

NEW POLYMER ARCHITECTURES FOR ARCHITECTURAL STONE PRESERVATION

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Abstract

A series of multifunctional polymeric systems have been designed, synthesized and their effectiveness in modifying the surface properties of different stone types have been evaluated. Both the synthetic strategy and the design of the macromolecular structures are aimed at achieving maximum flexibility in the introduction of structural features that are required to provide the resulting polymers with a range of potential properties. For this purpose, the controlled free radical polymerization of acrylic monomers by the so-called RAFT (Reversible Addition Fragmentation Transfer) technique has been adopted to obtain amphiphilic block copolymers. These may be used either as such in the modification of aqueous dispersions of inorganic nanoparticles (silica, titania, zirconia, zinc oxide among others), resulting in hybrid nanocomposite treatment materials, or as self-assembling reactive precursors for *ab initio* emulsion polymerizations, leading to the formation of colloidal aqueous dispersions of nanostructured multifunctional polymer nanoparticles. Among the innovative features of the polymers under investigation, the self-stabilisation against photooxidative degradation is worth mentioning as the durability of organic polymers is a well-known open issue in conservation. To achieve enhanced stability, free radical scavenging groups such as Hindered Amine Light Stabilizers (HALS) are introduced in the polymer structure through copolymerization with HALS derivatives. In addition, combination of polymers and UV-blocking inorganic particles (ZnO, TiO₂) are also expected to greatly enhance durability. These polymeric materials, and other presently under development, are intended as components of either protective or consolidant treatments to be tested first at a lab scale on various stones (both carbonatic and silicatic), then in situ on 5 different cathedrals distributed throughout Europe and on a contemporary opera theatre.

Keywords: block copolymer, hybrid latex, self-stabilisation, protection, consolidation

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1. Introduction

The stone materials undergo different kinds of alterations and degradation upon aging due to the different chemical, physical and mechanical characteristics of the stone and to the peculiar outdoor exposure. In the EU H2020 “NanoCathedral” project launched in 2015 five different medieval cathedrals and a contemporary opera theatre (Fig. 1) were selected as representative of both different macro- and micro-climatic conditions - continental vs. coastal; arid vs. humid - and different lithotypes - limestones, sandstones and marbles.

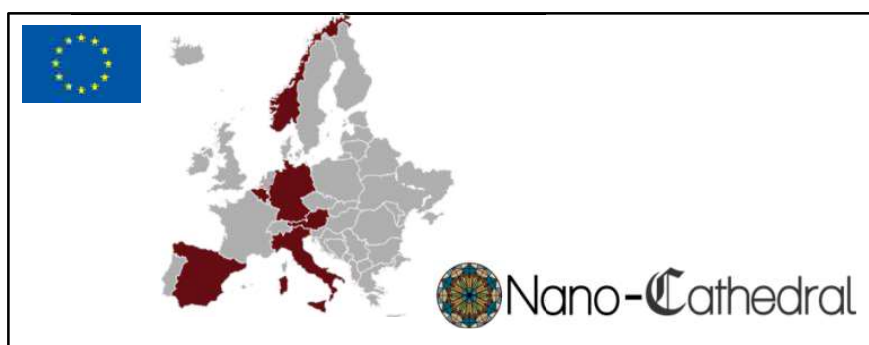


Fig. 1: Selected cathedrals within the “Nanocathedral” H2020 project: Pisa (Italy) and Santa María of Vitoria-Gasteiz (Spain) exposed to south European climate in coastal and continental regions, respectively; Sint-Baafs (Ghent, Belgium), St. Peter and Mary (Cologne, Germany) and St. Stephen (Wien, Austria) exposed to North European climate in either coastal or continental regions. Oslo Opera House, dipping into the North Sea.

The project aims at providing innovative consolidant and protective products tailored for the specific stone-environment combination, while granting improved effectiveness and durability. In particular, a wide range of inorganic nanoparticles, innovative polymeric structures, and their hybrid combinations are being investigated. The best products and formulations, selected according to their performance and durability tests performed in three different laboratories and on stone specimens representative of those present in the different monumental buildings (fig. 1), will be applied during the second year of the three-year project on the participating Cathedrals for in situ evaluation.

