

Thermal-ageing of paraloid acrylic protective polymers

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Abstract

The thermal-ageing of a series of commercial acrylic/methacrylic resins, homo- and copolymers which are extensively used as stone protectives, has been investigated under conditions of constant temperatures at 110, 135 and 150°C. Structural and molecular changes induced by the isothermal treatments in a forced-air circulation oven were followed by infrared and UV–Vis spectroscopy, and size exclusion chromatography (SEC), respectively. The stability of the resins appeared to be controlled by the reactivity of alkyl side groups, whose oxidative decomposition is favoured in the case of long ester groups, like the isobutyl and butyl ones. At the same time, the polymers containing long ester groups undergo fast and extensive cross-linking, together with loss of short chain fragments. In the acrylic/methacrylic resins where all or the majority of the alkyl side groups are short, chain scissions prevail over cross-linking and no insoluble fractions were formed. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymers based on acrylic and methacrylic esters are widely used in the formulation of paints, surface coatings and adhesives because of their good characteristics of film forming and mechanical properties, optical clarity and overall stability [1]. One particular niche market of acrylic resins that specifically exploits their good adhesion and water repellent properties regards the consolidation and protection of different substrates in monuments and works of art [2–4]. For such materials the durability is fundamental for the long term efficiency of the protective/consolidative treatment [5], particularly in the case of outdoor applications, e.g. stone façades of churches and ancient buildings, where the synergic effect of sunlight, temperature, moisture and pollution agents is maximum.

Lifetime prediction and mechanistic studies of the outdoor degradation processes may be made by accelerating the reactions involved through elevated temperature treatments or artificial weathering experiments, even though the simple increase of temperature or the contemporary exposure to light and water only permit an approximate simulation of the natural ageing [6]. Nevertheless, it was our interest to evaluate by short term laboratory experiments

the degradative behaviour of a series of commercial acrylic/methacrylic resins, homo- and copolymers, which are extensively used in the conservation of cultural heritage since the 1960s [7]. In order to better understand the reasons of their partial inadequacy in the long run [8], the resins have been submitted to a systematic investigation of their stability under different conditions of artificial ageing, after having been opportunely characterised in terms of chemical structures and composition [9].

It has been recently reported that under ultraviolet irradiation the main degradation pathway is chain scission, and the relative rates of degradation of the different resins may be related to the type of ester group and to the presence of the α -methyl in the main chain [10]. In the case of artificial solar light irradiation ($\lambda > 295$ nm), the beginning of degradation appears to be related to the initial presence of chromophores, while the oxidation itself is favoured by the presence of labile hydrogen atoms located on the tertiary carbon of acrylic units, or eventually of ester side groups, which may be easily extracted by radicals present in the system [11]. At the same time, the extension of cross-linking reactions has been related to both the size and the flexibility of the ester side group in the different units, as already reported for the photo-oxidation of partially fluorinated acrylic coatings [12].

In the present work, we report the results concerning the thermal-ageing of commercial resins known under the trade names of Paraloid B44, B82, B72, B48N, B66 and B67.

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Table 1
Composition of the Paraloid resins (mol%) [9]

Sample	MA	EA	MMA	EMA	BMA
B44	–	~ 28	70.3	–	~ 1
B82	–	~ 43	56.1	–	~ 1
B48N	–	–	74.5	–	25.5
B66	–	–	47.6	–	52.4
B72	32.0	–	–	65.8	2.2

Except B67 that is a isobutyl methacrylate homopolymer (PiBMA), all of them are copolymers with 2 or 3 components (Table 1). B44 and B82 may be considered as binary copolymers of ethyl acrylate/methyl methacrylate (EA/MMA), although the samples we have investigated contain a low amount of BMA units. B72 is generically indicated by the producer as a methyl acrylate/ethyl methacrylate (MA/EMA) copolymer [13], but it has already pointed out that its composition changes slightly over time [14]. B48N and B66 are MMA/BMA copolymers. The temperatures of the isothermal treatments, 110, 135 and 150°C, respectively, were chosen in order to magnify the differences of behaviour within the series of resins during the initial steps of degradation. The evolution of the system and in particular the structural and the molecular changes occurring during the treatment have been followed by infrared and UV–Vis spectroscopy, and size exclusion chromatography (SEC), respectively.

2. Experimental

The investigated materials are commercial acrylic resins produced by Röhm and Haas (USA) and sold in the European market as Paraloid, while in the US they were also traded under the name Acryloid. PMMA, PEMA and PBMA commercial secondary standards obtained by Aldrich (USA) were used as reference samples. Molecular and thermal characteristics of all samples are reported 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.

