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Polyvinylidene Fluoride: Reaction Engineering and Applications

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ABSTRACT

Polyvinylidene fluoride (PVDF) is a semicrystalline fluoropolymer mostly produced by free-radical suspension or emulsion polymerization. It has the second largest production capacity among all fluoropolymers, following only polytetrafluoroethylene. This great industrial attention is due to its excellent chemical and physical properties, among which its inertness and resistance to chemicals and heat, its high melting point and high tensile strength. As a result, it is one of the first materials of choice in the field of membrane separations, especially for micro and ultrafiltration. In addition, due to its piezoelectric, pyroelectric, and optical properties, PVDF is finding more and more extensive application in batteries and sensors. Given the important role played by PVDF in the polymer market, this review is aimed at reporting the latest advancements in its manufacturing, with particular reference to the innovations introduced following the new legislation on environmental protection from perfluoroalkyl substances. The main focus is on the emulsion polymerization process, where experimental conditions and models from the literature are presented and discussed. After having clarified the polymer reaction engineering aspects for this material, the latest advancements in the application of PVDF are reviewed, with the aim of highlighting its strengths as well as points for improvement.

1 | Introduction

Fluorinated polymers are specialty polymers where hydrogen is replaced by fluorine atoms in their backbone [1–4]. Several thermoplastic, elastomeric, semicrystalline, or amorphous materials belong to the family of fluorinated polymers. In general, they find applications in several areas, such as industrial coating and painting, aerospace, construction, petrochemistry, and automotive industry [4–10]. This interest is justified by their favorable properties including but not limited to resistance to aging, inertness toward many substances, and thermal stability [4–7, 11–13]. These properties are the result of the high electronegativity and low polarizability of fluorine atoms, with a short van der Waals radius (1.32Å), which causes the formation of a short C–F bond in a material having a large energy of dissociation (around 485 kJ/mol) [14]. As a matter of fact, the C–F bond is claimed to be "the strongest bond in organic chemistry" [15].

Figure 1 shows the main producers of fluoropolymers in the year 2022, with the first place in terms of manufacturing capacity belonging to Shandong Donyue, followed by Chemours and then Daikin. These three producers alone are responsible for more than one-third of the total fluoropolymer production.

In 2010, the production volume of fluoropolymers was around 200,000 tons per year. This value increased to 223,000 tons per year in 2012 [14], reaching 330,000 tons in 2021 [17]. In 2024, reports indicate 639,210 tons produced, confirming the great expansion experienced by the fluoropolymer market [18]. This fast growth is expected to proceed with a compound annual

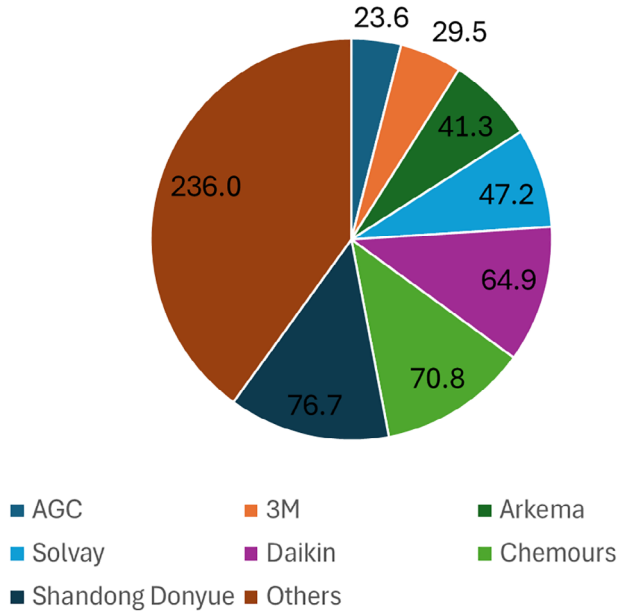

FIGURE 1 | Major fluoropolymer producers by mass of product manufactured per year (labels are in ktons/year). Data taken from [16] for the year 2022.

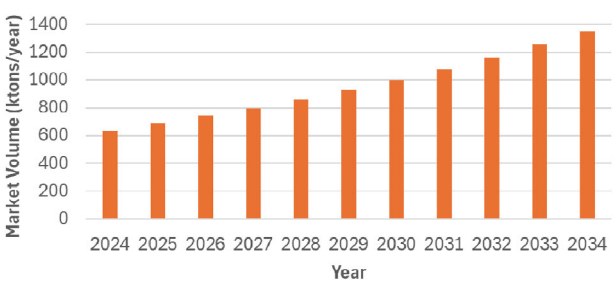

FIGURE 2 | Expected market growth for fluoropolymers in the upcoming years. Data taken from [18].

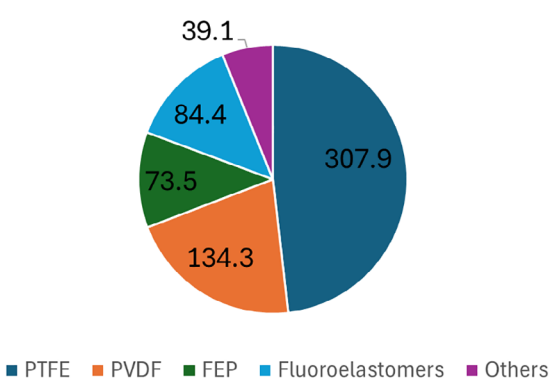

FIGURE 3 | Market share for fluoropolymers as of the year 2024 (labels are in ktons/year). Data taken from [18].

growth rate of 7.77% also in the coming years, with the forecasted manufacturing capacity shown in Figure 2 [18].

The share of the different fluoropolymers to the total installed capacity can be observed from Figure 3. Polytetrafluoroethylene (PTFE) has the largest share in the market, covering almost 50% of the installed manufacturing capacity. This is followed by polyvinylidene fluoride (PVDF), covering 21% of the whole market, while the third place belongs to fluorinated ethylene propylene (FEP) with 11.5% [18].

PVDF, a vinylidene fluoride homopolymer, is characterized by 2 fluorine atoms replacing hydrogen in a polyethylene backbone. It gained attention not only as a highly inert material [15], but also due to its high melting point (177°C), tensile strength (7.105 PSI), low thermal conductivity and resistance toward several chemical or physical factors (such as UV radiation, organic solvents, acids, etc.) [19].

In the early days of the discovery of PVDF, X-ray crystallography suggested that it could be used as a ferroelectric material. This would make it a unique material among a lot of organic and inorganic ferroelectric substances, being the first ferroelectric polymer. However, the experimental proof of this analysis took much more time than expected [15], as it was proven only 21 years after the discovery of the polymer [20]. Because of the aforementioned properties, PVDF is finding innovative applications in medical, electronical, pharmaceutical, petrochemical, and many more fields, which will contribute to the expansion of this fluoropolymer market in the coming years [19].

Because of the very favorable properties and great interest gravitating around PVDF, many articles reviewing its status [21–28] and application areas [29–33] have been published in the past. With this review, we aim at providing a discussion of the recent efforts and advances in its manufacturing, with a particular focus on emulsion polymerization. Indeed, more and more stringent regulations on the use of fluorosurfactants have pushed the manufacturers to adopt new formulations and reactor design to exclude these components while preserving the polymer quality. After having clarified the new technologies for the manufacturing, the focus is shifted to the description of the main applications for PVDF, with emphasis on the emerging fields that can lead to a further expansion in the market for this fluoropolymer. Through this analysis, we pinpoint the strengths of PVDF, while at the same time highlighting the aspects that can be improved for innovative applications.

2 | Production Strategies

PVDF is commercially produced mostly by free-radical emulsion or suspension polymerizations. The reason behind the popularity of these heterogeneous processes in water phase is due to the fact that free-radical polymerizations are subjected to high exothermicity. Indeed, the temperature control on the reactor is crucial to avoid undesirable thermal runaways. In this direction, water helps dissipating the heat of the reaction, mitigating the risk of runaway [34]. In addition, polymer particle dispersions, or latexes, are associated with significantly lower viscosity compared to polymer solutions. This allows processing much larger solid contents with less sophisticated reactor configurations [35]. Even though emulsion and suspension polymerizations are similar to each other, they have some key differences. These mainly include different distribution and concentration of free radicals, choice of the initiator (even though it is not strictly necessary, usually water soluble initiators are chosen for emulsion polymerization, and oil

soluble ones are selected for the suspension [4]) or the reactor conditions. Also, a surfactant, usually fluorinated, is necessary for emulsion polymerization, which is currently leading to a reevaluation of the manufacturing processes because of the restrictions imposed on the use of such molecules, as specifically discussed in the following. On the other side, surfactants are generally not needed for suspension polymerization, which exploits less dangerous suspending agents. Due to the mentioned differences, the produced polymers have different properties with respect to one other [36]. To compare these two processes, the product obtained from emulsion polymerization has a narrower molar mass distribution, lower head-to-tail defects, lower melting point, much smaller particle size (usually two orders of magnitude smaller), resistance to higher temperature, becomes more soluble after heating (while product from suspension polymerization is soluble in polar solvents) and high rate of polymerization could be achieved simultaneously with high molar mass (where these two are inversely proportional for suspension polymerization) compared to suspension polymerization [37]. Moreover, the choice of temperature, pressure, reaction recipe, the strategy of monomer feeding, and post-reaction processing changes the quality and the characteristics of the product [34, 38].

Commercially produced PVDF chains usually have a degree of polymerization from 1000 to 2500 VDF units [34]. Due to the structure of VDF, the produced chains can have two different ends, one ending with a $-CF_2$ unit and the other one with $-CH_2$. Various studies have proved that the $-CF_2$ chain end (head) dominates over the $-CH_2$ one (tail) [34, 39, 40]. However, "defects" forming head-to-head or tail-to-tail linkages in the chain can occur as well. Nuclear magnetic resonance (NMR) spectroscopy [41] shows that commercial products contain 3–7 mol% of defects [34, 41, 42], with this percentage increasing further as temperature increases [34, 43–45]. Besides NMR spectroscopy, matrix-assisted laser desorption ionization—time of flight (MALDI-TOF) spectroscopy is another technique to investigate the microstructure of PVDF [46, 47] and highlight the content of defects inside the chain.

In cases where such defects are highly undesired, the polymerization reaction could be carried out at low temperature by exploiting organocatalysts. Guo et al. [45] successfully reduced defects through an organocatalyzed photoredox polymerization in a temperature range −40 to 50°C. Another novel method by Asandei [48] describes reactions which could be carried out at ambient temperature under visible light through photomediated radical polymerization.

