Structure Control, Coating Properties, And Durability of Fluorinated Acrylic-Based Polymers

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Fluorinated acrylates were employed for the synthesis of conventional, side-chain fluorinated, fully acrylic random copolymers, and of more unusual hybrid copolymers with vinyl ethers. The latter can feature alternating structure and peculiar material properties associated with fluorine or fluorinated groups substitution onto the polymer backbone. Improved efficacy and durability of the resulting coating, highly desirable for the consolidation and protection of highly valued works of art, was achieved through a systematic approach involving a detailed study of their photodegradation behavior, and extensive testing of protection efficacy upon application onto micro- and macroporous stone substrates of different chemical composition and morphology.

INTRODUCTION

Coating formulations based on fluorinated polymers are well known for their excellent protective properties and stability.[1] The synthesis of fluorinated polymers from fluorinated olefins, vinyl ethers, or other more exotic precursors can be rather complex, however. In addition, it suffers from the scarce availability of the raw material on the free market due to captive consumption by the few industrial world leaders. Finally, their use does not allow, in many cases, sufficient flexibility for designing structures specifically tailored for different applications. Acrylic and methacrylic esters of fluorinated alcohols are often employed to overcome this problem. However, the presence of fluorine in specific positions of the monomer molecule can markedly affect reactivity and, consequently, a macromolecule's primary structure and material properties.[2,3]

In this context, our research group has been involved for several years in the investigation of the free radical polymerization of (meth)acrylic esters bearing fluorine atoms or fluorinated groups either directly connected to the double bond or in the side chain.[4] In this way, it was possible to evaluate how the position and extent of fluorine substitution can modify the polymerization process, as well as the chemical, physical, and protective properties of the resulting polymeric material. Monomers such as alkyl esters of 1-fluoro or 2,2-difluoro acrylic acid and esters of various short- and long-chain, linear, or branched fluorinated alcohols with acrylic, methacrylic, or 1-fluoroacrylic acid were copolymerized with different, not fluorinated, monomers such as acrylates, alkenyl ethers, and α-olefins. The microstructure of the copolymers was determined and related to glass transition temperature in order to build predictive capacity relative to the possibility of modulation of the copolymer's thermal properties by varying fluorine content and distribution.

The photochemical stability and protective properties of the prepared coating materials were also tested.[5,6] In the former case, GPC analysis and FTIR spectroscopy were employed to detect the extent of degradation of the macromolecular structure and the nature of chemical modification, respectively. In the latter case, the protective efficacy of the resulting coatings was evaluated upon application on micro- and macroporous substrates of different chemical compositions and morphologies, such as leather, textile, and stone materials. Both surface and technological properties were determined thereafter, by using simple

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Presented on behalf of FATIPEC (AITIVA) at the 78th Annual Meeting of the FSCT in Chicago, IL, on October 16-20, 2000.

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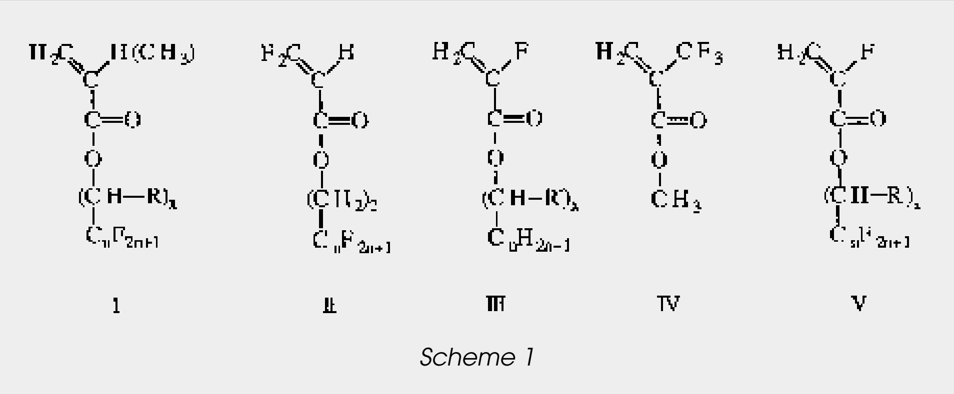

Scheme 1

techniques such as static and dynamic contact angle measurement, determination of water absorption, and transpirability.

EXPERIMENTAL

Materials and Techniques

Hoechst-Aventis provided 1,1,1,3,3,3-hexafluoroisopropyl α-fluoroacrylate (HFIFA). Methyl α-trifluoromethyl acrylate (MTFMA) and ethyl 3,3-difluoro-2-methylpropenoate (MFPE) were supplied by Prof. U. Matteoli, from the University of Venice (Italy). The remaining fluorinated acrylates were prepared from the corresponding alcohols and acryloyl- or methacryloyl chlorides by conventional nucleophilic substitution in the presence of triethylamine in diethyl ether at 0°C. All the fluorinated and unfluorinated acrylates (the latter purchased from Aldrich) were purified by distillation under nitrogen or, as in the case of XFDMA and XFDA,[7] by column chromatography, and stored under nitrogen at –25°C before use. Lumiflon® LF200 (Asahi—Zeneca) was used as supplied. All alkyl vinyl ethers (Aldrich) were purified by distillation over K/Na alloy just before use. Dioxane and toluene, employed as polymerization solvents, were refluxed and distilled under nitrogen over K/Na alloy. AIBN, α,α′-Azobisisobutyronitrile (Akzo) was recrystallized from ethanol. The remaining reagents and solvents were purchased from Aldrich and were used without further purification.

