

In Situ Polymerization of Unfluorinated and Fluorinated Acrylic Copolymers for the Conservation of Stone

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ABSTRACT: The effectiveness of butyl methacrylate/ethyl acrylate-based copolymers as consolidants for stone was investigated. The penetration of polymeric consolidating products is extremely slight because of their macromolecular nature and *in situ* polymerization of the monomers is suggested as an alternative technique to the use of macromolecular solutions. The efficiencies of three products synthesized *in situ* and fluorinated by various copolymers were comparatively evaluated in terms of surface properties, water permeability, and consolidation on a selected stone sub-

strate. Moreover, because the environmental stability of such polymeric products is one of the key factors for their extensive application for conservative treatments, the photooxidative stability of reference polymers prepared *in vitro* was also investigated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3202–3213, 2004

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INTRODUCTION

The use of polymeric materials for the preservation, consolidation, restoration, and protection of the stone surface of ancient buildings of great cultural importance is nowadays generally accepted.¹

Actually, organic consolidating products show an important advantage over inorganic products: if correctly chosen, they may also have a protective activity, thanks to their water-repellent properties. Inorganic consolidants do not have water-repellent properties and therefore a complete restoration treatment also requires a second operation that consists in the application of a protective, usually polymeric, material. The direct application of only one selected polymeric product may simultaneously achieve two results, with an improved feasibility of the restoration treatment.

On the other hand, some properties of polymeric consolidants should be improved, mainly those related to the organic nature of the polymer in contrast to the inorganic nature of the stone, such as, for example, the adhesion to the substrate; in many cases it is not satisfactory and small solicitations are sufficient to detach the matrix from the polymer.

However, some properties of the polymeric materials must still be fully studied: for example, their stability on aging and also their degradation products.²

The main problem of polymeric compounds is nonetheless related to their macromolecular nature. Whereas inorganic materials are made from substances with very small molecules, polymeric macromolecules have dimensions that increase with the square root of the molecular weight.^{3,4} Thus it is difficult for a polymeric compound to penetrate inside the stone because its pores may have a very small diameter (micropores have a diameter under 20 Å); as a consequence the penetration depth is limited and the polymer remains confined to the superficial layers. This is acceptable for a polymer with only a protective action, but not for a material that must also be a consolidating product, because in the latter case a deep penetration is required.

These considerations are the basis for consideration of *in situ* polymerization.⁵ According to our technique the monomer, not the preformed polymer, is introduced in the stone and it is polymerized *in situ* in a subsequent step. It is possible to foresee that the monomers, which are small molecules, can also reach the smallest pores and at the end of the polymerization the consolidating polymer is more evenly and deeply distributed into the stone.

The feasibility of *in situ* polymerization was explored in a previous work on the synthesis of an ethyl methacrylate/methyl acrylate (EMA/MA) copolymer in the presence of AIBN as initiator, at the optimal temperature of 50°C, and diffusing the polymerizing mixture in acetone as solvent.⁶ The ratio between the repetition units of EMA and MA (70/30 wt %) was purposely kept similar to a commercially available

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product (Paraloid B72[®]; Röhm and Haas),^{7,8} which is widely employed in the field of restoration.

In this research, the potentialities of such an approach are further considered for a series of products based on the copolymer of butyl methacrylate (BMA) with ethyl acrylate (EA).

It is important to remember that the polymer has characteristically better consolidating properties when the material, at the service temperature, is above its glass-transition temperature and thus it is in a viscoelastic, rather than glassy, state. The viscoelastic behavior may increase the polymer adhesion to the stone and it can also reduce its potential for fracture.⁹

The main limitation of Paraloid B72 (made by EMA/MA) is the T_g of 41°C, higher than room temperature; Paraloid B72 at the service temperature is in the glassy state and thus, being rigid and brittle, it may cause breaks because it does not follow the variations of volume of the stone where it is penetrated. For this reason the copolymer BMA/EA (with an original composition) was chosen. In particular the introduction of ethyl acrylate units, whose corresponding homopolymer has a very low T_g ($\sim -20^\circ\text{C}$) compared to the 20°C of poly(butyl methacrylate),¹⁰ leads to a material with a low T_g value, which makes the product very efficient as a consolidant.

We previously explored a possible solution by modifying the reagent system with the addition of a small quantity of plasticizer [poly(ethylene glycol) diacrylate].⁶ The selected plasticizer was able to copolymerize with the two monomers and simultaneously link the single macromolecular chains, creating a continuous network that has excellent consolidating properties. On other hand, the high mobility of polyoxyethylene chain ($T_g = -63^\circ\text{C}$) reduced the T_g of the system to values lower than room temperature.

In the previous experiments the selected temperature of *in situ* polymerization was 50°C⁶; this temperature was ideal for the initiator used in the polymerization reaction but it was not always applicable to the consolidation of large historical and artistic stone artifacts. In the actual work we present the data relative to the BMA/EA system, synthesized at 30°C. To simplify the reaction conditions, some of the polymerizations were carried out in the absence of solvent.

It is well known that the introduction of fluorine atoms into polymer structures has the effect of improving their chemical, thermal, and photochemical stability,¹¹ attributed to the stability of the C—F bond (bond energy = 116 kcal/mol). In addition, the formal substitution of hydrogen by fluorine atoms induces higher hydrophobicity as a consequence of the low surface energy conferred by the fluorinated groups.^{12–16} This characteristic was exploited in the present research through two different approaches, by the introduction in the polymerizing mixture (together with BMA and EA) of either (1) a fluorinated mono-

mer [i.e., 2,2,2-trifluoroethyl methacrylate (TFEMA)], a cheap and commercially available monomer, or (2) a low percentage of preformed fluoropolymer. The choice of the commercial copolymer Tecnoflon TN[®] (Ausimont) was based on its miscibility with acrylic copolymers, such as Paraloid.¹⁷

Following all of these indications, this article reports the assessment of the effectiveness of BMA/EA-based copolymers as consolidants for stone surfaces, in the framework of a systematic approach to the problem. The efficiencies of three products synthesized *in situ* and fluorinated by various copolymers were comparatively evaluated in terms of surface properties, water permeability, and consolidation on a selected stone substrate. Moreover, because the environmental stability of such polymeric products is one of the key factors for their extensive application for conservative treatments,¹⁸ the photooxidative stability of reference polymers prepared *in vitro* was also investigated.

