

Photo-oxidative stability of paraloid acrylic protective polymers

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Abstract

The photo-oxidative stability of a series of commercial acrylic/methacrylic protective resins, which find use in consolidation and protection of art works, monuments and historical buildings, and are known by the name of Paraloids, has been investigated. The structural and molecular changes occurring under conditions of artificial solar light irradiation have been followed by FTIR and UV–Vis spectroscopy, and size exclusion chromatography. In all the resins the first degradative event which is detected is the molecular weight distribution change due to chain scissions and/or coupling of macroradicals. The overall stability of the polymers is strongly influenced by the presence of long alkyl side groups, such as butyl or isobutyl, whose oxidation is favoured by the presence of relatively labile hydrogen atoms. At the same time these polymers containing long ester groups undergo fast and extensive cross-linking together with some fragmentation and consequent weight losses. The resins containing only ethyl and methyl esters showed a good stability towards oxidation, reaching an equilibrium between scission reactions and macromolecular coupling which permit them to maintain their molecular characteristics during the ageing. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photo-ageing; Photo-oxidation; Acrylic protective polymers

1. Introduction

Acrylic/methacrylic polymers are extensively used in many different industrial fields, for example as media in the formulation of paints and surface coatings, as well as bases for adhesives [1]. One important specific application is in the sector of artists' paints and cultural heritage conservation. Resins based on poly(butyl methacrylate) started to be used as picture varnishes in the late 30s [2], and more evolved commercial polymers have been later used, and are still being employed, for the conservation of many different materials and museum objects. Conservative treatments with acrylic resins have been reported for wood, paper, mosaics, pigments, lacquerwares, amber, fossils, ceramics, glass and stones [3–16]. Such uses specifically exploit the good adhesion and water-repellent properties of acrylic resins, requiring at the same time adequate environmental stability, particularly in those cases where the resins are intended to act as consolidants and/or protectives of monuments and works of art exposed to outdoor conditions [17–19]. The long-term efficiency of the consolidative/protective treatments is mainly influenced by the direct action of sunlight in promoting oxidation reactions, whose effects

may be exacerbated by temperature, moisture, and especially by the presence of atmospheric pollutants.

The complexity of natural ageing of materials may be reproduced in the laboratory only by considering a simplified approach through some kind of simulation with convenient short-term experiments. Lifetime prediction and mechanistic studies of the outdoor degradation processes are in general carried out by means of accelerated ageing experiments involving temperature and/or light treatments. The light sources which can be efficiently employed for such purposes must have high power output and the closest resemblance to the solar light spectrum, particularly in the UV range [20,21]. Lower-wavelength radiations must be removed, as it has been shown that they can cause the occurrence of reactions which do not take place outdoors [21].

The photo-ageing of acrylic protective resins has been scarcely investigated, and the photo-degradation induced by mercury high-pressure lamps with wavelengths lower than 300 nm, of some commercial protectives directly applied on stones has been recently discussed [22]. In order to better understand the reasons for the partial inadequacy to satisfactorily fulfil, in the long run, the required protective action [23], we have started a systematic investigation of the stability of a series of protective acrylic polymers under different conditions of artificial ageing. The samples have been chosen among the commercial resins

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Table 1
Composition of the paraloid resins (mol%) [24]

Sample	MA	EA	MMA	EMA	BMA
B66	–	–	47.6	–	52.4
B72	32.0	–	–	65.8	2.2
B82	–	~43	56.1	–	~1

most commonly used by restorers and conservators and their characterisation has been previously reported [24].

Such commercial consolidants/protectives are copolymers of acrylic and methacrylic esters and in order to make clear the role played by the different structural units in the copolymers, the degradation of the corresponding homopolymers has been investigated previously under the same ageing conditions [25]. Acrylate units were found to be more reactive towards oxidation in comparison with methacrylate ones, nevertheless in all the polymers the structures formed as a direct result of oxidation were similar. In both types of monomeric units, when the ester side group is short, scission reactions prevail over cross-linking ones, whereas when there is a butyl ester group the behaviour changes dramatically and the polymer samples undergo fast and extensive cross-linking. This behaviour was already observed also in other poly(alkyl methacrylate)s with long alkylic groups, even in the case of irradiation with longer wavelengths, such as visible light [26]. The photostability to solar light irradiation of poly(methyl methacrylate), (PMMA), on the other hand, is well recognised and under accelerated conditions very long irradiation times are necessary before any development of photo-induced oxidation is detected [27].

In this work we have investigated the photo-oxidative stability of commercial resins commonly employed for consolidation and protection of art works, monuments and historical buildings. The behaviour of the same samples under conditions of thermal ageing has been already discussed [28]. The polymers have been submitted to artificial solar light irradiation, and the structural and the molecular changes occurring during the treatment have been followed by infrared and UV–Vis spectroscopy, and by size exclusion chromatography (SEC), respectively.

Table 2
Molecular and thermal characteristics of the paraloid resins

Sample	M_n (10^{-3})	M_w (10^{-3})	M_w/M_n	T_g (°C) ^a	T_g (°C) ^b
B66	27	55	2.04	50	59
B67	24	48	2.00	50	64
B72	41	88	2.15	40	46
B82	38	96	2.53	35	35

^a Supplier's data.

^b Softening temperature determined by TMA.

2. Experimental

The investigated materials are produced by Röhm and Haas (USA) and traded with the names Paraloid B66, B67, B72 and B82. These resins are also known in the United States under the name Acryloid. B67 is an isobutyl methacrylate homopolymer (PiBMA), while the others are copolymers with two or three components, whose details are shown in Table 1. B72 and B82 may be considered as binary copolymers of methyl acrylate/ethyl methacrylate, (MA/EMA), and ethyl acrylate/methyl methacrylate, (EA/MMA), respectively, even though the samples we have investigated were found to contain a low amount of butyl methacrylate, (BMA), units [24]. B66 is an MMA/BMA copolymer. By reason of their structural similarity, the results are discussed separately for the two couples, B66 with B67, and B72 with B82. The molecular characteristics of all the resins are summarised in Table 2.