FTIR spectra were taken from cast films laid on KBr disks or, for the photodegradation studies, on silicon wafer, using a Perkin-Elmer 1710 instrument. ^{1}H-NMR spectra were recorded from $CDCl_3$ or acetone-d_6 solutions using a Varian Gemini 200 spectrometer. Differential scanning calorimetry (DSC) analyses were carried out on a Perkin-Elmer DSC-7 instrument equipped with a CCA7 temperature controller connected with a liquid nitrogen tank for subambient operation. Scan rates were 20°C/min with only the second heating scan considered for the analyses. Molecular weight characterization of initial and irradiated samples was performed by size exclusion chromatography (SEC) in tetrahydrofuran at 1 cm^3/min flux, using a Waters M45 pump, a Rheodyne 7110 injector, and four PL-Gel columns (Polymer Labs, England), with nominal porosity 500, 10^3, 10^4, and 10^5 Å. A series of poly(methyl methacrylate) standards (Polymer Labs, England) were employed for column calibration.

The accelerated photoaging was performed in a high-speed exposure unit Suntest CPS (Heraus, Germany), equipped with a Xenon light source. A glass filter with cutoff at $\lambda \leq 295$ nm was used in order to exclude radiation more energetic than that of common outdoor solar exposure. Irradiation was kept at 765 W/m^2. Film preparation, weight loss, and gel content determination, as well as the analyses carried out on samples submitted to different times of irradiation, were performed following the procedures already reported elsewhere.[8]

Polymerizations

All polymers were prepared by conventional AIBN-initiated radical polymerization, either in bulk

Table 1—Copolymers of Type I Side Chain Fluorinated Methacrylates with Unfluorinated Analogs[a]

Fluorinated Monomer	Unfluorinated Monomer	Fluor. Monomer in Feed (mol %)	Copolymer Fluor. Monomer (mol%)	Copolymer F (wt%)	Copolymer T_g (°C)
XFDMA	—	100	100	61	47
XFDMA	MA	6	6	17	15
XFDMA	MMA	50	50	51	46
XFDMA	MMA	7	5	13	110
XFDMA	BMA	60	62	52	45
XFDMA	BMA	10	14	22	29
XFDMA	OMA	20	21	25	-6
XFDMA	OMA	12	16	21	-2
XFDMA	LMA	42	45	38	27
XFDMA	LMA	15	15	17	-9
XFDMA	EHMA	20	20	24	20
XFDMA	EHMA	11	12	17	15
XFDMA	EHA	17	17	22	-52
XFDMA	EHA	7	7	10	-63
TFEMA	—	100	100	34	63
TFEMA	MA	67	66	27	43
TFEMA	BMA	62	60	22	69
TFEMA	BMA	35	37	14	57
TFEMA	OMA	67	64	21	43
TFEMA	OMA	43	42	13	27
TFEMA	LMA	74	70	20	38
TFEMA	LMA	28	28	7	1

(a) Free radical initiated polymerization in dioxane at 65°C [14]. MA = methyl acrylate, MMA = methyl methacrylate, BMA = butyl methacrylate, OMA = octyl methacrylate, LMA = lauryl methacrylate, EHMA = 2-ethylhexyl methacrylate, EHA = 2-ethylhexyl acrylate, XFDMA = 1H,1H,2H,2H-perfluorodecyl methacrylate, TFEMA=2,2,2-trifluoroethyl methacrylate.

or solution (dioxane or toluene), and purified twice by precipitation from the appropriate solvents. Copolymer compositions were determined by ^{1}H-NMR. Details on the synthetic procedures have been previously reported.[7,9-12]

RESULTS AND DISCUSSION

Synthetic Strategy

The general synthetic strategy was focused on the objective of preparing, through simple and mature polymerization processes, polymeric materials containing a predictable and optimized fluorine amount, functional groups to grant adhesion to various substrates, and characterized by thermomechanical properties suitable for the requested application.

Acrylic monomers appeared to respond to the above requisites as a result of the possibility of replacing H with F in different positions of acrylate or methacrylate esters, the excellent polymerizability by free radical processes in organic solvent or in water dispersion, and the easy polymerizability with different acrylic derivatives and other vinyl comonomers. Hydrogen replacement by fluorine, due to the high electronegativity of the latter, can strongly affect the chemical reactivity of acrylic monomers, depending on the position of such replacement in the monomer molecule. In this connection, two classes of acrylic monomers were investigated. The former includes acrylic (or more commonly methacrylic) esters containing fluorine only in the alkyl side chain, with at least one nonfluorine-bearing carbon next to the ester group (see, for example, structure I, in *Scheme* 1). Type I monomers were reasonably expected, and experimentally confirmed,[5,13] to show similar reactivity in free radical polymerization as their unfluorinated analogs. The latter group includes monomers where fluorine substitution occurs either on the C-atom involved in the double bond (structure II or III) or on the α-methyl in the case of methacrylates (structure IV). A type V monomer with fluorine both at the double bond and in the side chain was also investigated.

Monomers II-V display different reactivity, due to the electronic effect of F next to the double bond on the reactivity of the last,[5,10] as discussed later. Indeed, the high positive polarization of the double bond induced by F increases its electrophilicity and, therefore, affinity towards electron-rich, nucleophilic monomers, such as vinyl ethers. While homopolymerization of monomers I-V was tested to get information about their reactivity, a more extended investigation was devoted to evaluate their capacity to be included in more complex macromolecules jointly with alkyl acrylates and other vinyl monomers, including those bearing functional groups in the side chain.