EXPERIMENTAL

Materials

Monomers and solvents used in this research were commercial products from Aldrich (Milwaukee, WI). The polymerization initiator [2,2'-azobisisobutyronitrile (AIBN)] was supplied by Fluka (Buchs, Switzerland).

The monomers (i.e., ethyl acrylate, butyl methacrylate, 2,2,2-trifluoroethyl methacrylate) contained an inhibitor (hydroquinone monomethylether), which had to be removed before polymerization. Passing each product on a column of inhibitor removers (Aldrich) accomplished this; the pure monomers were subsequently stored at low temperature (4°C) and in the absence of light.

The solvents (acetone and methylethylketone) were laboratory-grade products and used without any further purification. Deionized water was used throughout the work.

Tecnoflon TN copolymer [composition: vinylidene fluoride (VF2), 64%; hexafluoropropylene (HFP), 19%; tetrafluoroethylene (TFE), 17%; fluorine, 67 wt %; $M_w = 495,000$, $M_n = 90,000$, D (dispersity index) = 5.5; $T_g = -14^\circ\text{C}$], was supplied by Ausimont (now Solvay Solexis, Bollate, Italy).

The stone for the *in situ* polymerization must present two basic requirements:

- High porosity, to reproduce a material degraded by the physical and chemical agents
- Easily supplied in the standardized forms

For these reasons we used a calcareous sedimentary stone of biological origin, easily available in Liguria, Italy called "Pietra di Finale."¹⁹ This is found in four

different formations, differing in the percentage of impurities and fragments; they also have different colors (from white to roseate) and different physical characteristics. We used the Mascia variety of the Finale stone, which presents a fairly high porosity (27%).

Polymer characterization: techniques

Measurements of intrinsic viscosity were carried out in methylethylketone at 25°C. In the case of our copolymer, the experimental constants K and a in the Mark-Houwink-Sakurada equation^{10,20} were not available and therefore it was not possible to calculate the molecular weights; the viscosity values are nevertheless interesting because they allow us to compare the results of copolymerization under different synthesis conditions.

Samples were submitted for determination of their molecular weight by size-exclusion chromatography (SEC), with a modular SEC system made of a Waters M45 pump, a Rheodyne 7071 injection valve with a 200- μ L sample loop, and an Erma 7510 differential refractometer as a detector.

Four PL-gel (Polymer Labs, Poole, UK) columns (30 \times 0.78 cm²), in series, were used for the separation. Gel particle (styrene/divinyl benzene based) diameter was 5 μ m and nominal porosity of the individual columns was 500, 10³, 10⁴, and 10⁵, respectively.

Sample solutions, approximately 0.3% wt/vol concentration, were prepared in distilled tetrahydrofuran, which was also the chromatographic eluent. Before the injections, solutions were filtered on 0.45- μ m membrane syringe filters in poly(tetrafluoroethylene). Injection volume was 200 μ L and the eluent flow rate was set at 1 cm³/min. Impurity solvent peaks were used as a flow rate internal standard.

Molecular weights were calculated relative to a poly(methyl methacrylate) (PMMA) calibration. Ten PMMA narrow-distribution standards (Polymer Labs), with M_w ranging from 1,600,000 to 2000, were used to construct a calibration curve in terms of $\log(M_w)$ as a function of elution time. A third-order polynomial equation was obtained from regression analysis.

To determine the composition of the copolymers, ¹H-NMR spectra were recorded in CDCl₃ on a Varian Gemini 200 spectrometer (Varian Associates, Palo Alto, CA) at 200 MHz, with TMS as internal standard. Chemical shifts ($\delta = [(\nu_{\text{sample}} - \nu_{\text{TMS}})/\nu_{\text{TMS}}] \times 10^6$) are expressed in ppm. Monomers and homopolymers were analyzed as references.²¹

BMA. δ 0.94 (3H, t, $J = 7.2$ Hz), 1.41 (2H, m), 1.66 (2H, m), 1.94 (3H, app s), 4.14 (2H, t, $J = 6.6$ Hz), 5.54 (1H, app t, $J = 1.7$ Hz), 6.09 (1H, app s).

PBMA. δ 0.95 (6H, m), 1.40 (2H, m), 1.61 (2H, br s), 1.90 (2H, m), 3.94 (2H, s).

EA. δ 1.30 (3H, t, $J = 7.1$ Hz), 4.21 (2H, q, $J = 7.1$ Hz), 5.81 (1H, dd, $J = 10.2$ and 1.5 Hz), 6.11 (1H, dd, $J = 17.2$ and 10.2 Hz), 6.40 (1H, dd, $J = 17.2$ and 1.5 Hz).

PEA. δ 1.25 (3H, m), 1.65 (2H, br s), 2.30 (1H, app s), 4.10 (2H, m).

TFEMA. δ 1.98 (3H, t, $J = 1.2$ Hz), 4.5 (2H, q, $J = 8.4$ Hz), 5.70 (1H, m), 6.2 (1H, m).
To determine the BMA amount in the copolymers the analyzed signals were those at 0.95 and 1.4 ppm, for the EA the methoxy group at δ 1.25 ppm, and for the TFEMA the signal of methylene at 4.5 ppm were considered.

The glass-transition temperatures (T_g) were evaluated using a Mettler differential scanning calorimeter (Model 30; Mettler, Greifensee, Switzerland) with a heating rate of 20°C/min from -100 to 150°C. To eliminate the effects deriving from earlier thermal histories, the second heating cycle was always considered, after heating the sample to 150°C at 20°C/min and then rapidly cooling it to -100°C.

