

Thioxanthone Sensitized Photodegradation of Poly(alkyl methacrylate) Films

Miguel G. Neumann, Carla C. Schmitt, Beatriz E. Goi

Instituto de Química de São Carlos, Universidade de São Paulo - Caixa Postal 780, São Carlos SP 13560-970, Brazil

Received 28 August 2008; accepted 28 April 2009

DOI 10.1002/app.30758

Published online 23 September 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The thioxanthone-sensitized photodegradation of poly(alkyl methacrylate) films [alkyl = methyl, ethyl, butyl, and hexyl] was studied using near UV-vis light. The photooxidation process continued even after the total consumption of the sensitizer, possibly due to the excitation of the ketyl groups formed during the first stages of the process. The rate of oxidation, as well as the formation of hydroxy, peroxy, and ketyl groups was faster for polymers with larger ester groups. The decrease of the molecular weight of the degraded polymers was also larger for the hexyl substituted polymer. The side-chain size

effect was attributed to the larger amount of secondary hydrogens available for abstraction by the triplet state of thioxanthone, present in the larger ester groups. The lower glass transition temperature of the hexyl substituted polymer allows a better diffusion of oxygen to the deeper layers of the films that also contributes to the faster photodegradation rate. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1283–1288, 2010

Key words: polymer photodegradation; sensitized photodegradation; poly(alkyl methacrylate) films

INTRODUCTION

The degradation of polymers continues to be a subject of intense interest, due mainly to the widespread use of these compounds in many industrial areas. Therefore, information about the stability and degradation of polymers has to be studied not only from the overall global efficiency of the oxidation processes, but also seeking mechanistic information, which might be useful in the design of new materials.^{1,2}

Of all poly(alkyl methacrylate) polymers, poly(methyl methacrylate) (PMMA) is the most studied because of its broad practical applications. Owing to its properties (high transparency, light weight, good mechanical and electrical properties, good resistance to high temperature, aging, and chemicals), poly(alkyl methacrylate) polymers are widely used in several fields like architecture, motorization, agriculture, medicine, pharmacy and in the textile, paper, and paint industries.^{3,4} The physical properties of these polymers change with the size of ester group. PMMA is a hard,

rigid material with high glass transition temperature ($T_g \sim 105^\circ\text{C}$).

The increase of the size of the ester side-chain promotes a decrease of the T_g , so that the polymers become softer and more flexible.⁵ Diffusion of gases in polymers depend on the flexibility of chain, i.e., as flexibility increases (lower T_g), the gas diffusion rate increases. In addition, the longer-side-chain polymers present larger fractional free volumes, increasing the concentration of oxygen in those sites.⁶

Polymers can be degraded by irradiation, either directly or using a photosensitizer.^{7,8} Although direct irradiation of polymers might be the simplest method, in some cases, the use of photosensitive structures has some advantages.⁹ The photosensitization method should be preferred when there is a need of controlling the photodegradation, as well as when the irradiation is performed at wavelengths that are not absorbed by the polymer.¹⁰

The excitation of the sensitizers may result in the production of free radicals that can initiate polymer degradation processes.¹¹ In general, these radicals abstract hydrogen atoms from the macromolecule forming polymeric alkyl radicals that react with oxygen, initiating an oxidative chain reaction. Photodegradation processes of this type have already been studied for polyethylene polymers sensitized by benzophenone and anthraquinone.^{12,13}

Most of the studies on photooxidation of acrylate and methacrylate polymers have been carried out using high energy UV radiation, typically in the 254-nm region. It has been reported that under these

Correspondence to: M. G. Neumann (neumann@iqsc.usp.br).

Contract grant sponsor: FAPESP, Brazil; contract grant numbers: Proc. 03/07770-4, 05/03692-4.

Contract grant sponsor: CNPq; contract grant number: Proc. 471310/2006-9.

