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Original Vinylidene Fluoride-Containing Acrylic Monomers as Surface Modifiers in Photopolymerized Coatings

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ABSTRACT: The syntheses of original acrylic monomers containing vinylidene fluoride (VDF) units, prepared through a four-step process starting from the telomerization of VDF with iodotrifluoromethane, are presented. By modifying the $[CF_3I]_0/[VDF]_0$ initial molar ratios, different $CF_3(VDF)_nI$ telomers of various molecular weights were obtained. VDF content and the microstructure of the VDF telomers were determined by ^{19}F NMR spectroscopy, while gas chromatography confirmed the average number of VDF units in each telomer. The radical addition of these telomers onto allylic alcohol led to original oligo(VDF)-containing iodohydrins that were reduced into novel ϖ-hydroxyl-VDF telomers. These latter were acrylated, and the resulting VDF-containing macromonomers were added in low amount (0−1% w/w) into a reference telechelic hydrogenated diacrylic resin and copolymerized through the UV-curing technique. The kinetics of the photopolymerization, monitored by IR spectroscopy, and the bulk properties of the film were independent of the amount of these PVDF additives, but peculiar surface properties were shown. The low concentration of the PVDF macromonomers made the surface of the cured networks both hydrophobic and oleophobic. The surface modification, assessed by contact angles and XPS spectroscopy, concerned one side of the films. The films coated on a polar surface showed on the air side a lower surface tension than that of the substrate side, which kept the same properties as those of the pure hydrogenated resin, including a good adhesion to the substrate.

Introduction

Introduction of fluorine compounds in coatings has proved to be interesting because of the outstanding bulk properties obtained[1−2] and also because they can give peculiar surface properties[3−5] that enable them to be involved as potential coatings for stone, textile, and optical fibers.

Therefore, it was worth preparing fluorinated coatings through the UV-curing technique. This technique is based on the polymerization of a multifunctional system induced by incident radiation to obtain a three-dimensional network.[6] The action allows one to transform, at room temperature in a fraction of a second, a liquid system into a solid having rubbery or glassy properties. It has been widely applied in many industrial fields for the manufacturing, decoration, and protection of different materials.[7] In fact, there are many advantages to producing coatings by the UV-curing method technique,[7] such as the following: (i) the energy needed for the process is low; (ii) the polymerization is very fast and highly efficient; (iii) the cure is selectively limited to the irradiated area; and (iv) no solvent is required (100% solid formulation), therefore the environmental pollution by VOC is avoided. Use of fluorinated monomers in the UV-curing field was first investigated by Torstensson et al.,[8] who employed a perfluorooctylacrylate and copolymerized it with acrylic resins. Fluorinated diacrylates were successfully cross-linked by UV irradiation and used for the cladding of optical fibers.[9] Original methyl-2,2,2-trifluoroethylacrylate telomers bearing acrylic side groups were also involved in photocuring for the protection of metals.[10] More recently, previous papers[11−15] reported the photopolymerization of different fluorinated esters of the structure

$$R_f{-}G{-}O{-}CO{-}CH{=}CH_2$$

where R_f is a perfluorinated alkyl group or a perfluoropolyether chain and G is a hydrogenated spacer. These acrylates were used as comonomers at a concentration lower than 1% w/w; their behavior in photopolymerization and the properties of the resulting films were investigated. The peculiar surface properties obtained were correlated with the structural parameters of the fluorinated comonomers. Interestingly, the surface modification achieved was found to be dependent on not only the molecular weight and the type of the fluorinated chain but also the identity of the end group and the length and nature of the spacer between the ester group and the perfluorinated end group.

Following that research topic we prepared new original fluorinated monomers containing vinylidene fluoride (VDF) units. Their general structure is

$$R_f{-}(CH_2CF_2)_n{-}(CH_2)_3{-}O{-}CO{-}CH{=}CH_2$$

where R_f is either a perfluoromethyl or a perfluorohexyl group and n is the average number of VDF units and ranges between 1 and 5. They were obtained by esterification of OH-functionalized telomers, prepared by a three-step procedure starting from the radical telomerization of VDF with the homologous perfluoroalkyl iodides.[16−18] Indeed, VDF-containing acrylates are scarce: to our knowledge, the only products belonging to this family were synthesized by Duc et al. from the

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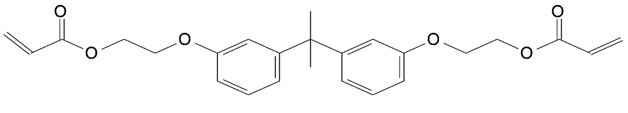
telomerization of VDF with methanol[19] or with diethylhydrogenphosphonate,[20] followed by the acrylation realized in one or three steps,[21,22] respectively.

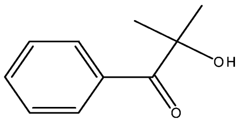
The objectives of this article concern the synthesis and use as surface modifiers of macromonomers containing VDF. The influence of the telomeric VDF chain length is compared with that of a telomeric tetrafluoroethylene one. The surface properties of films, which contain a small amount of these acrylic telomers, obtained by UV curing is another key point of this investigation.

Experimental Section

Materials for the Syntheses. CF_3I was purchased from Fluorochem (U.K.); allyl alcohol, tributyl stannane, triethylamine, trichloromethylisocyanate, *n*-hexadecane, and acryloyl chloride were provided by Aldrich (Saint Quentin, France). THF and acetonitrile were dried over calcium hydride and freshly distilled prior to use. VDF and *tert*-amylperoxypivalate (TAPPI) were kindly supplied by Solvay SA (Brussels, Belgium), while *tert*-butyl peroxypivalate (TBPPI) was kindly given by La Chalonnaise des Peroxydes (Chalons sur Marne, France). AIBN was purchased from Merck (Darmstadt, Germany). The diacrylic resin employed for the UV-curable formulations was bisphenol A-dihydroxyethyldiacrylate (BHEDA), kindly supplied by UCB Co. (Drogenbos, Belgium). The radical photoinitiator (PI) was kindly supplied by CIBA Specialty Chemicals (Basel, Switzerland). The structures of BHEDA and PI are shown below.



BHEDA



PI

Characterization of the Monomers. Gas chromatography (GC) analyses were performed using a Delsi apparatus. The nitrogen pressure at the entrance to the column was maintained in a range of 3−5 bar, and the temperatures of the injector and detector were 250 and 260 °C, respectively. The temperature program started from 30 °C and reached 240 °C at a heating rate of 10 °C/min.

The products were characterized by ^1H and ^{19}F NMR, all undertaken at room temperature. ^1H NMR spectra were recorded on a Bruker AC 200, while ^{19}F NMR spectra were recorded on a Bruker AC 250 with deuterated chloroform as the solvent and TMS as the internal reference. The letters s and m stand for singlet and multiplet, respectively. The experimental conditions for recording ^1H (^{19}F) NMR spectra were as follows: flip angle = 90° (30°), acquisition time = 4.5s (0.7 s), pulse delay = 2 s (5 s), number of scans = 16 (64), and pulse width = 5 μs for ^{19}F NMR.

The FTIR spectra were recorded by means of a Genesis ATI Mattson spectrometer.

