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Copolymers of Isopropenyl Alkyl Ethers with Fluorinated Acrylates and Fluoroacrylates: Influence of Fluorine on Their Thermal, Photochemical, and Hydrolytic Stability

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ABSTRACT: The homopolymer of butyl isopropenyl ether (pBPE) and a series of homo- and copolymers of BPE and decyl isopropenyl ether (DPE) with acrylates and methacrylates fluorinated on the vinyl and/or the alkoxy group were synthesized by cationic (pBPE) or free-radical process. The three structurally analogous 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFIMA), 1,1,1,3,3,3-hexafluoroisopropyl 2-fluoroacrylate (HFIFA), and isopropyl 2-fluoroacrylate (IFA) as well as ethyl 3,3-difluoro-2-methylpropenoate (EFMA) were used as the fluorinated comonomers. The thermal properties and aging behavior of the copolymers were correlated to their structure and particularly to the protective action of the fluorinated moieties against photooxidative and acid-catalyzed hydrolytic degradation triggered by the labile side chains of the BPE units. Depending on their distance from the primary center of photooxidation, the fluorinated groups can either slow down or largely modify the degradation pathway, as shown by the dominant cross-linking in the strictly alternating HFIFA/BPE which outweighs the prevailing chain fragmentation of the other copolymers.

Introduction

Polymer properties can be effectively modified by the introduction of fluorinated groups. The most evident and characteristic result is a significant decrease of the surface energy, affecting wettability, adhesion, and solvent resistance. Moreover, the presence of highly stable C−F bonds can substantially improve the chemical, thermal, and photochemical stability of the material. Fluorinated polymers are thus extensively applied as high-performance coatings to obtain water-repellent, antifouling, low-friction, and nonsticky surfaces. Unfortunately, highly fluorinated polymers such as of those based on perfluoroolefins are generally insoluble in most of the solvents commonly used for coating applications; in addition, their adhesive and mechanical properties are often poor and their cost is comparatively high. To bypass these drawbacks, most of the commercial products are based on partially fluorinated copolymers designed to balance the favorable properties and limitations associated with the unfluorinated components of the macromolecule. In particular, the latter provide adhesion and solubility but weaken the water repellence and the chemical stability.

Over the past 10 years an investigation on the development of partially fluorinated acrylic-based protective polymers for architectural surfaces has been undertaken by our group.[1,2] Among them, copolymers of fluorinated acrylates with vinyl ethers[3,4] were expected to bring about useful properties due to the absence of UV-absorbing chromophores, from which photodegradation processes can originate either directly or through sensitization mechanisms,[5] and to the conformational flexibility of vinyl ethers, lowering the glass transition temperature (T_g) and improving film formation. Unfortunately, these copolymers showed moderate to poor photochemical stability, mainly ascribed to the sensitivity of the labile hydrogen on the main chain tertiary carbon atom of the vinyl ether units.[6] Replacement of the sensitive vinyl ethers with their α-substituted homologues, alkyl 2-propenyl (hereafter isopropenyl) ethers, is a straightforward way of addressing the above problem.

In the presence of free radical or anionic initiators α-substituted vinyl ethers show a reactivity similar to their unsubstituted homologues, in that they tend to give at most low oligomers in poor yield or no chain propagation at all. Introduction of an electron-donating alkyl group at the α-carbon generally increases the reactivity of alkyl vinyl ethers toward electrophiles, although excess steric hindrance can result in the opposite effect. Indeed, methyl isopropenyl ether has been polymerized in fair to good yields with cationic initiators even in relatively mild conditions,[7,8] whereas higher alkenyl ether (AE) homologues such as butyl and propyl isopropenyl ether are reported to yield lower MW products.[9] However, the intrinsic higher reactivity of these electron-rich but sterically crowded AE toward electrophilic species is preserved, as shown by their higher reactivity in copolymerization experiments with unsubstituted vinyl ethers, where the steric hindrance is released due to comonomer alternation.[10]

Free radical copolymerization of unsubstituted AE with the nucleophilic fluorinated (meth)acrylates (FA) yields different structures, from those containing isolated vinyl ether units to strictly alternating copolymer sequences, depending on the nature of the monomers involved.[11] The combined F substitution on the vinyl group of the acrylate and α-methyl substitution on the vinyl group of the vinyl ether were expected to favor the formation of structurally regular alternating copolymers, owing to the greater difference in electrophilicity.

In the present work are reported the results of an investigation on the synthesis and polymerization behavior of two alkyl

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isopropenyl ethers, namely butyl isopropenyl ether (BPE) and decyl isopropenyl ether (DPE), with the three structurally analogous 1,1,1,3,3,3-hexafluoroisopropyl 2-fluoroacrylate (HFIFA), 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFIMA), and isopropyl 2-fluoroacrylate (IFA), as well as with ethyl 3,3-difluoro-2-methylpropenoate (EFMA).

The photochemical and hydrolytic degradation behaviors of the resulting homo- and copolymers were studied, and structure–properties relationships were investigated.

Experimental Section

Materials. Benzene, diethyl ether, dioxane, tetrahydrofuran (THF), toluene, and triethylamine were dried and purified by distillation with the appropriate procedure and stored under a dry nitrogen atmosphere prior to use. The solvents used in the polymerizations were distilled twice under a nitrogen atmosphere and immediately used. 2,2-Dimethoxypropane (acetone dimethyl acetal, Aldrich) was refluxed over Na and distilled under nitrogen. *n*-Butyl alcohol (Aldrich) was refluxed over CaH_2 and distilled under nitrogen. *n*-Decyl alcohol (Aldrich) was refluxed over K_2CO_3 and distilled under reduced pressure (bp 97–98 °C/70 Pa). Acetic anhydride was refluxed over P_2O_5 and distilled under reduced pressure (46 °C/0.7 kPa). All acrylates and methacrylates were distilled in the presence of 2,6-di-*ter*butyl-4-methylphenol (DTBP) inhibitor and stored at −25 °C under a dry nitrogen atmosphere. 1,1,1,3,3,3-Hexafluoroisopropyl α-fluoroacrylate (HFIFA, a gift from Hoechst-Aventis) and 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFIMA, Apollo) were distilled under a nitrogen atmosphere, collecting the fractions with bp 89–90 and 99 °C, respectively. Isopropyl α-fluoroacrylate (IFA) and ethyl 3,3-difluoro-2-methylpropenoate (EFMA)[12,13] were synthesized and kindly supplied by Prof. Stefano Paganelli and the late Prof. Carlo Botteghi (University of Venice) and purified by cryogenic distillation (10 Pa) before use. The EFMA distillate was a mixture still containing about 30 mol % of the corresponding saturated ester and traces of triethylamine. Azobis(1,1-dimethyl-2-propionitrile) (α,α′-azobis(isobutyronitrile), AIBN, Akzo) was purified by recrystallization from ethanol and stored at −25 °C. Iodine was purified by sublimation (40 °C/60 Pa). Perkadox 16 (4,4′-*tert*-butylcyclohexylperoxydicarbonate, Akzo), titanocene dichloride (Aldrich), and trimethylaluminum (2.0 N solution in toluene, Aldrich) were used as received. Boron trifluoride etherate (BF_3-OEt_2, Aldrich) was distilled at reduced pressure (52 °C, 2.2 kPa) and stored in the dark under a dry nitrogen atmosphere. ZnI_2 was dried under reduced pressure and stored in the dark under a dry nitrogen atmosphere. $FeCl_3$ was stirred for 24 h at 80 °C in refluxing thionyl chloride, filtered off, and stored under a dry nitrogen atmosphere. A hydrogen iodide solution was prepared by slow addition of 2 mL of aqueous HI (Aldrich, 57 wt %) to a flame-dried 500 mL three-necked flask containing a vigorously stirred slurry of P_2O_5 (11.8 g, 83.1 mmol) in dry hexane (155 mL). After the addition, carried out in the dark by accurate wrapping of the glassware with aluminum foil, P_2O_5 was removed by filtration under a dry argon atmosphere, and the obtained 0.02 M HI solution was stored under argon at −25 °C in the dark; the actual concentration was determined by extraction with deionized water of a known amount of the HI solution and titration of the aqueous extract with aqueous 0.1 N NaOH.

