

Aromatic triblock polymers from natural sources as protective coatings for stone surfaces

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ABSTRACT: Aromatic triblock polymers were synthesized, characterized, and tested as protective coatings for stone surfaces. Syntheses were carried out by a ring opening polymerization process from specifically synthesized monomers ((3S)-6-methyl-3-phenyl-1,4-dioxan-2,5-dione or 1,4-benzodioxepin-3-methyl-2,5-dione) and a perfluoropolyether diol (Fluorolink D10-H), as chain initiator. Polymers were characterized through spectroscopic and analytical techniques while their stability under photo-oxidative conditions was tested using a Solar Box. An excellent stability to environmental conditions was noticed with very low degradation during accelerated aging tests up to 1000 h, as detected by FTIR, molecular weight, DSC and weight loss. Furthermore, these polymers formed an excellent protective coating on the stone surface as shown by capillary water absorption test. Finally, as expected, very stable coatings were obtained as shown by aging tests. The stone surface showed negligible changes of color and a good hydrorepellency confirming a good durability of treatments. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43377.

KEYWORDS: biodegradable; coatings; glass transition; polyesters; ring-opening polymerization

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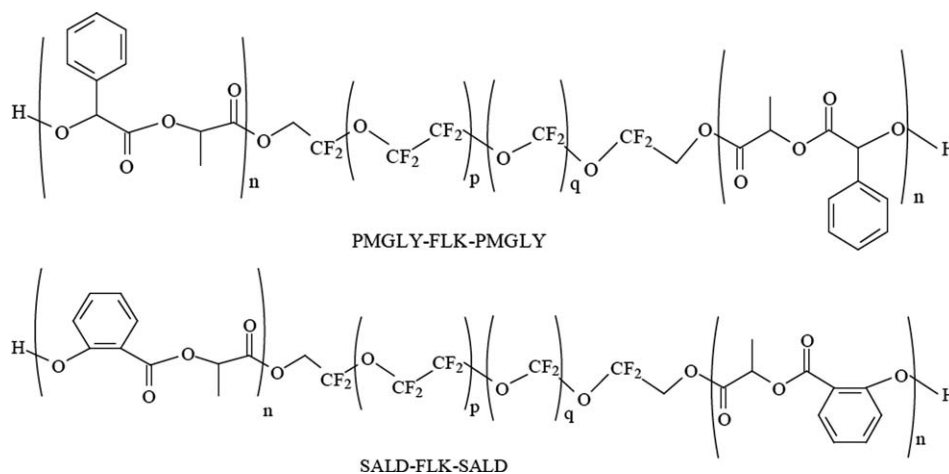
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INTRODUCTION

Perfluoropolyethers (PFPEs) are a well-known class of polymers with special properties, typical of fluorine chemicals, given by the large presence of C-F bonds in the molecule (bond energy = 116 kcal mol⁻¹). In particular, they are characterized by high chemical inertia, solvent and heat resistance, photochemical stability, low glass transition temperatures (about -120 °C), low friction coefficient, high barrier property, and high hydro- and lipo-phobicity, due to a very low surface energy.^{1,2} Thanks to their properties, several applications have been developed, including production of special textiles,^{3,4} flame retardants,⁵ micro and opto-electronics,² organic-inorganic hybrid coatings,⁶⁻⁹ and surface protection of stones.^{10,11} In recent years, PFPEs were employed for the protection of stone surfaces with a special attention to those involving works of historic and artistic interest^{10,11} due to their high hydro- and lypophobicity connected with their stability. It is well known that Cultural Heritage placed in an outdoor environment may undergo to a degradation process due to natural and pollution agents. Water, in fact, plays a central role in chemical, physical, and mechanical degradation of stone.¹² It is involved in the transport of pollutants present in the atmosphere (i.e., CO₂, SO₂, NO_x) inside stones, transport and crystallization of soluble salts, freezing/thaw cycles, and grow of biodeterioration agents (i.e., fungi, lichens).^{13,14} The protection of exposed stones with a hydrophobic polymer is a common practice in the conservation of stone artifacts.

However, PFPEs are extremely nonpolar substances, with very low solubility in common organic solvents, water solutions, and other polymers and consequently their application is a difficult task.

A possible way to overcome this limit has been proposed by joining PFPEs with common polymers, such as polyether, polyamides, polyurethanes, and polyacrylates.¹⁵⁻¹⁸ These materials always showed improved solubility with respect to PFPE and intermediate properties between perfluorinated and neat organic polymers. A new approach to the application of PFPE has been tried through the synthesis of biorenewable materials containing a fluorinated moiety such as polycaprolactone (PCL).^{7,8} In order to minimize the surface energy, PFPE-PCL block polymers were synthesized and applied as gels on stone surfaces showing a reduced wettability and surface segregation with respect to neat PFPEs. Recently, another approach was tried with the development of triblock polymers such as polylactide-perfluoropolyether-polylactide (PLA-PFPE-PLA) as a potential water repellent material for stone protection.¹⁹ These copolymers had a central block of a specific perfluoropolyether [coded as FLK, derived from Fluorolink D10-H (FLK-OH)] and two lateral moieties. These last moieties were made of PLLA (the L-form of the polymer obtained from L-lactide) or PLDA (the racemic form of the polymer obtained from rac-lactide), respectively, coded as PLLA-FLK-PLLA and PLDA-FLK-PLDA. Stone samples treated with these products showed a strong decrease of water uptake by capillarity and coating performances were kept



Scheme 1. Structures of PMGLY-FLK-PMGLY and SALD-FLK-SALD polymers.

after a long photochemical aging cycle. However, the T_g of these polymers was in the range between 25 and 55 °C, potentially causing the loss of the polymer film or the adhesion of particulate on the surface of coated stones. To overcome this problem, the potential employment of high T_g aromatic polyester coatings was tested using lactide/mandelide copolymers,^{20,21} containing a perfluoroalkyl moiety as a chain-end group. These polymers showed a high T_g and a significant increase of the hydrophobicity over conventional PLA showing a broad range of applications.

In this article, a further development of fluorinated PLA-based coatings for stone protection is reported. Triblock polymers were synthesized using the same procedure before reported.^{19–21} The monomers L-lactic acid and rac-lactic acid (rac-LA) were substituted with two different monomers such as salicylic and mandelic acids. Also the perfluoro alcohol was substituted with FLK-OH obtaining two different polymeric structures: (1) poly(lactic/mandelic acid)-FLK-poly(lactic/mandelic acid) (PMGLY-FLK-PMGLY) and (2) poly(lactic/salicylic acid)-FLK-poly(lactic/salicylic acid) (SALD-FLK-SALD) (Scheme 1).