Contract grant sponsor: FAPESP.

conditions the photodegradation of PMMA) proceeds via extensive random chain scissions, leading to low molecular weight gaseous products with little monomer production.^{14,15} The number of scissions is proportional to the radiation dose and is much higher in inert atmosphere than in air. The rate of scissions was found to vary with the radiation wavelength, reaching a maximum at 280 nm and falling to zero at $\lambda > 320$ nm.¹⁵ This finding suggests the presence of aldehyde or ketone groups, photoactive in the 280-nm region, and was supported by the absorption of irradiated samples.¹⁶ Poly(alkyl methacrylate) polymers with larger alkyl side chains degrade by a mechanism similar to that observed for PMMA, but when the alkyl side chain becomes longer, side-group scissions start to take place.¹⁷ The production of monomer decreases as the alkyl side chain length increases.¹⁸

In this work, we studied the degradation of several poly(alkyl methacrylates) photosensitized by thioxanthone (TX): PMMA, poly(ethyl methacrylate) (PEMA), poly(*n*-butyl methacrylate) (PBMA), and poly(*n*-hexyl methacrylate) (PHMA).

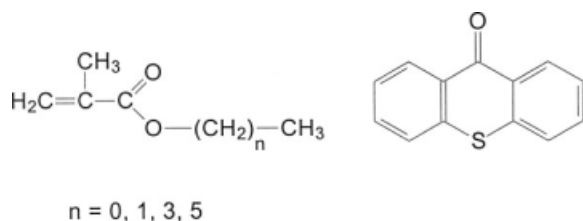
EXPERIMENTAL

Materials

The monomers used were methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), and hexyl methacrylate (HMA), all from Aldrich (St. Louis, MO). The thermal polymerization was initiated using dibenzoylperoxide (DBPO). The degradation photosensitizer was thioxanthone (TX, Aldrich) (Scheme 1). The solvents used in the different synthesis and analysis steps were methanol, tetrahydrofuran, and chloroform (HPLC grade, Tedia, Fairfield, OH).

Polymerization

Solutions in methanol containing 20 wt % of monomer and initiator (DBPO, 5 mM) were deaerated by bubbling oxygen-free nitrogen for 10 min. The solutions were heated at 70°C for 8 h, under continuous magnetic stirring. The formed polymers were dissolved twice in acetone, precipitated with methanol, and finally dried under vacuum at room temperature.



Scheme 1 Chemicals.

TABLE I
Physical Properties of Poly(Alkyl Methacrylates)

Sample	T_g (°C)	Molecular weight (\bar{M}_w)	Density ^a (g cm ⁻³)	Fractional free volume ^b
PMMA	109	300,000	1.144	0.135
PEMA	68	270,000	1.110	0.151
PBMA	35	290,000	1.056	–
PHMA	–5	440,000	1.028	–

^a Data from Ref. 19.

^b Data from Ref. 5.

Photodegradation

Thin polymer films (~ 0.200-mm thick) were casted from chloroform solutions (weight concentration: *ca.* 5%) and dried under vacuum at 60°C for 4 h. The photodegradation process took place in a thermostated stainless steel irradiation chamber using sixteen 6W G5 XELUX visible light lamps placed at 20 cm from the film. The temperature was kept at 40°C to assure a minimum contribution of the thermal process.

Analysis

Absorption spectra of the films placed in the film holder of the diffuse reflectance accessory were recorded on a Shimadzu UV-2550 spectrophotometer.

Photodegradation kinetics was determined by Fourier transform infrared (FTIR) spectroscopy. Samples were placed over a specular reflection accessory (Spectratec) in the compartment of a FTIR spectrometer (Bomem-100 MB Series spectrometer), and the absorbance was recorded at different times.

The average molar masses were determined by GPC on a Shimadzu LC-10 AD chromatographic system with a Shimadzu RID-6A refractive index detector. Twenty microliters of the sample solutions were injected in a combination of two Styragel HR4 and two Styragel HR5 columns. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min⁻¹. Narrow-distribution poly-MMA standards (American Polymers Standards) were used for calibration.

Glass transition temperatures were determined by differential scanning calorimetry using a TA Instruments SDT-Q600 Simultaneous Thermogravimetric Analyzer. Measurements were carried out between –30 and 130°C under nitrogen at heating and cooling rates of 10°C min⁻¹. Ten milligrams of samples in a covered 20 μ L aluminium pan were used for the determinations.

The physical properties of the poly(alkyl methacrylate)s are shown in Table I.

