

High glass transition temperature polyester coatings for the protection of stones

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ABSTRACT: Copolymers of lactic acid with mandelic or salicylic acid were synthesized through ring-opening polymerization (ROP) and tested as protective coatings for stones. Most notably, glass transition temperature (T_g), hydrophobicity, and UV barrier properties were increased, making these materials more suitable as protective coating for outdoor stones than poly(lactic acid). A T_g of 76°C was obtained for the alternating copolymer lactic acid/mandelic acid and it was considerably higher than the one of poly(lactic acid) with similar molecular weight (50–55°C). Furthermore, the introduction of a perfluorinated moiety as chain-end group, using a perfluoro alcohol as initiator of the ROP process, allowed to increase the hydrophobicity and stability of the new coatings. These polymers showed a good protective efficiency when applied on marble stones and preliminary stability tests under solar light showed low degradation, good stability to photo-oxidative conditions, and negligible color changes after an aging time of 1000 h. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42323.

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INTRODUCTION

In the past decades, synthetic polymers have been widely employed for the protection of stone artifacts, and polyacrylates, polysiloxanes, and synthetic waxes were the most used as protective coatings in Cultural Heritage.¹ However, these polymers were chosen among a plethora of commercially available products, and often they did not meet the requirements for application on historical and artistic artifacts (e.g., minimum alteration, high durability, and reversibility of the treatment).¹

The glass transition temperature (T_g) is an important property for protective coatings, especially when goods are exposed to an outdoor environment. It is a second-order transition, where a material changes from a rigid “glassy” to a softer “rubbery” state. A high and controlled T_g , far away from room temperature as reported by Schilling,² is an important characteristic for a polymeric coating, avoiding its permanence in a sticky-gummy state, so it is less influenced by aging processes induced by temperature cycles. In Table I, the T_g of some of the most used polymers for protective coatings are reported. Polymers will generally be quite tacky if the ambient temperature conditions are far above their T_g . These polymers may be better suited as pressure-sensitive adhesives since they remain tacky

under normal working conditions. They would be unsuitable for coating materials because they would attract dust and other particulates. However, a very strong increase of T_g may lead to a decrease of the protection due to breaking of the film caused by mechanical stress.

Recently some of us, following the principles of the green chemistry, developed a new class of polymers for conservation from renewable feedstock. Modified poly(lactic acid) (PLA) were synthesized, characterized, and tested for the protection of stone surfaces with a special attention to those of important historic and/or artistic objects.^{3,4} Hydrorepellence of the protective was improved through copolymerization with a perfluoroalkyl moiety. Good results were obtained either with a block copolymer containing PLA and perfluoropolyether (FLK) moieties (PLA–FLK–PLA)⁵ or with a chain-end perfluoroalkyl-functionalized PLA (PLA-F).⁶ However, the T_g of these copolymers ranged from 25 to 55°C, depending on the degree of crystallinity and molecular weight. Low T_g may cause the loss of the polymer film or the adhesion of atmospheric particulates on the surface of treated stones. Efforts to increase the T_g of PLA by cross-linking have led only to modest improvements.^{7,8}

Additional Supporting Information may be found in the online version of this article.

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Table I. Glass Transition Temperature (T_g) of Some Polymers Employed as Stone Coatings

Polymer	Code	T_g (°C)	Reference
Polyacrylate	Paraloid B-72	40	9
Polyacrylate	Paraloid B-44	60	9
Polyolefin	Cosmoloid H80	<0	1
Polysiloxane	Poly(dimethylsiloxane)	Liquid	1
Perfluoropolyether	Fomblin YR	Liquid	10
Poly(lactic acid)	PLA	55	3
Poly(lactic acid)/perfluoropolyether	PLA-FLK-PLA	40-50	5
Modified poly(lactic acid)	PLA-F	28-44	6

It is well known that replacing methyl with bulky aromatic rings as side groups increases the stiffness of the polymer chains and may significantly increase the T_g , as reported for polystyrene (PS) and poly(ethylene terephthalate) (PET). Following this approach, mandelic acid (2-hydroxyphenylacetic acid) and salicylic acid (2-hydroxybenzoic acid) may be tested as valuable products for the synthesis of copolymers with a high T_g , while preserving the availability from a natural source. The structures of poly(mandelide) and poly(salicylide) are reported in Scheme 1.

Although some early papers were reported on the syntheses of these polymers,^{11–16} a high-molecular-weight poly(mandelide) was obtained for the first time by Liu *et al.*¹⁷ These authors polymerized mandelide (the cyclic dimeric ester of mandelic acid) using a ring-opening polymerization (ROP) process and the polymer showed a T_g of 100°C. Poly(mandelide) shared several physical properties with poly(styrene); however, this polymer was obtained from renewable resources. Copolymers between lactic acid and mandelic acid having a low molecular weight were synthesized and suggested for biomedical applications in several papers.^{18–23}

Salicylic acid is another monomer available from natural sources and used for the synthesis of polymers for biomedical applications, such as drug release systems, surgical sutures, and implants for bone fixation.^{24–27} The ROP of salicylide (the cyclic dimeric ester of salicylic acid) was initially patented by Shalaby *et al.*²⁸ and more recently by Baker *et al.*²⁹ using 1,4-benzodioxepin-2,5-dione or its methyl-substituted analog 1,4-benzodioxepin-3-methyl-2,5-dione. These polymers showed properties very similar to aromatic polyesters PET and poly(butylene terephthalate) (PBT) such as thermal stability, chemical and mechanical resistance, and low gas permeability in

combination with the higher degradability of aliphatic polyesters with respect to PET and PBT when placed in appropriate conditions.

In this study, the monomers (3S)-6-methyl-3-phenyl-1,4-dioxan-2,5-dione (phenylmethylglycolide, (PMGLY)) and 1,4-benzodioxepin-3-methyl-2,5-dione (salicyl-lactide, (SALD)) were synthesized and then polymerized through an ROP process, obtaining a material having a T_g higher than PLA. Furthermore, copolymers containing a perfluoroalkyl segment were synthesized using a perfluoro alcohol as chain initiator to improve the hydrorepellency of the material. Finally, these polymers were checked as stone protectives together with tests on the stability of the new coatings.