Methods. All glassware to be used for the acid-sensitive isopropenyl ethers was washed with 5% aqueous Na_2CO_3 and dry acetone and flame-dried in a nitrogen atmosphere. Size exclusion chromatography (SEC) analyses were performed at room temperature on 0.2% (w/v) sample solutions in distilled THF. Solutions were filtered on 0.45 μm membrane syringe filters, and 200 μL was injected in the chromatograph with an eluent flow rate set at 1 cm^3/min. The system was equipped with four PL-Gel columns with different nominal porosities (500, 10^3, 10^4, and 10^5), a Waters M45 pump, and an Erma 7510 differential refractometer. Column calibrations were performed with PMMA narrow distribution polymer standards (Polymer Labs), and a third-order polynomial equation was obtained from regression analysis. Molecular weight evaluations were performed with internal standard corrections for flow rate fluctuations. Gas chromatographic analyses were performed on a Perkin-Elmer GLC Autosystem instrument equipped with a J&W Scientific DB-FFAP capillary column (15 m, 0.53 mm) and FID detector. GLC-MS analyses were performed on a Perkin-Elmer Q-Mass Api 3 plus (triple quadrupole) instrument, equipped with a DBI column (30 m, 0.25 mm).

Differential scanning calorimetry (DSC) measurements were performed at scan rates of 20 °C/min on 5–20 mg samples using a Perkin-Elmer DSC7 equipped with a CCA7 liquid nitrogen cooling system. Glass transition temperatures, T_g, were taken from the second heating scan as the midpoint of the curve inflection. Thermal gravimetric analyses (TGA) were performed on nitrogen-purged 10–12 mg samples at 10 °C/min in the 30–700 °C range using a Mettler TC11 TA processor connected with a Mettler TG 50 thermobalance. ^1H and ^{13}C NMR spectra were recorded on 5–10 wt % solutions in $CDCl_3$ (a $CDCl_3/CF_2Cl-CFCl_2$ mixed solvent in the case of the poorly soluble acid-treated HFIMA/BPE and HFIFA/BPE) with a Varian Gemini 200 instrument. Chemical shifts were related to the respective $CHCl_3$ signals for ^1H and ^{13}C nuclei. Peak multiplicity was denoted as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet), and b (broad signal). FTIR spectra were recorded either from neat liquids or from thin films cast from solution on KBr pellets, using a Perkin-Elmer 1600 instrument.

Accelerated Photoaging. The experiments were performed using a Sunset CPS exposure unit (Heraus, Germany) equipped with a xenon lamp. A glass filter with cutoff at $\lambda < 295$ nm was employed in order to better mimic ordinary outdoor solar exposure. Irradiation power density at the film surface was 765 W/m^2. Constant temperature (44 °C) was maintained throughout the photoaging experiment as the result of lamp heating and air recirculation within the chamber.

Film preparation, weight loss, and gel content determination, as well as the analyses carried out on samples submitted at different time of irradiation, were performed following the procedures already reported elsewhere.[14]

Hydrolytic Stability Tests. To the polymer sample (about 0.2 g) dissolved in acetone (10 mL) was added 0.1 mL of aqueous HCl, the concentration of which had been adjusted to obtain a final solution with the desired hydrogen ion concentration (that is, either 0.1 or 0.01 mol L^{-1}, corresponding to a nominal pH = 1 or pH = 2, respectively). The resulting homogeneous acetone solution was stirred in the dark at room temperature for 96 h, then neutralized with $NaHCO_3$, and filtered. The polymeric products were retrieved and purified by precipitation in a large excess of methanol, except for the hydrolysate of the BPE homopolymer which was collected by simple removal of the solvent and other volatile degradation compounds under a reduced pressure.

Monomer Preparation. *2,2-Dibutoxypropane* (acetone dibutyl ketal) (DBP) was synthesized following a modification of the method reported by Lorette et al.[15,16]

Butyl alcohol (20.1 mL, 0.22 mol), 2,2-dimethoxypropane (12.3 mL, 0.1 mol), benzene (34 mL), and *p*-toluenesulfonic acid monohydrate (0.67 mg, 0.34 mmol) were loaded into a Claisen apparatus under a dry nitrogen atmosphere and stirred for 3 h at 60 °C, while the benzene–methanol azeotrope was distilled off (57–59 °C). The temperature was then increased to distill off excess butyl alcohol. The remaining 11.5 mL of yellowish viscous liquid was further purified by distillation over Na under a reduced pressure (88–89 °C, 3.8 kPa), affording 13.2 g of GLC-pure DBP in a 70% yield. A higher conversion, roughly 90% according to GLC data on the raw reaction product, could have been obtained by neutralization of the acid catalyst prior to distillation of the excess butyl alcohol, thereby preventing some product loss due to retrocatalytic deacetalization.

GLC-MS: $m/z = 41$ (11.2%), 43 ($C_3H_7^+$, 8.8%), 55 (3.8%), 56 ($CH_2{=}CH-C_2H_5^+$, 6.0%), 57 ($C_4H_9^+$, 24.6%), 58 (6.6%), 59 ($C_3H_6OH^+$, 100%), 60 (7.7%), 61 (33.3%), 115 ($M^+ - OC_4H_9$, 80.7%), 116 (7.3%), 117 (3.8%).

^{1}H NMR ($\mathrm{C_6D_6}$): 0.9 (t, $\mathrm{C}\mathit{H}_3\mathrm{CH}_2$), 1.4 (s, $\mathrm{CC}\mathit{H}_3$), 1.5 (m, $\mathrm{CH_3C}\mathit{H}_2$), 1.6 (q, $\mathrm{C}\mathit{H}_2\mathrm{CH_2O}$), and 3.5 ppm (t, $\mathrm{CH_2O}$). ^{13}C NMR ($\mathrm{C_6D_6}$): 13.7 ($\mathit{C}\mathrm{H_3CH_2}$), 19.5 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$), 24.7 ($\mathit{C}\mathrm{H_2CH_2O}$), 32.2 ($\mathit{C}\mathrm{H_3C}$), 59.9 ($\mathit{C}\mathrm{H_2O}$), and 99.0 ppm ($\mathit{C}$).

IR (neat): 2960, 2934, 2872, 1462, 1380, 1212, 1164, 1074, 1020, 982, 896, 836 $\mathrm{cm^{-1}}$.

1-(2-Propenyloxy)butane (butyl isopropenyl ether, BPE) was synthesized following a modification of the method reported by Miginiac et al.[17]

A three-necked flask equipped with a magnetic stirrer, reflux condenser, and dropping funnel was loaded under a nitrogen atmosphere with two solutions of aluminum trichloride (5.89 g, 44.2 mmol) and triethylamine (8.95 g, 88.4 mmol) in dry diethyl ether (a total of 54 mL). After stirring the mixture for 2 h at room temperature, a solution of 2,2-dibutoxypropane (4.16 g, 22.1 mmol) in dry diethyl ether (5 mL) was slowly added to the milky slurry, and the mixture was stirred for 24 h at room temperature. After addition of 35 mL of 5 N aqueous NaOH, the mixture was extracted with diethyl ether (3 × 25 mL); distillation of the ethereal extract at reduced pressure (53 °C, 23 kPa) gave a mixture of BuOH (8%), $\mathrm{Et_3N}$ (53%), and BPE (39%), which was dissolved in pentane and washed with aqueous $\mathrm{CuCl_2}$ to remove the residual amine. A further distillation at reduced pressure (60−62 °C, 13 kPa) gave 1.5 g of BPE (purity >99% by GLC, yield 59.5%).

GLC-MS: $m/z = 39$ (6.5%), 41 ($\mathrm{C_3H_5^+}$, 13.7%), 42 (5.8%) 43 ($\mathrm{M^+ - CH_3 - C_4H_9}$, 17.5%), 53 (2.6%), 55 (12.6%), 56 ($\mathrm{CH_3{-}CH{=}CH{-}CH_3^+}$, 31.7%), 57 ($\mathrm{C_4H_9^+}$, 24.6%), 58 ($\mathrm{C_3H_6O^+}$, 100%), 59 (58.4%), 60 (3.8%), 85 (2.2%), 99 ($\mathrm{M^+ - CH_3}$, 53.8%), 100 (5.0%), 114 ($\mathrm{M^+}$, 1.7%).

^{1}H NMR ($\mathrm{C_6D_6}$): 0.9 (t, $\mathrm{C}\mathit{H}_3\mathrm{CH}_2$), 1.4 (m, $\mathrm{CH_3C}\mathit{H}_2$), 1.6 (m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2O}$), 1.85 (s, $\mathrm{C}\mathit{H}_3\mathrm{C{=}}$), 3.54 (t, $\mathrm{CH_2O}$), and 3.90−3.94 ppm (dd, $\mathrm{C{=}CH_2}$). ^{13}C NMR ($\mathrm{C_6D_6}$): 13.7 ($\mathit{C}\mathrm{H_3CH_2}$), 19.2 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$), 22 ($\mathit{C}\mathrm{H_3C{=}}$), 31.2 ($\mathit{C}\mathrm{H_2CH_2O}$), 66.5 ($\mathrm{CH_2O}$), 80.6 ($\mathrm{H_2C{=}}$), and 159.8 ppm ($\mathrm{H_2C{=}}\mathit{C}$).