RESULTS AND DISCUSSION

Absorption spectra in the UV-vis region

The UV-vis irradiation of poly(alkyl methacrylate) films containing TX causes an increase of the

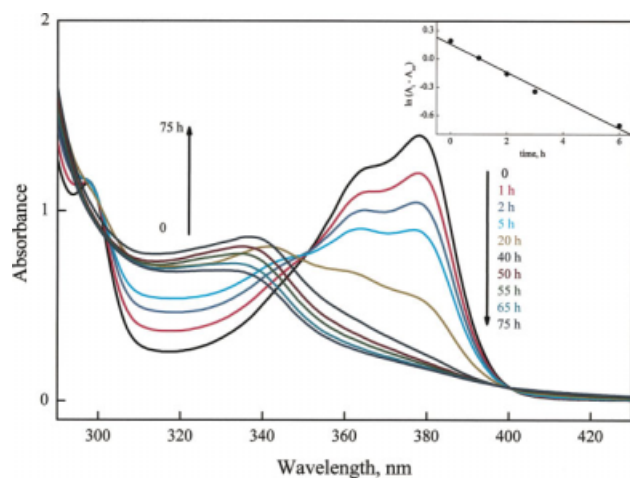


Figure 1 Absorption spectra of irradiated PEMA films at various irradiation times, up to 75 h. Inset: thioxanthone decay kinetics during the first 6 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

absorbance in the 300–400 nm range, as illustrated in Figure 1. Simultaneously, the absorbance at 380 nm, due to TX, rapidly decreases as a result of its bleaching. The disappearance of the TX absorbance can be approached by first-order kinetics, at least during the first 6 h of irradiation. The rate constant for the bleaching of TX in PEMA films is 0.14 h^{-1} , and similar values were found for the other polymers.

Two different stages can be observed in the 360–320 nm wavelength domain. There is a well-defined isosbestic point at 351 nm that can be assigned to the bleaching of the dye concomitant to the formation of new carbonyl groups on the polymer chain (Scheme 2).

The growth of the absorption band around 342 nm can be observed during the first 6 h of irradiation, which is gradually shifted to lower wavelengths. At longer times, this band starts decreasing, but continues shifting to the blue, as shown in Figure 1. This behaviour suggests that the newly formed ketyl groups do now disappear via their excitation and eventual oxidation. The behaviour of the other polymers used in this work was similar. There is a difference in the photodegradation rates of the different polymers that can be seen from the behaviour of the 340 nm peak. Initially there is an increase in the

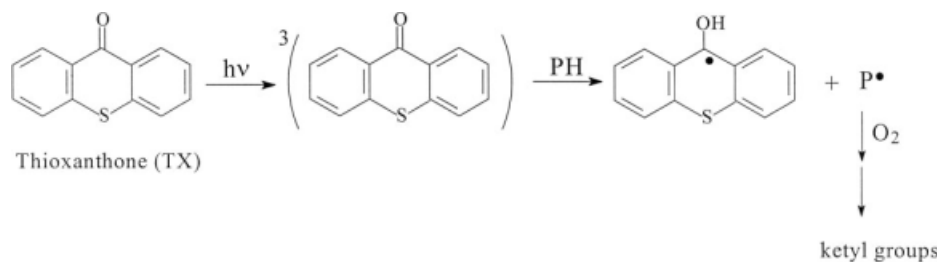
absorption due to the formation of ketone groups, but at longer times, between 10 and 20 h, the absorbance levels off, and starts to decrease due to the oxidation of these groups (Figure 2). Two features are apparent from the comparison of the different polymers. On one side, the initial rate of oxidation and the depletion of the TX concentration are faster for the polymers with larger side chains. On the other hand, there is a larger amount of ketyl radicals formed on the larger side-chain polymers.

When the maxima are reached, practically no TX remains in solution, so that the absorption at 340 nm, and lower wavelengths, must be assigned to the formed carbonyl and vinyl groups, which are responsible for continuing the photodegradation. During that process, these new formed groups will eventually be consumed as evidenced by the decrease of the absorbance in this region.^{16,20}

FTIR spectra analysis

Photochemical degradation of poly(alkyl methacrylate) is easily detected by FTIR. During UV-vis irradiation significant changes are observed practically over the whole ir region. The absorbance band in $3350\text{--}3500 \text{ cm}^{-1}$ region (with maximum at 3480 cm^{-1}) increases during UV-vis irradiation of PMMA, PEMA, PBMA, and PHMA films. This band is typical of hydroxyl and hydroperoxide groups free (non-associated) or hydrogen bonded.¹⁷ Kinetics curves of the intensity of this band indicate clearly that photo-oxidation leading to OH/OOH groups is faster for PHMA than for PBMA, PEMA, and PMMA (Fig. 3).