Table 2
Molecular and thermal characteristics of resins and references

Sample	M_n (10^{-3})	M_w (10^{-3})	M_w/M_n	T_g (°C) ^a
B44	23	105	4.56	60
B82	38	96	2.53	35
B48N	48	184	3.83	50
B66	27	55	2.04	50
B72	41	88	2.15	40
B67	24	48	2.00	50
PMMA	48	85	1.77	105
PEMA	146	328	2.28	63
PBMA	92	257	2.79	15

^a Supplier's data.

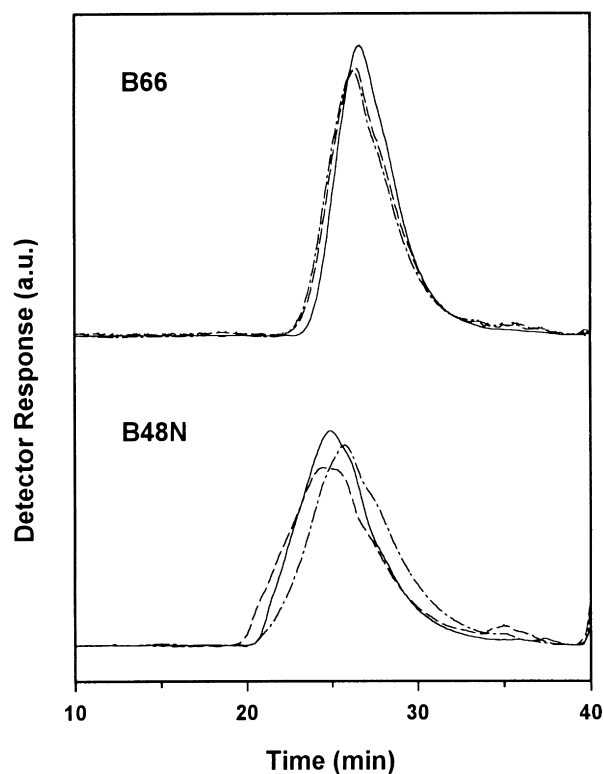


Fig. 1. SEC curves of B66 and B48N before (solid line) and after treatment for 115 h (dashed line) and 200 h (dash-pointed line) at 135°C.

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 .

The isothermal treatments were carried out in a forced-air circulation oven. Weight losses of polymer films induced by degradation were determined gravimetrically. Molecular characterisation of initial and treated 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, 10^3 , 10^4 , and 10^5 , respectively. Sample solutions, approximately 0.2% (w/v) concentration, were prepared in distilled tetrahydrofuran, which was also the chromatographic eluent. Before injections, the solutions were filtered on 0.45 μm membrane syringe filters. The injection volume was 200 μl and eluent flow rate set at 1 cm^3/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 normalised.

UV–Vis spectra were acquired with a Lambda 15 instrument (Perkin–Elmer, USA). Fourier transform infrared (FTIR) analysis was done on a 1710 Perkin–Elmer system,

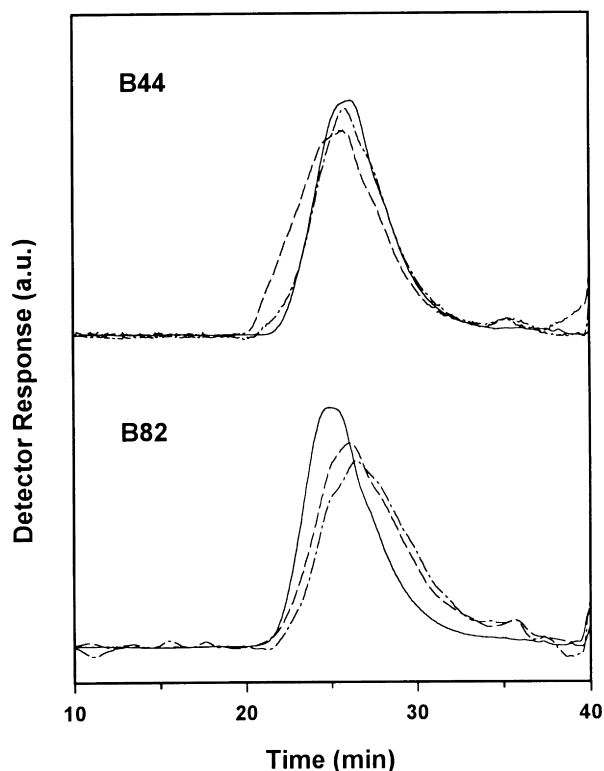


Fig. 2. SEC curves of B44 and B82 before (solid line) and after treatment for 115 h (dashed line) and 200 h (dash-pointed line) at 135°C.

with DTGS detector and 4 cm^{-1} resolution. Spectral acquisitions and data treatments were performed with Spectra Calc (Galactic Industries, USA) software.