Even though alternative methods, such as homogeneous phase reactions in supercritical carbon dioxide [49], are possible and could be advantageous due to reduced cost and pollution, they are still limited to laboratory scale.

The reactions can be carried out with the addition of chain transfer agents with the aim of controlling the molar mass and the end-group distribution [34]. In this direction, iodine transfer polymerization exploits organic iodides as transfer agents to both tune the molar mass distribution of the final polymer and to introduce iodine end-groups in the polymer chains, which are useful for subsequent processing [50–52]. Another appealing strategy to precisely control the molar mass distribution of PVDF is the reversible addition-fragmentation chain transfer polymerization (RAFT) [53–56]. Fuentes-Exposito et al. smartly exploited the RAFT/MADIX polymerization of VDF to introduced polyethylene glycol (PEG) chains at the polymer end, which provided colloidal stabilization in water, thus avoiding the use of fluorosurfactants [56].

2.1 | Synthesis of Vinylidene Fluoride Monomer

The monomer, vinylidene fluoride, can be obtained from different methods [4, 57], among which the most adopted ones are based on the dehydrohalogenation of halo hydrocarbons, such as dehydrobromation of 1-bromo-1,1-difluoroethane. The most common and commercially used process starts with the hydrofluorination of either acetylene (followed by chlorination), trichloroethane, or vinylidene chloride. All these three reactions result in producing 1-chloro-1,1-difluoroethane, which forms vinylidene fluoride after stripping a molecule of hydrochloric acid [57]. The reaction mechanisms of these three options are reported in the following.

Starting from acetylene

$$CH \equiv CH + 2HF \rightarrow CH_3 - CF_2H$$
$$CH_3 - CF_2H + Cl_2 \rightarrow CH_3 - CClF_2 + HCl$$

$$CH_3 - CClF_2 \rightarrow CH_2 = CF_2 + HCl$$

Starting from trichloroethane

$$CH_2Cl - CHCl_2 + 2HF \rightarrow CH_3 - CClF_2 + 2HCl$$

$$CH_3 - CClF_2 \rightarrow CH_2 = CF_2 + HCl$$

Starting from vinylidene chloride

$$CH_2 = CCl_2 + 2HF \rightarrow CH_3 - CClF_2 + HCl$$

$$CH_3 - CClF_2 \rightarrow CH_2 = CF_2 + HCl$$

2.2 | Production of PVDF in the Early Days

The production of PVDF was first reported in a patent submitted in 1948 by Ford and Hanford [58]. Polymerization of VDF was carried out in water media using a peroxide initiator in the temperature range from 50 to 150 °C and a pressure range from 50 to 100 MPa. During the polymerization in a batch system, no suspending agents or surfactants were used. The first process for the industrial manufacture of PVDF was developed in early 1960s by DuPont and after a short period of time, PVDF was introduced to the market as a commercial product [15, 57].

Another early patent [38], filed in 1965, reported extremely high yields using an organic polymerization initiator, namely, di-tertiary-butyl peroxide (DTBP). At the end of the reaction, lasting 18.5 h, a polymer yield around 83% was achieved [57]. Due to the impossibility of solubilizing the polymer, the absolute molar mass was not measured. Rather, an indication was provided through the measurement of the "plasticity number," defined as the area

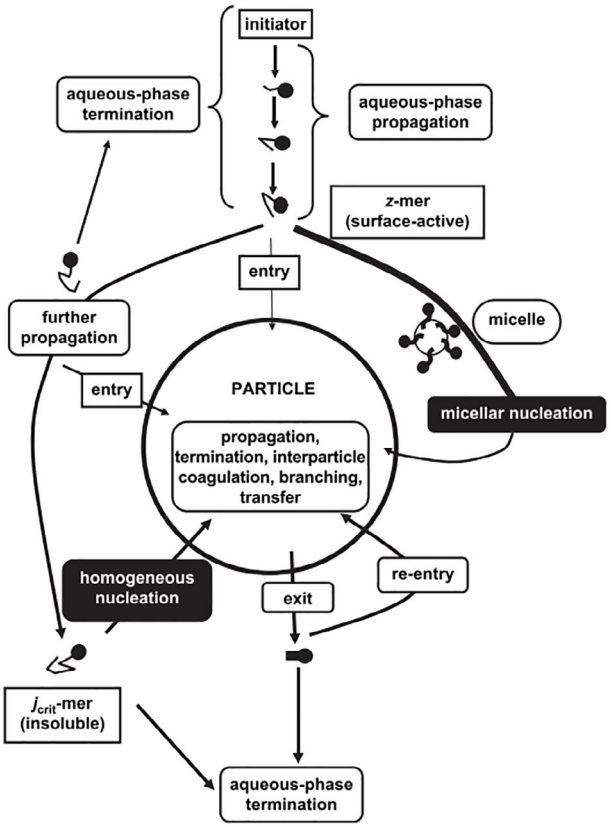

FIGURE 4 | Kinetic events for a generic emulsion polymerization reaction. Reproduced with permission from [60]. Copyright 2007, Elsevier.

(in mm^2) of a plaque formed by 0.5 g of polymer powder under pressure. The value of the plasticity number reported in this work is 3020, associated by the authors to a high molecular weight polymer. The thermal resistance of the polymer was assessed by incubation at 200°C for 100 h. The authors did not observe any decomposition or discoloration, hence they claimed the polymer had excellent thermal stability [38].

2.3 | Emulsion Polymerization of PVDF

Emulsion polymerization is a valuable process to produce polymer particle dispersions, which are also called latexes. The polymer particles forming the colloids, mostly suspended in water, usually have spherical shapes; however, the morphology is strongly dependent on the process and application area. The size of the particles could be as small as tens of nanometers up to the order of one micrometer [35]. In a common emulsion system, four main species are present: i) water as the medium, ii) one or more water-immiscible monomers forming droplets in the continuous phase, iii) initiator to start the reaction, and iv) surfactants to provide colloidal stability to the forming particles [35]. The temperature can be as low as 10 °C up to 130 °C and the pressures can range from 1 to 20 MPa [3, 34, 50, 59]. A schematic representation of the main kinetic events taking place in a generic emulsion polymerization system are shown in Figure 4 [60].

The polymerization reaction can be divided into three stages according to Smith and Ewart [60–62]. These three stages are named nucleation, particle growth, and monomer depletion and the relative rates define the properties of the latex, namely, the particle size distribution and morphology. The readers interested in deepening the fundamentals of emulsion polymerization are referred to the articles discussing these steps in detail [60–66].

With specific reference to the production of PVDF, the monomer VDF is usually in gaseous or supercritical form at the reaction conditions used during the emulsion polymerization, which introduces an additional resistance to the transfer of the monomer to the growing particles, which is its solubilization in the liquid medium. Indeed, this is most often the rate determining step of the process, so that the impeller geometry and stirring rates need to be carefully designed to approach the chemical regime as much as possible. The most common way of production of PVDF at an industrial scale is by semi-batch operation [36]. The gaseous monomer is continuously supplied to the reactor with a flowrate designed to have constant pressure, which comes from the balance between supplied monomer and amount transferred to the liquid phase and eventually consumed by propagation.

Until few years ago, the reactions were usually carried out in heterogeneous conditions with the use of a fluorinated surfactant, particularly compatible with fluorinated monomers, to form micelles and provide colloidal stability to the formed polymer particles [67]. However, regulations on the release in the environment of perfluoroalkyl substances (PFAS) became more and more stringent in the last years, after having recognized the danger of these molecules for their bioaccumulation and persistence. This pushed to the development of alternative PVDF manufacturing processes without the use of fluorosurfactants [68, 69]. The use of surfactant is not strictly required in the emulsion polymerization of VDF, but in cases where it is not used, low solid content latexes need to be produced to avoid polymer coagulum [34]. It is documented that poly(ethylene glycol) (PEG), acting as a hydrophilic stabilizer, can be used as an alternative to fluorinated surfactants for PVDF production [56]. Another patent [70] mentions acids such as polyvinyl phosphonic acid, polyacrylic acid or their salt forms can also be used for processes without any fluorinated surfactants. Other than these, charged initiator fragments, such as SO_4^- formed from persulfates, or other hydrocarbon salts such as sodium dodecyl sulfate (commonly used as an emulsifier for other emulsion polymerization processes) can provide a negative charge to the particle surface, which causes repulsion and helps providing stability. An industrial company, Arkema, which switched the production of their Kynar PVDF from traditional fluorinated surfactants to a new process without the use of fluorosurfactants in all their plants, claims they reached the same performance with respect to the traditional techniques [71].

The use of gaseous VDF monomer for the emulsion polymerization favors the nucleation of particles to occur by homogeneous mechanism [6, 34, 59]. This is happening because gaseous VDF dissolves uniformly in water phase, then it quickly reacts with the radicals in water and, upon forming oligomers with lengths of a few monomer units it becomes insoluble and precipitates before the possibility of being captured by eventual micelles.

The initiators can be water soluble [50], or a mixture of water-soluble and oil-soluble species [40]. Traditional choice

of initiators includes persulfates [50, 51], organic or inorganic peroxides [47]. Besides these, redox systems have been explored to initiate the reaction [45, 72, 73]. The advantage of using redox initiators with respect to thermal initiators lays in the possibility of running the reaction at a lower temperature, which slows down the termination reactions allowing the production of higher molar mass polymers. Indeed, fast rate of radical generation can be achieved even at low temperatures, which causes a high rate of nucleation and formation of smaller sized particles. However, as a disadvantage, it can induce the formation of chain-end defects. One can select the type of initiator depending on the final application. If high molar mass, small sized particles formed at low temperatures are desired, redox initiators should be preferred over the thermal initiators, and vice versa.

The polymerization conditions are usually at temperatures close to but below 100 °C and at relatively high pressures even up to a few hundreds of bars [36, 37, 50, 59]. The polymer is produced in the form of spherical particles with particle size around 250 nm [57]. The latex is stabilized by the use of a wax added to the reaction mixture, which is then removed from the latex at the end of the reaction by several post processing techniques [57].

