Photooxidative degradation of acrylic and methacrylic polymers

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Abstract

The photooxidative stability of poly(methyl acrylate), poly(ethyl acrylate), poly(ethyl methacrylate) and poly(butyl methacrylate) has been investigated under conditions of artificial solar light irradiation. Molecular and chemical changes induced by the light treatment were followed by size exclusion chromatography and Fourier transform infrared spectroscopy. The acrylate units were found to be more reactive towards oxidation, in comparison with the methacrylate ones. With short alkyl side groups chain scissions prevailed over cross-linking reactions both in acrylate and methacrylate samples. The degradation of poly(butyl methacrylate) proceeds in a completely different way, with extensive cross-linking and simultaneous fragmentation reactions. In all the samples the structure formed as result of oxidation reactions were similar. It has also been found that the first effect of degradation to be detected is that connected with the changes of samples molecular weight distributions. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Acrylic/methacrylic polymers derive from the polymerisation of esters of acrylic and methacrylic acid, and form materials, which are well known for their uses and applications in many important fields. Because of their characteristics of optical clarity, mechanical properties, adhesion and chemical stability one of their most important uses is in the formulation of paints and surface coatings [1]. The photostability of aliphatic acrylic and methacrylic polymers is generally very high, much higher for instance than that of polyolefins. The carbonyl ester group in the polymer units is not directly photochemically active, and the general content of trace impurities which could initiate the photoinduced degradation is inferred to be very low [2]. On the contrary, it has been reported that light induced oxidation of acrylic and methacrylic polymers is not autocatalytical, as in olefin polymers, but proceeds at constant rate of oxygen consumption, with direct proportionality of initiation rates on the number of chain ends [3]. This indicates that chromofores responsible for the photooxidation process initiation derive from polymerisation initiator fragments, or from transfer agent moieties incorporated as terminal groups.

Although acrylic and methacrylic polymers have also a generally good resistance to hydrolysis, there is some uncertainty in the evaluation of the role of water during their natural ageing: oxidation may precede hydrolysis, or it may take place on the hydrolysis products. Thin films of acrylic based artist's paints obtained from aqueous dispersions were reported to develop cross-linking and yellowing even when kept in the dark [4].

Most of the studies on photooxidation of acrylic and methacrylic polymers have been carried out with high energy UV radiation, typically 254 nm. Investigations performed with irradiation conditions comparable to those of solar light are limited, notwithstanding the relevance they can have for assessment of polymer stability in the natural environment.

In the photolysis and photooxidation at 254 nm of poly-(methyl methacrylate), PMMA, it is reported that the polymer undergoes extensive random chain scissions, with formation of low molecular weight gaseous products and limited monomer production [5–9]. The number of scissions is proportional to radiation dose, and it is much higher in an inert atmosphere than in air. Rate of scission was found to vary with radiation wavelength, reaching a maximum at 280 nm and becoming zero at $\lambda > 320$ nm [8]. This finding was explained by inferring the influence of aldehyde or ketone groups, photoactive at 280 nm, whose presence was supported by the absorptions seen in the UV spectra of the investigated samples. UV spectra of PMMA samples differ substantially from one case to the other, with some

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Table 1
Molecular and thermal characteristics of acrylic and methacrylic polymers

Sample	M_n	M_w	M_w/M_n	T_g (°C)[a]
PMA	6800	28 000	4.1	9
PEA	42 000	110 000	2.6	− 23
PEMA	140 000	310 000	2.2	63
PnBMA	110 000	220 000	2.0	15

[a] Supplier's data.

showing an absorption at 285 nm which is broadened up to 360 nm [5], and others having peak maximum at 277 nm shifting during irradiation to 267 nm. The absorption at 277 nm was attributed to the polymer ester groups and the displacement towards lower wavelength to the formation of ketone or aldehyde groups [8]. The photolysis of PMMA was therefore supposed to occur as a consequence of the UV radiation absorption from the ester groups, which induces deesterification through homolytic bond scission. Oxidation of the so formed tertiary polymeric radical produces, through decomposition of an hydroperoxide and scission of the polymer molecule, a terminal ketone [8].

At wavelengths higher than 300 nm the photostability of acrylic and methacrylic polymers must depend on the presence of undefined photoactivators in the material. Under such conditions, photooxidation of PMMA has been found to require very long irradiation times, with limited development of hydroxyl groups and of new carbonyl absorptions in the polymer [10]. Further it has been shown that residual monomer molecules or other unsaturations in the polymer do not act as photoinitiators of the degradation.

Poly(methyl acrylate) (PMA) and poly(ethyl acrylate) (PEA), when irradiated at 254 nm under vacuum, undergo both scissions on the side ester groups, with formation of volatile molecules, and extensive cross-linking [9,11,12]. Cross-linking occurs through macroradical recombination and is favoured in polymers with low glass transition temperatures. For polymers irradiated below their T_gs chain scissions prevail over cross-linking reactions [12].

Irradiation of polyacrylates in the presence of air produce radicals in the polymer chains which reacting with oxygen give rise to new carbonyl compounds and to hydroxyl groups, whereas cross-linking reactions are lower than under pure photolysis conditions [11]. Photooxidation at $\lambda > 300$ nm was found to produce similar structural changes, although with minor extent [13].

Methacrylate polymers are in general less prone to cross-linking, under any irradiation condition. This behaviour is explained by considering the higher stability of the tertiary macroradicals formed on the chains, which would preferentially undergo chain scissions in the absence of air, or reaction with oxygen in the presence of air, instead of recombination reactions between macroradicals from different polymer chains [9,14]. The trend, however, is influenced by the size and structure of the lateral ester

group. In poly(alkyl methacrylates) with long alkylic groups reactions on the side chains produce cross-linking even in the case of irradiation with longer wavelength, such as visible light [15]. With visible light irradiation in air, infinite network formation is produced with shorter lengths of alkyl side chains than under ionising radiation conditions [5].

The competition between chain scissions and cross-linking reactions was also found to depend on the temperature and thickness of the polymer film. Together with the development of cross-linked structures in such a type of methacrylate polymers, an increasing sample weight loss was observed, due to the formation of volatile fragments [9,15]. The use of weight loss has been indeed suggested as an index of the stability of acrylic polymers [15].

