PAT

Frontal polymerization of acrylic monomers for the consolidation of stone

Silvia Vicini[1]*, Alberto Mariani[2], Elisabetta Princi[1], Simone Bidali[2], Silvia Pincin[1], Stefano Fiori[2], Enrico Pedemonte[1] and Antonio Brunetti[3]

[1]Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy
[2]Department of Chemistry, University of Sassari, and local INSTM Research Unit, Via Vienna 2, 07100 Sassari, Italy
[3]Department of Mathematics and Physics, University of Sassari, Via Vienna 2, 07100 Sassari, Italy

Polymeric products are largely used for consolidation of stone in the field of cultural heritage. Nevertheless, the main problem of polymeric compounds is related to their macromolecular nature, it being difficult for a polymer to penetrate inside the pores which may have a very small diameter. These considerations are the starting points for *in situ* polymerization. According to this technique, not the pre-formed polymer, but the monomer is introduced into the stone and it is polymerized *in situ* in a subsequent step.

Frontal polymerization (FP) is a particular technique in which the heat released by the exothermal reaction of monomer to polymer conversion is exploited to promote the formation of a hot traveling front able to propagate and self-sustain the reaction.

In the present work, FP is performed inside the pores of the stone and the results lead to the conclusion that the hot front is still active in the presence of an inorganic material which dissipates partially the heat released during the polymerization. In addition some recent applications of FP are discussed in comparison with the traditional polymerization for the *in situ* consolidation and protection of stones. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: frontal polymerization; copolymerization; fluoropolymers; adhesion; stone consolidation and protection

INTRODUCTION

The use of polymeric materials for the consolidation of the stone surface of buildings of relevant cultural importance is nowadays generally accepted.[1]

Polymer products show an important advantage if compared to the inorganic materials: if correctly chosen, they may also have a protective activity, thanks to their water-repellent properties thus achieving two results at the same time, with an improved feasibility of the restoration treatment.

However, some of their properties 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 this is not satisfactory and small solicitations are sufficient to detach the polymer from the matrix.

Nevertheless, the main problem of polymeric compounds is related to their macromolecular nature. While inorganic materials are made out of substances with very small molecules, macromolecules have dimensions that increase with the square root of the molecular weight.[2,3] Therefore, it is difficult for a polymeric compound to penetrate inside the

stone since its pores may have too small a diameter (also less than 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 having only a protective action but not for a material that must also be a consolidating product, because in the latter case deep penetration is required.

These considerations are the starting points for *in situ* polymerization.[4] According to such a technique, the monomer is introduced in the stone instead of the polymer and it is polymerized *in situ* in a subsequent step. Obviously, monomers being 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 the traditional *in situ* polymerization has been explored in a previous work, by performing the synthesis of an ethyl methacrylate/methyl acrylate (EMA/MA) copolymer;[5] the ratio between the monomer units of EMA and MA (70/30 wt%) has purposely been kept similar to a commercially available product (Paraloid B72®, by Röhm and Haas),[6,7] which is widely employed in the field of restoration. Then, the potentialities of such an approach have been considered for copolymers based on butyl methacrylate with ethyl acrylate,[8] with adjusted glass transition temperature (T_g), in order to improve the polymer adhesion to the stone and therefore to reduce the possibility of fracture.[9]

*Correspondence to: S. Vicini, Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy.
E-mail: sivicini@chimica.unige.it

In this research, a new method of *in situ* polymerization is studied: the frontal polymerization (FP).[10] FP exploits the heat production due to the exothermicity of the reaction itself and its dispersion by thermal conduction. If the amount of dissipated heat is not too large, a sufficient amount of energy able to induce the polymerization of the monomer close to the hot zone is provided. The result is the formation of a hot polymerization front capable of self-sustaining and propagating through the reactor.[11,12] It is evident that, if FP occurs through a stone sample, the monomer must fill its pores and they must be in contact with each other to permit the hot front to propagate. For this reason, and in order to predict the possible efficiency of the consolidation treatment, it is mandatory to know to what extent the monomer is able to fill the stone pores and if the final FP allows for an optimal polymer dispersion inside the material. In this sense, X-ray tomography is proposed as a suitable technique that can provide information about the monomer propagation inside porous material.[13]