The samples were treated in the form of thin films, casted from chloroform solutions (weight concentration: ca. 5%) and dried under vacuum at 60°C for 4 h. Films with thickness in the range of 10–20 μm were supported for the infrared analyses on silicon wafers, and on quartz windows for UV–Vis spectroscopy. For all the other determinations, film thickness was between 20 and 50 μm .

Photo-ageing was carried out with a Suntest CPS apparatus (Heraeus, Germany) equipped with a Xenon light source filtered for $\lambda < 295$ nm, and having a constant irradiation at a power of 765 W/m². The maximum temperature on the samples, during irradiation, was 45°C. 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 pre-weighed membrane filters.

Molecular characterisation of initial and irradiated samples were performed by SEC with 4 PL-Gel (Polymer Labs, England) columns, 30 \times 0.78 cm, in series. Gel particle diameter was 5 μm , and nominal porosity of the individual columns: 500, 10³, 10⁴, and 10⁵, respectively. Sample solutions, approximately 0.2% (w/v) concentration, were prepared in distilled tetrahydrofuran, which was also the chromatographic eluent. Before injection, the solutions were filtered on 0.45 μm membrane syringe filters. Injection volume was 200 μl and eluent flow rate set at 1 cm³/min. *o*-dichloro benzene was added to the polymer solutions as a flow rate internal standard. Column calibration was performed with PMMA narrow distribution standards (Polymer Labs, England) and a third-order polynomial equation was obtained from regression analysis. For the comparison of chromatograms obtained from different samples the peak areas were always normalised by considering the amount that remained after subtraction of the volatile and the cross-linked fractions.

UV–Vis spectra were acquired with a Lambda 15

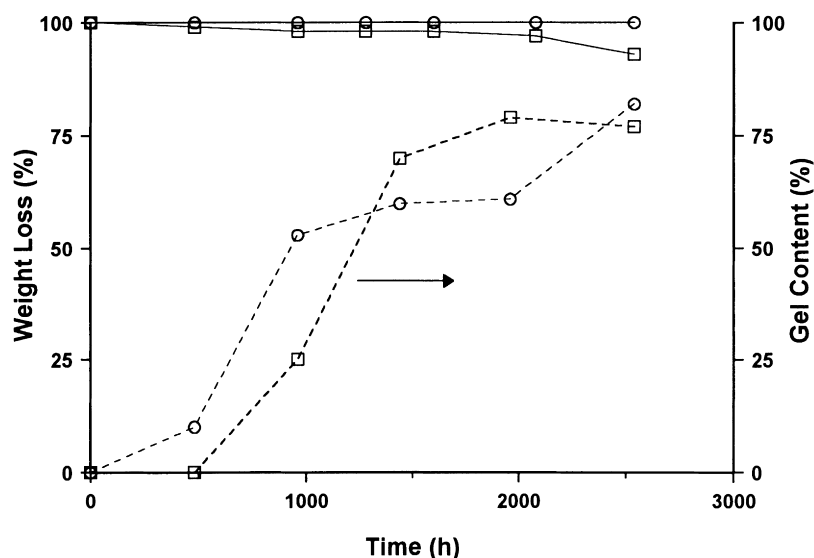


Fig. 1. Weight loss and gel content of B66 (W) and B67 (A) as a function of treatment time.

instrument (Perkin–Elmer, USA). Fourier transform infrared (FTIR) analysis was done on a 1710 Perkin–Elmer system, with DTGS detector and 4 cm^{-1} resolution. Spectral acquisitions and data treatments were performed with Spectra Calc (Galactic Industries, USA) software.

Thermomechanical analysis was accomplished with a TMA mod. 942 (DuPont, USA) driven by a 2100 Thermal Analyst (TA Instruments, USA) controlling system. The measure was made in penetration mode, with 0.25 mm^2

probe section and 50 g weight on the sample films, applying a $5^\circ\text{C}/\text{min}$ heating rate.

3. Results and discussion

3.1. Paraloids B66 and B67

Films of B66 and B67 were exposed to accelerated photo-ageing treatments for times up to 2500 h, and the changes induced by the irradiation were periodically checked. The apparent formation of low molecular weight volatile compounds was practically negligible for B66 and limited to a 5% weight loss at the longest treatment time for B67. Both polymers on the other hand showed a fast growth of insoluble fractions, as it can be seen in Fig. 1. In B66 the gel fraction was detected from the beginning, reaching the 85% of the total sample weight after 2500 h, whereas B67 showed an induction time of ca. 500 h, followed by a rapid development of an insoluble fraction remaining at a constant value of ca. 80% by weight after 1500 h.

The strong tendency to give cross-linking reactions was also clearly revealed by the SEC curves shown in Fig. 2. The SEC curve displacements are originated by two different processes: chain scissions which shift the chromatograms towards longer retention times, and formation of higher molecular weight molecules by branching and coupling reactions which produce a curve displacement at shorter retention times. From Fig. 2 it is seen that after 450 h the chromatograms of both samples are broadened towards lower retention times, indicating the predominance of cross-linking reactions. At longer irradiation times the chromatograms are only representative of the remaining uncross-linked chains and of the low molecular weight scission products.