Synthesis and Characterization of the Fluorinated Monomers. The monomers synthesized were

$$C_6F_{13}(CH_2CF_2)(CH_2)_3OCOCH{=}CH_2 \text{ (F1)}$$

$$CF_3(CH_2CF_2)_{2.3}(CH_2)_3OCOCH{=}CH_2 \text{ (F2)}$$

$$CF_3(CH_2CF_2)_{3.1}(CH_2)_3OCOCH{=}CH_2 \text{ (F3)}$$

$$CF_3(CH_2CF_2)_{4.8}(CH_2)_3OCOCH{=}CH_2 \text{ (F4)}$$

Table 1. Reagents Used in Radical Telomerization of Vinylidene Fluoride with Iodotrifluoromethane[a]

initiator (g)	type of initiator	acetonitrile (g)	VDF (g)	CF_3I (g)	obtained R_fI
2.21	TBPPI	59	15	75	$CF_3(VDF)_{2.3}I$
3.20	TAPPI	60	33	37	$CF_3(VDF)_{3.1}I$
0.68	TBPPI	57	14	41	$CF_3(VDF)_{4.8}I$

[a] TBPPI and TAPPI are *tert*-butyl and *tert*-amyl- peroxypivalate, respectively.

Table 2. VDF-Containing Telomers: Yield and Physical Characteristics

R_FI	yield (%)	bp (°C)	pressure (mmHg)
$CF_3(VDF)_{2.3}I$	11	50	20
$CF_3(VDF)_{3.1}I$	41	52	20
$CF_3(VDF)_{4.8}I$	8	55	20

Table 3. Reagents Used in the Radical Addition of VDF−Telomers onto Allyl Alcohol

	R_FI		$H_2C{=}CHCH_2OH$		AIBN	
R_FI	g	mol	g	mol	g	mol
$C_6F_{13}CH_2CF_2I$	70.1	0.14	9.56	0.16	1.35	0.008
$CF_3(VDF)_{2.3}I$	14.9	0.04	7.02	0.12	1.00	0.006
$CF_3(VDF)_{3.1}I$	20.2	0.05	24.03	0.41	2.00	0.012
$CF_3(VDF)_{4.8}I$	5.1	0.01	3.20	0.06	0.45	0.003

Telomerization of VDF with $C_6F_{13}I$ and Obtaining the Monoadduct. Synthesis of the VDF telomers from $C_6F_{13}I$ was reported in previous articles[16,17] by thermal telomerization of VDF followed by distillation of $C_6F_{13}CH_2CF_2I$ monoadduct.

Telomerization of VDF with CF_3I. In a 160-mL Hastelloy (HC-276) autoclave equipped with inlet and outlet valves, a manometer, and a rupture disk were placed the initiator (*tert*-amyl or *tert*-butyl peroxypivalate) and acetonitrile. Then, the autoclave was cooled, degassed, and pressurized with 20 bar of nitrogen to check for eventual leaks. CF_3I was first introduced in the autoclave, followed by VDF, the amount of both reactants being assessed by double weighing. Several trials were carried out to have different molar ratios between both reagents and to obtain various lengths of the VDF chains, as reported in Table 1.

After distillation (the conditions are reported in Table 2) the products were characterized by ^1H and ^{19}F NMR and GC and distinguished for a different average number of VDF units.

$CF_3(VDF)_nI$. ^1H NMR ($CDCl_3$): δ 3.8−3.6 (m, 2H, $-CF_2CH_2I$), 3.2 (m, 2H, CF_3CH_2-), 2.9 (m, 2H, $-CF_2CH_2CF_2-$). ^{19}F NMR ($CDCl_3$): δ −38 (tt, $^3J_{FH}$ = 11.0 Hz, $^4J_{FF}$ = 16.5 Hz, 2F, $-CH_2CF_2I$), −58 (q, $^3J_{FH} = {}^4J_{FF}$ = 10.0 Hz, 3F, CF_3CH_2-), −91 (m, ×2F, $-CH_2CF_2CH_2-$), −108 (m, y2F, $-CF_2\mathbf{CF_2}CH_2I$), −113 (m, z2F, $-CF_2CH_2\mathbf{CF_2}CF_2-$), −116 (m, z2F, $-CH_2\mathbf{CF_2}CF_2CH_2CH_2CF_2-$).

The chemical formula of the different VDF telomers and yields of the reactions are collected in Table 2.

Radical Addition of R_fI onto Allyl Alcohol. In a two-necked round-bottom flask equipped with a magnetic stirrer and a water condenser were put the iodofluorinated telomer R_FI, allyl alcohol, and AIBN as the initiator, as shown in Table 3.

When the temperature reached 75 °C, a similar amount of AIBN was introduced (as shown in Table 3). The temperature was maintained for 2 h, after which the same amount of AIBN was added again. After 2 h the solution was colorless. The mixtures were stirred at 75 °C for 5 h; the reactions were monitored by GC and stopped when a steady conversion of telomeric R_FI was obtained. This was also checked by NMR. The products were distilled (see conditions in Table 4) and characterized by ^1H NMR and ^{19}F NMR.

$C_6F_{13}CH_2CF_2CH_2CHICH_2OH$. ^1H NMR ($CDCl_3$): δ 5.5 (s, 1H, $-CH_2\mathbf{OH}$, shifted with dilution or with Cl_3CNCO), 4.2 (m, 1H, $-CH_2\mathbf{CHI}-$), 3.6 (m, 2H, $-\mathbf{CH_2}OH$), 2.8 (m, 2H, $-CF_2\mathbf{CH_2}CF_2-$), 2.6 (m, 2H, $-CF_2\mathbf{CH_2}CHI-$). ^{19}F NMR ($CDCl_3$): δ −82

Table 4. Yields and Characteristics of Synthesized Iodohydrins

R_F	$R_FCH_2CHICH_2OH$ g	$R_FCH_2CHICH_2OH$ mol	yield (%)	bp (°C)	pressure (mmHg)
$C_6F_{13}CH_2CF_2$	72.80	0.13	94	70	22
$CF_3(VDF)_{2.3}$	15.32	0.04	88	65	20
$CF_3(VDF)_{3.1}$	19.69	0.04	80	68	20
$CF_3(VDF)_{4.8}$	3.88	0.01	71	68	20

Table 5. Reagents Used in the Selective Reduction of Iodine Atom in Iodohydrins; Yields of the Reaction and Boiling Points of the Products

R_F	$R_FCH_2CHICH_2OH$ g	$R_FCH_2CHICH_2OH$ mol	$SnBu_3H$ g	$SnBu_3H$ mol	yield (%)	bp (°C)	pressure (mmHg)
$C_6F_{13}CH_2CF_2$	70.2	0.14	47.79	0.16	67	85	10^{-3}
$CF_3(VDF)_{2.3}$	15.3	0.04	12.90	0.04	70	78	10^{-3}
$CF_3(VDF)_{3.1}$	19.4	0.04	14.88	0.05	82	80	10^{-3}
$CF_3(VDF)_{4.8}$	4.1	0.01	4.10	0.01	60	80	10^{-3}

(m, 3F, $\mathbf{CF_3}CF_2-$), −94 (m, 2F, $-CH_2\mathbf{CF_2}CH_2-$), −113 (m, 2F, $-CF_2\mathbf{CF_2}CH_2-$), −124 (m, 6F, $C_2F_5\mathbf{C_3F_6}-$), −127(m, 2F, $CF_3\mathbf{CF_2}-$).

$CF_3(VDF)_nCH_2CHICH_2OH$. ^{1}H NMR ($CDCl_3$): δ 5.3 (s, 1H, $-CH_2O\mathbf{H}$, shifted with dilution or with Cl_3CNCO), 4.2 (m, 1H, $-CH_2\mathbf{CH}I-$), 3.8 (m, 2H, $-\mathbf{CH_2}OH$), 3.2 (m, 2H, $CF_3\mathbf{CH_2}-$), 2.8 (m, 2H, $-CF_2\mathbf{CH_2}CF_2-$), 2.6 (m, 2H, $-CH_2\mathbf{CH_2}CF_2-$), 2.2 (m, 2H, $-CF_2\mathbf{CH_2}CHI-$). ^{19}F NMR ($CDCl_3$): δ −61 (q, $^3J_{FH}$ = $^4J_{FF}$ = 10.1 Hz, 3F, $\mathbf{CF_3}CH_2-$), −92 (m, 2F, $-CH_2\mathbf{CF_2}CH_2-$), −109 (m, 2F, $-CH_2CF_2\mathbf{CF_2}-$), − 113 (m, $-CH_2\mathbf{CF_2}CF_2-$).

