

# HEREROGENEOUS POLYMERIZATION OF VINYLIDENE FLUORIDE IN $scCO_2$ IN THE PRESENCE OF PEFLUOROPOLYETHER SURFACTANTS

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**ABSTRACT:** heterogeneous polymerization of vinylidene fluoride (VDF) has been investigated in  $scCO_2$  in the presence of different perfluoropolyether surfactants using DECP as free radical initiator. When carboxylate perfluoropolyether was used higher monomer conversions were obtained with respect to precipitation processes. PVDF was collected at the end of the process under the form of a white powder and SEM analyses of the product have shown the existence of two different morphology: spongy coagulum and spherical particles. Preliminary results suggest that, in the case of ammonium carboxylate salt, the amount of particles increases when the initial concentration of the surfactant is augmented.

## INTRODUCTION

Free radical polymerization of fluorinated monomers is a crucial synthetic route for the preparation of macromolecules with excellent chemical resistance, high thermal stability, low dielectric constant and dissipation factor, unusual surface properties, low water absorptivities, excellent weatherability and low flammabilities.

Fluoropolymers are usually obtained by emulsion or suspension polymerization in aqueous systems. Owing to the adopted aqueous initiators unstable carboxylic acid and acid fluoride end groups are generated which must be removed before processing the polymer melt.

A possible way to reduce the level of thermally unstable end groups is the use of aprotic solvent such as CFCs or perfluorocarbons, perfluoroalkyl sulfide and perfluorinated cyclic amines which however are too expensive and/or not environmentally friendly [1].

In this context a sustainable alternative to such VOCs is constituted by dense  $CO_2$ , a low cost non-toxic solvent, inert to chain transfer reaction in free radical polymerization processes, which can be easily used both in the liquid state and in the supercritical region where medium density can be continuously changed from vapor-like to liquid-like values thus allowing the modification of chemico-physical and transport properties of the reaction medium.

$CO_2$  is a good solvent for most vinyl monomers but is an exceedingly poor solvent for most high molar mass polymer. Owing to this solubility consideration carbon dioxide has been used as a free-radical homogeneous polymerization media only for highly fluorinated amorphous polymers[2] while heterogeneous techniques have been adopted in the case of other vinyl monomers as reported in a recent exhaustive review [3].

In addition to solubility consideration a further relevant feature of dense  $CO_2$  to be taken into account is its capability of swelling polymers thus lowering their glass transition temperature ( $T_g$ ). This effect is particularly relevant in heterogeneous processes where polymer coagulum are formed as, by increasing the value of the diffusion coefficient of the monomer inside the coagulated particle, it allows the progression of the polymerization up to high value of monomer conversion.

Poly(vinylidene fluoride) (PVDF) is the second most important thermoplastic within the fluoropolymer family after poly(tetrafluoroethylene) PTFE. Even if thermal and chemical stability of PVDF are somewhat lower with respect to PTFE the hydrogenated polymer can be easily processed on conventional equipment thus leading to advantageous compromise between quality and price.

The synthesis of PVDF by precipitation polymerization in scCO<sub>2</sub> has been already investigated both in batch [4] and in continuous stirred tank reactor [5,6]. Apart from the limited monomer conversion an important drawback which can prevent the scale-up of the process to industrial plant is the flowability of the polymer particles that can block the lines largely increasing the complexity in the management of the production plant. To avoid this possibility and to improve the performances of the polymerization it could be appealing the use of suitable surfactants to stabilize polymer particles thus changing the process from precipitation to dispersion or microemulsion.

In this context we have investigated the effect of different highly CO<sub>2</sub>-philic perfluoropolyether carboxylate salts on the performances of VDF polymerization and on the morphology of collected polymer.