A key requirement for *consolidants* is its effective penetration by capillarity into the stone porous network; this is often not achieved, as shown by the failure of many past consolidation treatments causing damage by formation of surface scales. Lack of chemical/physical compatibility or uncontrolled reactivity with the stone substrate is another reason of failure; poor durability of the consolidant a third one. Last but obviously not least, a consolidant material has to perform its main role of strengthening the micro-structure of the decayed stone by replacing lost original mineral bridges, partially recovering lost mechanical properties, and in some cases even converting unstable material into stable one (e.g. soluble into insoluble salts). Several reviews report on the state of art in stone consolidation (Clifton, 1980; Doehne and Price, 2010). Alkoxysilanes are currently the most commonly used consolidating materials, followed by acrylics. While the former may perform poorly due to bridging capacity limited to narrow fissures, long term shrinkage causing the formation of a secondary porosity, hydrolytic instability and poor chemical affinity with carbonatic stones, acrylics may develop better bridging properties but, as most organic polymers, their durability is poor and degradation products may be detrimental to the stone substrate.

Novel nano-materials may overcome penetration depth issues, while their extremely large surface area may promote the reactivity required to build up cohesive and adhesive forces. Nano-lime systems, also applied in combination with alkoxysilane treatments, have shown encouraging results, although the penetration and durability of such treatment has not been clearly demonstrated yet (Daehne and Herm, 2013). The so-called (nano)particle modified consolidant (PMC), typically based on tetraethoxysilane (TEOS) formulations with silica nanoparticles, can reduce the internal stone damages caused by the shrinkage and cracking during sol-gel condensation of TEOS (Ksinopoulou *et al.*, 2016). However, shortcomings are still related to the hydrolytic sensitivity and poor control of the time evolution of the consolidant nanophase during the sol-gel process. On the other hand other types of inorganic nanoparticles (e.g. Ti, Zn, Al, Si oxides or hydroxides) and hybrid organic-inorganic systems have been much less extensively investigated, although they may provide additional useful features such as biocidal (Gómez-Ortiz *et al.*, 2013) and self-cleaning properties, synergistic mechanical reinforcement, hydrophobicity, etc..

When dealing with hydrophobic *protection* the main open issues are durability inertness towards the stone substrate and lack of undesired aesthetic modifications upon and after application. Even in this case the limited durability of organic polymers is raising major objections, among conservators, against their application, although they are undoubtedly superior materials in providing hydrophobic and even self-cleaning surfaces. Even in this case, however, novel polymeric, hybrid or nanocomposite systems may provide solutions to overcome these drawbacks and even introduce additional useful features such as e.g. biocidal activity (van der Werf *et al.*, 2015). Among the various materials under development within the H2020 Nanocathedral project, here the design and synthetic approach to novel polymeric structures and their water based formulations will be presented, along with the preliminary results concerning their characterization and the evaluation of their performance and durability.

2. Approach and Results

2.1. Design of multifunctional polymer structures

The underlying criteria for the newly developed polymers are:

- a) A synthetic approach that may allow easy adaptation of the polymer structure according to the specific requirements of either consolidation or protection;
- b) Self-dispersibility in water (i.e. without added low molecular weight surfactants) in the form of nanoparticles with controllable (< 100 nm) size, for solvent-free application and effective penetration within the porous stone network;
- c) Functional groups for enhanced durability, water repellency, specific interaction and binding with inorganic nanoparticles (for nanocomposite treating materials) and with the stone substrate, respectively.

For such purposes, a synthetic scheme for multifunctional acrylic copolymers based on the controlled RAFT (Radical Addition–Fragmentation-Transfer) free radical polymerization is adopted. The relatively recent RAFT technique (Wang A.R. and Zhu S., 2003) has become very popular in recent years due to its tolerance towards most functional groups (thus allowing the synthesis of multifunctional polymers) and solvents (from hydrocarbon to water). Besides, the so-called “ab initio” RAFT emulsion polymerisation, may be

performed in “soapless” conditions (without added surfactant) by using amphiphilic RAFT mediators, leading to the formation of amphiphilic block copolymers self-assembled into nanoparticles of controlled size (typically 50-150 nm) (Chenal *et al.*, 2013).