Chemical modifications caused by photooxidation were evaluated by FTIR analysis on a Perkin-Elmer 1710 system (Perkin Elmer Cetus Instruments, Norwalk, CT), with a DTGS (deuterated triglycine sulfate) detector and 4 cm⁻¹ resolution. Spectral acquisitions and data treatments were performed with Spectra Calc [Thermo Galactic (formerly Galactic Industries), Salem, NH] software.

In vitro polymerization

Polymerizations of BMA/EA (feed composition: 75/25 vol %) and BMA/EA/TFEMA (feed compositions: 67.5/22.5/10 and 73/24.5/2.5 vol %) were also processed outside the stone (*in vitro*) to characterize the properties of the obtained polymer. The reaction was performed in solution and in the absence of solvent at 50 and 30°C, following the conventional mechanism of free-radical polymerization, by a previously described technique.⁴

The half-life time of the initiator increased with the decrease of temperature; thus at 50°C the reaction was considered complete after 24 h and at 30°C, after 96 h.

Fractionation

Polymers are mixtures of molecules of various chain lengths and/or molecular weight and fractionation was carried out for the purpose of evaluating the heterogeneity of the synthesized polymer.²²

The usual procedures for polymer fractionation involve the distribution of the polymer molecules between two phases. In particular in the fractional precipitation the polymer (3 g of BMA/EA copolymer polymerized at 50°C *in vitro*) was dissolved in a suitable solvent (600 mL of acetone, to obtain a 5% wt/vol solution) and an appropriate nonsolvent (water) was

added gradually to this solution at constant temperature. At the same time, the solution was subjected to vigorous agitation.

After a certain amount of water was added (50 mL), the addition of one more drop of nonsolvent caused turbidity, which is not easily removed by agitation. At this stage the addition of nonsolvent was continued more carefully until the solution turned milky. The precipitated phase, which contains the fraction consisting of the highest molecular weight species, was separated from the supernatant phase.

The supernatant liquid was treated with a further volume of water (20 mL), using the same procedure described above, to obtain the next fraction. This procedure was repeated until adequate amounts of nonsolvent had to be added to obtain the succeeding fraction. The final fraction was obtained by evaporating the supernatant liquid to dryness.

Six fractions were separated (with, respectively, 50, 10, 20, 30, and 80 mL of water, where the last one is the residue), and then dissolved in a small amount of acetone; polymeric films were obtained by casting. Each fraction was analyzed by $^1\text{H-NMR}$ and viscosimetry and some fractions also by DSC and SEC.

Mixture

In the literature it has been reported that poly(vinylidene fluoride) is among the few partially crystalline polymers that exhibit thermodynamic compatibility with other polymers,²³ in particular acrylic or methacrylic resins.²⁴

The miscibility of BMA/EA copolymer and Tecnoflon TN was studied by measuring the glass-transition temperatures of the mixtures.

The mixtures of BMA/EA copolymer with Tecnoflon TN, in the desired weight ratios, were obtained from solutions in acetone at 5 wt % of the two polymers by evaporation of the solvent to obtain thin films of the desired thickness. Evaporation was carried out initially under a ventilated hood at room temperature (for 2–3 days) and then in a vacuum oven at room temperature for 1 week to remove all the residual solvent.

The experimental T_g values as a function of the compositions were compared with those of the following theoretical equations.

Flory–Fox²⁵

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

where W_1 and W_2 are the weight fractions of polymers 1 and 2, and T_{g1} and T_{g2} are their glass-transition temperatures, respectively.

Gordon–Taylor²⁶

$$T_g = (W_1T_{g1} + KW_2T_{g2})/(W_1 + KW_2)$$

Utracki²⁷

$$\ln T_g = (W_1 \ln T_{g1} + KW_2 \ln T_{g2})/(W_1 + KW_2)$$

In the last two equations K is a parameter that derives from the ratio of the difference between the thermal expansion coefficients of the pure rubber and the glassy components: $K = \alpha_{1,2} - \alpha_{g,2} / \alpha_{1,1} - \alpha_{g,1}$.

Accelerated aging and analysis

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

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

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

In situ polymerization

The *in situ* polymerization was carried out in bulk and in acetone solution with different percentages of solvent and initiator.

The experimental procedure consists of three steps:

1. *Absorption.* The stone absorbs by capillarity the different mixtures that must be polymerized (BMA/EA, BMA/EA/TFEMA, and BMA/EA + 2 wt % of Tecnoflon TN) by placing the sample on a thick layer of cotton soaked in the reaction mixture; the operation was carried out at 4°C , in the absence of light, and the absorption time was standardized to 4 h.

2. *Polymerization*. The polymerization was carried out at 30°C for 96 h (at this temperature the catalytic action of AIBN is not maximum and preliminary tests have shown that the time is sufficient for a nearly complete conversion).
3. *Purification*. Traces of solvent and of unreacted monomers were still present after the polymerization were removed in a vacuum oven at 30°C for 2 days.

To compare the results of *in situ* polymerization with those obtainable from the traditional technique of application of the consolidant, a series of stone samples were treated by capillarity for 4 h with a 3% wt/vol solution in acetone of BMA/EA polymerized preliminarily *in vitro*. The treated surfaces were kept in a horizontal position at room temperature to release all the solvent until a constant mass was reached.

Evaluation of treatments

To evaluate the consolidating and protective properties of the *in situ* polymerized copolymers, some tests were carried out.^{28,29} Each test was performed on three specimens (5 × 5 × 2 cm) of the following Finale stone samples:

- Untreated samples (blank)
- Samples containing the *in situ* polymerized copolymer BMA/EA
- Samples containing the *in situ* polymerized copolymer BMA/EA with 2 wt % Tecnoflon TN
- Samples containing the *in situ* polymerized terpolymer BMA/EA/TFEMA (respectively, with 2.5 and 10 vol % in fluorinated monomer)
- Samples treated with preformed polymer BMA/EA

Preliminarily, the quantity of absorbed product ($\Delta\%$) was evaluated as follows:

$$\Delta\% = [(M_f - M_0)/M_0] \times 100$$

where M_0 is the weight of untreated stone (g), M_f is the weight of stone after treatment (g), and

$$X = (M_f - M_0)/S$$

where S is the contact surface of stone (cm²).