EXPERIMENTAL

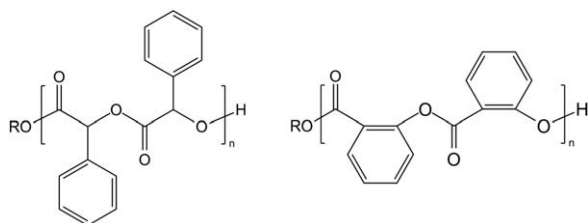
Materials

Reagents: L-lactide (L-LD), (S)-mandelic acid, salicylic acid, triethylamine 99.5% (TEA), 2-bromopropionyl bromide, 4-dimethylaminopyridine (DMAP), tin(II) 2-ethylhexanoate (SnOct₂), and anhydrous benzyl alcohol 99.8% were purchased from Aldrich and employed without any treatment. 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (PFOct) was purchased from Fluka. Solvents such as chloroform (CHCl₃), tetrahydrofuran (THF), acetonitrile (MeCN), ethyl acetate (EtOAc), acetone, *n*-hexane, and deuterated solvents (CDCl₃, DMSO-d₆) were purchased from Aldrich and used without any further purifications.

A calcitic white marble coming from residues of a quarry in the Carrara basin was used as reference stone. It was selected from an ancient front of Gioia quarry (Carrara), a block probably extracted in the Roman age. This lithotype was characterized by a total open porosity of 2.8% and a water accessible porosity of 1.1%. Stone samples were prepared with the dimension of 5 × 5 × 2 cm.

Instruments

¹H- and ¹⁹F-NMR spectra were collected using a Varian VXR 200 MHz spectrometer, using CDCl₃ or DMSO-d₆ 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.

**Scheme 1.** Structures of poly(mandelide) and poly(salicylide).

FT-IR spectra were recorded with a Shimadzu FT-IR 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 instruments model Pyris 1 DSC equipped with an 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 color space),³⁰ with the standard illuminant D65 and observer at 10°. Five measurements 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.³¹

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,³² irradiance was kept at 550 W/m² and black standard temperature (BST) at 65 ± 2°C.

PMGLY Synthesis

In a 100 mL three-neck flask, (S)-mandelic acid (8.0 g, 52.6 mmol), TEA (8.4 mL, 60.7 mmol), and MeCN (90 mL) were introduced and stirred for 20 min. The flask was cooled in an ice bath and purged several times with nitrogen, and then a mixture of 2-bromopropionyl bromide (6.1 mL, 58.1 mmol) and MeCN (10 mL) was slowly added drop-wise to the solution under mechanical stirring in about 30 min and the solution stirred for 30 min at room temperature. The white solid was removed by filtration and the solution evaporated to obtain the crude linear Br-ester. ¹H-NMR (S,S) (2-((2-bromopropanoyl)oxy)-2-phenylacetic acid) (CDCl₃): δ 7.82 (1H, m) 7.60–7.30 (5H, m), 5.97 (1H, s), 4.56–4.44 (1H, q, *J* = 6.9 Hz), 1.89 (3H, d, *J* = 6.9 Hz). ¹H-NMR (S,R) (2-((2-bromopropanoyl)oxy)-2-phenylacetic acid) (CDCl₃): δ 7.82 (1H, m) 7.60–7.30 (5H, m), 5.98 (1H, s), 4.56–4.44 (1H, q, *J* = 6.9 Hz), 1.83 (3H, d, *J* = 6.9 Hz). Elemental analysis for C₁₁H₁₁BrO₄ (%) calcd.: C, 54.59; H, 0.05. Found: C, 54.65; H, 0.08.

The viscous liquid was mixed with 1000 mL of acetone and 20.0 g of NaHCO₃ and refluxed overnight under mechanical stirring. The solid was removed by filtration, and then acetone solution was evaporated to dryness. The residue was dissolved in ethyl acetate, washed with HCl 2M (1 × 10 mL), H₂O (1 ×

20 mL), and brine (3 × 20 mL), and then dried over MgSO₄. Ethyl acetate was evaporated to give 8.0 g of the rac/meso mixture. The crude product was purified by column chromatography (SiO₂, *n*-hexane/EtOAc, 5 : 1). ¹H-NMR (CDCl₃): δ 7.60–7.35 (5H, m), 5.95 (1H, s), 5.20 (1H, q, *J* = 6.9 Hz), 1.67 (3H, d, *J* = 6.9 Hz). ¹³C-NMR (CDCl₃): δ 168.98, 167.21, 137.03, 129.97, 128.97, 127.37, 74.72, 72.84, 16.56. Elemental analysis for C₁₁H₁₀O₄ (%) calcd.: C, 64.07; H, 4.89. Found: C, 64.05; H, 4.91. *T*_m: 138.0–138.5°C.

SALD Synthesis

The same procedure of the section “PMGLY Synthesis” was followed starting from salicylic acid (7.5 g, 54.2 mmol) and obtaining the intermediate linear Br-ester (2-((2-bromopropanoyl)oxy)benzoic acid). ¹H-NMR (CDCl₃): δ 8.16 (1H, m) 7.71 (1H, m), 7.45 (1H, m), 7.24 (1H, m), 4.73 (1H, q, *J* = 6.6 Hz), 3.24 (1H, m), 2.04 (3H, d, *J* = 6.6 Hz). Elemental analysis for C₁₀H₉BrO₄ (%) calcd.: C, 57.14; H, 4.76. Found: C, 57.54; H, 4.62.

In the subsequent step, following the procedure reported in the section “PMGLY Synthesis”, the crude SALD was obtained and purified by column chromatography (SiO₂, hexane–EtOAc, 5 : 1). ¹H-NMR (CDCl₃): δ 7.95 (1H, m) 7.68 (1H, m), 7.41 (1H, m), 7.25 (1H, m), 4.94 (1H, q, *J* = 6.6 Hz), 1.67 (3H, d, *J* = 6.6 Hz). ¹³C-NMR (CDCl₃): δ 168.81, 163.32, 150.29, 134.25, 131.94, 126.40, 123.72, 119.35, 69.55, 16.67. Elemental analysis for C₁₀H₈O₄ (%) calcd.: C, 62.50; H, 4.20. Found: C, 62.16; H, 4.05. *T*_m: 128.3–129.0°C.