The first studies on FP were performed in the former USSR on methyl methacrylate that was polymerized under drastic pressure conditions (>3000 atm).[14] Lately, several other vinyl monomers have been polymerized at ambient pressure by Pojman and coworkers.[10,11,15] Furthermore, FP has been applied to the curing process of epoxy-based materials.[16–18]

FP might represent a possible valid alternative technique to obtain polymeric products, having practical and economical advantages, also because high conversions are obtained in a short time.

The lack of heat sources, generally requested for carrying out many traditional chemical reactions, results in many advantages in terms of cost and environmental impact. Furthermore, FP is generally (but not exclusively) applicable to solvent-free systems. Monomers can be used as received, i.e. without the usual elimination of the dissolved inhibitor.[5] Moreover, as mentioned earlier high conversions are often found, thus making the final common purification procedures not necessary.

Following all of these indications, this paper reports the assessment of the effectiveness of poly(1,6-hexanediole diacrylate) (PHDDA) as a consolidant for stone, in the framework of a systematic approach to the problem.

Recently, FP has been applied to the consolidation of porous materials (i.e. stones, woods, textiles, papers), in particular—but not only—those having a historical-artistic interest. In this work the efficiencies of products synthesized *in situ* and variously fluorinated have been comparatively evaluated in terms of vapor and water permeability and consolidation on a selected substrate: the Finale stone (see Experimental section).

It is well known that the introduction of fluorine atoms into polymer structures has the effect of improving their chemical, thermal, and photochemical stability,[19] due 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 brought about by the fluorinated groups.[20–23] This characteristic has been exploited in the present research by the introduction in the polymerizing mixture (together with

HDDA) of a cheap and commercially available fluorinated monomer, i.e. 2,2,2-trifluoroethyl methacrylate (TFEMA).

EXPERIMENTAL

Materials

Monomers employed in this research were commercial products from Aldrich. The polymerization initiator (AIBN: 2,2′-azobisisobutyronitrile) came from Fluka. Deionized water was used throughout the work.

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

- high porosity, in order to reproduce a material degraded by the physical and chemical agents;
- easily supplied in standardized forms.

For these reasons a calcareous sedimentary stone of biological origin was used, easily available in Liguria, Italy, called ''Pietra di Finale''.[24] This is found in four different formations, differing in the percentage of the impurities and fragments; they also have different colors (from white to roseate) and different physical characteristics. The pale variety of the Finale stone was used, which presents a fairly high porosity.[25] Sample size was: 5 cm × 5 cm × 2 cm.

In vitro traditional polymerization

The polymerizations of HDDA and HDDA/TFEMA (feed composition: 97.5/2.5 vol%) was carried out outside the stone (*in vitro*). The reaction was performed in solution and in the absence of solvent at 50°C with AIBN (3 wt%), following the conventional mechanism of free-radical polymerization. The employed technique has already been described.[3]

In situ traditional and frontal polymerizations (FPs)

The *in situ* polymerizations were carried out in bulk and the experimental procedure consists of two steps:

(1) Absorption: the stone absorbs by capillary action so the different mixtures must be polymerized (HDDA and HDDA/TFEMA) by putting 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 hr.
(2) Polymerizations: (i) the FP was carried out by heating only one side of the sample, by placing one of the stone faces onto a hot plate ($T \cong 200$°C). Immediately after the formation of an ascending hot polymerization front, the sample was removed from the hot plate in order to avoid the occurrence of spontaneous polymerization simultaneously to FP. (ii) In order to compare the results of the FP with those obtained from the traditional *in situ* polymerization, a series of stone samples were polymerized for 24 hr in an oven at 50°C.

Evaluation of treatments

To evaluate the consolidating and protective properties of the *in situ* obtained polymers, some tests were carried out. Each test was performed on three specimens (5 cm × 5 cm × 2 cm) of the following Finale stone samples, i.e.

