Effect of Interfacial Area on Heterogeneous Free Radical Grafting of Vinyl Monomers in Supercritical Carbon Dioxide: Grafting of Acrylic Acid on Poly(vinylidenefluoride) Nanoparticles

Sonia Lanzalaco, Onofrio Scialdone, Alessandro Galia

Dipartimento Ingegneria Chimica Gestionale Informatica Meccanica, Università di Palermo, Viale delle Scienze Ed.6, 90128 Palermo, Italy

Correspondence to: A. Galia (E-mail: alessandro.galia@unipa.it)

ABSTRACT: The role of the polymer interfacial area on free radical grafting of acrylic acid (AA) onto poly(vinylidenefluoride) (PVDF) was studied at 65°C using supercritical carbon dioxide ($scCO_2$) as a solvent and swelling agent, benzoylperoxide (BPO) as chemical initiator and PVDF nanoparticles as polymer matrix. Under adopted conditions PVDF particles do not melt neither dissolve in the reaction medium and FTIR analyses performed on carefully washed nanoparticles confirmed the achievement of high grafting levels. The mass fraction of grafted AA increased with the grafting time and the BPO concentration while it decreased when the density of the fluid phase was enhanced. Collected results suggest that the grafting level obtained by free radical grafting of vinyl monomers onto solid polymer in $scCO_2$ can be significantly enhanced by increasing the interfacial area of the matrix. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41541.

INTRODUCTION

Poly(vinylidenefluoride) (PVDF) exhibits excellent mechanical and physicochemical properties somehow similar to those of polytetrafluoroethylene (PTFE) but with much easier processability with respect to its perfluorinated homologue. It has found widespread industrial applications and research interest.[1,2] For example, PVDF membranes are suitable for carrying out microfiltration (MF) and ultrafiltration (UF) due to their outstanding chemical resistance, well-controlled porosity and good thermal properties.[3] Moreover, this polymer is also frequently used in bio-medical application owing to its good biocompatibility. Klinge et al., for instance, have studied the utilization of nets constituted by PVDF monofilaments as a repair tissue in the walls of abdominal hernias.[4] Tissue contacted with the PVDF net showed significantly lower inflammation and fibrosis in comparison with those treated with polypropylene-based nets. Moreover, the physiologic reaction was found to be slightly affected by the amount of material that is a clear indication of improved biocompatibility.[4]

On the other hand, the use of PVDF membranes in biomedical applications is somehow limited by the hydrophobicity of their exposed area. For example, fouling of the membrane surface as well as within the pores occurred when such membranes were used for filtering protein-containing solutions.[5] Consequently, chemically and physically modified hydrophilic PVDF membranes have been widely studied in recent years.[6–8] Several approaches have been developed to confer hydrophilicity to conventional hydrophobic membranes, including coating and grafting techniques.[5] In the former approach, the membrane is introduced into a solution of polymer functionalized with hydrophilic groups.[9,10] Alternatively, covalent immobilization of hydrophilic species onto membrane surface can be achieved by either surface grafting of hydrophilic polymers or surface graft copolymerization between the membrane and dissolved hydrophilic monomers or macromonomers.[11–15] For instance, acrylic acid (AA) has been grafted onto the surface of PVDF membranes to endow hydrophilic and pH-sensitive properties.[8,16] Worth noting, both methods present some drawbacks. In the former one, the coatings tend to be loose and may become easily detached under some conditions.[5,17] As for the second method, changes in membrane pore size as well as in pore size distribution have been reported, thereby reducing the membrane permeability.[18] Also, the grafted chains may not be homogenously distributed on both, the membrane surface and the pore surface.[5,17] Therefore, bulk or chain modification of PVDF

arises as a promising alternative to overcome some of these problems, thus allowing the preparation of membranes with the desired properties.

Supercritical carbon dioxide (scCO$_2$) has been investigated as processing medium to modify PVDF membranes by free radical grafting.[19–21] The utilization of dense CO$_2$ allows working in the absence of any toxic solvent as well as the preservation of the original morphology, since the modification process is performed without dissolution of the polymer matrix.

Supercritical carbon dioxide has been successfully used also as dispersing medium to perform heterogeneous free radical polymerization of VDF.[22–27] When the polymerization is carried out in the presence of effective surfactants micron-size polymer particles are generated since the polymer is highly insoluble in scCO$_2$. When high enough total interfacial area of the polymer phase is reached in the reactor the main polymerization locus is constituted by the polymer particles since free radicals generated in the less viscous continuous medium are trapped by the PVDF particles before they are terminated and there propagates using monomer replenished from the fluid phase.[28]

Prompted by these considerations, in the present work, we have studied the modification of commercial nanoparticles of PVDF with AA polymer side chains attached to the fluorinated backbones by molecular graft copolymerization using scCO$_2$ as reaction medium. The study was performed using Hylar 461 PVDF synthesized by suspension polymerization in aqueous system that is already used in its native form for the preparation of micro-filtration membranes and it is constituted by spherical nanoparticles with sub-micron average size and crystallinity lower than 40%.[29]

Aim of this research was to test the possibility of using such a high specific area matrix to reach high grafting level of AA on the polymer backbone thus obtaining the preparation of a modified material that could be mixed with as-polymerized PVDF to impart hydrophilicity to the final membrane.

EXPERIMENTAL

Materials
PVDF used in this study is Hylar 461, obtained in powdery form (250 nm average particle size) from Solvay Specialty Polymers. Anhydrous acrylic acid (AA) (99%, stabilized with 200 ppm of monomethylether hydroquinone as inhibitor, reagent grade) and ethanol (ACS, 99.8%) were purchased from Aldrich, CO$_2$ was Air Liquide (99.998%). All chemicals were used without further purification. Benzoyl peroxide (BPO), obtained from Aldrich (USP grade with a 75% w/w titolum, the remainder constituted by water), was recrystallized from methanol (HPLC grade, Riedel-de Haën). KBr for FTIR analyses (Potassium bromide 99+%, FT-IR grade) was purchased from Aldrich.

