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Photochemical Stability of Partially Fluorinated Acrylic Protective Coatings. 2. Copolymers of 1*H*,1*H*,2*H*,2*H*-Perfluorodecyl Methacrylate with Unfluorinated Acrylic Esters

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The photochemical stability of a series of copolymers of 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (XFDMA) with acrylic or methacrylic unfluorinated esters has been investigated under artificial solar light irradiation. Molecular and chemical changes induced by the light treatment were monitored by weight loss and gel content determination, size exclusion chromatography, and Fourier transform infrared spectroscopy. In XFDMA/methyl acrylate the degradation mainly occurs on the tertiary position of the acrylic units, followed by extensive chain scissions. In the copolymers with butyl acrylate, butyl methacrylate, and lauryl methacrylate, the XFDMA units are not affected by oxidative degradation reaction, and the mechanism of degradation is influenced by the specific reactivity of the unfluorinated comonomer. For these samples the principal degradation effect is the cross-linking of the polymer structure promoted by radicals formed on the alkyl side groups, and it is only partially attenuated by the fluorinated units.

1. Introduction

The outstanding properties of fluoropolymers have stimulated their application in several fields characterized by a high technological level, from the days of the first strategic uses during World War II to the aerospace and advanced materials industries.[1] In particular, their intrinsic excellent chemical, thermal, and photochemical stability[2,3] has favored the development of polymeric structures containing fluorinated urethanes, alkyds, vinyl ethers, silicones, and acrylics, which are gaining growing interest as coating materials for diverse applications, such as oil repellents, water repellents, antifouling agents, and components for nonstick surfaces.[4,5]

The use of coatings based on fluoropolymers for the conservation of cultural heritage is still quite limited, and only recently perfluoropolyethers and fluoroelastomers have been tested for the protection and consolidation of degraded surfaces of ancient buildings.[6] An investigation project aimed at the development of new polymeric protectives with improved performance has been undertaken in the framework of the Special Program “Safeguard of Cultural Heritage” of the Italian National Research Council (CNR). Due to the limited environmental stability of the acrylic protective coatings commonly used for conservation of monuments and stone surfaces,[7] the focus of the research is the design, synthesis, and testing of new partially fluorinated acrylic-based polymers suitable as efficient and durable water-repellent stone coatings. The systematic investigation of photochemical stability and degradation pathways of the new polymers is an essential part of the project.

The first results concerned the study of the photooxidative behavior of poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) and copolymers of 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate with 2-ethylhexyl methacrylate (XFDMA−EHMA).[8] PTFEMA exposed up to 2000 h under conditions of artificial solar light irradiation showed only minor molecular changes due to limited extent of chain scissions; by contrast the XFDMA−EHMA copolymers underwent much more extensive degradation, mainly associated with the reactivity of the EHMA unit. In the present work are reported the results concerning the investigation of a further series of XFDMA copolymers with both acrylic and methacrylic unfluorinated units (methyl acrylate, MA; butyl acrylate, BA; butyl methacrylate, BMA; and lauryl methacrylate, LMA), embracing a wide range of

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Table 1. Polymer Synthesis: Experimental Data

polymer	monomer[a] (mol/L)	T (°C)	comonomer mole ratio	AIBN[b] (mol %)	copolymer composition	yield (%)
XFDMA/MA	1.32	65	1/15	3.0	1/16	94
XFDMA/BA	0.93	70	1/9	3.0	1/4.8	53
XFDMA/BMA 1	0.85	70	1/5	2.7	1/4.3	77
XFDMA/BMA 2	1.01	70	1/9	3.1	1/6.5	78
XFDMA/LMA	0.57	70	1/3	3.3	1/2.3	86
PLMA	c	70		3.7		97

[a] Overall feed concentration in dioxane. [b] Versus monomer. [c] In bulk.

compositions, with molar ratios of XFDMA/unfluorinated unit between 1/2.3 and 1/16. Their photochemical stability was also compared with that of homopolymers of the corresponding unfluorinated co-units already presented in a previous paper[9] or herewith reported as original results. All the copolymers present good solubility in common organic solvents, allowing their potential use in the formulation of coatings. Some of the above polymers have already demonstrated their good protective action when applied on stone, particularly in terms of water repellency and film-forming properties.[10−12] These earlier studies also showed that fluorinated units having appropriate fluorine amount and distribution should be combined with polar co-units in order to give a good anchorage onto the working surface and allowing, in addition, a modulation of the glass transition temperature, T_g, and of other material properties.[13]