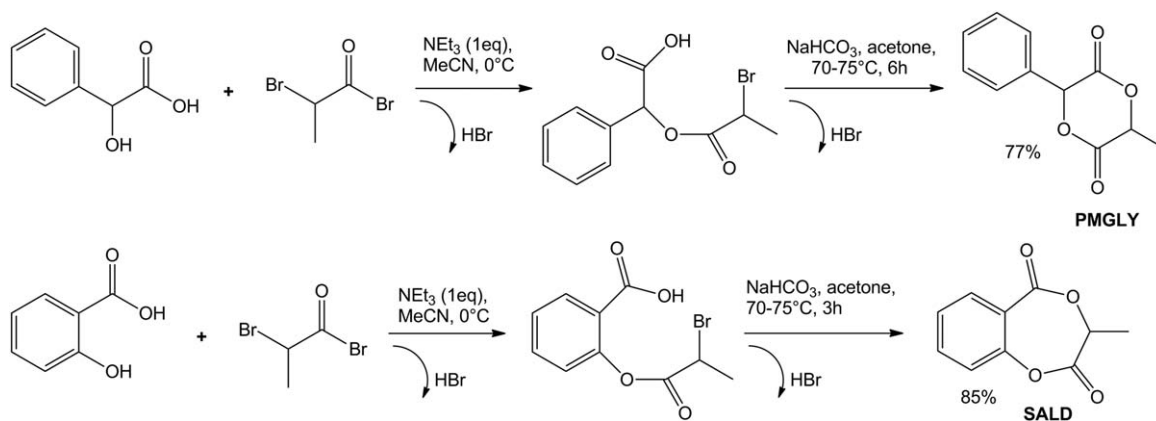
PMGLY or SALD Bulk Polymerization

In a nitrogen atmosphere, PMGLY (0.50 g, 2.4 mmol, previously dried overnight at 40°C under reduced pressure) or SALD (0.50 g, 2.6 mmol) was introduced in a dried Schlenk tube. 0.5 mol % of SnOct₂ or 0.5 mol % of DMAP for SALD and an amount between 0.5 and 10.0 mol % of the desired initiator (benzyl alcohol or PFOct) were added. The Schlenk tube was purged several times with nitrogen and then heated at 140°C under mechanical stirring. After 24 h for PMGLY, or 3 h for SALD, the reactor was cooled down to room temperature and the mixture was dissolved in CHCl₃. The crude polymer was purified 2 times by dissolution in CHCl₃ followed by precipitation through addition of *n*-hexane and finally dried at reduced pressure overnight.

Polymer Coatings

Marble samples were initially brought to constant weight in a drier and the treatment was applied on one of the wider surfaces. Glass slides (dimension 38 × 26 mm, from Aldrich) were washed and dried before coating. NaCl disks were used without any previous treatment. Polymer (40 mg) were dissolved in CHCl₃ (2 mL) and the solution casted on the selected surface with the aid of a pipette. The solvent was allowed to evaporate in laboratory conditions (25°C, 60% relative humidity) overnight and a uniform coating was obtained, and then treated samples were kept in a drier until constant weight was reached.

Protective Efficiency (P.E.). It was evaluated according to the UNI15801 (2010) method³³ by capillary water absorption and calculated as:



Scheme 2. Synthesis of phenylmethylglycolide (PMGLY) and salicyl-lactide (SALD).

$$\text{P.E.}\% = ((A_{un} - A_t) / A_{un}) \times 100$$

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

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^* is the colorimetric value (L^* , a^* , or b^*) of the treated stone and x_u^* is 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 method³⁰:

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

Accelerated Aging

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 FT-IR, ¹H-NMR, GPC, DSC, solubility, and weight loss of the irradiated samples. Chromatic changes and P.E. were measured on stone samples and the mean value of the three tests was reported.

RESULTS AND DISCUSSION

Polymers were obtained from the corresponding PMGLY or SALD with the aim to obtain precise alternating copolymers, using the ROP process and benzyl alcohol or PFOct as chain initiator.

Synthesis of Monomers

Natural and commercially available mandelic and salicylic acids were used as starting materials obtaining PMGLY or SALD following the procedures reported in Scheme 2.^{34–40} Racemic forms of these cyclic esters were obtained, due to a lack of stereoselectivity in the ring-closure step, in line with the data reported in the literature.⁴¹

Table II. Reaction Conditions and Polymers Characterization

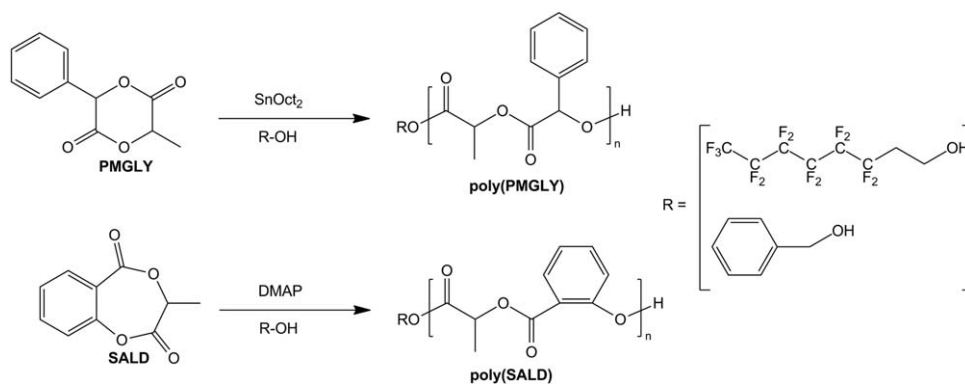
Run	Monomer	PFOct (% mol)	DP ^b	M_n (g/mol)	M_w (g/mol)	PDI ^c	T_g (°C)	ΔC_p ^d (J/g)
1	PMGLY	0 ^a	66	13,540	20,160	1.49	76.5	0.424
2	PMGLY	0.5	63	12,890	21,164	1.65	75.0	0.419
3	PMGLY	3.0	51	9665	11790	1.22	74.7	0.535
4	PMGLY	5.0	15	3036	4405	1.45	65.2	0.461
5	PMGLY	10.0	12	2435	4805	2.39	58.9	0.498
6	SALD	0 ^a	18	3886	6635	1.71	76.8	0.704
7	SALD	0.5	17	3212	5429	1.55	70.3	0.871
8	SALD	3.0	12	1819	3247	1.79	54.9	0.643
9	SALD	5.0	9	1326	2810	2.12	45.2	0.584
10	SALD	10.0	10	2108	2949	1.40	59.6	0.776

^a 0.5 mol % of benzyl alcohol was used as chain initiator.

^b Degree of polymerization.

^c Polymer dispersion index.

^d Specific heat capacity variation.



Scheme 3. ROP of PMGLY and SALD to obtain copolymers of lactic acid/mandelic acid and lactic acid/salicylic acid.

Table III. Products Tested as Coating of Stones

Code	Polymer	Fluorine content (% w/w)	M_w (g/mol)	PDI ^a	T_g (°C)
PLA	L-LD homopolymer	0.0	14,396	1.38	50.0
PLA-F	Fluorinated L-LD homopolymer	3.6	7697	1.26	40.5
Poly(PMGLY)	PMGLY homopolymer	0.0	20,160	1.49	75.0
Poly(PMGLY)-F	Fluorinated PMGLY homopolymer	3.5	11,790	1.22	74.7
Poly(SALD)	SALD homopolymer	0.0	6635	1.71	76.8
Poly(SALD)-F	Fluorinated SALD homopolymer	3.8	3247	1.79	54.9

L-LD: L-lactide.

^a Polymer dispersion index.

