li>- MWD independent of temperature (T= 75 °C; T= 85 °C).</li> <li>- MWD independent of residence time (t= 10 - 50 min).</li> <li>- R<sub>p</sub> dependent of mixing at high monomer concentration.</li> </ul> <p><i>Estimation of the MWD:</i></p> <ul style="list-style-type: none"> <li>- Recursive algorithm based on homogeneous model accounting for chain transfer to polymer and termination by combination.</li> <li>- Model is not robust enough to predict bimodality.</li> </ul>
Ahmed et al. 2010 <sup>[41]</sup>	Continuous mode VDF in scCO <sub>2</sub> .	Precipitation T= 65 - 85 °C / P= 210 - 305 bar	<p><i>Modeling of the entire MWD:</i></p> <ul style="list-style-type: none"> <li>- Homogeneous model accounting for chain transfer to polymer, chain-length dependency of the termination rate, and the possibility that termination reaction is either kinetically or diffusion controlled (dependent on macro-radical chain length).</li> <li>- Good agreement with experimental results, overestimation of PI values.</li> </ul>
Mueller et al. 2005 <sup>[42]</sup>	Batch mode VDF in scCO <sub>2</sub> .	Precipitation T= 50 °C / P= 204 - 332 bar	<p><i>Modeling of the entire MWD and time evolution of conversion:</i></p> <ul style="list-style-type: none"> <li>- Heterogeneous model (two reaction loci) accounting for termination by combination and/or disproportionation, chain transfer to polymer, mass transport of radicals and interphase partitioning.</li> <li>- Good agreement with the experimental results, discrepancy with the MWD at high density.</li> <li>- Model reliability is conditioned to the total interphase area.</li> </ul>

Costa et al. 2011 <sup>[43]</sup>	Continuous and batch from VDF and VDF-HFP in scCO <sub>2</sub> .	Precipitation: CSTR (T=75 °C / P=277 bar; T=40°C, 400 bar). Batch (T=50 °C, P=204 bar)	<p><i>Modeling reaction rates:</i></p> <ul style="list-style-type: none"> <li>- Identification of the number of reaction loci in a heterogeneous polymerization, using specific rate ratio (<math>\theta</math>).</li> <li>- VDF polymerization in scCO<sub>2</sub> occurs in the two-phases.</li> <li>- Homogeneous model can be used to describe diluted solution and/or when the <math>\theta</math> is small.</li> <li>- Homogeneous model provides good prediction of overall Rp.</li> </ul>
Apostolo et al. 1999 <sup>[44]</sup>	Semi-continuous VDF-HFP in water.	Emulsion T=85 °C / P= 11 bar, P= 19 bar.	<p><i>Modeling of MWD and chain end group distribution:</i></p> <ul style="list-style-type: none"> <li>- Pseudo-kinetic polymerization accounting termination by disproportionation, chain transfer to monomer and polymer, and chain transfer to a CTA.</li> <li>- To compute the chain end group backbiting reaction has to be included</li> <li>- CTA reduced the number of branches, molecular weight and PI.</li> <li>- Chain transfer to CTA is comparable with the initiator decomposition of chain initiating capacity.</li> <li>- MWD is slightly affected by the monomer concentration</li> <li>- Mn increased with the pressure - High pressure favors chain propagation over branching reactions.</li> <li>- Thermodynamic equilibrium using Henry's law.</li> <li>- Satisfactory model predictions.</li> </ul>
Pladis et al. 2014 <sup>[45]</sup>	Semi-continuous VDF in water	Emulsion T= 83 °C / P= 85 bar.	<p><i>Modeling of PSD and MWD:</i></p> <ul style="list-style-type: none"> <li>- Kinetic polymerization model accounting for initiator decomposition, initiator reaction, propagation, chain transfer to monomer and polymer, chain transfer to a CTA, backbiting reaction, termination by combination.</li> <li>- Development of PBE model</li> <li>- Modeling of the homogenous nucleation.</li> <li>- Thermodynamic equilibrium using the Sancez-Lacombe equation of state (SL).</li> <li>- Reliability of the model questioned by the number of adjusted parameters.</li> <li>- PSD model predictions satisfactory at high surfactant concentration.</li> <li>- MWD well predicted.</li> </ul>

The group of DeSimone have performed a range of studies on homogeneous and heterogeneous polymerization of fluorinated monomers in supercritical CO<sub>2</sub><sup>[46]</sup>. One part of their studies was focused on the development and understanding of the continuous homo-polymerization of VDF in scCO<sub>2</sub> using simplified models. In an initial paper<sup>[39]</sup>, they modeled the kinetic rate as a homogeneous polymerization, assuming:

- (i) Initiation decomposition, monomer consumption and dead polymer formation in the solid polymer negligible compared to the reactions that take places in the fluid phase.
- (ii) Steady-state approximation.
- (iii) Rate constants independent of the chain length.