2. Experimental Section

2.1. Materials and Techniques. Diethyl ether was dried over $CaCl_2$ and then distilled from $LiAlH_4$. Dioxane was dried over $CaCl_2$ and then distilled from Na. Toluene was distilled from Na. Azobis-1,1-dimethyl-2-propionitrile (α,α′-azobisbutyronitrile, AIBN, Akzo) was purified by recrystallization from ethanol. Triethylamine (Fluka) was distilled from CaH_2. 1*H*,1*H*,2*H*,2*H*-Perfluorodecan-1-ol (Strem Chemicals) was used as received. Methacryloyl chloride (Fluka) was distilled from quinoline in the presence of di-*tert*-butyl-*p*-cresol (DTBC) as polymerization inhibitor. *n*-Dodecyl methacrylate, LMA (Aldrich), BA, and BMA (Salchi) were distilled at reduced pressure in the presence of DTBC. MA (Aldrich) was added to DTBC and distilled under nitrogen. 1*H*,1*H*,2*H*,2*H*-Perfluorodecyl methacrylate (XFDMA) was synthesized as described below. All monomers were stored under nitrogen at −25 °C before use.

^1H NMR spectra were recorded from 5% to 10% $CDCl_3$ solutions on a Varian Gemini 200 spectrometer at 200 MHz. Chemical shifts were related to the $CHCl_3$ signal at 7.24 ppm vs TMS. ^{19}F NMR spectra were recorded on a Varian-VxR-300 instrument at 282.24 MHz, using $CFCl_3$ as external reference.

UV−vis spectra were acquired from thin films on quartz windows with a Lambda 15 instrument (Perkin-Elmer). FTIR spectra were recorded from films on KBr disks or silicon wafers, using a Perkin-Elmer 1600 instrument or a 1710 system with a DTGS detector and 4 cm^{-1} resolution. Spectral acquisitions and data treatments were performed with Spectra Calc (Galactic Industries) software. Differential scanning calorimetric analyses were carried out with a Perkin-Elmer DSC7 instrument equipped with a CCA7 temperature control apparatus operating with liquid nitrogen; indium and mercury standards were used for calibration. Thermal analyses were carried out at 20 °C/min scan rate, and the reported T_g values were taken from the second heating scan. 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 eluent flow rate set at 1 cm^3/min. The system was equipped with 4 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.

2.2. Synthesis and Characterization. *1H,1H,2H,2H-Perfluorodecyl Methacrylate.* (XFDMA) was synthesized from the fluorinated alcohol (25 g, 54 mmol) and methacryloyl chloride in diethyl ether, in the presence of triethylamine and DTBC (alcohol/chloride/amine mole ratio 1/1.3/2). Methacryloyl chloride was added dropwise to the reaction solution at 0 °C under nitrogen, stirred for 1 h, and left at room temperature overnight. The mixture was then poured onto ice, extracted with 5% HCl, 5% NaOH, washed with water to neutrality, and dried over Na_2SO_4. After removal of the solvent the raw product was purified by chromatography over silica using a 5/1 *n*-hexane/chloroform mixture as the eluent. The >99% pure product (by gas chromatography) was obtained in 88% yield (25 g). IR (neat): 3100−2900, 1728, 1640 (C=C), 1350−1120 (C−F, C−O), 946 (out-of-plane C−H bending) cm^{-1}. ^1H NMR: 6.15 (s, =C−H cis), 5.60 (s, =C−H trans), 4.45 (t, O−CH_2), 2.50 (m, CH_2–CF_2), 1.95 (s, CH_3) ppm. ^{19}F NMR: −82.0 (t, CF_3), −114.6 (m, CH_2–CF_2), −122.8, −122.9, −123.0, −123.9, and −124.7 (s, −$(CF_2)_5$−), −127.3 (m, CF_2–CF_3) ppm.

Poly(lauryl methacrylate) (PLMA). LMA (1.03 g, 4.04 mmol) and AIBN (0.024 g, 0.15 mmol) were introduced in a Schlenk tube, degassed, and stirred 24 h at 70 °C. The glassy product was purified by precipitation from $CHCl_3$/methanol and dried under vacuum at room temperature, yielding 1.00 g (97%) of polymer. ^1H NMR: 4.1−3.7 (O−CH_2), 2.1−1.7 (main chain CH_2), 1.7−1.45 (OCH_2–CH_2), 1.45−1.2 (−$(CH_2)_9$–CH_3), 1.2−0.6 (2 × CH_3) ppm.

All XFDMA copolymerizations were carried out in dioxane solution, following the same general procedure reported below for XFDMA/LMA. The experimental data are summarized in Table 1.

Poly(1H,1H,2H,2H-perfluorodecyl methacrylate-co-lauryl methacrylate) (XFDMA/LMA). XFDMA (0.313 g, 0.59 mmol), LMA (0.814 g, 3.2 mmol), and AIBN (0.018 g, 0.11 mmol) were introduced in a 25 mL Schlenk tube with 6 mL of dry dioxane. After freeze−pump−thaw degassing the polymerization was carried out at 70 °C under magnetic stirring for 24 h. The obtained product was precipitated in 200 mL of methanol, giving 1.06 g (94% yield as calculated from weight ratio of the purified polymer vs monomer feed) of XFDMA/LMA copolymer.