Cross-linked structures influence the physical properties

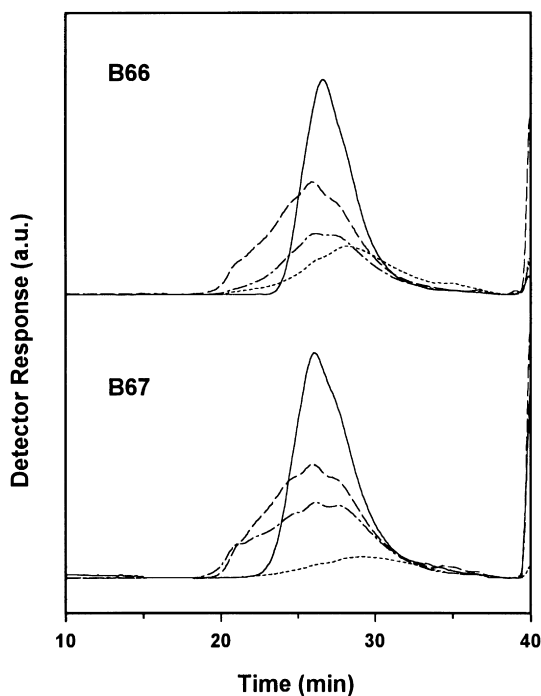


Fig. 2. SEC curves of B66 and B67 before (solid line) and after treatment for 450 (dashed line), 1500 (dash-pointed line) and 2500 h (short-dashed line).

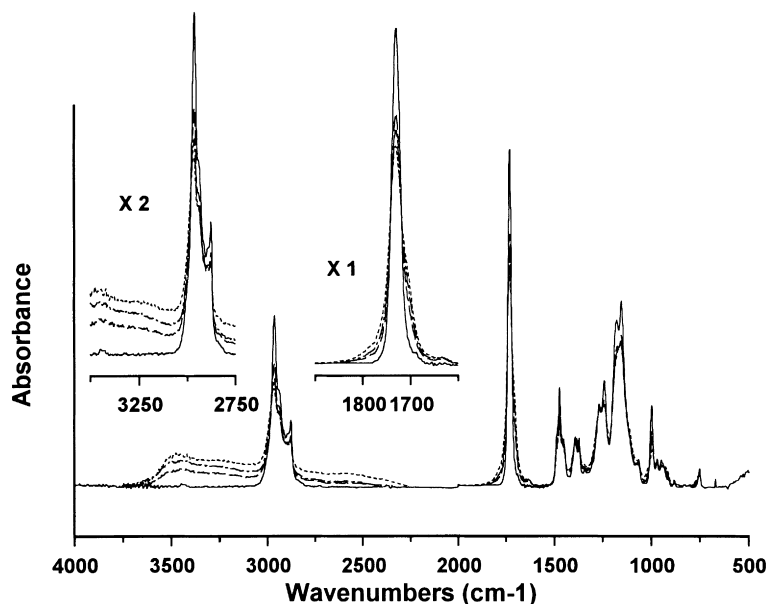


Fig. 3. FTIR spectra of B67 before (solid line) and after treatment for 750 (dashed line), 1500 (dash-pointed line) and 2500 h (short-dashed line).

of the polymer films. TMA measurements showed that in the case of B66 both the softening temperature and the temperature at which the polymer shows viscous behaviour increase during the degradation from the initial values of 59 and 150°C, respectively, to the final ones of 78 and 170°C. In Paraloid B67 the softening temperature remains practically constant during the whole treatment time but the viscous behaviour shifts at temperatures higher than those of B66. In both types of polymers extensive surface cracking developed during the ageing, but with dissimilar visual patterns, which may be tentatively attributed to different cross-link densities. In B66 extended crackings appeared

since the beginning of the ageing treatments, whereas B67 showed only a few cracks during the whole treatment.

The films remained completely transparent during the treatment and, apart from cracking, no variations were visually detected. Only in the case of B67 the UV-Vis spectra before and after different ageing times showed that irradiation in the presence of air causes a progressive increase of an absorption in the range between 240 and 300 nm, attributed to the formation of chromophore groups. A similar behaviour has been already reported for other acrylic and methacrylic polymers [25,29,30].