From those assumptions, they derived that the rate of chain initiation is equal to the rate of chain termination, which are a very standard assumption in free radical polymerization. After algebraic treatment, they found a correlation between the polymerization rate, the monomer concentration and the initiator at the outlet stream and some parameters related with the rate constant. Those parameters were obtained from data fitting of their experimental results. After including the presence of an inhibitor, the nature of which was not clearly defined, but attributed to chain transfer to monomer (leading to the formation of an unreactive radical for some reason), they managed to find a good agreement between the experimental polymerization rate and the rate model, for a residence time between 10 - 50 min, for temperatures ranging from 65 - 85 °C, and for pressures of 210 - 305 bar. They showed that the rate of polymerization was of first order with respect to the monomer and half order with respect to the initiator (diethyl peroxydicarbonate - DEPDC), which is what one expects from a free radical polymerization in a single phase.

In subsequent papers<sup>[40,47]</sup> the same group analyzed the effect of the reaction conditions on the average molecular weights. Specifically, they investigated the impact of the inlet monomer concentration, the residence time, the agitation rate and the temperature. Their experimental data shows that at low monomer concentration the MWD is monomodal with a polydispersity index (PI) close to 1.5. They reported that with the increasing of monomer concentration ( $[M]_{in} = 0.8 - 1.5 \text{ M}$ ) the MWD broadens and bimodality appears. The residence time and the agitation rate seem to do not affect the

MWD, but agitation affects the polymerization rate at high monomer concentration<sup>[39,40]</sup>. Monomodality of the MWD is favored by increasing the temperature from 75 °C to 85 °C.

In order to explain the bimodality of the MWD, they first used the homogeneous kinetic scheme already presented in [39] adding chain transfer to polymer (CTP). The presence of this reaction was also proposed by Maccone et al.<sup>[48]</sup> to explain the presence of long chain branching in a ter-polymer of 72%mol of VDF, 18%mol hexafluoropropylene (HFP), and 10%mol tetrafluoroethylene (TFE). This hypothesis was confirmed by Saraf et al.<sup>[40]</sup> by NMR analysis indicating the presence of CF<sub>2</sub>-CH<sub>3</sub> end groups.

A kinetic model was written as a function of the active radical and dead polymer species, and the molecular weight was expressed in terms of the first three moments. The initiator decomposition rate constants (i.e. initiator efficiency " $f$ ", and decomposition rate coefficient " $k_d$ ") used were reported in Charpentier et al.<sup>[49]</sup>, while the other rate constant was obtained by fitting rate data or PI for a single experiment. The model under-predicted the experimentally observed number average molecular weight ( $M_n$ ), using the efficiency value  $f$  from [49]. The authors therefore, used  $f$  as an adjustable parameter to fit the data, which allowed them to obtain a better prediction for monomodal MWD.

The entire MWD was modeled in a later publication<sup>[41]</sup>, where they demonstrated that the MWD of PVDF obtained by continuous precipitation polymerization in scCO<sub>2</sub> can be described if the homogeneous kinetic model accounts for CTP reaction, chain-length dependency on the termination rate (as previous paper), but also diffusion-controlled possibility needs to be accounted to describe the radical termination. The radical termination by diffusion depends on the size of the macro-radical, radicals contained monomer units with a chain-length longer than a defined critical value tends to diffuse.

Specifically, they developed a model based on the classical reaction steps for a homogenous free radical polymerization, i.e. initiator decomposition, chain initiation, propagation, and termination; in which the termination step was separated by three cases, regulated by the macro-radical chain lengths. Specifically:

- Both radicals are shorter than the critical chain length, the termination is assumed to be kinetically controlled and termination rate constant is assumed to be independent of the chain-length for these steps.
- One of the radicals exceeds the critical chain length, the termination is diffusion controlled, the termination rate is chain-length dependent.
- Both radicals of chain length greater than the critical chain length, the termination rate occurs by combination of two radicals limited by diffusion.