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Table 2. Structure and Composition of Original Polymers

polymer	molar ratio	F (wt %)	T_g (°C)	M_n	M_w/M_n
XFDMA/MA	1/16	17	15	6 300	3.5
XFDMA/BA	1/4.8	28	−34	36 000	1.4
XFDMA/BMA 1	1/4.3	28	23	24 000	1.6
XFDMA/BMA 2	1/6.5	22	29	27 000	1.6
XFDMA/LMA	1/2.3	29	−47; 5[a]	19 000	2.3
PLMA			−47	144 000	2.7

[a] A second T_g at the same temperature as the PLMA homopolymer was detected, possibly indicating the occurrence of microphase-separated unfluorinated domains comprising either long LMA homosequences or, more simply, aggregations of side chains from LMA units.

^{1}H NMR: 4.3−4.1 (XFDMA, O−CH_2), 4.1−3.7 (LMA, O−CH_2), 2.6−2.2 (CH_2–CF_2), 2.2−1.65 (2 × CH_2, main chain), 1.65−1.45 (LMA, OCH_2–CH_2), 1.45−1.2 (LMA, −$(CH_2)_9$–CH_3), 1.2−0.6 (3 × CH_3) ppm.

Poly(1H,1H,2H,2H-perfluorodecyl methacrylate-co-butyl methacrylate) (XFDMA/BMA). ^{1}H NMR: 4.4−4.1 (XFDMA, O−CH_2), 4.1−3.7 (BMA, O−CH_2), 2.6−2.2 (CH_2–CF_2), 2.1−1.7 (2 × CH_2, main chain), 1.7−1.45 (BMA, OCH_2–CH_2), 1.45−1.2 (CH_2–CH_3), 1.2−0.6 (3 × CH_3) ppm.

Poly(1H,1H,2H,2H-perfluorodecyl methacrylate-co-butyl acrylate) (XFDMA/BA). ^{1}H NMR: 4.4−4.1 (XFDMA, O−CH_2), 4.1−3.7 (BA, O−CH_2), 2.7−2.0 (CH−COOBu, CH_2–CF_2), 2.0−1.7 (2 × CH_2, main chain), 1.7−1.45 (BA, OCH_2–CH_2), 1.45−1.2 (CH_2–CH_3), 1.1−0.7 (2 × CH_3) ppm.

Poly(1H,1H,2H,2H-perfluorodecyl methacrylate-co-methyl acrylate) (XFDMA/MA). ^{1}H NMR: 4.4−4.1 (O−CH_2), 4.0−3.2 (O−CH_3), 2.8−2.2 (CH_2–CF_2), 2.5−2.0 (CH−COOMe), 2.1−1.2 (2 × CH_2, main chain), 1.2−0.8 (C−CH_3) ppm.

The compositions of the copolymers were calculated from integrals of the well-resolved ^{1}H NMR O−CH_2 (or O−CH_3) resonances in the 4.4−4.1 and 4.1−3.2 ppm range for XFDMA and the unfluorinated co-units, respectively. Copolymer compositions, T_g, and molecular weight data are listed in Table 2. The reported M_n and M_w/M_n data are relative rather than absolute values, as they are calculated by SEC analysis using a calibration curve established with homopolymer standards. A further source of uncertainty in the molecular weight and molecular weight distribution determination is due to the possible presence of composition drifts in the copolymer chains, which will affect the response of the refractometric detector. A not negligible structural heterogeneity in the copolymer samples of this work is to be expected, considering the fact that the batch copolymerizations were allowed to reach relatively high conversions and that the fluorinated and unfluorinated comonomers are characterized by different reactivity, thereby producing a continuous change in the composition of the polymerizing mixtures.

2.3. Accelerated Aging and Analysis. The accelerated photoaging was performed in a high-speed exposure unit Suntest CPS Heraus, equipped with a xenon light source; a glass filter with cutoff at $\lambda \leq 295$ nm was used to exclude radiation more energetic than that of outdoor solar exposure. Irradiation was kept at 765 W/m^2. The maximum temperature of the samples, during irradiation, was 45 °C.

The samples for degradation were in the form of thin films, cast from chloroform solutions (weight concentration ca. 5%) and dried under vacuum at 60 °C for 4 h. Samples for infrared analyses were supported on silicon wafers, and on quartz windows for UV−vis spectroscopy, with film thickness in the range of 10−20 μm. For all other determinations film thickness was between 20 and 50 μm. The films of all the samples were uncolored and perfectly transparent.