The FTIR spectra in Figs. 3 and 4 show the structural

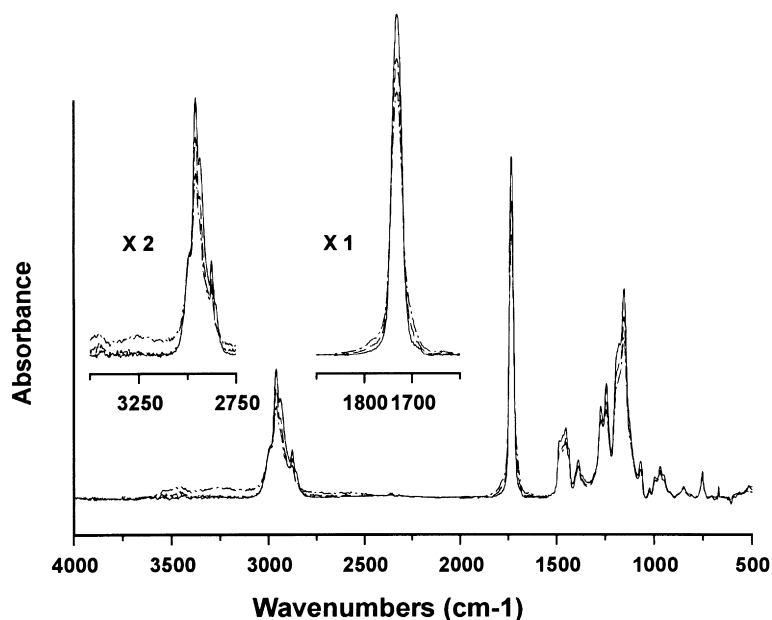
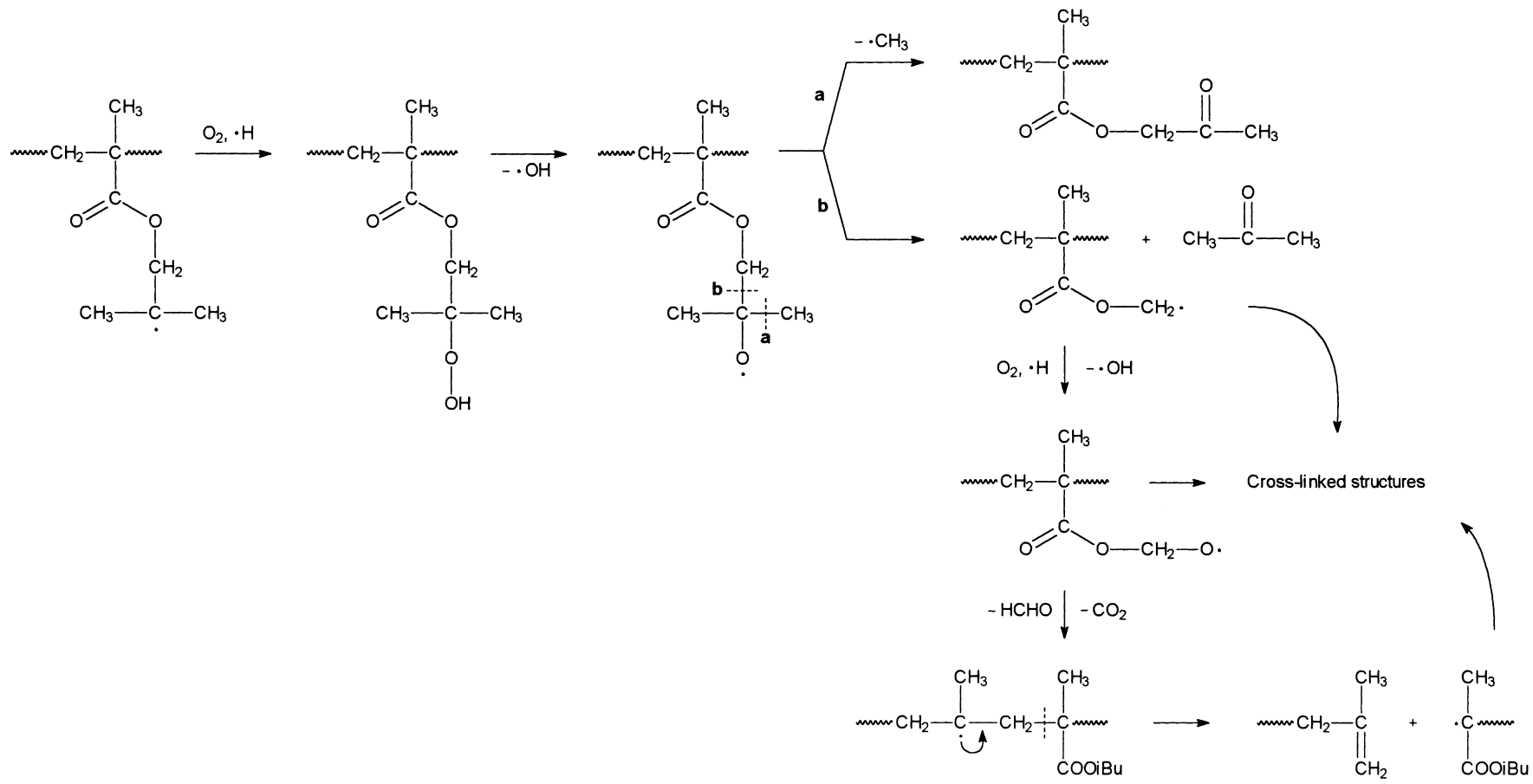
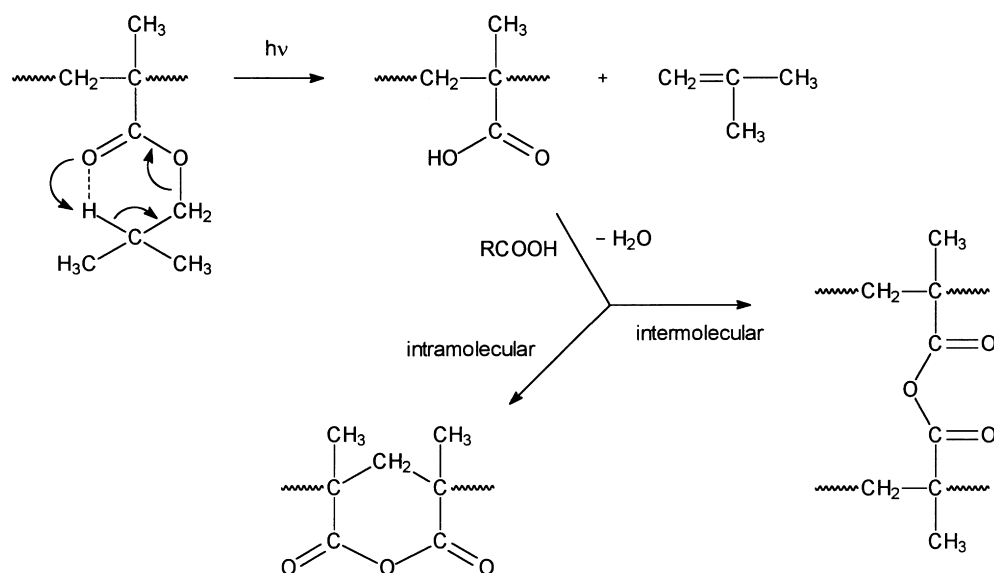


Fig. 4. FTIR spectra of B66 before (solid line) and after treatment for 1200 (dashed line) and 2500 h (dash-pointed line).