The assumptions presented in previous model were assumed as valid, viz. CO<sub>2</sub> phase being the only locus of polymerization<sup>[50]</sup>, the quasi-steady-state approximation applied, and in the CTP reaction the hydrogen atom is taken from the dead polymer, so the rate constant will be proportional to the chain length of this dead polymer.

Their model predicts the appearance of a second peak in the MWD when the monomer concentration increases to 1.7 M, in agreement with the experimental results. However, the model underestimates the location of the peaks, and the average molecular weight. No calculations were carried out to explain the bimodality reduction with temperature; they alleged that diffusion coefficient as well as the critical chain-length increases with the increase of temperature, which favors a kinetic controlled termination and so the formation of just one family.

Regarding the PI, the trends are adequately predicted, the values are better computed compared to the previous publication<sup>[40]</sup>, but at high concentration of monomer (e.g. 2.8 M) the model tended to overestimate the value of the PI. The authors explained that the divergences may come from the assumption that there is no initiator partitioning, we remember that they considered that the initiator is only in the fluid phase. Moreover, they remarked the uncertainty of the experimental data, the M<sub>w</sub> obtained by GPC is relative to PMMA standards, plus some samples were hard to handle due to their high gel content.

The group of Morbidelli studied the polymerization of VDF in scCO<sub>2</sub> as well as the copolymerization of VDF and hexafluoropropylene (HFP) in emulsion polymerization.

Contrarily to what was done in the studies of DeSimone, the group of Morbidelli considered the polymerization of VDF took place in both the supercritical phase and in

the dispersed polymer phase. They followed the path of the radicals, noting that the radicals are generated in the supercritical phase and then diffuse in to the dispersed phase. However, some radicals do not reach the dispersed phase, terminating in the preceding phase. Mueller et al.<sup>[42]</sup> employed a sophisticated treatment that accounts for:

- (i) Two reaction loci, the CO<sub>2</sub> phase and the polymer phase.
- (ii) Low molecular weight species diffused very rapidly between the phases, so they are at the equilibrium conditions, for larger molecular weight interphase mass transport kinetics is considered.
- (iii) Partitioning of the polymer chains is related to their chain length.
- (iv) Number of particles is assumed to be constant, the nucleation time is very short and it is not simulated.
- (v) Crystalline part does not intervene in the interphase partitioning. Sanchez Lacombe is used to estimate the equilibrium of VDF/PVDF/CO<sub>2</sub>, and constant partitioning coefficient describes the initiator phase behavior.
- (vi) Kinetic scheme includes the initiation, propagation, and bimolecular termination is said to occur only by combination and CTP.

The model uses population balance equations (PBE) of the chain lengths to account for the active and terminated polymer chains, as well as mass balance for low molecular weight species involving interphase equilibrium. The resulting system is a mix of algebraic and differential equations with a very large number of parameters. The authors determined some of the parameters from independent experimental data, and others by fitting. Specifically, they adjusted the value of VDF/PVDF interaction parameters, chain transfer to polymer rate constant and the interphase surface area. A particular effect of the CTP constant value on the broadness of the MWD was remarked, in coherence with the observations of Saraf et al.<sup>[40]</sup>, but overall the other two estimated parameters play an important role in the system behavior conditioning the existence of the bimodal MWD. For instance, the ratio of the characteristic times of interphase mass transport and termination introduced in Mueller et al. <sup>[42]</sup>, is a function of the interphase surface area. This ratio determines whether the active chains terminated in the same phase where they were formed.

The ratio of the chain transfer reaction rate constant to the propagation rate constant ( $1 \cdot 10^{-6}$ ) is at least 3 orders of magnitude smaller than the reported by the group of DeSimone<sup>[40,41]</sup> ( $1.5 \cdot 10^{-3}$ ), the difference comes precisely because the latter authors consider just a single polymerization phase, whereas Mueller et al.<sup>[42]</sup> considered 2 phases. This allowed Mueller et al. to find good agreement between the experimental data and the model results, in terms of the evolution of the conversion, and the MWD as a function of conversion, both at different monomer concentrations and pressures. Based on their results, at low conversion the polymerization occurs predominantly in the continuous phase, and low molecular chains are produced. With the rising number of polymer particles, a second mode appears in the MWD. In so far as the monomer concentration is concerned, higher concentrations promote the polymerization in the dispersed phase. There is a discrepancy between the model and the experimental MWD at high monomer concentration, attributed to the assumption of the constant value for the specific surface area of the polymer particle.