These polymers showed a wide range of application of the coatings with improved UV protection and stability while keeping the T_g and hydrophobicity of the previously reported polymers. The new materials may be less affected by environmental parameters like temperature cycles and adhesion of particulate on the protected surface.

The performance as coating was tested on selected Carrara marble samples and stability in the course of time was verified using accelerated aging tests. Change of molecular weight and FTIR spectra of the polymers was checked in the course of time. Finally, hydrophobicity and chromatic changes of the coating were also checked at the end of the aging cycle.

EXPERIMENTAL

Materials

Reagents: L-lactide (L-LD), (S)-mandelic acid, salicylic acid, triethylamine 99.5%, 2-bromopropionyl bromide, 4-dimethylaminopyridine (DMAP), tin(II)-2-ethylhexanoate (SnOct₂), and anhydrous benzyl alcohol 99.8% were purchased from Aldrich and employed as received. Fluorolink D10-H (FLK-OH) was a commercial perfluoro-

polyether containing two terminal hydroxyl moieties, supplied by Solvay Solexis ($M_w = 1400 \text{ g}\cdot\text{mol}^{-1}$). Solvents: chloroform (CHCl₃), tetrahydrofuran (THF), acetonitrile, ethyl acetate, acetone, *n*-hexane, and deuterated solvents (CDCl₃, DMSO-*d*₆) were purchased from Aldrich and used without any further purifications.

White calcitic Carrara marble, with a total porosity of 0.2%, was employed to test the performances of polymers as stone protective using specimens of $5 \times 5 \times 2 \text{ cm}$.

Instruments

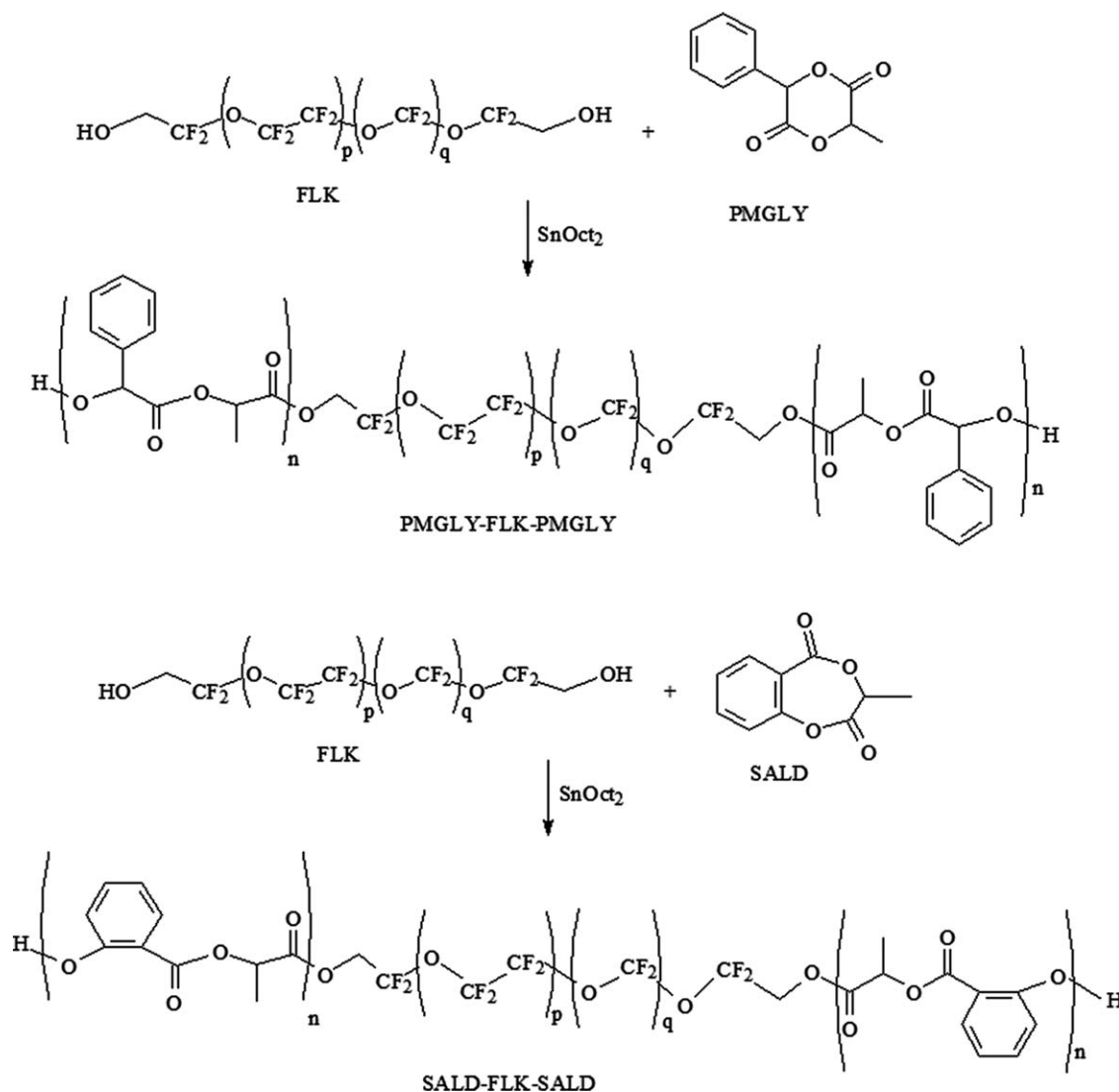
¹H- and ¹⁹F-NMR spectra were collected using a Varian VXR 200 MHz spectrometer, using CDCl₃ or DMSO-*d*₆ as solvents. ¹³C-NMR spectra were obtained using a Mercury 400-MHz spectrometer, using CDCl₃ as solvent. ¹H- and ¹³C-NMR spectra were referenced to TMS as external standard using residual hydrogen of the solvent as internal reference. ¹⁹F-NMR spectra were referenced to CFCl₃ as external standard.

FTIR spectra were recorded with a Shimadzu FTIR spectrometer model IRAffinity-1 in transmission mode on polymer casted on NaCl disks or using a Specac Golden Gate single reflection diamond attenuated total reflectance (ATR) accessory.

GPC data were collected with a Waters system equipped with a pump Waters model Binary HPLC 1525, three columns Shodex KF-803 (length: 300 mm; diameter: 8.0 mm) and a refractive-index detector Waters model 2414, calibrated against polystyrene standards. Analyses were performed on THF solutions (1 mg/mL of polymers) at 35 °C, using THF as eluent, with a flow rate of 1.0 mL/min.