Scheme 1.



changes induced by irradiation in B67 and B66, respectively. Large spectral modifications can be seen in B67, with the appearance of new oxygen-containing functional groups since the initial steps of degradation. The main features observed are the following:

- increase of absorption in the whole hydroxyl region between 3600 and 3100 cm^{-1} with two main components centred at around 3450 and 3220 cm^{-1} , and extended also in the region below 2800 cm^{-1} , indicating a strong association of $-\text{OH}$ groups [31];
- progressive decrease of the $\text{C}-\text{H}$ stretching absorptions, with a shift of the main band attributed to asymmetric stretching of isobutylic CH_3 from 2961 to 2970 cm^{-1} ;
- decreasing of the carbonyl ester band at ca. 1730 cm^{-1} , with simultaneous broadening at both sides;
- development of a small absorption at ca. 1640 cm^{-1} , which does not grow further after 750 h irradiation, possibly related to the formation of chain-end double bonds [32,33];
- overall decrease of the main absorptions and loss of resolution in the fingerprint region.

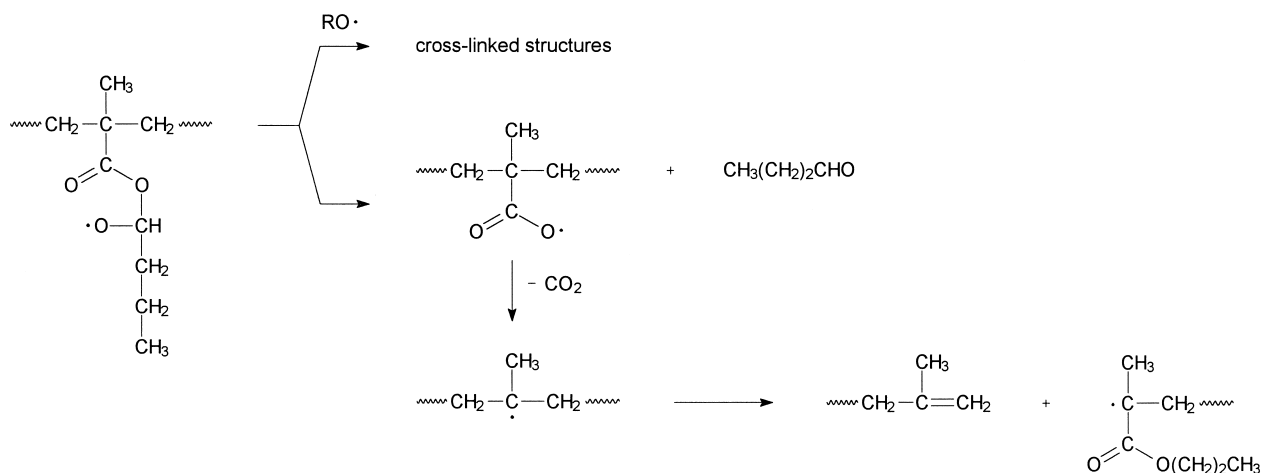
Hydroxyl absorptions are partially due to hydroperoxides. Their presence was verified by heating an oxidised polymer film under vacuum at 150°C for 20 h: such treatment produced a one-third decrease of the hydroxyl absorption. These relatively stable hydroperoxides are probably tertiary, formed on methacrylic chain ends or in γ position with respect to the carbonyl ester [34]. In the last case, oxidation reactions are favoured by the labile hydrogen atom located on the tertiary carbon of the isobutyl group, which may be easily abstracted.

One possible mechanism of the oxidation is reported in Scheme 1. The formation of new $\text{C}-\text{O}$ bonds on the alkyl

groups increases the polarity of isobutylic CH_3 , whose absorption is shifted to higher wavenumbers, i.e. asymmetric stretching from 2961 to 2970 cm^{-1} . The β scission of the alkoxy radicals may follow two paths. The first one leading to ketones probably occurs to a limited extent, since their presence has not been detected by UV-Vis analysis, in disagreement with the results reported for thermal ageing of the same polymer [28]. On the other hand, ketones may decompose by Norrish cleavage as soon as they are formed [35]. The second pathway may account for the development of carbon-carbon double bonds and the formation of low molecular weight scission products, while cross-linked structures are produced by any bimolecular combination of radicals.

The hydroxyl groups remaining after the thermal treatment that decomposes the hydroperoxides belong to $\text{R}-\text{OH}$ structures. In particular, the absorption at 3220 cm^{-1} and its extension in the region below 2800 cm^{-1} can be assigned to the stretching vibrations of free and bonded acid OH groups, respectively [31]. The carbonyl absorption component growing at low wavenumbers may be attributed to the carboxylic $\text{C}=\text{O}$. Acid formation occurs by photo-induced decomposition of the isobutyl groups through a molecular mechanism involving interaction between the carbonyl group and hydrogen atoms on the β carbon atom of the ester (Scheme 2) [30]. The evolution of acids to anhydrides, either by inter- or intramolecular elimination of water, and the corresponding infrared absorptions of the different $\text{C}=\text{O}$ groups, may justify the broadening of the carbonyl peak at wavenumbers higher than 1750 cm^{-1} [31,36]. The formation of intermolecular anhydrides could be the main route to cross-linking, and the delay in detection of gel fractions may be related to the time interval necessary for reaching the required concentration of acid groups.

The FTIR spectra of photo-oxidised B66 (Fig. 4) show



Scheme 3.

less structural modifications than those seen in B67, even though the final amount of gel fraction is the same. An overall decrease of all spectral absorptions is visible but the new spectral features resulting from the oxidation are limited. Hydroxyl groups, for example, grow extensively only after 1200 h of irradiation. By comparing the spectral changes of Fig. 4 with those found during the photo-oxidation of PBMA [25] it may be deduced that in B66 mainly the BMA units are involved in the degradation process.