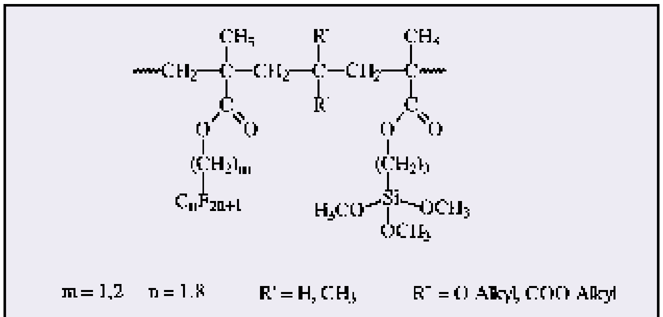

Figure 1—General structure of fluorinated, reactive acrylate-vinyl ether polymer.

Within this broad context, the copolymerization of type I monomers with alkyl methacrylates was first investigated with the aim of obtaining materials with variable content and distribution of fluorine and variable glass transition temperature (T_g). The monophase morphology of the material, and then the homogenity of the derived films, was anticipated by the predictable random structure of these copolymers. Investigated examples are reported in *Table* 1, where it is shown how appropriate selection of comonomers and composition allows for the independent modification of fluorine content and T_g within a rather broad range. Such variations can be even larger if monomers of a different nature, such as vinyl ethers or vinyl esters, are employed instead of unfluorinated methacrylates.

Positive charge density on the double bond, in addition to allowing conventional semirandom copolymerization with unfluorinated acrylates, opens new possibilities in terms of the introduction of different units and, particularly, of such electron-rich monomers as vinyl ethers (VE) and α-olefins. Good conversion with these fluorinated acrylates indeed was obtained in the copolymerization with alkyl vinyl ethers. These latter are incapable of polymerizing under free radical conditions but, as a result of the high electron density on their double bond, can form charge transfer complexes or polarized adducts with the fluorinated monomers, thereby producing alternating or quasi-alternating copolymer sequences.[5]

Type I fluorinated monomers showed different tendencies to alternation, depending on fluorine position. Indeed, HFIMA (I, R=CF$_3$, x=1, n=1) produced copolymers of vinyl ethers with a mainly alternating structure,[9] while XFDMA, with a dimethylene spacer between the perfluorinated group and the acrylate moiety, showed a similar reactivity in the radical copolymerization as the unfluorinated methacrylates, and TFEMA displayed an intermediate behavior. This indicates that two methylene groups are necessary for proper spacing, unless specific

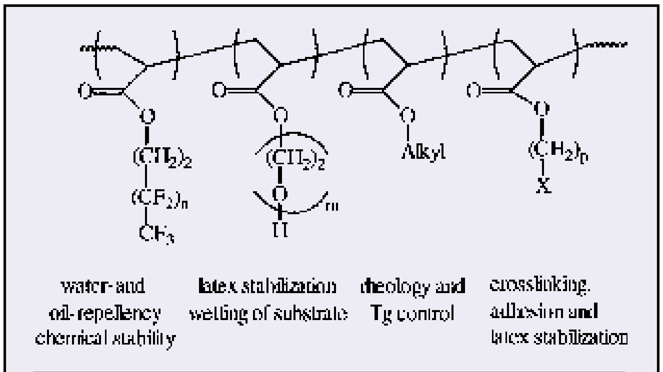

Figure 2—General structure of multicomponent polymers.

Table 2—Phootoxidative Degradation of Fluorinated Copolymers

Copolymer	Molar Composition	F (wt%)	Mn (x 10^{-4})	Mw/Mn	Irradiation Time (hr)	Weight Loss (%)	Gel Formation (%)
TFEMA/BMA	60/40	22	2.55	3.3	250	n.d.	0
					500		1
					1000		2
TFEMA/BVE	77/23	29	3.14	1.6	250	n.d.	0
					500		2
					1000		5
EMA/BVE	71/29	/	2.00	3.4	250	n.d.	6
					500		10
					1000		13
XFDMA/BA	17/83	28	3.58	1.4	250	n.d.	4
					500		5
					1000		43
XFDA/BMA	18/82	28	4.06	1.7	250	n.d.	2
					500		4
					1000		52
XFDMA/BMA-1	19/81	28	3.8	1.6	250	1	2
					500	2	4
					1000	2	50
XFDMA/BMA-2	13/87	21	4.2	1.5	250	1	2
					500	2	4
					1000	3	76
XFDMA/LMA	30/70	29	1.9	2.3	250	1	6
					500	1	38
					1000	3	77
XFDMA/EHMA-1	20/80	24	n.d.	n.d.	200	2	0
					400	9	28
					900	17	61
XFDMA/EHMA-2	12/88	16	n.d.	n.d.	200	2	0
					400	10	34
					900	19	72
MTFMA/EHVE	60/40	22	1.79	3.3	250	n.d.	1
					500		3
					1000		11
MFPE/BVE	51/49	15	2.17	4.1	200	8	5
					400	11	50
					600	11	—
HFIFA/BVE	50/50	39	17.4	2.8	200	5	9
					400	16	16
					600	20	—

changes in the reactivity of the fluorinated acrylate is desired.

By combining the data collected for the copolymerization with a primary vinyl ether as the unfluorinated comonomer, it is possible to conclude that the tendency to alternation of the investigated fluorinated monomers is in the order:

$$\text{HFIFA} \sim \text{MFPE} > \text{MTFMA} \sim \text{HFIMA} > \text{IFA} \sim \text{TFEMA} > \text{XFDMA} \sim \text{MMA}$$

One may also conclude that by using different fluorinated monomers, copolymer macromolecules with isolated VE units, quasi-alternating distributions, or strictly alternating distributions were obtained. Of course, the nonrandom, mainly alternating distribution of these last copolymers does not allow one to predict T_g on the basis of simple semiempirical relations such as the Fox equation.

