

# PRECIPITATION COPOLYMERIZATION OF VINYLIDENE FLUORIDE AND ACRYLIC ACID IN SUPERCRITICAL CARBON DIOXIDE

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**Abstract:** the free radical copolymerization of vinylidene fluoride (VDF) and acrylic acid (AA) was carried out in supercritical carbon dioxide using a precipitation technique in the absence of any surfactant. Formation of a copolymer was confirmed by NMR spectroscopy. Synthesized materials are going to be tested as matrixes for the preparation of pH sensitive biofiltration membranes.

## INTRODUCTION

Fluoropolymers exhibit outstanding chemical and thermal stability, excellent weatherability together with good mechanical and dielectric properties.[1]

Among these polymers, poly(vinylidene fluoride) (PVDF) is particularly interesting as it joints aforementioned properties with biocompatibility and a much easier processability with respect to its perfluorinated homologue. For these reasons PVDF is widely used in the chemical and petrochemical industry, in electronics and biomedical applications. In particular VDF copolymers have been proposed for the manufacture of materials that are particularly adapt to be used in the preparation of pH sensitive membranes. For these applications it could be very interesting to impart to the fluorinated matrix stimuli responsive capabilities such as sensitivity to pH variation. This could be accomplished by adding acid or base functionalities on the polymer chains.

An interesting method to reach this goal was based on the precipitation of the fluoropolymer, dissolved in N-methylpyrrolidone (NMP) or N,N-dimethylformamide, by ozone treatment. After precipitation and drying, the peroxide containing PVDF is redissolved in NMP and reacted in homogeneous phase with acrylic acid (AA) or 4-vinylpyridine [2,3]. This method is anyway based on the utilization of low volatile toxic solvents that must be thoroughly removed from the polymer before its utilization in biomedical applications.

In the last decade the synthesis and modification of fluoropolymers using supercritical carbon dioxide (scCO<sub>2</sub>) as a solvent and swelling agent has been intensively studied [4]. Dense CO<sub>2</sub> is a dispersing medium particularly interesting for the synthesis of fluoropolymers given its inertia to highly electrophilic fluorinated radicals. Moreover when it was used to perform copolymerization of fluorinated and hydrocarbon monomers it was observed a marked decrease of chain transfer reactions occurring in conventional liquid systems probably owing to the faster mass transfer kinetics of comonomers inside polymer coaguli [5].

Prompted by these considerations we have investigated the precipitation copolymerization of VDF and AA in supercritical carbon dioxide to evaluate the possibility of using such route to prepare a copolymer with architecture adapt to be used in the preparation of pH sensitive membranes for biomedical applications.

## MATERIALS AND METHODS

Vinylidene fluoride monomer (VDF) was kindly donated by Solvay Solexis; CO<sub>2</sub> was Air Liquide 99.998 pure. Acrylic acid (AA) was purchased from Aldrich. All chemicals were used without further purification.

The DEPDC initiator was synthesized, according to a procedure described in the literature [6,7] 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.

Polymerizations were carried out in an AISI 316 fixed volume (27 mL in the completely assembled set-up) batch reactor, stirred by a magnetic bar and inserted in an automated control system of the temperature as described elsewhere [8]. The proper amounts of AA were charged in the reactor, the vessel was then purged by a controlled flow rate of CO<sub>2</sub> maintained for at least 20 min to remove air. After sealing the reactor, VDF was added at room temperature, by using ISCO syringe pump. The vessel was then inserted in the control system and heated at the reaction temperature (50°C). After, liquid CO<sub>2</sub> and initiator, the latter under the form of liquid solution in Freon 113, were added by an air driven Maximator pump. The temperature  $T_r$  and pressure  $P_r$  of the polymerization mixture were recorded together with the temperature of the heating water bath  $T_w$ .

At the end of polymerization the reactor was cooled down to room temperature by changing the set-point of the control system (cooling time from 50 to 25°C about 15 minutes) and slowly depressurized. After drying under vacuum at room temperature overnight the polymer was weighted and stored in a dry atmosphere without further treatments.

The prepared copolymers were characterized by NMR spectroscopy, scanning electronic microscopy, X-ray diffraction and DSC analyses.

## RESULTS

The free radical copolymerization of vinylidene fluoride (VDF) and acrylic acid (AA) was carried out in supercritical carbon dioxide using a precipitation technique in the absence of any surfactant. Prior polymerization experiments the phase behaviour of the CO<sub>2</sub>/comonomers system was investigated by coupling visual observation of the mixture to the recording of the pressure trend inside a fixed volume view cell, as a function of the temperature during the slow heating and cooling of the system, according to a procedure elsewhere described [8]. At room temperature all the investigated systems are constituted by two fluid phases, which merge into a single one, during the heating cycle.