Synthesis and Characterization of Polymers

Monomers were polymerized in the melt phase through ROP using benzyl alcohol as chain initiator (conditions are reported in Table II), obtaining two classes of copolymers of lactic acid with mandelic acid (poly(PMGLY)) or salicylic acid (poly(SALD)) (Scheme 3). The homopolymer of lactic acid (PLA) was also synthesized as previously reported^{5,42} for comparative purposes. In some polymerizations, PFOct was used as chain initiator obtaining end-capped copolymers with a perfluoroalkyl moiety (poly(PMGLY)-F, poly(SALD)-F, and PLA-F). Fluorine content in the copolymers was calculated as weight percent of fluorine on total product, considering the PFOct insertion and the molecular weight of the polymers (Table III).

NMR Spectra. ¹H-NMR spectra of PFOct functionalized copolymers are reported in Figures 1 and 2 (Poly(PMGLY)-F and poly(SALD)-F, respectively) and these spectra confirmed the presence of an PFOct moiety in the macromolecules. The resonance of methylene units of free PFOct (δ 4.01 ppm, absorption **d** in Figure 1) due to the formation of the ester linkage. The multiplicity of this group was increased from a quartet in the starting alcohol into a multiplet in the polymer due to a long-range coupling with the hydrogens of the polymer backbone. An analogous behavior was shown by Giuntoli *et al.* in the polymerization of lactic acid using a benzotriazole-1-methanol as chain initiator.⁵⁸ Furthermore, the resonances of the ¹H-NMR spectrum of poly(PMGLY)-F support the link between the perfluoro alcohol

and the repeating unit from mandelic acid, because it is presented that the resonance of the terminal $\underline{\text{CH}}(\text{CH}_3)\text{OH}$ group of lactic acid (δ 4.23 ppm, **c'** in Figure 1) as the prevailing linkage of chain end groups. On the contrary, the ¹H-NMR spectrum of poly(SALD)-F (Figure 2) does not show this resonance, suggesting the link between the perfluoro alcohol and the lactic acid as the prevailing linkage of the chain end group. A further support to this hypothesis is given by the resonance at 5.25 ppm attributed to the $\underline{\text{CH}}(\text{CH}_3)\text{COO-PFOct}$ group.

¹⁹F-NMR spectra of these copolymers (reported as Supporting Information) showed the resonances of fluorine atoms, with

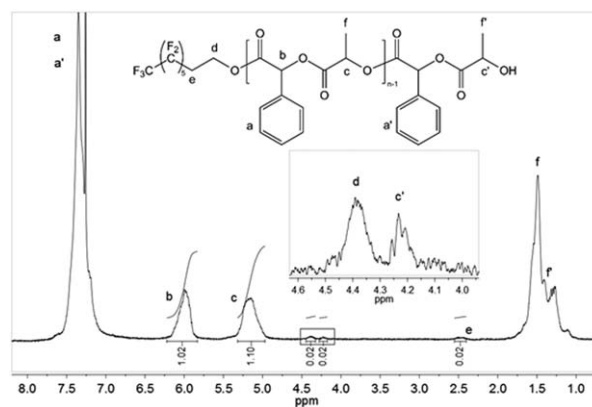


Figure 1. ¹H-NMR spectra of poly(PMGLY) functionalized with PFOct (run 3, Table I).

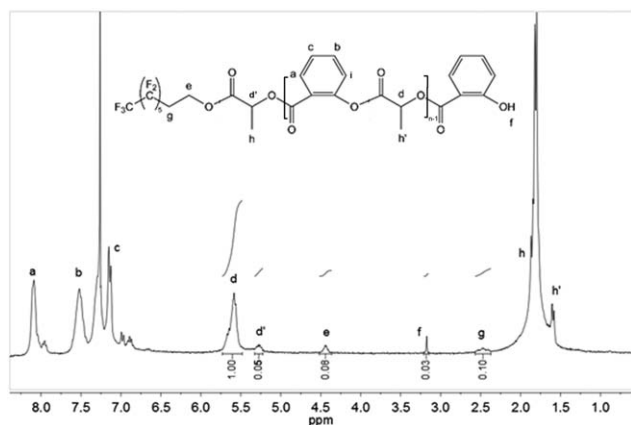


Figure 2. ^1H -NMR spectra of poly(SALD) functionalized with PFact (run 10, Table II).

chemical shifts very close to those detected for the starting alcohol, confirming the insertion of a perfluoroalkyl moiety in the polymers.^{43–45} The invariance of the ^{19}F -NMR spectra of the fluorinated polymers with respect of the starting alcohols was in agreement with previous study on the synthesis of end-capped perfluoroalkyl PLA.^{5,6}

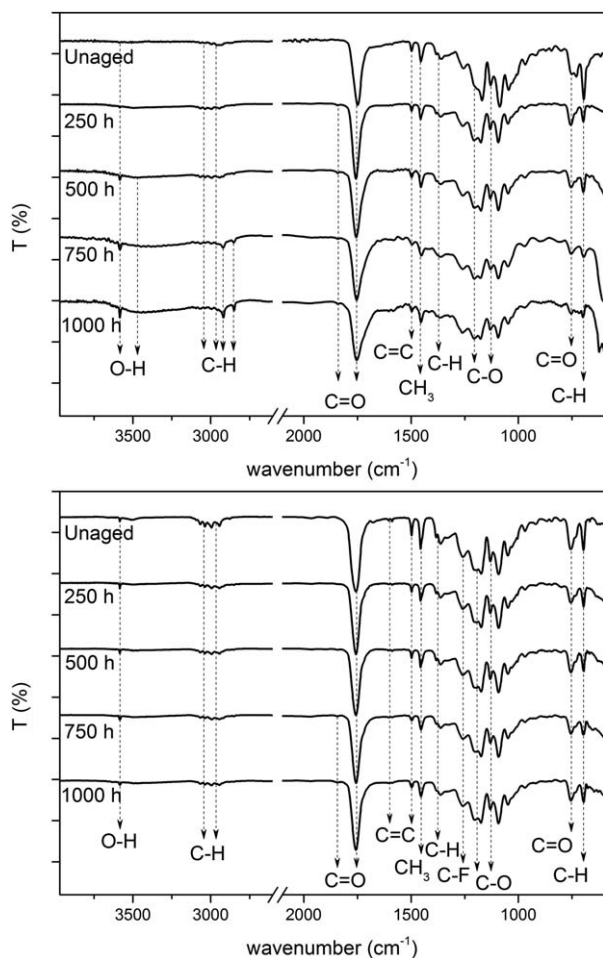


Figure 3. FT-IR spectra of poly(PMGLY) (top) and poly(PMGLY)-F (bottom) samples after different steps of the artificial aging process.