The reproducibility of measurements was sufficient in spite of the irregular porosity of stone, with a deviation within 5%.

The penetration depth should be as large as possible and the purpose of the present research was to increase this value significantly through *in situ* polymerization.

The consolidating properties were evaluated with an original instrument, consisting of a wood rail [100 × 5 cm (length × width)] having a strip of sandpaper (granulometry: 60 mesh) on the top. The sample with the largest surface area (5 × 5 cm) was set on the rail and loaded with a weight of 2.0 kg; it ran 30 times (equivalent to 30 m of sandpaper) along the sandpaper with a constant driving force of 2.5 kg; every 5 m it was weighed and the weight loss percentage (WL%) was calculated.

Our test allows calculation of the efficacy of aggregation (EA) with the formula

$$EA = [(WL_0 - WL_t)/WL_0] \times 100$$

where WL_0 is the average value of the weight loss percentage of three untreated stones after 30 m and WL_t is the average value of the weight loss percentage of three treated stones after 30 m.

The quantity of removed material is a function of the aggregation of the sample, and thus it is different for treated and untreated samples.

The protective properties were evaluated by three tests: (1) capillary water absorption; (2) permeability to water vapor; and (3) contact angle.

Capillary water absorption

This determination was carried out using the gravimetric sorption technique, according to Normal Protocol 11/85.³⁰ The stone specimen was laid on a filter paper pad around 1 cm thick, partially immersed in deionized water, with the treated surface in contact with the pad. The amount of water absorbed by capillarity forces was determined by weighing the specimen after 10, 20, and 30 min, and 1, 2, 4, 6, 24, 48, 72, and 96 h, to obtain the wet specimen mass M_i ($M \pm 0.0001$ g).

The amount of absorbed water Q_i , at the time t_i per surface unit, is defined as

$$Q_i = (M_i - M_0)/S$$

where M_i is the specimen mass (g) at time t_i (s), M_0 is the dry specimen mass (g), and S is the contact surface (cm²).

The Q_i values (g/cm²) are plotted against the square root of time ($t^{1/2}$), to give the capillarity absorption curve.

The angular coefficient of the first part of the curve enables us to evaluate the capillary absorption coefficient (CA) and its value should be reduced with treatment. The results can also be expressed as protective efficacy (EP%):

$$EP\% = [(Q_0 - Q_t)/Q_0] \times 100$$

TABLE I
Characteristic Data of the New Copolymers BMA/EA 75/25 vol % (68/32 mol %)

T (°C)/ t (h) of polymerization	Acetone (%)	AIBN (%) ^a	BMA/EA (wt %) ^b	$[\eta]$ (g/dL)	T_g (°C)
50/24	40	3	70/30	0.77	7
30/96	40	3	69/31	1.55	14
30/96	40	4	69/31	1.49	4
30/96	30	3	70/30	2.33	15
30/96	30	4	72/28	1.98	5

^a wt % of monomers.

^b Obtained by ¹H-NMR (CDCl₃).

where Q_0 is the average value of water absorbed by the untreated stones series after 1 h and Q_t is the average value of water absorbed by the treated stones series after 1 h.

Permeability to water vapor

This determination was carried out according to the corresponding Normal Protocol 21/85³¹ on the $5 \times 5 \times 1$ -cm specimen, using a measurement cell consisting of a cylindrical PVC chamber with open top fitted with an O-ring rubber seal, where the stone specimen was used as the lid of the chamber; the chamber was sealed with the lid by means of an aluminum flange with an O-ring.

The cell was partially filled with deionized water, thus allowing measurement by gravimetry of the amount of water vapor that diffuses through the stone specimen with fixed thickness (1 cm) between two parallel surfaces. The test was carried out at constant temperature ($20 \pm 0.5^\circ\text{C}$), with the cell placed in a desiccator. The driving force for the diffusion of water vapor is, therefore, the constant difference between the water vapor pressure inside and outside the cell (in the presence of activated silica gel desiccant).

The permeability was monitored by determining the weight decrease per surface unit (S , m²) in the unit time (24 h):

$$\Delta M_i = (M_i - M_{i-1})/S$$

where M_i is the weight system (cell and stone) at the i th day (g).

The cell was weighed ($M \pm 0.0001$ g) and ΔM_i (daily weight variation) was calculated when a stationary condition (constant vapor flow through the stone) was reached; stationary flow was considered to be reached when

$$(\Delta M_i - \Delta M_{i-1}) \times 100 / \Delta M_i \leq 5\%$$

The permeability to water vapor, after the treatment, must be as high as possible and not too different from the value of the untreated material.

Besides the water vapor permeability, we also evaluated the reduction in permeability (RP%) attributed to the treatment, according with following equation:

$$\text{RP}\% = [(P_0 - P_t)/P_0] \times 100$$

where P_0 is the permeability to water vapor of the untreated stones, used as reference, and P_t is the permeability to water vapor of the treated stones.

Contact angle

The measurements of the contact angle³² were carried out with a Lorentzen Wettre surface wettability tester by depositing 30 microdrops (3–5 μL) of deionized water on the surface of the sample and by measuring their height h and diameter at the base d . The contact angle (in degrees) was calculated as

$$\alpha = 2 \arctan(2h/d)$$

The resulting contact angle measurements were averaged for each specimen and standard deviation was calculated.

RESULTS AND DISCUSSION

In vitro polymerization

The characteristic data of our new copolymers are listed in Table I. The polymer obtained at 50°C with 3 wt % of initiator and 40 vol % of solvent analyzed by SEC has the following molecular weight: $M_w = 475,900$, $M_n = 181,000$, and $D = 2.63$; the polydispersity index is in accordance with the statistic radical mechanism of polymerization.