IR (neat): 3120 ($\mathrm{{=}CH_2}$), 2960, 1656 ($\mathrm{C{=}C}$), 1450, 1366, 1282, 888 (δ_{as} $\mathrm{CH_2{=}C}$), 512 $\mathrm{cm^{-1}}$.

n-Decyl Acetate (DAC). Acetic anhydride (8.2 mL, 58 mmol), *n*-decyl alcohol (11.2 mL, 58 mmol), and triethylamine (12.2 mL, 88 mmol) were stirred for 12 h at room temperature in a three-necked flask under a dry nitrogen atmosphere. Diethyl ether (30 mL) was added, and the obtained solution was washed with 1 N HCl (3 × 30 mL) and then with 5% aqueous $\mathrm{NaHCO_3}$ to neutrality. The collected organic phases were dried overnight over $\mathrm{Na_2SO_4}$; after removal of the solvent under reduced pressure, fractional distillation (88 °C, 65 Pa) gave 8.9 g of DAC (purity >99% by GLC, yield 76.2%).

GLC-MS: $m/z = 39$ (3.9%), 41 (21.9%), 42 (11.3%), 43 ($\mathrm{CH_3\text{-}CO^+}$, 79.3%), 44 (3.2%), 53 (4.5%), 54 (8.9%), 55 (77.6%), 56 (72.9%), 57 (42.2%), 58 (6.2%), 61 (74.3%), 67 (13.2%), 68 (24.6%), 69 (76.5%), 70 (100%), 71 (21.6%), 73 (12.7%), 81 (5.0%), 82 (31.5%), 83 (69.7%), 84 (44.8%), 85 (11.3%), 87 (2.0%), 96 (8.1%), 97 (40.2%), 98 (23.2%), 99 (2.0%), 101 (2.9%), 110 (2.7%), 111 (22.1%), 112 (23.2%), 113 (2.2%), 116 (6.0%), 140 ($\mathrm{C_{10}H_{20}^+}$, 4.8%).

^{1}H NMR ($\mathrm{CDCl_3}$): 0.85 (t, $\mathrm{C}\mathit{H}_3\mathrm{CH}_2$), 1.1−1.4 (bs, 14H, $\mathrm{CH_3\text{-}(C}\mathit{H}_2\mathrm{)_7}$), 1.65 (m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2O}$), 2.0 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{C{=}O}$), and 4.1 ppm (t, 2H, $\mathrm{CH_2O}$). ^{13}C NMR ($\mathrm{CDCl_3}$): 14.1 ($\mathit{C}\mathrm{H_3CH_2}$), 21.2 ($\mathit{C}\mathrm{H_3C{=}O}$), 24.1 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$), 26.9 ($\mathrm{C_2H_5}\mathit{C}\mathrm{H_2}$), 28−30 ($\mathrm{C_3H_7(}\mathit{C}\mathrm{H_2)_4}$), 31 ($\mathit{C}\mathrm{H_2CH_2CH_2O}$), 32.3 ($\mathit{C}\mathrm{H_2CH_2O}$), 66.1 ($\mathrm{CH_2O}$), and 172.1 ppm ($\mathrm{C{=}O}$).

IR (neat): 2956, 2926, 2856, 1744 (s, $\mathrm{C{=}O}$), 1468, 1386, 1366, 1240, 720 (δ $\mathrm{CH_2}$) cm-^{1}.

1-(2-Propenyloxy)decane (n-decyl isopropenyl ether, DPE). A three-necked round-bottomed flask, equipped with a magnetic stirrer, reflux condenser, and dropping funnel, was loaded with titanocene dichloride (8.7 g, 35 mmol) and trimethylaluminum (70 mmol, as a 2 M solution in toluene) under a dry nitrogen atmosphere. The resulting red solution was stirred at room temperature for 72 h, while the methane evolved from the reaction was allowed to vent off. The Tebbe reagent thus formed was used in situ: after cooling the obtained solution to −17 °C, a solution of DAC (8.5 mL, 3.5 mmol, in 35 mL of dry THF) was added dropwise. The mixture was stirred at −17 °C for 30 min, then a further 90 min while slowly increasing the temperature from −17 to 0 °C, and finally at room temperature for a further 90 min. To increase the yield, the conversion of decyl acetate was monitored by gas chromatography. When no further increase in the concentration of DPE could be detected the reaction mixture was diluted with 100 mL of dry diethyl ether, then 43 mL of aqueous 1 N NaOH was gradually added for 20 min to stop the reaction. The raw product was filtered through a Celite pad by vacuum suction, washed with diethyl ether, and dried over $\mathrm{Na_2SO_4}$ and purified by column chromatography on basic alumina, using a 1/10 diethyl ether/hexane mixture as the eluent. Fractional distillation at reduced pressure (75−77 °C, 7 Pa) gave 0.38 g of GLC-pure DPE as a colorless liquid (yield 5.5%).

Table 1. Cationic Homopolymerization of BPE

BPE (mol/L)	solvent	*T* (°C)	initiating species	initiator (10^{-3} mol/L)	time (h)	conv (%)
1.0	$\mathrm{Et_2O}$	−78	$\mathrm{I_2}$	1.0	96	97
1.0	toluene	−78	$\mathrm{I_2}$	0.5	4	31
0.14	$\mathrm{CH_2Cl_2}$	0	$\mathrm{HI/ZnI_2}$	2.0[a]	1.5	71
1.0	toluene	−78	$\mathrm{FeCl_3}$	0.5	4	2
1.0	toluene	−78	$\mathrm{BF_3OEt_2}$	0.5	4	4

[a] HI concentration; $\mathrm{HI/ZnI_2}$ mole ratio = 10.

GLC-MS: $m/z = 39$ (4.9%), 41 (26.3%), 42 (8.3%), 43 ($\mathrm{CH_3\text{-}CO^+}$, 43.0%), 53 (4.3%), 54 (5.0%), 55 (55.0%), 56 (39.6%), 57 (51.9%), 58 ($\mathrm{CH_3C(OH){=}CH_2^+}$, 34.5%), 59 (100%), 60 (4.9%), 67 (6.9%), 68 (9.6%), 69 (42.0%), 70 (50.7%), 71 (17.8%), 73 (3.9%), 81 (2.3%), 82 (10.9%), 83 (32.0%), 84 (19.3%), 85 (9.6%), 96 (2.4%), 97 (14.6%), 98 (5.6%), 99 (2.6%), 111 (5.4%), 112 (5.9%), 138 (3.0%), 183 ($\mathrm{M^+ - CH_3}$, 8.9%).

^{1}H NMR ($\mathrm{C_6D_6}$): 0.95 (t, $\mathrm{C}\mathit{H}_3\mathrm{CH}_2$), 1.2−1.5 (bs, 14H, $\mathrm{CH_3\text{-}(C}\mathit{H}_2\mathrm{)_7}$), 1.6 (m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2O}$), 1.9 (s, $\mathrm{C}\mathit{H}_3\mathrm{C{=}}$), 3.58 (t, $\mathrm{CH_2O}$), and 3.9−4.0 ppm (s, $\mathrm{H_2C{=}}$). ^{13}C NMR ($\mathrm{C_6D_6}$): 13.7 ($\mathit{C}\mathrm{H_3CH_2}$), 20.9 ($\mathit{C}\mathrm{H_3{-}C{=}}$), 22.5 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$), 26.9 ($\mathrm{C_2H_5}\mathit{C}\mathrm{H_2}$) 29.4−28.9 ($\mathrm{C_3H_7\text{-}(}\mathit{C}\mathrm{H_2)_5}$), 31.0 ($\mathit{C}\mathrm{H_2CH_2CH_2O}$), 66.9 ($\mathrm{CH_2{-}O}$), 88.7 ($\mathrm{H_2}\mathit{C}\mathrm{{=}C}$), and 159.7 ppm ($\mathit{C}\mathrm{{=}CH_2}$).

IR (neat): 3120 ($\mathrm{{=}CH_2}$), 2960, 1654, 1450, 1366, 1282, 888 (ν_{as} $\mathrm{CH_2{=}C}$), 512 $\mathrm{cm^{-1}}$.

Polymerizations. *Cationic Homopolymerization of BPE (pBPE).* All polymerizations were carried out under a dry nitrogen atmosphere in flame-dried Schlenk tubes equipped with a magnetic stirrer. The relevant experimental data are summarized in Table 1.

(a) Polymerization Initiated by Iodine. Two experiments were carried out. According to the general procedure, the initiator, dissolved in the polymerization solvent, was added with a syringe to the monomer solution at −78 °C and stirred at that temperature for a given time. After quenching the reaction with methyl alcohol the crude product was washed with aqueous sodium thiosulfate and then with water and dried over $\mathrm{Na_2SO_4}$. Excess solvent was then removed, and the polymer was dried in a vacuum at room temperature, without further purification, to give a colorless polymeric material with either a very viscous or a semisolid appearance which was stored in the dark under nitrogen.