Selective Reduction of the Iodine Atom for the Synthesis of Telomeric VDF-Containing Alcohols. In a two-necked round-bottom flask, cooled in an ice bath and saturated with nitrogen, the VDF-containing iodohydrin was dissolved into dried THF; then 1.051 g of AIBN and tributylstannane were dropwise added. After complete addition of the tributylstannane, the solution was stirred at room temperature. The mixture was warmed to 80 °C for 4 h, and the reaction was monitored by GC. After partial evaporation of THF, the mixtures were distilled (Table 5), and the products were characterized by ^{1}H- and ^{19}F NMR.

$C_6F_{13}CH_2CF_2CH_2CH_2CH_2OH$. ^{1}H NMR ($CDCl_3$): δ 3.6 (m, 2H, $-\mathbf{CH_2}OH$ shifted to 4.5 ppm with CCl_3NCO), 3.1 (m, 2H, $-CF_2\mathbf{CH_2}CH_2-$), 2.8 (m, 2H, $-CF_2\mathbf{CH_2}CF_2-$), 2.2 (s,H, $-CH_2O\mathbf{H}$ shifted by dilution and with CCl_3NCO), 1.8 (m, 2H, $CH_2\mathbf{CH_2}CH_2-$). ^{19}F NMR ($CDCl_3$): δ −82 (m, 3F, $\mathbf{CF_3}CF_2-$), −94 (m, 2F, $CH_2\mathbf{CF_2}CH_2-$), −113 (m, 2F, $-CF_2\mathbf{CF_2}CH_2-$), −124 (m, 6F, $C_2F_5\mathbf{C_3F_6}CF_2-$), −127 (m, 2F, $CF_3\mathbf{CF_2}-$).

$CF_3(VDF)_nCH_2CH_2CH_2OH$. ^{1}H NMR ($CDCl_3$): δ 3.6 (m, 2H, $-\mathbf{CH_2}OH$, shifted to 4.5 ppm with CCl_3NCO), 3.2 (m, $CF_3\mathbf{CH_2}-$), 2.9 (m, $-CF_2\mathbf{CH_2}CF_2-$), 2.8 (m, $-CF_2\mathbf{CH_2}CH_2CH_2-$), 1.8 (m, 2H, $-CH_2\mathbf{CH_2}CH_2-$), 1.6 (s, 1H, $-CH_2O\mathbf{H}$, shifted with dilution and with CCl_3NCO).

^{19}F NMR ($CDCl_3$): δ −62 (m, 3F, $\mathbf{CF_3}CH_2-$), −92 (m, 2F, $-CH_2\mathbf{CF_2}CH_2-$), −109 (m, $-CH_2\mathbf{CF_2}CF_2-$), − 113 (m, $-CH_2CF_2\mathbf{CF_2}-$).

Synthesis of VDF-Containing Macromonomers by Acrylation of the Alcohols. The alcohols were dissolved in anhydrous THF in a two-necked round-bottom flask equipped with a stirrer, a water condenser, a nitrogen flow, and an addition funnel.

After stirring the solution of the alcohol under nitrogen for 30 min, acryloyl chloride, dissolved in dry THF, was added dropwise at room temperature under stirring according to the quantities reported in Table 6. When the addition was complete, triethylamine (Et_3N) dissolved in THF (Table 6) was dropwise added while stirring and cooling the flask with an ice bath. The solution was then warmed to 60 °C and left stirring for 4 h.

After evaporation of the solvent, the product was dissolved in diethyl ether while the precipitate (chlorinated salt of triethylamine) was filtered off. Then, the excess amount of acryloyl chloride dissolved in the filtrate was evaporated under reduce pressure.

Table 6. Reagents Used in the Acrylation of ω-Hydroxy Oligo(VDF)s; Yield of the Reaction

R_F	$R_F(CH_2)_3OH$ g	$R_F(CH_2)_3OH$ mol	$H_2C{=}CHC(O)Cl$ g	$H_2C{=}CHC(O)Cl$ mol	Et_3N g	Et_3N mol	yield of acrylate (%)
$C_6F_{13}CH_2CF_2$	19.46	0.05	15.94	0.18	17.80	0.18	79
$CF_3(VDF)_{2.3}$	5.57	0.02	7.26	0.08	8.09	0.08	96
$CF_3(VDF)_{3.1}$	8.50	0.03	11.01	0.12	12.35	0.12	86
$CF_3(VDF)_{4.8}$	2.68	0.01	1.90	0.02	2.13	0.02	82

The amounts of the products left after evaporation and yields of the reactions are reported in Table 6. The products were characterized by ^{1}H and ^{19}F NMR spectroscopies.

$C_6F_{13}CH_2CF_2CH_2CH_2CH_2OCOCH{=}CH_2$.

^{1}H NMR ($CDCl_3$): δ 6−6.5 (m, 3H, $O\mathbf{CH{=}CH_2}$), 4.2 (t, $^3J_{HH}$ = 6.9 Hz, 2H, $-CH_2\mathbf{CH_2}O$), 3.6 (m, 2H, $-CF_2\mathbf{CH_2}CH_2-$), 3.4−3.2 (m, 4H, $-CF_2\mathbf{CH_2}CF_2-$), 1.8 (m, 2H, $CH_2\mathbf{CH_2}CH_2-$). ^{19}F NMR ($CDCl_3$): δ −82 (m, 3F, $\mathbf{CF_3}CF_2-$), −94 (m, 2F, $CH_2\mathbf{CF_2}CH_2-$), −113 (m, 2F, $-CF_2\mathbf{CF_2}CH_2-$), −124 (m, 6F, $C_2F_5\mathbf{C_3F_6}CF_2-$), −127 (m, 2F, $CF_3\mathbf{CF_2}-$).

$CF_3(VDF)_nCH_2CH_2CH_2OCOCH{=}CH_2$.

^{1}H NMR ($CDCl_3$): δ 6.0−6.5 (m, 3H, $O\mathbf{CH{=}CH_2}$), 4.2 (t, $^3J_{HH}$ = 7.0 Hz, 2H, $-CH_2\mathbf{CH_2}O-$), 3.6 (m, 2H, $-CF_2\mathbf{CH_2}CH_2-$), 3.2 (m, $-CF_2\mathbf{CH_2}CF_2-$), 3.0 (m, 2H, $CF_3\mathbf{CH_2}-$), 1.9 (m, 2H, $-CH_2\mathbf{CH_2}CH_2-$). ^{19}F NMR ($CDCl_3$): δ −61 (q, $^3J_{FH}$ = $^4J_{FF}$ = 10.0 Hz, 3F, $\mathbf{CF_3}CH_2-$), −92 (m, 2F, $-CH_2\mathbf{CF_2}CH_2-$), −109 (m, $-CH_2\mathbf{CF_2}CF_2-$), − 113 (m, $-CH_2CF_2\mathbf{CF_2}-$).

Film Preparation and Characterization. The fluorinated macromonomers were photocopolymerized in bulk with the hydrogenated acrylic resin (BHEDA) in the presence of the radical photoinitiator (PI) at a concentration of 4% w/w.