- untreated samples (blank);
- samples containing the *in situ* traditionally polymerized polymer HDDA;
- samples containing the *in situ* traditionally polymerized copolymer HDDA/TFEMA;
- samples containing the frontally polymerized polymer HDDA;
- samples containing the frontally polymerized copolymer HDDA/TFEMA.

Preliminarily, the quantity of absorbed product was evaluated using the following equations:

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

where M_0 is the weight of the untreated stone (in grams) M_f is the weight of the stone after treatment (in grams) and

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

where S is the surface of the stone (in cm^2).

The reproducibility of the measurements is sufficient in spite of the irregular porosity of the stone and the deviation is within 5%.

The penetration depth should be as high as possible and the purpose of *in situ* polymerization is to increase significantly this value.

The consolidating properties were evaluated using an original instrument, made up using a wood rail (100 cm in length × 5 cm in width) having a strip of sandpaper (granulometry: 60 mesh) on the top. The sample was set with the largest base (5 cm × 5 cm) on the rail and loaded with a weight of 2.0 kg; run 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 percent (WL%) calculated.

The test allows the 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 percent of three untreated stones after 30 m, WL_t is the average value of the weight loss percent of three treated stones after 30 m. The quantity of removed material is a function of the aggregation of the sample, and so it is different for treated and untreated samples.

The protective properties were evaluated by three tests:

(a) capillary water absorption;
(b) water absorption by complete immersion;
(c) permeability to water vapor.

Capillary water absorption

This determination was carried out using the gravimetric sorption technique, according to the Normal protocol.[26] The stone specimen is laid on a filter paper pad *ca.* 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 is determined by weighing the specimen after 10, 20, and 30 min and 1, 2, 4, 8, 24, 48, 72 and 96 hr, 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 follows:

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

where M_i is the specimen mass (in grams) at time t_i (in seconds), M_0 is the dry specimen mass (in grams), and S is the contact surface (in cm^2).

The Q_i values (in g/cm^2) are plotted against the square root of time ($t^{1/2}$) to give the capillary 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 efficiency, EP%:

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

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

Water absorption by complete immersion

The measurements of water absorption by complete immersion have been carried out by using the gravimetric method, according to the Normal protocol.[27] The stone specimen is completely immersed in deionized water, at room pressure and temperature. The amount of absorbed water is determined by weighing the specimen after 10 and 30 min and 1, 4, 6, 8, 24 and 48 hr.

The amount of absorbed water Q_i, at the time t_i, is defined as follows:

$$Q_i = [(M_i - M_0)/M_0] \times 100$$

where M_i is the specimen mass (in grams) at time t_i, M_0 is the dry specimen mass (in grams).

The Q_i values (in percent) are plotted versus t_i (in hours), to give the absorption curve. The results can also be expressed as capacity of imbibition CI%:

$$CI\% = [(M_{max} - M_0)/M_0] \times 100$$

where M_{max} is the specimen mass (in grams) at the end of the test and M_0 is the dry specimen mass (in grams).

Permeability to water vapor

This determination was carried out according to the corresponding Normal protocol[28] on 5 cm × 5 cm × 1 cm specimens, using a measurement cell consisting of a cylindrical poly(vinyl chloride) (PVC) chamber with an open top fitted with an O-ring rubber seal, where the stone specimen is employed as the lid of the chamber; the chamber is sealed with the lid by means of an aluminum flange with an O-ring.

The cell is partially filled with deionized water, therefore allowing measurement by gravimetry of the amount of water vapor that diffuses through the stone specimen with a fixed thickness (1 cm) between two parallel surfaces. The test is carried out at constant temperature (20 ± 0.5°C), with the cell placed into a desiccator. Therefore, the driving force for the diffusion of water vapor is the constant difference between the water vapor pressure inside and outside the cell (in the presence of activated silica gel desiccant). The permeability is monitored by determining the weight decrease per surface unit (S, in m^2) in the unit time (24 hr):

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

where M_i is the weight system (cell and stone) at i-day (in grams).