^{1}H NMR ($\mathrm{C_6D_6}$): 0.7−0.9 ($\mathrm{C}\mathit{H}_3\mathrm{CH}_2$), 1.2−1.4 ($\mathrm{CH_3(C}\mathit{H}_2\mathrm{)_2}$), 1.45−1.6 ($\mathrm{CCH_3}$), 1.9−2.1 (main chain $\mathrm{CH_2}$), and 3.2−3.4 ppm ($\mathrm{CH_2O}$). ^{13}C NMR ($\mathrm{C_6D_6}$): 14 ($\mathit{C}\mathrm{H_3CH_2}$), 20 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$), 24−25 ($\mathrm{C}\mathit{C}\mathrm{H_3}$), 32−33 ($\mathrm{C_2H_5}\mathit{C}\mathrm{H_2}$), 47−49 ($\mathrm{C}\mathit{C}\mathrm{H_2}$), 60 ($\mathrm{CH_3}\mathit{C}$), and 78 ppm ($\mathrm{CH_2O}$).

IR (film): 2958, 2932, 2870, 1458, 1376, 1356, 1260, 736 $\mathrm{cm^{-1}}$ ($\mathrm{CH_2}$).

(b) Polymerization Initiated by $\mathit{HI/ZnI_2}$. To a stirred solution of BPE (0.4 g, 3.5 mmol) in 22 mL of $\mathrm{CH_2Cl_2}$, cooled to −25 °C, were added 1.75 mL of a 0.025 M solution of HI in hexane (4.4×10^{-5} mol of HI) containing 1.4 mg (4.4×10^{-6} mol) of $\mathrm{ZnI_2}$. The resulting mixture was stirred for 90 min at 0 °C, then quenched with ammoniacal methanol, washed with aqueous sodium thiosulfate and water, and then dried over $\mathrm{Na_2SO_4}$. Evaporation of the solvent

and vacuum-drying at room temperature afforded 0.28 g of a colorless viscous oil.

(c) Polymerization Initiated by $FeCl_3$. To a stirred solution of 0.5 g of BPE in toluene maintained at −78 °C with an acetone−CO_2 cooling bath was added 0.36 mg of $FeCl_3$. After 4 h at that temperature the resulting mixture was quenched with ammoniacal methanol, washed with deionized water, and dried over Na_2SO_4. Solvent evaporation and vacuum-drying at room temperature afforded 0.01 g of a viscous oil.

(d) Polymerization Initiated by BF_3OEt_2. A solution of 0.31 mg of BF_3OEt_2 in dry toluene was quickly added to stirred a solution of 0.5 g of BPE in toluene at −78 °C. After 4 h at that temperature the resulting mixture was quenched with ammoniacal methanol, washed with deionized water, and dried over Na_2SO_4. Solvent evaporation and vacuum-drying at room temperature afforded 0.02 g of a waxy, colorless material.

Homopolymerization of HFIMA, HFIFA, and IFA. Homopolymers of HFIMA, HFIFA, and IFA were prepared by free radical polymerization in bulk at 60 °C (50 °C in dioxane solution in the case of the more reactive IFA), using 1−2 mol % AIBN as the free radical initiator, as reported elsewhere.[4,12]

Copolymerization of BPE and DPE with Fluorinated (Meth)-acrylates (FA). The syntheses of the copolymers of BPE with HFIMA and HFIFA have been reported elsewhere.[18]

HFIFA/DPE. HFIFA (0.27 g, 1.1mmol), DPE (0.22 g, 1.1 mmol), AIBN (5.41 mg, 3.3×10^{-5} mol), and 0.1 mL of dry THF to achieve miscibility were stirred under a nitrogen atmosphere at 60 °C for 72 h. After cooling at room temperature the solid product was dissolved in acetone, precipitated in methanol, and dried to constant weight to give 0.42 g of polymer (86% yield).

^{1}H NMR ($CDCl_3$): 0.8−1.0 (CH_3CH_2), 1.2−1.7 ($CH_3(CH_2)_8$−; CCH_3), 2.2−2.7 (main chain CH_2), 3.2−3.6 (OCH_2), and 6.2−6.5 ppm (CH). ^{13}C NMR ($CDCl_3$): 14 (CH_3CH_2), 21−22 (CH_3CH_2), 24−25 (CCH_3), 25 ($C_2H_5CH_2$), 28−32 ($C_3H_7(CH_2)_5$), 33 (CH_2-CH_2O), 42−50 (CCH_2), 62−64 (CH_3C), 66−71 (m, $CH(CF_3)_2$), 76−78 (CH_2O), 92−98 (d, CF, $J_{C-F} = 192$ Hz), 114−130 (q, CF_3, $J_{C-F} = 282$ Hz), and 168−170 ppm (C═O).

IR (neat): 2966, 2940, 2878, 1800−1779 (C═O), 1466, 1382, 1356−1200 (ν CF_3, C−F), 1200−1112 (ν C−O), and 690 cm^{-1} (ρ CF_3).

IFA/BPE. IFA (0.99 g, 7.5 mmol), BPE (0.85 g, 7.5 mmol), and AIBN (15 mg, 0.091 mmol) were stirred under a nitrogen atmosphere at 60 °C for 50 h. After cooling at room temperature, the crude product was dissolved in 1:1 chloroform/hexane mixture, precipitated in methanol, and then dried to constant weight to give 0.77 g of polymeric product (42% yield).

^{1}H NMR ($CDCl_3$): 0.8−1.0 (CH_3CH_2), 1.0−1.5 (13H, CH_3CH + $CH_3(CH_2)_2$ + CCH_3), 1.7−2.9 (main chain CH_2), 3.0−3.3 (CH_2O), 4.8−5.1 ppm ($OCH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): 14 (CH_3-CH_2), 20 ($CHCH_3$), 21 (CH_3CH_2), 22 (CH_3C−O), 31 ($C_2H_5CH_2$), 46−48 (main chain CH_2), 60−61 (CH_3C−O), 68−69 (CH), 75 (CH_2O), 90−96 (d, CF, $J_{C-F} = 280$ Hz), and 168−170 ppm (C═O).

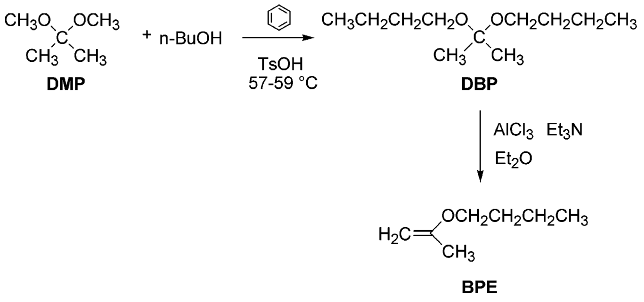
IR (neat): 2966, 2874, 1738−1762 (C═O), 1464, 1428, 1378 (ν_{sym} CH_3 isopropyl group), 1350−1200 (ν CF_3), 1202−1112 (ν C−O), and 920 cm^{-1} (ν CH_3 isopropyl group).

EFMA/BPE. EFMA (1.69 g, 70% mixture, 7.8 mmol), BPE (1.29 g, 11.2 mmol), and AIBN (50 mg, 0.3 mmol, 1.8 mol %) were stirred under a nitrogen atmosphere at 60 °C for 72 h. After cooling at room temperature, the crude product was precipitated in methanol and then dried to constant weight to give 0.21 g of polymeric product (5% overall yield, or 10% yield with respect to the theoretical quantitative conversion of the limiting BPE to give an alternating copolymer).

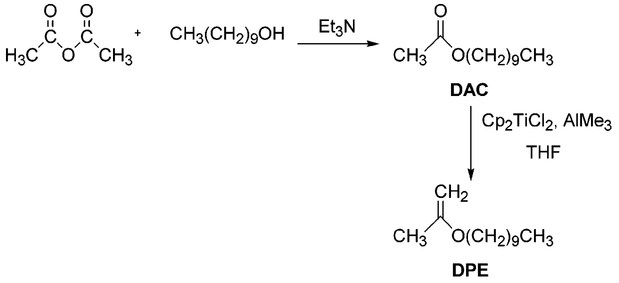
^{1}H NMR ($CDCl_3$): 0.8−1.0 (t, $CH_3C_3H_7$), 1.1−1.6 ($2 \times CCH_3$ + $CH_3(CH_2)_2$ + CH_3CH_2O), 2.2−2.7 (main chain CH_2), 3.2−3.6 ($C_3H_7CH_2O$), and 3.95−4.25 ppm (CH_3CH_2O). ^{13}C NMR ($CDCl_3$): 12−14 ($CH_3C_3H_7$), 16−18 (CH_3CC═O), 19 (CH_3CH_2-C_2H_4), 30−31 (CH_3C−OBu), 31−32 ($C_2H_5CH_2$), 36−38 (CH_3-CH_2O), 48−50 (CCH_2), 50−53 (CCF_2), 60−62 (CH_2OC═O), 64−66 (CH_2OC), 80−82 (CCH_2), 118−130 (t, CF_2, $J_{C-F} = 280$ Hz), and 171−172 ppm (C═O).