The mixtures were composed of 3−4 g of BHEDA, 4% w/w of PI, and a variable amount of macromonomer ranging from 0% to 1.5% w/w. They were spread on a glass slide or onto a polypropylene sheet with a calibrated wire-wound applicator to obtain a thickness of about 100 μm. The curing reaction was performed under nitrogen atmosphere by UV irradiation with a medium-pressure Hg lamp equipped with a water jacket for IR radiation screening. The intensity at the film surface was 6 mW/cm^2. The overall time of exposure to the UV light was 45 s (alternating 15 s of irradiation and 15 s of dark).

On all the films dynamic contact angle measurements were performed with a Kruss G10 instrument, equipped with a video camera and image analyzer, at room temperature with the sessile drop technique. The films were peeled off the substrates and analyzed on both sides: the side in contact with air was labeled as air side, the opposite one as the substrate side. On each examined surface at least five measurements were done; the difference from the average value was no more than 2° for the advancing angle and 3° for the receding angle. The measuring liquids were doubly distilled water and n-hexadecane (γ = 72.1 and 28.1 mN·m^{-1}, respectively).

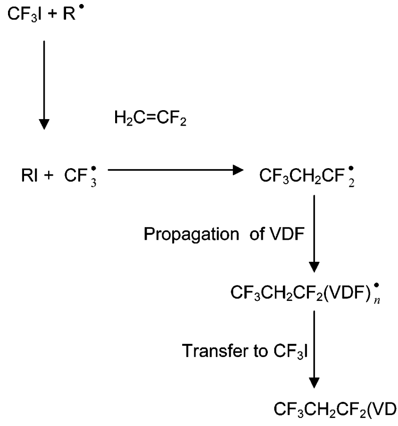
The gel content was determined by measuring the weight loss of the sample after extraction with $CHCl_3$ for 24 h at room temperature.

The adhesion test was performed according to the cross-cut method (ASTM D3359).

The glass-transition temperatures, T_gs, of the films were measured by DSC analyses, performed by a Mettler DSC 20 (initial T = −50 °C, final T = 150 °C, heating rate = 10 °C/min). A second scan was always realized on each sample, and the values of the T_gs were taken as the inflection point of the curve.

XPS measurements were carried out on the films containing the fluorinated additives by a VG Instrument electron spectrometer using a Mg Kα,1,2 X-ray source (1253.6 eV). The X-ray source in the standard conditions was working at 100 W, 10 kV, and 10 mA. The base pressure of the instrument was 5×10^{-10} Torr, and an operating pressure of 2×10^{-8} Torr was used typically. A pass energy of 100 and 50 eV was used for wide and narrow scans, respectively. Depth profile information was obtained by running measurements on electrons taking off from the sample surface with angles of 90°, 45°, and 25°. According to the equation $d = 3\lambda \sin \theta$, sample

Scheme 1. Telomerization Reaction of Vinylidene Fluoride with Iodotrifluoromethane[a]



[a] $R^\bullet$ coming from the initiator (tBuO•, CH_3•, or tBu•).

depths (*d*) were lower when the take off angle (t.o.a.) was smaller. All data analyses (linear background subtraction and peak integration) were accomplished using VGX900x (version 6) software. Binding energies were referenced to the C−H level at 285.0 eV.

Results and Discussion

Synthesis of the Fluorinated Telomers. Telomeric F1 precursor was synthesized from $C_6F_{13}CH_2CF_2I$ obtained by distillation of the monoadduct achieved in the thermal telomerization of vinylidene fluoride (VDF) with $C_6F_{13}I$, as reported in previous papers.[16,17]

The synthesis of original VDF-containing macromonomers was realized from a four-step procedure, starting from the radical telomerization of VDF with iodotrifluoromethane under radical conditions as in Scheme 1. All the steps are detailed hereafter.

To prepare various fluorotelomers that exhibit a different number of VDF units, the telomerization of VDF with CF_3I was performed with different initial $[CF_3I]_0/[VDF]_0$ (R_0) and $[initiator]_0/[VDF]_0$ (c_0) molar ratios (Table 1). Different initiators were used.

The amount of CF_3I controls the transfer step of the telomerization: when the concentration of the initiator was the same, it was noted that the higher the R_0 values, the lower the degree of telomerization (DP_n), as expected.

Comparing the yields, η, obtained for the three products, the difference between that of the $CF_3(VDF)_{3.1}$ telomer ($\eta = 41\%$) and those of the other ones (which are lower) is remarkable. Higher yields were obtained when *tert*-amyl peroxypivalate (TAPPI) was involved as the initiator, while in the other cases the *tert*-butyl homologue (TBPPI) was employed. This confirms the strong influence of the nature of the initiator chosen for the reaction, as already described in previous studies on the radical telomerization of VDF with branched or linear perfluoroalkyl iodides,[16−18,23,24] telechelic diiodoperfluoroalkanes,[25] or iodoperfluoropolyether.[26]

The DP_n values of these telomers were assessed from gas chromatography (GC) and NMR analyses. The GC chromatograms of all the products exhibit the presence of different multiadduct VDF telomers. An example of a GC chromatogram is reported in Figure 1 and clearly shows the first eight VDF adducts of the $CF_3(VDF)_{4.8}I$ telomer while those of $CF_3(VDF)_{2.4}I$ and $CF_3(VDF)_{3.1}I$ exhibit the presence of the first six adducts.

It is a classical gas chromatogram, indicating that the reaction was clean and showing the presence of few byproducts, arising from addition of the radicals (generated from the initiator) onto the transfer agent, besides the reversed VDF adducts.

In agreement with previous work,[16−18,22−26] we did not observe any oligomers produced from the direct addition of the radical initiator onto VDF as in the cases of radical oligomerization of VDF[23] that occurred concomitantly in the telomerization of VDF with methanol.[19]

The GC data enable one to assess the average DP_n from the following formula

$$DP_n = \sum c_i n_i / \sum c_i$$

where c_i and n_i represent the area percentage of the *i* peak and its number, respectively. The results, reported in Table 7, are in good agreement with those obtained by ^{19}F NMR.

The ^{19}F NMR spectra of the iodofluorinated telomers show the presence of four major signals centered at around −38, −57, and −91 and −113/−116 ppm corresponding to CH_2CF_2I end groups,[16−18,25,26] CF_3[18,27,28] end groups, and head-to-tail (or normal addition) and head-to-head (reverse addition) VDF chaining[16−28] in the VDF propagation, respectively. They can clearly be seen in Figure 2, showing the ^{19}F NMR spectrum of the $CF_3(VDF)_{4.8}I$ telomer (F4).

On the basis of the integrals of the signals, according to the following formula

$$DP_n = \frac{\dfrac{\sum [I_{-38} + I_{-91} + I_{-113} + I_{-116}]}{2}}{\dfrac{I_{-57}}{3}}$$

the degree of telomerization was predicted and reported in Table 7.

Because of the absence of any signal centered at −83 ppm assigned to the CF_3 end group in $CF_3CF_2CH_2$, it can be claimed that the addition reaction of $\bullet CF_3$ radical onto VDF is selective on the CH_2 side of the fluoroalkene. This is not in agreement with Chambers' work,[29] but it confirms recent investigations in the telomerization of VDF.[16−26,28] In fact, as can be seen from the spectrum of Figure 2 concerning the longest telomer, there is no signal at −118 ppm, which is attributed to the CF_2 group of $CF_3CF_2CH_2-$ as mentioned by Apsey et al.,[30] who investigated the telomerization of VDF with C_2F_5I.