3. Results and discussion

3.1. Ageing at 110 and 135°C

Isothermal treatments at the lowest temperature of 110°C, extended up to 200 h did not induce significant molecular nor structural changes detectable by SEC or FTIR analysis. On the contrary, UV spectra of all the samples showed some changes, in particular a slow decrease of absorption at wavelength $>240\text{ nm}$. This may be correlated to a consumption of chromophores already present in the starting polymers, probably as impurities [15], rather than to the real beginning of degradation.

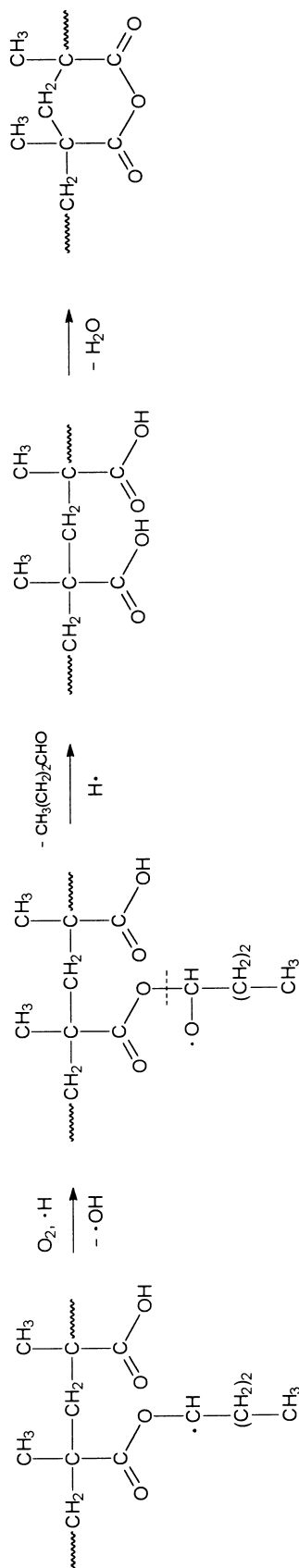
By treating the samples at 135°C, in addition to accelerate the degradation processes occurring at 110°C, new oxidation and/or thermal degradation reactions could start. All the resins showed a comparable weight loss of about 5% during the first 115 h of treatment at 135°C, not followed by any other apparent weight loss, at least for ageing extended up to 200 h. A similar trend was also detected for the polymethacrylates, with weight losses after 115 h of 5, 15 and 9% for PMMA, PEMA and PBMA, respectively. Throughout the whole treatment time, all the polymers, except B67 and PBMA, remained completely soluble.

In Figs. 1 and 2 are reported the SEC chromatograms of the two couples of twin resins, B66 and B48N, and B44 and B82, respectively, before and after 115 and 200 h of treatment. In general, the curve displacements can highlight the occurrence of two different types of processes: the shift of the chromatograms towards longer retention times, indicating the occurrence of chain scissions, and the opposite shift, as a consequence of branching and coupling reactions producing higher molecular weight molecules. In the case of B66 and B82, a simple behaviour is visible, with the gradual development from the beginning of ageing of cross-linking and chain scission reactions, respectively. B72, whose curves are not reported, shows the same pattern of B82. The displacements of B44 and B48N curves indicate that degradation takes place with the initial formation of higher molecular weight fractions, followed by a phase where scission processes prevail. The chromatograms of B67, PEMA and PBMA (figures not reported) show patterns in agreement with the simultaneous occurrence of cross-linking and fragmentation reactions, similar to the behaviour found in the initial steps of PEMA and PBMA photooxidation [16]. The tendency to give the formation of cross-linked structures is particularly strong in PBMA, where the gel point is reached before 115 h.

The infrared spectra of the resins remained almost unchanged throughout the investigated time. In the spectra of B67, all the common features, such as slight decrease of peak intensity in the C–H and carbonyl zones, are visible, together with a peculiar limited broadening of the carbonyl absorption. Among the reference polymethacrylates only PBMA showed a more advanced ageing (Fig. 3). In particular, the following spectral modifications are visible:

- increase of absorption in the hydroxyl region between 3600 and 3100 cm^{-1} ;
- appearance of a broad band centred at around 2600 cm^{-1} ;
- broadening and initial decreasing of the carbonyl peak, with appearance of three new components at 1804 , 1762 and 1705 cm^{-1} .