IR (neat): 2962, 2958, 2874, 1734 (ν C═O), 1462, 1386, 1350−1220 (ν CF_2), 1202−1112 (ν C−O), and 690 cm^{-1} (b CF_3).

Scheme 1. Synthesis of BPE



Scheme 2. Synthesis of DPE



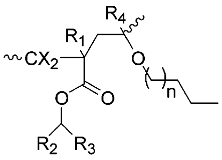
Results and Discussion

To investigate the hydrolytic, thermal, and photochemical stability of the copolymers of BPE with the structurally analogous but differently fluorinated HFIMA, HFIFA and IFA all the respective homopolymers were preliminarly synthesized. Among them, the behavior of the BPE homopolymer had not been studied until now. The homopolymers were to be taken as the reference materials, to help sorting out the specific contribution of each comonomer type. Such an approach was adopted as an alternative to that followed in our previous investigations, when unfluorinated copolymer analogues had been comparatively evaluated instead. In the present case, in fact, the different reactivity of the unfluorinated acrylates would have led to copolymers with different structures and significantly lower AE content, unsuitable as reference materials.

Synthesis and Polymerization of Alkyl Isopropenyl Ethers. Several synthetic routes to alkyl isopropenyl ethers are reported.[10,19−25] Aiming at milder synthetic conditions from inexpensive precursors, a modification of a procedure based on the $AlCl_3$-promoted dealcoholation of symmetrical acetone dialkyl ketals in triethylamine was adopted (Scheme 1).[17]

The BPE precursor, 2,2-dibuthoxypropane (acetone dibutyl ketal, DBP), was prepared by acid-catalyzed transacetalization of acetone dimethyl ketal. Butyl isopropenyl ether (BPE) was then obtained in good chromatographic yield by addition of a diethyl ether solution of DBP to a solution of $AlCl_3$ and Et_3N in anhydrous diethyl ether at room temperature, presumably through deprotonation of an activate ketal−$AlCl_3$ complex promoted by triethylamine.

The ketal precursors of higher AE homologues are obtained with decreasing yields as the bulkiness of the alkoxy chain increases. Therefore, DPE was synthesized according to a different synthetic route based on the Tebbe reaction,[26] where the methylenation of decyl acetate by a two-step reaction involves the in-situ formation of the intermediate Tebbe reagent, $Cp_2Ti{=}CH_2$ (Scheme 2).



X=H	R_1=F	R_2=R_3=CF_3	R_4=CH_3	n=1	HFIFA/BPE
X=H	R_1=F	R_2=R_3=CF_3	R_4=H	n=1	HFIFA/BVE
X=H	R_1=F	R_2=R_3=CF_3	R_4=CH_3	n=7	HFIFA/DPE
X=H	R_1=CH_3	R_2=R_3=CF_3	R_4=CH_3	n=1	HFIMA/BPE
X=F	R_1=CH_3	R_2=H R_3=CH_3	R_4=CH_3	n=1	EFMA/BPE
X=H	R_1=F	R_2=R_3=CH_3	R_4=CH_3	n=1	IFA/BPE
X=H	R_1=F	R_2=R_3=CH_3	R_4=H	n=1	IFA/BVE

Figure 1. Copolymers of AE with FA.

The structures of both BPE and DPE were confirmed by the presence of the ^{1}H NMR vinylidene resonances at 3.94 and 3.90 ppm as well as by ^{13}C NMR and GC-MS.

Several attempts to polymerize BPE by cationic initiation were carried out, generally resulting in very low yields of oily, low molecular weight products as summarized in Table 1.

A high yield of a tacky, highly viscous product with a comparatively high molecular weight ($\bar{M}_n = 7000$ g mol^{-1} referred to a polystyrene calibration curve, $\bar{M}_w/\bar{M}_n = 2.3$) and good solubility in diethyl ether, benzene, and $CHCl_3$ was only obtained by polymerization at −78 °C in diethyl ether using I_2 as the initiator. The expected structure of the homopolymer, pBPE, was confirmed by ^{1}H and ^{13}C NMR.

Poly(butyl isopropenyl ether) is amorphous, showing a $T_g = -13$ °C, which is about 40 °C higher than that of poly(butyl vinyl ether). As expected, replacement of the α-C−H in pBVE with a C−CH_3 group in pBPE significantly reduces the conformational mobility of the main chain. The methyl substituent on the main chain of pBPE plays a major role also in lowering its stability with respect to pBVE due to the inductive stabilization of the cationic and free-radical intermediates deriving from the heterolytic and homolytic cleavage of the alkoxy side chain, respectively. This results in a marked hydrolytic instability of pBPE under acidic conditions, as discussed later, and it might be a factor promoting its thermal degradation under mild conditions. In fact, the TGA analysis showed the onset of pyrolytic weight loss at about 80 °C, possibly occurring as a multistage (although unresolved) process leading to complete volatilization at about 400 °C. As a straightforward explanation of such a poor thermal stability, one could refer to the presence of the ether linkage on a quaternary carbon. On the other hand, it is well-known that one macromolecule's end group can effectively activate unzipping mechanisms leading to thermally induced depolymerization, as in the case of poly(methyl methacrylate).[27] A similar situation could concern at least a fraction of pBPE, where an unzipping might be activated by a thermally induced elimination of HI from the chain ends carrying a iodine from the initiator.

Copolymerization of Alkyl Isopropenyl Ethers with FA. Copolymerization of BPE and DPE with the three fluorinated acrylates (Figure 1) was carried out under free radical initiation in bulk or, in the case of HFIFA/DPE, with a little THF as the cosolvent to ensure initial miscibility of the comonomers. Equimolar feed compositions were used in all copolymerizations, by analogy with other studies involving butyl vinyl ether (BVE).[4,12]

Only with HFIMA additional syntheses were carried out at higher BPE molar fraction in the feed to compensate for the less efficient incorporation of BPE in the copolymer. Details on the various polymerizations are summarized in Table 2.

Table 2. Copolymerization of Isopropenyl Ethers with FA[a]

run	acrylate (10^{-3} mol)	composition[b] feed	copolymer[c]	yield[d] (%)	yield[e] (FA %)
HFIMA/BPE1	3.0	0.50	0.74	73	93
HFIMA/BPE2	1.5	0.25	0.64	41	79
HFIMA/BPE3	1.0	0.17	0.60	18	46
HFIFA/BPE	2.1	0.50	0.50	86	86
HFIFA/DPE	1.1	0.50	0.50	89	89
IFA/BPE	7.5	0.50	0.75	42	61
EFMA/BPE[f]	7.9	0.42	0.52	5	6

[a] Bulk polymerizations, $T = 60$ °C, 72 h, AIBN = 1.5 mol %. [b] Mole fraction of acrylate. [c] Determined by ^{1}H NMR. [d] g of polymer/g of monomers. [e] g of FA in copolymer/g of FA in feed. [f] The slight molar excess of BPE in the feed is the result of an initial overestimation of the title of EFMA, later found to contain some saturated ester analogue as a side product of its synthesis.

The copolymerizations with HFIMA and HFIFA resulted in good conversions of the FA, whereas incorporation of BPE in the HFIMA copolymer was less efficient than that previously reported for BVE.[4] It should be pointed out that in these FA/AE copolymers, due to the virtual lack of AE homopropagation under free radical conditions, the highest level of incorporation of BPE corresponds to the equimolar composition of an alternating copolymer, while a molar excess of FA units implies the presence also of homoacrylate blocks of variable length. Therefore, the final composition of the material can be considered as a measure of the tendency of the AE to be incorporated in an acrylate-based material. The copolymer compositions were evaluated from the diagnostic ^{1}H NMR resonances of BPE at 3.2−3.4 ppm (O−CH_2) and between 5.7 and 6.4 ppm (methine of the hexafluoroisopropoxy group) for HFIFA and HFIMA; the analogous methine resonance is shifted about 1 ppm upfield in the case of the unfluorinated side chain of IFA, while in the EFMA units the diagnostic resonance of the side chain methylene occurs at about 4.0 ppm.