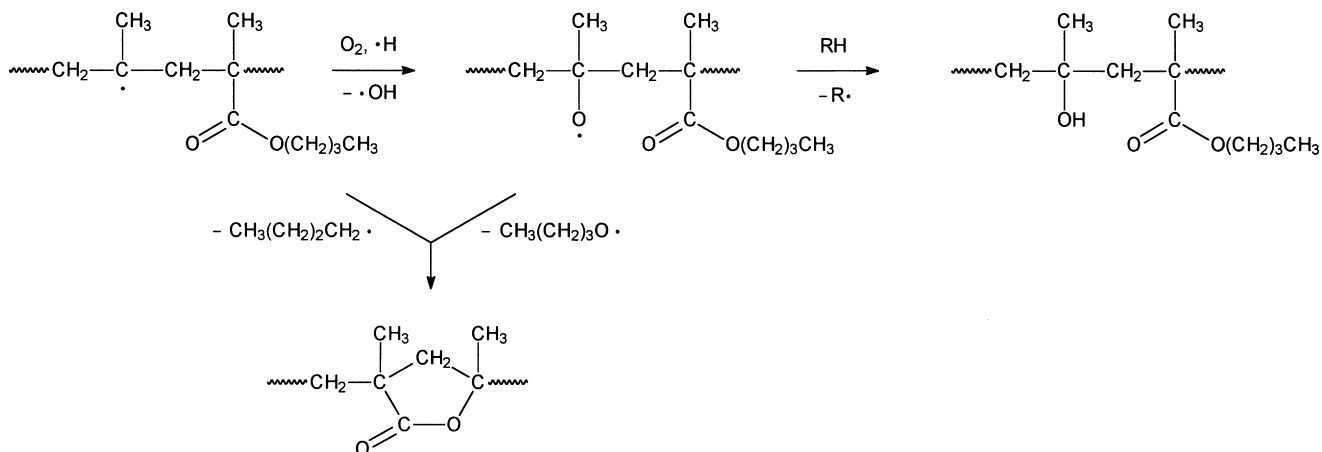
The high cross-linking rate of the sample during the first phases of ageing, comparable with that of PBMA [25], is attributed to oxidation of the butyl groups, which gives rise to unstable secondary hydroperoxides, immediately photolysed to alkoxy radicals [34]. Owing to high mobility of the side chains such radicals rapidly decay via bimolecular combinations [37]. At longer irradiation times the stiffness of the formed polymeric network makes other reactions competitive, such as the radical fragmentation shown in Scheme 3, with complete loss of ester groups and formation of tertiary internal macroradicals. The latter ones will induce scission reactions with production of unsaturated

chain ends, responsible for the small infrared absorption visible after 2500 h at ca. 1640 cm^{-1} , and of lower molecular weight products.

Oxidation of the tertiary radicals will lead, as reported in Scheme 4, to hydroperoxides and alcohol groups or, in presence of adjacent ester groups, to γ -lactones which absorb around 1780 cm^{-1} . Formation of acids and their evolution to anhydrides, in the same way as proposed for B67, cannot be excluded as a secondary mechanism of ester group decomposition.

3.2. Paraloids B72 and B82

Photo-oxidation of both B72 and B82 up to 2500 h occurred without formation of insoluble fractions and with a similar weight loss of about 5% that after 2000 h remains practically constant. Neither cracking nor other optical variations were detected on the polymer films. This behaviour is different from that reported for Paraloid B72 irradiated with UV light, which was found to develop fast yellowing [22].



Scheme 4.

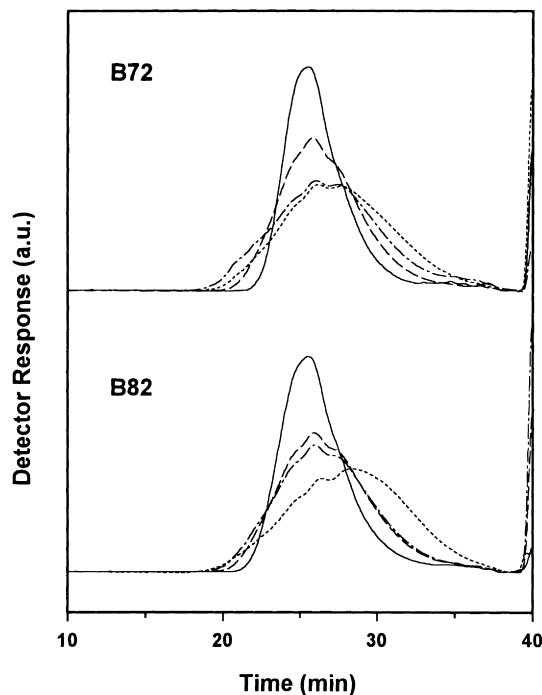


Fig. 5. SEC curves of B72 and B82 before (solid line) and after treatment for 450 (dashed line), 1500 (dash-pointed line) and 2500 h (short-dashed line).

The SEC chromatograms obtained from the two resins after different treatment times are shown in Fig. 5. New polymer fractions are visible, eluting at retention times both shorter and longer than those of the initial polymers. This indicates that degradation takes place from the beginning with simultaneous cross-linking and fragmentation reactions, as was also found in the initial steps of their thermal ageing [28]. For longer irradiation times, particularly in B82, the formation of lower molecular weight products appears favoured in comparison with molecular

weight increase. This tendency was also supported by the results of TMA analyses, which showed a decrease of the softening temperature in both resins. A progressive lowering of glass transition temperature has been already reported during the photo-ageing of Paraloid B72 under an unfiltered xenon lamp [38].