DSC measurements were performed with a Perkin Elmer instrument model Pyris 1 DSC equipped with a Intracooler 2P cryogenic system. Samples were initially heated from 0 to 200 °C under a nitrogen atmosphere at 20 °C/min, cooled to 0 °C, then DSC curves were collected in a second heating run up to 200 °C at 20 °C/min.

Colorimetric measurements were performed on stone samples before and after treatments with the protective products using a KONICA-MINOLTA CM2600d spectrophotometer, following the UNI EN 15886/2010 protocol (CIELAB colour space),²² with the standard illuminant D65 and observer at 10°. Five measurements



Scheme 2. Synthesis of FLK block copolymers PMGLY-FLK-PMGLY, and SALD-FLK-SALD.

were taken by repositioning the instrument on the same spot each time, and data were averaged.

Water vapor diffusivity was checked with a home-made apparatus as reported in a previous article.¹¹

Photochemical aging was run using a Solar Box *CO.FO.ME.GRA* model 3000e equipped with a Xenon-arc lamp and an outdoor type UV filter with cut-off <290 nm. According to the ISO 1134/2004 protocol,²³ irradiance was kept at 550 W/m² and black standard temperature (BST) at 65 ± 2 °C.

PMGLY and SALD Synthesis

Monomers were synthesized following the procedure reported in a previous article,²¹ using L-LD, (S)-mandelic acid, and salicylic acid as starting materials, thus monomers were obtained having the same characteristics of those previously reported.²¹

Polymerizations

The previously reported polymerization procedure²¹ was followed using FLK-OH instead of perfluorooctyl alcohol as chain initiator. In this way PMGLY-FLK-PMGLY and SALD-FLK-

SALD polymers were obtained and their characteristics are reported in Table II.

Polymer Coatings

Stone samples were previously brought to constant weight in a drier and the treatment was applied on one of the wider faces. A CHCl₃ solution of polymer (40 mg) in 2 mL of solvent (20 mg/mL) was casted on a 5 × 5 cm surface of the stone with the aid of a pipette. The solvent was evaporated in laboratory conditions (T 25 °C, RH 60%) overnight up to a constant weight obtaining a uniform coating. Glass slides were washed and dried, then the solution of the polymer was applied and the solvent was allowed to evaporate. Treated samples were kept in a drier until constant weight was reached. NaCl disks were also treated in the same way. Each treatment was applied on three samples and each data was reported as the mean value of these samples.

Protective Efficiency

It was evaluated according to the UNI15801 (2010) method²⁴ by capillary water absorption and calculated as:

Table I. Polymerization Conditions and Characterization of FLK Copolymers

Run	Monomer	FLK/monomer (molar ratio %)	Copolymer code	DP ^a	M_n (g/mol)	M_w (g/mol)	PDI ^b	T_g (°C)	ΔC_p^c (J/g)	Fluorine content (w/w %)	Ref.
1	PMGLY	3.61	PMGLY-FLK-PMGLY	17	11,310	17,180	1.51	62	0.407	13.6	
2	PMGLY	9.63	PMGLY-FLK-PMGLY	12	3166	3888	1.22	58	0.227	40.0	
3	SALD	3.61	SALD-FLK-SALD	9	1417	2520	1.78	51	0.237	13.6	
4	rac-LD	3.61	PLDA-FLK-PLDA	18	10,710	13,790	1.29	32	0.275	13.6	19
5	L-LD	3.61	PLLA-FLK-PLLA	15	6727	8207	1.22	42	0.219	13.6	19
	PMGLY	3.00	PMGLY-F ^d			11,790	1.22	75		3.5	21
	SALD	3.00	SALD-F ^e			3247	1.79	55		3.8	21
	PMGLY	0	PMGLY			20,160	1.49	75		0	21
	SALD	0	SALD			6635	1.71	77		0	21
	L-LD	0	PLLA			62,000	2.0	60		0	21
	Rac-LD	0	PLDA			83,000	2.4	56		0	21

^aDegree of polymerization (referred to the lactone monomer).

^bPolymer dispersion index.

^cSpecific heat capacity variation.

^dChain end perfluorooctyl polymandelic acid.

^eChain end perfluorooctyl polysalicylic acid.

$$PE \% = \frac{(A_{un} - A_t)}{A_{un}} \times 100$$

where A_{un} and A_t are, respectively, the amount of water absorbed by an untreated sample or sample treated with a polymer.

Colorimetric Performances

Chromatic variations of marble samples treated with the products were evaluated according to the CIE- $L^*a^*b^*$ chromatic system. The chromatic differences were defined as

$$\Delta x^* = x_t^* - x_u^*$$

where x_t^* was the colorimetric value (L^* , a^* , or b^*) of the treated sample and x_u^* the colorimetric value of the untreated sample. The ΔE^* value, that is the color change between treated and untreated surfaces, was calculated according to the UNI method²²:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Accelerated Ageing

The stability of the coatings was tested through accelerated artificial aging in a Solar-box up to 1000 h. Three coated stones, several coated glass slides, and treated NaCl disks with selected polymers were aged in the climatic chamber. Every 250 h coatings were analyzed by FTIR-ATR, GPC, DSC, solubility, and weight loss of the irradiated samples. Chromatic changes and PE were measured on stone samples and the mean value of the three tests was reported.

RESULTS AND DISCUSSION

Polymer Synthesis

The synthesis of polyester/FLK block polymers was carried out by ring-opening polymerization (ROP). FLK-OH is an oligomer of a perfluoropolyether bearing two chain-end hydroxyl groups.

Each molecule is able to start the polymerization of two polyester chains (Scheme 2).

The monomers employed in the syntheses were (3S)-6-methyl-3-phenyl-1,4-dioxan-2,5-dione (PMGLY) and 1,4-benzodioxepin-3-methyl-2,5-dione (SALD), both synthesized from natural and commercially available materials. Racemic 3,6-dimethyl-1,4-dioxan-2,5-dione (rac-lactide or rac-LD) was also employed for comparison purposes. Details about the synthesis of these monomers were reported in a previous paper.²² Polymerization were carried out in the melt phase, using the desired amount of FLK initiator (20 or 40% w/w). Catalyst for rac-LD and PMGLY copolymerizations was SnOct₂, whereas DMAP was used for SALD polymerization.

Copolymers had a perfluoropolyether as a central unit and two lactic acid/mandelic acid or lactic acid/salicylic acid moieties as terminal polymeric units. Owing to the choice of the monomers, terminal alternating units of lactic acid/mandelic acid or lactic acid/salicylic acid in a 1:1 ratio was obtained.