Only HFIFA gave an alternating copolymer, and an excess of BPE in the feed resulted not only in a lower overall yield but also in a lower conversion of HFIMA, similarly to what observed with the analogous BVE copolymers. As it is generally the case with AE, also for BPE this can be ascribed to some chain transfer activity, which is more pronounced when a large molar excess of the AE with respect to the FA is fed to the reactor and cannot be incorporated in the copolymer. Such a chain transfer activity had been confirmed in previous studies on FA/BVE copolymers, showing a reduction of molecular weight when a molar excess of BVE was used.[28]

The two fluoroacrylates IFA and, particularly, EFMA gave lower copolymerization yields than the side-chain fluorinated HFIMA and HFIFA, possibly due to a combination of steric and electronic factors. This was somehow expected in the case of the not homopropagating EFMA,[29] although the conversion of a similar copolymerization with BVE was reported to be significantly higher.[18] Apparently, the bulkiness of the α-methyl group of BPE and of the neighboring −CF_2− from the alternating EFMA plays a particularly important role in slowing down the copolymerization.

The conversions of BPE and DPE in the copolymerization with HFIFA were nearly the same, suggesting that the reactivity of isopropenyl ethers is not significantly affected by the bulkiness of their alkoxy chain.

All the above results point out that fluorination either in the α-position on the acrylic double bond or in the ester group as in IFA and HFIMA is not sufficient to grant an efficient

Table 3. Thermal Properties of Homo- and Copolymers of Isopropenyl Ethers with FA

polymer	composition (acr mole fract)	F (wt %)	T_g (°C)	$T_{\mathrm{d,onset}}$[a] (°C)	$T_{\mathrm{d,max}}$[b] (°C)	R_{600} (wt %)
pBPE	0	0	−13	80	95, 127	1
pBVE	0	0	−55	335	370	0
pHFIMA	1	48	81	316	345[c]	7
pHFIFA	1	55	108	408[d]	448	7
pIFA[e])	1	14	99	294	307	14
HFIMA/BPE1	0.74	41	49	320	250; 353*	0
HFIMA/BPE2	0.64	38	51	315	250; 362*	0
HFIMA/BPE3	0.60	36	55	313	250; 362*; 520	3
HFIFA/BPE	0.50	37	55	343	373	0
HFIFA/DPE	0.50	30	24	347	380	0
IFA/BPE	0.75	12	71	290	310*; 417	12
EFMA/BPE	0.52	14	88	320	275; 363*	0

[a] Onset calculated as the intercept between the zero weight loss line and the tangent to the inflection point of the weight loss curve corresponding to the maximum decomposition rate of the main weight loss step; heating rate 10 °C/min. [b] Temperature of maximum weight loss rate. When applicable, an asterisk (*) indicates the main decomposition step. [c] Main decomposition process; two additional weight loss steps are centered at 180 °C (3 wt %) and 250 °C (−9 wt %). [d] Shallow onset of weight loss at 330 °C. [e] Polymerization in dioxane at 50 °C.

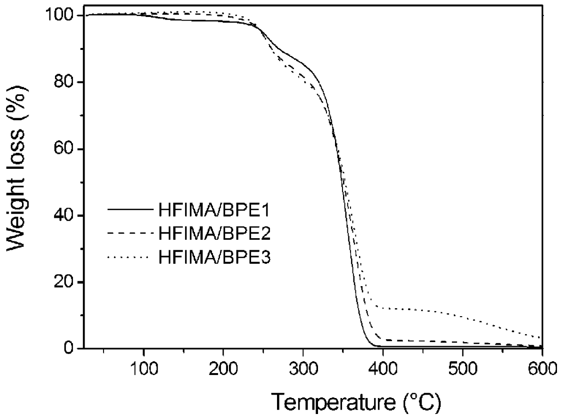


Figure 2. Thermogravimetric analyses of HFIMA/BPE copolymers.

Table 4. Weight Loss Data from the TGA Thermograms of HFIMA Copolymers

polymer	weight loss (% at 280 °C)	equiv wt % BuOH	R_{400} (wt %)
HFIMA/BPE1	12	10	1
HFIMA/BPE2	15	14	3
HFIMA/BPE3	17	16	12

copolymerization with the nucleophilic BPE. Only the increased electrophilicity provided by the simultaneous presence of two fluorinated substituents, as in HFIFA and EFMA, results in the effective incorporation of BPE in an alternating copolymer structure.

Thermal Stability and Thermal Behavior. The thermal behavior of all homo- and copolymers was investigated by TGA and DSC. The thermogravimetric data, summarized in Table 3, show that the presence of up to 50 mol % of BPE units causes a moderate to negligible reduction of the thermal stability typical of most FA copolymers, indicating that the reactivity of pBPE is effectively offset when each BPE unit is shielded by two neighboring FA within alternating comonomer sequences.

The two alternating copolymers of HFIFA with BPE and DPE undergo a sharp single-stage pyrolytic decomposition with onset at about 345 °C, suggesting that either the AE alkyl side chains are not involved or they participate to a kinetically fast stage of the overall degradation process. None of the remaining copolymers show such a clear-cut behavior, their pyrolytic degradation occurring generally through a multistage process.

In particular, the TGA curves of EFMA and HFIMA copolymers show a moderate weight loss well below 300 °C, followed by the main degradation process common to all copolymers investigated. In the case of IFA/BPE and the least fluorinated HFIMA copolymer the main degradation is followed, above 450 °C, by the slow decomposition of a highly cross-linked material, resulting in a charred residue at 600 °C. From Figure 2 it is apparent that an increasing content of BPE in the HFIMA copolymers corresponds to a larger weight loss in the first step, but also to a slower weight loss rate in the main degradation process. This can be ascribed to a combination of poor stabilization of the BPE units by EFMA and HFIMA neighbors and of moderate reactivity of the unfluorinated methine of the hexafluoroisopropyl ester side chains, which are known to promote cross-linking reactions. In fact, the data reported in Table 4 are in good agreement with a nearly quantitative cleavage of the alkoxy side chains from the BPE units according to the mechanism depicted in Scheme 3.

This is further confirmed by the IR spectra recorded in the 25 < T < 300 °C range, showing the thermally induced disappearance of the C−O−C stretching absorption from the BPE units at 1084 cm^{-1} which appears initially as a broad shoulder of the HFIMA ester absorption at 1110 cm^{-1}. Such a process is possibly superimposed to an additional pyrolytic reaction involving the HFIMA units, and corresponding to that occurring in pHFIMA within the same temperature range, which must involve the ester group since the thermal treatment at T > 220 °C causes an irreversible shift of the C═O absorption from 1778 to 1773 cm^{-1}. Furthermore, the residue at 400 °C increasing along with the content of BPE in the HFIMA copolymers (up to 12 wt % for HFIMA/BPE3, see Table 4) and the charred residue at 600 °C in IFA/BPE and HFIMA/BPE3 (also observed in pIFA, pHFIMA, and pHFIFA) suggest the occurrence of a cross-linking reaction involving the hexafluoroisopropyl side chain, possibly enhanced by the products of cleavage of the butoxy side chains.

All copolymers are fully amorphous according to the results of the DSC analyses. Their T_g is generally about 20 °C higher than that of the BVE analogues, the only exception being EFMA/BPE with a T_g 67 °C higher than that of EFMA/BPE.[1] In the latter case a larger reduction of conformational mobility is probably caused by the steric crowding from the neighboring quaternary $-CF_2-$ and $-C(CH_3)-$ of alternating BPE−EFMA sequences. The apparently anomalous increase of T_g at lower content of T_g-lowering BPE counits in the HFIMA series, opposite to what is expected from a simple additive behavior, is the result of a shift of comonomer distribution from a nearly alternating in HFIMA/BPE3 toward an increasingly random one. In fact, the Fox approximation gives for HFIMA/BPE1 a T_g = 49 °C, matching the experimental one.

Hydrolytic Stability. The homopolymers of low-MW isopropenyl ethers are reported to poorly withstand acidic condi-

Scheme 3. Proposed Mechanism of Pyrolytic Cleavage of the Butoxy Group

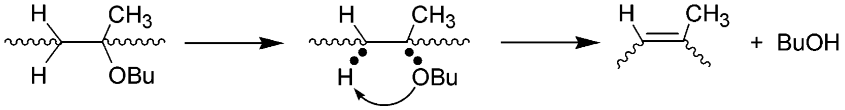


Table 5. Hydrolytic Tests on Representative Samples

polymer	weight loss (%)	acrylate mole fraction^a			T_g (°C)		
		original	pH = 2^b	pH = 1^b	original	pH = 2	pH = 1
pBPE	*c*				−17	oligomers	n.d.
HFIFA/BPE	23	0.50	0.54	0.56	55	56	58
HFIMA/BPE1	33	0.74	0.77	n.d.	49	66	n.d.