Weight losses of polymer films induced by degradation were determined gravimetrically. Gel content after the different treatment times was also determined gravimetrically, after soaking the sample films in chloroform and collecting the insoluble fractions with vacuum filtration on 0.2 μm preweighted membrane filters. In the comparison of the SEC chromatograms obtained from treated samples, the peak areas were always normalized relative to the soluble part of the polymers.

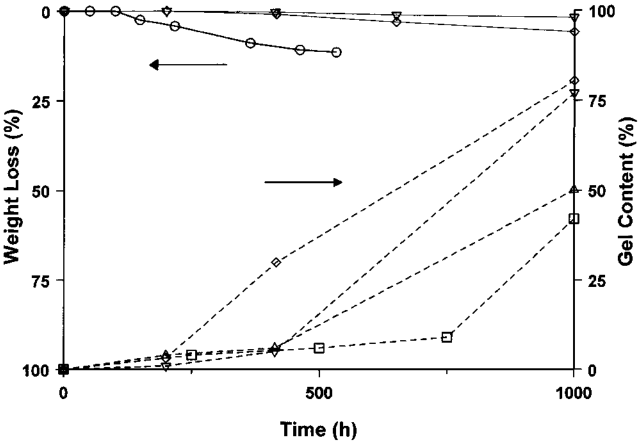

Figure 1. Weight loss and gel content of XFDMA copolymers with MA (○), BA (□), BMA 1 (△), BMA 2 (▽), and LMA (◇) as a function of treatment time.

3. Results and Discussion

In Tables 1 and 2 are reported synthesis conditions, average compositions, glass transition temperatures, and apparent molecular weights of the different polymers. The broad polydispersity determined by SEC for some of the copolymers might be the result of different comonomer reactivities and chain transfer effectiveness between fluorine-rich and hydrogenated monomers, and of the polymerizations carried out to high yields where diffusion-controlled termination reactions play a role in broadening the molecular weight distributions.

3.1. Copolymers with MA and BA. Films of two XFDMA copolymers with MA (molar ratio 1/16) and BA (1/4.8) were exposed to accelerated photoaging treatments for times sufficient to obtain clear indications on their photooxidative trends, while corresponding physical and chemical changes were periodically checked. XFDMA/MA remained soluble in chloroform and THF throughout the whole irradiation and started to lose weight after the first 100 h of aging, reaching a 12% weight loss at around 500 h. In the case of XFDMA/BA, on the other hand, a negligible formation of volatile compounds was accompanied by the formation of insoluble fractions with the rate increasing after 750 h irradiation (Figure 1).

The strong tendency of XFDMA/BA to give cross-linking reactions in comparison with those relative to XFDMA/MA was also revealed by the SEC chromatograms shown in Figure 2. The initial distribution after 250 h irradiation is broadened mainly toward shorter retention times, indicating the predominance of coupling and branching reactions, which produce higher molecular weight molecules. With continuation of the treatment, and specifically after 750 h, the chromatograms become only representative of the remaining soluble part, containing both lower molecular weight fractions of the initial sample and fragments formed during the degradation. On the other hand, the displacement of the XFDMA/MA curves in Figure 2 indicates that only chain scissions occur which develop extensively in correspondence with the beginning of weight loss.

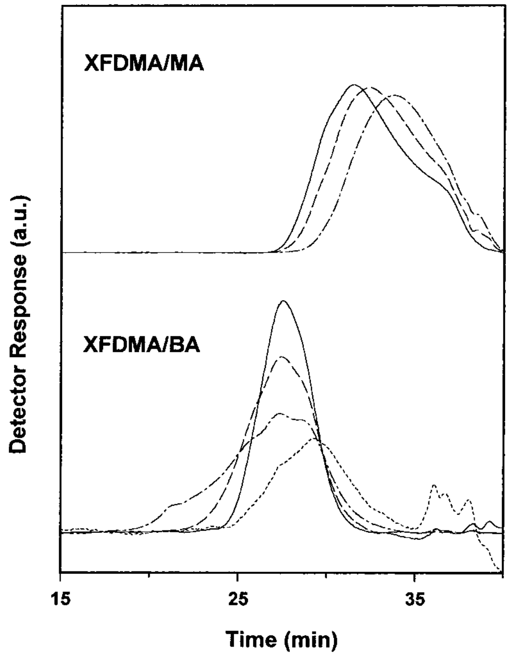

Figure 2. SEC chromatograms: XFDMA/MA before (solid line) and after treatment for 150 (dashed line) and 360 h (dash−dotted line); XFDMA/BA before (solid line) and after treatment for 250 (dashed line), 500 (dash−dotted line), and 1000 h (short-dashed line).