As shown, the viscosity of the copolymers obtained at 30°C is higher than that at 50°C and this means that the molecular weight is much higher; moreover, the higher molecular weight is not a problem because, in the *in situ* polymerization, the monomers, but not the preformed polymer, were carried inside the stone. By increasing the AIBN concentration from 3 to 4, the molecular weight and the T_g both decreased and also

TABLE II
Characterization of Fractions

Fraction	Quantity (g)	Composition BMA/EA (wt %)	M_n	M_w	D	$[\eta]$ (g/dL)	T_g (°C)
1	1.301	75/25	320,000	586,000	1.63	0.92	17
2	0.490	70/30	167,800	317,300	1.89	0.73	8
3	0.377	67/33	—	—	—	0.62	—
4	0.048	64/36	—	—	—	0.54	—
5	0.068	57/43	—	—	—	0.47	—
6	0.203	40/60	31,500	117,000	3.72	0.33	-12
Total BMA/EA	2.487	70/30	181,000	475,900	2.63	0.77	7

by increasing the amount of solvent the molecular weight decreased. The compositions of the copolymer obtained in different conditions were very similar.

Table I shows the results obtained by using acetone as a solvent; some experiments were carried out in bulk at 50 and 30°C and the resulting copolymers had a comparable T_g and a higher viscosity. Nevertheless, this type of polymerization cannot always be used in every kind of stone for the *in situ* procedure because the volume contraction associated with the copolymerization determines tensions inside the stone, causing it to break. To avoid this effect, it was necessary to perform solution polymerization.

We must point out the T_g values, which were below room temperature, make the product elastic and efficient as a consolidating material.

The terpolymers BMA/EA/TFEMA were polymerized at 50°C with 2 wt % of AIBN and, with the aim of a practical application, with only 20 vol % of acetone. Characteristics of various compositions of BMA/EA/TFEMA are as follows:

- 65/30/5 wt %, 58/38/4 mol %: $T_g = 14^\circ\text{C}$
- 61/28/11 wt %, 56/35/9 mol %: $T_g = 16.5^\circ\text{C}$; $M_w = 306,000$; $M_n = 83,400$, $D = 3.67$

The influence of fluorinated monomer (T_g of the homopolymer = 62°C) causes a slight increase of the T_g in both terpolymers. In any case, the small quantity of TFEMA allowed the T_g to be maintained to a value lower than room temperature.

Fractionation

To determine the heterogeneity of the synthesized polymer, it was fractionated by precipitation with nonsolvent; every fraction was characterized.

At constant temperature, the fractionation occurred as a function of both molecular weight and composition of the copolymer. The solubility depends not only on the molecular weight, but also on the percentage of the comonomers and, by fixing a molecular weight,

the critical parameter for the interaction polymer-solvent X_c changes if the copolymer composition has been changed. This aspect could complicate the interpretation of the results, when both the factors are changing at the same time.

The results of fractionation are shown in Table II.

First, it may be observed that in fractions 1, 2, and 3 some 87% of the total polymer is present, and this means that the polydispersity is narrow; the characteristics of the second fraction correspond to those of the whole polymer.

From the table one may observe a decrease of the quantity of butyl methacrylate, followed by changes of the T_g values.

The intrinsic viscosity decreases; this effect could depend not only on the decrease of molecular weight, but also on the affinity of the polymer with the system solvent/nonsolvent. Actually, this affinity changes, thus changing the polymer composition. Unfortunately the two effects are not distinguishable.

Although the goodness of the solvent system (acetone and water) for the polymer was not evaluated, we can deduce that the ethyl acrylate is the most soluble. Looking at the reactivity ratios, the chains richer in BMA are the first to be formed ($r_{\text{BMA}} > r_{\text{EA}}$) when the system has plenty of initiator and low molecular weight chains are mostly formed. If the fractionation depended only on the molecular weight they would precipitate later. In Table II it is evident that the fraction richer in butyl methacrylate precipitates earlier, meaning that the amount of ethyl acrylate causes the copolymer to be more soluble and thus hampers the precipitation.

Nothing can be reported about the presence of homopolymers because the $^1\text{H-NMR}$ gives a mean value of composition of the sample without distinguishing the composition of the different chains.

Molecular weights obtained by SEC are consistent with viscosity values. As expected, the fractions have a lower polydispersity index than that of the whole sample, except for the last fraction, where the residuals are present.

TABLE III
Calculated and Experimental T_g Values of the Mixtures Between
Copolymer BMA/EA and Tecnoflon TN®

Weight percentage Tecnoflon TN®	Experimental	Flory-Fox	Gordon-Taylor (K = 1)	Utracki (K = 1)
0	284	284	284	284
20	278	279	279	279
40	272	273	274	274
50	265	271	271	271
60	263	268	268	268
80	259	264	264	264
100	259	259	259	259

Mixture

The experimental results of the T_g of the mixtures BMA/EA, polymerized *in vitro* at 50°C, and Tecnoflon TN with different ratios, are listed in Table III.

As shown, for all compositions the thermograms are characterized by only one glass transition, in which the T_g is intermediate between those of the pure components. As a consequence, the polymers are miscible in the whole concentration range.

Figures 1 and Table III show the experimental outline of the T_g versus the composition of the mixture and the behavior is compared with those of theoretical equations of Flory-Fox, Gordon-Taylor, and Utracki (assuming the empirical parameters, $K = 1$, in Gordon-Taylor and Utracki equations). As shown, there is good agreement of the experimental data with the three equations for quantity of Tecnoflon TN < 40% wt. For higher amounts of Tecnoflon the experimental outline of the T_g versus the composition of the mixture is characterized by strong negative variations from linearity.

In our ordinary polymerization conditions, the two acrylic monomers were mixed with a small amount of fluorinated polymer (2 wt %), enough to achieve better protective performances.