The behaviour of PEMA and PBMA can be assumed to correspond to four successive fast-slow-fast-slow stages, i.e., rapid surface degradation, slow degradation due to oxygen diffusion to the lower layers, followed by the fast degradation of the newly exposed surface, and finally an even slower degradation when oxygen has to diffuse to the bulk of the film to promote oxidation. PMMA only shows the fast first surface oxidation stage, followed by a plateau, as the oxygen diffusion to the inner layers is much slower due to its higher density. On the other hand, PHMA will be rapidly oxidized in all layers as oxygen can easily diffuse to the bulk of the film.



Scheme 2 Photoinitiation reactions.

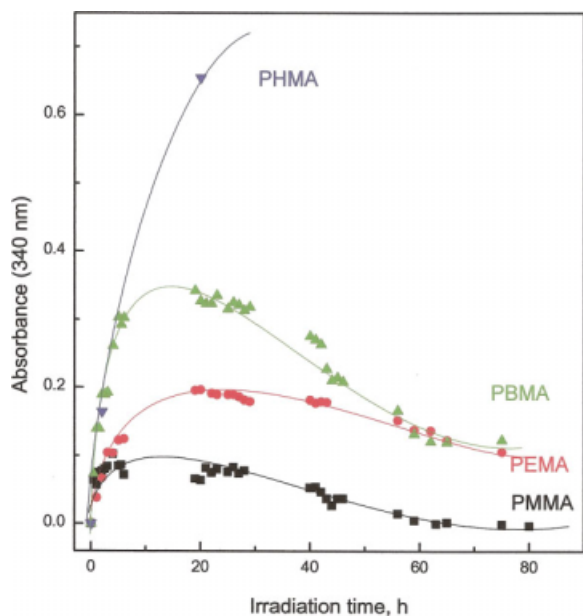


Figure 2 Absorption at 340 nm during UV-vis irradiation of PMMA, PEMA, PBMA, and PHMA films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The spectral analysis in the carbonyl region ($1600\text{--}1800\text{ cm}^{-1}$) is more complicated. Three well-distinguished peaks centred at 1740 , 1685 , and 1640 cm^{-1} are present in the unirradiated samples. The peaks at 1740 and 1685 cm^{-1} grow with irradiation, so that they may be associated with the creation of aliphatic ketones.²¹ On the other hand, the decrease of the smaller peak at 1640 cm^{-1} might be due to the ester groups that are being consumed during the photodegradation process.²²

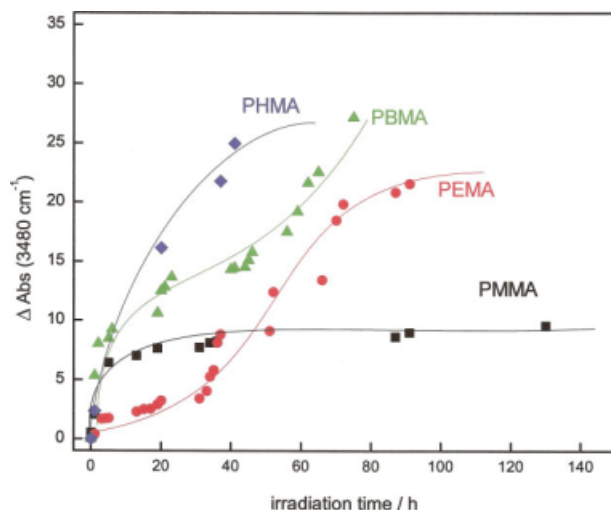


Figure 3 Formation of hydroxyl/hydroperoxide groups (absorption at 3480 cm^{-1}) during irradiation of PMMA, PEMA, PBMA, and PHMA films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

As shown in Figure 4, the ketone groups also show a faster growth when the poly(alkyl methacrylate) bears larger side groups on the ester. It can be also noticed that the behavior is rather similar to that found for the hydroxyl region.

The obvious mechanism for the TX-sensitized photodegradation goes through the excitation of the dye to its singlet state, intersystem crossing to the triplet and abstraction of an hydrogen, leading to radicals that will react with oxygen to initiate the oxidative degradation chain.²³ Therefore, the following reaction steps should be taken into consideration (Scheme 3).