Until this point, we see that reasonable predictions can be obtained using either one single phase or two phase model, but that 2-phase models manage to better describe the bimodality of the MWD. The disadvantages of this approach are that it is complex and a large number of variables need to be defined. The 1-phase model is much simpler since their equations are derived for CO<sub>2</sub>-rich phase, so active chains transport can be neglected. Nevertheless, knowledge of where the polymerization occurs is not only theoretically important, but also practical, since it can help to tailor some important properties of the final product, as well as to control the reaction.

One factor that can help to elucidate the reactive sites of the polymerization is the equilibrium sorption of VDF/CO<sub>2</sub>/PVDF. Some studies<sup>[47,51,52]</sup> showed that the concentration of VDF in PVDF is very low in presence of scCO<sub>2</sub> (P<100 bar), so very low rate polymerization in polymer phases can be expected, which justifies the choice of DeSimone for one phase reaction.

More recently, Costa et al.<sup>[43]</sup> proposed a general procedure based on a specific rate ratio ( $\theta$ ) to identify the number of reaction loci in a heterogeneous polymerization system. To obtain  $\theta$ , the formulated polymerization rate for each phase are based on the previously mentioned assumptions<sup>[42,43]</sup>. After analyzing the data, published by Ahmed et al.<sup>[50]</sup>,

they conclude that the experimental data is well described using one-locus polymerization since the value of  $\theta$  is small.

In fact, the comparative evolution of the models in terms of the reaction rates vs. polymer holdup confirmed that the precipitation polymerization of VDF is always taking place in both phases. Nevertheless, at diluted condition, or when  $\theta < 50$  homogeneous model can provide reasonable approximations.

To summarize, homogenous models are suitable for describing the overall reaction rate, and are preferred for their relative simplicity. Heterogeneous models can be used when radical transport cannot be neglected, for instance, to describe the entire MWD, or more important in EP system where they are generated in one phase and propagate in another. In any case, to properly describe the kinetic both models should account the chain transfer to (at least) polymer.

One aspect that could be quite important in VDF emulsion polymerization that is rarely discussed in either the patent or academic literature is the role of agitation. The group of DeSimone<sup>[39,40]</sup> noticed that at high monomer concentration the agitation affects the polymerization rate and monomer conversion. But their attention focused on the variables that directly affect the MWD, so mixing was not treated in their publications. Morbidelli's group did not mention the possible impact that agitation can have on VDF polymerization. As mentioned above, one suspects that in a reactor with gaseous (or supercritical) monomer it would be quite likely that mass transfer resistance could become a rate limiting step as it is in ethylene-vinyl acetate copolymerizations under conditions of similar temperature and pressure.

We will now focus on the kinetic studies of VDF emulsion polymerization. Apostolo et al.<sup>[44]</sup> examined the emulsion co-polymerization of VDF and HFP based on the polymerization rate and characterization of the polymer structure, specifically the MWD and the chain end group distribution. The fluoropolymers under investigation were composed by 79 %mol of VDF and 21 %mol of HFP. Reactions were carried out at constant temperature (85 °C) and at constant pressure (11 bar or 19 bar), using ethyl acetate as CTA and ammonium persulfate as initiator.

The kinetics of copolymerization was described in terms of equivalent homo-polymer, using the following assumptions:

- (i) Negligible mass-transport limitation, they verified that at the working stirring speed there are no transport limitations of the monomers between gas and liquid. (N.B. The experiments were not shown or explained.)
- (ii) Quasi-steady-state assumption for the radical species.
- (iii) Long-Chain assumption for large molecular weights, chain composition is independent of the chain length.
- (iv) Reactivity of the active chain is conditioned by the last monomer unit.
- (v) Pseudo-bulk approximation, i.e. the isolation of radical in separate particles can be neglected. Particles of the same size are assumed to have the same average number of radicals. Nucleation stage is not modeled, and the particle number is not computed.
- (vi) Reactants are homogeneously distributed inside the polymer particles.
- (vii) Negligible water solubility due to the hydrophobic nature of the monomers. The monomer will be partitioned between the gaseous and polymer phase.