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

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

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

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

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

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

RESULTS AND DISCUSSION

HDDA-based polymers and copolymers obtained *in vitro* are crosslinked because of the two acrylic groups present in the monomeric units, therefore it was not possible to solubilize them for the characterization of molecular weight. Moreover, no T_g value was observable.

The quantities of product present in the stones at the end of the *in situ* polymerizations are summarized in Table 1 and are in the range 6–8 wt%. Those of frontally polymerized samples, with or without fluorinated monomer, are always larger than those treated by traditional polymerization and the reason is the complete conversion of the monomers in the first case. Indeed, no unreacted monomer was found by solvent extraction on the grinded stone. This is the first outstanding result of the research since it was questionable if the FP may take place also in the presence of large amounts of an inert material which absorbs partially the heat developed in the polymerization reaction.

As reported elsewhere, $\Delta\%$ of stones treated with the pre-formed polymer is very low (0.3%).[5] 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 deep penetration can be reached.

These considerations are very important when the performances will be evaluated, since the properties are obviously strongly affected by the amount of the polymer in the stone. On the base of the high $\Delta\%$ value, it can be foreseen that the

Table 1. Percentile weight variation, $\Delta\%$, of *in situ* treated stones

Samples	$\Delta\%$	X (g/m^2)
HDDA (FP)	8 ± 0.3	2789 ± 20
HDDA (traditional)	7 ± 0.3	2453 ± 20
HDDA/TFEMA (FP)	7 ± 0.2	2686 ± 10
HDDA/TFEMA (traditional)	6 ± 0.3	2414 ± 20
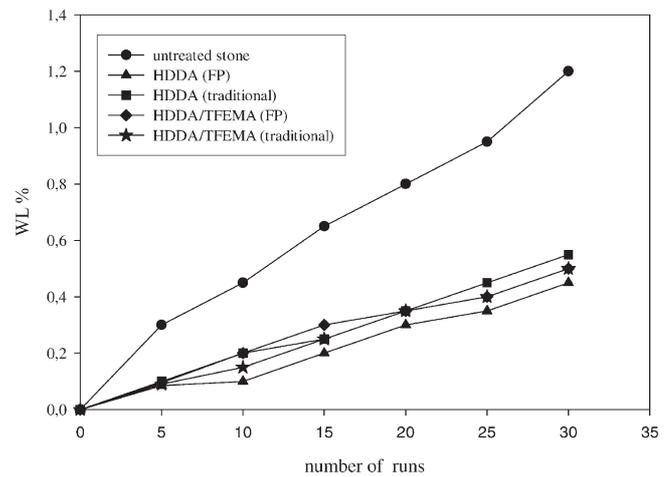
Figure 1. Abrasion test.

Table 2. Efficacy of aggregation (EA) of the products

Samples	EA (%)
HDDA (FP)	62 ± 2
HDDA (traditional)	54 ± 2
HDDA/TFEMA (FP)	58 ± 2
HDDA/TFEMA (traditional)	58 ± 2

in situ obtained polymer materials will be good consolidating and protective products for stones, as supported by the experimental results. The treated stones, due to the large amount of polymer inside, could be considered as a particular composite material.

In Fig. 1, abrasion test results are reported. The weight loss of the sample after 30 runs on the sand paper is maximum for the untreated stone and very low for all the stones treated with polymers and copolymers; therefore the two treatments of *in situ* polymerization are excellent from the consolidation point of view. The efficacy of aggregation (see Table 2) is comparable for all the samples.