Table 3. Scissions per Initial Molecule of PMA and XFDMA/MA as a Function of Treatment Time

time (h)	PMA	XFDMA/MA
0	0	0
100	0.24	0.03
150	0.57	0.36
216	0.60	0.44
360	0.69	0.74

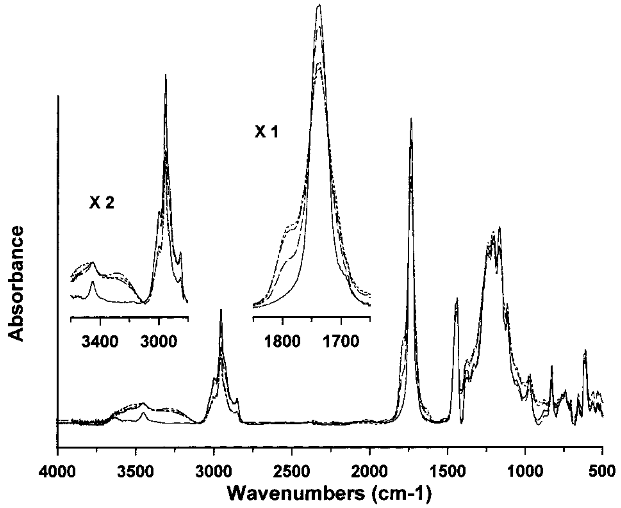

Figure 3. FTIR spectra of XFDMA/MA before (solid line) and after treatment for 100 (dashed line), 360 (dash−dotted line), and 500 h (short-dashed line).

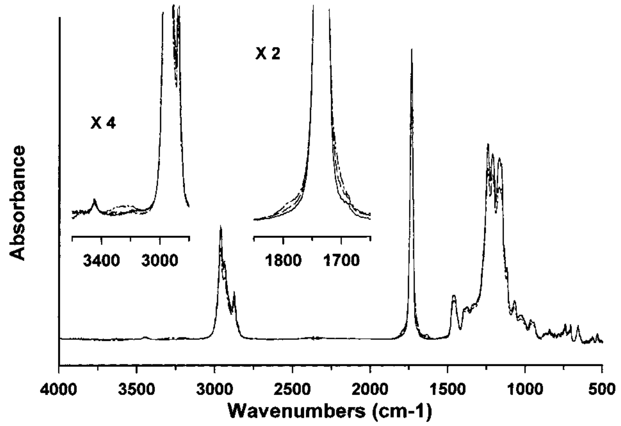

Figure 4. FTIR spectra of XFDMA/BA before (solid line) and after treatment for 500 (dashed line) and 1000 h (dash−dotted line).

The complete solubility of XFDMA/MA allows comparison of the progression of the apparent number of chain scissions per initial polymer molecule, *S*, with that relative to the completely unfluorinated homopolymer, PMA, submitted to identical degradation conditions.[9] The values of *S* were calculated through the relationship[14]

$$S = [M_{n,0}(1 - x)/M_n] - 1$$

where $M_{n,0}$ is the initial number-average molecular weight, M_n is its value at different times, as calculated from SEC curves, and x is the fraction of volatilized polymer. The number of scissions occurring in the copolymer increases in an almost linear mode, but it is worth stressing that in the initial phase of degradation the values are always smaller than those calculated for PMA (Table 3). This suggests a certain stabilizing effect of the fluorinated methacrylate units, whose limited presence is sufficient to slow the main chain rupture, at least in the early stage of irradiation. The relatively high F content, 17 wt %, corresponds to less than 6% by mole of fluorinated units in this copolymer with "light" MA co-units; the few XFDMA units are nonetheless capable of reducing the weight loss by about 30% (from 18% of PMA[9] to 12% of XFDMA/MA) after the first 500 h of irradiation. A reduced number of chain scissions means a lower number of radicals capable of propagating the degradation process, and therefore lower formation of volatile compounds.

The extent of structural modifications taking place during irradiation is different in the two acrylic copolymers, as may be appreciated from the FTIR spectra in Figures 3 and 4. After 100 h of treatment new oxygen-containing functional groups are formed in XFDMA/MA, responsible for the broad absorption in the hydroxyl region between 3600 and 3100 cm^{-1}, while at the same time the carbonyl peak broadens on both sides with the simultaneous appearance of a shoulder at lower wavelength (Figure 3). At longer irradiation time the spectra show a progressive decrease of the C−H stretching absorptions possibly related to the evolution of small molecules as supported by the weight loss results. Moreover, apart from the increase of the OH peak, the evolution of C=O absorptions is the main signal of the occurrence of the oxidative process: in particular, at the final treatment time, i.e., ca. 500 h, the complex carbonyl band extends between 1850 and 1600 cm^{-1} and shows several new components, the main ones being recognizable at around 1780 and 1710 cm^{-1}.