Grafting Procedure
The reactions were carried in an AISI 316 stainless steel reactor having a free volume of about 27 mL, consisting of a cylindrical body and a threaded cap. In the central position of the reactor closure was settled a thermo well for the Pt 100 temperature

sensor. In the cap two threaded ports ($^1/_4$ inch NPT) used to mount the pressure sensor and a valve for the loading and the venting of gaseous substances were also present. The pressure sensor was a Barksdale type UPA 3 transducer, calibrated against a precision manometer, the gas valve was of the needle type supplied by Parker. The reactor was heated to reaction temperature using an electric heating mantle controlled by a PID electronic controller (Eurotherm).

The loading of the reactor before each grafting reaction was carried using the following sequence: about 1 ± 0.1 g of the PVDF powder previously dried in an oven at 80°C for 3 h under vacuum was initially loaded followed by the weighed amount of monomer and initiator. All these components were added under a stream of inert gas to limit the contact with the atmospheric air. The reactor was then closed and before solvent loading purged at least five times with low pressure CO$_2$ to remove residual atmospheric oxygen. After purging the oxygen, liquid CO$_2$ was loaded at room temperature using an ISCO syringe pump, up to reach the desired nominal density. The total amount of CO$_2$ introduced was measured by weighing the vessel with an electronic scale (Sartorius LP 8200S, precision 0.01 g). After loading the heating mantle was mounted and the autoclave was heated up to 65°C. Heating time lasted <15 min and the reaction time was counted from the instant at which the reaction temperature was reached. The temperature and the pressure in the reactor were monitored during the whole test. At the end of the desired reaction time, the system was cooled down in ice water and slowly depressurized by bubbling the gaseous effluent in water.

After venting, the reactor was opened and the product was recovered and washed at room temperature with ethanol (25 mL) for 2 h to remove unreacted monomer and initiator. The polymer powder was separated by centrifugation (3,500 rpm for 5 min) and extracted six times with hot ethanol at 90°C in the sealed reactor to recover any ungrafted PAA chains (extraction time for each batch 1 h, cumulative volume of alcohol used 150 mL). The treated PVDF was again recovered by centrifugation, and then it was dried in an oven at 70°C overnight, to eliminate residual traces of ethanol.

Characterization of Grafted PVDF
An estimation of the amount of grafted AA in the PVDF powder was made by infrared (IR) spectra recorded on a Perkin-Elmer Spectrum 2000 Explorer FTIR with an averaging of 16 scans at a resolution of 1 cm^{-1} using a near-IR fast recovery deuterated tryglicinesulfate detector using a procedure described in the literature.[30,31] Weighed amounts of grafted samples were mixed with KBr in a mortar and pressed into discs with a 10 tonn strenght. The determination was made by calculating the ratio of the absorbance of the 1,716 cm^{-1} band (A_{CO}) corresponding to the stretching of the carbonyl group in polyacrylic acid chain to the absorbance of the CF$_2$ stretching band at 877 cm^{-1} (A_{CF2})[32] which was used as the internal reference in the normalization of the different spectra.

Assuming validity of the Lambert-Beer law, the absorbance of aforementioned characteristic peaks can be expressed by equations:
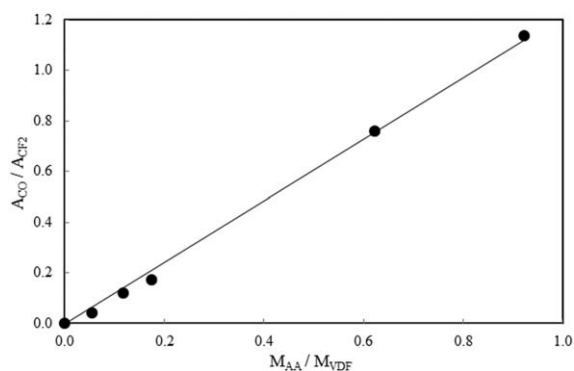
Figure 1. Calibration curve for FT-IR quantitative analysis of the grafting degree.

$$A_{CO} = K_{CO} \; C_{AA} L, \tag{1}$$

$$A_{CF2} = K_{CF2} \; C_{VDF} L, \tag{2}$$

where K_{CO} and K_{CF2} are the molar absorption coefficients at the specific wavenumbers, C stands for the molar concentration of repeat units in the KBr disc, and L is its thickness.

By dividing member to member eq. (1) and (2) and by introducing the cumulative mass of repeat units in the analyzed sample, we obtain the eq. (3):

$$\frac{A_{CO}}{A_{CF2}} = \frac{K_{CO}}{K_{CF2}} \frac{C_{AA}}{C_{VDF}} = F \frac{M_{AA}}{M_{VDF}}, \tag{3}$$

where $F = (K_{CO}/K_{CF2})(PM_{VDF}/PM_{AA})$.

The grafting level DG in the modified polymer was given by the following equation:

$$DG = 100 \frac{M_{AA}}{M_{VDF}} = 100 \frac{1}{F} \frac{A_{CO}}{A_{CF2}}. \tag{4}$$

According to eq. (3), a plot of A_{CO}/A_{CF2} versus M_{AA}/M_{VDF} should yield a straight line, and its slope would represent the ratio F.

To verify the validity of the assumptions and to obtain the calibration line, several mixtures of PVDF and PAA powders at different weight ratios were mixed with KBr in a mortar, pressed into discs with a 10 tonn strenght and analyzed by FT-IR to obtain the absorbances of the bands at 1,716 cm^{-1} (C=O stretching from the polyacrilylic acid) and 877 cm^{-1} (CF$_2$ stretching from PVDF) whose ratio was plotted against the mass ratio of the polymers adopted to prepare the samples. Experimental data are plotted in Fig. 1 and they can be fitted quite well by a straight line with a slope $F = 1.22$ ($R^2 = 0.98$).

FT-IR analyses were also used to confirm the efficacy of the ethanol washes performed on the grafted polymer. To this purpose a synthetic sample of PVDF powder contaminated with PAA was prepared by mixing PVDF and PAA at 40°C overnight in ethanol that is a solvent of the acrylic polymer and a nonsolvent of PVDF. The physical precipitation of PAA on the fluropolymer particles was obtained by solvent evaporation. The obtained synthetic sample was subjected to the washing procedure previously described. KBr pellets prepared with the virgin PVDF powder, the contaminated sample and the washed polymer were analyzed by FTIR. While the carbonyl absorption band was clearly detected in the case of pellet prepared with the untreated contaminated sample, no signal was detected both in the virgin and in the washed PVDF thus confirming the elimination of physically adsorbed PAA within detection limit of the infrared spectrophotometer.