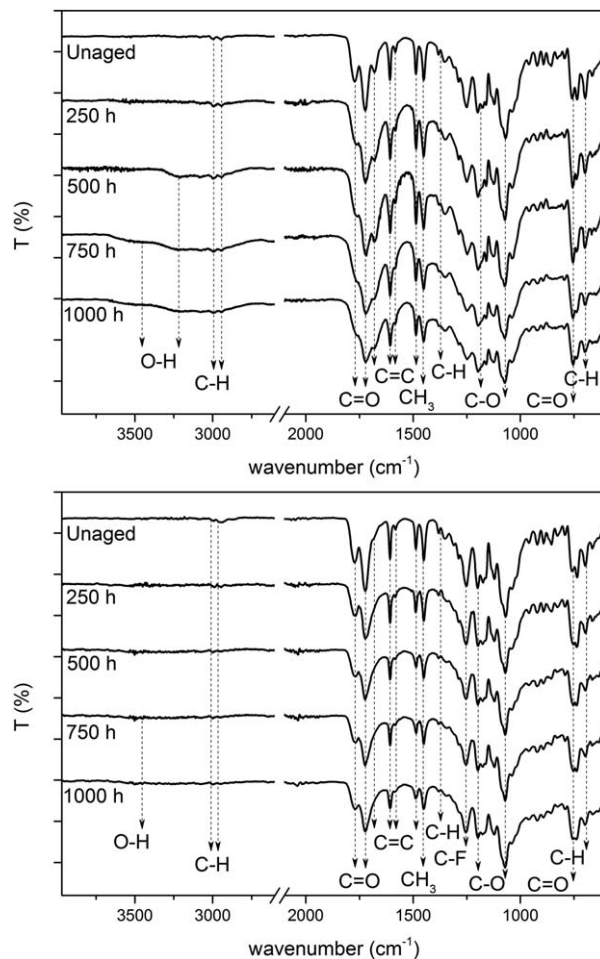


Figure 4. FT-IR spectra of poly(SALD) (top) and poly(SALD)-F (bottom) samples after different steps of the artificial aging process.

FT-IR Spectra. FT-IR spectra of polymers are reported in Figures 3 and 4 and they confirm the synthesis of poly(PMGLY) and poly(SALD) copolymers. The main absorptions were attributed on the basis of data reported in the literature.^{46,47}

Poly(PMGLY) spectrum showed the following signals: 3580 (w, O—H stretching), 3066 and 3038 (w, symmetric and asymmetric aromatic C—H stretching), 2993 and 2943 (m, symmetric and asymmetric aliphatic C—H stretching), 1750 (s, C=O stretching), 1498 (w, aromatic C=C stretching), 1457 (m, CH₃ bending), 1384 and 1359 (m, symmetric and asymmetric C—H bending), 1290–990 (s, C—H bending and C—O stretching), 1210 and 1095 (s, C—O stretching and C—O—C asymmetric bending), 871 (w, amorphous PLA), 753 (m, C=O bending) 696 (s, C—H bending) cm^{-1} .

Poly(SALD) spectrum showed the following absorptions: 3580 (w, O—H stretching), 3118 and 3083 (w, symmetric and asymmetric aromatic C—H stretching), 2993 and 2949 (m, symmetric and asymmetric aliphatic C—H stretching), 1774 (s, C=O stretching lactic moiety), 1722 (s, C=O stretching salicylic moiety), 1681, 1607, 1583 1490 (s, aromatic C=C stretching and bending), 1449 (m, CH₃ bending), 1384 and 1351 (m, symmetric and asymmetric C—H bending), 1330–970 (s, C—H bending

Table IV. Protective Efficiency of Treated Samples

Polymer	P.E. %
PLA	37
PLA-F	78
poly(PMGLY)	67
Poly(PMGLY)-F	94
PSALD	60
Poly(SALD)-F	85

and C—O stretching), 1210 and 1095 (s, C—O stretching and C—O—C asymmetric bending), 860 (w, amorphous PLA), 761 and 737 (m, C=O bending) 696 (w, C—H bending) cm^{-1} .

Additional signals in the 950–1200 cm^{-1} region, relative to stretching and bending of C—F bonds, were also present in perfluoroalkyl containing polymers, but they were not univocally attributable due to overlapping with other bands of polymers.

Rheological Characterization. The polymers, due to the use of racemic monomers, showed a random stereochemistry and amorphous materials lacking any crystalline domain were obtained. In agreement with the data reported for lactide/mandelide copolymers with higher mandelide content,⁴² poly(-PMGLY) showed only a T_g without a T_c and a T_m (Tables II and III). The bulky phenyl groups as side chains may be the cause of the high increase of T_g . Poly(PMGLY), due to the monomer employed and the polymerization adopted (ROP), showed an alternating sequence with a 1 : 1 ratio between lactic acid and mandelic acid as repeating units. The same behavior was shown by poly(SALD); however, its T_g was lower than the one of poly(PMGLY) due to its lower molecular weights. The synthesis of poly(PMGLY) with low M_w was attributed to the use of DMAP catalyst, fairly active in trans-esterification reactions,^{35,48} with respect to $\text{Sn}(\text{Oct})_2$. Unfortunately the tin catalyst was not active in the polymerization of SALD, nevertheless the T_g of poly(SALD) was significantly higher than neat PLA.

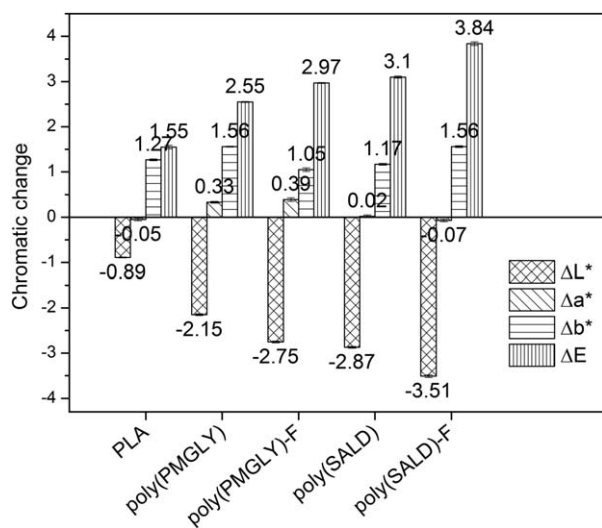


Figure 5. Chromatic variations of samples after coating with selected polymers.