[a] Formal copolymer composition as calculated from the integrals of the ^{1}H NMR resonances at 5.5−5.9 and 3.0−3.4 ppm, respectively. [b] The hydrogen ion activity reported here as "pH" is actually a nominal value referred to the HCl molar concentration and uncorrected for the actual K_a of HCl in the acetone solvent. [c] Only a small fraction of viscous oligomeric product was recovered.

tions,[7,30] promoting the cleavage of the ether bond with the formation of a relatively stable tertiary carbocation intermediate. The presence of bulky alkoxy side chains, as in BPE, had been anticipated to possibly reduce such hydrolytic sensitivity. A further strengthening of the polymeric material against hydrolytic degradation was expected as the result of copolymerization with fluoroacrylic comonomers, providing a hydrophobic character to the macromolecule and an electron-depleting effect which could destabilize a vicinal carbocationic species.

The hydrolytic stability of pBPE and of its copolymers with HFIMA and HFIFA was comparatively investigated by exposing their solutions to given activities of HCl at room temperature. After the acidic treatment both copolymers could be retrieved by precipitation into a large excess of methanol, whereas only a small fraction of highly hydrolyzed oily material could be collected from the acid-treated pBPE upon removal of the solvent and of other volatile degradation compounds under a reduced pressure. The latter undergoes fast degradation under these conditions. On the other hand, the presence of FA counits strongly increases the hydrolytic stability of the polymeric material; indeed, the weight losses between 23 and 33% reported in Table 5 for HFIFA/BPE and HFIMA/BPE, respectively, are probably overestimated since the repeated purification procedures may have caused a loss of material due to polymer fractionation based on molecular weight rather than composition.

The molecular weight distribution of the fluorinated BPE copolymers was unaffected by the acid treatment. On the contrary, SEC analysis of the oligomeric material recovered as a highly hygroscopic pBPE hydrolysate gave $\bar{M}_n$ = 1200 g mol^{-1} and $\bar{M}_w/\bar{M}_n$ = 1.9, corresponding to a molecular weight reduction exceeding that expected in the case of a quantitative cleavage of the side chains. FT- IR as well as ^{1}H and ^{13}C NMR analyses of the pBPE residue (see Figure 3) showed that a relatively large fraction of the original butoxy side chains was still present together with additional alcoholic and olefinic functional groups, a clear indication of a more complex degradation pathway involving also the cleavage of the main chain.

Differently from pBPE, the fluorinated BPE copolymers were only slightly affected by a similar acidic treatment, as indicated by solubility tests, spectroscopic data, and thermal behavior. The main structural changes are revealed by the appearance of a weak and broad absorption above 3400 cm^{-1} in the FTIR spectrum of the acid-treated HFIFA/BPE (see Figure 4) and to higher ratios of the integrated resonances at about 5.7 ppm (methine from acrylate) and 3.2 ppm (methylene from BPE) in the ^{1}H NMR spectra of both copolymers. The former can be ascribed to buildup of hydroxyls from the reaction of water with the carbocationic centers generated by the hydrolytic cleavage of the butoxy groups; the latter, reported in Table 5 as formal variations of copolymer composition, are actually associated with the loss of butoxy side chains. The fraction of cleaved butoxy groups in HFIFA/BPE is only slightly increased at higher acidity, that is at nominal pH = 1.

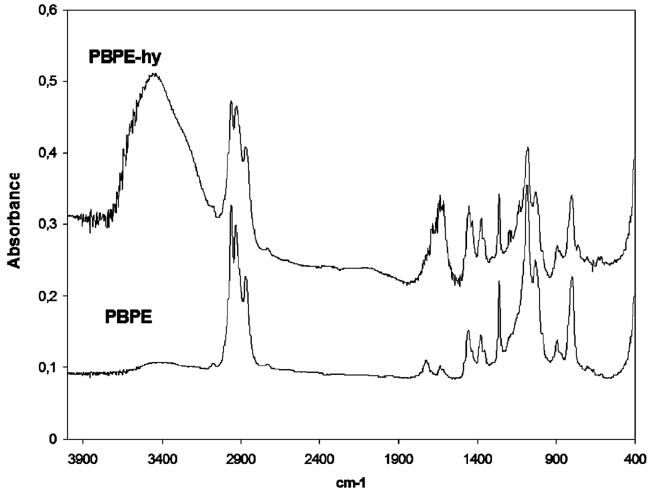


Figure 3. FTIR spectrum of the acid-treated pBPE residue.

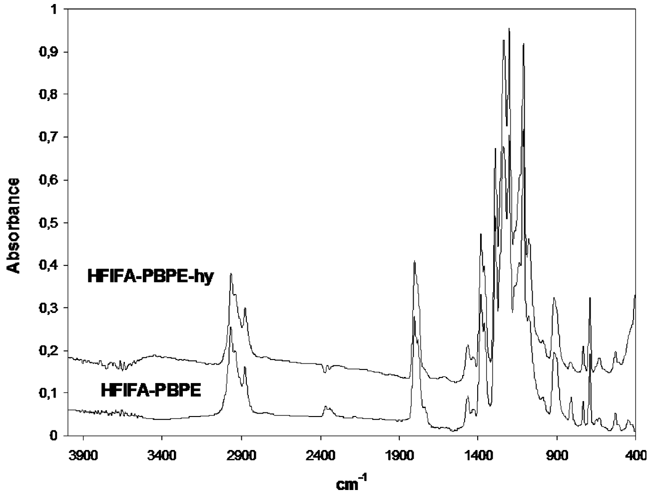


Figure 4. FTIR spectrum of the acid-treated HFIFA/BPE.

According to the TGA data, the thermal stability of the HFIMA and HFIFA copolymers was only slightly affected by the structural alterations caused by the hydrolytic treatment. Furthermore, the results from the DSC analyses suggest that the hydrolytic protection provided by HFIFA be slightly better than that of HFIMA, since an appreciable increase of T_g after the hydrolytic treatment was only detected for the latter.

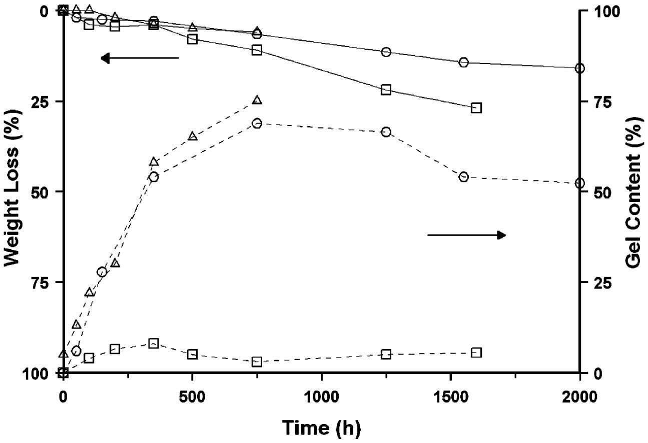


Figure 5. Weight loss and gel content of HFIMA/BPE (□), HFIFA/BPE (○), and IFA/BPE (△) as a function of treatment time.

Table 6. Number-Average Molecular Weights of PBPE, HFIMA/BPE, HFIFA/BPE, and IFA/BPE Determined by SEC, as a Function of the Photooxidative Treatment Time[a]

	$\bar{M}_n$ (10^3 g mol^{-1})			
time (h)	pBPE	HFIMA/BPE2	HFIFA/BPE	IFA/BPE
0	7.0	19	190	353
100	1.0	19	71	270
200	0.87	21	67	112
750		12		
1250		3		

[a] Polydispersity index $\bar{M}_w/\bar{M}_n$ at $t = 0$: pBPE = 2.3; HFIMA/BPE2 = 2.3; HFIFA/BPE = 5.1; IFA/BPE = 2.1.

Photochemical Stability. An investigation on the photooxidative behavior of the homologous series of BPE copolymers with HFIMA, HFIFA, and IFA was carried out in order to assess the effect of fluorine content and distribution on the photochemical stability. The homopolymers pBPE, pHFIMA, and pHFIFA were also investigated in order to provide a set of reference data. A thin film of each polymer was irradiated in air under artificial solar light, and their molecular and structural changes were periodically checked by SEC and FTIR spectroscopy. The progress of photooxidation, which often occurs with the formation of volatile and cross-linked degradation byproducts, was also followed by gravimetry and determination of the buildup of insolubles.

The time evolution of the weight loss and gel fraction buildup, as illustrated in Figure 5, present significant differences for the various copolymers, suggestive of distinct dominant oxidative pathways. This was confirmed by the results of SEC analyses (Table 6) showing that the overall photodegradation pathway leads to extensive chain scission in the case of HFIMA/BPE, while for the HFIFA and IFA copolymers the observation of shorter and shorter chains cannot be considered as indicative of the overall degradative behavior, as it only refers to limited fractions of still soluble polymer (e.g., already lower than 80 wt % for both copolymers after just 100 h of treatment). Both mechanisms are likely to be related to the presence of the unstable BPE units. In fact, pHFIMA and pHFIFA undergo a negligible volatilization of small cleaved fragments and limited gel formation (less than 10 wt % for times up to 2000 h) when compared with the almost complete decomposition of pBPE in just hundreds of hours (see the evolution of molecular weights in Table 6). Correlation was also found between the molecular changes and the appearance of the films, as only the FA homopolymers remained transparent throughout the irradiation.