The main results of polymerizations are reported in Table I.

Polymer Characterization

Multinuclear NMR. The linkage between FLK and polyester chains was detected by NMR spectroscopy. ¹³C-NMR spectra showed new signals in the region 100–130 ppm, in addition to those relative to polyester chains, and they were attributed to FLK moieties in the polymer (marked as “f” in Figure 1). ¹⁹F-NMR (Figure 2) confirmed the formation of a block polymer. The spectra were similar to the FLK-OH precursor, but the signals of CF₂-CH₂-OH terminal groups at –82.4 and –84.9 ppm were shifted toward lower fields at –77.7 and –79.7 ppm (marked as “b” and “c” in Figure 2) due to the formation of the ester linkages CF₂-CH₂-OOC-R. In agreement with this interpretation, the shift was the same for PMGLY and SALD polymers. Also the ¹H-NMR spectrum (here not reported) showed a shift of the 3.9 ppm signal of

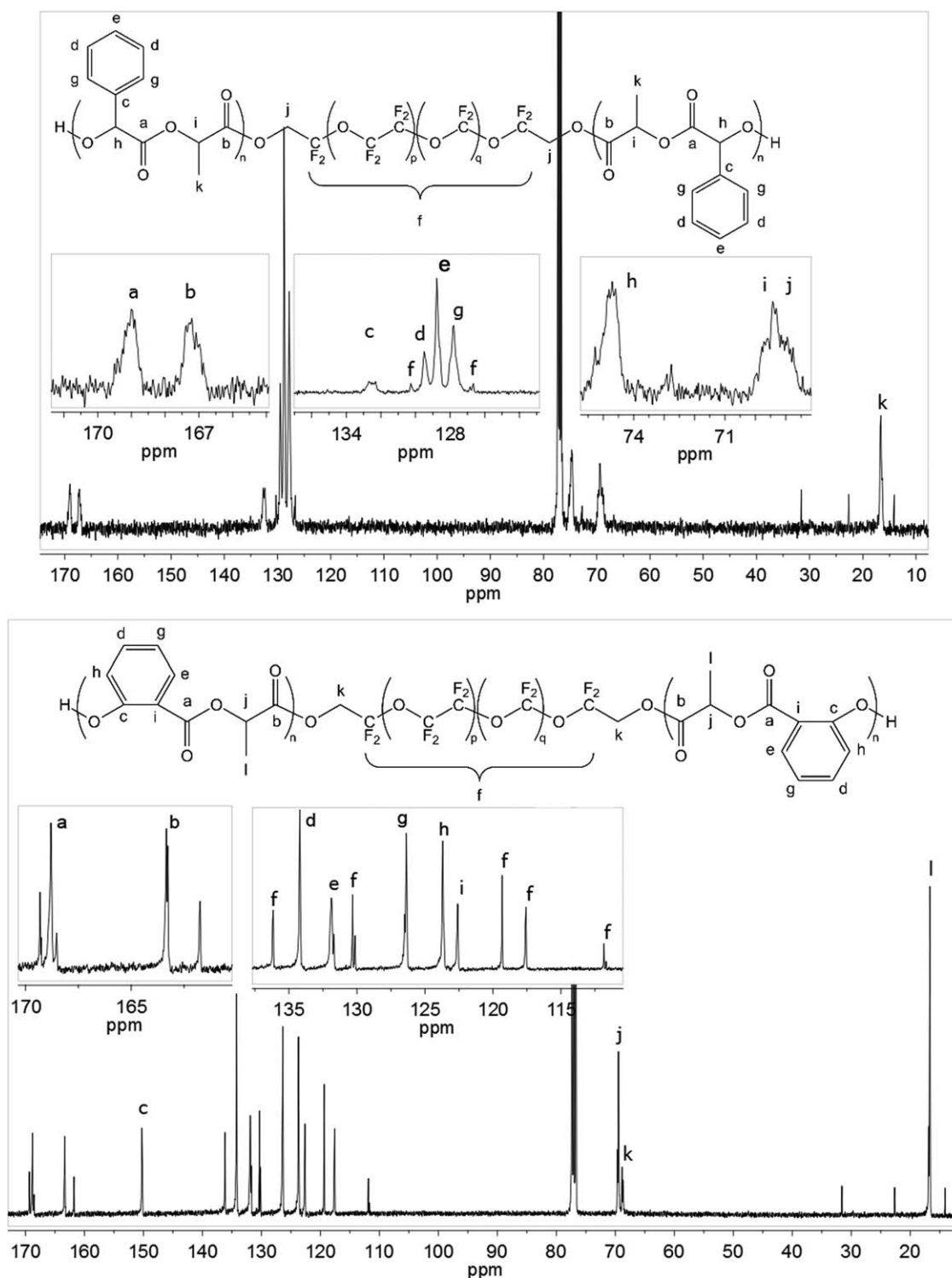


Figure 1. ¹³C-NMR spectra of PMGLY-FLK-PMGLY (top) and SALD-FLK-SALD (bottom).

CF₂CH₂-OH terminal groups of FLK-OH. The new signal was present at 4.6 ppm due to the formation of the ester bond. These shifts were analogous to those of PLDA-FLK-PLDA reported in a previous article¹⁹ and the spectra collected were in agreement with those previously reported on the synthesis of PLA/PFPEs copolymers.^{19,25} These data confirmed the bonds between lactic acid and FLK moieties of the polymer.

FTIR. The FTIR spectra of polymers are reported in Figure 3. The main absorptions were attributed on the basis of data reported in the literature.^{26,27}

The spectrum of PMGLY-FLK-PMGLY showed the following bands: 3582 (w, O-H stretching), 3066 and 3033 (w, symmetric and asymmetric aromatic C-H stretching), 2999 and 2943 (m, symmetric and asymmetric aliphatic C-H stretching), 1754 (s,