The data summarized show the very broad possibility of the synthetic approach to modulate fluorine content and T_g allowed by the use of the different monomers and by copolymerization. It is easily understandable how this flexibility can be further improved by using a third monomer. This last, in addition to further modulating F content and T_g, can allow for the introduction of additional and useful functional groups.

Thus, the adhesion to different substrates can be improved by the introduction of a modest amount of a third monomer containing a functional group capable of linking more or less strongly with the coating substrate. In particular, in the case of a silicatic stone or masonry surface, co-units with an alkoxysilane group in the side chain, as shown in *Figure* 1, can undergo partial hydrolysis and provide strong adhesion through hydrogen or even covalent bonds with the silanol groups of the stone. Therefore, the consequent terpolymer can combine the already mentioned useful structural properties with the good wetting of an inorganic surface and convenient adhesion to the same. This will ultimately allow for a significant improvement of the homogeneity of the final film and of the actual extent of surface covering, that is, both at the outer surface and within the pores of the substrate itself.

The application of the previously mentioned polymer as protective film is dependent on the solution rheology (viscosity). Indeed, when the film-forming material is a reactive low molecular weight compound, such as a silane derivative, viscosity can be too low for appropriate film formation. In addition, these products may form films with modest mechanical properties. On the contrary, the use of high molecular weight macromolecules, which can be more convenient for modulating the many necessary properties, commands application from a viscosity-reducing medium. While dilute solutions in organic solvents present the required rheological properties, they are also increasingly replaced by water dispersions (latexes) for obvious environmental reasons. Accordingly, acrylic multipolymers with either fluorinated or alkoxysilane groups in the side chains, or both, were prepared by the emulsion polymerization process. In order to obtain a stable latex, one or more additional comonomers with a water compatible side chain, such as that reported in *Figure* 2, were added to the basic structure of either simple or functional (reactive) fluorinated copolymers.[11] The final goal of the present activity will be the optimization of the application properties of such latexes as either water repellent coatings or stone consolidant materials, according to the specific copolymer composition.

Stability to Photoaging

The photodegradation processes of the various fluorinated copolymers, as compared to those of selected unfluorinated analogs, were studied by means of accelerated photoaging under strictly controlled conditions using a fluorescent xenon lamp to mimic solar irradiation. Chromatographic and spectroscopic techniques were used to monitor the evolution of the different structures[12] during and up to 2000 hr of irradiation.

Copolymers of type I side-chain fluoroalkyl methacrylates with unfluorinated methacrylates having linear or branched (2-ethylhexyl) side chains have shown that the presence of the fluorinated comonomer slows down the photodegradation process, which is still determined by the intrinsic reactivity of the alkyl group.[6] As a consequence, progressive gelification of the material is due to photoinduced crosslinking reactions that take place in the presence of oxygen (*Table* 2). Such reactions are sped up by the presence of branched (e.g., 2-ethylhexyl-) or by longer (e.g., butyl, lauryl-) unfluorinated side chains; indeed, the former increase the probability of free radical formation through abstraction of labile tertiary hydrogens, the latter increase molecular and, hence, free radical mobility. In all the samples containing vinyl ether units, crosslinking is much lower. Moreover, it is further verified that the crosslinking rate is comparatively greater when the unfluorinated methacrylate units have long side chains.

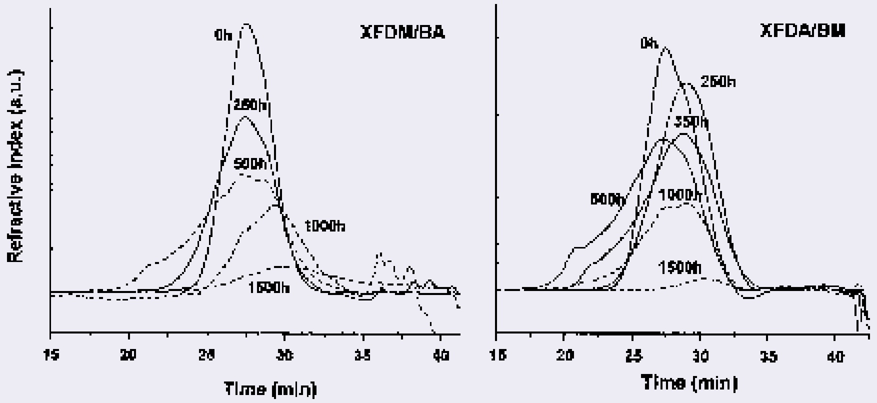

Figure 3—Normalized SEC analyses: XFDMA/BA and XFDA/BMA copolymers irradiated up to 1500 hr.

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The two XFDMA and XFDA (XFDA = 1H, 1H, 2H, 2H-perfluorodecyl acrylate) copolymers with, BA (butyl acrylate) and BMA respectively, present a similar amount of insoluble polymer fraction generated by the photooxidative treatment. The tendency of these structures to undergo a degradation pathway where gel formation is the main output may be revealed, even at relatively short degradation times, by looking at the changes in the size exclusion chromatography curves of the polymers.

In fact, one can see from *Figure* 3 that at the beginning of the degradation the molecular weight distributions broaden on the lower retention volume side, indicating the formation of molecules with molecular weights higher than the initial ones. At longer degradation times, on the other hand, the curves are only representative of the soluble fractions remaining in the samples.