By comparison with the spectral characteristics of poly(methacrylic acid), the new band growing at 1705 cm^{-1} is assigned to carboxylic C=O, and the absorptions at ca. 3250 and 2600 cm^{-1} to the stretching vibrations of free and bonded acid OH groups, respectively [17]. These changes can be explained through the decomposition of the lateral butyl groups, induced by the oxidation on the side chains (Scheme 1). The alkoxy radicals formed by decomposition of the unstable secondary hydroperoxides may give β -scission followed by hydrogen abstraction or eventually decay via cross-linking. At the same time, the peaks at 1804 and 1762 cm^{-1} may be assigned to asymmetric and symmetric stretching of carbonyl groups, respectively, belonging to six-membered glutaric type anhydrides [18], whose formation in the ageing conditions can easily occur by dehydration of two adjacent acid groups [17,19,20]. Moreover, the growth of the main carbonyl absorption at



1730 cm^{-1} after the initial decrease can be due to the formation of ketone and aldehyde groups.

3.2. Ageing at 150°C

The weight losses consequent to ageing at 150°C are of the same order of those measured at 135°C, apart from the case of B67 where a 30% weight loss is reached after 200 h. The molecular weight distribution modifications of B66 and B48N, B44 and B82, and B72 and B67 are shown in Figs. 4–6, respectively, where the SEC chromatograms determined before and after 115 and 200 h of ageing are reported. Their patterns confirm the indications on the degradation mechanism obtained by the chromatograms relative to samples treated at 135°C (Figs. 1 and 2). In the case of B66 the curves reveal a main tendency to give cross-linked structures, together with the occurrence from the beginning of degradation of processes that involve the formation of lower molecular weight products. A similar behaviour is also visible for B67, where also at this temperature the polymer which underwent the larger changes: the curve after 115 h of treatment is broadened towards the higher molecular weight side as a result of the branching reactions, whereas at the longer time cross-linking is so extensive that the chromatogram, representing the soluble part only, contains the lower molecular weight fractions of the initial sample together with shorter fragments formed during the decomposition processes. In all the other resins, chain scission is either the only or the main process of degradation. In particular, in B44 and B82 (Fig. 5) polymer fragmentation competes with cross-linking reactions, and the efficiency of the two processes may depend on the molecular weight of the polymer chains.

Comparison between the structural changes occurring on the twin samples B66 and B48N confirms the differences of behaviour previously found. FTIR analysis shows that B48N remained almost unchanged after 200 h of treatment, whereas in B66 (Fig. 7) several spectral changes can be seen. A broad absorption grows in the hydroxyl region between 3600 and 3100 cm^{-1} and three new components are visible in the carbonyl region, at 1805, 1760 and around 1700 cm^{-1} , respectively, together with an initial decrease of the main peak at 1730 cm^{-1} followed by a successive growth. These latter features are practically the same shown in Fig. 3 for the ageing of PBMA at 135°C, where the oxidative decomposition of adjacent lateral butyl groups to give acids and anhydrides was hypothesised as the main mechanism of degradation. In the same conditions, on the contrary, the homopolymer of the other structural unit of these samples, i.e. MMA, do not present evidences of degradation. The lower oxidative stability of PBMA in comparison with PMMA and PEMA has been already reported under conditions of accelerated photo-ageing [16]. The lower stability of B66 compared to B48N may be therefore attributed to the composition difference (BMA/MMA 52/48 and 25/75, respectively) and in particular to the higher

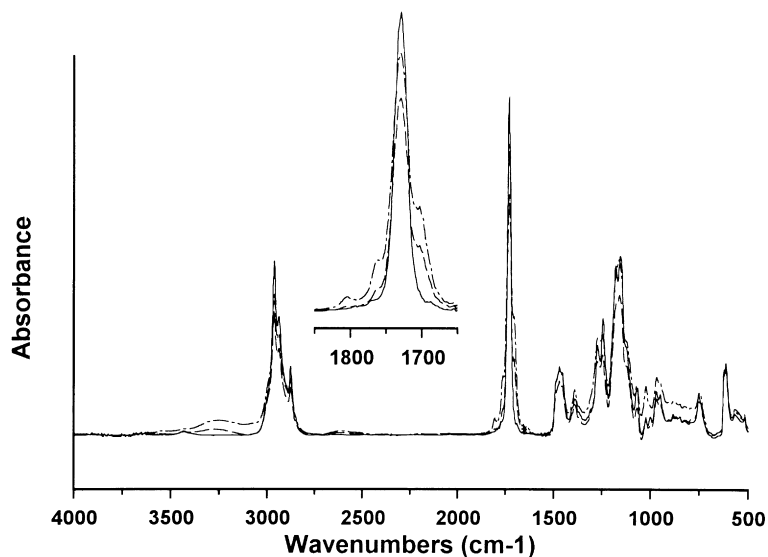


Fig. 3. FTIR spectra of PBMA before (solid line) and after treatment for 115 h (dashed line) and 200 h (dash-pointed line) at 135°C.

probability of BMA sequences in the B66 chains. When sequences of BMA units are present, formation of cyclic anhydrides can easily occur, while in case of isolated units the decomposition is likely to be blocked owing to the more stable adjacent MMA units.