With the above approach, water-based polymer dispersions with controlled composition and a range of functional groups have been prepared, for desirable properties such as:

- colloidal stability (for extended shelf life and easy application), by using a RAFT mediator leading to the formation of polymers with a short “block” of either poly(acrylic acid) (PAA) or poly(ethylene oxide) (PEO) at one chain end;
- adhesivity by incorporation of comonomers with either Ca^{2+} binding (e.g. carboxylate, for carbonatic stones) or sol-gel reactive (e.g. trialkoxysilyl groups for specific bonding to silicatic stones) functional groups;
- film cohesivity, by balancing the main copolymer composition (methyl methacrylate/butyl acrylate) for a polymer glass transition, T_g , slightly below room temperature, while keeping the polymer photooxidative sensitivity at a minimum;
- self-stabilisation against photo-oxidative aging, by incorporation of HALS group in the side chain (stabilisation against UV-induced photooxidation is based on a cyclic deactivation of photogenerated free radicals and peroxiradicals, followed by regeneration of the free-radical scavenging nitroxyl-amine active species).
- water repellency, by introduction of semifluorinated comonomers (in progress).

2.2. Polymer synthesis

The general synthetic scheme starts with an amphiphilic trithiocarbonate RAFT mediator extended with a short hydrophilic oligomer through controlled free radical polymerization. The obtained RAFT-active amphiphilic oligomers (Fig. 2) can then be used as block copolymer precursors of functional polymer nanoparticles (Fig. 3).

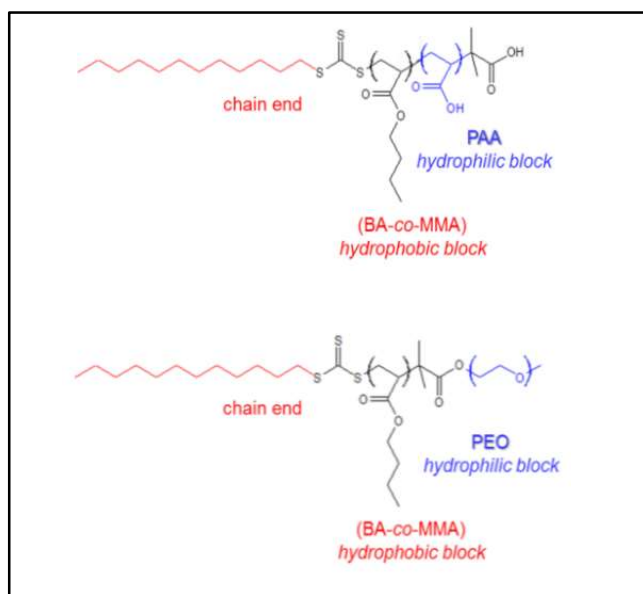


Fig. 2: RAFT-active amphiphilic block copolymer precursors.

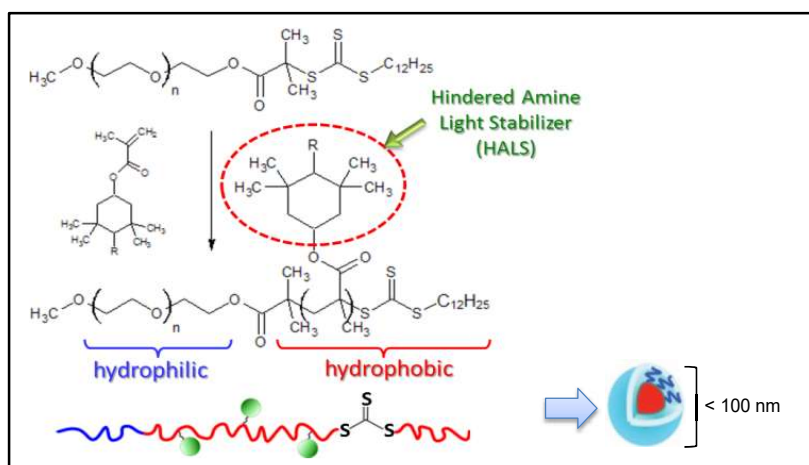


Fig. 3: synthetic scheme for self-stabilized multifunctional block copolymer nanoparticles by *ab-initio* RAFT emulsion polymerization of amphiphilic precursors.