To confirm that a calibration line obtained using physical mixtures of the homopolymer can be used to estimate the composition of grafted copolymers, we performed a graft copolymerization experiment in such a way that the grafting degree can be gravimetrically estimated and compared with the IR calculated one.

To reach this goal, a fixed amount of PVDF powder was loaded in a stainless steel cylindrical container of known mass and closed by a glass sintered cap to avoid mechanical entrainment of the fine powder during the experiments. BPO and AA were loaded outside the cylinder in such amount to reach 0.05 and 0.40 mol/L concentration respectively. The reactor was sealed, loaded with liquid CO$_2$ up to generate a nominal density of 0.5 g/mL and heated at 65°C for 20 h. Grafted PVDF powder was completely segregated inside the cartridge also after venting of the reactor while polymer outside the basked was identified as PAA homopolymer by FTIR analysis.

The PVDF powder was carefully washed with hot ethanol several times without recovering it from the cylinder and after drying the grafting degree was determined gravimetrical using the equation:

$$DG = 100 \frac{M_{Pol}^{f} - M_{PVDF}^{0}}{M_{PVDF}^{0}}, \tag{5}$$

where M_{Pol}^{f} is the mass of the polymer in the cartridge after washing and M_{PVDF}^{0} is the initial mass of PVDF powder loaded in the cartridge.

The gravimetric degree of grafting determined by this method was 18.0% while that estimated by FTIR analyses of the powder with previously reported procedure gave a DG of 17.6% thus confirming the reliability of the spectroscopic method of estimation of the grafting level.

Calorimetric analyses of the copolymers were performed with a Perkin Elmer Jade differential scanning calorimeter (DSC). A pre-weighed amount M$_{POL}$ of the copolymer (3–5 mg) was loaded into an aluminium pan sealed with an aluminium lid pressed slightly using a metal plunger and placed into the calorimeter holder under a N$_2$ flow of 20 mL min^{-1}. The sample was heated twice from 18°C up to 220°C with a heating rate of 10°C min^{-1}. The cooling rate between the two scans was 10°C min^{-1} too. The melting enthalpies, ΔH_m, were determined from the peak areas, whereas the melting temperatures, T_m, where measured at the maximum of the peaks. The percentage of crystallinity of the grafted and pristine powders, χ_c, was then calculated from the measured melting enthalpies values by using the eq. (6):

$$\chi_c = 100 \frac{\Delta H_m * \left(1 - \frac{DG}{100}\right)}{M_{POL} \; \Delta H_{100\%} \text{crystalline}}, \tag{6}$$

where $\Delta H_{100\%crystalline}$ is the specific heat of fusion of pure crystalline PVDF, which is reported to be 104.6 J g^{-1}.[33]

Table I. Test Performed to Study the Influence of scCO$_2$ and BPO on the Polymer Matrix

Entry	BPO (mmol/L)	ρCO_2 (g/mL)	time (h)	T (°C)
1	–	0.5	20	65
2	0.5	0.5	20	65

ρCO_2: density of the supercritical carbon dioxide loaded in the reactor.

The particle morphologies were analyzed and imaged with a Philips scanning electron microscope. Samples were sputter-coated with gold to a thickness of 200 Å.

Contact angles between powders of grafted PVDF and water were measured by compressing polymer particles into a disc to generate a flat and compact solid surface. A FTA 1000 (Ten Angstrom) equipment with deionized water as test liquid was used.

RESULTS AND DISCUSSION

Grafting of AA on PVDF Powders: Effect of the AA Concentration

Solubility of acrylic acid in supercritical carbon dioxide is quite high. Up to 40% (w/w) concentration of this vinyl monomer can be dissolved in CO$_2$ at 65°C and pressure higher than 13 MPa.[34] The phase behavior of the ternary mixture of CO$_2$, AA, and BPO in the adopted reaction conditions was previously studied by visual observation in a view cell.[19] Also at the highest concentration of AA and BPO adopted to perform grafting experiments in this study it was observed that the ternary system was single phase at 65°C provided that pressure higher than 13 MPa are reached inside the vessel.[35] On the other hand to dissolve low molecular weight PVDF ($M_n = 3,031$ g mol^{-1}, PDI = 3.65) in scCO$_2$, pressure of 150 MPa and temperature of 140°C were necessary.[36] This means that under operative conditions adopted to perform grafting experiments, an heterogeneous reaction system was obtained constituted by solid PVDF powders contacted with an homogeneous fluid phase formed by the supercritical solvent, BPO and AA.

Preliminary experiments were performed to study the influence of the solvent and the initiator on the morphology and the crystallinity of PVDF powder using recipes reported in Table I. The tests were performed in the absence of AA with a density of carbon dioxide of 0.5 g/mL.

The FTIR spectra (not shown) and SEM micrographs (Fig. 2) of polymer samples treated in the absence of AA showed no significant changes with respect to that of the virgin PVDF. Calorimetric crystallinity of the starting PVDF powders was 42% and remained substantially not affected by the swelling in scCO$_2$ and by the action of free radicals generated from the thermal decomposition of the organic peroxide.

The effect of monomer concentration on the degree of grafting (DG) was investigated at 65°C and using a density of CO$_2$ of 0.5 g/mL, changing the AA concentration from 0.03 to 0.40 mol/L. Reaction time was 20 h in all runs.

A plot of the DG obtained as a function of the acrylic acid concentration is diagrammed in Fig. 3, each experimental point is the average of two values obtained in different tests carried out at the same operative conditions, grafting degree in these duplicate tests differed always for <5%. A not monotonic trend was obtained with a shape similar to that obtained when the grafting process was performed in scCO$_2$ using PVDF membranes as polymeric matrixes.[19]

The observed trend of the DG when the monomer concentration is increased was already observed studying the maleation of polyolefins both in scCO$_2$[37] and in conventional reaction systems and it can be tentatively attributed to the kinetic competition between graft copolymerization and AA homopolymerization. According to the reaction mechanism generally accepted to describe the grafting process[38] free radicals arising from peroxide decomposition (Scheme 1, reaction a) can add a monomer unit thus initiating homopolymerization (Scheme 1, reaction d) or extract hydrogen from the polymer backbone (Scheme 1, reaction b) thus generating macroradicals that can add AA monomers forming grafted chains (Scheme 1, reaction c).