Some thermal contribution to the ester decomposition [21] is thought to be active in the samples discussed here,

as proved by results obtained on B66 treated under inert atmosphere at 150°C up to 200 h. Infrared analysis in fact showed a progressive formation of acids and cyclic anhydrides, though in limited amounts, suggesting that in addition to the main process of direct oxidation of the side alkyl groups, partial thermal decomposition may be also taken into account at the investigated temperatures.

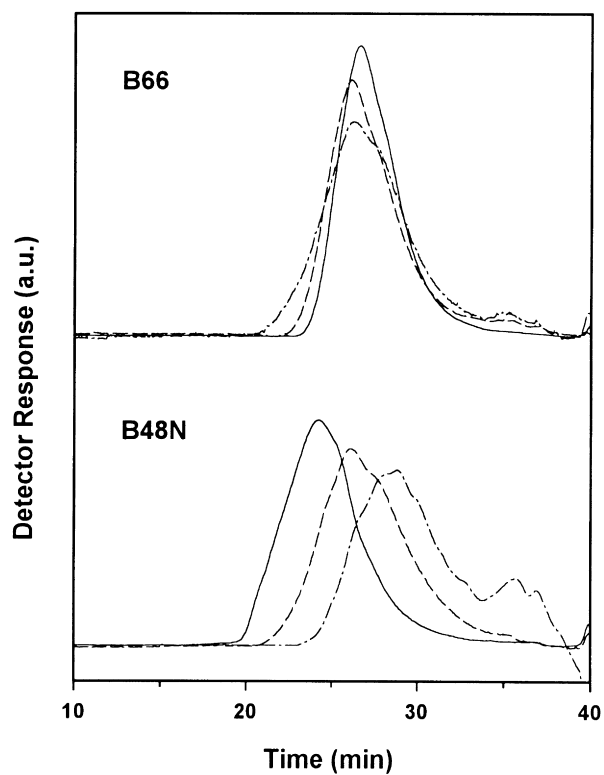


Fig. 4. SEC curves of B66 and B48N before (solid line) and after treatment for 115 h (dashed line) and 200 h (dash-pointed line) at 150°C.

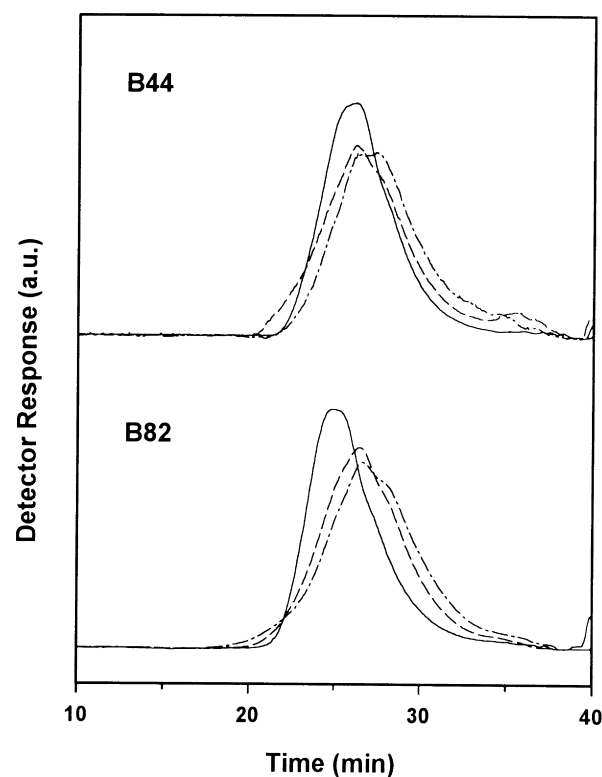


Fig. 5. SEC curves of B44 and B82 before (solid line) and after treatment for 115 h (dashed line) and 200 h (dash-pointed line) at 150°C.