As mentioned, the selection of process parameters like temperature and species present inside the reactor such as the initiator or the surfactant could significantly affect the final polymer properties. Therefore, the polymerization recipe needs to be defined with care, having in mind the desired final polymer properties. Guan et al. [74] developed a method to synthesize ultrahigh molar mass PVDF by initiating he reaction with trichloroacetic acid and silver nanoparticles at 50 °C and 70 bar (Figure 5). The final polymer had a number average molar mass of 1.72 MDa, which could be useful for specific applications where elevated thermal stability, mechanical strength, and chemical resistance are required [74, 75].

2.3.1 | Reactor Configurations

Emulsion polymerization of VDF is usually carried out in a stainless-steel reactor. A recent article by Gelinski et al., [59] aiming to compare model predictions with experimental data used a stainless steel 316 reactor, with external jackets in order to control the temperature. The reactor had a height to diameter ratio of 5. Mixing is particularly critical in this system, to overcome the important mass transfer limitations across the different phases, among which the most relevant one from the gas phase to the liquid one. Therefore, a careful design of the stirring system is particularly crucial to approach the chemical regime. Indeed, the impeller geometry is often from dedicated studies and constitutes a trade secret from the specific manufacturer, making it hard to find details about it. In general, stirring is typically achieved by the use of six-bladed 45° type impellers, with a diameter of the impeller to the inner diameter of the reactor ratio of 0.5. Other than the impellers, in the specific case of Gelinski et al., [59] the reactor was equipped with a thermocouple, a dip tube and a hydrofoil which had a diameter of the hydrofoil to the inner diameter of the reactor ratio of 0.9.

Two other recent patents [76, 77] by Solvay Specialty Polymers describe a process where a stainless steel horizontal reactor is used. In this case, stirring is performed by the use of a paddle agitator. In an earlier patent [78] by the researchers from the same company, the reaction is carried out in a horizontal autoclave, mixing is achieved by baffles and a stirrer operating at 60 rpm. In this same patent, they also describe a copolymerization process where they used an AISI 316 steel vertical autoclave still connected to baffles and a stirrer, this time they were stirring the mixture at 570 rpm.

The entire commercial production of PVDF is carried out in discontinuous or semicontinuous reactors. This is the result of the difficulty associated to the process, mainly coming from the necessity of handling a dangerous monomer in supercritical conditions at high pressure. However, batch (or semi-batch) processes have some significant disadvantages, the major ones could be summarized as [79]:

i. Batch-to-batch variations: Every lot is associated to differences in the polymer properties due to slight variations in polymerization recipe and reaction conditions.
ii. Downtime: The reactor has to be emptied, cleaned, and reloaded for the new reaction; this causes not to have an ongoing operation for hours.
iii. Heat and mass transfer limitations: These are common when dealing with a multiphase system.

To avoid these disadvantages, laboratory examples of continuous emulsion polymerization of PVDF have been recently reported. Herrmann et al. [79] recently conducted a research using a continuous flow reactor and developed a well-controlled process without the use of a fluorosurfactant. They claimed that their process could improve mass and heat transfer, hence reducing energy requirements and speeding up the process to achieve higher yields. The setup used in this study (shown in Figure 6) consists of a tubular membrane, with water flowing inside and gaseous VDF monomer outside the tube. The diffusion of VDF across the membrane supplies the monomer required to sustain the reaction, carried out at 85 °C and pressure in the range of 5–15 bar. The flow rate of liquid inside the reactor was in the range of 0.03–0.12 mL/min. This pioneer work could stimulate new ideas and perhaps motivate researchers and companies to investigate on continuous processes.

2.3.2 | Mass Transfer in Emulsion Polymerization of VDF

Transfer limitations usually become non-negligible when one deals with multiphasic systems like emulsion polymerization with a gaseous monomer [9, 79]. This has been documented as the case when emulsion polymerization of vinylidene fluoride is carried out [3, 36, 59]. Several studies report that the measured rate of reaction changes under different speeds of agitation or even the choice of the impeller [36]. Mendez Ecoscia et al. [36] conducted experiments using two different impeller types and various agitation rates. The main conclusion they had was that type of agitators and rate of agitation play a significant role on parameters like the rate of polymerization, size of particles, and temperature control. The plot of the rate of polymerization with respect to different rates of agitation is reported in Figure 7.

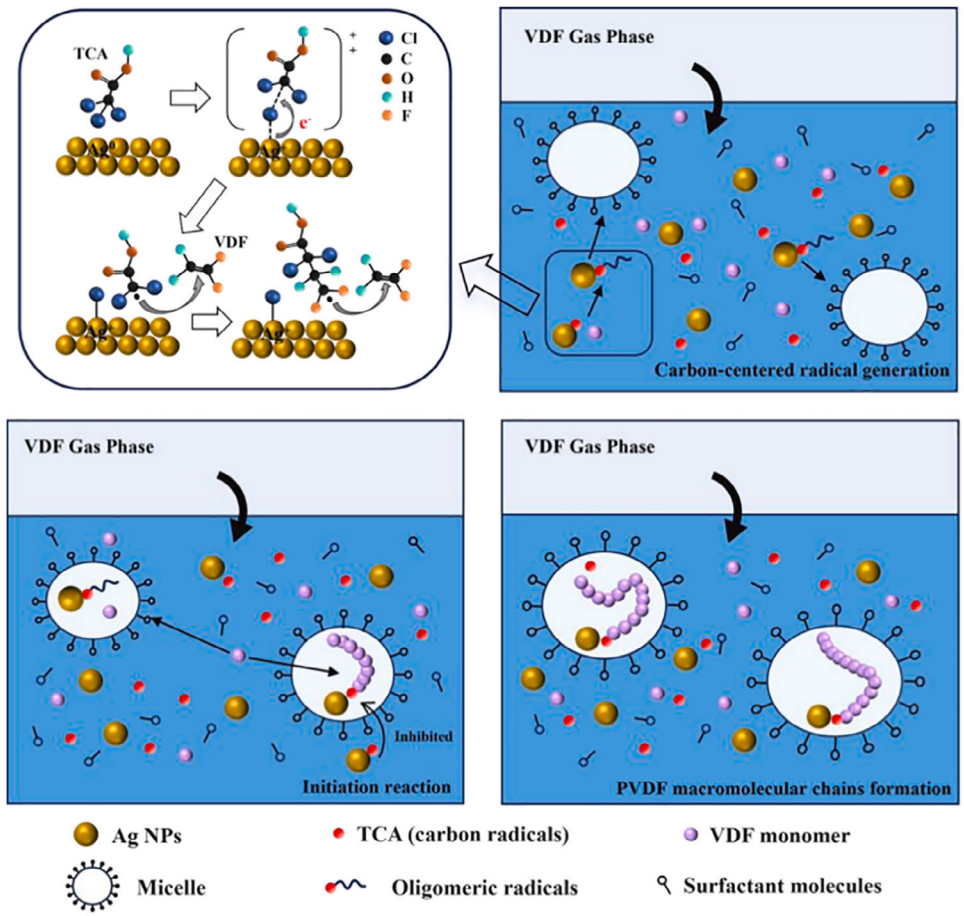

FIGURE 5 | Reaction scheme of ultrahigh molar mass PVDF reaction by Guan et al. Reproduced with permission from [74]. Copyright 2026, Elsevier.

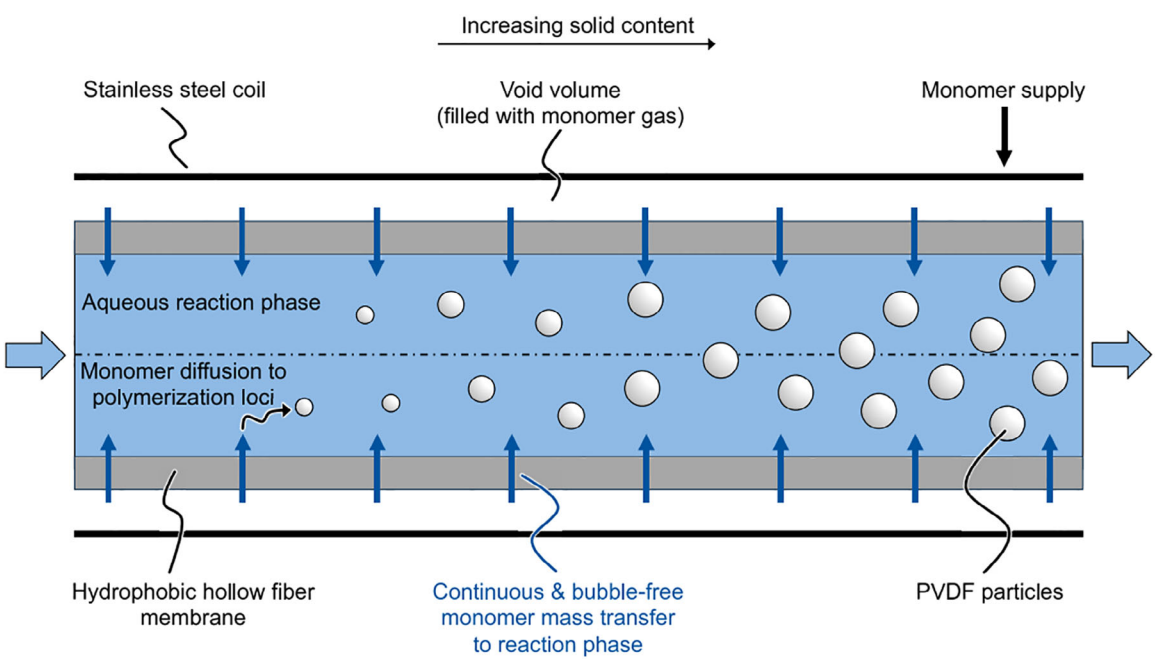

FIGURE 6 | Illustration of a continuous flow VDF emulsion polymerization reactor. Reproduced with permission from [79]. Copyright 2025, American Chemical Society.

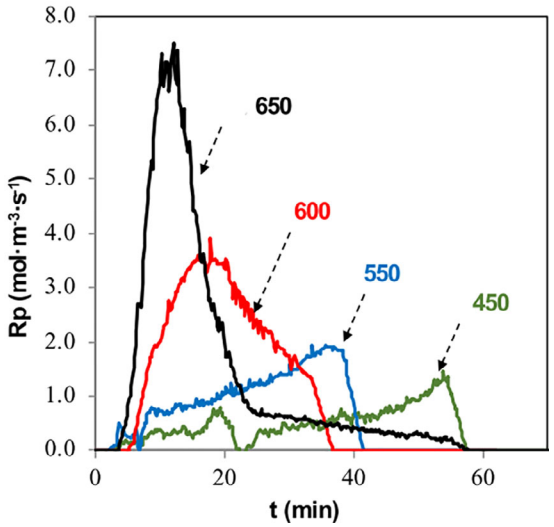

FIGURE 7 | Rate of polymerization with respect to rate of agitation (in rpm). Reproduced with permission from [36]. Copyright 2021, Wiley.