In addition to the molecular weight distribution changes and the gel formation, the structural changes in the XFDMA and XFDA copolymers are also very similar, and consist in the formation of hydroxyl-bearing groups through the typical mechanism of hydrocarbon oxidation,[15] and of lactone groups, detectable from their characteristic absorption at 1785 cm^{-1}. The latter ones are invariably found as the photooxidation products of different types of structures like polyolefins[16-18] and acrylate homopolymers.[8]

The irradiation in air of TFEMA/BVE and of its unfluorinated analogous, EMA/BVE, induces large changes in the samples, from both a structural and a molecular point of view. The main effects on the two copolymers are the development of oxidized structures (hydroperoxides, alcohols, lactones, and acids), as detected from the FTIR spectra, and the extensive chain scissions, which may be visually appreciated by the displacement towards higher retention times of the SEC curves (*Figure* 4). By comparing the number of chain scissions per

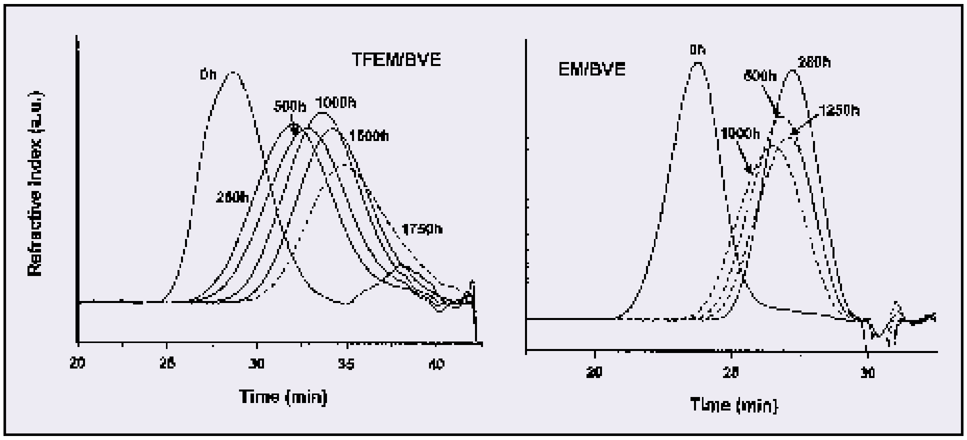

Figure 4—Normalized SEC analyses of irradiated copolymers of BVE with fluorinated (TFEMA) and corresponding unfluorinated methacrylates.

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initial polymer molecule, as calculated from the Mn values measured during degradation,[19] the progress of these reactions appears to be faster in the EMA/BVE copolymer. Indeed, this latter yields a sharp increase to about seven events within the first 200 hr, a value reached by TFEMA/BVE only after 1500 hr.

Vinyl ether units in polymer samples are quite sensitive to photooxidation,[20] with the development of new carbonyl containing functional groups and the homolysis of the backbone carbon–carbon bonds. The sharp molecular weight decrease measured in our copolymer samples after the irradiation indicates that the same chain scission mechanism is present, which can be attributed to the effect of the vinyl ether units. In fact the TFEMA and EMA homopolymers, subjected to the same irradiation conditions, undergo chain scissions to a much lesser extent, and very little or no oxidation of the macromolecular structure can be observed.[6,12] On the other hand, oxidation in the vinyl ether copolymer with TFEMA is lower than with EMA, as it is shown by the respective increments of the lactone absorption in the IR spectra.

All copolymers of vinyl ethers with acrylic monomers fluorinated at, or close to, the vinyl group exhibit some degree of comonomer alternation. It was argued that such structural regularity, with α- or β-fluorinated acrylate units alternating with acrylate or vinyl ether units containing a labile tertiary hydrogen, could stabilize the systems by inhibiting the backbone oxidation and the chain scission reactions. The first copolymer of this type that was studied, MTFMA/EHVE,[21] showed a moderate effect of the CF_3 group. The molecular weight distribution changes, evaluated from SEC analysis, were compared with those of a side-chain fluorinated acrylic-vinyl ether copolymer, TFEMA/BE, and its unfluorinated analogous, EMA/BVE. The main difference is a slowed displacement of the curves towards longer elution times, corresponding to a lower number of chain scissions. The oxidation reactions in MTFMA/EHVE are similar to those already described for the other samples, indicating that, in this case, the F atoms are too far from the tertiary C–H bond of the vinyl ether unit to allow for a significant electronic effect for polymer stabilization.

The preliminary results obtained with the copolymers HFIFA/BVE and MFPE/BVE indicate that the photoinduced reactivity of the vinyl ether units is still significant, and polymer degradation is not suppressed. Structural modifications probably are controlled also in these samples by the reactions on the vinyl ether units, although the infrared spectra changes are quite different in comparison with the previous cases. Detailed evaluation of the photooxidative degradation reactions taking place in the above polymers will be reported in a forthcoming paper. The commercial Lumiflon, an alternating copolymer of vinyl ethers with chlorotrifluoroethylene (CTFE), was also analyzed as a reference commercial coating material. Here again the labile C–H bond of the vinyl ether unit is in α position to a CF_2 group, thereby allowing an interesting although loose comparison with the MFPE copolymer. In this case, very fast and complete photo-crosslinking was observed, possibly as a result of the presence of reactive hydroxyl and/or other undisclosed functional groups in the side chain, participating to secondary reactions following the primary free radical photogeneration. However, the FTIR spectra showed very small changes even after more than 2000 hr of irradiation, indicating that the $–CF_2–CFCl–$ units strongly inhibit the formation of oxidized structures.

Coating and Protective Properties of Fluorinated Copolymers

Among the many possible applications of the described copolymers, our attention has been focused on their use as transparent protective coating for surfaces having aesthetic importance. In this connection, the present work deals with the screening of fluorinated acrylic coatings applied over either monumental stone surfaces, with reference to cultural heritage maintenance, or textile, with reference to the clothing/fashion industry.