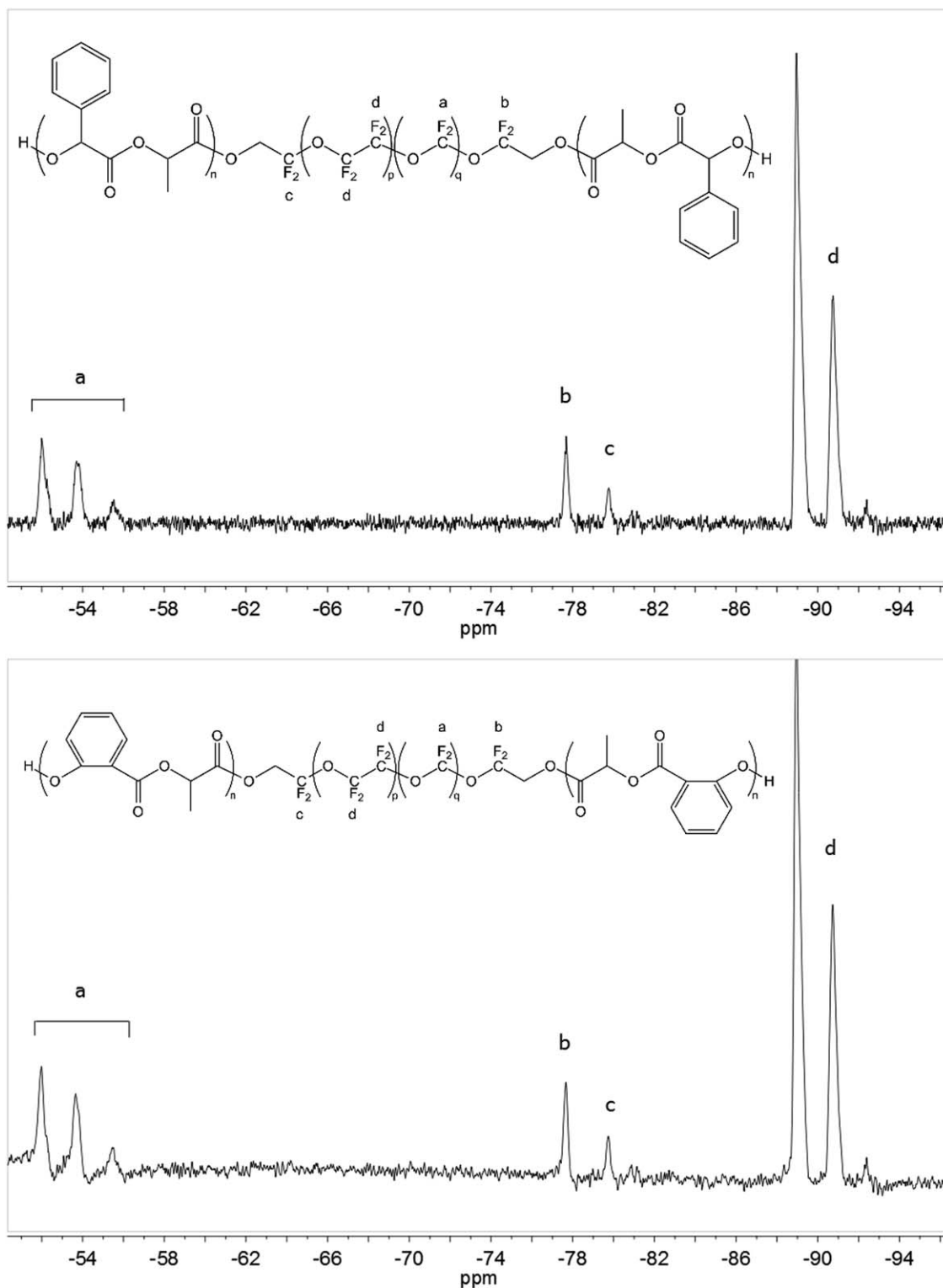


Figure 2. ^{19}F -NMR spectra of PMGLY-FLK-PMGLY (top) and SALD-FLK-SALD (bottom).

C=O stretching), 1497 (w, aromatic C=C stretching), 1453 (m, CH_3 bending), 1384 and 1363 (m, symmetric and asymmetric C-H bending), 1290–990 (s, C-H bending, C-F stretching and C-O stretching), 1201 and 1127 (s, C-O stretching and C-O-C asymmetric bending), 875 (w, amorphous phase of PLA), 749 (m, C=O bending), and 697 (s, C-H bending) cm^{-1} .

The spectrum SALD-FLK-SALD showed the following bands: 3581 (w, O-H stretching), 3115 and 3046 (w, symmetric and asymmetric aromatic C-H stretching), 2960 and 2947 (m, symmetric and asymmetric aliphatic C-H stretching), 1774 (s, C=O stretching of lactic acid moiety), 1726 (s, C=O stretching of salicylic acid moiety), 1676, 1611, 1583, 1485 (s, aromatic C=C

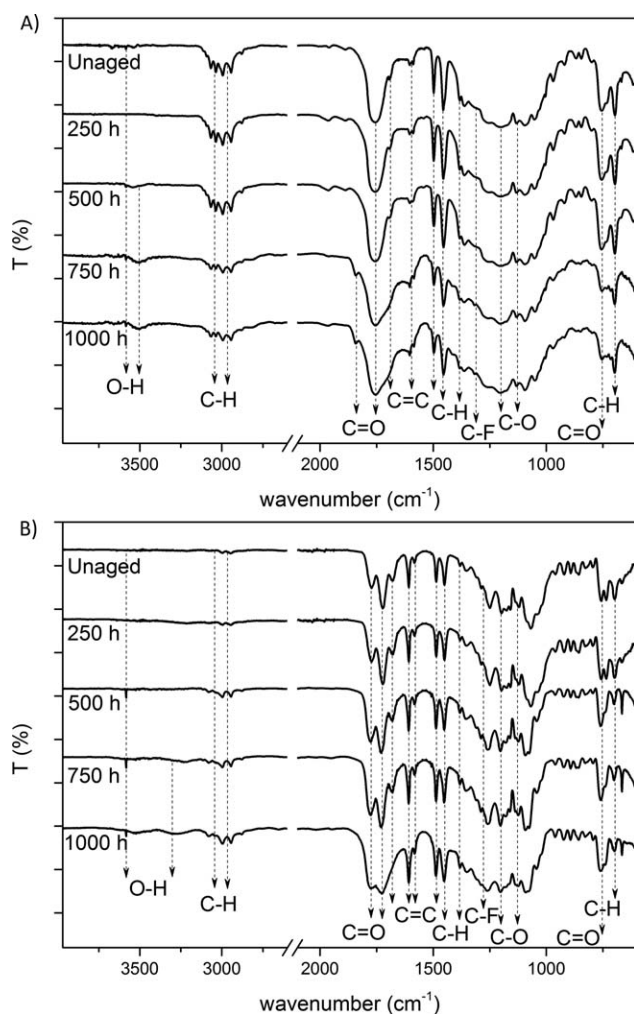


Figure 3. FTIR spectra of polymers after different steps of the artificial aging process: (A) PMGLY-FLK-PMGLY and (B) SALD-FLK-SALD.

stretching), 1453 (m, CH₃ bending), 1384 and 1360 (m, symmetric and asymmetric C-H bending), 1330–970 (s, C-H bending, C-F stretching and C-O stretching), 1201 and 1023 (s, C-O stretching and C-O-C asymmetric bending), 859 (w, amorphous phase of PLA), 758 and 733 (m, C=O bending), and 697 (w, C-H bending) cm⁻¹.