The complete solubility of the degraded samples allows the determination of the apparent number of chain scissions per initial polymer molecule, S , during the degradation, through the relationship [39]:

$$S = [M_{n,0}(1 - x)/M_n] - 1$$

where $M_{n,0}$ is the initial number average molecular weight, M_n is its value at the different times, as calculated from the curves in Fig. 5, and x the fraction of volatilised polymer. The plot of S vs. time for B72 and B82 is shown in Fig. 6. The rate of chain scissions increases with time, due to the fact that more and more photo-induced scission reactions are promoted with the proceeding of oxidation.

The infrared spectra of B72 (Fig. 7) and B82 reflect the good stability of their methacrylic component, i.e. EMA and MMA, respectively [25,27]. The observed structural changes are fully comparable with those observed for the homopolymers of the corresponding acrylic structural units [25]. In B72, the presence of oxidated structures is detectable only after 2500 h of ageing, with the appearance of hydroxyl groups responsible for the broad absorptions centred at about 3450 and 3250 cm^{-1} and with the broadening of the carbonyl peak on both sides. In addition to the growing of a small absorption at ca. 1640 cm^{-1} , one can also notice a progressive decrease of all the principal absorptions of the spectrum, due to the loss of monomers and small fragments formed as a result of the chain scissions.

The process of oxidation on B72 is likely to be initiated through addition of oxygen to the radicals formed by

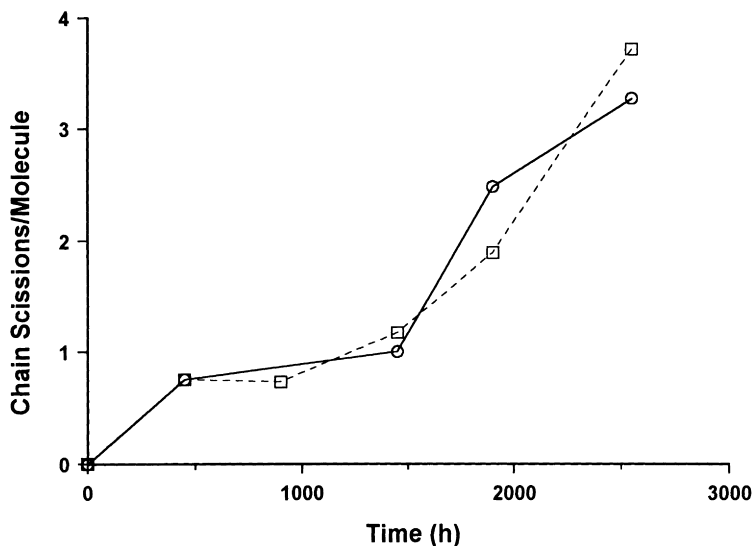


Fig. 6. Scissions per initial molecule of B72 (w) and B82 (A) as a function of treatment time.

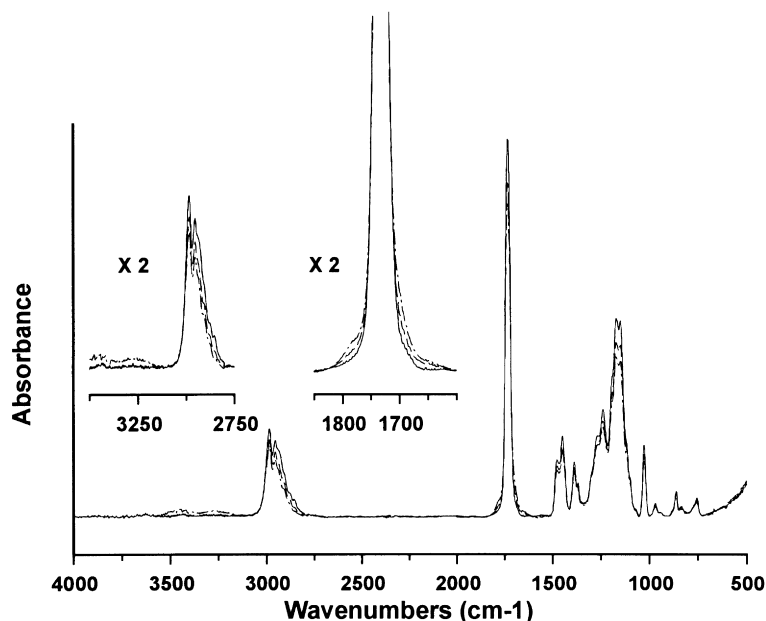


Fig. 7. FTIR spectra of B72 before (solid line) and after treatment for 1200 (dashed line) and 2500 h (dash-pointed line).

abstraction of the tertiary hydrogen atoms of the MA units (Scheme 5). The subsequent decomposition of hydroperoxides leads to the formation of ketones absorbing at 1710 cm^{-1} [33]. Scheme 5 also suggests the generation of acid groups starting from the photolytically induced decomposition of ketones, as well as their evolution to open chain anhydrides, whose main absorption is around 1800 cm^{-1} . However, the broadening of the carbonyl peak at the higher wavenumber side, and in particular its component centred at ca. 1780 cm^{-1} which starts to appear at 2550 h of irradiation, is attributed to the formation of γ -lactones in the way already reported in Scheme 4. The absorptions of $-\text{OH}$ groups is due to the formation of carboxylic acids and hydroperoxides, and also to alcohol groups formed on the alkoxy radicals. The development of double bonds can be explained by photo-induced main chain scissions followed by macroradical disproportionation and formation of unsaturated terminals, in the same way as found for PEMA [25].