Moreover, as noted in previous work,[19,23] the ^1H NMR spectra show the absence of any signal centered at 1.8 ppm which is attributed to the methyl end group of $CH_3CF_2CH_2$ sequence arising from the direct addition of a radical (generated from the initiator) onto VDF.[19,23] As an example, the ^1H NMR spectrum of the longest telomer is given in Figure 3.

The presence of the reversed adducts containing sequences of the type $-CH_2CF_2CF_2CH_3$ and $-CH_2CF_2CF_2CH_2I$[16−26] could be observed by the characteristic signals in the ^{19}F NMR spectra, in particular those indicated below

$$-CH_2CF_2CF_2CH_3 \qquad R_FCH_2CF_2CF_2CH_2I$$
$$(b)\,(a) \qquad\qquad (c)\,(d)$$

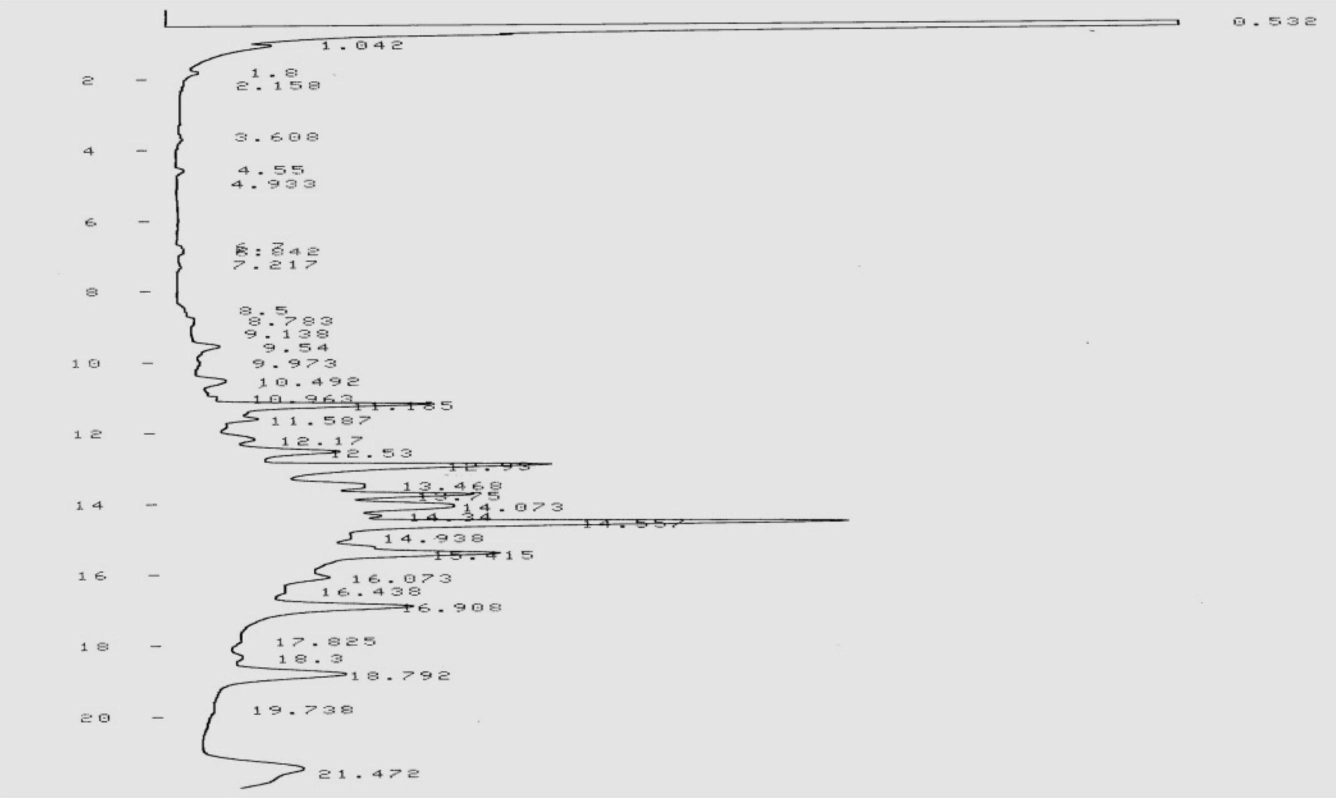


Figure 1. Gas chromatogram for the telomer precursor of F4.

Table 7. Experimental Conditions of Telomerization Reactions and Molar Masses

telomer obtained	VDF	CF_3I	R_0[a]	c_o[a]	yield η (%)[a]	DP_n (by GC)	DP_n (by NMR)	initiator
$CF_3(VDF)_{2.4}I$	15	75	1.63	0.02	11	2.6	2.4	TBPPI
$CF_3(VDF)_{3.1}I$	33	37	0.37	0.02	41	3.2	3.1	TAPPI
$CF_3(VDF)_{4.8}I$	14	41	0.96	0.02	9	5.1	4.8	TBPPI

[a] $R_0 = [CF_3I]_0/[VDF]_0$, $c_o = [\text{initiator}]_0/[VDF]_0$, $\eta = [CF_3(VDF)_nI]/[CF_3I]_0$.

which have the following chemical shifts: (a) −108, (b) −114.3, (c) −112.6, and (d) −107.4 ppm.

From the experimental data (both ^{19}F and ^1H NMR spectra) few reversed adducts coming from the reversed VDF chaining occurred while the others were not present at all. These results confirm those developed by Tatemoto,[31,32] Carlson,[33] Hung,[34] and Arcella et al.[35,36] regarding the living character of the polymerization called iodine transfer polymerization (ITP)[2].

It is also possible to estimate the defect of the VDF chaining (i.e., the percentage of the $-CH_2CF_2CF_2CH_2-$ head-to-head addition in the PVDF chain formed) that corresponds to

$$\%\mathbf{U} = \frac{I_{-116}}{I_{-116} + I_{-91} + I_{-38} + I_{-113}}$$

U shows the number of groups $-CF_2CF_2-$ with regard to all the $-CF_2-$ groups present in the molecules. We calculated this value for each sample and obtained the results shown in Table 8.

The small values indicate that a certain livingness has appeared, as noted by various industries quoted above[31−36] in the iodine transfer polymerization of fluoroalkenes (mainly VDF, TFE, and VDF/HFP).

Interestingly, the quasi absence of tail-to-tail addition is observed in the ^1H NMR (Figure 3), i.e., the absence of the multiplet centered at 2.2 ppm due to the $CF_2CH_2-CH_2CF_2$ diad that also confirms this pseudo-living behavior.[2]

Synthesis of the Fluoroacrylates. As presented in previous studies,[11−15] the synthesis of fluoroacrylates was realized by a three-step procedure starting from the iodofluorinated telomers, as depicted in Scheme 2.

First, the radical addition of VDF telomers onto an excess of allyl alcohol (up to an 8-fold excess, Table 3) initiated by AIBN enabled us to obtain VDF-containing iodohydrines (**1**) in high yields (ranging from 71% to 94%). This was evidenced by the ^{19}F NMR spectrum that exhibits a high-field shift of the signal assigned to CH_2CF_2I from −38 to −94 ppm (assigned to the difluoromethylene in $-CH_2CF_2CH_2CHI-$ sequence in the iodohydrin). Furthermore, adding one drop of trichloromethyl isocyanate in the NMR tube enabled the triplet centered at 3.6 ppm (attributed to the methylene group in CH_2OH end group) to undergo a ca. 1 ppm downfield shift.