The capillary water absorption test shows the protective properties of the different treatments: Fig. 2 makes evident that the untreated stones absorb rapidly a large quantity of water, and this effect is reduced immediately by every treatment.
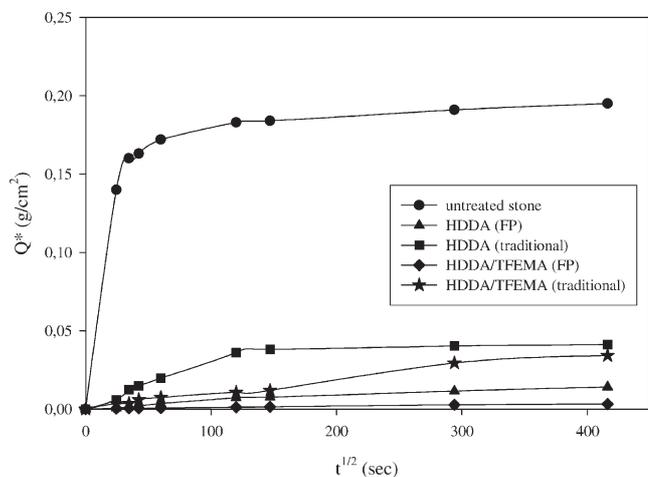
Figure 2. Water capillary absorption curves for Finale stone.

Table 3. Capillary water absorption test results

Samples	CA (g/cm^2 $t^{1/2}$)	EP (%)
Untreated stone	$2.3\ (\pm0.02) \times 10^{-4}$	—
HDDA (FP)	$0.35\ (\pm0.01) \times 10^{-4}$	98 ± 0.1
HDDA (traditional)	$0.94\ (\pm0.01) \times 10^{-4}$	88 ± 0.1
HDDA/TFEMA (FP)	$0.078\ (\pm0.001) \times 10^{-4}$	99 ± 0.2
HDDA/TFEMA (traditional)	$0.87\ (\pm0.01) \times 10^{-4}$	95 ± 0.2
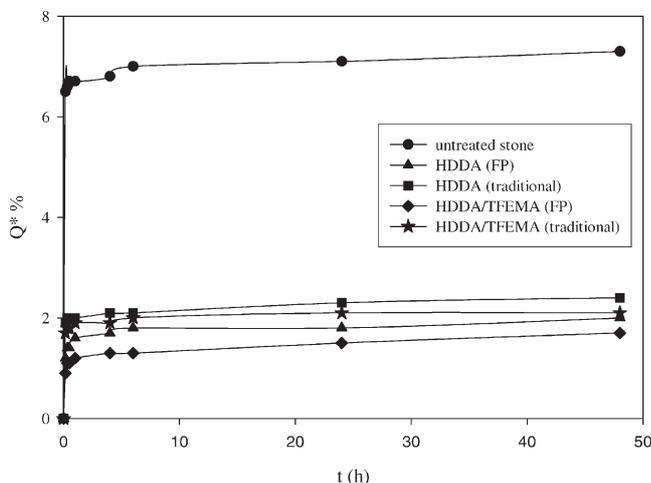
Figure 3. Water absorption by complete immersion curves for Finale stone.

The values of the capillary absorption coefficient and of protective efficiency, calculated from the curves of Fig. 2, are listed in Table 3. The capillary absorption coefficient with traditionally polymerized polymers is lower than that of the untreated stone, but higher than in the case of FP; all the value of protective efficiency are very high, particularly in the case of the copolymer polymerized frontally in the presence of the fluorinated monomer (99%). These results are coherent with the large amount of polymer present in the stones; the stones treated with fluorine containing materials are more resistant to water penetration than the other ones.

The same conclusions are obtained by considering the results of the water absorption by the total immersion test (Fig. 3). The untreated samples absorb a large amount of water, especially in the first hours, and quickly reach the saturation value. In the treated samples the quantity of absorbed water is much smaller and, once again, the FP guarantees a larger efficient protection compared to the traditionally polymerized polymer, because of the higher amount of polymer inside the stone, that coat the surface of pores.