In the case of stone, an accurate evaluation of the protective properties is very challenging, due to the lack of homogeneity of the thin polymer film. This follows from both the method of application and the roughness and porosity of the stone surface. In the case of the subject copolymers, two carbonatic lithotypes differing to a large extent in porosity were selected for the application tests: these were Candoglia Marble and Noto calcarenite, with about 1% and 30-40% porosity, respectively. Copolymers of XFDMA or TFEMA as the fluorinated acrylate, with either methyl methacrylate (MMA), 2-ethylhexyl meth-

Table 3—Polymer Coatings Employed for Stone Protection

Polymer	Molar Composition[a]	F (wt%)	T_g (°C)	Mn (x 10^{-4})	Mw/Mn	Applied Coating[b] (g/m^2) Marble	Applied Coating[b] (g/m^2) Calcarenite
XFDMA/MMA	1/7	24	97	1.7	1.5	7.7	23.3
XFDMA/EHMA-1	1/4	24	20	0.5	2.0	1.2	3.1
XFDMA/EHMA-2	1/7	17	15	1.2	2.8	3.0	19.8
XFDMA/LMA	1/2.4	28.3	5[c]	6.6	1.1	13.9	144.7
PLMA	—	—	-47	1.5	2.6	11.7	102.4
TFEMA/MA	2/1	27.0	43	2.1	1.7	7.1	396.0
EMA/MA[d]	2/1	—	43	1.7	3.7	3.1	299.4
TFEMA/BVE	2.5/1	27.4	34	4.2	2.9	19.2	91.6
EMA/BVE	2.5/1	—	26	9.8	1.2	29.8	82.9

(a) Determined by ^{1}H-NMR.
(b) Polymers applied on 2-cm thick stone specimens, either by brush as 10 wt % solutions in ethyl acetate, or by capillary absorption from 5% solutions (EMA/MA and TFEMA/-MA); XFDMA/MMA and XFDMA/EHMA copolymers applied by brush as 3-5 wt% solutions, according to solubility.
(c) Additional T_g at -47°C, associated to microseparated homo-LMA domains.
(d) Acryloid™ B72 (Rohm and Haas).

acrylate (EHMA), lauryl methacrylate (LMA), methyl acrylate (MA), or n-butyl vinyl ether (BVE) as the unfluorinated monomers were used (*Table* 3). The assessment of the effectiveness of the side-chain fluorinated acrylic-based copolymers was performed by comparing their behavior to that of their unfluorinated analogs. Also, the influence of replacing acrylic units with vinyl ether units having the same alkoxy side chain was examined.

Great care was taken in the preparation of the stone specimens, which were accurately washed with deionized water and dried under vacuum (0.1 mm Hg.) at room temperature before being stored in a dessiccator. Application of the coating polymer solution was carried out either by brush until refuse, or by capillary absorption from a filter paper pad saturated with the polymer solution. After the treatment, the specimens were dried following the same procedure adopted for the initial conditioning.[7] The evolution was followed using such techniques as sessile contact angle determination, capillary water absorption, water vapor permeability, and colorimetric analysis. The relevant data are reported in *Tables* 4 and 5 for Candoglia Marble and Noto Stone, respectively.

As shown by the data reported in *Table* 3, the penetration into the two stones is very different for each polymer solution. Indeed, depending on the type of polymer, the calcarenite specimen absorbs four to 10 times as much product as that absorbed by the marble specimen, when the coating is applied by brush. The two types of stone behave even more differently when the products are applied by capillarity, being from 40 to 100 times larger in the case of the more porous calcarenite. These data anticipate that the protective behavior can be strongly affected by both the characteristics of the substrate and the application technique.

Accordingly, contact angles with water are generally larger for the Noto calcarenite than for the Candoglia Marble, irrespective of the type and amount of fluorine in the polymer. Strictly speaking, a comparison among different polymers can then be done only on the basis of contact angles observed on the same type of stone. For both types of investigated stones, the contact angle becomes larger upon random replacement with fluorinated XFDMA units in the relatively hydrophobic PLMA homopolymer. However, differences are not very large, as the long aliphatic chains of PLMA units also exert a fair water repellence. For these two polymers the improvement due to fluorine substitution is better evidenced at higher polymer loading, that is, on the calcarenite. The effect of fluorine in reducing surface wettability is more evident with the short chain acrylic polymers, as in the case of TEFM/MA as compared to its parent unfluorinated copolymer Acryloid® B72. Upon replacement of MA with BVE in copolymers with TFEMA and EMA (ethyl methacrylate), respectively, the effect of fluorine is almost completely lost on the marble, i.e., at low polymer loads, whereas it is still apparent on the Noto stone.

Information about the coating behavior can also be derived from the determination of water absorption through the stone surfaces before and after treatment with various polymers. All untreated stone specimens were quickly saturated by water, reaching a plateau of 30-50 g/m^2 within the first 3-6 hr (100-150 $sec^{1/2}$) for the marble and of as much as 4500-5000 g/m^2 within the first 20-40 hr for the calcarenite (2-cm thick samples). Application of the polymeric coatings led to a more or less pronounced reduction in absorption, at least at short times. *Tables* 4 and 5 report the short- and long-term water absorption

Table 4—Protective Properties on Candoglia Marble: Type I Acrylates Copolymers and Unfluorinated Polymer Analogs

Polymer	Water Contact Angle (deg)	Capillary Water Absorption (mg/cm^2)[a] After 4 hr	Capillary Water Absorption (mg/cm^2)[a] After 96 hr	Water Vapor Permeability[b] (% Reduction)
None	42	2.5 – 4.3	3.3 – 5.1	—
XFDMA/MMA	115	1.5	n.d.	n.d.
XFDMA/EHMA-1	132	1.9	n.d.	32
XFDMA/EHMA-2	127	1.9	n.d.	42
XFDMA/LMA	117	0.4	3.8	75
TFEMA/MA	94	0.9	2.9	78
TFEMA/BVE	92	0.4	2.3	70
PLMA	115	0.7	4.0	76
EMA/MA	82	1.6	4.2	47
EMA/BVE	89	0.5	3.1	43

(a) Gravimetric measurements on 2-cm thick samples.
(b) Gravimetric measurements on 1-cm thick samples.