Assessment of Synthetic Polymers as Stone Coatings

A selection of the synthesized polyesters was chosen to evaluate their performances as coating of stones. The products, selected from those reported in Table I, were a poly(PMGLY) (run 1), a chain-end perfluorinated alkyl containing poly(PMGLY) [poly(-PMGLY)-F] (run 3), a poly(SALD) (run 6) and a chain-end perfluorinated alkyl containing poly(SALD) [poly(SALD)-F] (run 8). PLA and PLA-F were synthesized as reference materials and employed to correlate the results with those previously reported.^{5,6}

White calcitic marble with low porosity was chosen as stone substrate to evaluate the performances of the coatings. Products were applied by solution casting, a common practice for film formation, successfully employed to form thin polymer coatings of acrylates, methacrylates,^{49–51} fluorinated acrylic resins,^{52–55} polysiloxanes,^{52,56} polyolefins,⁵⁷ and polylactic acid.^{1,5,6,42,58,59} Taking into account the goals of this study, two sets of samples were prepared: (a) polymer coatings on glass slides and NaCl disks, for the characterization of films and to study their stability after an aging process under solar radiations (coating were checked by optical microscopy, FT-IR, ¹H-NMR, GPC, DSC, and weight loss), and (b) polymer coatings on marble surfaces, to evaluate the protective efficiency, as well as color change, that is the performances as stone protective.

The new polymers showed almost the same solubility of PLA, in acetone, THF, but CHCl_3 was overall the best solvent. CHCl_3 or THF solutions were employed for solution casting without any significant differences on the performance of the final coatings.

The penetration of polymer solutions was allowed only to a low extent, due to the low porosity of marble, leading to a rapid solvent evaporation and reduced times for film formation. The polymers remained largely on the surface, so their behavior as surface coating was readily studied and phenomena such as product migration and diffusion in the bulk of marble were limited. Finally, the white color of the substrate allowed an easy detection of chromatic variations.

Uniform and crack-free coatings were obtained after solvent evaporation in laboratory conditions and the absence of fractures in the final coatings was confirmed by visual inspection using an optical microscope. Pictures of these coatings were reported as Supporting Information.

Protective Efficiency (P.E.). The P.E. of poly(PMGLY) and poly(SALD) was higher than that one of PLA due to the presence of phenyl groups (Table IV) and it increases in the following order: $\text{PLA} < \text{Poly}(\text{SALD}) < \text{Poly}(\text{PMGLY})$. As expected, the introduction of a chain-end perfluoroalkyl group in the polymers further increases the P.E., in agreement with results previously reported.^{5,6,31,59} The presence of a perfluoroalkyl moiety in the polymer is the most important factor to reduce the penetration of liquid water in the stone. Among all polymers tested, poly(PMGLY)-F showed the best performance, with a P.E. = 94%.

Water Vapor Diffusivity. Residual water vapor diffusivity of marble coated with poly(PMGLY)-F was 47.1% with respect to

untreated sample and very close values were obtained with PLA-F (48.3%) used as reference.

Chromatic Performances. Chromatic variations of marble samples treated with the products are reported in Figure 5. The most significant contribution to chromatic changes was due to the lightness parameter L^* . All treatments reduced the lightness of the stones, that is, they showed a darker aspect. The effect was more evident when poly(SALD) and poly(SALD)-F were employed.

A similar behavior was already reported for PLA-FLK-PLA and PLA-F treatments.^{5,6} However, in these latter treatments, almost negligible changes in the a^* and b^* parameters were reported. Treatments employing copolymers of lactic acid with mandelic or salicylic acid caused a low decrease of a^* values, while the changes of b^* values was higher, that is a variation of the color toward a more yellow hue was shown. The yellowing may be attributed to the presence of phenyl groups, although neat polymers did not show any absorption in the visible region. Phenyl groups must be also responsible of the higher decrease of lightness with respect to PLA-FLK-PLA and PLA-F coatings.

The color variation usually considered acceptable for stone treatments is $\Delta E^* = 3$,²⁶ because it was undetectable by naked eyes. All treatments were under this limit with the exception of poly(SALD) and poly(SALD)-F, even in a low extent. The effect

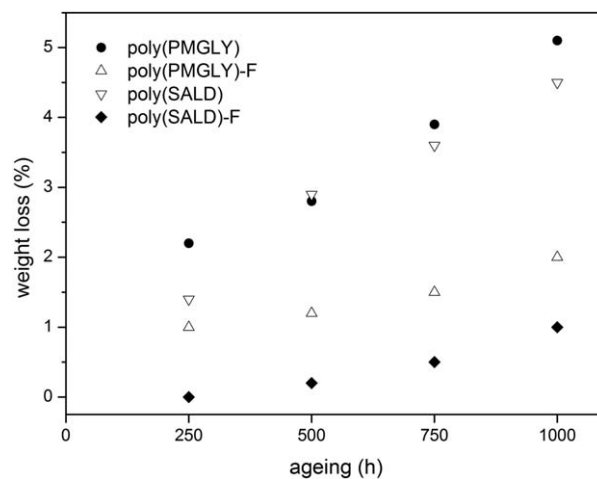


Figure 6. Weight loss of samples during artificial aging.

of yellowing and darkening was just barely noticeable by visual inspection.

Coating Stability

The stability of the coatings was checked through accelerated artificial aging, up to 1000 h using the following tests.

Weight Loss. The weight of all coatings was gradually reduced by different amounts, due to degradation processes; however,

Table V. Physicochemical Characteristics of Polymers at Different Steps of the Artificial Aging Process

Polymer	Aging time (h)	Weight loss (%)	M_n (g/mol)	M_w (g/mol)	PDI	T_g (°C)	ΔC_p^a (J/g)
Poly(PMGLY)	0	-	13,540	20,160	1.49	75.0	0.419
Poly(PMGLY)	250	2.2	6045	11,243	1.86	70.1	0.400
Poly(PMGLY)	500	2.8	1478	2868	1.94	58.1	0.414
Poly(PMGLY)	750	3.9	1134	2378	2.10	52.3	0.381
Poly(PMGLY)	1000	5.1	607	2377	3.91	40.4	0.353
Poly(PMGLY)-F	0	-	9665	11,790	1.22	74.7	0.461
Poly(PMGLY)-F	250	1.0	7328	9952	1.36	76.4	0.420
Poly(PMGLY)-F	500	1.2	6807	9860	1.45	74.1	0.493
Poly(PMGLY)-F	750	1.5	5077	8266	1.63	71.7	1.094
Poly(PMGLY)-F	1000	2.0	4925	8565	1.74	66.6	0.516
Poly(SALD)	0	-	3886	6635	1.71	76.8	0.704
Poly(SALD)	250	1.4	2776	5811	2.09	73.3	0.201
Poly(SALD)	500	2.9	2206	4985	2.26	78.4	0.839
Poly(SALD)	750	3.6	2554	5330	2.08	69.3	0.337
Poly(SALD)	1000	4.5	2424	4974	2.05	71.1	0.428
Poly(SALD)-F	0	-	1819	3247	1.79	54.9	0.643
Poly(SALD)-F	250	0	1800	3384	1.88	54.2	0.530
Poly(SALD)-F	500	0.2	2015	3450	1.71	53.9	0.675
Poly(SALD)-F	750	0.5	1925	3229	1.68	46.7	0.421
Poly(SALD)-F	1000	1.0	1697	3261	1.92	38.0	0.658

PDI, polymer dispersion index.