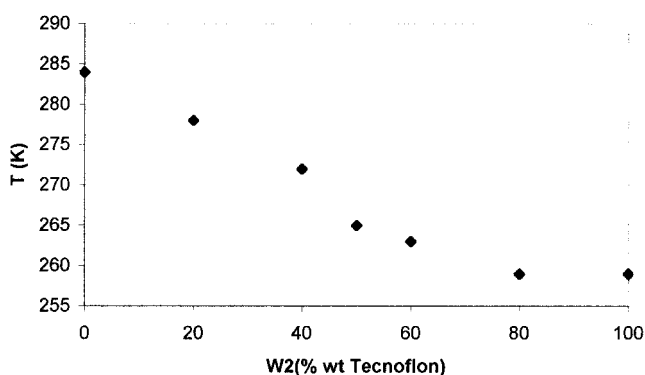


Figure 1 Experimental T_g values for the BMA/EA/Tecnoflon TN mixtures.

Accelerated photoaging

Films of BMA/EA (70/30 wt %, 62/38 mol %) and BMA/EA/TFEMA (61/28/11 wt %, 56/35/9 mol %) were irradiated in air under artificial solar light for times sufficient to obtain clear indications on the influence of the different monomeric units on the photooxidative behavior. Weight loss and gel determination, SEC, FTIR spectroscopy, and $^1\text{H-NMR}$ were used during treatment times of up to 2000 h to monitor molecular and chemical changes.

Throughout the whole irradiation process the apparent weight losses of the two copolymers were limited to less than 10%, whereas the amount of insoluble polymer became very large. Such crosslinked structures grew rapidly in both copolymers after an induction time of less than 200 h up to about 90% at the final time of treatment.

The common tendency to promote crosslinking was also revealed by the SEC chromatograms. For example, in Figure 2 are shown the curves of BMA/EA before and after up to 500 h of irradiation, where a clear displacement is visible since the first 100 h.

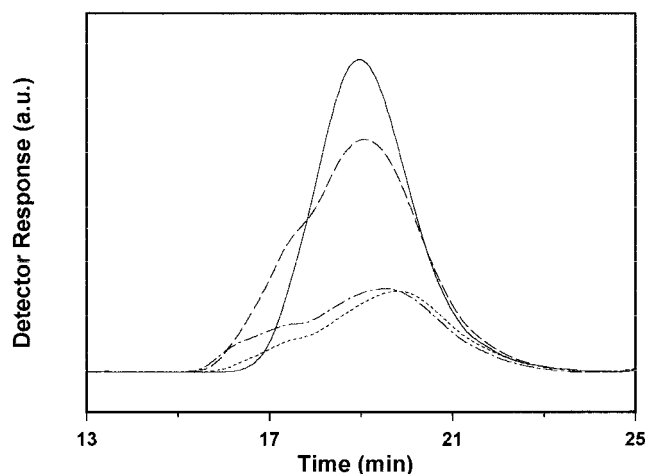


Figure 2 Size-exclusion chromatograms of BMA/EA before (solid line) and after treatment for 100 (dashed line), 200 (dash-dotted line), and 500 h (short-dashed line).

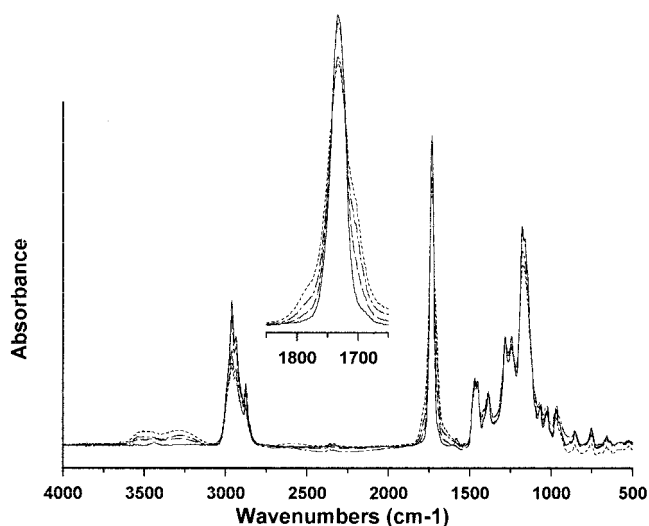


Figure 3 FTIR spectra of BMA/EA/TFEMA before (solid line) and after treatment for 600 (dashed line), 1000 (dash-dotted line), and 2000 h (short-dashed line).

Broadening toward shorter retention times indicated that degradation occurred since the first stages, with the occurrence of coupling and branching reactions producing higher molecular weight molecules. For treatments longer than 150 h insoluble polymer fractions were formed and the chromatograms mainly concern uncrosslinked chains. The $^1\text{H-NMR}$ analysis performed on the uncrosslinked fraction (soluble on CDCl_3) indicated a composition in EA richer than the initial; the composition changed from BMA/EA 62/38 to 58/42 mol %.

The extent of structural modifications induced by photoaging was almost identical in the two copolymers. Some results relative to the spectral changes in the infrared region in BMA/EA/TFEMA are shown in Figure 3, and the main features are the following: A progressive growth in the hydroxyl region between 3600 and 3100 cm^{-1} , with two main components centered at about 3500 and 3250 cm^{-1} attributed to alcohols and hydroperoxides, respectively.³³ The decrease

of the carbonyl ester absorption at about 1730 cm^{-1} during the light treatment was accompanied by the appearance of new carbonyl groups that contributed to the peak broadening, with the components at the lower wavenumber growing faster than those at higher wavenumbers. In particular, two principal components were recognizable around 1780 and 1700 cm^{-1} , which may be tentatively attributed to γ -lactone structures and acid groups, respectively. The spectra also showed a progressive decrease of the C—H stretching absorptions in the region 3000–2800 cm^{-1} , possibly indicative of the loss of aliphatic ester groups. Despite the structural changes, it is worth mentioning that the polymeric films remained transparent throughout the photoaging, without showing any evident yellowing or color formation, which would preclude the use for conservation treatments.