Then, the selective reduction of the iodine atom was performed in the presence of tributylstannane and led to fluoroalcohol (**2**) with satisfactory yields (60−82%). Proof was shown in the ^1H NMR spectrum of $R_FCH_2CHICH_2OH$, where the multiplet attributed to CHI got a high-field shift from 4.2 to 1.8 ppm after selective reduction of the iodine atom.

Finally, acrylation of the alcohols was carried out in the presence of an excess of acryloyl chloride, and acrylates (**3**) obtained were purified. The FTIR spectra of the final products showed the absence of the wide band at about 3500 cm^{-1} assigned to the hydroxy end groups and the presence of the characteristic acrylic double bond at frequencies of $\nu = 1650$ and 810 cm^{-1}.

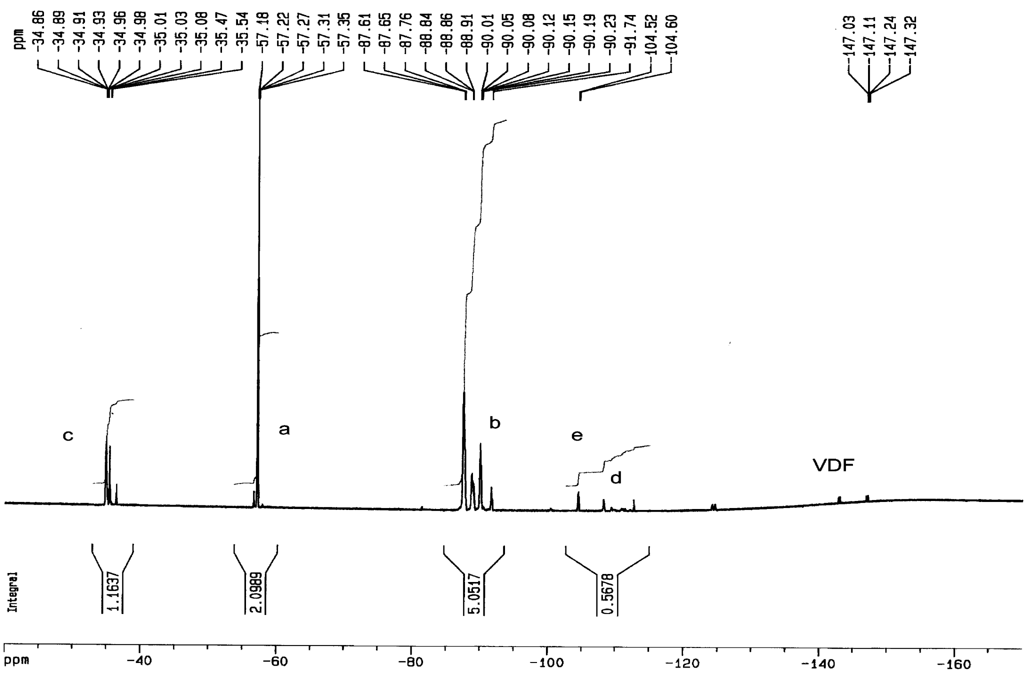


Figure 2. ^{19} F NMR spectrum for the telomer precursor of F4.

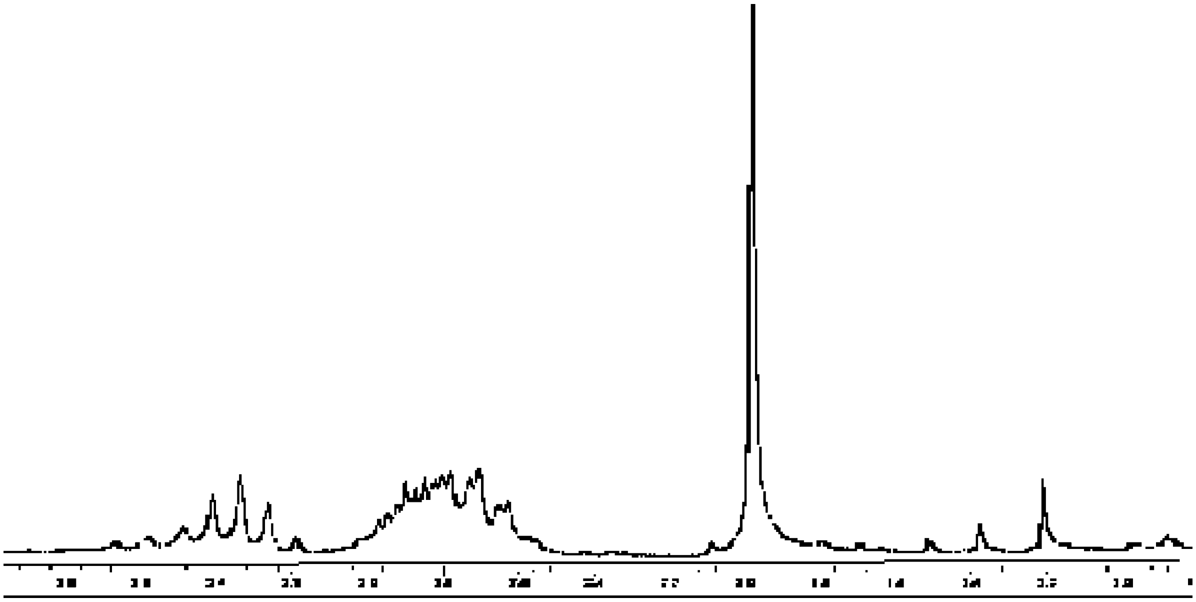


Figure 3. ^{1}H NMR spectrum for the telomer precursor of F4.

Table 8. Amount of Defects (*U*) of Oligo(VDF) Chaining, $-CH_2CF_2CF_2CH_2-$, in F2, F3, and F4 Telomers

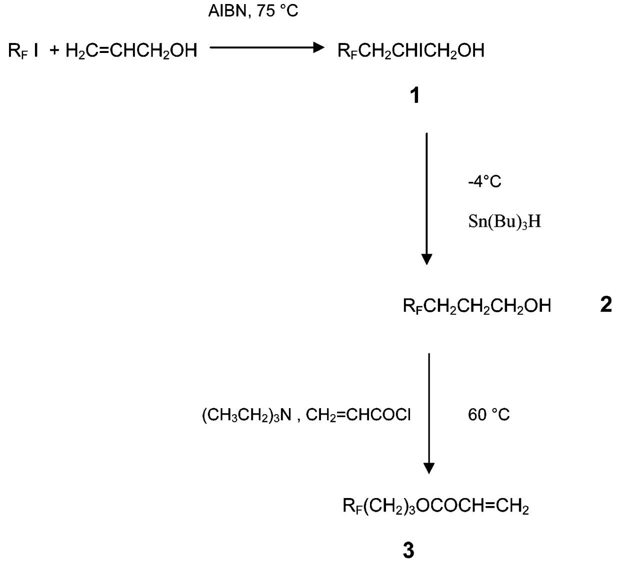
	U (%)
$CF_3(VDF)_{2.3}I$	1.4
$CF_3(VDF)_{3.1}I$	2.9
$CF_3(VDF)_{4.8}I$	2.7

The ^{1}H NMR spectrum shows the expected complex system of peaks centered at 6−6.5 ppm assigned to the protons of the acrylate function and the low-field shift of the signal attributed to CH_2OH group from 3.6 to 4.2 ppm. In that of $C_6F_{13}(CH_2CF_2)(CH_2)_3OCOCH{=}CH_2$ are observed major signals characteristic of the $-\mathbf{OCH{=}CH_2}$ group centered in the 6.0−6.5 ppm range, the signal at 4.2 ppm of$-CH_2\mathbf{CH_2}O-$, at 3.6 ppm the signal for $-CF_2\mathbf{CH_2}CH_2-$, and around 3.2 ppm the signals for $-CF_2\mathbf{CH_2}CF_2-$ and $-CH_2\mathbf{CH_2}CH_2-$.