When the vinyl monomer concentration in the fluid phase is low, the macroradical generation prevails on the AA homopolymerization and one expects that DG increases with the AA concentration. The Fig. 3 shows that when AA concentration increased from 0.06 to 0.11 mol/L DG slightly decreased. This trend could be explained considering that increasing the
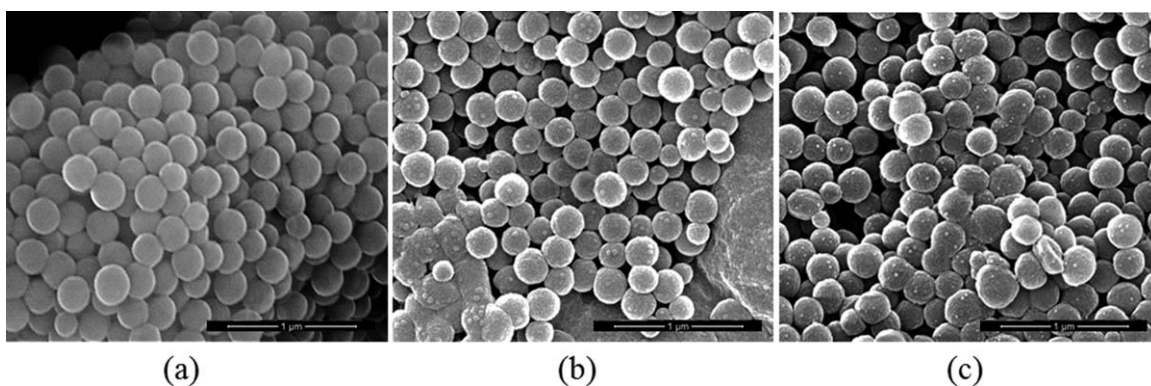

Figure 2. SEM micrographs of pristine PVDF powder (a), PVDF powder soaked with scCO$_2$ (entry 1 Table I) (b), PVDF powder soaked with scCO$_2$ and BPO (entry 2 Table I) (c).
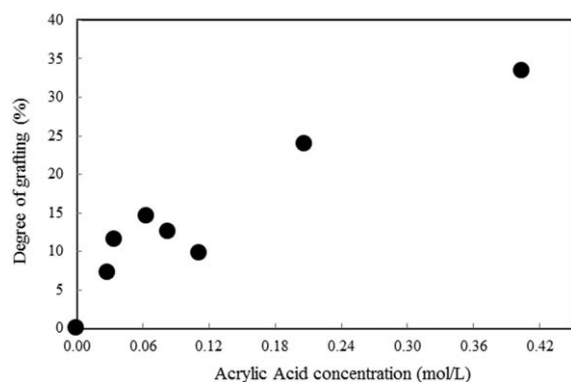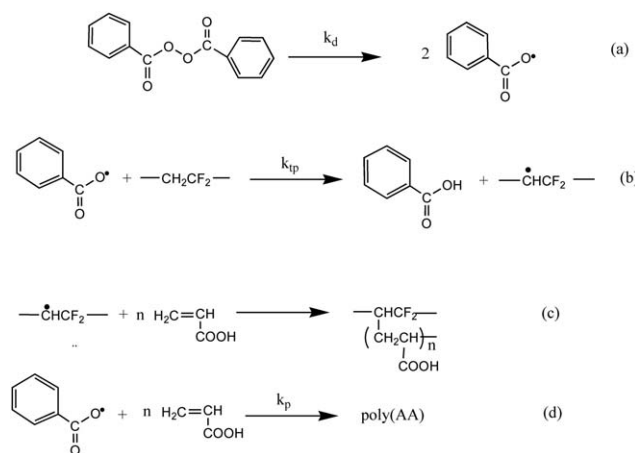
Figure 3. Effect of monomer concentration on the grafting of AA on PVDF powders in scCO$_2$. Concentrations of BPO 0.50 mmol/L. Reaction temperature 65°C, carbon dioxide density 0.5 g/mL, and reaction time 20 h.

Table II. Effect of the Polymer Morphology on the Grafting Degree

PVDF morphology	a_s (m^2/g)	AA (mol/L)	DG (%)
Powder	13.6	0.20	24.8
Membrane	2–3	0.20	16.5
Powder	13.6	0.40	33.4
Membrane	2–3	0.40	24.0

Experimental conditions: CO$_2$ density 0.5 g/mL, BPO concentration 0.50 mmol/L, reaction time 20 h, reaction temperature 65°C.

monomer concentration in the supercritical solution a kinetic regime can be reached at which the rate of the initiation and propagation steps of the AA homopolymerization become faster than the chain transfer reaction to PVDF. In this regime, the rate of generation of the macroradical precursors of grafted copolymers decreases thus inducing the observed decrease of the DG with the AA concentration. The significant increase of the DG observed when the AA concentration changes from 0.11 to 0.40 mol/L can be attributed to the faster monomer addition to macroradicals made possible by the higher local concentration of AA so that the new increase of the grafting degree should be mainly attributed to an increase in the length of grafted chains.

A marked difference with respect to grafting experiments performed on the PVDF membranes in the same range of monomer concentration[19] is the larger grafting degree obtained with PVDF powders. This result could be attributed both to the higher initial concentration of BPO adopted to perform experiments with PVDF nanoparticles and to the higher specific interfacial area a_s of the polymer matrix estimated using the equation:

$$a_s = \frac{6D}{\rho},$$

(7)

where D is the average diameter of the polymer particles and ρ the polymer density.

In fact an higher value of specific area improves the fraction of free radicals generated in the fluid phase that are trapped by polymer nanoparticles thus increasing the kinetic competition of graft copolymerization with respect to AA homopolymerization.