Based on their NMR analysis, they found that the chemistry of the copolymerization is characterized by the mobility of hydrogens atoms of VDF, so the reactions involving radicals of the type  $CF_2^*$ - are dominant (i.e. more head-head defects), namely chain transfer to monomer and to polymer, and bimolecular termination by disproportionation. Chain transfer to polymer leads to long-chain branching. This observation is coherent with that one given by the group of DeSimone<sup>[41]</sup>. On the other hand, the reactions that involves the radical type  $CH_2^*$ -, that is the backbiting reactions (which leads only to short chain branching) were considered important to compute the chain end distribution, but not the MWD.

To solve the mass balance equation, the distribution of the monomers, initiator and chain transfer species need to be known. As we mentioned in the previous section, Morbidelli's group calculated the partitioning of monomers between gaseous and polymer phase using a Henry's Law constant obtained from an internal report, so no experiments were shown. The initiator was considered completely water soluble, and

the partitioning of the chain transfer agent between the aqueous and polymer particles were obtained by data fitting.

The entire MWD was modeled using fractionated moment equations. Here the MWD is obtained by summing the MWDs of each generation. Those generations were discretized as function of the size and number of long-chain branches. Furthermore, the chain end groups were calculated through the balances of:

- (i)  $\text{CH}_3$  that were formed by chain transfer to monomer and by backbiting.
- (ii)  $\text{CF}_2\text{H}$  and  $\text{CH}_3\text{COOCH}(\text{CH}_3)$  formed from chain transfer to CTA, and terminal double bond (TDB) that resulted from chain transfer to monomer and termination by disproportionation.

Considering the lack of information in the open literature and the number of parameters required to solve the proposed a set of ordinary differential equations, the authors evaluated most of the model kinetic parameters by experimental data fitting. Two sets of copolymerization reactions were used, one obtained at different conversion values without CTA, and the other using CTA at an equivalent conversion value. The model was found to predict correctly the MWD as well as the chain end distribution of the produced polymer.

From the modeling of the MWD by generations, in the reactions performed without CTA, it can be seen that as the polymerization progresses, the first generations decrease, due to the predominance of the two branching mechanisms, CTP and propagation to TDB reactions. It is assumed that the monomer concentration in the polymer particles is constant (reactor at constant pressure), and only a chain reactivation mechanism explains a higher MWD that leads to long-chain branching.

When CTA is present, the molecular weight and the number of branches per macromolecules are reduced. Consequently, the PI is reduced and it is constant during the polymerization. In presence of CTA the relative concentration of  $\text{CF}_2\text{H}$  groups is higher than  $\text{CH}_2\text{OH}$  concentration, suggesting the role of the chain transfer to CTA as chain initiating mechanism compared to initiator decomposition.

The MWD is not strongly influenced by the initiator concentration as a consequence of minor impact of the termination provoked by two radicals on the polymer chain length.

The increase of the monomer concentration in the polymer particles provokes an augmentation of the molecular weight. Particularly, linear chains are favored with respect to branched polymer, indicating that chain propagation reactions are promoted at high monomer concentration.

Pladis et al. [45,53] also proposed a mathematical model to describe the emulsion polymerization of VDF that included the elementary reactions that can describe the kinetic mechanism of VDF emulsion and the derived polymerization rate expressions. They selected the PSD as quality parameter to describe the evolution of the polymerization, so a population balance to model the particle size was proposed. In reference [53] the authors just showed the general form of the equations, without further development or derivation, the parameters employed were not presented, and no explanations about the parameter determination were given.

In their earlier work<sup>[45]</sup> a model for the VDF emulsion polymerization performed at 83 °C and 85 bar in semi-continuous mode is presented in more detail. Their kinetic scheme was similar to that one proposed by Apostolo et al.<sup>[44]</sup> to describe the produced polymer chain end groups. Namely the elementary free-radical reactions (i.e. initiator decomposition, chain propagation, and termination), joined with the initiation reaction, chain transfer to monomer and to polymer, chain transfer to a CTA, and backbiting reaction. Here, the propagation to a terminal double bond was not accounted for, and the termination was assumed to occur by combination, and not by disproportionation as signaled by Morbidelli's group. The overall polymerization rate was calculated as the sum of the rate in the aqueous phase and in the polymer phase.