We have started a systematic investigation on the photooxidative stability under conditions of artificial solar light irradiation of acrylic and methacrylic based polymers, which have real or potential interests as protective coatings for many different substrates. In the course of this study we have evaluated the characteristics and performances of commercial polymer systems and of new acrylic based partially modified polymers. In this paper we report the results so far obtained on PMA, PEA, poly(ethyl methacrylate) (PEMA) and poly(n-butyl methacrylate) (PBMA), which contain structural units present in many commercial acrylic coatings, and whose stability characteristics will be used as comparison terms.

2. Experimental

The investigated acrylic/methacrylic polymers were commercial secondary standards obtained by Aldrich Chimica (Italy), whose molecular and thermal characteristics are collected in Table 1. 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.

Photooxidations were carried out with a Suntest CPS apparatus, (Heraeus, Germany) equipped with a Xenon light source filtered for $\lambda < 295$ nm. Irradiation was kept at a constant power of 765 W/m^2 during the lamp operating life. 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 with chloroform and collecting the insoluble fractions with vacuum filtration on 0.2 μm pre-weighted membrane filters.

Molecular characterisation of initial and irradiated samples were performed by size exclusion chromatography (SEC) with 4 PL-Gel (Polymer Labs, England) columns,
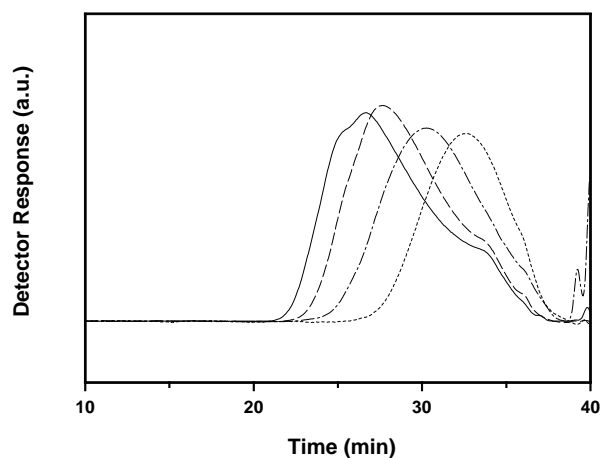
Fig. 1. SEC curves of PMA before (solid line) and after treatment for 100 h (dashed line), 364 h (dash-pointed line) and 1550 h (short dashed line).

30×0.78 cm^2, 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 solutions were filtered on 0.45 μm membrane syringe filters. 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 the chromatograms obtained from different samples the peak areas were always normalised, by taking into account the fraction of polymer not lost by volatilisation or by cross-linking.

UV–Vis spectra were acquired with a Lambda 15 instrument (Perkin–Elmer, USA). Fourier transform infrared (FTIR) analysis was carried out on a 1710 Perkin–Elmer system, with DTGS detector and 4 cm^{-1} resolution. Spectral

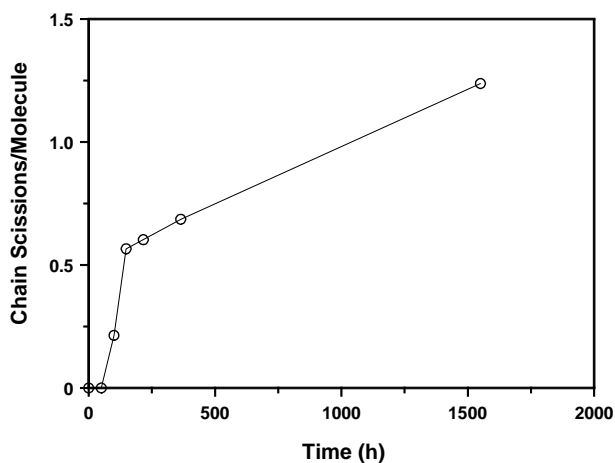acquisitions and data treatments were performed with Spectra Calc (Galactic Industries, USA) software.

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. Samples were pre-cooled by circulating liquid nitrogen around the measuring cell, constantly kept under nitrogen flow, and the temperature programme was 5°C/min heating rate.

3. Results and discussion

3.1. Poly(methyl acrylate)

The accelerated photooxidative ageing of PMA was extended up to 1550 h. The polymer sample started to loose weight after the first 100 h treatment, reaching 27% weight loss at the final treatment time. No cross-linked polymer was detected at any stage. The molecular modifications occurring during ageing are shown in Fig. 1, where are reported the SEC chromatograms determined on the polymer after different treatment times. It is clear that only chain scissions take place, starting to develop even before any weight loss could be detected. Under irradiation conditions with a light source having wavelengths < 300 nm it has been reported for PMA in air that no cross-linking occurs but only initial increase of molecular weights followed by chain scissions [9].

From the SEC chromatograms the number average molecular weights, M_n, were calculated at the different treatment times and, taking into account the fraction x of volatilised polymer, the number S of chain scissions per initial polymer molecule was obtained through the relationship [16]:

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

where $M_{n,0}$ is the initial number average molecular weight.

The plot of S vs. time is shown in Fig. 2. One can see that after a short induction period, the number of chain scissions increases in a linear mode at an higher rate up to ca. 150 h, and than at a lower rate for longer times. This behaviour implies that in the two different kinetic regimes chain scissions occur randomly along the polymer molecules [17].

The UV spectra of PMA films in Fig. 3 show that irradiation in presence of air causes development of an absorption in the range between 240 and 320 nm, which looks very similar to that reported in the literature for the case of an acrylate copolymer [13].

This broad absorption initially increases with time, due to the formation of chromofore groups in the polymer molecules. After ca. 200 h the absorption reaches a maximum and then starts to decrease, indicating consumption of the chromofores previously formed.

The structural changes occurring in the PMA are revealed

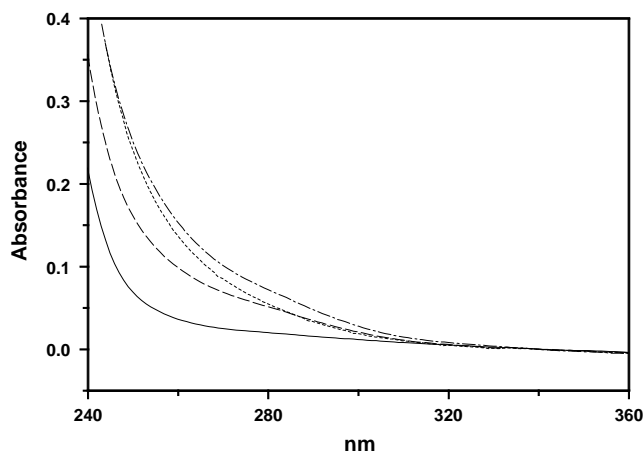Fig. 2. Scissions per initial molecule of PMA as a function of treatment time.