Then, it was studied the effect of the feed composition on the precipitation copolymerization of VDF and AA changing the relative amount of the comonomers, at fixed total density of the reaction mixture (0.90 g/mL), by keeping constant the amount of VDF and increasing that of the AA (Table 1).

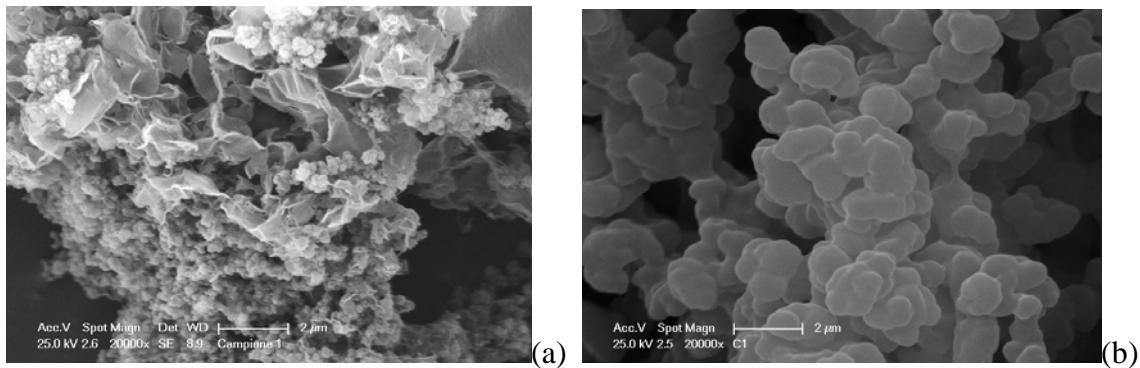
Formation of a copolymer was confirmed by HSQC NMR spectroscopy. The copolymer composition, estimated through NMR spectroscopy, maintained close to the initial feed composition.

All samples collected in the form of a white powder, were also analyzed by SEM analysis. In the case of pure PVDF synthesized without surfactant we observed sponge like portions and some particle with irregular shape. The same morphology was observed in copolymers prepared at lower AA concentration in the feed (Figure 1a). When the AA content increased, the morphologies of the copolymers became more similar to that of agglomerated single particles (Figure1b).

**Table 1.** Precipitation copolymerization of VDF and AA: effect of the feed composition.

Entry	f	P <sup>0</sup> , MPa	Yield,(%)	F
1	0.00	25	72 <sup>a</sup>	---
2	0.10	24	25	0.13
3	0.20	24	28	0.20
4	0.30	26	36	0.37
5	0.40	26	33	0.40
6	---	25	82 <sup>a</sup>	---

DEPDC iniizator concentration 0.5 mM; CO<sub>2</sub> added in such amount to reach the density of 0.90 g/mL; T= 50 °C. Reaction time 120 min. f: initial molar ratio of AA to VDF in the feed, entry 6 was a homopolymerization of AA. F: molar ratio of AA and VDF repeat units in the copolymer (C<sup>13</sup>-NMR determined). P<sup>0</sup>:initial pressure. <sup>a</sup>Reaction time 240 min.



**Figure 1.** SEM micrographs of: (a) entry 2, table 1; (b) entry 5, table 1.

The crystallinity of the synthesized copolymers was studied by XRD and DSC analyses. Comparison of the XRD patterns of copolymers with those of pure PVDF and PAA revealed some differences. The diffraction peaks of pure PVDF clearly indicate that this polymer is semi-crystalline. The diffraction pattern of PAA does not show any characteristic crystalline peak, indicating that the polymer is amorphous. At lower AA monomer loading, poly(VDF-co-AA) still retains the semi-crystalline nature of PVDF. When the AA content in the feed composition increased, diffraction peaks gradually broadened, until the samples became completely amorphous. These results were confirmed by DSC analyses. The observed trend of the crystallinity can be considered a further element confirming the formation of a copolymer.

## CONCLUSION

Acrylic acid and vinylidene fluoride were copolymerized in supercritical CO<sub>2</sub> by a free radical mechanism without the use of a surfactant. HSQC NMR was used to confirm the formation of copolymers and to estimate their compositions.

The crystallinity of the copolymers decreased with the increase of the AA content in the feed compositions, as shown by XRD and DSC analyses.

Synthesized materials are going to be tested as matrixes for the preparation of pH sensitive biofiltration membranes.

## ACKNOWLEDGEMENTS

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