They<sup>[45]</sup> developed a PBE model to compute the PSD during the emulsion polymerization included the coagulation rate. The coagulation rate value can be determined if the stability ratio is known. No experimental data is presented for the estimation of this parameter, and in this publication no details are given about the choice of Fuch's stability ratio or related parameters.

The nucleation stage was modeled, and considering that they work at concentration below the critical micelle concentration, particle nucleation was assumed to be homogenous. An important parameter to compute the rate of nucleation is the critical length of the polymer chains; this value was treated as an adjustable model parameter.

Their estimations based on empirical correlation from Gilbert et al.<sup>[54]</sup> suggested that the saturated monomer concentration in the aqueous phase is  $10^{-1} \text{ mol}\cdot\text{L}^{-1}$ , so the critical length for VDF equal to 20, which seems to be very high value compared to what is typically obtained in a system where the monomer solubility is low. Radical transport between the aqueous and polymer phase was also treated; calculations are based on the quasi-steady-state approximation. Thermodynamic equilibrium was assumed to be able to compute the monomer phase behavior using the Sanchez Lacombe equation of state. The characteristic SL parameters were given, but the VDF/PVDF interaction parameter was not. Finally,  $M_n$ ,  $M_w$ , and PI were computed in terms of the methods of moments.

The monomodal PSD and the molecular weight agree with the model prediction, suggesting a good performance of the proposed model. However, we recognized that a certain number of parameters were not reported and we do not know if they were estimated by data fitting or based on independent measurement. The authors also showed a better fit between experimental and simulation results at high surfactant concentration. We know that when the surfactant concentration is higher the particles will be better stabilized and the particle coagulation will be limited. So, the disagreement between experimental observations and model prediction might come from the estimation of the coagulation rate (which is, in itself, quite difficult), so it is possible that their model performs better when coagulation becomes unimportant. This can also explain the difficulties that their model has to predict a broad PSD, at low surfactant concentration, when a limited particle aggregation is present in the system.

Concerning the experimental part, they found that the polymerization rate increased with the total amount of initiator (potassium persulfate, KPS) and decreased with the amount of CTA (Ethyl acetate). This last effect was said to be accentuated when the total amount of CTA is added in one shot. Pladis et al.<sup>[45]</sup> suggested that the rate decrease provoked by the CTA can be attributed to the increase of the radical desorption rate of chain length radicals and to the decrease of the gel-effect, this last promotes the mobility of the growing radical chains. Additionally, they computed an average number of radicals that exhibit a U-shape behavior, from 0.68 to 0.85, related to the PVDF crystallinity and particle size. They indicate that these changes are promoted by a variation in the radical concentration in the particles due to radical entry, and to termination rates. Authors of patent US 3,475,396-A<sup>[15]</sup> signaled that surfactant amount

can be reduced as function of the amount of CTA added. In other words, the CTA seems to have a stabilizing effect, probably through the production of oligoradicals.

A final point that is potentially important from a product point of view, but that it is rarely taken into consideration is the impact of chain defects on the polymerization rate. Defects such as head to head, or tail to tail additions can lead to changes in crystallinity and other properties<sup>[4,7]</sup>. The existence of these defects were discussed in some modelling papers<sup>[44,53]</sup>, and Pladis et al. <sup>[53]</sup> seem to consider the appearance of these defects for calculation of polymer crystallinity. However, given that the chain end radicals generated by the different modes of addition will have different reactivity, one might need to consider including this type of information in process models. The kinetics of vinylidene fluoride in free-radical polymerization were investigated by quantum chemistry in an effort to differentiate between the different possible propagation reactions were accounted for (head to head, head to tail, tail to tail, head to monomer, tail to monomer); and the Arrhenius parameters for each system were estimated assuming the terminal model.<sup>[55]</sup> It was found that the “head to tail” propagation is more favorable than the “tail to head” that has a kinetic constant 2 orders of magnitude smaller. The propagation reactions “head to head” and “tail to tail” were of the same or higher importance than the “head to tail” propagation. This indicates that the homopolymerization of VDF is complicated and can necessitate under some conditions to be modelled as a copolymerization. The proportion of these reactions can however be affected by the reactions conditions and the radical types.