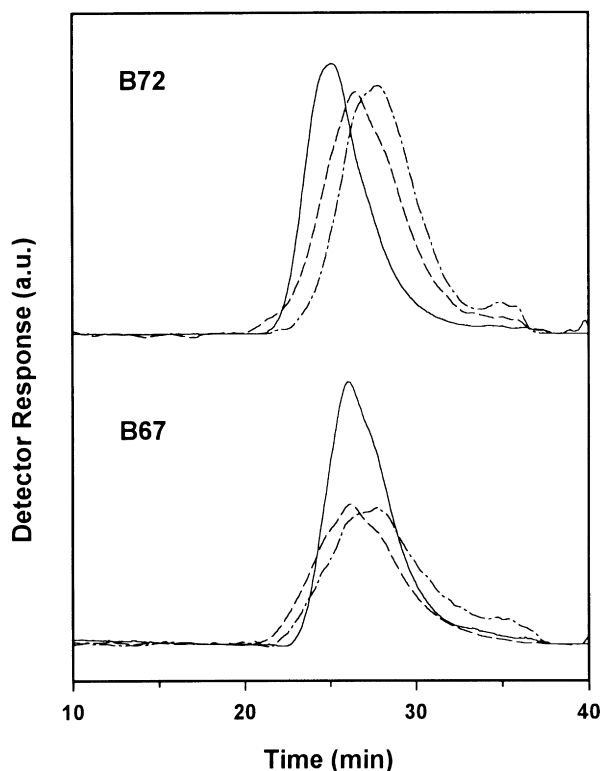


Fig. 6. SEC curves of B72 and B67 before (solid line) and after treatment for 115 h (dashed line) and 200 h (dash-pointed line) at 150°C.

Small infrared spectral modifications were also detected in B82 and B44, very similar for the two samples, and essentially consisting of the gradual decreasing and the partial broadening of the carbonyl esters absorption. The infrared spectra of B72 showed only a slight decrease and a very limited broadening of the carbonyl

peak, suggesting a good stability towards decomposition of ester groups.

The relatively low stability of B67 found a confirmation in the FTIR and UV–Vis spectra (Figs. 8 and 9, respectively). Large infrared spectral differences can be seen, in particular:

- overall progressive decreases of the main absorptions and extensive loss of structural resolution in the region between 1500 and 600 cm^{-1} ;
- appearance of a very broad absorption in the whole hydroxyl region with two relative maxima at ca. 3500 and ca. 3250 cm^{-1} , and extended also in the region of 2800–2400 cm^{-1} , indicating strong association of –OH groups [17];
- broadening of the carbonyl peak with formation of new components centred at about 1805, 1760 and 1700 cm^{-1} , and development of absorptions at lower frequencies, down to ca. 1600 cm^{-1} .

Such variations are similar to those found in PBMA degradation and indicate that the isobutyl groups underwent extensive decomposition, accounting for the observed weight losses, and also leading to formation of anhydrides. The hydroxyl absorptions show an intensity decrease in the interval between 115 and 200 h of treatment, which is greater for the band centred at 3500 cm^{-1} . This trend together with the assignment of the absorptions [22], suggests the initial accumulation and the following thermal decomposition of tertiary hydroperoxides, absorbing at 3500 cm^{-1} . In B67, oxidation reactions are promoted by the labile hydrogen atom located on the tertiary carbon of the isobutyl group, which may be easily abstracted by any radical formed during the treatment. The possible mechanism

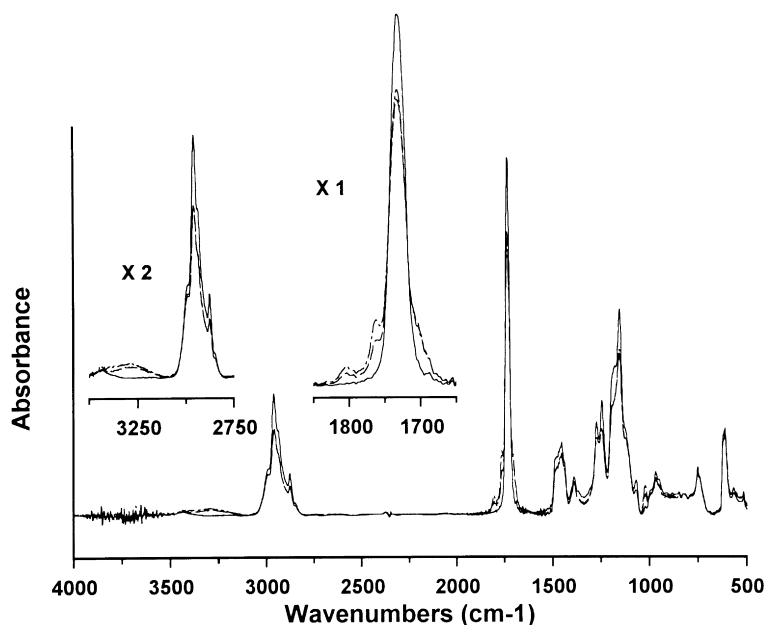


Fig. 7. FTIR spectra of B66 before (solid line) and after treatment for 115 h (dashed line) and 200 h (dash-pointed line) at 150°C.