The minimum overall yield of the syntheses, excluding the telomerization step, was about 40% from $R_F(VDF)_nI$.

Bulk Properties of the UV-Cured Films. The fluorinated monomers synthesized in this work were copolymerized in bulk with hydrogenated acrylic resin bisphenol A-dihydroxyethyl etherdiacrylate (BHEDA). This was carried out in the presence of 2-hydroxy-2-methyl-1-phenyl-1-propanone as the photoinitiator by means of the UV-curing technique. The concentration of the fluorinated monomer varied from 0.01% w/w up to their solubility limit in the BHEDA resin (around 1.5% w/w, as assessed by visual inspection). First, the mixtures were coated on a glass substrate (the thickness of the films was about 100 μm) and then irradiated under UV light. As expected, the presence of a small amount of the fluorinated comonomer did not change

Scheme 2. Steps of the Telomer Functionalization Reactions[a]



[a] $R_F \equiv C_6F_{13}CH_2CF_2$ or $CF_3(CH_2CF_2)_n$.

the kinetics and the double-bond conversion of the systems. Through FTIR analyses, monitoring the typical acrylic double bond signal at 1650 cm^{-1}, the photopolymerization yield was measured and found to be almost quantitative in all cases. Also, the gel percentage of the UV-cured mixtures was always higher than 97%.

The films obtained were both homogeneous and transparent when a maximum amount of 1.5% w/w of the fluorinated monomer was present. For higher amounts of fluoroacrylates, the films became hazy and then opaque.

The glass-transition temperature of the films (T_g), assessed by DSC analyses, was independent of the chemical composition: as the amount of comonomer was always very low, T_g was found to be equal to 70 °C for all systems. This value was also the same as that obtained from the pure BHEDA resin. In conclusion, the fluorinated comonomer, present in low amount, did not modify both the state of the films and their main bulk properties.

Surface Properties of the UV-Cured Films. The wettability of the films was studied by contact angle measurements with water. The contact angles of the pure acrylic resin, coated on a glass substrate, were around 78° and 47° on the air side and glass side, respectively.

When a fluorinated monomer was added to the curable product and the mixture was coated on the same substrate, a dramatic change of the wettability on the air side of the films was assessed. As shown in Figure 4, in the presence of any comonomer, the contact angle was found to be higher than 90°. This means that hydrophobic surfaces were obtained.

At the same time, on the glass side of the films there was no modification, whatever the type and amount of fluoroacrylate. In Figure 5 the behavior of comonomer F2 is shown as an example.

The values of the contact angles plotted as a function of the comonomer F2 concentration show that the fluorinated additive is effective only on the air side of the films and the surface modification was highly selective.

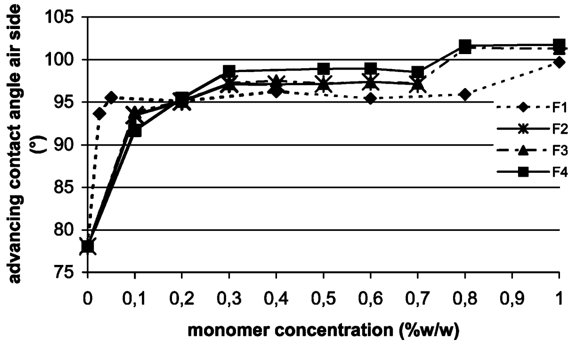


Figure 4. Advancing contact angle of the air side of films prepared onto glass.

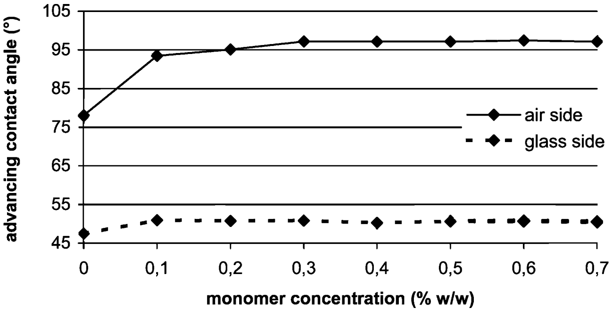


Figure 5. Advancing contact angle for the air side and the glass side of a film containing the F2 comonomer.

As reported in Figures 4 and 5, the wettability depends on the monomer concentration, i.e., on the fluorine content. A very small amount of any fluoroacrylate is enough to make the surface hydrophobic (or nonwettable by water). This condition, corresponding to a contact angle higher than 90°, is reached for concentrations as low as 0.03−0.10% w/w. Increasing the monomer concentration, the contact angle value can reach and even overcome 100° and indicates a hydrophobic surface, as is usually found for apolar materials such as the polyolefins and also the poly(fluoroolefin)s.

It is interesting to discuss the characteristics of the surfaces comparing the different monomers. The effect of the chemical structure on the surface activity of the product is not obvious. To explain this behavior it is useful to compare the products, examining, inside their chain, a spacer group (Sp), a fluorinated chain (R_F), and a fluorinated end group (FG), according to a general model FG−R_F−Sp−.

In our case it is clear that FG is always a perfluorinated methyl group, which is known to play a major role on the surface activity of the molecules.[37−39] Also Sp, whose effect is discussed in the literature,[14,15,37] is not changed in the series of comonomers used, as it can be identified as $CH_2CF_2CH_2CH_2CH_2$. As for R_F, the structure is different between F1 and the other products as we compare a perfluoroalkyl chain and a partially fluorinated chain of VDF type. The latter has an increasing length going from F2 to F4. Therefore, the fluorine content should be rather different in the order of the increasing fluorine content: F1 ≈ F4 > F3 > F2. However, F1, F2, and F3 show a very similar surface activity; F4 has a better activity than F1, while in terms of fluorine concentration, it should be similar to F1.

These facts can be explained considering that the VDF-based acrylates contain different isomers, as reported by the GC analyses and NMR. Any of them contain a fraction of products with a longer chain, which

Table 9. Surface Atomic Composition of the Cured Film Containing 0.3 % of F3 Monomer (as determined by XPS analyses)

t.o.a.	F1s/C1s	O1s/C1s
25°	0.39	0.28
45°	0.28	0.32
90°	0.19	0.32
calcd values	0.0019	0.25

Table 10. Results of Cross-Cut Adhesion Tests

	BEDHA	F1	F2	F3	F4
monomer concentration (w/w %)	0	0.6	0.7	0.4	0.6
% adhesion	100	100	95	97	100

can have a strong effect on the surface activity even at low concentration. In particular, F2 and F3 contain isomers with six VDF units, 15% and 30% mol/mol, respectively. F4 contains a fraction of eight VDF units (around 10%).

On the basis of the surface characteristics found, comparing the results with previous data,[11−15] it can be assumed that the surface composition of these systems is different from the bulk composition, as it was enriched in the fluorinated monomers, which migrated to the air interface before the curing was performed. This migration is due to the difference in surface tension between the comonomers (i.e., the acrylic resin and the fluoroacrylates). Since the fluorinated compounds have a low surface tension, lower than that of the hydrogenated diacrylate, they tend to move to the air interface. This behavior is in agreement with both our previous results for other UV-cured systems which contained low amounts of acrylic monomers having perfluoroalkyl branches or perfluoroalkyl ether chains[11−15] and the abundant literature on the surface segregation of fluorinated copolymers and blends.[2,40−44]

The surface enrichment was confirmed by studying the surface composition by XPS spectroscopy. The results of the elemental surface chemical analysis, concerning the films containing 0.3% w/w of F4, are reported in Table 9 and show that the concentration of this monomer at the film surface (air side) is 2 orders of magnitude higher than the calculated value, i.e., the bulk concentration.