Assuming an average diameter of 0.25 μm and a polymer density of 1.76 g/mL we could estimate a value of a_s of 13.6 m^2/g that is about 4–5 times higher than that of the commercial PVDF membrane used in our previous study.[19]

To discriminate between the two previous mentioned possibilities and to highlight the effect of the polymer morphology on the grafting process a set of experiments was performed, at the same operative conditions, loading in the reactor similar amount of PVDF under the form of nanoparticles and microporous membranes.

Higher grafting levels were reached using powders (Table II) thus confirming that higher interfacial area can lead to larger grafting degree. This result can be of interest since the Hylar PVDF used in this study is a fluoropolymer grade already used for the preparation of membranes and the modified matrix could be mixed with untreated polymer to impart the final membrane hydrophilic and pH responsive behavior.

To further confirm the occurrence of graft copolymerization of AA to PVDF chains a control experiment was carried out. A polymer sample with estimated degree of grafting of 33.4% was dissolved in dimethylacetamide (DMA), a solvent that solubilizes both PVDF and PAA chains. Water was added to this solution to induce the precipitation of the hydrophobic PVDF chains while any residual PAA homopolymers in the polymer nanoparticles would remain in the aqueous solution being hydrophilic.

The polymer precipitated was recovered, dried, and analyzed by FTIR to reestimate the degree of grafting. IR analysis confirmed
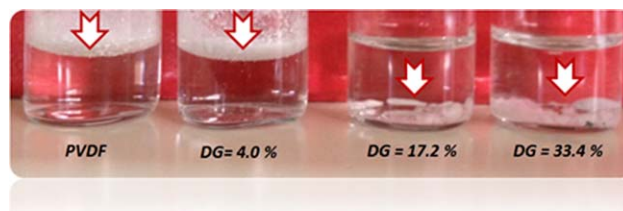

Scheme 1. Schematic description of the postulated grafting process.

Figure 4. Effect of the grafting level on the hydrophobicity of the polymer particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
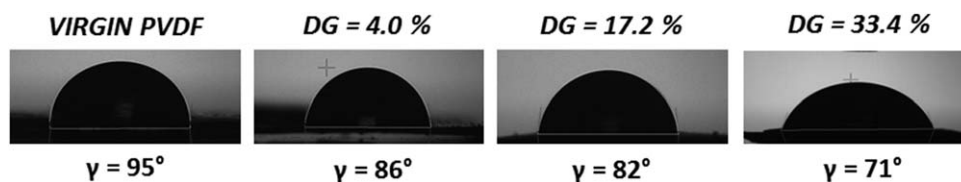
Figure 5. Contact angle as a function of the grafting level for thin plates of compressed grafted PVDF powder.

that PAA chains remained chemically grafted to PVDF backbones, since DG equal to 33.0% was determined.

To have an indication of the effect of the grafting process on the properties of the polymer particles, we have studied the hydrophilicity of PVDF-g-PAA samples obtained with different levels of grafting namely 4.0%, 17.2%, and 33.4% w/w whose behavior in water suspension was compared with that of the untreated PVDF powder (Fig. 4). Pure PVDF powder floats at the water air interphase and the same occurs for PVDF-g-PAA with the lowest grafting level. The powders of PVDF-g-PAA particles with higher degree of grafting (17.2%–33.4%), immediately interact with water falling to the bottom of the container.

To study better the correlation between the grafting level and the hydrophilicity of the polymer particles, we performed contact angle measurements on thin plates with flat surface obtained by compression of the PVDF powder (Fig. 5). The contact angle γ measured with unmodified PVDF was 95° and decreased to 86° when DG was 4.0%. When the DG increased to 17.2% and 33.4% measured values of the contact angles decreased to 82° and 71° respectively, thus confirming that polymer hydrophilicity increased with the grafting level.

Effect of BPO Concentration, Carbon Dioxide Density, and Reaction Time

Both the initiator concentration and the density of the fluid phase can be used as operative parameters to adjust the grafting level. To study their effect on the grafting on nanoparticles a set of experiments was performed changing the initiator concentration at two different CO_2 densities namely 0.5 and 0.7 g/mL (Fig. 6).

It can be seen that the degree of grafting markedly increased when the concentrations of initiator changed from 0.14 to
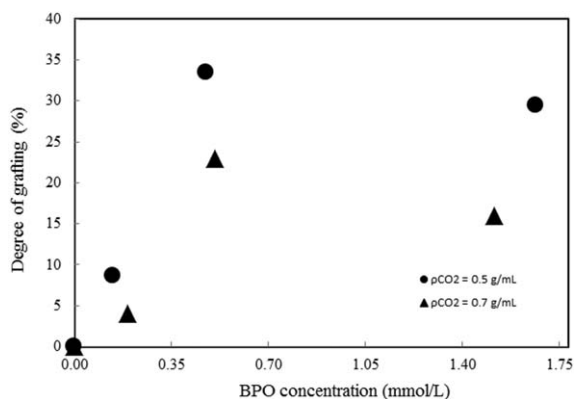
0.47 mmol/L reaching values higher than 30% w/w and slightly decreased when BPO concentration was further enhanced to 1.65 mmol/L. This trend could be explained considering that, for sufficiently low concentrations of BPO, the extraction of the hydrogen atoms from the PVDF chains prevails, while at high concentrations, AA homopolymerization reactions are favored.

DG decreased upon increasing the density of carbon dioxide. This result could be explained by the enhancement of the solvent power of the supercritical solvent when its density is increased. The dense gaseous phase becomes then a better solvent for the monomer and the initiator thus making more favorable the homopolymerization of AA with respect to its graft copolymerization to the PVDF chains.

Also reaction time can be used to modify the grafting level in $scCO_2$. To study this parameter a set of copolymerization tests were performed changing the reaction time from 4 to 16 h, by fixing the concentrations of acrylic acid and BPO to 0.40 mol/L and 0.50 mmol/L, respectively. All experiments were carried out at 65°C with a carbon dioxide density of 0.7 g/mL.

Plot of the degree of grafting as a function of time is shown in Fig. 7. Each point is the average of two experiment with uncertainty in the grafting degree that was ±5% of the average value.