It is evident that, the lower the stirring rate, the lower the measured polymerization rate. This is attributed to mass transfer limitations from the gaseous to the liquid phase becoming the rate determining step, limiting the overall throughput of the process.

Torres Aladro et al. [3] conducted an experiment with a setup similar to that of Mendez Ecoscia. The authors tested three different impeller types at different agitation rates, however their experiment added additional topics of discussion for the mass transfer. They mentioned the number and the space between impellers also affect the mass transfer. When agitation takes place, impellers cause a vortex in the water. Their theory is that the size and shape of the vortex affects mass transfer significantly. To prove this, the reaction was conducted under different vortex conditions by changing the volume of water in the reactor, as shown in Figure 8. One important conclusion they had was that at 550 rpm, they could make mass transfer limitations almost negligible for their setup and recipe. This is achieved by the changes in the size and the shape of the formed vortex for one reference case (constant reaction recipe and same agitation setup). This same value of agitation speed is also reported by both Gelinski et al. [59] and Apostolo et al. [50] where they explicitly claim negligible mass transfer limitations.

One final comment on the mass transfer limitations is that they depend on many factors such as impeller type, number, rate of agitation, and spacing. Even though studies claim they had difficulties removing mass transfer limitations, as reported earlier in this subsection some researchers could make it negligible by playing with some of their operating conditions.

2.3.3 | Modeling Studies

The kinetics of the emulsion polymerization of vinylidene fluoride is still not well documented in the literature [40, 56, 50]. There could be several reasons behind that, among which the complex multiphase reacting system. Due to these difficulties, it is not an easy task to have a comprehensive description of the chemical events taking place in the aqueous and polymer particle phases [80]. However, due to the popularity of PVDF among other fluoropolymers and its industrial applicability, researchers from several academic institutions dedicated extensive effort to the description of its emulsion polymerization [6, 40, 59, 50]. The most established kinetic scheme considered in the literature is reported in Table 1.

In addition to the very typical initiation, propagation and bimolecular terminations, chemical reactions often reported during the emulsion polymerization of VDF are the chain transfer to monomer and to polymer. Both chain transfer reactions rely on the H abstraction from the $-CH_2-$ group. In case of chain transfer to monomer, the growing radical undergoes H abstraction. This, together with the termination by disproportionation, is responsible for the formation of unsaturated polymer chains with a characteristic terminal double bond (shown as $P_n^=$ in the kinetic scheme). These species with terminal double bonds, in turn, could undergo a propagation reaction, leading to the formation of long-chain branches. These branches are particularly relevant as, when their number becomes consistent, they may lead to high molar mass polymers and, eventually, to gel formation. On the other side, backbiting reactions may occur [6, 40, 50], leading to short-chain branches, not as critical as their long-chain counterparts.

Another comment about the termination reactions is that termination by combination is usually assumed to be dominant over termination by disproportionation [4, 6, 59]. However, some works [40, 50] claim their case to be the opposite (i.e. disproportionation is the dominant termination mechanism). In their work, Hanamirian et al. [40] give an explanation for the dominance of disproportionation reaction based on the experimental measurement of chain-ends.

Starting from this basic kinetic scheme, Pladis et al. [80] developed a model for a 30 L semi-batch reactor at a reaction temperature of 83 °C using potassium persulfate as initiator and a nondisclosed chain-transfer agent. Their model contains both differential and algebraic equations to describe reaction kinetics and the particle size distribution. They used the free-volume theory to calculate the gel effect. They also take the crystalline phase physics as well as partitioning of the monomer into consideration. It is mentioned that the polymerization occurs in the particle phase; however, they took consumption of monomer in the water phase into account as well. They compared the model predictions to properties such as rate of consumption of monomer and molar mass distribution. The authors concluded that conversion is affected by the addition rates of the initiator and the chain transfer agent, where the former is in favor of increasing the conversion and the latter provides an inverse effect. Almost a decade after the development of their model, the same researchers published another work [6] reporting the use of fluorinated surfactants, potassium persulfate as initiator, and ethyl acetate as a chain-transfer agent. The reaction was carried out at 83 °C and 85 bar in a semi-batch reactor. In this work, the authors developed and validated a comprehensive nucleation model for PVDF, considering homogeneous nucleation as the dominant mechanism. They proposed a simple equation, derived from the mechanistic approach of Hansen and Ugelstad [65], for the description of particle nucleation function of the rates of initiator

FIGURE 8 | Size and shape of vortex at different liquid volumes. Reproduced with permission from [3]. Copyright 2024, Wiley.

TABLE 1 | Kinetic scheme of emulsion polymerization of PVDF.

Initiation	$I_2 \xrightarrow{k_d} 2I^{\bullet}$
Propagation	$I^{\bullet} + M \xrightarrow{k_{pM}} R_1^{\bullet}$
	$R_n^{\bullet} + M \xrightarrow{k_{pM}} R_{n+1}^{\bullet}$
Chain transfer to monomer	$R_n^{\bullet} + M \xrightarrow{k_{fM}} R_1^{\bullet} + P_n^{=}$
Propagation to terminal double bond (TDB) [40, 50]	$R_n^{\bullet} + P_m^{=} \xrightarrow{k_{TDB}} R_{n+m}^{\bullet}$
Chain transfer to CTA	$R_n^{\bullet} + T \xrightarrow{k_{fT}} P_n + T^{\bullet}$
Chain transfer to polymer	$R_n^{\bullet} + P_m \xrightarrow{k_{fP}} R_m^{\bullet} + P_n$
Back-biting [6, 40, 50]	$R_n^{\bullet} \xrightarrow{k_{bb}} R_{n,MC}^{\bullet}$
Bimolecular termination (disproportionation) [40, 50]	$R_n^{\bullet} + R_m^{\bullet} \xrightarrow{k_{td,dis}} P_n^{=} + P_m$
Bimolecular termination (combination) [6, 59]	$R_n^{\bullet} + R_m^{\bullet} \xrightarrow{k_{td,com}} P_{n+m}$

consumption, terminations in water, monomer consumption in water, the rate of radical entry and the value of the critical chain length. Due to the amount of surfactant being smaller than the CMC, they claimed that the nucleation occurred by homogeneous nucleation mechanism. The key conclusion they had from their kinetic model in combination with a thermodynamic and a particle population model, which is validated through lab and pilot scale experiments, was the demonstration that the level of crystallinity of PVDF during the process strongly affects the rate of polymerization, the molar mass and the particle size distribution. More in detail, as crystallinity increases, radical concentration in particles, affecting the rate of reaction in a positive direction, starts decreasing first. However, after reaching the minimum of 0.68 radicals per particle around 35% crystallinity, it starts to increase up to 0.83 while the crystallinity reaches 50%. A similar "U-shape" like behavior is seen for the particle

size, which first decreases from 190.8 to 185.5 nm when the crystallinity goes from negligible values to 15%. However, as the crystallinity increases further to 50%, the average particle size experiences a decisive augmentation to 227.8 nm. On the other hand, the number average molar mass is almost constant with the crystalline content in the polymer, only slightly decreasing from 274 kDa at negligible crystallinity to 272 kDa when PVDF is 50% crystalline. Another important result showed that the addition policy of the chain transfer agent affects the molar mass as well as the concentration of radicals and the rate of polymerization. That means that the molar mass distribution can be tuned for the specific application of the material by simply changing the policy of addition of the chain transfer agent, with no major interventions on the process conditions and reaction recipe. In both of their works, the authors assumed that termination reactions occur by combination, while the extent of disproportionation is negligible. They also did not consider the propagation to terminal double bond (TDB) in their models, which, as discussed, is particularly critical in the formation of high molar mass chains.

Another important modelling work is from Gelinski et al., [59] who studied the emulsion polymerization of VDF in a semi-batch system in conditions similar to those of Pladis et al. [6]. The reactor they used was a 3.8 L stainless steel 316 reactor, equipped with jackets and three impellers of the six-bladed 45° type which are 5 cm in diameter, besides that a single hydrofoil with diameter of 9.1 cm, a thermocouple and a dip tube was present inside the reactor. The reaction mixture included the monomer, VDF, a nondisclosed surfactant, potassium persulfate (initiator) and ethyl acetate (chain transfer agent) and finally sodium acetate salt to buffer the continuous phase. The reaction temperature was the same as the one of Pladis et al., [6] namely, 83 °C with a pressure of 88 bar. Using this setup, the authors claimed that the optimal agitation speed to overcome mass transport limitations was 550 rpm. Indeed, the transport of a gaseous monomer to the reaction locus, that is, polymer particles, may represent a rate determining step in the process, with implications on the overall reaction rate, as it affects the monomer concentration in the particles, and, in case of co-polymers, on their composition. This aspect, therefore, should not be overlooked, in the direction of producing a polymer with the required properties. Their model considers only the initiation, propagation, chain transfer to monomer as well as to the transfer agent and termination reactions. The termination reactions, just like Pladis et al., [6, 80] are assumed to be taking place by combination only. A key difference between the works of Gelinski et al. [59] and Pladis et al. [6] is that the former included in the model mass transport limitations, which were also investigated experimentally, while the latter assumed chemical regime. This, in turn, took into account the surface crystalline fraction, as a property determining the rate of different chemical and physical processes, as the rate of coagulation for example. Also, the equation to calculate the number of particles is reported as a function of the particle density distribution in the work of Gelinski et al., [59] while for the model of Pladis et al. [6] a mechanistic equation was specifically derived, as mentioned earlier.