Thermal Properties. The random configuration of the carbon atoms in the monomers led to amorphous materials lacking of any crystalline domain. The polymers showed only a T_g from glassy to amorphous state^{28,29} and no crystallization (T_c) or melting temperature (T_m) (Table I), and this behavior was already observed in a previous work using PMGLY and SALD monomers.²¹

The glass transition temperatures (T_g) of PMGLY-FLK-PMGLY and SALD-FLK-SALD were higher than that one of PLDA-FLK-PLDA. These results were expected since aromatic groups improve the stiffness of the polymer chains, increasing the energy required for chain rotation. An important fraction of the polymer (20–40% w/w) was constituted by amorphous, low T_g FLK moiety with high chain mobility. However, the increment was remarkable if compared to amorphous PLA: the T_g of

PMGLY-FLK-PMGLY (61.5 °C) was 29.3 °C higher than PLDA-FLK-PLDA (32.2 °C) with very close molecular weight.

Assessment of Polymers as Protective Coating of Stone

Two selected FLK block polymers (PMGLY-FLK-PMGLY and SALD-FLK-SALD) were applied as a protective coating on marble surfaces and their characteristics are reported in Table II (runs 1 and 3) together with those of closely related polymers. Fluorine content was calculated as weight percentage on total weight product.

The stone specimens selected were obtained from a white calcitic marble with very low porosity ideal to study the behavior of these products as surface coating. The substrate allowed only a low penetration of the polymer solutions and a rapid evaporation of solvent. The polymers remained almost entirely on the surface, so polymer migration and diffusion in the bulk of samples were limited. Furthermore, the white color allowed an easy detection of chromatic variations. Some coatings were also placed on glass slides to evaluate the behavior of the polymers during accelerated aging tests and on NaCl disk to collect transmission FTIR spectra.

Polymers were applied on the surfaces by solution casting, following the same procedure used in previous works.²² Polymer solutions in THF or CHCl₃ were used without any significant differences on the final coatings. Polymer coatings placed on stone surfaces were used to evaluate the performance as stone protective; polymer coatings on glass slides or NaCl windows were used for the characterization of films through optical microscopy, FTIR, ¹H-NMR, GPC, and DSC. Optical microscopy was also used to check the formation of uniform crack-free coatings.

Protective Efficiency. The protective efficiency (PE %) of the coating applied on marble surfaces, defined as reported in the experimental part, and after 1000 h of the aging process, is reported in Table III. Initial values of PE % of PMGLY-FLK-PMGLY and SALD-FLK-SALD were higher than plain PLA, PMGLY, and SALD and were comparable with data previously reported for a FLK block polymer and chain-end fluorinated polymers.

Water Vapor Diffusivity. Residual water vapor diffusivity of marble coated with PMGLY-FLK-PMGLY or SALD-FLK-SALD was 50% with respect to untreated sample. These values were very close to those of PLLA-FLK-PLLA used as reference and that of chain-end perfluorooctyl polymandelic acid (PMGLY-F) previously reported.²¹

Chromatic Variations. Chromatic variations between coated and uncoated marble samples were checked with a colorimeter and reported in Figure 5. The treatment initially caused a decrease of the lightness of the surface (L^*) for the two coatings. The variation was respectively $\Delta L^* = 2.80$ and $\Delta L^* = 1.23$ for PMGLY-FLK-PMGLY and SALD-FLK-SALD, respectively. An analogous behavior was already reported for other chain-end perfluorooctyl PLA³⁰ and PLA-FLK-PLA block polymers.¹⁹

Stability of Coatings

The stability of the polymer coatings placed on the surfaces of stone specimens was tested after accelerated artificial aging, up to 1000 h. Polymer coatings on glass slides and NaCl windows

Table II. Physicochemical Characteristics of PMGLY-FLK-PMGLY and SALD-FLK-SALD and Analogous Polymers During the Accelerated Ageing Process

Polymer	Ageing time (h)	Weight loss (%)	M_n (g/mol)	M_w (g/mol)	PDI ^a	(°C)	ΔC_p^b (J/g)	Ref.
PMGLY-FLK-PMGLY	0	–	11,310	17,180	1.51	57.5	0.227	
PMGLY-FLK-PMGLY	250	0	10,410	14,530	1.40	51.8	0.207	
PMGLY-FLK-PMGLY	500	0	8689	14,800	1.70	49.5	0.672	
PMGLY-FLK-PMGLY	750	0.5	10,580	15,890	1.50	50.8	0.320	
PMGLY-FLK-PMGLY	1000	0.9	10,830	16,230	1.50	50.1	0.422	
SALD-FLK-SALD	0	–	1417	2520	1.78	51.1	0.237	
SALD-FLK-SALD	250	0	1343	2367	1.76	51.2	0.232	
SALD-FLK-SALD	500	0.3	1000	2101	2.10	43.7	0.207	
SALD-FLK-SALD	750	0.6	1086	2376	2.19	45.1	0.629	
SALD-FLK-SALD	1000	1.2	1082	2568	2.38	37.4	0.479	
PLLA-FLK-PLLA	1000							19
PLDA-FLK-PLDA	1000							19
PMGLY-F	0	–	9665	11,790	1.22	74.7	0.461	21
PMGLY-F	1000	2.0	4925	8565	1.74	66.6	0.516	21
SALD-F	0	–	1819	3247	1.79	54.9	0.643	21
SALD-F	1000	1.0	1697	3261	1.92	38.0	0.658	21
PMGLY	0	–	13,540	20,160	1.49	75.0	0.419	21
PMGLY	1000	5.1	607	2377	3.91	40.4	0.353	21
SALD	0	–	3886	6635	1.71	76.8	0.704	21
SALD	1000	4.5	2424	4974	2.05	71.1	0.428	21

^aPolymer dispersion index.^bSpecific heat capacity variation.

were used to study the polymer stability when exposed to environmental conditions (coating were checked by optical microscopy, FTIR-ATR, ¹H-NMR, GPC, DSC, weight loss).