The values of the soakage capacity, CI, expressed as the percentage of the absorbed water at the end of the test, are listed in Table 4. It is interesting to point out that, from the

Table 4. Water absorption by complete immersion test results

Samples	CI (%)
Untreated stone	7.3
HDDA (FP)	2.0
HDDA (traditional)	2.4
HDDA/TFEMA (FP)	1.7
HDDA/TFEMA (traditional)	2.1

Table 5. Permeability (*P*) to water vapor and reduction of permeability (RP)

Samples	P (g/m^2 per 24 hr)	RP (%)
Untreated stone	47 ± 2	—
HDDA (FP)	2.5 ± 0.2	95
HDDA (traditional)	4.8 ± 0.2	90
HDDA/TFEMA (FP)	2.3 ± 0.2	95
HDDA/TFEMA (traditional)	4.4 ± 0.2	91

experiments of total immersion, it can be concluded that the polymer, during the polymerization, reaches all the surfaces of the sample and it is not concentrated only on the surface in which the polymerization starts.

As far as the permeability to water vapor is concerned, the value for permeability of the protective system based on both types of polymerization indicates that these systems have very low vapor permeability, as shown in Table 5. The lowest permeability is observed with the use of frontally polymerized polymers, even if the values are not too different from those obtained with traditionally obtained polymers. Also the reduction of permeability reaches a very high percentage (90–95%) and confirms that the permeability to water vapor is very low. This indicates that with *in situ* polymerizations stone porosity is almost completely filled and the larger quantity of absorbed product indicates a larger penetration depth.

CONCLUSIONS

Two alternative ways of *in situ* polymerization inside stones have been suggested: traditional polymerization and FP of HDDA and HDDA/TFEMA copolymer. It has been demonstrated that the absorption of monomers, instead of the pre-formed polymer, followed by a polymerization process inside the stone, has the advantage to ensure a better absorption of the polymer and a deeper penetration in the substrate.

Moreover FP represents an interesting synthesis technique having practical and economical advantages, as the high reaction rate and conversion. This research demonstrates that FP can be performed successfully also when a material, which absorbs partially the heat developed by the polymerization, is present in relatively large amounts of weight.

In this way, the protective and consolidating properties of the stone are improved, in respect to the traditional application method of a pre-formed polymer, which remains confined only into the more external layers.

By adding a fluorinated component to the monomer/initiator system, water repellence can be improved. For this reason a low percentage of fluorinated monomer was incorporated into the reaction mixture and an improvement on the protective efficacy of the material together with good consolidating characteristics were obtained.

The main effect of using a monomer with two double bonds in the molecule is the extensive formation of insoluble polymer by crosslinking; even though the irreversibility is an unwanted characteristic of materials potentially applicable for the safeguard of cultural heritage, the use of the

investigated polymers as consolidants is 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; however, the reduction of reversibility in the consolidation treatment is a negligible factor. Overall these results are satisfactory and therefore it can be concluded that the *in situ* traditional polymerization and FP techniques deserve further attention.