Under adopted operative conditions experimental data suggest the presence of an induction time of about 4 h. After this time, the graft polymerization starts with an average rate decreasing with the increase of the polymerization time up to reach negligible reaction rate after approximately 14–16 h, as demonstrated by the stabilization of the degree of grafting to a value of 13.8%–13.9% w/w.

In Fig. 8 are reported the FTIR spectra of untreated PVDF powder [Fig. 8(a)] and of the fluoropolymer treated for different
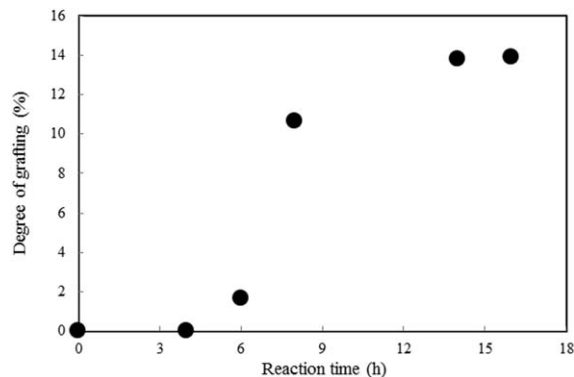

Figure 6. Trend of the degree of grafting as a function of the BPO concentration at two different values of the CO_2 density. Concentration of AA 0.40 mol/L. Reaction temperature 65°C, reaction time 20 h.

Figure 7. Effect of reaction time on the grafting of AA on PVDF powders in $scCO_2$. Concentrations of AA and BPO 0.40 mol/L and 0.50 mmol/L respectively. Reaction temperature 65°C, carbon dioxide density 0.7 g/mL.
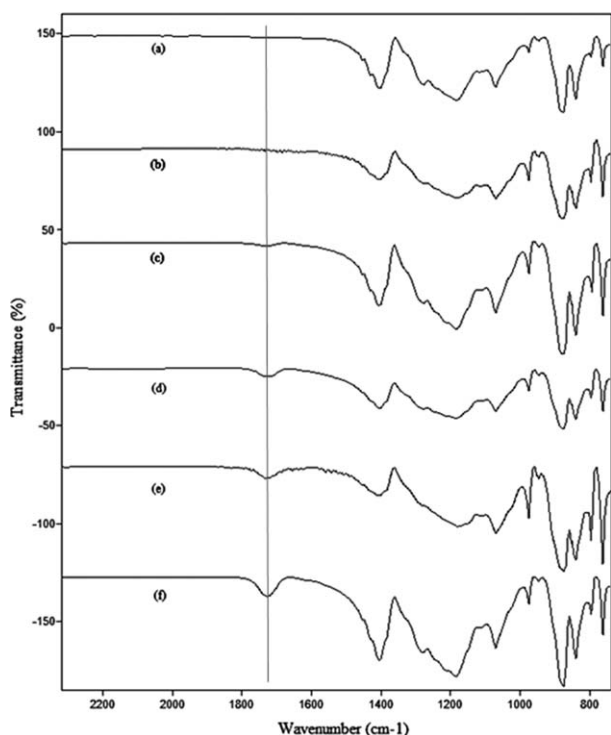
Figure 8. FT-IR spectra of PVDF (a) and of PVDF-g-PAA powder treated at different reaction time under operative conditions reported in the legend of Fig. 7: (b) 4 h, (c) 6 h, (d) 8 h, (e) 14 h, and (f) 16 h. The solid line marks the position of the carbonyl peak of the AA repeat units incorporated in PAA chains.
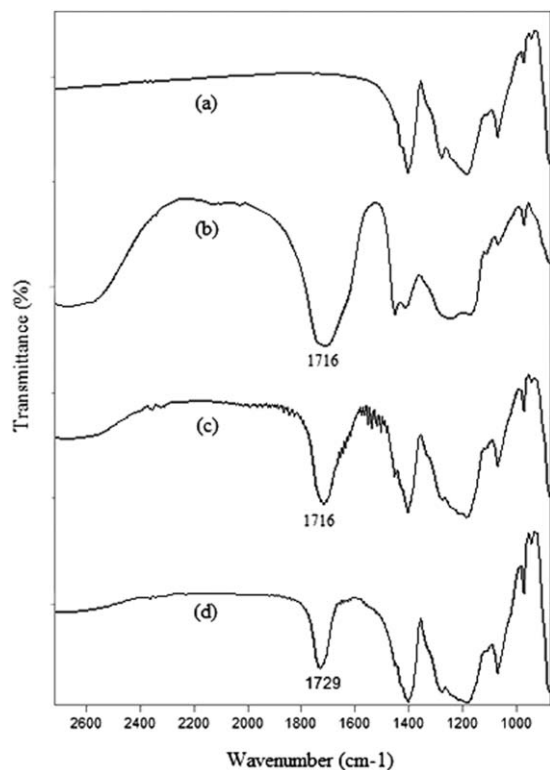

Figure 9. FT-IR spectra of PVDF (a), PAA (b), physical mixture of PVDF and PAA (c), and PVDF-g-PAA powder (d).