Apostolo et al. [50] developed a model for the copolymerization of VDF with hexafluoropropylene (HFP). The content of VDF was much higher than that of HFP, where the former was 79 mol% and the latter was only 21%. Given this large excess of VDF, their model uses the pseudo-homopolymerization approximation, which allowed them to use a single pseudo-kinetic rate constant for the reactions instead of having separate rate constants for the co-monomers (for example, instead of having two different propagation rate constants, for VDF and HFP propagation, they used a single pseudo-kinetic propagation rate constant). Thanks to the mentioned approximation, they solved the governing equations as if they were derived for a homopolymerization of PVDF. Hence, this work demonstrates how to simplify the governing equations for a copolymerization system through the introduction of averaged rate constants to consider the different nature of the comonomers. Of course, this approach is valid only when one comonomer is much more abundant than the other, so that the resulting polymer chain can be approximated to a homopolymer. The model equations are solved numerically by the use of the method of moments [81]. They compared the model results in terms of conversion, chain-ends, branches as well as average and molar mass distributions with experimental data. The important contribution of this work to the literature is the presentation of a trustable kinetic scheme with kinetic parameters evaluated in this work. The reactions reported in this work include initiation, chain transfer to monomer, to ethyl acetate (chain transfer agent) and to the polymer. A striking difference compared to the contributions discussed so far is that they assumed termination taking place only by disproportionation. Other than these, propagation to terminal double bond and backbiting reactions are included in their kinetic scheme. They evaluated the kinetic parameters of these reactions through fitting their model predictions to the highly detailed set of experimental data.

A very recent model published in 2025 is developed by Hanamirian et al. [40]. Their work investigates a system where only water, the initiator (di-tertiary-butyl peroxide) and the monomer (VDF) are present inside the reactor. They mention that the chain transfer agent (which is added as a separate species in other works) is formed inside the reactor by the decomposition of the initiator. It is worth mentioning their work because unlike the other mentioned studies, tracking only the chain length distribution of the polymer, their model is multidimensional. In other words, even though the population balance equations are solved using the method of moments [81] just like in the case of Apostolo et al., [50] two different properties of the polymer chains are tracked during the reaction time (or monomer conversion), specifically the length and the TDB content of each polymer chain. As of our knowledge, no other work related to polymerization of VDF followed this approach before. Tracking TDBs for their system is important for the final applications since, as already mentioned, TDB content of a chain affects its reactivity (high TDB content causes high reactivity of the chains) and processability, being the responsible of long-chain branches. Their model contains almost all the reactions reported in Table 1, with addition of a second chain transfer to monomer and a second backbiting reaction. The former is included because that reaction forms a TDB, which is important for their model to keep track as precise as possible. The latter reaction is included for the good predictions of chain-ends, more precisely for CH_3 and CF_2H type of chain-ends. Like the claims of Apostolo et al., [50] they consider termination reactions to occur only by disproportionation. In fact, while combination reactions lead to two chain ends derived from

initiator fragments, disproportionation causes only one initiator-related chain end, which was the experimental observation reported in this work.

2.4 | Suspension Polymerization of PVDF

Another process frequently used in the industry by companies such as Solvay [82–84] to produce PVDF is suspension polymerization. In this case, the produced polymer particles are characterized by larger size (larger than 50 μm), the polymer has higher crystallinity with high melting point and a relatively narrow molar mass distribution with respect to emulsion polymerization [37]. Another key difference is, unlike the emulsion polymerization, the rate of polymerization tends to slow down as larger molar mass polymer is produced [37]. In suspension polymerization, the droplets of monomer, where polymerization takes place, are dispersed in the water phase. The decomposition of the organic initiator inside these same droplets leads to the formation of free radicals that eventually propagate as growing polymer chains. The concentration of radicals per particle is typically much larger than in the case of emulsion polymerization, which causes the system to behave as a pseudo-bulk process. Due to the same reason, the rate of termination is large and chains with smaller molar mass are formed, and a narrow molar mass distribution is obtained [85].

The main reason behind using suspension polymerization is to limit the loss of polymer which is sticked to the walls of the reactor [57]. In this process, as mentioned earlier, no fluorinated surfactants are used. On the other hand, to keep the level of coagulation minimum, a water soluble suspending agent such as polyvinyl alcohol, or derivatives of cellulose are used [34, 37]. As initiator, organic peroxides find application and just like emulsion polymerization, the oil-soluble chain transfer agent controls the molar mass distribution of the polymer [34, 37]. In a conventional initiation system, the reactions are usually carried out at temperature and pressure values similar to those of emulsion polymerization [34]. The slurry, recovered from the reactor, contains large (usually 30–100 μm) PVDF particles suspended in water, the polymer can be obtained in powder form after some post treatment [34, 37].

Suspension polymerization is required when large particle size and more uniform, smaller sized chains, causing a narrow MWD, are desired. On the other hand, suspension polymerization includes more head-to-tail defects in the polymer chain. Therefore, applications where low concentrations of these defects is crucial, such as those requiring high resistance to temperature, should privilege emulsion polymerization over suspension polymerization [37].

2.5 | Solution Polymerization of PVDF

The third type of polymerization, which is not as common as the first two, is solution polymerization [86]. Some of the reasons of not having industrial applicability for solution polymerization compared to the emulsion and suspension polymerization is because of the necessity of a solvent that dissolves both VDF and PVDF. This kind of solvent is most often a fluorinated one, which is banned by the current regulation. In addition, polymer solutions are associated to very high viscosity, which limits the solid content achievable while ensuring processability. Also, a large amount of heat is produced during the polymerization process, and even though the used solvent can help to dissipate the produced heat, water used in the heterogeneous processes is a great source for that purpose [34]. Besides the peroxides, radiation can also be used to initiate or induce the reaction, which also serves to avoid contamination of PVDF with other reaction components [37].

3 | PVDF Properties

Properties of materials belong to two categories, namely, the physical and the chemical properties. The former relates to the characteristics which are not related to the chemical reactivity of the material under investigation, such as the melting and boiling points, color, density and so on. The latter is related to the transformation of a specific material to another one, which includes chemical reactions. PVDF properties, defining its application fields, are discussed in the following based on this classification.

3.1 | Physical Properties

PVDF is a nonreactive polymer comprising VDF repeating units, $-(CH_2CF_2)_n-$. It contains both amorphous and crystalline phases, hence it is a semicrystalline polymer [87]. The simplicity of the structure causes it to be a strong and a tough material, which is seen from the tensile strength (7.105 PSI) and the impact toughness (160–530 J/m) [15]. Besides these, it is known to have remarkable resistance toward creep and fatigue [15]. Depending on the application area, if a thin film or filament of PVDF (where PVDF becomes a transparent material) is used, the material achieves a flexible behavior. Other superior properties of PVDF compared to other materials include a large value of dielectric constant, high thermal stability, high strength as well as resistance to different weather conditions, UV, nuclear radiation and chemicals [88]. The crystal structure of PVDF is strongly affected by the sample preparation technique [15]. Some of the main physical properties are reported in Table 2.

PVDF has four polymorphs, namely, α, β, γ, and δ. Their schematic representation is shown in Figure 9. The first form (α) is a nonpolar and the most common phase which can simply be obtained from melt, while the remaining three forms (β, γ, and δ) are associated to permanent dipoles [15]. Out of these three, the polarity of the β-phase is higher than both γ and δ phases. It is known that a material made from α phase can be converted into δ once an electric field of about 100 MV/m is applied. Similarly, a β-phase material can be obtained if about 500 MV/m of electric field is applied on a material with δ-phase [90].

α-phase is the most stable one at room temperature. Even though it is mechanically strong, it does not exhibit piezoelectric properties [91]. That is why it finds applications mostly in areas where mechanical strength and chemical resistance are important. Some examples include structures like pipes, valves, coatings, and membranes. The β-phase has very strong

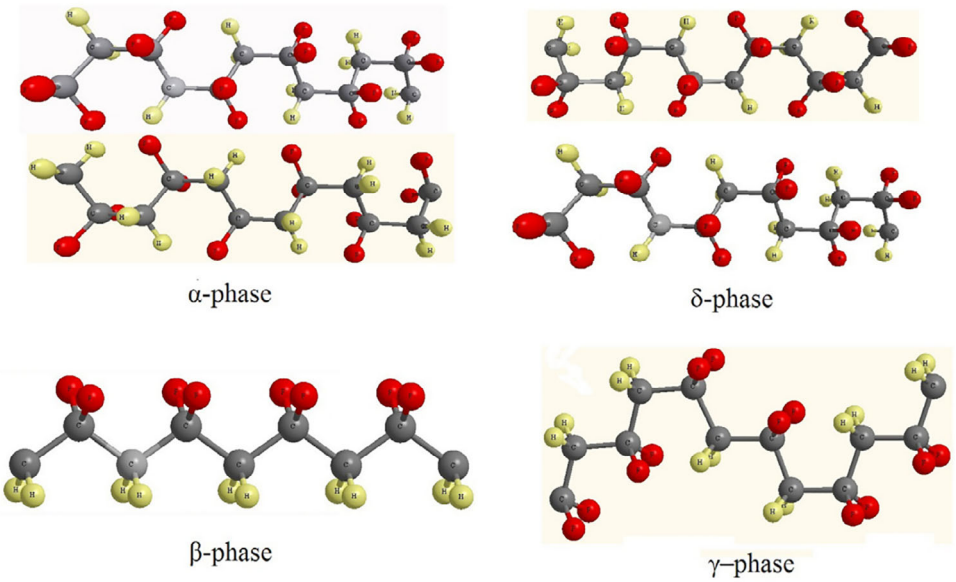

FIGURE 9 | Polymorphs of PVDF. Reproduced with permission from [91]. Copyright 2017, IOP Publishing.

TABLE 2 | Physical properties of PVDF [15].

Property	Value
Color	Colorless and opaque
Density (at room temperature)	1.77 g/cm^3
Melting point	177 °C
Glass transition temperature	−35 °C
Thermal stability	0.17–0.19 W/m-K
Crystallinity	50%–60%
Dielectric constant	5.6
Tensile strength (at 23°C)	35–55 MPa
Elongation (at 23°C)	25%–500%
Young's modulus (at 23°C)	1340–2000 MPa
Thermal expansion coefficient [89] (1/°C)	Around 0.0001
Processing temperature range (°C)	200-300

piezolecetric properties, it also has the highest dipole alignment among all the polymorphs. As such, it is very frequently used for electrical applications such as sensors and actuators. The γ-phase is found less commonly than the previously mentioned phases, and it has properties laying between the α and β-phases. It has high polarization and is used for capacitors and optoelectronic devices. The last phase, namely the δ-phase is formed under high electric fields and has ferroelectric properties. Because of that, it is used for applications where ferroelectricity is desired, such as microelectromechanical systems or thin-film electronics [92].