REFERENCES

1. Amoroso GG, Fassina V. *Stone Decay and Conservation*. Elsevier: Losanna, 1983.
2. Flory PJ. *Principles of Polymer Chemistry*. Cornell University Press: Ithaca, NY, 1962.
3. Vicini S, Princi E, Moggi G, Pedemonte E. Consolidation and protection of stone manufactered object of artistic interest with polymeric materials prepared by *in situ* polymerization. *La Chimica e l'Industria* 1999; **81**: 1013.
4. Vicini S, Margutti S, Moggi G, Pedemonte E. *In situ* copolymerisation of ethylmethacrylate and methylacrylate for the restoration of stone artefacts. *J. Cultural Heritage* 2001; **2**: 143.
5. Vicini S, Margutti S, Princi E, Moggi G, Pedemonte E. *In situ* copolymerization for the consolidation of stone artefacts. *Macromol. Chem. Phys.* 2002; **203**: 1413.
6. www.rohmhaas.com/coatings/ (last visited 02/02/2005).
7. Chiantore O, Lazzari M. Photo-oxidative stability of paraloid acrylic protective polymers. *Polymer* 2001; **42**: 17.
8. Vicini S, Princi E, Pedemonte E, Lazzari M, Chiantore O. *In situ* polymerisation of unfluorinated and fluorinated acrylic copolymers for the conservation of stone. *J. Appl. Polym. Sci.* 2004; **91**: 3202.
9. Ferry JD. *Viscoelastic Properties of Polymer* (3rd edn). John Wiley: New York, 1980.
10. Pojman JA. Traveling fronts of methacrylic acid polymerization. *J. Am. Chem. Soc.* 1991; **113**: 6284.
11. Khan AM, Pojman JA. The use of frontal polymerization in polymer synthesis. *Trends Polym. Sci.* 1996; **4**: 253.
12. Mariani A, Fiori S, Chekanov Y, Pojman JA. Frontal ring-opening metathesis polymerization of dicyclopentadiene. *Macromolecules* 2001; **34**: 6539.
13. Brunetti A, Princi E, Vicini S, Pincin S, Bidali S, Mariani A. Visualization of monomer and polymer inside porous stones by using X-ray tomography. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 2004; **222**: 235–241.
14. Chechilo NM, Khvilivitskii RJ, Enikolopyan NS. On the phenomenon of polymerization reaction spreading. *Dokl. Akad. Nauk SSSR* 1972; **204**: 1180.
15. Fortenberry DI, Pojman JA. Solvent-free synthesis of polyacrylamide by frontal polymerization. *J. Polym. Sci., Part A: Polym Chem.* 2000; **38**: 1129.
16. Chekanov Y, Arrington D, Brust G, Pojman JA. Frontal curing of epoxy resin: comparison of mechanical and thermal properties to batch cured materials. *J. Appl. Polym. Sci.* 1997; **66**: 1209.
17. Kim C, Teng H, Tucker CL, White SR. The continuous curing process for thermoset polymer composites. Part 1: Modeling and demonstration. *J. Comp. Mater.* 1995; **29**: 1222.
18. Pojman JA, Elcan W, Khan AM, Mathias L. Binary polymerization fronts: a new method to produce simultaneous interpenetrating polymer networks (SINs). *J. Polym. Sci., Part A: Polym Chem.* 1997; **35**: 227.
19. Brady RF, Laronson C. Elastomeric fluorinated polyurethane coatings for nontoxic fouling control. *Biofouling* 2003; **19**: 63.
20. Brewis DM. Adhesion to polymers: how important are weak boundary layers? *Int. J. Adhesion & Adhesives* 1993; **13**: 251.
21. Castelvetro V, Aglietto M, Montagnini di Mirabello L, Toniolo L, Peruzzi R, Chiantore O. Adapting the properties of new fluorinated acrylic polymers to suit the conservation of ancient monuments. *Surface Coat. Intern.* 1998; **11**: 551.
22. Ciardelli F, Aglietto M, Montagnini di Mirabello L, Passaglia E, Giancristoforo S, Castelvetro V, Ruggeri G. New fluorinated acrylic polymers for improving weatherability of building stone materials. *Prog. Org. Coat.* 1997; **15**: 43.
23. Alessandrini G, Aglietto M, Castelvetro V, Ciardelli F, Peruzzi R, Toniolo L. Comparative evaluation of fluorinated and unfluorinated acrylic copolymers as water-repellent coating material for stone. *J. Appl. Polym. Sci.* 2000; **76**: 962.
24. Carpene' F. *Le meraviglie della Pietra di Finale*. Bacchetta Ed: Alberga, 1997.
25. Vicini S, Princi E, Gattorno S, Massa B, Pedemonte E. Pietra di Finale: caratterizzazione petrografia e problemi di reversibilità nel consolidamento mediante polimerizzazione *in situ*. Proceedings of the XIX Convegno Internazionale Scienza e Beni Culturali ''La reversibilità nel restauro'', Bressanone, 2003; 243.
26. Normal Protocol 11/85. *Water Absorption by Capillarity—Capillarity Absorption Coefficient*. ICR-CNR: Rome, 1986.
27. Normal Protocol 7/81. *Water Absorption by Complete Immersion—Capacity of Imbibition*. ICR-CNR: Rome, 1981.
28. Normal Protocol 21/85. *Water Vapour Permeability*. ICR-CNR: Rome, 1986.