Comparisons of such results on BMA/EA and BMA/EA/TFEMA with those already reported for homopolymers of the corresponding co-units^{34,35} and for a series of acrylic copolymers (and Paraloid products) containing different amounts of BMA and TFEMA^{35–39} confirm that the overall stability was controlled by the unfluorinated comonomers, and in particular by the most abundant (i.e., BMA). Oxidation on the side chains of BMA units occurred through the typical pathway of hydrocarbon oxidation,⁴⁰ leading to the formation of labile secondary hydroperoxides, immediately photolyzed into alkoxy radicals.³⁴ Because of the high mobility of side chains such radicals may decay rapidly by crosslinking. On the other hand, the consequent increase of stiffness of the polymeric network makes other reactions competitive, such as the partial decomposition of the butyl esters, which lead to the development of acid groups,³⁸ visible in the IR spectra. Hypothesis of the mechanism is well known from the literature.^{34,35,37}

The faster formation of insolubles during the photoaging of both the BMA/EA-based copolymers compared with PBMA exposed to the same conditions (e.g., more than 50% gel content at 200 h against about

TABLE IV
Percentile Weight Variation $\Delta\%$ of Treated Stones

Acetone (%)	AIBN (%)	Feed composition (vol %)	$\Delta\%$	X (g/m ²)
30	4	BMA/EA 75/25	1.5 \pm 0.2	850 \pm 20
—	3	BMA/EA 75/25	1.5 \pm 0.2	850 \pm 20
—	3	BMA/EA 75/25 + 2 wt % Tecnoflon TN [®]	1.0 \pm 0.2	350 \pm 10
—	3	BMA/EA/TFEMA 67.5/22.5/10	1.3 \pm 0.2	450 \pm 20
—	3	BMA/EA/TFEMA 73/24.5/2.5	1.3 \pm 0.2	450 \pm 20
Solution of prepolymerized BMA/EA 75/25			0.2 \pm 0.02	60 \pm 10
Solution of prepolymerized BMA/EA 75/25 with 5 wt % Tecnoflon TN [®]			0.05 \pm 0.01	10 \pm 2

20% in PBMA³⁴) suggests that the photodegradation of EA units facilitates the first stages of BMA oxidation, probably by hydrogen abstraction on the lateral butyl groups from main-chain radicals. Moreover, the tertiary radicals formed on the EA units also accounts for the observed γ -lactone structures, whose development may occur through an intermolecular backbiting process.^{34,41} Obviously when the copolymer is present more deeply within the stone, it is not exposed to sunlight and therefore the photoaging will be reduced.

In conclusion, BMA/EA and BMA/EA/TFEMA showed a good light stability, comparable at least to that of acrylic commercial products actually in use for conservative treatments,³² with a negligible effect of the fluorinated monomer on the overall photodegradation behavior. The main effect of aging is the extensive formation of insoluble fractions by crosslinking, and even though the irreversibility is an unwanted characteristic of potentially applicable protection for the safeguarding of artifacts and structures of irreplaceable cultural heritage,⁴² the use of the investigated polymers as consolidants was not compromised. By contrast, the formation of a three-dimensional network after the consolidation treatment may be considered as a positive factor that facilitates its long-term durability.

In situ polymerization

The quantities of product absorbed by the stone at the completion of polymerization are summarized in Table IV. The $\Delta\%$ is 1.5% polymerizing BMA/EA in bulk and in solvent.

In the presence of a small quantity of Tecnoflon in the reaction system, the percentage of absorbed material by Finale stone decreases to 1.0%, attributed to a lower fluidity of the products because of the presence of preformed macromolecules. This is the reason that the third fluorinated monomer was added. With 2.5 and 10% of TFEMA $\Delta\%$ increases, compared to that of the sample with Tecnoflon.

By treating the stones with the preformed acrylic polymer with and without Tecnoflon, the $\Delta\%$ is very

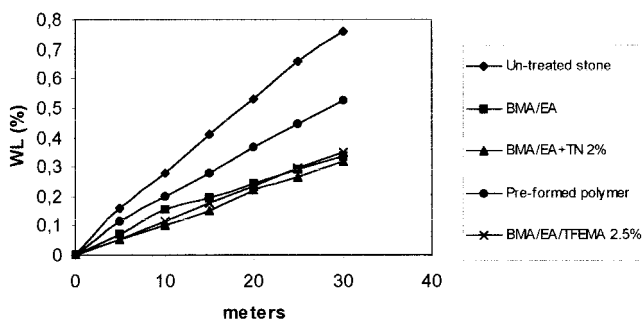


Figure 4 Abrasion test.

TABLE V
Aggregation Efficacy of the Products

Sample	EA (%)
BMA/EA 75/25	55 ± 2
BMA/EA 75/25 + 2 wt % Tecnoflon TN®	58 ± 2
BMA/EA/TFEMA 73/24.5/2.5	54 ± 2
Prepolymerized BMA/EA 75/25	30 ± 2

low. This is the evidence that with the traditional application method of consolidating products the polymer remains in the superficial layers, whereas with the *in situ* polymerization deeper penetration may be achieved.

Consolidating and protective properties

Given the high $\Delta\%$ value and the low T_g value, we predict that the *in situ* polymerized material will serve as a good consolidating and protective material for stones, as shown by the experimental results.

In Figure 4 abrasion test results are reported; the weight loss of the sample after 30 runs on the sandpaper is maximum for the untreated stone and minimum for the treated stone with *in situ* polymerized copolymers. After adding the Tecnoflon and 2,2,2-trifluoroethyl methacrylate, the behavior does not change. The efficacy of aggregation (see Table V) obtained with preformed BMA/EA applied in solution is 30%; using the *in situ* polymerized copolymers the EA increases to 55%, with a relative increase of roughly 50%.

The water capillary absorption test shows the protective properties of the different treatments: Figure 5 makes evident that the untreated stones rapidly absorb a great quantity of water, and this effect is reduced immediately by every treatment.