3. Materials and characterizations

3.1. Latex Polymers

A selection of the functional polymer dispersions (polymer latexes) prepared during the first year of the project is listed in Tab. 1. Macro-RAFT is the alkyl-dithiocarbonate terminated oligo (acrylic acid) (PAA-TTC) or oligo(ethyleneglycol) (MPEG-TTC) of Fig. 2, used as a reactive surfactant and RAFT mediator in the *ab initio* emulsion polymerization of the butyl acrylate/methyl methacrylate (BM) mixture. The polymer latex acronyms indicate the amount of hydrophilic PAA or MPEG block (1 to 5 wt.-%) and of the HALS comonomer (1 and 3 wt.-% in H1 and H3 samples, respectively).

Tab. 1: Water borne polymer particles.

Polymer Latex		Macro-RAFT	PMPMA	Solids content	Particle size
		wt.-%	wt.-%	wt.-%	nm
BM-PAA5-H1	(DS4)	PAA-TTC	1	7.8	170
BM-PAA3-H1	(DS7)	PAA-TTC	1	9.0	143
BM-PAA1	(DS10)	PAA-TTC	//	9.1	188
BM-PAA1-H1	(DS11)	PAA-TTC	1	9.2	55
BM-PEG5	(DS9)	MPEG-TTC	//	8.0	79
BM-PEG5-H1	(DS12)	MPEG-TTC	1	7.9	181

The latexes were cast to clear films, and after dilution to 1 wt.% solids were applied by capillarity to Carrara marble and Schleitdorf sandstone (Cologne), respectively, to a nominal 1 μm -thick coating (actually thinner due to absorption into the porous stone). The

water contact angles (Tab. 2) and the surface Zeta potential data (Fig. 4) show that even at low concentration and without structure optimisation, these relatively hydrophilic materials are effective hydrophobic modifiers.

Tab. 2: Static water contact angle on polymer films and treated stones.

Polymer Latex		Smooth polymer film	Sandstone	Marble
		deg	deg	deg
Untreated stone			35.2 ± 2.3	35.2 ± 2.0
BM-PAA1	(DS10)	90.0 ± 2.0	105.3 ± 3.5	99.4 ± 5.4
BM-PAA1-H1	(DS11)	86.5 ± 0.8	104.5 ± 5.6	81.7 ± 7.0
BM-PEG5	(DS9)	91.6 ± 0.2	100.5 ± 8.6	67.7 ± 7.4
BM-PEG5-H1	(DS12)	97.2 ± 0.9	113.9 ± 5.8	99.8 ± 3.8

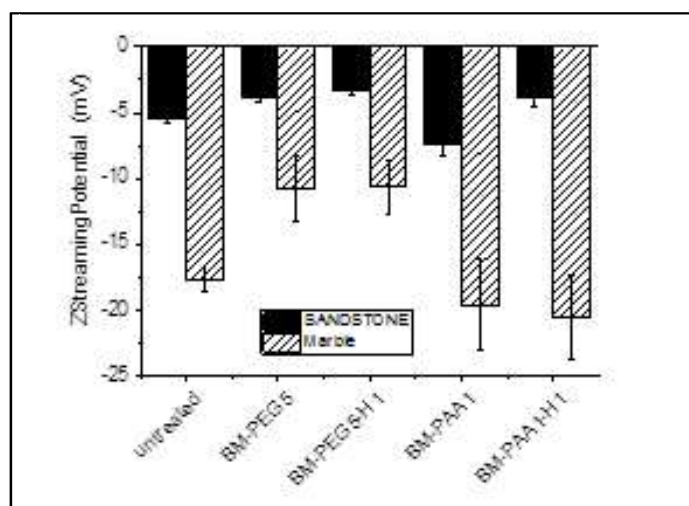


Fig. 4: ζ potential of uncoated and coated stone surfaces (measured with the Anton PAAR SurPASS® Electrokinetic Analyser).