Table 5—Protective Properties on Noto Stone: Type I Acrylates Copolymers and Unfluorinated Polymer Analogs

Polymer	Water Contact Angle (deg)	Capillary Water Absorption (mg/cm^2)^a		Water Vapor Permeability^b (% Reduction)
		After 4 hr	After 96 hr	
None	n.d.^{c}	454-508	516-588	—
XFDMA/MMA	146	5	n.d.	n.d.
XFDMA/EHMA-1	145	11	n.d.	-9
XFDMA/EHMA-2	140	6	n.d.	5
XFDMA/LMA	141	67	554	51
TFEMA/MA	130	14	43	39
TFEMA/BVE	129	14	52	28
PLMA	132	482	544	27
EMA/MA	118	30	368	39
EMA/BVE	109	14	162	33

(a) Gravimetric measurements on 2-cm thick samples.
(b) Gravimetric measurements on 1-cm thick samples.
(c) The equilibrium contact angle on the untreated calcarenite could not be determined, due to fast capillary absorption.

data, together with the absorption range of the stone samples before application of the coating polymers. The broadness of the latter is indicative of the intrinsic variability of the natural stones, and of the difficulty of making a direct comparison of the efficacy of the various coating polymers. In the case of Candoglia Marble the fluorinated polymers determine a higher reduction of water absorption than their unfluorinated analogues. Such improvement is particularly apparent for TFEMA/BVE and XFDMA/LMA at shorter times (less than 24 hr). TFEMA/BVE is the most effective in maintaining a moderate long-term water repellency which, on the contrary, is lost on the EMA/BVE-coated stone; indeed at longer times TFEMA/BVE is the best performer among all the acrylic copolymers studied. On the other hand, XFDMA/LMA is the most effective at short contact times. The short side-chain TFEMA/MA copolymer is slightly less effective than the TFEMA/BVE copolymer and performs better than XFDMA/LMA at times exceeding 48 hr. This apparently strange behavior can be understood in terms of local reorganization of the coating material at the polymer-water interface. Such reorganization is certainly favored by a T_g close to or above the working temperature (the T_g of the polymers showing the worst long-term performance, XFDM/LM and EM/BVE, are 5° and 26°C, respectively). On the contrary, the relatively low molecular weights of some of the polymers did not seem to markedly affect their water resistance (see TFEMA/MA), either because they are above the entanglement threshold or because entanglement is not a crucial factor. In the case of the TFEMA/MA copolymer, containing a mole fraction of fluorinated units much higher than in XFDMA/LM, the CF_3 groups are more likely to be homogeneously distributed in the bulk of the polymer with little enrichment at the polymer-air interface. Therefore, the good but not outstanding performance of the coating at short contact times is balanced by its fair and long-lasting water repellency, which is only overrun by the highly hydrophobic TFEMA/BVE.

It must be noted, however, that although these polymers perform relatively well, the appearance of the coated marble surface is in some cases very poor, due to darkening, undesired gloss and, particularly for the long side-chain polymers, tackiness caused by the low T_g and insufficient penetration in the compact marble.

The higher polymer uptake allowed by the porous Noto stone determines a much sharper decrease of the water absorption on the coated specimens. Again, all fluorinated polymers perform better than their unfluorinated analogues, particularly at longer contact times. XFDM/LMA is the worst performer among all fluorinated copolymers, with initial loss of efficacy after less than six hours and complete ineffectiveness after 24 hr. The performance of TFEMA/MA, TFEMA/BVE, and EMA/BVE are, on the other hand, very interesting. TFEMA/MA displays its improved behavior, with respect to its fluorinated analogous Acryloid B72, after the first four hours, when the fluorinated coating preserves its efficacy while the unfluorinated one shows a slow recovery of the water permeability. The difference between the fluorinated and unfluorinated polymer is less evident in the case of the vinyl ether copolymers, simply because both materials perform extremely well up to 72 hr, when only the unfluorinated coating starts losing efficacy. The lower T_g determined by the replacement of MA with BVE in the TFEMA copolymers, in addition to the lower polarity of the vinyl ether unit and, therefore, to its reduced affinity for water, positively affects the coating performance.

Water vapor permeability of the stone should not be strongly reduced by the coating polymer. The permeability of the marble, already very low for the untreated stone (13-18 g/m^2 over a 24-hr period at stationary flux, for 1-cm thick specimens), is however disadvantageously reduced by the application of the fluorinated copolymers (*Tables* 4 and 5). The situation is very different in the case of the highly porous calcarenite (untreated stone permeability 260-330 g/m^2·24 hr). The introduction of fluorine does not produce a pronounced reduction in the permeability of the coated surfaces, while, in some cases, a reduction can be observed if one compares the same copolymer at higher concentration of the treating solution—that is, at higher polymer uptake. As a general rule, the data reported here suggest that the introduction of fluorine determines a certain reduction of the water vapor permeability; however, this kind of property is strongly affected by the treating methodology (e.g., by capillarity or by brush) and by the porous structure of the stone.