Let us now return to considerations about the reactor and eventual mass transfer limitations. As noted above, the case of the emulsion polymerisation of vinylidene fluoride can be a bit more complicated than for other emulsion polymerization processes because the monomer is typically either a gas or a supercritical fluid under the polymerization conditions of interest (N.B. henceforth we will refer to undissolved VDF in the reactor as the gas phase while we discuss mixing and mass transfer to avoid serial repetition of “gas or supercritical” phases). Thus, since we are working with a reaction where the monomer must transfer from the lightest of the 3 phases in the reactor to the polymerizing particles, it is quite possible that the polymerization can be limited by the rate of mass transfer in certain conditions (this can also present a certain number of challenges in terms of scale up as well!). Since very little information is

available in the open literature (or the patent literature), we can infer certain things about reactor design and performance from cases like ethylene – vinyl acetate polymerizations, or the general literature on gas-liquid-solid reactors.

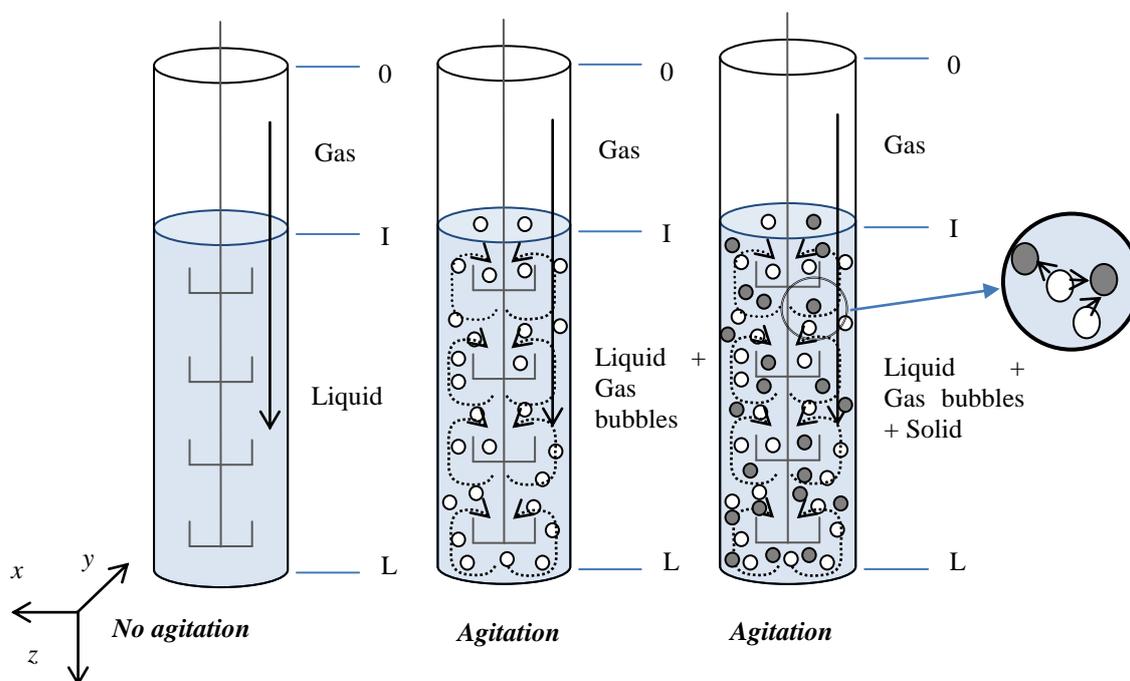


Figure 1. Illustration of the mass transport phenomena between the gas-liquid-solid phases.

A schematic representation of the mass transport phenomena taking place during this reaction is shown in Figure 1. Regardless of whether the VDF is true gas or supercritical fluid, it is lighter than the aqueous phase, and dispersed in the form of bubbles, so the transfer of the monomer to the reaction medium and thus to the growing particles particles is achieved by dispersing the gas in the form of bubbles in mechanically agitated vessels.<sup>[32]</sup> In other words, it is probable that the quality and intensity of mixing will have a non-negligible impact on the kinetics of polymerization, and on the properties of the final polymer. As the mixing of the gas and liquid phases grows more intense, the bubbles are divided more finely. This increases the surface area available for mass transfer and permits an effective dispersion of the gas into the liquid.