3.2. Ageing tests

The FT-IR spectra of fig. 5 were recorded on cast films of selected polymers (DS#, as listed in Tab. 1) and of their nanocomposites with TiO₂ nanoparticles (DS#n), before and after the first 250 hours of simulated solar irradiation (Hereus Suntest CPS solar box, Xenon lamp, 300 nm cutoff filter, 750 W/m²). The preliminary results indicate that:

- After 250 hours of ageing only a slight oxidation is detected from the appearance of weak OH absorptions at 3220 cm⁻¹ and of a shoulder at 1640 cm⁻¹ due to chain-end double bonds (compare DS9 in Fig. 5a, and DS10 in Fig. 5b, before and after ageing).
- The HALS moiety inhibits the oxidation phenomena, as shown by the further reduction of the weak OH absorption at 3220 cm⁻¹ (compare DS12 with DS9 in Fig. 5a, and DS11 with DS10 in Fig. 5b)

- The photocatalytic action of TiO₂ promotes polymer oxidation phenomena (compare DS9 and DS9n in Fig. 5a) as shown by the growth of a broad absorption above cm⁻¹ due to formation of hydroxy groups, irrespective of the presence of HALS groups (compare DS12 and DS12n in Fig.5a).

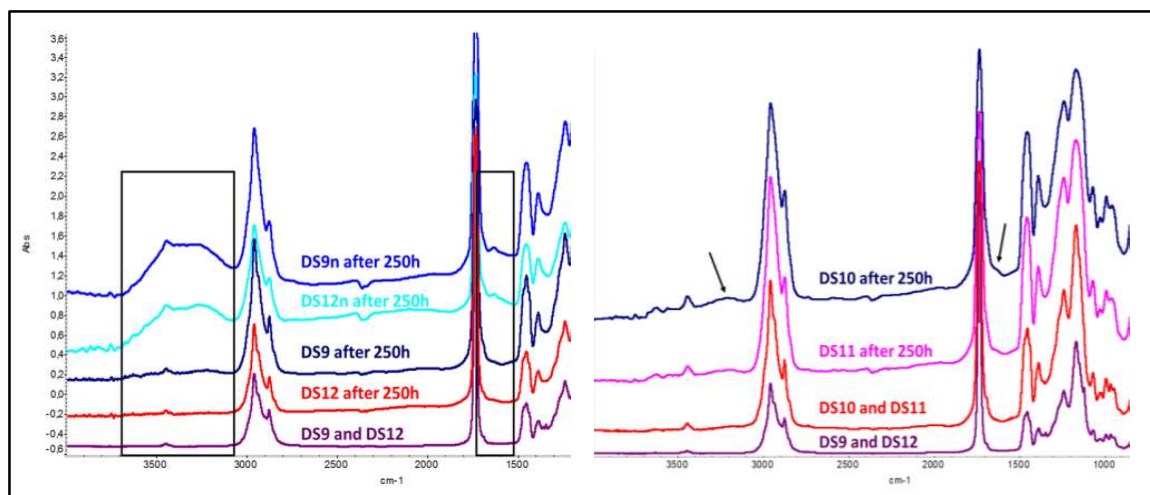


Fig. 5: FT-IR transmission spectra of films on silicon wafer.

4. Conclusions

A range of amphiphilic block copolymers and of self-stabilized, surfactant-free colloidal polymer dispersions (polymer latex) with small particle size (< 100 nm, for improved capillary absorption into the stone porous network) and reactive functional groups (carboxylate, for polymer anchoring onto stone substrates or inorganic nanoparticles) have been synthesized by means of the RAFT controlled polymerization method.

The amphiphilic block copolymers may be useful as modifiers of inorganic nanoparticles (ZnO and TiO₂ for protection, calcite, ZrO₂ and hydroxyapatite for consolidation) and as precursors of multifunctional latex particles or water-borne nanocomposite materials. Encouraging results have already been obtained from preliminary tests of application of the colloidal polymer dispersions onto sandstone and marble different stone samples (, respectively). In particular, very low amounts of applied polymer are sufficient to make the stone surface hydrophobic.

Aging tests have confirmed the foreseen stabilizing effectiveness of the HALS groups introduced by means of functional comonomers. On the other hand, the photocatalytic activity of embedded TiO₂ nanoparticles was shown to cause, as expected, accelerated degradation of the polymer matrix in nanocomposite films. Finally, a better understanding of the stone-polymer and stone-nanoparticle interaction and distribution at and within the porous stone surface may be achieved thanks to a combination standard (water absorption, water vapour permeability, contact angle) and less conventional techniques; among them, the Zeta potential may provide useful insights on the effectiveness of a treatment and on the evolution of the treated stone surface upon aging.

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