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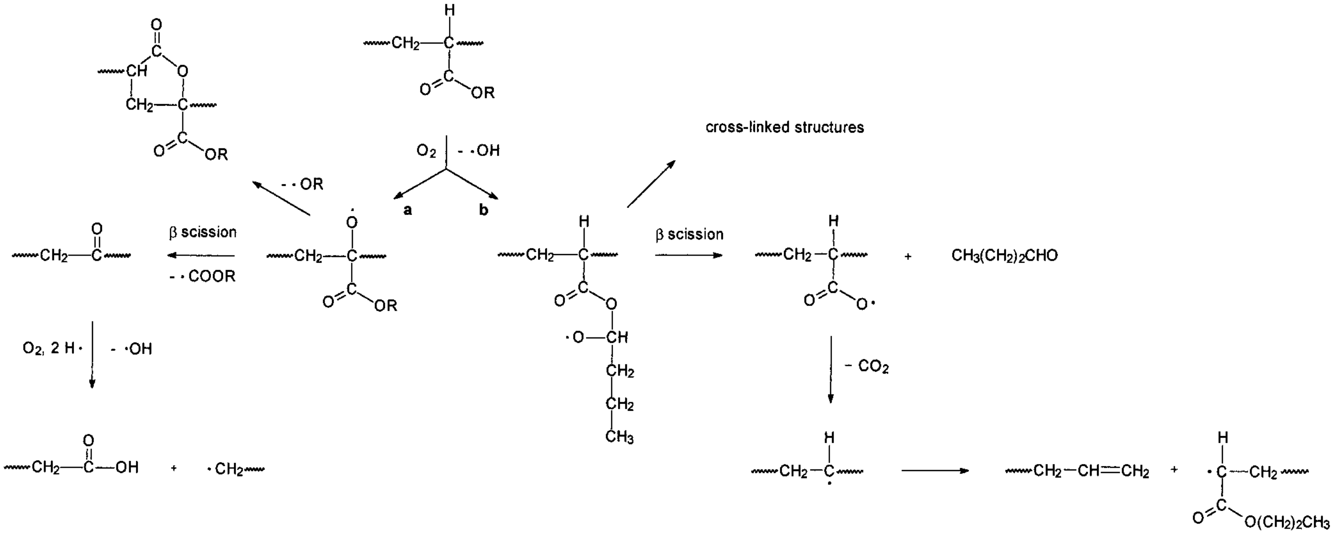
Scheme 1



By comparing the spectral changes in XFDMA/MA with those already found in PMA,[9] it is evident that very similar structural variations occur in the two polymers, suggesting the unfluorinated part of the copolymer as the reactive site of oxidation. This finding is also supported by the stability of XFDMA units, whose infrared absorptions due to C−F stretching at 1300−1100 cm^{-1} [8,15,16] apparently remain constant during the considered irradiation interval. The oxidation is likely to initiate through the addition of oxygen molecules to the tertiary radical formed by abstraction of the labile hydrogen atom of the MA units, followed by the typical pathway of hydrocarbon oxidation (Scheme 1, route a). Ketones formed by decomposition of alkoxy radicals, and responsible for the component at 1710 cm^{-1},[15] may undergo Norrish type photoinduced cleavage leading to acid groups,[17] which absorb in the same region. The latter ones can evolve by bimolecular water elimination to open chain anhydrides responsible for the absorption around 1800 cm^{-1}. The principal new component of the carbonyl band at ca. 1780 cm^{-1} is attributed to γ-lactone structures, which may be formed through an intramolecular backbiting process, similar to that first proposed for the oxidation of polypropylene.[18] The presence of γ-lactones is ubiquitous in all types of aliphatic polymer oxidation,[19,20] and their formation was already revealed in other acrylic copolymers.[21] The described mechanism accounts for the observed molecular weight decrease of the polymer, and also for the weight losses due to volatilization of chain fragments.

The FTIR spectra of photooxidized XFDMA/BA (Figure 4) show less structural changes than those of XFDMA/MA, even though the features are almost the same. The presence of oxidized structures is clearly detectable only after 1000 h, with appearance of hydroxyl groups responsible for the broad band centered at about 3250 cm^{-1} and the contemporary broadening of the carbonyl absorption at both sides, with two new components around 1780 and 1700 cm^{-1}. In addition, the growing of a small absorption at 1640 cm^{-1} is visible from the first 500 h.

The oxidation of XFDMA/BA is likely to take place extensively with the same mechanism seen for XFDMA/MA, through attack of oxygen onto tertiary radicals of the BA units, which then evolve to either hydroperoxides, ketones, and acids, or lactones. However, the tendency to form insolubles indicates that other processes of degradation occur earlier, probably on the ester side group. Radicals on the butyl group can lead to the formation of unstable secondary hydroperoxides immediately photolyzed into alkoxy radicals (route b of Scheme 1).[21] Because of the high mobility of the side chains,[22] the formed radicals can decay rapidly via cross-linking. An alternative route is the radical propagation through chain scission and production of unsaturated chain end. Scission products are shown by the size exclusion chromatograms, and olefinic groups by the growing absorption at 1640 cm^{-1}.