3.2 | Chemical Properties

PVDF, an organic polymer, is soluble only in a limited number of organic solvents [4, 15], although it is worth mentioning its solubility in a wider group of polar solvents compared to other fluoropolymers [11, 93]. A common approach to investigate the solubility of a material in different solvents is to use the Hansen solubility parameters [94]. The idea behind this theory is that a hypothetical sphere is drawn in the space defined by the dispersion (δ_D), polar (δ_P), and hydrogen bonding (δ_H) forces, whose centre and radius are specific features of the material of interest. More specifically, δ_D represents the dispersion interaction energy, δ_P is related to polar cohesive energy, and δ_H takes hydrogen bonding energy into account [95]. Every solvent has its own set of characteristic values for these same forces. Therefore, using the formula $R^2 = 4(\delta_{D,2} - \delta_{D,1})^2 + (\delta_{P,2} - \delta_{P,1})^2 + (\delta_{H,2} - \delta_{H,1})^2$ it is possible to estimate the distance R of the investigated solvent from the center of the characteristic sphere of the material of interest [94]. The subscripts 1 and 2 in this equation represent PVDF and the solvent of interest. The larger this distance, the poorer the compatibility of the two molecules. In fact, if the distance between the solvent and the molecule of interest is shorter than the Hansen's sphere radius, that is a good solvent for the molecule itself, while the molecule is insoluble in the solvent if this falls outside the sphere. The Hansen solubility parameters and the distance from the center of the sphere of PVDF and some common solvents are reported in Table 2. The value of the radius of the solubility sphere is reported in the literature as 5.0 MPa$^{0.5}$ for PVDF [95, 96]. Hence, any good solvent has to have a value of R smaller than 5.0 MPa$^{0.5}$.

Table 3 shows that the most suitable solvents for PVDF are dimethyl acetamide (DMAc) and dimethyl formamide (DMF), followed by acetone and dimethyl sulfoxide (DMSO). Another common solvent, tetrahydrofuran (THF), is not as compatible as the other solvents according to the solubility parameters presented in the literature (since the value of R is larger than R_0 of PVDF).

Besides these organic solvents, PVDF resins tend to be insoluble in several other solvents (alcohols, acids, bases, halogens, aliphatic compounds, etc.). This being said, due to lower levels

TABLE 3 | Hansen solubility parameters of PVDF and some common solvents [95–98].

Substance	δ_D (MPa$^{0.5}$)	δ_P (MPa$^{0.5}$)	δ_H (MPa$^{0.5}$)	R (MPa$^{0.5}$)
PVDF	17.2	12.5	9.2	R_0= 5.0
DMSO	18.4	16.4	10.2	4.69
DMF	17.4	13.7	11.3	2.45
THF	16.8	5.7	8.0	6.95
DMAc	16.8	11.5	10.2	1.62
Acetone	15.5	10.4	7.0	4.56

of crystallinity, the copolymers of PVDF [99–101] usually have higher solubility in several solvents compared to the homopolymer of PVDF [15]. The resistance (in terms of solubility) of PVDF toward several solvents, alcohols, acids, bases, and food products around room temperature (20 °C) and at a higher temperature (50 °C) up to one month are reported in the work of Saxena and Shukla [15].

Resistance of a polymer toward other chemicals (being chemically stable) is a very important property in order for the materials to be working with good performance over a long period of time [15]. Due to its superior properties mentioned earlier, PVDF is said to be one of the most resistant materials. Even though this is true for the contact with most of the materials, it is documented that materials made from PVDF tend to get weaker once they get into contact with strong alkaline solutions [102]. This is a major drawback for its implementation since alkaline solutions (NaOH solutions) are widely used in several applications [103].

Thermal stability is a highly important property especially for industrial applications, since polymeric materials are usually exposed to high temperatures during operations [15]. When talking about thermal stability, two separate parameters play a crucial role for determining the application limits of a material, namely the glass transition temperature and the melting temperature. The former is usually more important for amorphous polymers, while the latter for crystalline polymers. The glass transition temperature is related to brittleness or ductileness of a material. At temperatures below this value, the material tends to be brittle and easily breakable, while above that value, the materials are ductile and elastic. On the other hand, the melting temperature is the temperature for which phase transformation from solid state to liquid state occurs. The values of these specific temperatures for PVDF are reported in Table 2. PVDF shows changes in its chemical structure at temperatures below the glass transition temperature or above the melting temperature. It is also mentioned in the literature that the thermal decomposition occurs above 316 °C [15]. The process of thermal decomposition is usually measured by applying moderate to high temperatures on the polymer in the presence of vacuum (with no oxygen). The result of this kind of analysis showed that the thermochemical decomposition of PVDF takes place by dehydrofluorination, which either causes formation of a double bond between the carbons that contain CH_2 and CF_2 groups, or cause crosslinking between two separate PVDF chains (in this case one loses one H atom and the other one loses one F atom) [15].

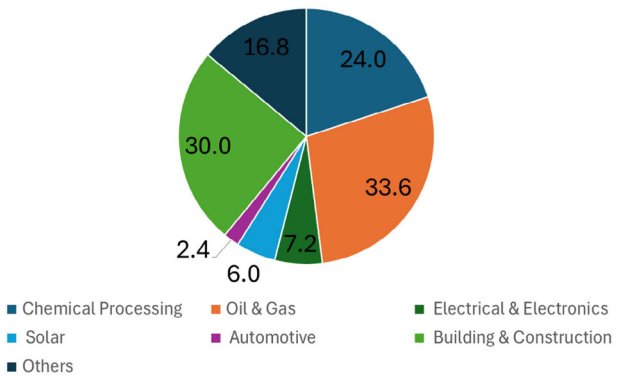

FIGURE 10 | End-user shares of PVDF materials in the industry for the year 2023 (labels in ktons/year). Data taken from [104].

4 | Industrial Applications for PVDF

Due to its appealing properties, materials made from PVDF find use in many areas. Figure 10 shows the end-user shares of PVDF materials in the industry for the year 2023.

By looking at Figure 10 it is clear that almost 50% of the user demands are in the fields related to chemical processing and oil & gas. Then, the favorable electrical properties of this polymer make it a requested material for electrical and solar applications. Finally, the good resistance makes it appealing in the field of coating and painting, mainly in the automotive and building & construction areas. Hence, various properties and structures allow different applications. For example, a branched polymer could be desired for adhesives but not for medical applications. These main applications are reviewed in details in the following sections, highlighting the advantages that made PVDF the material of choice as well as the points for improvement that could drive to a further expansion in its market share.

4.1 | Chemical Processing

One of the most common uses of PVDF is in the field of chemical processing equipment including tubes, valves and pumps [105]. Besides these, another important application area of PVDF is in the field of chemical separations, more specifically for the realization of membranes [4, 15, 23, 25, 106–112]. These applications require polymers with high chemical resistance and high mechanical strength, which puts PVDF on top places of the list of candidates [108]. Besides the resistance and strength, easy

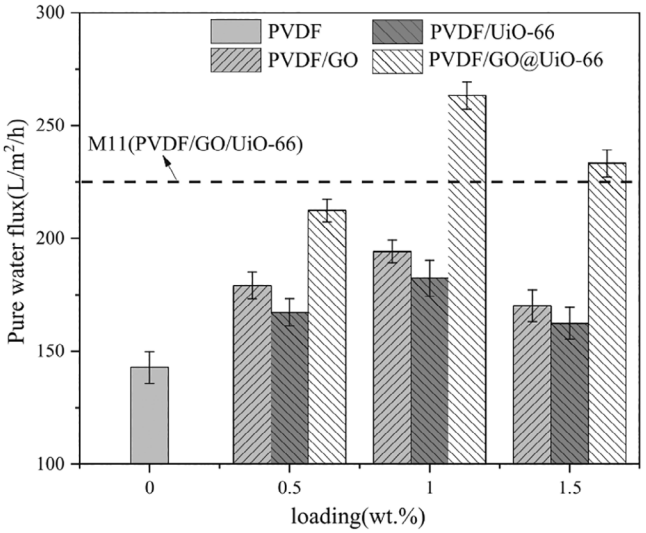

FIGURE 11 | Effect of additive amount on water flux for PVDF-based membranes. Reproduced with permission from [115]. Copyright 2021, Elsevier.

processability and being a highly durable material caused it to be frequently used for membrane applications. Several factors including the method of preparation, polymer composition or the used additives and solvent affect the membrane characteristics [113, 114]. For example, copolymers rich in VDF are claimed to increase the mechanical properties of the membrane, as well as its hydrophobicity, with decreased water flux [108]. PVDF membranes have been used for several purposes such as water treatment, oil-water separation, ultra and microfiltration among the others for many years.

One of the greatest challenges in the field of polymeric membranes is to achieve high permeability together with high rejection and resistance to fouling/ease of cleaning [115]. The research on this suggests that these properties could be achieved using nanocomposite membranes of PVDF. Liang et al. [115] carried out a study where they formed this kind of membranes with the use of graphene oxide (GO) nanosheets. They claimed that even with the use of small amount of the additives on PVDF membranes, they could reach much higher water flux compared to the pure PVDF, as shown in Figure 11. Not only this, they also improved the rejection ratio of the system they studied to 93% from 68%, while having good antifouling features. These results show promising future for PVDF nanocomposite membranes.

4.2 | Oil and Gas

The excellent chemical resistance of PVDF made it particularly valuable for the insulation of oil and gas transport pipelines as well as pressure sheath, which requires materials able to sustain high operating pressures [19, 116].

The performance of the pipes used for oil and gas transportation are significantly affected by the temperature, pressure and the acidity of the medium. Thermoplastic materials gained attention due to their resistance to corrosion. However, they have poor temperature resistance and some problems in the long run due to

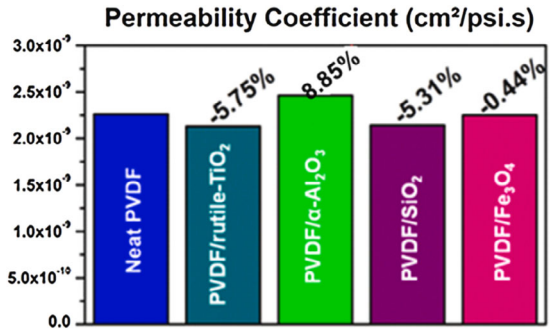

FIGURE 12 | Permeability coefficients of different PVDF composites. Reproduced with permission from [116]. Copyright 2020, Elsevier.

aging [117]. High-performance plastics, such as PVDF, are good alternatives to thermoplastics. Not a lot of sources investigate the behavior of PVDF tubes when in contact with gaseous and acidic oil environments. Qi et al. [117] tried to fill this gap by carrying out an experiment where they investigated the aging performances of the samples by changing temperature and the exposure time. They checked the effect of aging on properties such as size of the samples, mass, tensile properties and thermal stability. Their results showed important decrease of performance and some cracks of the material as the exposure time and temperature increased. This is showing the limit of applicability of PVDF, a very important result to make sure process conditions are not beyond the limits of the used material. This study could be used for determining the tube material based on the temperature and the duration of operation. Also, in order to provide a more general information, this study could be expanded to different pressures and different acidic mediums.