^aSpecific heat capacity variation.

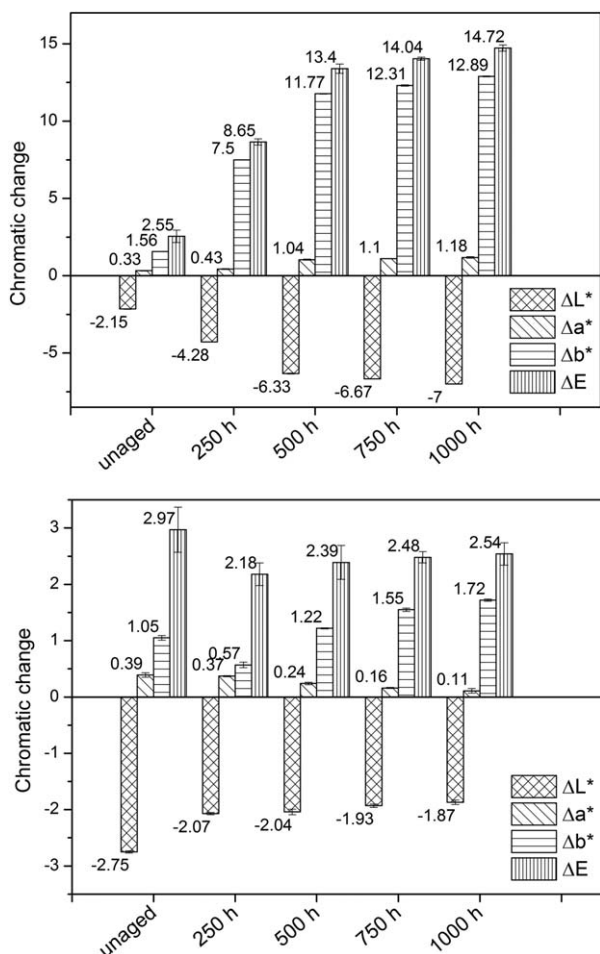


Figure 7. Chromatic variations of marble samples after treatment with poly(PMGLY) (top) and poly(PMGLY)-F (bottom) coatings after different aging times (error bars represent standard deviations).

the maximum weight loss was only 5% (poly(PMGLY), Figure 6 and Table V). The rate of this decrease was in the following order: poly(PMGLY) > poly(SALD) > poly(PMGLY)-F > poly(SALD)-F with fluorine-containing polymers showing a higher stability (weight loss 1.0–2.0% after 1000 h of aging).

Solubility. All polymers remained completely soluble after all aging times. This behavior ruled out cross-linking of the polymer chains with formation of insoluble materials. These results were confirmed by GPC analyses of the aged polymers (chromatograms were reported in Supporting Information), where additional peaks or shoulders at high molecular weights were not showed. These findings were in agreement with the other determinations, suggesting chain scission and depolymerization as the predominant mechanisms of degradation.

Molecular Weight. A decrease of molecular weight in the course of the aging process was shown for all samples, but the entity of this degradation was different among copolymers (Table V). Generally fluorine-containing polymers showed a higher stability than nonfluorinated ones and molecular weights were not very far from those of the starting polymers, in agreement with data reported on fluorine-containing PLA in previous works.^{4,5}

The presence of a perfluoroalkyl groups increases the stability of the polymer; in fact poly(SALD)-F did not show any significant change of M_w , and only a slight decrease of M_n was observed, while poly(SALD) showed a decrease of M_w of 25%. Also, the M_w for poly(PMGLY)-F decreased by 27% after 1000 h of UV aging while M_w of poly(PMGLY) was 88% of the initial value after the same aging time.

Photodegradation of polymers involves two main processes: chain scission and cross-linking, both affecting the molecular weight. In the absence of cross-linking, chain scission causes a decrease of M_n and M_w . Polydispersity index (PDI) (M_w/M_n) tends to 2 in the presence of a random chain scission.⁶⁰ If chain scission and cross-linking occur simultaneously and the probability of chain scission is smaller than cross-linking, PDI increases.⁶¹ The data collected confirmed chain scission as the main process, while cross-linking was not evidenced; in fact, M_w and M_n decreased and, at the same time, PDI increased for all samples. This behavior may be attributed to the weak CH protons in the chain of poly(PMGLY), due to the presence of a phenyl and a carboxyl group in α -position. As a consequence, a radical eventually formed on this tertiary carbon atom is stabilized by conjugation with the aromatic ring and the carboxyl group. Degradation processes may be preferentially originated on this position; hence, these CH groups may be the causes of the lower stability of poly(PMGLY). In agreement with these considerations, poly(PMGLY) showed the higher weight loss. When comparing poly(PMGLY) with poly(SALD), another aspect must be taken into account, that is, the lower molecular weight of poly(SALD) due to the synthetic conditions adopted, so the same absolute change of M_w is strongly reflected on the change percent of its M_w . The same considerations can be done for poly(PMGLY)-F and poly(SALD)-F but these polymers showed very limited changes of M_w and M_n .

Thermal Properties. The T_g of copolymers decreased in the course of the aging process with a behavior in good agreement with M_w variations. The higher decrease of T_g was shown by poly(PMGLY) ($\Delta T_g = 34.6^\circ\text{C}$) followed by poly(SALD) ($\Delta T_g = 5.7^\circ\text{C}$), while among perfluorinated polymers, poly(-PMGLY)-F showed a ΔT_g of 8.1°C while poly(SALD)-F showed a ΔT_g of 16.9°C . In this last case, due to the low molecular weight of the polymer, the small changes of molecular weight caused an important decrease of T_g . This behavior confirmed chain scission as the main mechanism of degradation excluding cross-linking because a decrease of T_g was always shown.

ΔC_p values remained substantially constant during the aging process, only slight variations were noticed.