reaction times. It seems interesting to underline that the resonance band of the carbonyl in graft-copolymer samples is located at about 1,729 cm^{-1} [Fig. 9(d)] while it can be found at 1,716 cm^{-1} in the case of PAA homopolymers [Fig. 9(b)] or of PAA/PVDF physical mixtures [Fig. 9(c)]. The slight shift to higher wavenumber of the characteristic peak of carbonyl group, i.e., from 1,716 to 1,729 cm^{-1}, gives a hint of the successful grafting of monomers AA to PVDF probably because of the strong electronegative polarity effect of the fluoride atoms. Moreover from FT-IR spectra in Fig. 9(d), there exists a very small peak at around 1,650 cm^{-1}, which could be attributed to the stretch of carbon-carbon double bond (–C=C–), and that could be indicative of the possibility of physical adsorption of
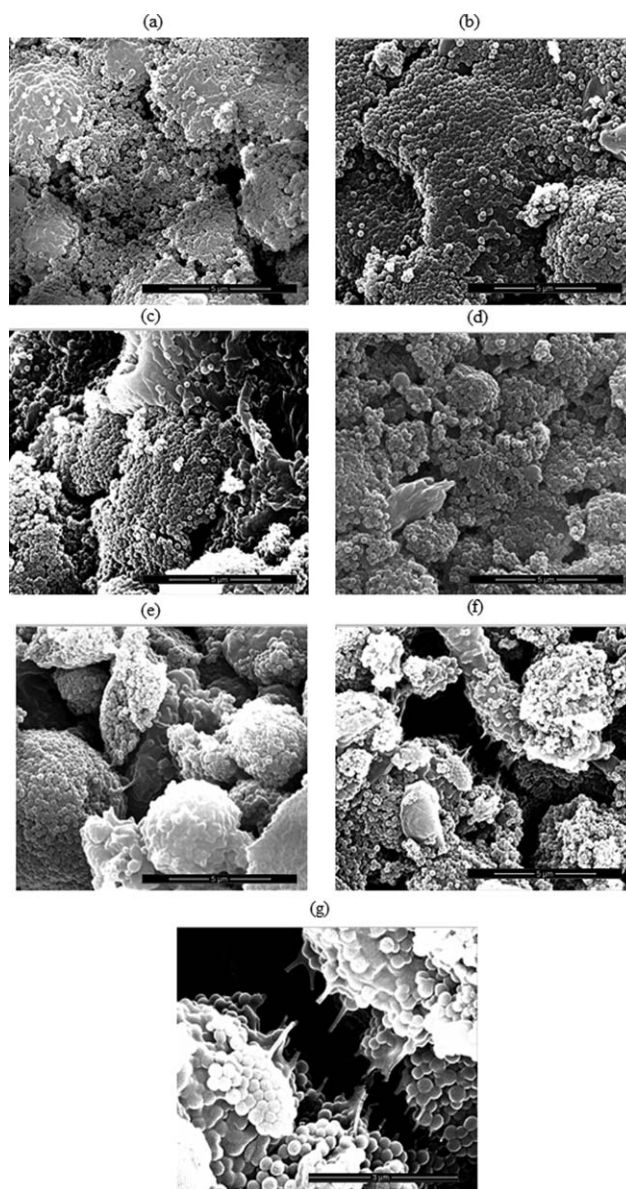

Figure 10. SEM micrographs of virgin PVDF powder (a) and of PVDF-g-PAA samples treated in scCO$_2$ for: (b) 4 h, (c) 6 h, (d) 8 h, (e) 14 h, (f) 16 h, (g) magnification of micrograph (f) highlighting the coalescence among PVDF particles when high grafting levels are reached.
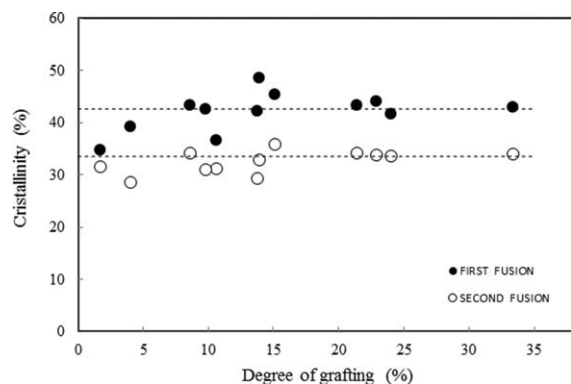
Figure 11. Cristallinity trend of AA grafted PVDF particles at different value of degree of grafting.

residual free AA monomer on PVDF owing to the ubiquitous intermolecular attractive forces.[39–43]

Sample of grafted polymer obtained with different reaction times were analyzed by SEM to study the effect of the grafting process on the morphology of the polymer powder. From the comparison of the micrographs [Fig. 10(b–g)] with that of virgin PVDF powder [Fig. 10(a)] we can clearly observe that no significant morphological modification can be detected when the grafting level is 10.7% or lower (corresponding to a reaction time up to 8 h). When the grafting level reached values close to 13.8%, as in the samples obtained at the highest investigated reaction time, PVDF particles are coated with a sticky layer and glued in agglomerates probably as a consequence of the higher surface concentration of grafted polyacid chains but the spherical morphology of nanoparticles can be anyway recognized in the micrographs.

Grafted PVDF powders were also characterized by DSC. Figure 11 reports the calorimetric crystallinity of PVDF powders as a function of the DG obtained at different CO_2 density and AA and BPO concentrations. We have found a small variation of the crystallinity that was $42 \pm 4\%$ from the first melting endotherm and $32 \pm 2\%$ from the second melting endotherm independently on the grafting level and any other operative conditions.

When we have studied the grafting of AA on preformed PVDF membranes we found that the 2nd heating melting enthalpy of the modified membranes decreased significantly with the grafting level.[19] This trend was attributed to the accumulation of grafted chains in the amorphous domains of the membranes so that the grafting level is the cumulative result of surface linked poly(AA) chains and of chains buried in the polymer.

Since the calorimetric crystallinity of the powder do not exhibit the same behavior one can hypothesize that the higher surface area of PVDF powder induces segregation of the grafting process at the polymer interface with minor effects on the amorphous domains of the PVDF particles.

CONCLUSIONS

Free radical grafting of AA on PVDF nanoparticles was successfully performed in $scCO_2$ using benzoyl peroxide to initiate the process at mild temperature condition.

Grafting levels could be adjusted by changing the concentration of the vinyl monomer and of the initiator, the reaction time and the density of the supercritical solvent.

The values of the degree of grafting obtained with PVDF nanoparticles were significantly higher than that obtained on PVDF membranes at similar operative conditions as a consequence of the larger specific interfacial area of the polymeric system. This result is a clear indication that the polymer morphology can be used as additional parameter to modify the grafting degree.

By proper selection of operative conditions, degree of grafting of about 33.4% w/w were obtained without significant modification of the spherical morphology of the polymer particles thus obtaining PVDF-g-PAA nanoparticles with high grafting level that can be potentially used as additive of untreated PVDF for the preparation of hydrophilic and pH sensitive membranes.