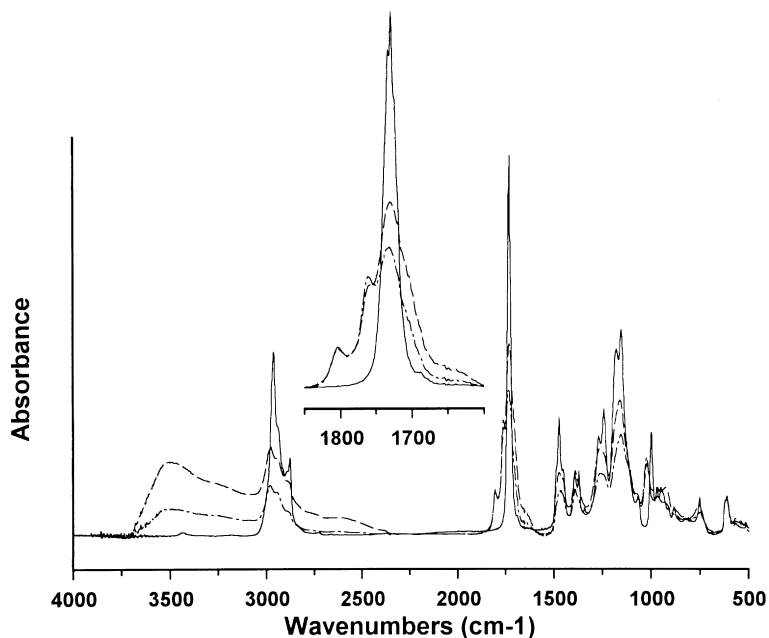


Fig. 8. FTIR spectra of B67 before (solid line) and after treatment for 115 h (dashed line) and 200 h (dash-pointed line) at 150°C.

through which such reactions take place is shown in Scheme 2. The β -induced scissions of alkoxy radicals may follow two paths, the first one leading to ketones, whose formation may account for the broad absorption growing at 280 nm in the UV–Vis spectra shown in Fig. 9 [15]. The second pathway produces new alkoxy radicals mainly leading to acid groups, which easily evolve to anhydrides. Moreover, it may lead to scission products, clearly visible by SEC (Fig. 6) and also containing C=C double bonds (Fig. 8), and to cross-links. Cross-linked structures are also obviously formed through any bimolecular combination of radicals.

4. Conclusions

The above results allow us to clarify the degradative behaviour under conditions of low temperature treatments in air, relevant for natural ageing, of acrylic resins used as commercial protective coatings. SEC analysis could determine the molecular changes even before any structural variations may be detected, demonstrating that the first reactions to take place in all the resins are chain scissions and/or macromolecular couplings.

The stability of the resins appeared to be controlled by the reactivity of alkyl side groups. The first step of ageing