3.2. Copolymers with BMA and LMA. Photooxidation of XFDMA copolymers with BMA (two samples with composition 1/6.5 and 1/4.3, respectively) and LMA (1/2.3) takes place with formation of insoluble fractions after only 200 h of treatment, followed by a fast increase up to the values shown in Figure 1. A slight weight loss, <5%, was measured in the three samples after 1050 h of irradiation. In the XFDMA/BMAs the amount of cross-linked structures responsible for the presence of insoluble fractions may be related to the content of BMA units, whose tendency to cross-link has been recently investigated.[9,21] In the case of XFDMA/LMA such behavior may be ascribed to the LMA units, as is demonstrated by the corresponding homopolymer which after 1050 h of exposure to the same radiation showed a gel fraction close to 80%. At the same time, at longer irradiation time the polymeric films showed a progressive loss of transparency, whereas no new absorptions were detected on their UV−vis spectra.

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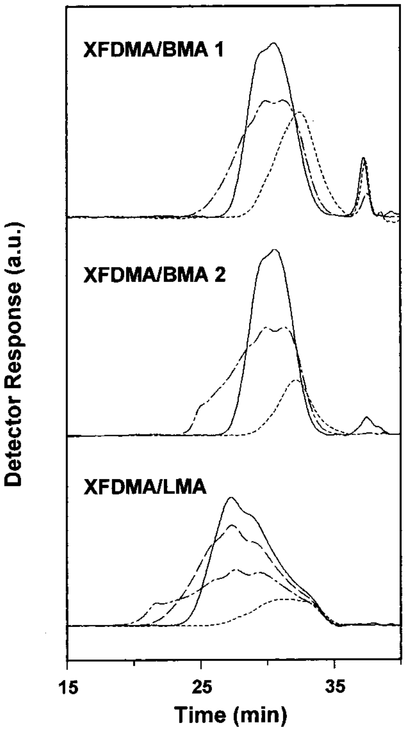

Figure 5. SEC chromatograms of XFDMA/BMA 1, XFDMA/BMA 2, and XFDMA/LMA before (solid line) and after treatment for 200 (dashed line), 400 (dash–dotted line), and 1000 h (short-dashed line).

The SEC curves obtained from the three copolymers after different treatment times are shown in Figure 5. The chromatograms of XFDMA/BMAs after 400 h and that of XFDMA/LMA at 200 h may still be considered as representative of the overall behavior, even though a certain amount of insoluble fraction has already been formed. Fractions eluting at retention times shorter than those of the initial polymers are clear evidence of the extensive occurrence of coupling reactions between macroradicals. At longer times the curves represent only the un-cross-linked chains, and in the case of the BMA copolymers also show the presence of low amounts of scission products formed during the degradation.

The infrared spectra of these three copolymers showed very similar modifications, although with different extensions. The main spectral variations observed in XFDMA/BMA (copolymer 1/6.5 in Figure 6) and XFDMA/LMA (Figure 7) are the following: a progressive growth in the hydroxyl region between 3600 and 3100 cm^{-1}, visible in the LMA copolymer only at 1050 h, and extended in XFDMA/BMA 1/6.5 also in the 2800–2400 cm^{-1} region, indicative of strong association of –OH groups, probably carboxylic.[23] Decrease of the carbonyl ester peak at 1730 cm^{-1} was accompanied by the appearance of γ-lactones and acid group absorptions around 1780 and 1705 cm^{-1}, respectively.

Comparison of such results with those already reported for PBMA,[9] and with the FTIR spectra of an irradiated PLMA used as reference, permits the conclusion that also in the XFDMA copolymers with methacrylates the overall stability is controlled by the comonomers. Moreover, taking into account the almost

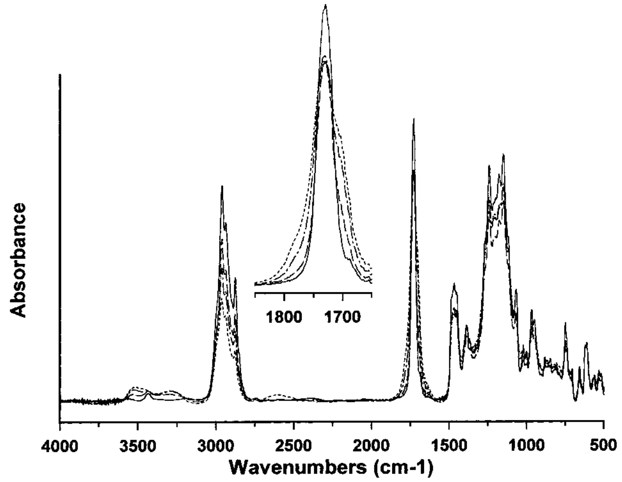

Figure 6. FTIR spectra of XFDMA/BMA 2 before (solid line) and after treatment for 400 (dashed line), 650 (dash–dotted line), and 1000 h (short-dashed line).