So far, in the literature the mass transport limitation has not been treated explicitly for system in presence of vinylidene fluoride, so we will need to consider works on similar

polymerization systems. For instance, the group of Penlidis worked on ethylene-vinyl acetate emulsion polymerization, and showed that mass transfer limitations (ethylene bubbles to polymer particles) can be important.<sup>[56,57]</sup> They showed that an increase in the agitation rate leads to increased ethylene levels in the final product, presumably because of enhanced mass transfer of the gaseous component. While the authors did not discuss the impact of the agitation rate on the rate of polymerization, one can infer that if increasing the mass transfer rate of the gaseous components to the polymerizing particles leads to an increase in its incorporation. In an earlier paper, it was shown by Senrui et al.<sup>[58]</sup> that for the particular case of the radiation-induced emulsion polymerization of ethylene this is indeed the case. So while one can draw parallels between the ethylene-vinyl acetate and ethylene systems on the one hand, and the VDF system of interest here, it is clear that this matter requires further investigation.

In a related issue, the few works cited above that look at the modelling of VDF polymerization assume (implicitly) that thermodynamic equilibrium is established instantaneously between the monomer, the water phase and the polymer particles. The vast majority of experimental solubility studies in PVDF that can be found in the literature were carried out in supercritical CO<sub>2</sub><sup>[51,59]</sup>. In those studies dealing with VDF in emulsion, Pladis et al.<sup>[45]</sup> reported the characteristic parameters for the Sanchez-Lacombe equation of state that they used, but did not give values for the binary interaction parameter that is required. Apostolo et al.<sup>[44]</sup> investigated the emulsion polymerization of vinylidene fluoride and hexafluoropropylene at 85 °C and pressures between 11 bar and 19 bar. In this case, they studied the monomer solubility between the gaseous and the polymer phase using Henry's Law, and reported a Henry's Law constant of 3.1E-4 mol·Pa<sup>-1</sup>·m<sup>-3</sup>, obtained by data fitting from an Ausimont internal report (no further details on this were available either). It should be noted that Henry's law can be employed to calculate the equilibrium between the gas monomer and polymer phase as a function of the partial pressure of monomers at low to moderate pressure. However, as mentioned above, even the equilibrium behavior can deviate from Henry's law if we are working at higher pressures typical of VDF homopolymerization processes. In these cases, a more sophisticated approach such as SL-EoS is required, and a full range of model parameters that cannot be predicted *à priori* is required.

In closing, a final brief remark about reactor design. As mentioned rapidly above, the patent literature is of little help here. Some patents cite the use of horizontal autoclaves, others vertical. While there are undoubtedly reasons to use the horizontal configuration, they are not immediately clear. It is widely accepted in the chemical reaction engineering literature that a high aspect ratio is desirable to enhance gas/liquid contacting.<sup>[57]</sup> It seems obvious that if the gas phase can be entrained (or fed) to the bottom of the reactor, then it will take a reasonably long time to rise back to the vapor space at the top of the reactor, giving the system more time to absorb the species in question. One would suspect that this less true in a horizontal configuration, and that this configuration would require very well-designed agitators (that will be particularly difficult to scale up beyond a certain point) to ensure that mass transfer limitations are not an issue.

In summary, there is not enough information about the monomer solubility and monomer-polymer interaction parameters to model the partitioning of VDF under realistic reaction conditions *à priori*. Furthermore, all the models and semi-empirical approaches are based on the hypothesis that equilibrium is rapidly achieved. However, if the systems are mass transfer limited, then this assumption will be incorrect!

## **CONCLUSIONS**

From this review of the literature, we can conclude that despite the economic importance of the VDF emulsion polymerization the knowledge of the kinetic mechanism is incomplete, and the available data to estimate model parameters is still limited in the open literature. The model developed by the group of Morbidelli presents a complete evaluation of the MWD, and they managed to obtain reliable estimation parameters based on the combination of different experimental approaches. The estimation of PSD demands that more parameters be known, and the stability studies begin to play an important role. With this in mind, the model developed by the group of Kiparissides based on PBE, seems to account for almost all the phenomena that affect the particle size. However, their predictive power is limited by the number of adjusted variables. In this sense, the objective of this work is to contribute, in broad terms, to the kinetic investigation of the VDF emulsion to provide sufficient data parameters that lead to the development of reliable models, and to capture most of the important features that control this system.

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