Fig. 3. UV spectra of PMA before (solid line) and after treatment for 100 h (dashed line), 216 h (dash-pointed line) and 532 h (short dashed line).

by the FTIR spectra of Fig. 4. Oxidated structures appear in the polymer molecules soon after a 100 h treatment: hydroxyl groups are responsible of the broad absorptions at ca. 3400 and 3230 cm^{-1}; the carbonyl peak broadens at 1710 cm^{-1} and at lower wavenumbers. With irradiation times longer than 100 h spectral changes are more extensive. The general and progressive decrease of the principal polymer peaks reflects the volatilisation of small molecules, in agreement with the weight loss results. Such decrease involves not only the ester side groups, but also the backbone structure, as chiefly shown by the spectral changes in the zone of the –C–H stretchings, 3000–2850 cm^{-1}. This suggests that monomer molecules are also formed as a result of the chain scissions.

The main signal of advancing oxidation during this interval time is the gradual increase in the carbonyl region of new absorptions, extending up to 1830 cm^{-1}, with maximum at 1793 cm^{-1}. The hydroxyl absorptions, on the contrary, either decrease to an almost constant value (at 3400 cm^{-1}), or slightly increase (at 3230 cm^{-1}).

The oxidative degradation of PMA at $\lambda > 295$ nm initiates through reaction of oxygen molecules with the radicals much probably formed by abstraction of the tertiary hydrogen atoms of the structural units, followed by β-scission and formation of ketones absorbing at 1710 cm^{-1} [18] according to Scheme 1.

Acid groups which would absorb at 1705 cm^{-1} [19] may be also formed at this stage, as a result of the photolytically induced scission of ketones (Scheme 2).

The formation of carboxylic OH groups, their association as well as that with other OH groups (alcohols, hydroperoxides) could justify the absorptions at 3400 and 3230 cm^{-1}. The growing of the broad absorption between 1830 and 1760 cm^{-1} could partially be attributed to the formation of γ-lactone structures, which absorb at 1780 cm^{-1} and are ubiquitous in all types of aliphatic polymers photodegradation [20–22], but as well to the formation of open chain anhydrides whose main absorption is around 1800 cm^{-1} [23]. Such structures may be generated according to reactions of Schemes 3 and 4.

From the spectral changes reported in Fig. 4 it may be seen that the formation of anhydrides according to Scheme 4 takes place after a given concentration of terminal carboxylic acid groups is reached. The open chain anhydride molecules have higher molecular weights than the initial acidic reactants, and this may explain the lower rate of apparent chain scissions shown in Fig. 2 for irradiation times higher than 150 h.
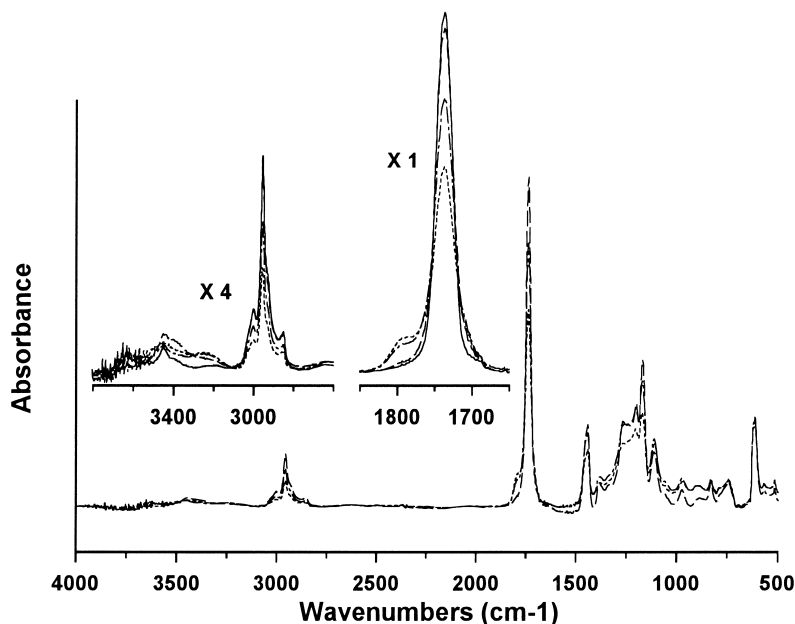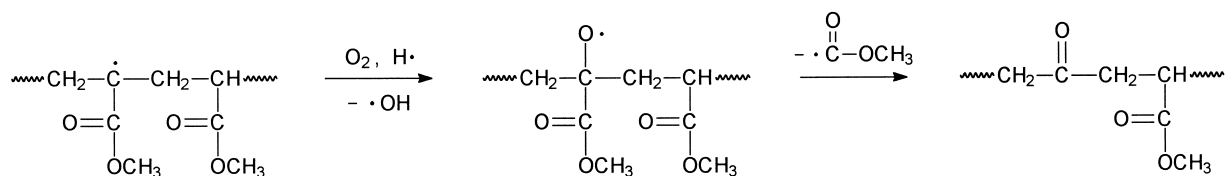

Fig. 4. FTIR spectra of PMA before (solid line) and after treatment for 100 h (dashed line), 216 h (dash-pointed line) and 532 h (short dashed line).

Scheme 1.

3.2. Poly(ethyl acrylate)

No apparent weight loss was measured on PEA irradiated for 1500 h, in contrast with what found in the case of PMA. Also no gel formation was detected. The SEC chromatograms in Fig. 5 show patterns in agreement with a degradation process where extensive chain scissions take place, with formation of shorter polymer molecules. Fragmentation does not proceed randomly at the beginning: at the shorter irradiation time a bimodal molecular weight distribution is formed, containing a small fraction of molecules with molecular weights higher than the initials.

The UV spectra of the polymer, Fig. 6, show the presence in the starting polymer of a broad absorption between 260 and 290 nm, which may be attributed to chromofore impurities. These structures are soon eliminated during the degradation and no other chromofores build-up in the polymer.