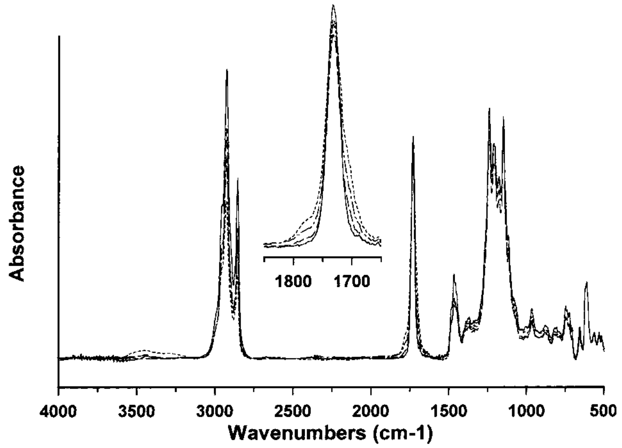

Figure 7. FTIR spectra of XFDMA/LMA before (solid line) and after treatment for 400 (dashed line), 650 (dash–dotted line), and 1000 h (short-dashed line).

comparable photooxidative behavior of PBMA and PLMA, it is possible to correlate the observed order of relative stability to oxygen attack, XFDMA/LMA 1/2.3 > XFDMA/BMA 1/4.3 > XFDMA/BMA 1/7, with the molar, rather than mass, fraction of unfluorinated units. This also means that the overall fluorine weight fraction of the copolymer is not strictly correlated with its photochemical behavior, the latter being more clearly influenced by the frequency of the fluorinated co-units along the macromolecular chain and by the length of the unfluorinated side chains. The role of the unfluorinated ester groups is clearly displayed by such a comparison. Oxidation occurs on the side chain of methacrylic units through the formation of secondary hydroperoxides. The alkoxy radicals formed by their photolysis decay via cross-linking or decompose following the mechanisms already reported in Scheme 1 for BA units. The secondary macroradicals formed by CO_2 elimination (see Scheme 1) may also add oxygen, leading to new hydroperoxides and later to alkoxy radicals. Finally, the latter ones can react intramolecularly via the elimination of an adjacent ester group to form γ-lactones. As in PEHMA,[8] the development of acids may be ascribed to an intramolecular cyclic elimination of alkyl side groups or to the hydrogen abstraction of the carboxylic radicals

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[23] Lazzari, M.; Kitayama, T.; Hatada, K.; Chiantore, O. *Macromolecules* **1998**, *31*, 8075.

as an alternative to the aforementioned CO_2 evolution. Oxidation reactions are less likely to occur on the alkoxy CH_2 group of the XFDMA units than on the hydrocarbon ester groups because of the stabilizing electronic effect due to the fluorine atoms in the β-position. A similar stabilizing effect was already observed in other side chain fluorinated polyacrylates, such as PTFEMA[8] and poly(hexafluoroisopropyl methacrylate).[24]

The different rates of insoluble fraction formation seen in Figure 1 and the higher tendency of PLMA to cross-link compared with PBMA (e.g., ca. 40% vs 14% of insoluble fraction after 300 h) is attributed to the high mobility of the side ester groups, directly proportional to their lengths.[9,25]

4. Conclusions

The relative stability and the mechanism of photooxidative degradation of the investigated XFDMA copolymers depend on both the molar fraction and the specific reactivity of the unfluorinated comonomer. In XFDMA/MA the degradation occurs mainly through oxidation on the tertiary position of the MA units, followed by extensive chain scissions of the polymer molecules. By contrast, in the copolymers with long side ester chains the principal degradation effect is the cross-linking of the polymer structure, promoted by the radicals formed on the alkyl side groups. The XFDMA units are not affected by oxidative degradation reactions, and the fact that their presence reduces the formation of volatiles in XFDMA/MA and the amount of gel formation in the other copolymers may be ascribed to a direct protective effect due to a local reorganization of the long fluoroalkyl side chains which tend to form a physical barrier of microphase-segregated domains at the film surface.[12]

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(24) Lazzari, M.; Chiantore, O.; Castelvetro, V.; Aglietto, M. Proceedings of the First International Conference on Polymer Modification, Degradation and Stabilisation, Palermo, Italy, 2000; 1-W-1000.

(25) Feller, R. L.; Curran, M. In *Photodegradation and Photostabilization of Coatings*; Pappas, S. F., Winslow, F. H., Eds.; ACS Symposium Series 151; American Chemical Society: Washington, DC, 1981; p 183.