The macroradicals created by the abstraction of an hydrogen by the TX triplet do react with oxygen to form peroxide radicals, which might abstract another hydrogen from the polymer chain to form peroxide groups and a new polymer macroradical, thus propagating the degradation chain.²⁴ Alternatively, these radicals can split homolytically to form macroalcoyl and hydroxyl radicals.^{25,26} The former will eventually give raise to ketones and hydroxy groups on the chain, whereas the later radicals will add new degradation cycles to the mechanism.¹¹

Two different factors might contribute to the faster degradation of methacrylates with large ester groups. On one side, there will be a larger number of easier abstractable secondary hydrogen atoms in hexyl esters than in methyl esters, so that the probability of forming macroradicals, as well as ketone groups, will be higher.

On the other hand, as PMMA is more rigid than PHMA (glass transition temperature of 105 and -5°C , respectively),⁵ oxygen diffusion in the latter will be easier. This permits that polymer chains of the deeper layers of the film be also oxidized increasing the overall oxidation rate of the softer materials.^{6,27,28}

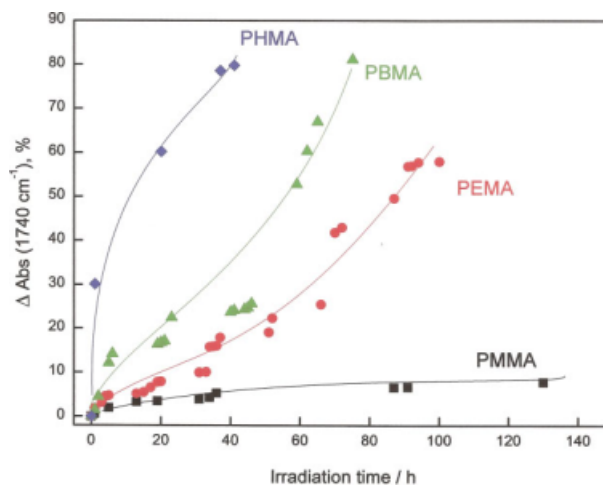
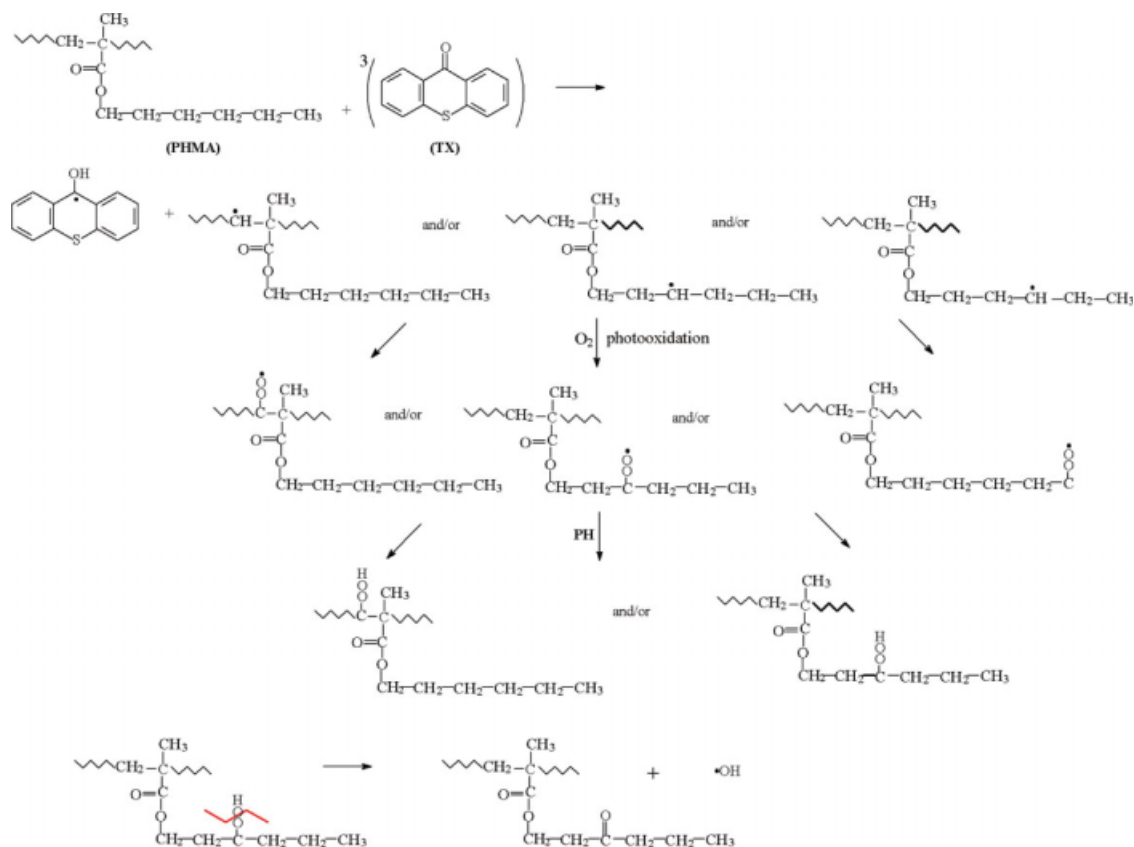