FT-IR Spectra. Changes in FT-IR spectra during the aging process were qualitatively the same for all products tested, that is, the same groups were involved in the degradation process. However, differences were observed on the extent of these changes (Figures 3 and 4). The more relevant variations were (1) formation of a broad absorption in the $3600\text{--}3000\text{ cm}^{-1}$ region; (2) broadening and weakening of the carbonyl bands ($1770\text{--}1720\text{ cm}^{-1}$ and 750 cm^{-1}) and formation of a shoulder at 1840 cm^{-1} ; (3) a decrease of the intensity and broadening of all bands in the fingerprint region. The broad absorption at

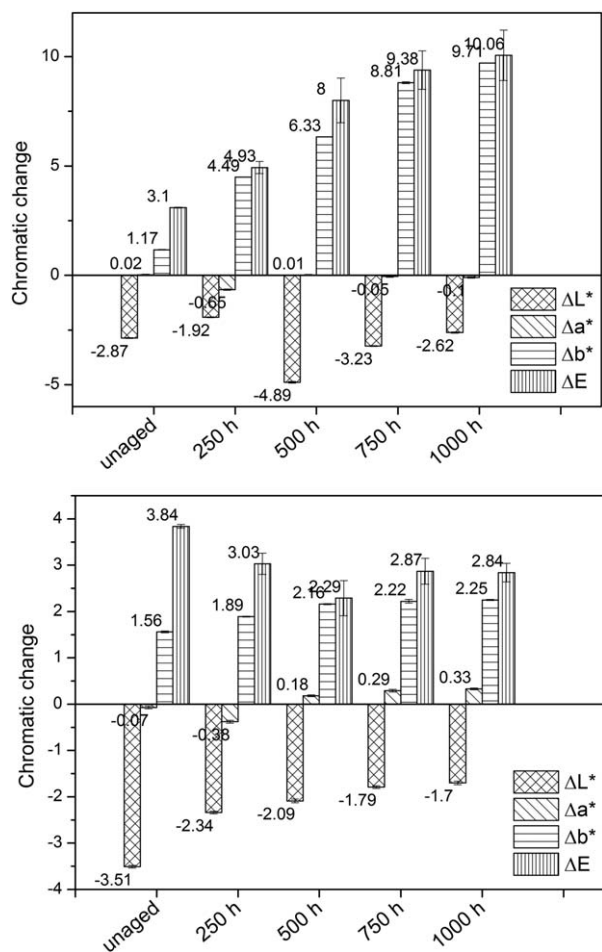


Figure 8. Chromatic variations of marble samples after treatment with poly(SALD) (top) and poly(SALD-F) (bottom) coatings after different aging times (error bars represent standard deviations).

3600–3000 cm^{-1} may be attributed to depolymerization and chain-scission processes with formation of $-\text{OH}$ and $-\text{COOH}$ end groups and the subsequent oxidation of $-\text{OH}$ end groups to $-\text{COOH}$ groups. This oxidation may take place through formation of hydroperoxides causing extensive hydrogen bonding. The band at 1840 cm^{-1} may be attributed to the stretching of anhydrides formed during photo-oxidation. Minor changes in the spectra of perfluoroalkyl-containing copolymers were shown (Figures 3 and 4).

Table VI. Hydrorepellence of Coatings (P.E. %) After 1000 h of Artificial Aging

Treatment	P.E. %	References
Poly(PMGLY)	23	
Poly(PMGLY)-F	83	
Poly(SALD)	19	
Poly(SALD)-F	80	
PLLA-FLK-PLLA	85	5,6
PLDA-FLK-PLDA	55	5,6

Chromatic Properties. The aging of polymers caused on all samples the progressive increase of the b^* parameter, corresponding to a yellowing of the coatings (Figures 7 and 8). The lightness (L^*) was lowered immediately after the coating deposition but returned toward the initial values during the aging process. This behavior was followed by all treatments, even if some fluctuations for poly(PMGLY) and poly(SALD) coatings (but these treatments also showed higher photo-oxidation and variations of other parameters) were shown. A similar behavior was already reported by Giuntoli *et al.*⁶ for PLA-F and by Frediani *et al.*⁵ for PLA-FLK-PLA and it was ascribed to a rearrangement of the film at the polymer–air interface due to exposition at a temperature over its T_g during the photo-oxidative aging. The same explanation may be claimed for poly(SALD)-F but, the other polymers (poly(-PMGLY), poly(PMGLY)-F, and poly(SALD)) had a higher T_g than the temperature employed in the aging tests. However, a partial reorganization of the coatings cannot be excluded even if the polymers were exposed at a temperature lower than their T_g . The increase of L^* in the course of the aging process was beneficial because it contributed to restore the original aspect of the stone, with a smoother and brighter surface. The yellowing process was more evident for poly(PMGLY) than poly(SALD) samples showing, $\Delta b^* = 12.89$ and 9.71, respectively. Perfluorinated polymers poly(PMGLY)-F and poly(SALD)-F showed less variations with a maximum change of $\Delta b^* = 2.27$. The contributions of Δb^* to the total color variation was limited and coupled with an increase in lightness.

At the end of the aging cycle, a ΔE^* higher than 3 was shown only for poly(PMGLY) and poly(SALD) coatings, while the fluorine-containing polymers showed a very low change of ΔE^* , if referred to the untreated stones, that is, the variation cannot be observed by naked eyes.

Protective Efficiency. In agreement with their low photo-oxidative stability, poly(PMGLY) and poly(SALD) showed also a decrease of P.E. and these values, after an aging time of 1000 h, were 2–3 times lower than the initial values (Table VI). This behavior may be connected with a partial loss of the protective film and/or to the formation of hydrophilic species in the course of the aging process. The protective efficiency of fluorinated polymers remained almost constant: the P.E. decreased only 5% for poly(SALD)-F and 11% for poly(PMGLY)-F. The conservation of hydrophobic properties was comparable with that of PLA-FLK-PLA⁵ and only slightly lower than PLA-F,⁶ previously reported.

CONCLUSIONS

Alternating copolymers of lactic acid with mandelic or salicylic acid were synthesized through an ROP process using specifically designed monomers. Amorphous polymers with a higher T_g than conventional PLA, far above room temperature, were obtained. These polymers are more suitable as stone protective because the influence of temperature cycles, when stones were located in an outdoor environment, was reduced. Chain-end perfluoroalkyl copolymers were also prepared and they showed a high P.E.

Polymers were fully characterized and their stability and protective performances in the course of a photo-oxidative weathering

were tested. Poly(PMGLY) and poly(SALD) copolymers partially lost their performance when exposed to photo-oxidative conditions, mainly through depolymerization and chain-scission processes. Chain-end perfluoroalkyl copolymers—poly(PMGLY)-F and poly(SALD)-F—showed better protective performances as shown by their stability, retention of solubility, and hydrophobic properties together with low chromatic variations at the end of the aging process.

The main advantages of these materials with respect to traditional coatings (e.g., acrylic polymers) are (1) good solubility in low toxic solvents, (2) flexible and controlled syntheses, (3) readily functionalization, (4) negligible color variations of the stone, (5) good stability to photo-oxidative conditions, and (6) use of monomers from natural sources. New features of these polymers as stone protectives are (a) amorphous, high T_g materials, (b) UV barrier properties, (c) tunable properties (molecular weight, T_g), (d) low content of fluorine atoms, (e) high stability, and (f) low color variation. Taking into account the performances of these polymers, they may be employed as suitable coatings for protection and conservation of stone surfaces with special attention to those involved in Cultural Heritage.

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