The values of the capillary absorption coefficient and of protective efficacy, calculated from the curves of Figure 5, are listed in Table VI. The capillary ab-

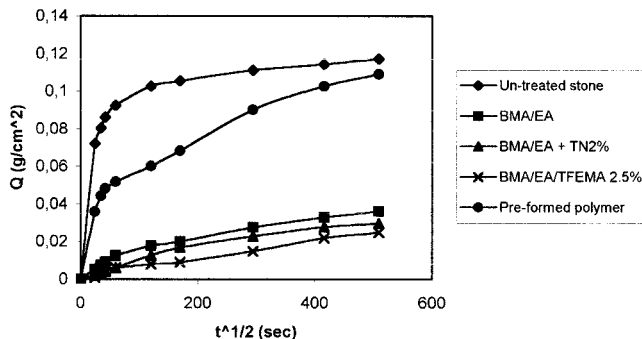


Figure 5 Water capillary absorption curves for Finale stone.

TABLE VI
Water Capillary Absorption Test Results

Sample	CA (g/cm ² t ^{1/2})	EP (%)
Untreated stone	15.4 (±0.02) × 10 ⁻⁴	—
BMA/EA 75/25	2.0 (±0.01) × 10 ⁻⁴	86 ± 0.1
BMA/EA 75/25 + 2 wt % Tecnoflon TN®	1.1 (±0.01) × 10 ⁻⁴	93 ± 0.1
BMA/EA/TFEMA 73/24.5/2.5	1.1 (±0.01) × 10 ⁻⁴	93 ± 0.2
Prepolymerized BMA/EA 75/25	8.8 (±0.02) × 10 ⁻⁴	44 ± 0.2

sorption coefficient with the preformed polymer is lower than that of the untreated stone, but higher than that in the case of *in situ* polymerization: this means that the polymer, present in small quantities only in the superficial layer, forms a continuous film that does not allow the water to penetrate inside the stone only for a short time; after 1 h of absorption the preformed polymer is efficient (see values of protective efficacy), but when the absorption is prolonged, the polymer does not show any protective efficacy.

The stones treated *in situ* with the presence of fluorine (in monomer end/or in polymer) are more resistant to water penetration than untreated stones.

The permeability to water vapor is maintained to acceptable values. The lower permeability is observed with the use of preformed polymers, even if the values are not too different, as shown in Table VII. This indicates that with *in situ* polymerization the stone porosity is only partially filled and the higher quantity of absorbed product means a higher penetration depth, whereas the prepolymerized polymer forms a superficial continuous film that reduces the evaporation of the water.

Reduction of permeability data show that the permeability to water vapor is maintained even if in smaller measure.

Finally, the values of the contact angle are listed in Table VIII; this measure is useful for evaluating the water repellence of different polymers.

The contact angles were measured on polymeric films, not on stone surfaces, to obtain more accurate measures, given that the effect of roughness and heterogeneity of the stone affect the results.⁴³

Films were obtained from polymer solutions in acetone at 5% in weight, by evaporation of the solvent

on a glass support; the investigated surfaces were those exposed to air. As foreseen, the samples containing fluorine atoms (even in low percentage) show higher contact angles.

CONCLUSIONS

The *in situ* polymerization of a copolymer butyl methacrylate/ethyl acrylate, a variation of the well-known Paraloid B72, fluorinated by various copolymers was investigated; we demonstrated that the vehiculation of monomers, instead of the preformed polymer, followed by a polymerization process inside the stone has the advantage of ensuring a better absorption of the polymer. In this way, the protective and consolidating properties on the Finale stone are improved over those of the same stone treated with a preformed polymer (actually this one remains confined to the more external layers).

At the service temperature, the chosen copolymer was above its glass-transition temperature and was therefore in the viscoelastic state. Because of its excellent adhesive characteristics, it makes the stone resistant to mechanical stresses.

By adding a fluorinated component to the monomer and initiator system the water repellence can be improved. For this reason we incorporated into the reaction mixture a low percentage of fluoropolymer. We chose the Tecnoflon TN copolymer because we had previously verified that it reaches a good level of mixing with acrylic polymer. Unfortunately, the addition of a preformed polymer in the system has some drawbacks, among them the decrease of penetration depth into the stone because of the high molecular weight of a constituent in the polymerizing mixing.

TABLE VII
Permeability to Water Vapor and Reduction of Permeability

Sample	P (g/m ² 24 h)	RP (%)
Untreated stone	30 ± 3	—
BMA/EA 75/25	20 ± 3	33
BMA/EA 75/25 + 2 wt % Tecnoflon TN®	15 ± 2	50
BMA/EA/TFEMA 73/24.5/2.5	17 ± 2	43
Prepolymerized BMA/EA 75/25	13 ± 2	57

TABLE VIII
Contact Angle Results on Finale Stone

Sample	α (°)	Standard deviation
Film BMA/EA 75/25	86	5
Film BMA/EA/TFEMA 73/24.5/2.5	93	5
Film BMA/EA/TFEMA 67.5/22.5/10	95	5
Film BMA/EA + 2 wt % Tecnoflon TN®	93	6

This research has been focused on finding a good method for introducing a fluorine atom in the polymer without impairing the penetration depth. By polymerizing *in situ* a terpolymer that (beside the two acrylic monomers) contains in the third monomer a fluorinated function, we obtained an improvement in the protective characteristics of material and good consolidating characteristics. The research was carried out with the goal of finding the cheapest fluorinated monomer able to confer, at the lowest contents, the best performances.

BMA/EA and BMA/EA/TFEMA showed a good light stability, at least comparable with that of acrylic commercial products actually in use for conservative treatments (i.e., Paraloid). The main effect of aging is the extensive formation of insoluble fractions by crosslinking, and even though the irreversibility is an unwanted characteristic of potentially applicable protection for the safeguarding of artifacts and structures of irreplaceable cultural heritage, the use of the investigated polymers as consolidants was not compromised. The formation of a three-dimensional network, not free to flow, after the consolidation treatment may be considered positively, leading to a facilitation of long-term durability; and the reduction of reversibility, concerning the consolidation, is a negligible factor.

Overall, these results are satisfactory and we therefore can conclude that the *in situ* polymerization technique deserves further attention.

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