## MATERIALS AND METHODS

Vinylidene fluoride monomer was kindly donated by Solvay Solexis; CO<sub>2</sub> was Air Liquide 99.998 pure. Both chemicals were used without further purification. The perfluoropolyether salts tested as stabilizers were supplied from Solvay Solexis (Bollate, Italy) and their formula is here reported:



Fluorolink FLK 7004A  $M_n = 920$ , H<sub>2</sub>O 1.0 % w/w



Fluorolink FLK Ca  $M_n = 920$  for each macroanion, H<sub>2</sub>O 1.0-2.0 % w/w

All other chemicals were obtained from Aldrich and used as received.

The DEPDC initiator was synthesized, according to a procedure supplied by Solexis, using water as the solvent and extracting the peroxydicarbonate into Freon 113 (HPLC grade). The concentration of active peroxide in the solution was determined by iodine titration technique, ASTM method E 298-91. All manipulations of the initiator solution were performed at 0°C and the final product was stored under dark at -22°C.

Experiments have been carried out in a stainless steel reactor (total volume 32 cm<sup>3</sup>) heated by a water bath controlled by a PID based cascade control system. The reactor is equipped with a Pt-100 temperature sensor and a pressure transducer whose signals are continuously recorded together with the temperature of the water in the bath.

Polymer morphology was analysed and imaged with a Philips scanning electron microscope (SEM). Samples were sputter coated with gold to a thickness of ~200 Å.

Polymer yields were determined gravimetrically.

## RESULTS AND DISCUSSION

The batch polymerization of VDF was performed at 50°C in the presence of different perfluoropolyether stabilizers with an average density of the polymerization mixture of about 0.85 g/mL and an initial monomer concentration fixed to 3.5 mol/L.

Experimental results are summarized in Table 1 where are also reported the results of a precipitation polymerization used as a reference.

When the stabilizer was present a faster polymerization kinetics was obtained as indicated by the higher values of yields determined at the same reaction time.

In all the experiments the polymer was collected under the form of a white powder but when analyzed by SEM different morphologies were observed. In the case of the polymer synthesized by precipitation a spongy structure was recognized (Fig. 1a). Upon addition of the perfluoropolyether Ca salt the comparison of a limited number of spherical particles was observed (Fig. 1b). When FLK 7004A was used as stabilizer the spherical aggregates increased in numbers and their statistical occurrence become comparable with that of the coagulated polymer.

**Table 1.** Batch polymerization of VDF in the presence of different stabilizers.

Surfactant (% w/w) <sup>a</sup>	$P^{\circ}$ (MPa)	$\Delta P$ (MPa)	Yield (%)	Product morphology
---	28.3	2.7	21	powder
FLK 7004A (5.0)	26.8	3.1	35	powder
FLK Ca (5.0)	22.6	3.4	30	powder

<sup>a</sup> Based on the monomer. VDF concentration 3.5 M; DEPDC concentration 5.5 mM; T=50°C; CO<sub>2</sub> added in such amount to reach the density of 0.85 (±0.02) g/mL; reaction time 180 min.  $P^{\circ}$ : initial pressure;  $\Delta P$ : final pressure drop.

In the case of FLK 7004A we have investigated the effect of the perfluoropolyether concentration on the performances of the polymerization. When the polyether concentration was increased higher yields were obtained and the amount of spherical particles increased even if residual amount of coagulated polymer was detected also at the highest adopted concentration of the stabilizer.

**Table 2.** Effect of FLK7004A concentration on the polymerization of VDF in scCO<sub>2</sub>.

FLK 7004A (% w/w) <sup>a</sup>	$P^{\circ}$ (MPa)	$\Delta P$ (MPa)	Yield (%)	Product morphology
2.5	26.9	2.0	17	powder
5.0	26.8	3.1	35	powder
10.0	26.6	4.2	42	powder

<sup>a</sup> Based on the monomer. VDF concentration 3.5 M; DEPDC concentration 5.5 mM; T=50°C; CO<sub>2</sub> added in such amount to reach the density of 0.85 (±0.02) g/mL; reaction time 180 min.  $P^{\circ}$ : initial pressure;  $\Delta P$ : final pressure drop.