The FTIR spectra of PEA at various irradiation times, in Fig. 7, show the following structural modifications occurring in the sample:

- increase of absorption in the whole hydroxyl region, between 3650 and 3100 cm^{-1}, after an induction period of 450 h;
- progressive broadening of the carbonyl band, with simultaneous increasing of new components at 1780 and at 1705 cm^{-1};
- decreasing intensity of the main carbonyl peak at 1734 cm^{-1} at times longer than 450 h.

The progressive decrease of all the absorptions between 3000 and 2800 cm^{-1}, and in the fingerprint region between 1400 and 700 cm^{-1}, may be attributed to the loss of low molecular weight material formed during the degradation. In the photooxidation of PEA the tertiary macroradicals which are initially formed in the polymer may react intramolecularly, in the same way as in PMA (Scheme 3), to

form γ-lactones, responsible of the 1780 cm^{-1} absorption. Alternatively, the same radicals may react with atmospheric oxygen to produce, after chain scission, unsaturated ketones which may account for the absorption at 1700 cm^{-1} [24,25] which increases from the beginning of the process without induction time (Scheme 5).

At this stage the carbonyl peak at 1734 cm^{-1} remains practically constant: this means that the loss of part of the carbonyl ester groups is compensated by the formation of new oxidation products absorbing in the same region, which could be terminal aldehyde groups formed, as shown in Scheme 5, by reaction of the secondary macroradical with oxygen. At irradiation times longer than 450 h the degradation proceeds with formation of the same photoproducts, and with a growing concentration of –OH groups responsible of the broad absorption between 3600 and 3100 cm^{-1}.

The recombination of a fraction of tertiary macroradicals could justify the formation of higher molecular weight molecules. At the same time, carbonyl ester groups are progressively eliminated from the structure.

The absence of any absorption at 1640 and 909 cm^{-1} in the IR spectra seems to show no formation of vinyl unsaturations during degradation, in disagreement with what reported for the photooxidation of ethylene–ethyl acrylate copolymers [13].

3.3. Poly(ethyl methacrylate)

Photooxidation of PEMA up to 1500 h occurs without formation of insoluble fractions and no apparent weight loss. The SEC chromatograms in Fig. 8 show that chain scissions take place in the polymer, but again the shape of the distribution curves excludes the case of a purely statistic chain scission mechanism. Polymer fragmentation and cross-linking reactions by macroradical recombination probably compete, and it is likely that the efficiency of the
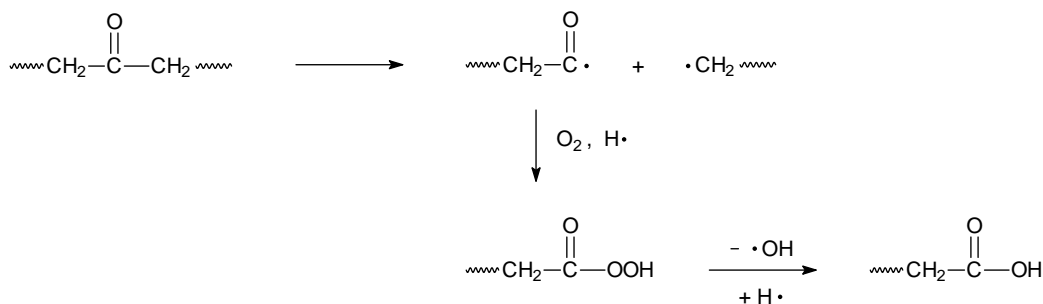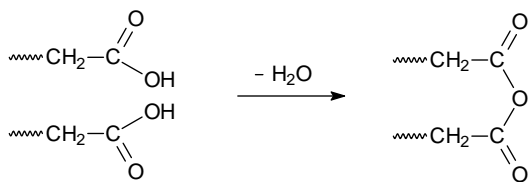
Scheme 2.
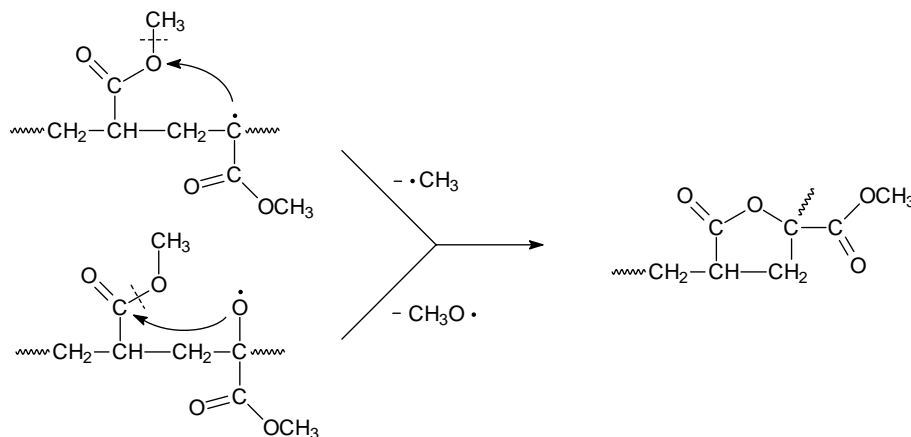
Scheme 3.

two processes depends on the molecular weight of the polymer chains.

The changes of UV spectra after polymer irradiation are reported in Fig. 9. The spectrum of the initial polymer is very similar to that of PEA in Fig. 6, showing the absorption between 260–290 nm due to some chromofore impurity. Spectral variations, however, differ from the previous case, as the above absorption initially increases and disappears only at longer irradiation times, with a contemporary slow growth of an absorption above 310 nm.

The infrared spectra of PEMA remained almost unchanged throughout the investigated time intervals of irradiation. After 1500 h a slight decrease of peak intensity in the –C–H stretching zone may be noticed together with a very limited broadening of the carbonyl peak below 1700 cm^{-1}, and with small absorptions at 1654 and 1638 cm^{-1} (Fig. 10). These results indicate very high stability of PEMA towards oxidation, similarly to that reported for PMMA [10]. Elimination of ester groups is limited and the photoinduced degradation consists in main chain scissions followed by macroradical disproportionation and formation of terminal double bonds (1638 cm^{-1}). The reactions at these chain ends can proceed as shown in Scheme 6, with formation of a conjugated double bond system which may explain the UV absorption above 310 nm, and the IR one at 1654 cm^{-1}.