FTIR-ATR Spectra. The spectra of polymers after several aging cycles are reported in Figure 3. Changes were very small indicating a high stability of the coating tested. The following variations were observed:

PMGLY-FLK-PMGLY (a) formation of a very weak broad absorption band centered at 3500 cm⁻¹; (b) a slight broadening and weakening of the carbonyl absorption bands (1770–1720 and 750 cm⁻¹) and formation of a shoulder at 1840 cm⁻¹; (c) a slight decrease of the intensity and broadening of absorptions in the fingerprint region. The broad absorption at 3500 cm⁻¹ may be attributed to formation of –OH and –COOH end groups and to the subsequent oxidation of –OH to –COOH groups. The band at 1840 cm⁻¹ may be attributed to the stretching of anhydrides formed by photochemical oxidation. Other changes were the slight broadening and weakening of the absorptions already present.

SALD-FLK-SALD (a) formation of a very weak broad absorption band centered at 3500 cm⁻¹ and another band at 3250 cm⁻¹; (b) a slight broadening and weakening of the carbonyl absorption bands (1770–1720 and 750 cm⁻¹); (c) a slight broadening of absorptions in the fingerprint region. The broad absorption at 3500 and 3250 cm⁻¹ may be attributed, as above reported, to depolymerization through chain scission processes with formation of –OH and –COOH end groups and to the subsequent oxidation of –OH to

–COOH groups. Another interpretation may be the oxidation of –OH groups with formation of hydroperoxidic intermediates. Beside these reactions, other changes were the very slight broadening and weakening of the absorptions already present.

Molecular Weight. Molecular weights of aged polymers are reported in Table II together with data of close related polymers. Mean molecular weights M_n and M_w remained almost constant during the aging process for PMGLY-FLK-PMGLY, whereas a slight decrease of M_n for SALD-FLK-SALD was observed, leading to a partial increase of the polydispersion index (PDI). Initial molecular weight of the SALD-FLK-SALD was lower than that of

Table III. Protective Efficacy (PE %) of Several Coatings before and after an Ageing Time of 1000 h

Treatment	PE % Unaged	PE % 1000 h	Ref
PMGLY-FLK-PMGLY	96	89	
SALD-FLK-SALD	91	84	
PMGLY-F	94	83	21
SALD-F	85	80	21
PLLA-FLK-PLLA	97	85	19
PLDA-FLK-PLDA	84	55	19
PMGLY	67	23	21
SALD	60	19	21
PLLA	53	37	19

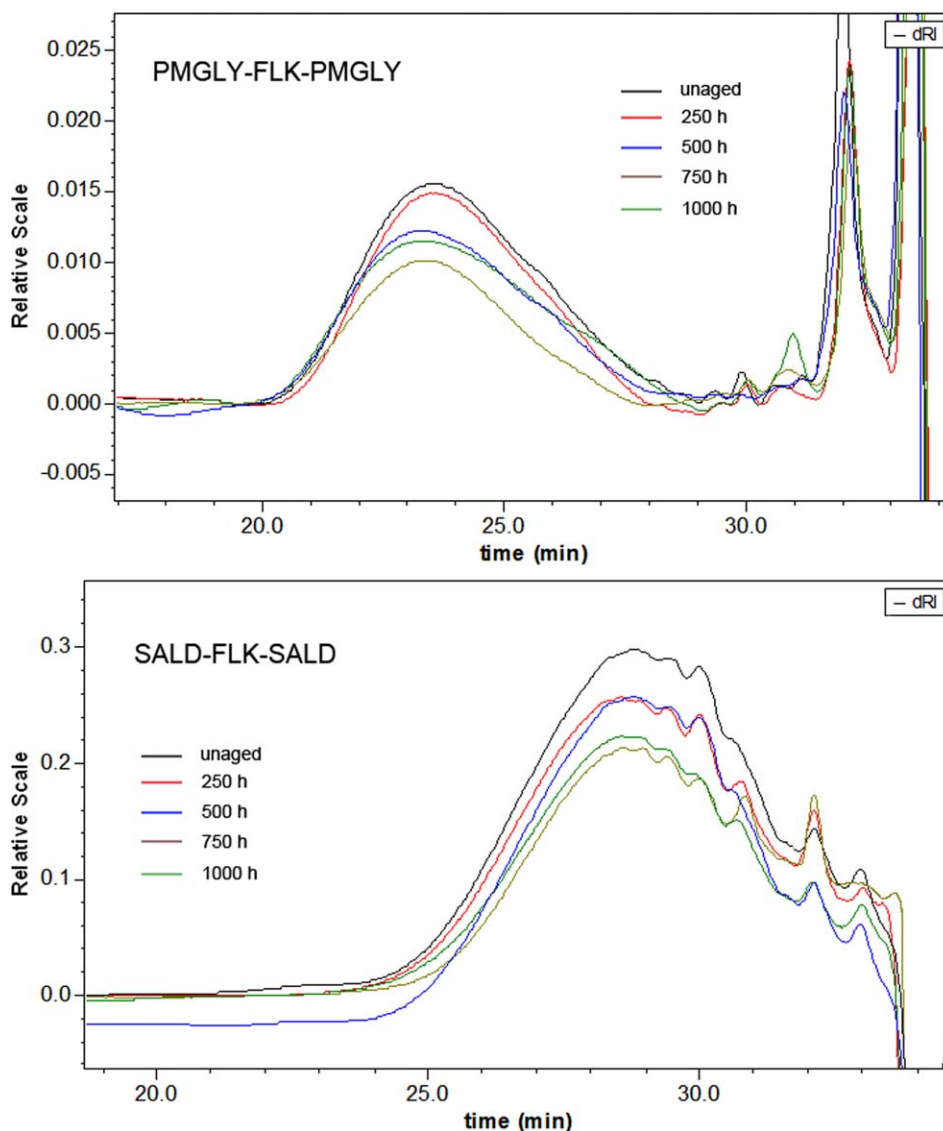


Figure 4. GPC chromatograms of PMGLY-FLK-PMGLY (top) and SALD-FLK-SALD (bottom) unaged and at different steps of the artificial aging process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PMGLY-FLK-PMGLY; hence, in this case, a comparable decrease of M_n caused a higher increase of PDI. It should also be noted that such small variations of M_n and M_w are hardly detected by instrument. This behavior is in agreement with the higher stability showed by other, previously reported, fluorinated polymers particularly for those containing a FLK moiety.¹⁹

Fluorine containing block polymers showed a remarkable higher stability than the corresponding homopolymers without fluorine atoms.

This behavior is confirmed by the GPC chromatograms reported in Figure 4, the shape of the curves and molecular weight distributions are essentially unchanged for the two samples during the artificial aging process.