Figure 4 Formation of ketone groups (absorption at 1740 cm^{-1}) during irradiation of PMMA, PEMA, PBMA, and PHMA films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 3 Photooxidation reaction mechanism. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The degradation of the polymers may become a diffusion-limited oxidation process (DLO) when the amount of dissolved oxygen in the polymer is used up faster than it can be replenished by diffusion from the oxygen-containing atmosphere surrounding the material. As this process is faster in PHMA than in the other polymers, a larger amount of oxidation will occur in deeper layers of the film, leading to higher oxygen concentrations which result in higher oxidation levels in the interior of the samples, which will be reduced or non-existent for lower side-chain polymers.²⁷

Gel permeation chromatography

Molecular weights and chain scissions of the irradiated poly(alkyl methacrylate) polymers were obtained using GPC techniques and are listed in Table II. The molecular weights of the undegraded samples have molecular weights ranging in the 150,00–250,000 Dalton interval. The average number of chain scissions (S) per macromolecule can be calculated using^{18,18}

$$S = (\overline{M}_n)_0 / (\overline{M}_n)_t - 1$$

where $(\overline{M}_n)_0$ and $(\overline{M}_n)_t$ are the number-average molecular weights of the polymer before and after irradiation for t hours, respectively.

It can be seen from the values in Table II that the number of scissions per macromolecule for PHMA is much higher than for PMMA. This trend is compatible with the results found from spectroscopic analyses, where the rate of photodegradation, as well the amount of intermediaries formed during the irradiation process is much higher for poly(hexyl methacrylate) than for the other polymers.

In addition, the chromatograms shown in Figure 5 illustrate the behaviour of the different poly(alkyl methacrylates) when submitted to photodegradation. For the polymer with the smaller side-chain, PMMA, there is only a slight widening of the peak observed at ~ 29 min. On the other hand, for PHMA the original peak is shifted significantly toward longer times, indicating an important decrease of the size of the polymer after irradiation.

TABLE II
Average Molecular Weights (\overline{M}_n) Before and After Irradiation (75 h) of the Polymers, and Number of Chain Scissions (S)

	$(\overline{M}_n)_0$	$(\overline{M}_n)_{75 \text{ h}}$	S
PMMA/TX	180,000	160,000	0.08
PEMA/TX	150,000	118,000	0.25
PBMA/TX	145,000	115,000	0.27
PHMA/TX	250,000	110,000	1.22

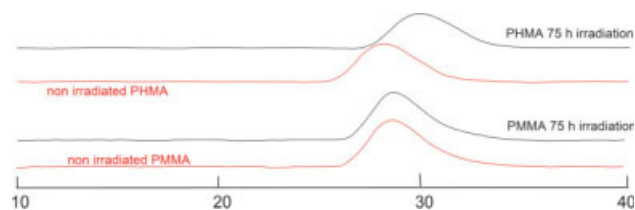


Figure 5 GPC chromatograms of PMMA and PHMA films before and after 75-h irradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

Poly(alkylmethacrylate) films with different size of side groups were irradiated with visible light in the presence of TX. During their degradation all the polymer films showed the presence of oxidized intermediates, like hydroxy, peroxy, and ketyl containing species. A decrease of the molecular weight of the polymers was also observed.