Moreover, quantitative data of the F1s/C1s atomic ratios collected at different take off angle (t.o.a.), i.e., at different depths, evidence the existence of a concentration gradient from the outermost layers of the film toward the bulk of the film. The comonomer concentration in weight percent varies from 62% (at t.o.a.= 25°) to 30% (at t.o.a. = 90°).

While the fluorine content is higher in the surface than in the bulk, the oxygen amount decreases in moving toward the external layers of the films. At highest t.o.a., the O/C ratio approaches the calculated value of the non-fluorinated resin. This confirms the preferential distribution of the fluorinated additives toward the air interface.

As the glass side of the films was not modified, the adhesion was not expected to be influenced by the presence of the fluorinated comonomers. The results of the cross-cut adhesion test are collected in Table 10 for a series of films containing the different fluoroacrylates.

The data clearly show that adhesion to glass is good for both the homopolymeric film and the fluorine-containing copolymers. As the fluorinated products are known to show poor adhesion, these results further confirm the selectivity of the surface modification obtained with these products, i.e., their self-stratification on the air side of the films.

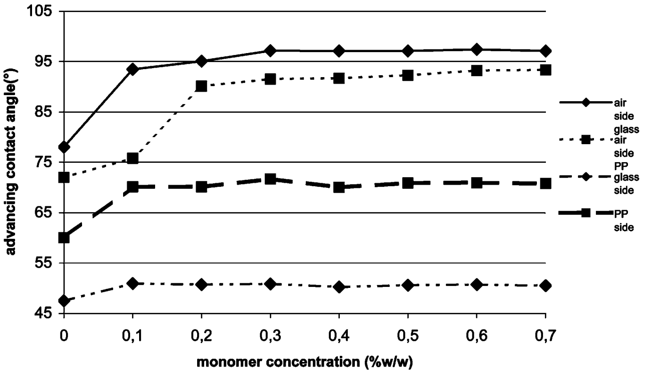


Figure 6. Advancing contact angles for films containing F2 when different substrates are used.

Table 11. Surface Properties of the UV-Cured Films: Effect of the Substrate

	$\theta_{\max}$	F1	F2	F3	F4
glass	$\theta_{\text{maxairside}}$ for the pure resin = 78	105	97	101	102
	$\theta_{\text{maxglassside}}$ for the pure resin = 47	51	51	51	51
PP	$\theta_{\text{maxairside}}$ for the pure resin = 72	110	97	98	97
	$\theta_{\text{maxpolypropyleneside}}$ for the pure resin = 60	72	70	70	70

When the substrate employed for making the films was highly apolar, as in the case of polypropylene or polyethylene, both sides of the polymeric networks were made hydrophobic. This was evidenced in previous studies[37,38] and is also revealed in the present systems. In fact, using a PP substrate a modification of the contact angle on both sides of the films was noted. In Figure 6, concerning the behavior of monomer F2, the upper curves correspond to evolution of the contact angles on the air side of the films having the same composition but coated on different substrates, while the lower curves permit a comparison of the film surfaces in contact with the substrate.

It is clear that the air side is always made hydrophobic in the presence of the fluorinated comonomer, independent of the type of substrate employed. On the contrary, the film surface in contact with the substrate has a different performance: when the substrate is polar (glass), there is no change of the wettability in the presence of the fluoromonomers, while for an apolar substrate (e.g.,PP), a neat effect of the additives was noted (Figure 6).

Table 11 lists the maximum value of the obtained contact angles for the films containing the different comonomers, evidencing the substrate effect.

Further information on the film surfaces has been obtained by the contact angle hysteresis, which is the difference between the advancing and receding angles. The hysteresis of the films increased in the presence of the fluorinated additives with an asymptotic trend, as shown in Figure 7, for the systems containing the F2 additive.

The surface heterogeneity, i.e., the presence of different chemical compositions or various physical state phases, is likely to be the major factor for controlling the hysteresis of these films. The asymptotic trends observed are justified assuming that the systems have similar surface compositions and morphologies. As expected, on the glass side the hysteresis value of the films with the fluorinated monomer is equal to the value measured on the glass side of the pure BHEDA resin.

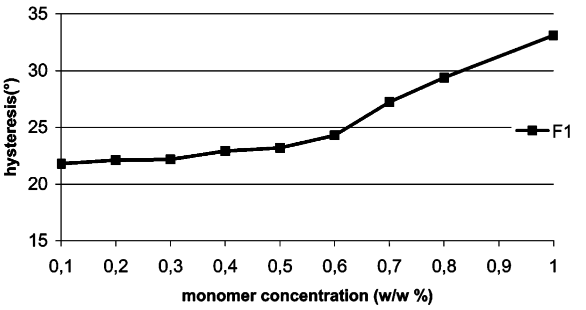


Figure 7. Hysteresis of the contact angle measurements for the air side of films containing the F2 comonomer.

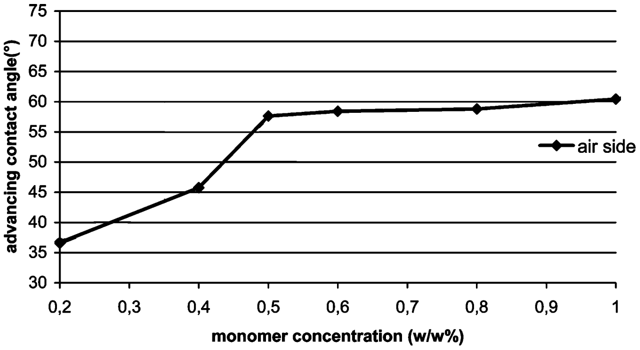


Figure 8. Advancing contact angles with hexadecane on the air side of films containing the F1 comonomer.

Tests of wettability with hexadecane were also carried out. In this case, a high value of contact angle indicates that the surface was oleophobic. Oleophobicity is an interesting property as it also means that the film behaves as a dirt repellent and antigraffiti. The influence of the fluorinated monomers is shown in Figure 8 for monomer F1, and similar trends were also found for the other copolymers.

Conclusions

The radical telomerization of VDF enabled us to synthesize different telomers to be used as useful precursors of original VDF-containing fluoroacrylates. These products (although their syntheses need to be optimized), via the presence of the acrylic unsaturation, can be photocopolymerized with hydrogenated resins. In particular, by means of the UV-curing technique, using diacrylic resins, we obtained networks in the form of films. The fluorinated monomers were used in a very low amount (less than 1.5%), so that the bulk properties of the films were the same as those of the pure hydrogenated resin. However, due to the high surface activity of the fluorinated products, they migrated to the film surface in contact with air and enriched the external layer of the films, so that the copolymeric films obtained by curing showed interesting changes in surface properties. A deep decrease of the wettability with water was selectively obtained on the air side of the films, which could be made very hydrophobic. Simultaneously, a high oleophobicity was achieved. The opposite surface of the films, in contact with glass, was not modified and maintained the polar characteristics of the pure resin, including its adhesion. Interestingly, no drastic change of the surface property was noted between fluoroacrylates bearing a perfluoroalkyl chain of the C_nF_{2n+1} type and those based on VDF units with a CF_3 end group. Hence, VDF telomers could be potential precursors of novel fluoroacrylates, as competitors of commercially available acrylates containing tetrafluoroethylene base units.

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Supporting Information Available: Introduction on UV-curing systems, experimental part on the synthesis of longer VDF telomers and other F-acrylates, and measurements of XPS. This material is available free of charge via the Internet at http://pubs.acs.org.

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