Less systematic data are available for copolymers of acrylic derivatives bearing fluorinated groups in the close vicinity of the double bond. Among them, a Type V copolymer with butyl vinyl ether, HFIFA/BVE (see *Table* 2, T_g = 35°C, F = 39 wt%), and the CTFE—vinyl ethers copolymer Lumiflon, were applied on the same stones (Noto and Candoglia). Their protection efficacy and the surface properties of the treated stones were analyzed immediately after application and upon accelerated photoaging under the same conditions adopted for the photodegradation studies carried out on the cast films, as previously discussed. Copolymers of BVE with both Type I fluoroalkyl acrylate TFEMA and its unfluorinated analogous EMA (see *Table* 2) were also studied, and their behavior compared with that of the main chain-fluorinated copolymers HFIFA/BVE and Lumiflon.

The preliminary results obtained so far[22] confirm the expected superior photooxidative stability of the alternating CTFE/vinyl ethers copolymer, which undergoes fast crosslinking due to the presence of reactive groups in the side chain, but remains otherwise unaffected by the most common radiation- and oxygen-induced chemical reactions occurring on most acrylic-vinyl ether copolymers. This coating material is also an excellent performer in terms of protective behavior on both stone substrates. The short- and long-term (96 hr) reduction of water capillary absorption is comparable with that obtained using the highly water repellent TFEMA/BVE, slightly better than HFIFA/BVE, and much better than EMA/BVE, at longer contact times. While the performance and surface properties (contact angle with water) of Lumiflon remain almost unaffected by irradiation up to 1500 hr, the protection efficacy of the acrylic-based coating materials is largely reduced by the accelerated photoaging, although not as much as in the case of the unfluorinated EMA/BVE. Separate studies still in progress have allowed for the highlighting of the key roll of a fluorinated carbon in α position with respect to the reactive O–C–H bond of the vinyl ether units, such as in MFPE/BVE (*Table* 2). Indeed its presence can modify, and possibly hinder, the chemical reactions involving photogenerated radicals, those that will eventually lead to crosslinking and/or C–C cleavage with volatilization of small fragments.

CONCLUSIONS

Fluorinated acrylates were employed for the synthesis of conventional, side-chain fluorinated, fully acrylic random copolymers and of more unusual hybrid copolymers with vinyl ethers. While perfluoroalkylethyl acrylates such as XFDMA show a similar reactivity in the radical polymerization as unfluorinated (meth)acrylates, the same does not apply when fluorine substitution occurs closer to the vinyl bond as in MTFMA, HFIMA, and TFEMA. These latter can feature alternating copolymer structure and peculiar material properties associated with fluorine or fluorinated groups substitution onto the polymer backbone. The tendency to alternation with vinyl ethers in the order HFIFA ~ MFPE > MTFMA ~ HFIMA > IFA ~ TFEMA > XFDMA ~ MMA, allows copolymers to be obtained with isolated VE units, quasi-alternating, or strictly alternating distribution by appropriate selection of the fluorinated comonomer.

The accelerated photoaging studies, carried out on fluorinated copolymers and their unfluorinated analogues, confirmed that the photochemical instability is mainly due to the reactivity of the unfluorinated co-units, and is particularly high in the presence of long unfluorinated side chains. Some control on the photooxidative instability can be achieved using main chain fluorinated copolymers of fluoroacrylates with vinyl ethers. Indeed, the photoinduced reactivity of the vinyl ether units in MTFMA, HFIFA, and MFPE copolymers indicate that the photodegradation is still significant, although the two latter fluoroacrylates induce a change in the reaction path. The best results were obtained with the commercial Lumiflon® LF200; in fact, its fast photocrosslinking is likely to be due mainly to the presence of reactive groups purposely introduced in the macromolecule, rather than to intrinsic polymer instability.

Extensive testing of the protection efficacy on various stone substrates commonly found in historic buildings and works of art have shown, as expected, improved performance of the fluorinated coatings. However, such improvement is particularly apparent at shorter contact times with water. The short side-chain TFEMA copolymers generally perform better than those with XFDMA at times exceeding 48 hr, due to the effects of macromolecular rearrangement at the polymer-air interface. Furthermore, the introduction of fluorine negatively affects the water vapor permeability of the coated substrate. Therefore, particular attention must be paid to the choice of application conditions and amount of applied coating material. Again, excellent and durable performance is exhibited by Lumiflon, although its behavior is likely to be largely influenced by its network-forming nature.

Penetration of the polymer beyond the stone surface, film formation, film morphology, and adhesion are important factors determining the ultimate properties of the coating on the porous stone exposed to natural weathering. Further studies are presently carried out concerning the synthesis, the application behavior, and the coating properties of multifunctional fluorinated acrylic copolymers, bearing either reactive or otherwise suitably selected functional groups on the side chain, according to the specific effect or property desired for the coating material.

Reactive terpolymers with the general structure reported in *Figure* 1 have already shown promising efficacy as water repellent coatings. While the reactivity of the trialkoxysilane groups makes their application virtually irreversible, and, therefore, not particularly suitable in the protection of valuable works of art or monuments, the same reactivity makes them interesting candidates for combined consolidation and protection treatments of heavily deteriorated objects. Multifunctional polymers are also required for the successful synthesis of stable fluorinated latexes, which can be employed as solvent-free, environmentally safer protective base materials for stone coatings. In this case, however, the nature of the porosity and the chemical composition of each specific stone represents an additional constraint to the requirements of the polymeric material. In fact, the latex particle size and size distribution, as well as its stability in the microenvironmental conditions within the pores (pH, salt concentration, etc.), should be compatible with those of porous matrix, since the latter can markedly affect the penetration of the solid waterborne particles and, therefore, the efficacy and durability of the protective treatment.

ACKNOWLEDGMENT

Financial support from the C.N.R. Special Project "Safeguard of Cultural Heritage" is gratefully acknowledged.

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