3.4. Poly(n-butyl methacrylate)

Photooxidation of PBMA takes place with formation of insoluble polymer fractions as the initial steps of the

process, and fast growth of gel amount: 14% after 300 h, 58% after 900 h, and 70% after 1500 h. A limited polymer weight loss of 2% is measured after 1500 h irradiation.

The strong tendency of PBMA to give cross-linking reactions, bringing finally to an almost completely insoluble polymer, is also clearly revealed by the SEC curves, in Fig. 11. The initial molecular weight distribution after 300 h irradiation is broadened on both sides as the result of cross-linking and scission reactions occurring simultaneously. At this point gel fraction is a minor part of the whole material, and therefore the chromatogram is still representative of the whole polymer transformations. At longer times of irradiation cross-linking is so extensive that the chromatograms, obviously representing the soluble part only, contain either the lower molecular weight fractions of the initial sample together with shorter fragments formed during the degradation (sample irradiated for 900 h), or the latter ones alone (sample irradiated for 1500 h).

The extensive formation of cross-linked structures strongly influences the physical properties of the polymer
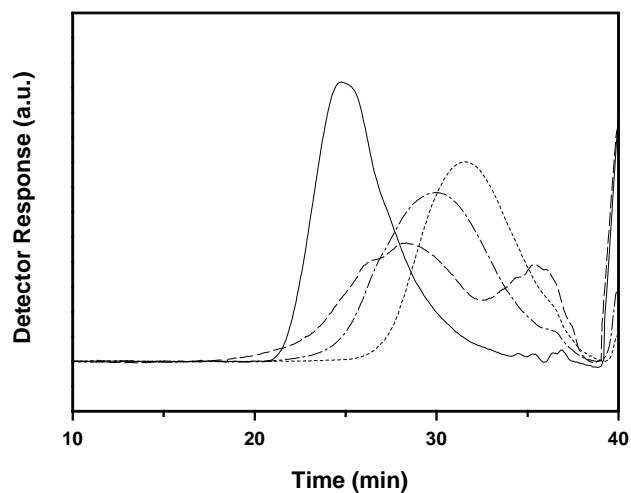

Fig. 5. SEC curves of PEA before (solid line) and after treatment for 300 h (dashed line), 900 h (dash-pointed line) and 1500 h (short dashed line).
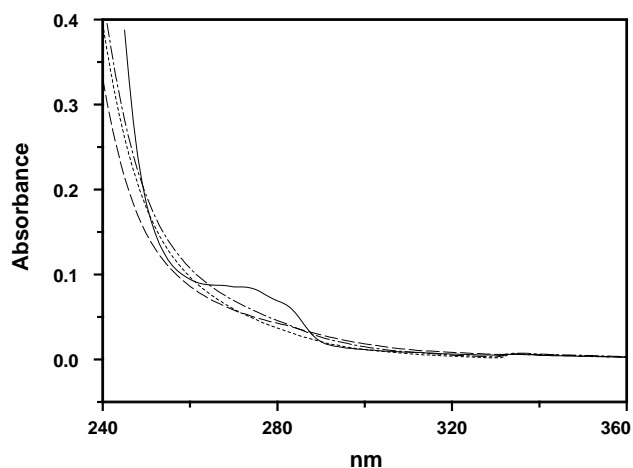

Scheme 4.

Fig. 6. UV spectra of PEA before (solid line) and after treatment for 160 h (dashed line), 320 h (dash-pointed line) and 1500 h (short dashed line).

at 1732 cm^{-1} and of those at 1242, 1177, 1153 cm^{-1} associated to the C–O–C groups. The new spectral features resulting from the photoinduced oxidation are:

- a very broad absorption covering the whole hydroxyl region between 3600 and 3000 cm^{-1}, and extended also in the region of 2800–2400 cm^{-1}, indicating a strong association of –OH groups [26]. From Fig. 13 it may be seen that the hydroxyl bearing groups begin to be formed only after more than 1000 h of irradiation;
- the broadening of the carbonyl peak, with progressive increase of the absorption at low frequencies side, down to ca. 1670 cm^{-1}, and the retarded development, after more than 700 h treatment, of absorptions between 1810 and 1760 cm^{-1};
- a small absorption at about 1640 cm^{-1}, which does not grow further after 700 h irradiation.

The lower photooxidative stability of PBMA in comparison with PEMA, which is evident from the comparison of the respective IR changes, must be attributed to the effect of the side chain oxidation. The high cross-linking rate is accounted for by the fact that oxidation on the side chains produces unstable secondary hydroperoxides which are immediately photolised giving alkoxy radicals [27]. The latter decay rapidly via cross-linking, due to the high mobility of the side chains [28]. Butyl group fragmentation will also occur, with complete loss of ester groups, as shown in Scheme 7.

The tertiary internal macroradicals produced as in Scheme 7 could be the main responsible of the chain scission reactions with formation of unsaturated chain ends, absorbing at 1640 cm^{-1}. Such reactions take place from the beginning of the degradative process, at the same time with the coupling of radicals bringing to cross-linked

films. The film property changes have been measured by TMA, and in Fig. 12 the behaviour of the initial polymer can be compared with that after 2000 h photooxidation. For the initial PBMA the softening temperature is at ca. 25°C, and at ca. 80°C the polymer shows viscous behaviour. In the photooxidised film a limited 10% rod penetration is reached between 50 and 80°C, and complete softening of the film is obtained only above 120°C.