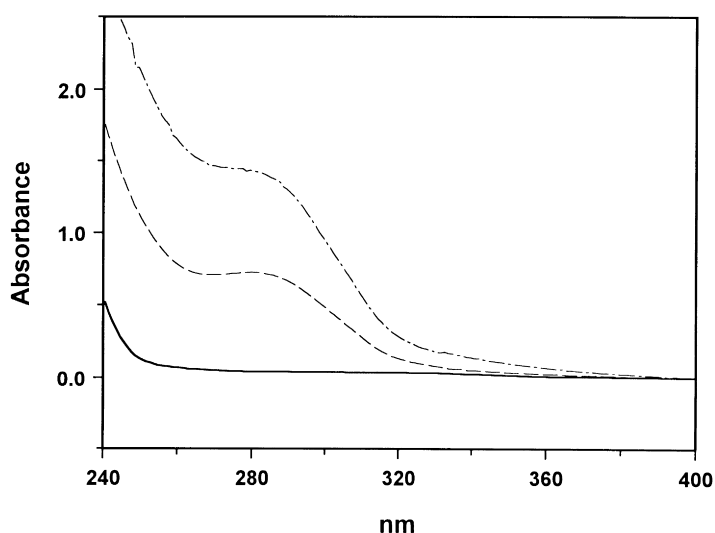
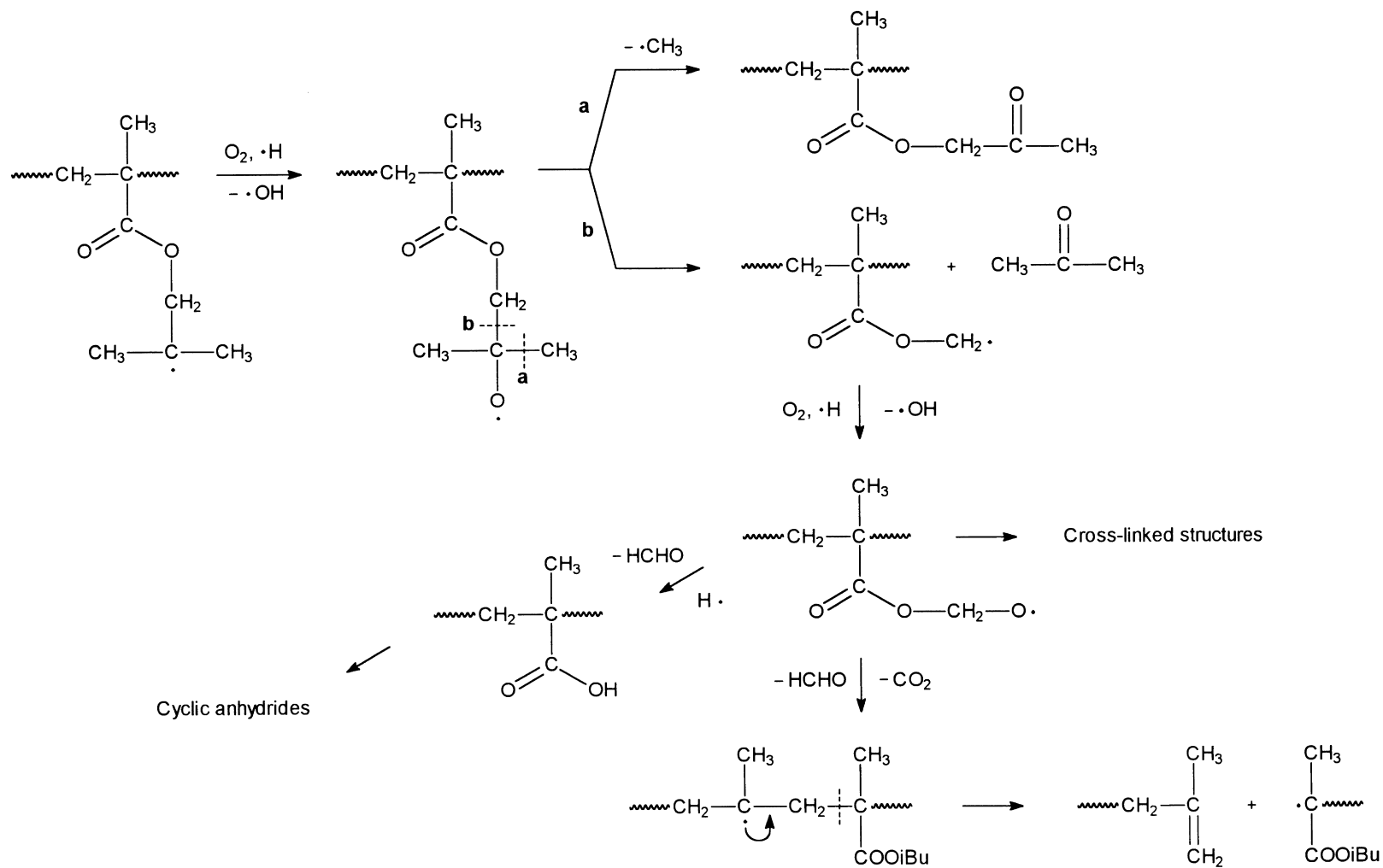


Fig. 9. UV spectra of B67 before (solid line) and after treatment for 115 h (dashed line) and 200 h (dash-pointed line) at 150°C.



Scheme 2.

involves the thermal decomposition of labile structures formed during synthesis, probably the same trace impurities, which induce the photoinitiated degradation [23]. At longer times of treatment the oxidative decomposition of side groups may occur, favoured for longer esters as in B67 (isobutyl group) and B66 (butyl group), while in the case of B48N, containing a lower amount of BMA units, the formation of anhydrides is blocked by the presence of the more stable co-units. At the same time, these polymers containing long ester groups, and in particular B67, undergo fast and extensive cross-linking together with fragmentation and consequent weight losses.

On the contrary, only a limited decomposition of esters occurs in B44, B82 and B72, and mainly molecular changes are visible. On this basis, it may be concluded that in both acrylic and methacrylic resins where all or the majority of the alkyl side groups are short, chain scissions prevail over cross-linking and no insoluble fractions are formed.

In general the resins showed good stability towards oxidation: the formation of oxygen-containing functional groups has been observed only for B66 and B67, and the higher reactivity of B67 has been explained by the presence of labile tertiary hydrogen atoms on the alkyl side chains, which promote the oxidation process. As a final remark, it is also worth to say that SEC, being sensitive to very small changes of molecular weight distribution [24], has been confirmed to be one of the more suitable tools for detecting initial events of degradation [16].

Acknowledgements

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