The degradation mechanism involves the initial formation of macroradicals originated by the abstraction of hydrogen from the polymer chain by the triplet state of TX. These macroradicals react with oxygen to form ketyl groups that will absorb light after the complete consumption of the sensitizer, continuing the photodegradation process.

The rate of degradation, as well as the rate of formation of the intermediate groups depends on the size of the ester side group in the polymer. Poly(hexyl methacrylate) was degraded faster than the other three, i.e., PBMA, PEMA, and PMMA, in this order. The effect is attributed to the larger proportion of abstractable secondary hydrogen atoms on the side chains and/or the higher permeability of oxygen and free volume in the large size alkyl side groups, which allows oxygen to penetrate deeper into the polymer film.

References

- Torikai, A.; Hasegawa, H. *Polym Degrad Stab* 1999, 63, 441.
- Nagai, N.; Matsunobe, T.; Imai, T. *Polym Degrad Stab* 2005, 88, 224.
- Mark, H. F. In *Encyclopedia of Polymer Science and Engineering*; Bikales, N. M.; Overberger, C. H. G.; Menges, G.; Kroschwitz, J. I., Eds.; Wiley: New York, 1985.
- Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley: New York, 1989.
- Donth, E.; Beiner, M.; Reissig, S.; Korus, J.; Garwe, F.; Vieweg, S.; Kahle, S.; Hempel, E.; Schroter, K. *Macromolecules* 1996, 29, 6589.
- Tiemblo, P.; García, F.; García, J. M.; García, C.; Riande, E.; Guzmán, J. *Polymer* 2003, 44, 2661.
- Lawrence, J. B.; Weir, N. A. *J Polym Sci Polym Ed* 1973, 11, 105.
- Ikeda, T.; Von-Euler-Chelpin, H. S.; Okumura, S.; Yamaoka, H. *Macromolecules* 1984, 17, 1655.
- Hosono, K.; Kanazawa, A.; Mori, H.; Endo, T. *J Appl Polym Sci* 2007, 105, 3235.
- Kaczmarek, H.; Kaminska, A.; Swiatek, M.; Sanyal, S. *Eur Polym J* 2000, 36, 1167.
- Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers. Theory and Applications*; Wiley: Chichester, 1987.
- Taylor, L. J.; Tobias, J. W. *J Appl Polym Sci* 1977, 21, 1273.
- Kubota, H.; Takahashi, K.; Ogiwara, Y. *Polym Degrad Stab* 1989, 24, 201.
- Fox, R. B.; Isaacs, L. G.; Stokes, S.; Kagarise, R. E. *J Polym Sci A* 1964, 2, 2085.
- Torikai, A.; Ohno, M.; Fueki, K. *J Appl Polym Sci* 1990, 41, 1023.
- Rabek, J. F. *Photodegradation, Photooxidation and Photostabilization of Polymers: Principles and Applications*; Wiley: London, 1975.
- Kaczmarek, H.; Kaminska, A.; Van Herk, A. *Eur Polym J* 2000, 36, 767.
- Chiantore, O.; Trossarelli, L.; Lazzari, M. *Polymer* 2000, 41, 1657.
- Hempel, E.; Beiner, M.; Donth, E. *Acta Polym* 1996, 47, 525.
- Rabek, J. F. *Polymer Photodegradation: Mechanisms and Experimental Methods*; Chapman and Hall: London, 1995.
- Liu, P.; Su, Z. *Polym Bull* 2005, 55, 411.
- Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*; Wiley: New York, 1975.
- Corrales, T.; Peinado, C.; Catalina, F.; Neumann, M. G.; Allen, N. S.; Rufs, A. M.; Encinas, M. V. *Polymer* 2000, 41, 9103.
- Morimoto, K.; Suzuki, S. *J Appl Polym Sci* 1972, 16, 2947.
- Allen, N. S.; Parker, M. J.; Regan, C. J.; McIntyre, R. B.; Dunk, W. A. E. *Polym Degrad Stab* 1995, 47, 117.
- Millan, M. D.; Locklin, J.; Fulghum, T.; Baba, A.; Advincula, R. C. *Polymer* 2005, 46, 5556.
- Mattson, B.; Stenberg, B.; Gillen, K. T.; Clough, R. L.; Östman, E. *Polym Degrad Stab* 1993, 41, 211.
- Wright, C. T.; Paul, D. R. *Polymer* 1997, 38, 1871.