The IR spectra of photooxidised PBMA, Fig. 13, show both general and specific structural changes. The progressive decrease of all principal absorptions indicate loss of low molecular weight molecules produced by the degradation and involving all parts of the structural units. The loss of butyl ester groups may be considered the main occurrence, as shown by the decrease of the carbonyl absorption
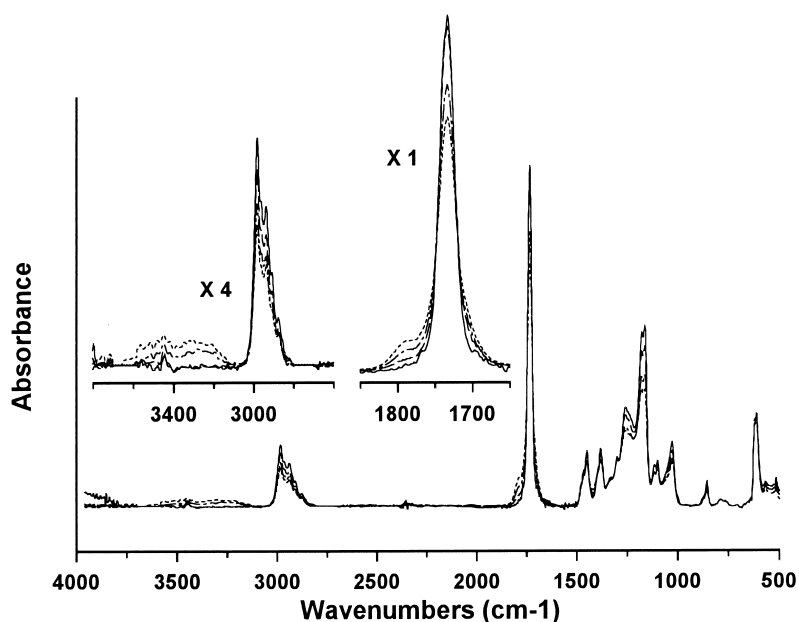

Fig. 7. FTIR spectra of PEA before (solid line) and after treatment for 450 h (dashed line), 800 h (dash-pointed line) and 1500 h (short dashed line).
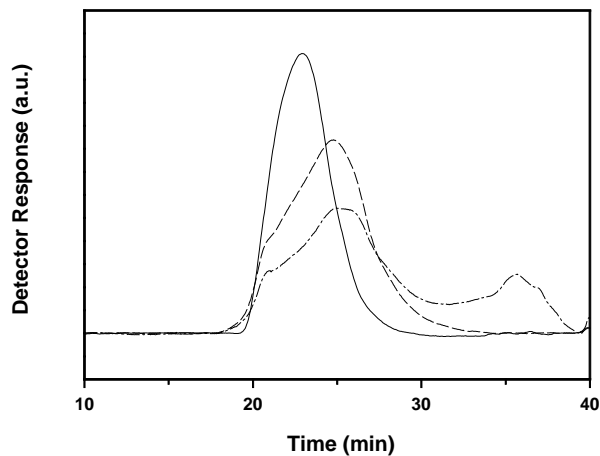
Fig. 8. SEC curves of PEMA before (solid line) and after treatment for 400 h (dashed line) and 1500 h (dash-pointed line).
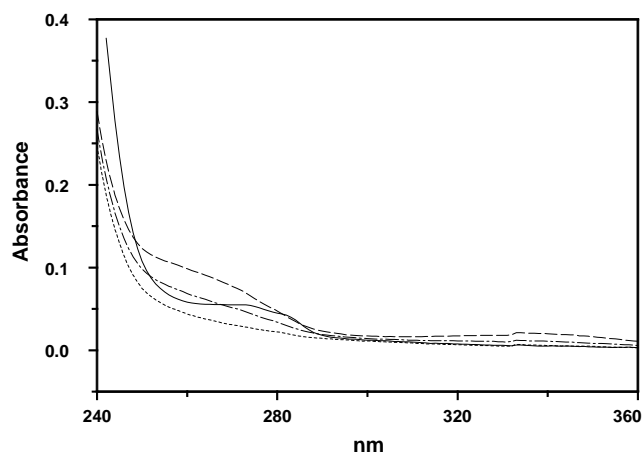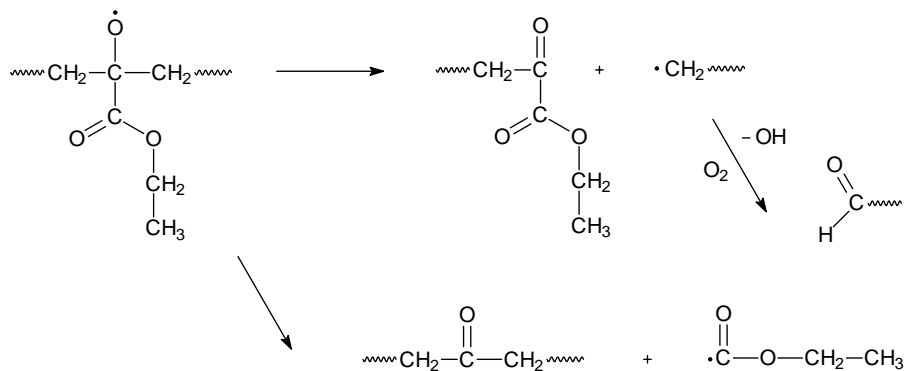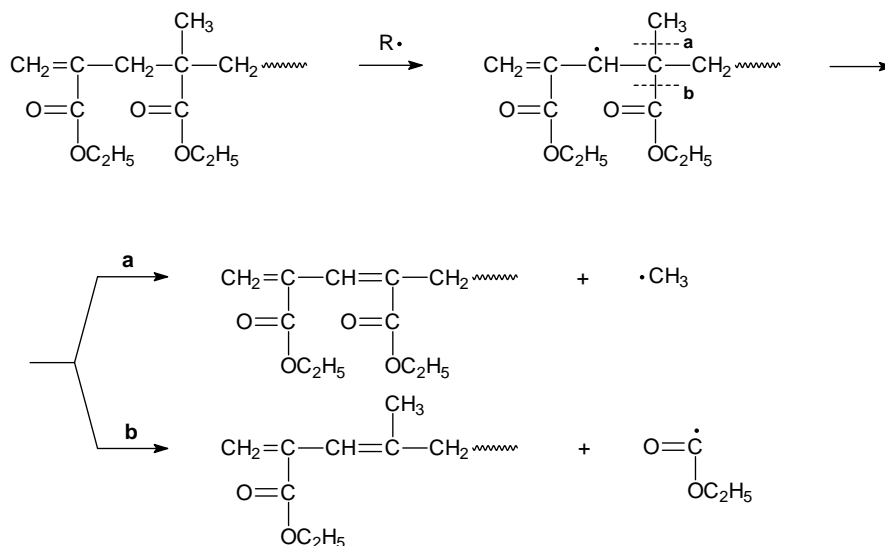

