Photodegradation of poly(methyl methacrylate)/ bisphenol A polycarbonate blends

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Summary
Poly(methyl methacrylate) [PMMA], Bisphenol A polycarbonate [BAPC] and its blends of different weight compositions irradiated under static vacuum conditions, were investigated by UV spectroscopy and gel permeation chromatography. Analysis indicated that photolysis of PMMA is retarded by blending with BAPC. This effect is attributed to photo products formed in the BAPC, most probably due to Fries rearrangement, that reduces the photodegradation of PMMA.

Introduction
Earlier, from the photodegradation study of PMMA-BAPC blends 1:1 by weight under static vacuum conditions, it was reported (1) that the degradation of the PMMA is retarded when it is blended with BAPC. In the present work, the degradation behavior of PMMA-BAPC blends of 10:90, 20:80, 30:70, 40:60 and 50:50 weight compositions, under similar conditions, is studied. The results are compared with those published by Osawa and Fukuda (2,3) for a similar system when photodegraded under nitrogen at room temperature.

Experimental
Polymers of PMMA and BAPC (Aldrich) were employed. Both polymers were purified by reprecipitation from a chloroform solution using methanol as non solvent and dried under vacuum. The number average molecular weights ($\overline{Mn}$) of PMMA and BAPC were 45,300 and 20,100, respectively. Blends of PMMA and BAPC of different compositions were obtained by mixing appropiate volumes of the homopolymer solutions prepared in dichloromethane (20mg/ml). Films were obtained by evaporation of the dichloromethane solutions on stainless-steel plates which were later dried under dynamic vacuum for 24 hours. The average film thickness (22μm) was calculated from the mass deposited, its density and the covered area (3.8 cm^2). Because of the limited accuracy in the determination of the film thickness,

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The photodegradation experiments were made on several samples and the average values thus obtained are reported.
The photodegradation experiments were performed under static vacuum (10^{-3} mm Hg) at $20\pm0.5°C$ for 12, 24, 48 and 72 hours. A 250 watts medium-pressure mercury arc lamp (Photophysics Ltd) was used as irradiation source. The characteristic output of the lamp reported by the manufacturer was over 40% below 400nm.
Molecular weight distributions (MWD) and average molecular weight of the original and degraded polymers were estimated by GPC at $40\pm0.5°C$ using polystyrene as standard. Chloroform as eluent with a flow rate of 1 ml/min and polymer solutions of 0.2% w/w were used.
Ultraviolet absorption spectra of the original and degraded films were obtained using a Perkin-Elmer spectrophotometer (model 124) connected to a Perkin-Elmer recorder (model Coleman 165).
Intrinsic viscosity [η̄] of the polymers and PMMA-BAPC blends were measured in chloroform at $25\pm0.5°C$. Single-point determinations of [η̄] were evaluated using the Salomon-Ciuta equation(4).

Results and discussion

Molecular weight changes

The GPC chromatograms of PMMA, BAPC and 1:1 by weight PMMA-BAPC blend before and after 72 hours of exposure are shown in figs. 1 (a) and (b). This UV irradiation produces a broadening of the GPC curve and a shift of the average molecular weight to lower values. The MWD of PMMA undergoes a larger change than BAPC and PMMA-BAPC. This behavior indicates that the polymers undergo chain scission.

Fig.1 Molecular weight distribution of BAPC (---), PMMA (-·-) and PMMA-BAPC system (---) before (a) and (b) after irradiation for 72 hours.
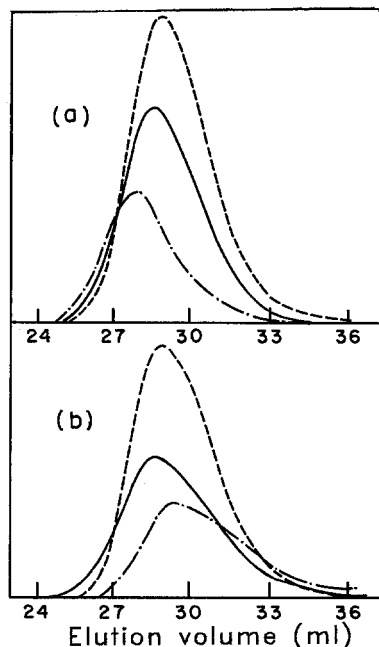
Relative change of weight average molecular weight ($\bar{M}w/\bar{M}wo$) as a function of exposure time for different polymers and blends

is shown in fig. 2. It can be noted that $\bar{M}w/\bar{M}wo$ of PMMA decreases much faster with exposure time than BAPC and PMMA-BAPC blend. These results indicate the latter to be more photostable to UV light.