## CONCLUSION

Perfluoropolyether carboxylate salts have been tested as stabilizers in the heterogeneous polymerization of VDF. When polymerization was performed in the presence of polyethers a faster kinetics was obtained testified by an increase in the polymer yield at fixed reaction time. More interestingly, a clear modification in the morphology of the collected powder was

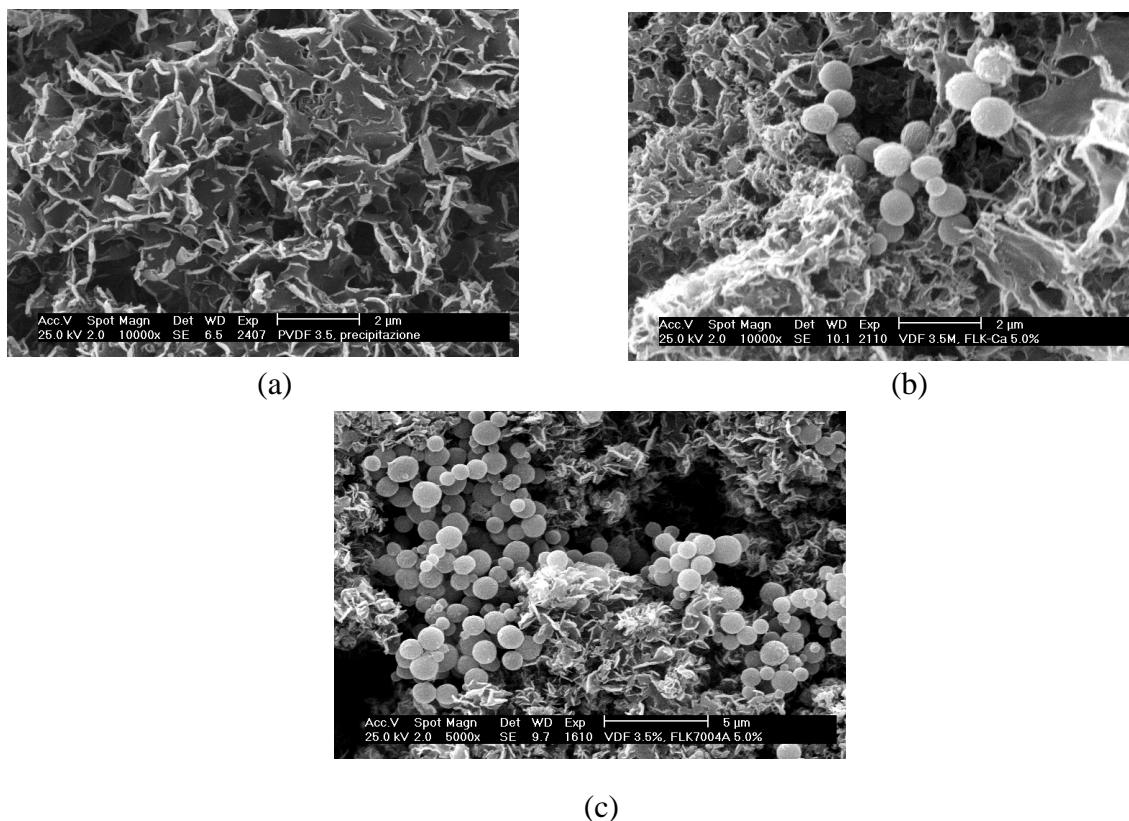


Figure 1. SEM micrographs of PVDF powder synthesized in supercritical carbon dioxide. Operative conditions as in table 1. (a) precipitation polymerization, (b) FLK Ca, (c) FLK 7004A.

observed when FLK 7004A was used. In fact, apart from the coagulated spongy structure typical of a precipitation process, spherical particles were observed by SEM analyses. The amount of spherical particles increased when the initial concentration of FLK 7004A was increased. This preliminary results suggest that perfluoropolyether carboxylate salts can exhibit interfacial activity in the polymerization of fluorinated monomers.

#### ACKNOWLEDGEMENTS

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