Fig. 9. UV spectra of PEMA before (solid line) and after treatment for 200 h (dashed line), 450 h (dash-pointed line) and 1500 h (short dashed line).
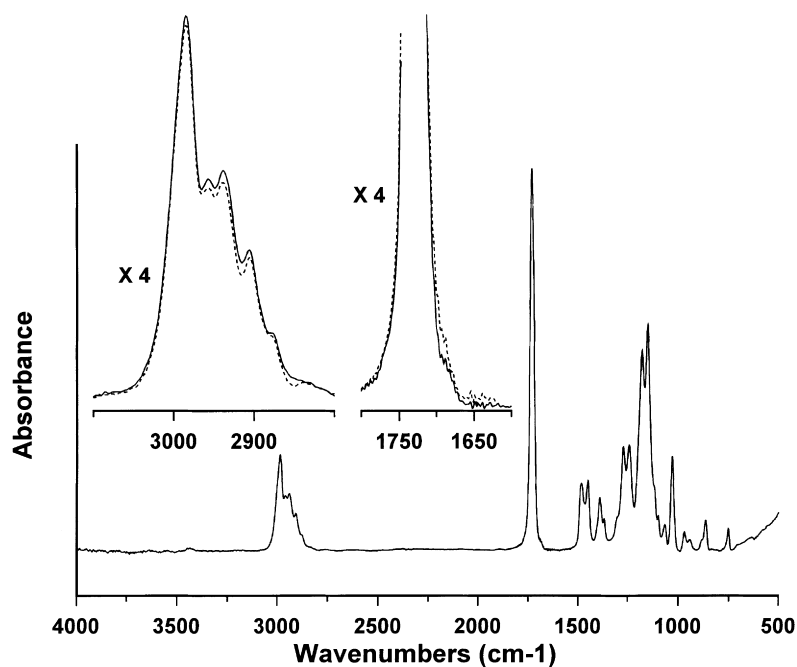

Scheme 5.

Scheme 6.

Fig. 10. FTIR spectra of PEMA before (solid line) and after 1500 h of treatment (dashed line).

structures. Additionally, oxidation of the tertiary macro-radicals will bring to hydroperoxide and alcohol groups, whose growth is seen in the infrared spectra at the longer irradiation times. Intramolecular reactions of the tertiary macroradicals with adjacent ester groups can produce γ-lactones absorbing at 1780 cm^{-1}, as already shown in Scheme 3. Another possible reaction for formation of lactones is reported in Scheme 8.

The intramolecular reactions producing lactones require favourable geometric conformation, possibly due to high segmental mobility. It is therefore likely that such structures are preferentially formed in the dangling chains of the polymeric network and also in the still soluble lower molecular weight chains produced by the polymer fragmentation.
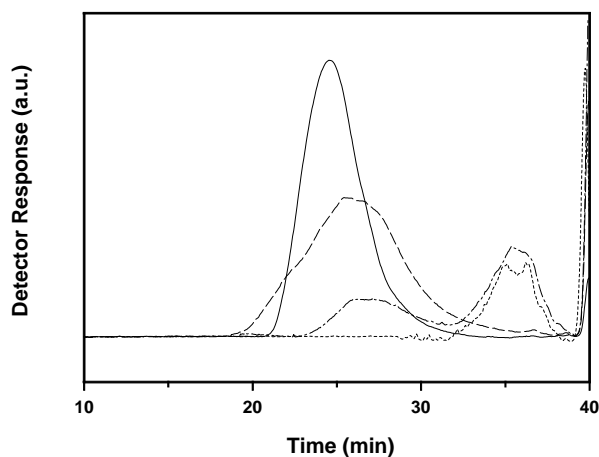

Fig. 11. SEC curves of PBMA before (solid line) and after treatment for 300 h (dashed line), 900 h (dash-pointed line) and 1500 h (pointed line).

Unsaturated ketones and, at longer irradiation times, carboxylic acids are also in this case the photoproducts responsible of the absorptions around 1700 cm^{-1}.

4. Conclusions

The above results allow to make a comparison of the photooxidative stability, under conditions relevant for natural ageing, of acrylate and methacrylate polymers used as components of many commercial protective coatings. When alkyl side groups are short, in both type of polymers chain scissions prevail over cross-linking and no, insoluble fractions are formed. Further, the comparison between PEA and PEMA shows that acrylates are much more reactive towards oxidation than methacrylates. In particular, PEMA shows a very high stability towards the formation of oxidised groups in the polymer, with behaviour similar to the one reported for PMMA [10]. When the aliphatic side ester groups is longer, as in the case of PBMA, the behaviour changes completely: the polymer undergoes fast and extensive cross-linking, together with fragmentation. The overall chemical stability is affected, with effects on both the molecular and the structural side. Formation of cross-linked fractions is the first process, which can be monitored, with the growth of oxidated products appearing at longer times. The reactivity and influence of side butyl groups was also reported in the case of polyacrylates under thermal [28] or photoinduced oxidation [29].

In the competition between scission and cross-linking reactions induced by photooxidative treatments it has been
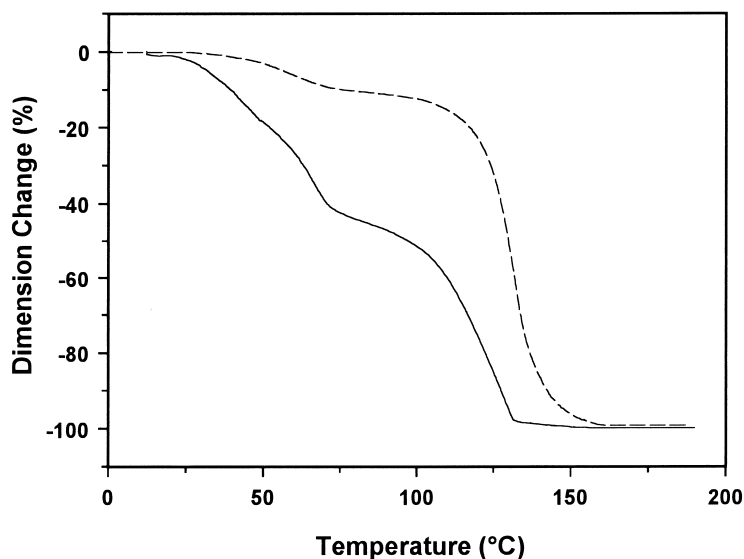
Fig. 12. TMA curves of PBMA before (solid line) and after 2000 h of treatment (dashed line).

often suggested that the glass temperature T_g of the polymer is a controlling parameter [9,15]: polymer chains above their T_gs, with high segmental mobility, would preferentially undergo cross-linking. Under the experimental conditions of this investigation, however, the results for PMA and PEA show that scission reactions are the prevailing ones. It is obvious that for such samples chain mobility is not the controlling reaction parameter, whereas in the case of PBMA the side chain flexibility facilitates mutual recombination of macroradicals to produce the polymer network.