The spectra relative to B82 showed lower structural changes than those of Paraloid B72. Common features are the broad band appearing in the hydroxyl region, with a main component centred at around 3250 cm^{-1} , and the broadening of the carbonyl peak with appearance of the new component at 1780 cm^{-1} . Oxidation of the resin takes place with the same mechanism seen for B72, through initial attack of oxygen on tertiary radicals of the EA units (Scheme 5). Also in this case among the main oxidation products are the γ -lactones, which appear to be ubiquitous in photo-oxidation of all types of aliphatic polymers [40–42]. The development of cross-linked structures in both resins is the result of recombination reactions between the macroradicals.

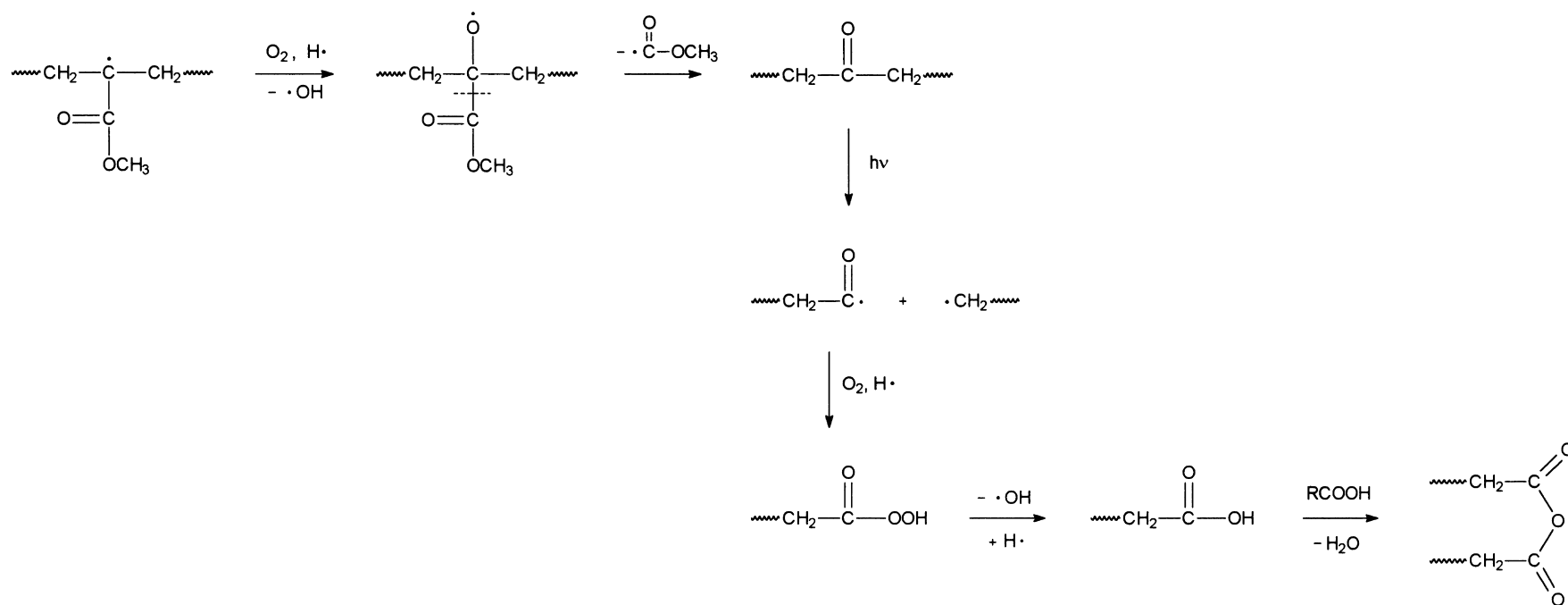
4. Conclusions

The photo-oxidative behaviour and the differences of stability of acrylic resins used as protective coatings has been investigated under accelerated photo-ageing conditions. In all the resins the first degradative event which is detected is the molecular weight distribution change due to chain scissions and/or coupling of macroradicals. The overall stability of the polymers is strongly influenced by the alkyl side groups, particularly in the case of B66 and B67, where relatively longer esters are present. Here the oxidation is favoured by hydrogen atoms either on the methylenes of the *n*-butyl groups in B66, or on the tertiary carbon of the isobutyl groups in B67. The relative sample stability reflects in fact the order of lability of such hydrogens. At the same time these polymers containing long ester groups undergo fast and extensive cross-linking together with some fragmentation and consequent weight losses.

Paraloids B72 and B82 showed a good stability towards oxidation, which reflects that of their main components, the methacrylic units EMA and MMA, respectively. The degradation takes place through the initial oxidation on the acrylic units, i.e. MA and EA, and mainly leads to the formation of γ -lactones.

Finally, it is worth noticing that in B72 and B82 the balance between scission reactions and macromolecular couplings is such that the polymers do not become insoluble. This is a favourable characteristic for a coating to be applied for protection of monuments and historical buildings, as it must maintain its molecular characteristics for a long time, with the possibility of being removed by solution in appropriate solvents [16].

Comparison of the results obtained in this and in a previous work [25], with those reported for the case of



Scheme 5.

irradiation of the same acrylic polymers with a light source containing wavelengths lower than 290 nm [22] shows that the degradation rates are very dissimilar, but also indicates that the acceleration effects are not homogeneous in the two cases. The principal reactions promoted by the high-energy radiation are homolysis of all types of chemical bonds, bringing the polymer structure to complete fragmentation soon [22]. Under such ageing conditions cross-linked structures cannot develop and the oxidation process is not relevant in the degradation, although in the two different types of irradiation some common intermediates are found.

It is clear that the difficulty of accelerated weathering experiments arises from the fact that by changing not only the light intensity but also the energy level of irradiation, new reactions may take place and the rate ratios of parallel or competitive reactions will be affected. It must be stressed therefore that for the closest reproduction of natural outdoor ageing conditions, it is necessary to employ radiation sources matching the sunlight spectrum, like the xenon arc lamp.

Acknowledgements

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