Another study [116] investigated the effect of adding nanoparticles, namely, rutile-TiO_2, Fe_3O_4, SiO_2, and α-Al_2O_3, to PVDF on mechanical, thermal, morphological, and chemical properties of the pipes. The addition of nanoparticles caused an increase of the β crystals, which is a sign of homogenization of the investigated nanocomposite. The results also showed a decrease in both the storage and the loss modulus (the decrease when α-Al_2O_3 was used was more significant than those with rutile-TiO_2 and SiO_2). They claim that, due to experimental results, the nanocomposites with rutile-TiO_2 and SiO_2 showed good potential in terms of the reduction of CO_2 permeability (shown in Figure 12), both decreased by more than 5%, and an increase of lag time. This is an important research because it could provide a solution to the aging problem due to operating parameters. Similar studies should be conducted with different additives and also different percentages in order to make the pipeline materials to resist any possible harsh conditions.

4.3 | Electrical/Electronical and Solar

PVDF materials are also commonly used for sensors [118–127], batteries [52, 128–131], and energy harvesting [32, 33, 132–138] applications due to their piezoelectricity [139], pyroelectricity, and nonlinear optical properties [15, 140]. Piezoelectric materials are the ones that allow the production of electricity from vibrational energy, hence an acoustic wave is transformed into an electric wave [135]. One noticeable example of the use of PVDF in

batteries is documented by Ren et al. [128]. The authors found that optimizing the phase ratio of the polymorphs of PVDF can have a significant effect on battery life. The optimization of the polymorphs is conducted using LiCl salt. In today's world, the need for long battery life is non-negotiable, and more and more research, including but not limited to, PVDF should be carried out on that topic.

Another point of attention is in the field of photovoltaic cells where PVDF is one of the key materials for the backsheets of these cells [141, 142]. Ahn et al. [143] carried out an experiment where they added PVDF-HFP copolymer on perovskite solar cells. The authors claimed that the fluorine atoms of the copolymer form strong hydrogen bonds with the perovskite. Their results showed that they achieved almost a 3% increase in the power conversion efficiency. They tested their solar cell in a vacuum environment to investigate if it is suitable for space applications and found that the solar cell still works at 70% of the initial power conversion efficiency even after 600 h. This showed the effect of the added copolymer on the stability and the performance. Similar research on PVDF additives could help to develop new areas, not only on space applications, but also for those where high stability is needed.

4.4 | Building and Construction

Last but not least, PVDF finds application in many different areas of the field of building and construction, especially in the coating and painting industry [144–148]. Due to the photostability and resistance, it is used for long lasting binding and weather resistant finish applications [34]. Indeed, the weather and corrosion resistant properties [144] made it to be the material of choice worldwide and it is even documented that PVDF coatings can resist up to 35 years of use in outdoor applications [149]. This has extreme importance for the users, as it is highly desirable to have structures that require very small amount of maintenance in years, and PVDF is the material of choice even at harsh conditions. Similarly, due to weather and chemical resistance, it is frequently used on the surfaces of cars and airplanes [4, 34].

5 | Future Perspectives

The previous sections aimed to show the most established application areas and advantageous properties of PVDF. These highlighted a bright future for fluoropolymers, and more specifically for PVDF. Reports show that the market share of PVDF is around 21% among the fluoropolymers for the year 2024, and it is expected to reach 24.5% by 2034. Given the anticipated growth mentioned in the beginning of the fluoropolymer industry, this change in the percentage represents a huge difference for the amount of PVDF produced [18]. This increase in the market demand will come from those fields that are currently facing challenges that fluorinated polymers may solve. Some possible examples come from the increasing necessity of corrosion and weather resistant coatings, flexible tubes which would find application in oil transport, high temperature wiring and insulation materials, biomedical applications, microporous membranes, and the increasing demand for lithium-ion batteries, where PVDF is one of the top choices as binder of the cathode [4, 11, 150–152].

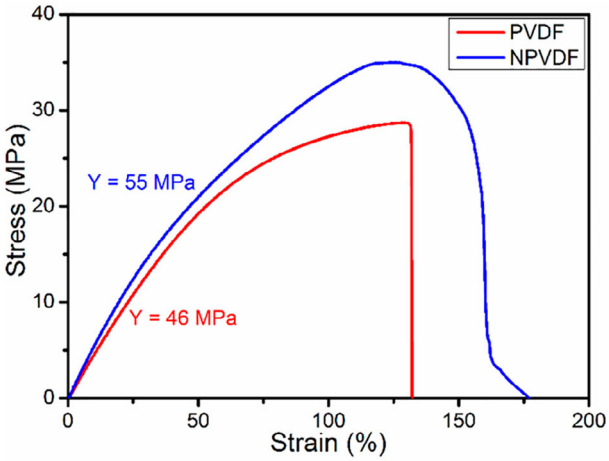

FIGURE 13 | Stress vs. strain curve for PVDF and Ni-MOF incorporated PVDF (NPVDF). Reproduced with permission from [154]. Copyright 2023 by the authors. Licensee MDPI, Basel, Switzerland. Article distributed under the terms and conditions of the CC BY license.

As already mentioned, PVDF is one of the most commonly used materials for the realization of microporous membranes, hence one can expect some developments and additional revenues from this field. To realize this latent potential, the research is exploring the integration of metal–organic frameworks (MOFs) for enhancing the separation capabilities, particularly welcome in wastewater treatment, membranes for desalination, and in dairy filtration [153–155].

Sasmal et al. [154] investigated the incorporation of Ni-MOF in a PVDF matrix. The authors mentioned that they could improve polarity significantly as well as Young's modulus compared to neat PVDF, which increased the performance for mechanical energy harvesting. In particular, the significant improvement on Young's modulus when incorporating Ni-MOF in PVDF can be appreciated in Figure 13.

Another research is done by Pisarenko et al. [155] They used electrospinning to incorporate different MOFs into PVDF and observed different crystalline phase behaviors with respect to the chosen metal. The main conclusion they had was that Cr-MOF and Zr-MOF incorporation showed capacity of fast adsorption, demonstrating the potential of MOF-PVDF hybrid membranes for applications like dye removal or wastewater treatment. An additional improvement is related to the fabrication techniques. Specifically, electrospinning is proposed for the fabrication of nanofibrous materials with large surface area and high β-phase fraction [155], highly desired for applications like sensors and energy harvesting, due to enhanced piezoelectric properties.

Another important expansion in the market share for PVDF may be directly connected to its piezoelectric properties. Only a few materials have such properties, and the piezoelectricity of PVDF is much stronger than that of any other polymer [105]. This property makes it a strong candidate for tissue engineering, surgical meshes, drug delivery, implants, and other medical applications [156]. The reason behind the applications of piezoelectric materials in these examples is because of the conversion of mechanical stresses into electrical signals, which is caused by the

structural asymmetry of the used material. Once a mechanical stress is applied, the material has an altered internal polarization, that is causing a surface voltage. This, in turn, can be used to stimulate cellular growth for tissue engineering, control drug release by electrically regulated mechanisms, promote cellular migration to have fast healing of a wound [157].

A recent study by Gryshkov et al. [158] investigated PVDF scaffolds in nerve engineering. The authors provided a comparative analysis of the PVDF electrospun scaffolds for the in vitro performance analysis as well as piezoelectric and structural properties for the first time. They evaluated the cytotoxicity and the performance on neonatal rat and human Schwann cells and they claim not to have any apparent cytotoxicity and good level of biocompatibility. Finally, thanks to the piezoelectric properties, scaffolds based on PVDF have promising applications in the field of artificial nerve development and repairments for nerve injuries.

Another application in the field of neural tissue engineering is carried out by Forouharshad et al. [159] The authors developed electrospun PVDF scaffolds to increase the efficiency in stem cell transplantation in order to regenerate cells for spinal cord injuries. Their study investigates the effects of incorporation of additives (such as self-assembling peptides) and different electrospinning techniques. They conclude their studies mentioning to have achieved uniform, thin fibers with high alignment and high hydrophilicity. These additives also result in an increase of the content of the electroactive phase. Finally, they claim their study opened a way for the development of electroactive scaffolds with good level of applicability in the field of neural tissue engineering. The aforementioned works related to bio applications of PVDF-based materials show low toxicity and high applicability, which is providing a motivation for carrying out similar studies.

Besides the medical applications, piezoelectric materials are useful for energy harvesting, that is why it is highly likely that PVDF will be used in sensors and other applications where energy harvesting is required [156]. Chamankar et al. [160] conducted a research on a pressure sensor based on PVDF fibers that are doped with lead zirconate titanate particles. They gradually increased the volume fraction of lead zirconate titanate (from 0.011 to 0.37 with 6 different samples) on the nanocomposite material formed by electrospinning. They analyzed the samples they formed and concluded that the formed ceramic-polymer nanocomposites allowed to improve the piezoelectric coefficient and dielectric constant proportionally with the fraction of lead zirconate titanate, which is important for the applications where harvesting of energy is aimed.

A very recent work by Devi et al. [161] followed a similar ideology. They constructed a nanocomposite film piezoelectric generator. They used PVDF matrix and barium strontium titanate. They fabricated the nanocomposites by solution casting method, and mentioned that the fraction of barium strontium titanate is highly related to the β-phase content (as mentioned earlier, this was the desired phase for piezoelectric properties), and the highest measured content of β-phase (of 41.8%) was obtained when the nanocomposite is formed by 10% barium strontium titanate. They also mentioned to reach an efficiency of 73.9%. For the dielectric constant, they observed an improvement at room temperature from 23 (pure PVDF) to 132 when 20% of barium strontium titanate was incorporated. The energy storage density showed an increase as well, as the barium strontium titanate increased without having a peak at intermediate content.