Thermal Properties. A low decrease of T_g values (Table II) was showed in the course of the aging process and this behavior may be attributed to the partial oxidation of the polyester chains, as above reported analyzing the FTIR spectra. The decrease was

lower for PMGLY-FLK-PMGLY (7.4 °C) than SALD-FLK-SALD (13.7 °C). These differences may be attributed to the lower molecular weight of the starting SALD-FLK-SALD polymer, as already discussed for molecular weight variations. On the contrary, nonfluorinated polymers showed a higher T_g variation.¹⁸

Specific heat capacity (ΔC_p) values did not show any particular variation in the course of the aging process.

Weight Loss and Solubility. Weight loss of new samples and close related polymers during artificial aging are reported in Table II. The weight loss of the new polymers was very low, and close to experimental errors, in line with the low degradation observed through the other techniques. Furthermore, these polymers remained completely soluble after all aging tests, in agreement with a lack of crosslinking process in the course of the aging process.

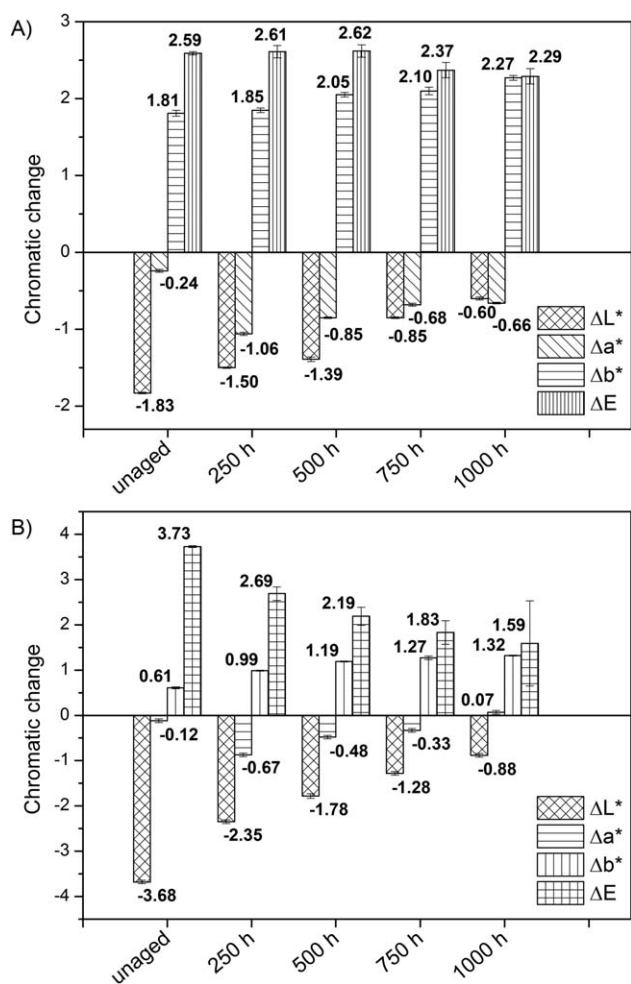


Figure 5. Chromatic variations of coated marble samples after different aging times (error bars representing standard deviations): (A) PMGLY-FLK-PMGLY and (B) SALD-FLK-SALD.

Chromatic Variations. Chromatic variations of coated marble samples at different steps of the artificial aging were checked with a colorimeter and reported in Figure 5. The lightness of the surface (L^*) was initially decreased due to the application of the two coatings, however, in the course of the aging process, returned toward the initial color of marble. The increase was, respectively, $\Delta L^* = 2.80$ and $\Delta L^* = 1.23$ for PMGLY-FLK-PMGLY and SALD-FLK-SALD, respectively. This behavior was already reported for other fluorinated PLA³¹ and PLA-FLK-PLA block polymers¹⁹ and was attributed to a rearrangement of the film at the polymer-air interface as a result of the exposition at a temperature over its T_g , 65 °C according to ISO 11341/2004 protocol.²³ A slight yellowing (b^*) of the samples was also shown in the course of the aging process, attributable to a partial oxidation of polyester chains, as showed by FTIR spectra. The increase of b^* values was $\Delta b^* = 0.71$ for PMGLY-FLK-PMGLY and $\Delta b^* = 0.46$ for SALD-FLK-SALD.

The two samples showed limited chromatic variations after 1000 h of exposition to photo-oxidative weathering conditions. The yellowing was coupled with an increase of the lightness towards the initial value, causing a decrease of the total color

variation (ΔE^*). The colorimetric changes were always lower than $\Delta E^* 3$, established as the limit of the human eye perception and commonly accepted as the limit of imperceptible changes.

Protective Efficiency. The PE % of the coating applied on marble surfaces, after 1000 h of artificial aging, is reported in Table III together with the data for close related polymers. As expected there was a slight decrease of the PE % in the course of the aging process for both coatings. After 1000 h PE % was lowered by 7% from the initial values, and this reduction may be attributed to a partial loss of protective film. A penetration inside the material and/or formation of hydrophilic species on the surface in the course of the aging process can't be completely excluded. The loss of PE % however was lower than that previously reported for similar products in the same conditions (−12% for PLLA-FLK-PLLA and −29% for PLDA-FLK-PLDA,¹⁹ respectively). This behavior happened in spite of the presence of chromophores as side groups or in the main chain, enhancing the absorption of radiations. The higher stability of the new coatings with respect to PLLA-FLK-PLLA and PLDA-FLK-PLDA may be due to their higher T_g , making more difficult some oxidation processes (in this case, the propagation of radicals) in a “frozen” glassy structure.

CONCLUSIONS

Triblock polymers containing a central perfluoropolyether (FLK) moiety and two chain-end group poly(PMGLY) or poly(SALD) were synthesized, characterized and tested as coatings for the protection of stone. These products were structurally similar to PLDA-FLK-PLDA and PLLA-FLK-PLLA, two products previously reported¹⁹ as potential stone coatings. Three main effects may be ascribed to the presence of phenyl groups: (1) an increase of T_g , as a consequence of the higher stiffness of polyester chains, (2) the formation of a completely amorphous material, as opposed to partially crystalline PLA, and (3) an increase of light absorption and UV-barrier properties due to the aromatic groups.

The higher T_g of these products if correlated to PLDA-FLK-PLDA expands the range of application of these polymers as surface coating of stone, especially if exposed to an outdoor environment. This higher T_g reduces the amount of particulate stuck on the surface and decreases the volume variations due to temperature cycles,³¹ but are not so high to cause an easy cracking of the coating in the course of the aging process.

The new polymers, when compared to previously reported coatings, showed a slightly higher stability to photo-oxidative conditions, even with a higher level of absorption of radiations due to the presence of chromophores in the structure. The coating performances of these polymers were slightly better than PMGLY-F and SALD-F polymers previously reported.

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