REFERENCES

1. Seiler, D. A.; Scheirs, J. Modern Fluoropolymers, 2nd ed., Wiley: Chichester, UK, **1998**; p 487.

2. Malcolm, P. S. Polymer Chemistry: An Introduction, 3rd ed., Oxford University Press: New York, **1999**; p 168.

3. Wang, D.; Li, K.; Teo, W. K. *J. Membr. Sci.* **2000**, *163*, 211.

4. Klinge, U.; Klosterhalfen, B.; Ottinger, A. P.; Junge, K.; Schumpelick, V. *Biomaterials* **2002**, *23*, 3487.

5. Ying, L.; Wang, P.; Kang, E. T.; Neoh, K. G. *Macromolecules* **2002**, *35*, 673.

6. Kushida, A.; Masayuki, Y.; Akihiko, K.; Teruo, O. *J. Biomed. Mater. Res.* **2001**, *154*, 37.

7. Pasquier, A. D.; Warren, P. C.; Culver, D.; Gozdz, A. S.; Amatucci, G. G.; Tarascon, J.-M. *Solid State Ionics* **2000**, *135*, 249.

8. Tarvainen, T.; Nevalainen, T.; Sundell, A.; Svarfvar, B. *J. Control Release* **2000**, *66*, 19.

9. Kim, K. J.; Fane, A. G.; Fell, C. J. D. *Desalination* **1998**, *70*, 229.

10. Brink, L. E. S.; Elbers, S. J. G; Robbertsen, T.; Both, P. J. *J. Membr. Sci.* **1993**, *76*, 281.

11. Wang, Y.; Kim, J. H.; Choo, K. H.; Lee, Y. S.; Lee, C. H. *J. Membr. Sci.* **2000**, *169*, 269.

12. Ulbricht, M.; Belfort, G. *J. Membr. Sci.* **1996**, *111*, 193.

13. Ulbricht, M.; Richau, K.; Kamusewitz, H. *Colloid Surf. A* **1998**, *138*, 353.

14. Iwata, H.; Oodate, M.; Uyama, Y.; Amemiya, H.; Ikada, Y. *J. Membr. Sci.* **1991**, *55*, 119.

15. Iwata, H.; Matsuda, T. *J. Membr. Sci.* **1988**, *38*, 185.

16. Iwata, H.; Hirata, I.; Ikada, Y. *Macromolecules* **1998**, *31*, 3671.

17. Zhai, G.; Ying, L.; Kang, E. T.; Neoh, K. G. *Macromolecules* **2002**, *35*, 9653.

18. Yu, M.; Deng, B.; Yang, X.; Zang, B.; Li, L.; Xie, L.; Li, J.; Lu, X. *J. Membr. Sci.* **2010**, *350*, 252.

19. Ferro, L.; Scialdone, O.; Galia, A. *J. Supercrit. Fluids* **2012**, *66*, 241.

20. Qiu, G. M.; Zhu, L. P.; Zhu, B. K.; Xu, Y. Y.; Qiu, G. L. *J. Supercrit. Fluids* **2008**, *45*, 374.

21. Qiu, G.; Zhu, B.; Wang, X.; Xu, Y. *Acta Polym. Sin.* **2005**, *5*, 783.

22. Charpentier, P. A.; Kennedy, K. A.; DeSimone, J. M.; Roberts, G. W. *Macromolecules* **1999**, *32*, 5973.

23. Saraf, M. K.; Gerard, S.; Wojcinski, L. M. II; Charpentier, P. A.; DeSimone, J. M.; Roberts, G. W. *Macromolecules* **2002**, *35*, 7976.

24. Galia, A.; Caputo, G.; Spadaro, G.; Filardo, G. *Ind. Eng. Chem. Res.* **2002**, *41*, 5934.

25. Tai, H.; Wang, W.; Howdle, S. M. *Macromolecules* **2005**, *38*, 1542.

26. Tai, H.; Wang, W.; Martin, R.; Liu, J.; Lester, E.; Licence, P.; Woods, H. M.; Howdle, S. M. *Macromolecules* **2005**, *38*, 355.

27. Galia, A.; Giaconia, A.; Scialdone, O.; Apostolo, M.; Filardo, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2406.

28. Costa, L. I.; Scialdone, O.; Storti, G.; Filardo, G.; Morbidelli, M.; Galia, A.; Ferro, L. *Macromolecules* **2010**, *43*, 9714.

29. Solvay. http://www.solvayplastics.com/sites/solvayplastics/EN/specialty_polymers/Markets/Membranes/Pages/fluoropolymers-membranes.aspx. Last accessed October 4, 2014.

30. Mascia, L.; Hashim, K. *J. Appl. Polym. Sci.* **1997**, *66*, 1911.

31. Xuejuan, Z.; Jing, C.; Shuangjun, C.; Jun, Z.; Xiaolin, W. *Colloid Polym. Sci.* **2010**, *288*, 1327.

32. Deng, B.; Yu, Y.; Zhang, B.; Yang, X.; Li, L.; Yu, M.; Li, J. *Radiat. Phys. Chem.* **2011**, *80*, 159.

33. Gaur, U.; Wunderlich, B. B.; Wunderlich, E. *J. Phys. Chem. Ref. Data* **1983**, *12*, 29.

34. Romack, T. J.; Maury, E. E.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 912.

35. Wang, Y.; Liu, Z.; Han, B.; Dong, Z.; Wang, J.; Sun, D.; Huang, Y.; Chen, G. *Polymer* **2004**, *45*, 855.

36. Beuermann, S.; Imran-Ul-Haq, M. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 5626.

37. Galia, A.; De Gregorio, R.; Spadaro, G.; Scialdone, O.; Filardo, G. *Macromolecules* **2004**, *37*, 4580.

38. Clark, K.; Lee, S. *Polym. Eng. Sci.* **2005**, *45*, 631.

39. Sun, W.; Zeng, Q.; Yu, A.; Kendall, K. *Langmuir* **2013**, *29*, 7825.

40. Sun, W.; Zeng, Q.; Yu, A. *Langmuir* **2013**, *29*, 2175.

41. Sun, W. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5846.

42. Sun, W. *Nanoscale* **2013**, *5*, 12658.

43. Sun, W.; Li, Y.; Wu, W.; Mai, Y.-W. *RSC Adv.* **2014**, *4*, 34500.