The works of Chamankar et al. [160] and Devi et al. [161] showed the improvements on the properties related to energy harvesting applications as the content of the additives changes. Both studies mentioned that PVDF is a highly desirable material, thanks to many factors including cost effectiveness and electrical properties. Following their ideas, new studies using different materials can be conducted to optimize a formulation for an application of interest.

Most of the research is currently conducted on a small size (and using small size models). In the future, the scale up of the fabrication strategies need to be investigated, to bring the mentioned novel applications for PVDF to industrial maturity. This being said, PVDF is an easily processible material, which could be produced in different shapes/forms, and different fabrication methods can cause it to have different final properties. Thanks to these differences, it could fulfil the requirements for many applications in terms of properties and the formed shapes. Therefore, it is highly likely that it will be a very frequently used material in the future [156]. At the same time, the expansion in the PVDF market cannot disregard the constantly evolving regulatory landscape. The most important turning point was introduced by the new law embodiment related to the use of perfluoroalkyl substances (PFAS), which led to a drastic change in the manufacturing processes for fluoropolymers. According to the definition of the Organization for Economic Cooperation and Development (OECD), PFAS are the fluorinated substances containing one or more completely fluorinated methyl (in form of $-CF_3$) or methylene (in form of $-CF_2-$) groups (not having any H, Cl, Br, or I atom connected to the carbon atom) [162]. The carbon-fluorine bond they contain, as mentioned before, is one of the strongest bonds in chemistry, which causes PFAS to be highly resistant to degradation. Indeed, many of them are known to be more persistent than any other synthetic chemical [163]. It is also documented that contaminations from these substances could travel far away from their source of release, and accumulate not only in the environment but also in food products and drinking water [163]. These contaminants are small molar mass oligomers (<1000 g/mol), less stable and more soluble in water than fluoropolymers, and typically include polar groups such as carboxylates ($-COO^-$) and sulfonates ($-SO_3^-$) [164]. With current technologies, it is both highly expensive and difficult to clean the polluted areas. Researchers claim that even if the release of PFAS is stopped today, their presence in nature will continue for generations [165]. At the same time, given their unique ability to repel water and grease, PFAS found large industrial application in the past years, mainly as surfactants [163, 165, 166].

Starting from 2009, the European Union (EU) proposed to limit the use of substances similar to PFAS with the regulations on "Persistent Organic Pollutants." Authorities from Germany, Norway, Denmark, Sweden and Netherlands have submitted a proposal to the European Chemicals Agency (ECHA) in 2023 to ban the usage of all the known PFAS completely unless their use is essential (there are no alternatives) for an application. The final decision on this proposal is expected to come in 2026 [165, 167].

The restrictions aim to reduce the environmental impact of PFAS, prevent damages on human health and encourage industrial companies to use safer alternatives.

The ideal solution, which is the main focus of research of many companies nowadays, is to develop new technologies for the manufacturing of fluoropolymers, such as the non-fluorosurfactant processes [68]. This initiative is currently exploring different alternatives to provide colloidal stability to the fluoropolymer latexes, by exploiting conventional surfactants or the electrostatic charges introduced on the polymer chains by the initiator fragments, to cite a few. On the other hand, since it is not likely to stop using such molecules with so large number of applications in a short period, a plan for the short term, not as environmentally friendly as the previously mentioned long term solution, is to shift the production to the locations where no major regulations limiting the production are present [168]. This is unfortunately a practice that is finding adherence, even though we recognize it cannot be a solution and efforts need to be concerted from both industry and academia to find viable alternatives to PFAS.

Among these alternatives, recycling and reuse of PVDF can be considered, although this is not an easy task either [169]. The thermal and mechanical properties of PVDF make recycling processes highly technical and expensive [170]. Some of the properties causing challenges in recycling are the polymer high density, tensile strength, and tensile modulus.

At an industrial scale, the most common approach to recycle is to use thermochemical defluorination. However, this comes with problems like corrosion for the pipelines and shortening the equipment operating life [169].

Unfortunately, there are not sufficient studies to conclude that the chemical and mechanical properties of the virgin PVDF could be preserved after recycling. One promising work is carried out by Veiga et al. [170]. The authors performed mechanical recycling on different samples and analyzed them through spectroscopy as well as thermal and mechanical tests. Their results showed no significant change of properties, hence they obtained highly promising results. This type of experiments should be continued in other research projects and the techniques proposed by the authors could represent important validation approaches to assess the potential of a specific recycling process.

Another innovative approach to recycling is to use a solution that selectively decomposes additives, fillers, and other components allowing to collect PVDF exploiting its high chemical tolerability. Morita et al. [171] investigated hydrolysis with the use of an alkaline solution on photovoltaic backsheets to decompose materials other than PVDF. However, this approach should be carried out with caution. In fact, as mentioned earlier, PVDF is sensitive to strong alkaline solutions, hence the concentration of the alkaline solution plays a crucial role to ensure the integrity of the polymer.

Liang et al. [172] described a procedure to recover PVDF micropowders from waste PVDF membranes. The process scheme proposed in this work is shown in Figure 14. The first step is the ultrasonic cleaning of the membranes, then parts of them are dissolved in DMAc that, as reported earlier in Table 3, is one of the most suitable solvents for PVDF. This solution is then added to water, which allows precipitation of PVDF powder that can be recovered by filtration. A second dissolution-precipitation cycle is then performed to further improve the purity of the recovered polymer. The solid powder of PVDF is once again dissolved in DMAc, this time with the addition of polyvinyl alcohol (PVA), and a precipitant solution containing deionized water and PVA is added on top drop by drop. The final mixture is centrifuged in order to separate DMAc and PVA leaving only the PVDF micropowders at the bottom of the centrifuge tube, with a yield of 83.5%.

Despite these early and mostly lab scale investigations, further experiments and research are urgently required to identify new and efficient recycling and reuse strategies to replace the traditional and poorly environmentally friendly approaches like landfilling [173]. These are expected to reduce the environmental impact of PVDF, mainly in the form of reducing PFAS emissions and reliance on fossil-derived raw materials for the synthesis of virgin polymer, altogether introducing important economic returns.

6 | Conclusions

Fluoropolymers are gaining attention worldwide due to their unique set of properties. As of the year 2024, their annual production reached 639,210 tons and this value is expected to grow in the future. The top two fluoropolymers based on worldwide production are PTFE and PVDF, respectively. The aim of this work was to provide a recent review for PVDF uses and manufacturing processes. Properties such as chemical and physical inertness, mechanical strength, easy processability, thermal resistance and ferroelectric properties enlarged its application areas to gas and oil transport, membranes, sensors, batteries, and energy harvesting.

On an industrial scale, PVDF is mainly produced by emulsion and suspension polymerizations, conducted at temperatures around 100 °C and a few tens of bar. A significant effort is being put in the understanding and rationalization of the multitude of chemical and physical events taking place in these heterogeneous processes. Modelling studies in the literature are contributing by providing a trustable kinetic scheme with reliable sets of rate parameters. They also showed that many factors can affect molar mass, particle size distribution, or the reaction rate, for example, the rates of addition of the chain transfer agent and initiator, or the crystallinity of the PVDF inside the reactor. The importance of these conclusions is that, given polymer properties of interest (such as molar mass or particle size), one can use these models to predict experimental conditions that will produce the required polymer grade, reducing the process development burden, which is significant for a molecule known for its flammability and toxicity. Another result from these studies showed that the polymerization system could have strong mass transport limitations, that is why the choice of stirring rate and the stirring equipment plays a crucial role on approaching the chemical regime. So far, the large majority of the modelling studies available tracked with precision the chain length distribution of the polymer produced, describing other important properties like chain ends and number of terminal double bonds through average values. To improve the precision in the description of the polymer microstructure, higher order models are raising,

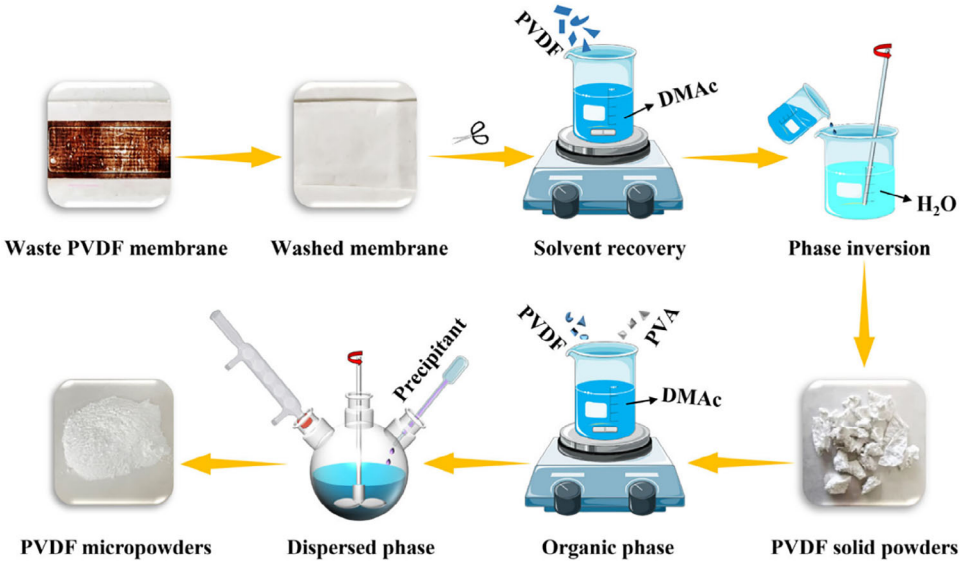

FIGURE 14 | An example scheme of recycling of PVDF materials. Reproduced with permission from [172]. Copyright 2023, Wiley.

allowing to track the distribution of multiple properties with the progress of the reaction. Despite the higher computational demand, these models are able to provide a better picture of the heterogeneity of the polymer, which strongly impacts its final properties in application.

As a final conclusion, it is expected that PVDF will be used for many applications in the future as well. Studies especially stress that applications related to the piezoelectric properties of this material, such as the realization of medical devices and sensors, are going to continue to grow in the future. The aspects where the researchers have to focus on in the close future are related to the scale-up of the fabrication processes and to their sustainability. Regulations on the use of PFAS are stimulating the development of greener manufacturing processes, avoiding the use of fluorosurfactants. In this direction, academia and industry need to work side by side to come up with sustainable processes that are able to preserve the unique properties of these fluoropolymers.

Author Contributions

B.H.: Investigation, data curation, writing – original draft; G.S.: writing – review & editing, supervision; M.S.: writing – review & editing, supervision, project administration.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

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