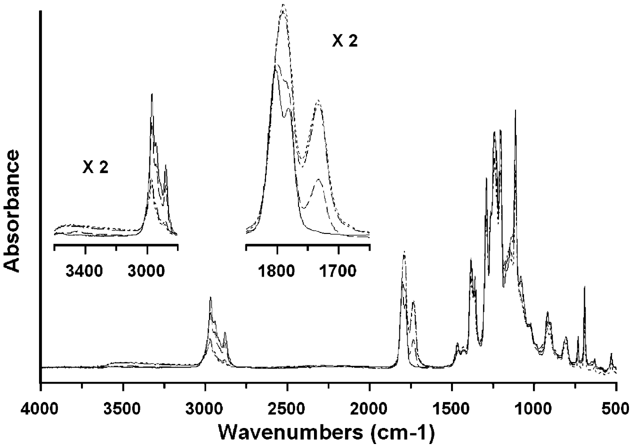


Figure 6. FTIR spectra of HFIFA/BPE before (solid line) and after 350 h (dashed line), 1000 h (dash-pointed line), and 2000 h (short-dashed line) treatment. The splitting of the C=O stretching absorption, possibly due to Fermi resonance[31] with the absorption at 902 cm^{-1}, is lost during the progressive deterioration of the sample.

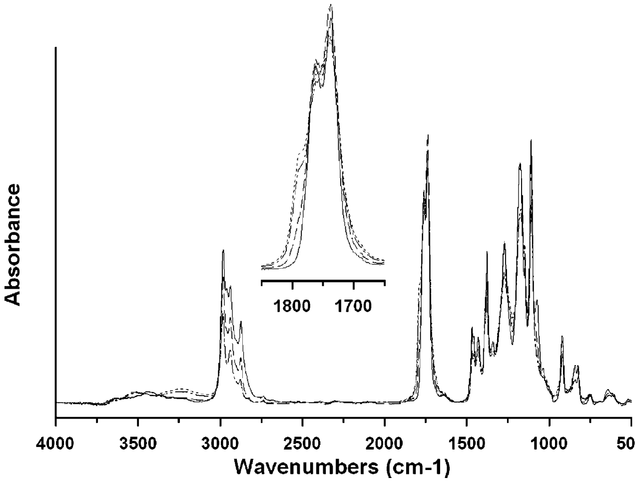
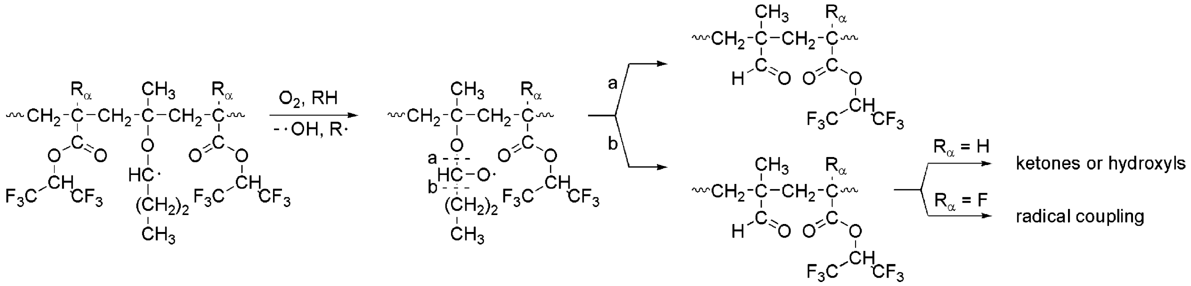


Figure 7. FTIR spectra of IFA/BPE before (solid line) and after treatment for 250 h (dashed line), 1000 h (dash-pointed line), and 2000 h (short-dashed line).

The FTIR measurements confirmed that in pHFIMA and pHFIFA there were practically no structural changes even after more than 2000 h of irradiation. On the other hand, large and somehow similar spectral modifications were detected in the copolymers (Figure 6 and Figure 7). New oxygen-containing groups are formed already at short irradiation times, as shown by the broad absorption due to hydroxyl groups in the region between 3600 and 3100 cm^{-1} and the appearance of new absorptions in the carbonyl region. The growth of a new peak at around 1730 cm^{-1}, observed in the spectra of HFIMA/BPE, HFIFA/BPE, and pBPE, was attributed to the presence of formates (see Figure 6 as example), their occurrence being confirmed by ^{1}H NMR analysis. In the case of IFA/BPE (Figure 7) the broadening of the carbonyl band toward higher wavenumbers, with clear formation of a new component at ca. 1780 cm^{-1}, was tentatively ascribed to γ-lactone formation, as already proposed for the photooxidation of different (fluoro)acrylic homo- and copolymers.[32−34] A general decrease of the original carbonyl absorptions is also evident in all the spectra.

Based also on the behavior of the reference homopolymers, a mechanism of aging of the copolymers may be suggested in which a more or less complex photooxidation pathway is generally started at the ether units.[18] The initial attack of dioxygen is likely to occur on the secondary radicals formed by abstraction of the labile hydrogen atom of the side group,[35] followed by the typical pathway of hydrocarbon oxidation (main

Scheme 4. Proposed Mechanism for the Oxidation-Degradative Pathway in FA/BE Copolymers



routes reported in Scheme 4). The alkoxy radicals formed by hydroperoxide decomposition may then undergo β-scission, leading to either the observed formates or new tertiary alkoxy radicals, with the latter possibly evolving to photounstable ketones (e.g., by further β-scission) or, alternatively, to hydroxyls by hydrogen abstraction.

Cleavage of ketones is in agreement with the rapid molecular weight decrease and the formation of volatiles observed in the HFIMA/BPE copolymer, while for HFIFA a stabilizing effect of the fluorine on the main polymer chain can be assumed. However, the α-fluorine from the FA units alternating with the AE are unlikely to interfere with the reactivity of the initial alkoxy radicals, whereas they may be quite effective in stabilizing closer radical intermediates.[36] This would inhibit or slow down the formation of ketones and hydroxyls and redirect the mechanism toward otherwise less important coupling reactions. The production of α-lactone in the IFA/BPE copolymer can be considered as a direct evidence that chemical transformations also involve the acrylic units, possibly through oxygen addition at the tertiary radicals formed by hydrogen abstraction from the unfluorinated isopropyl group, followed by decomposition of such group and its cyclization with an adjacent FA.[33]

Conclusions

A series of poly(acrylate-*co*-isopropenyl ether)s variously fluorinated in the main and/or the side chain of the acrylic units have been synthesized and the physical properties and chemical stability of their film investigated. The main purpose was one of testing these materials as water-repellent, intrinsically photostable coating materials, with special attention to the requirements for the protection of stone surfaces of artistic or historical importance.

Strictly alternating BPE copolymers were obtained with the highly electrophilic HFIFA and EFMA, both carrying two fluorinated substituents or F atoms on the acrylic double bond, while the “monosubstituted” HFIMA and IFA gave the corresponding copolymers in a lower yield and with a less effective incorporation of BPE. A similarly behavior had been previously observed in the copolymerization of the same FA with BVE, indicating that introduction of an α-methyl group into the BVE structure does not substantially alter the reactivity of the AE in the free radical copolymerization with a FA.

The poor thermal, photochemical, and hydrolytic stability of pBPE, related to the facile cleavage of the alkoxy side chain, is only partially suppressed by copolymerization with a FA, although the chemical stabilization provided by the latter depends strongly on the type of comonomer. As a general rule, the alternating HFIFA/BPE showed the best performance among the three structurally analogous series of side-chain fluorinated copolymers, irrespective of its higher BPE mole fraction, although a quite effective hydrolytic stabilization is also achieved in the HFIMA copolymer. On the other hand, the photooxidative behavior indicates that the main effect of the presence of fluorine on the ester side groups is one of stabilizing the FA units (e.g., with respect to unfluorinated analogues), whereas fluorination of the polymer backbone, as in HFIFA, IFA, and EFMA, has a profound effect on the reactivity of the neighboring unfluorinated AE units and therefore of the copolymer as a whole. In fact, depending on the relative position of fluorine atoms with respect to the common center of photoactivated oxidation, the dominant mechanism can lead to rapid cross-linking or to comparatively slow but progressive chain fragmentation.

The obtained results indicate that tailoring of the application properties of partially fluorinated copolymers, and specifically of their durability as coating materials, can be achieved by selecting the more convenient distribution of fluorine or fluorinated substituents on the main and the side chain, rather than relying only on the overall degree of fluorination.

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