In all the investigated polymers the principal new groups formed as a result of the oxidation reactions are similar. Identification of the precise points of oxidative attack on the polymer chains, and of the preferred reaction pathways would require the analysis of the low molecular weight products formed at the different stages of degradation [29,30]. Our main objective, however, was to obtain the overall photooxidative stability pattern for the polymers investigated and, under the experimental conditions employed in this investigation, the determination of volatile degradation products was not performed.

The production of low molecular weight compounds by oxidation and/or fragmentation obviously corresponds to weight losses in the starting polymer sample. On recognising this fact it has been suggested [15] to use weight loss measurements as an index for classifying the photostability
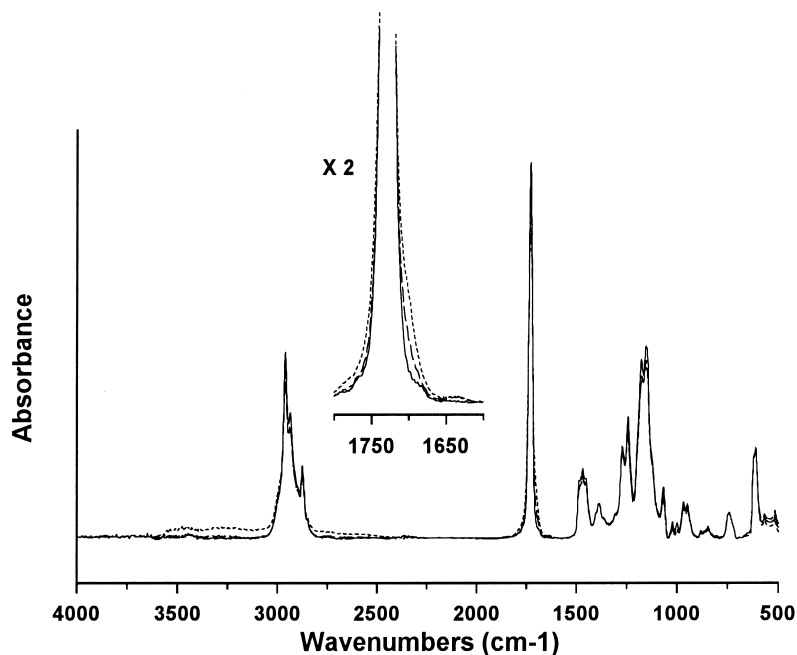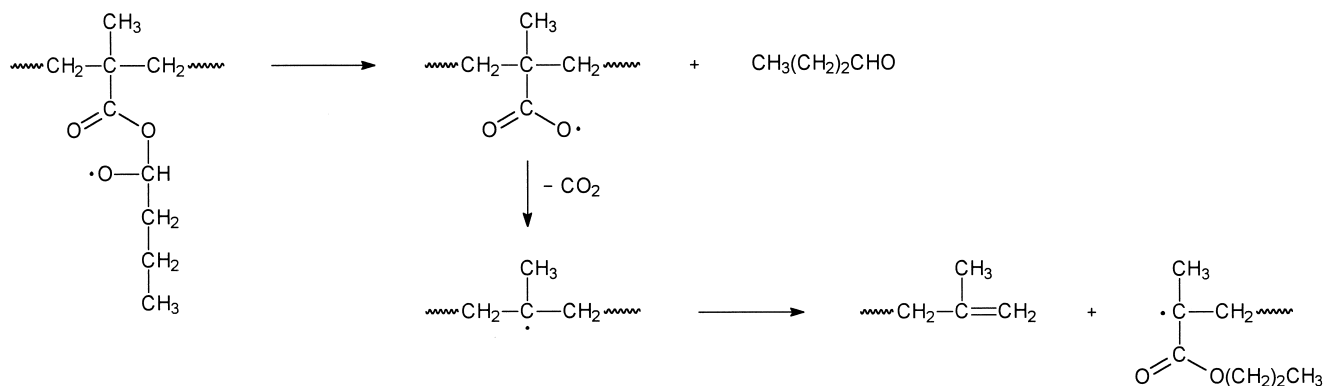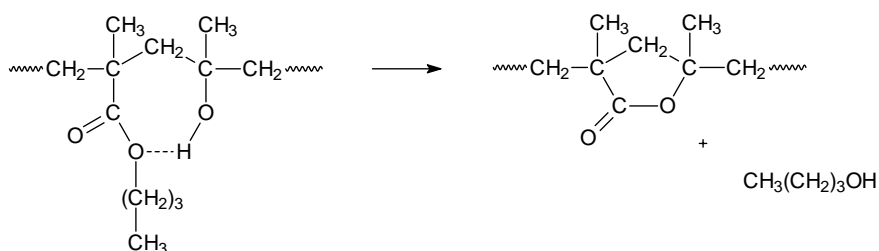

Fig. 13. FTIR spectra of PBMA before (solid line) and after treatment for 700 h (dashed line) and 1500 h (dash-pointed line).

Scheme 7.

Scheme 8.

of acrylic polymeric protectives. The results reported here indicate that such a method is not suitable for assessing the relative polymer stabilities. Even when there were evidences of material losses during the degradation, weight loss measurements could not detect them. The main reason is that oxygen atoms are incorporated in the polymer structure during the degradation, partially or completely compensating the effective weight losses of the original polymer. Only with extended formation of volatile products, as it happens in the case of substantial monomer evolution or of polymers having large lateral groups, weight loss may be easily detected.

Finally, it is worth to point out that in most cases the first reactions to take place in the degradation are chain scissions and/or macroradical recombinations. The systematic determination by size exclusion chromatography of molecular weight distribution changes occurring in the polymer samples during the degradation process, being sensitive to even very small molecular changes [31], is the most suitable tool for detecting any initial degradation event.

Acknowledgements

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