Fig. 2 Change of weight average molecular weight ($\bar{M}w/\bar{M}wo$) for PMMA (◑), BAPC (▪) and PMMA-BAPC of composition: 10:90 (Δ), 20:80 (⊠), 30:70 (⊙), 40:60 (□) and 50:50 (▽), as a function of exposure time (h).
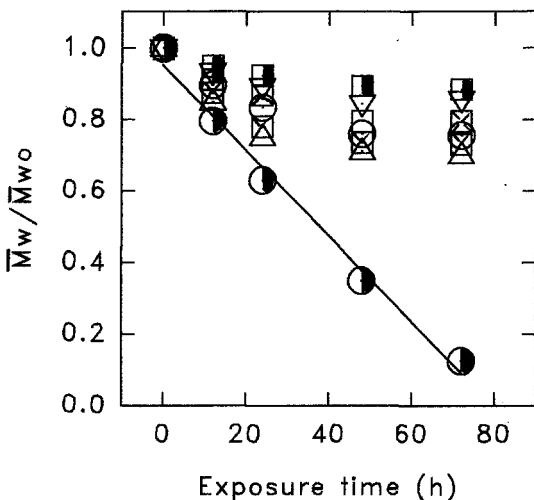
The variation of average number of chain scission ($\bar{M}no/\bar{M}n-1$) of homopolymers and PMMA-BAPC of different compositions with exposure time is shown in fig. 3. It can be observed that PMMA undergoes chain scission very nearly linear with exposure time. However, chain scission decreases with the increase of BAPC in the PMMA-BAPC blend.

These results are in good agreement with earlier findings under nitrogen atmosphere (2).

Fig. 3. Average number of chain scission ($\bar{M}no/\bar{M}n-1$) for PMMA (◑), BAPC (▪), and the PMMA-BAPC of composition: 10:90 (Δ), 20:80 (⊠), 30:70 (⊙), 40:60 (□) and 50:50 (▽) as a function of exposure time (h).

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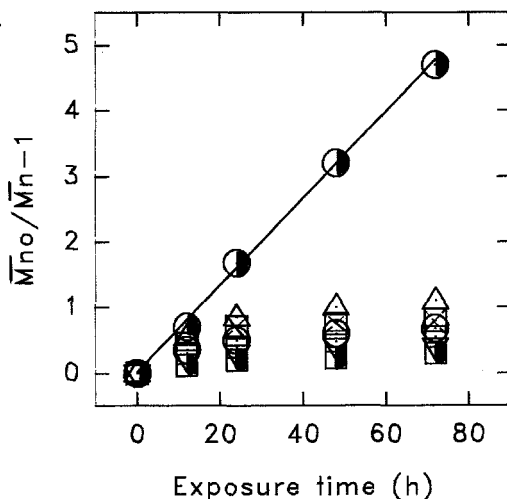
Spectral changes

The UV spectra of films of PMMA, BAPC and PMMA-BAPC blend 1:1
after irradiation for different times are indicated in figs.
4. (a), (b) and (c), respectively. PMMA and BAPC show a single
absorption band with maxima at 210 and 260 nm, respectively.
The spectra of undegraded PMMA-BAPC blends resemble those of
the homopolymers. After irradiation, an increase in UV
absorption of the homopolymer and the blend is observed. In
the case of irradiated PMMA a shift of the absorption between
240 to 280 nm is noted. These shifts are attributed (2,5,8) to
the formation of: (i) short polymer fragments with olefinic
end groups that absorb at λmax = 240 nm, and (ii) aldehyde
groups which absorb at λmax = 280 nm. BAPC, after irradiation,
shows two new extensively superimposed bands which have been
assigned to: polymer fragments with phenolic end groups
with λmax = 287, and polymeric phenyl esters of salicylic acid
and polydihydroxybenzophenone at λmax = 280, 320 and 360 nm.
The PMMA-BAPC blend shows bands possibly related to photo
products similar to those given by the homopolymers.

Fig. 4. UV absorption of films of PMMA (a), BAPC (b) and PMMA- BAPC blend (1:1) (c), after irradiation in static vacuum for 0(---), 12(···), 48 (---), and 72 (ooo) hours.
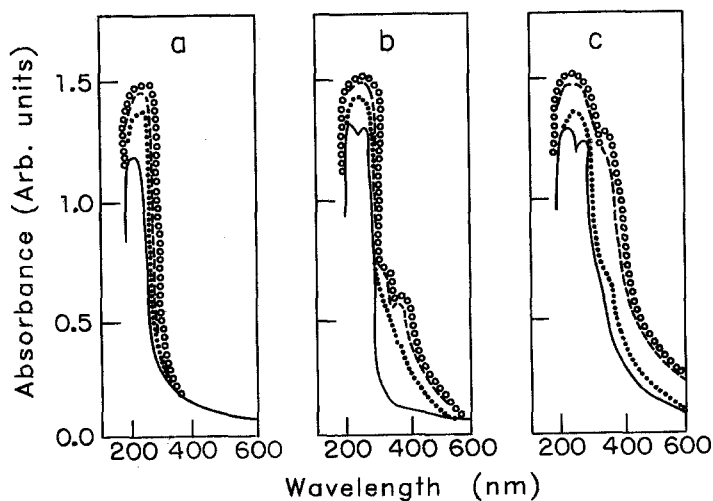
The normalized intrinsic viscosity $[\bar{\eta}]$ of homopolymers and their blends as function of exposure time (h) is shown in fig. 4. The $[\bar{\eta}]$ change for PMMA is more rapid at all times of irradiation than those of BAPC and PMMA-BAPC. At the initial stage of irradiation of BAPC, the change in $[\bar{\eta}]$ occurs at a higher rate. PMMA-BAPC blends and BAPC show similar behaviors.
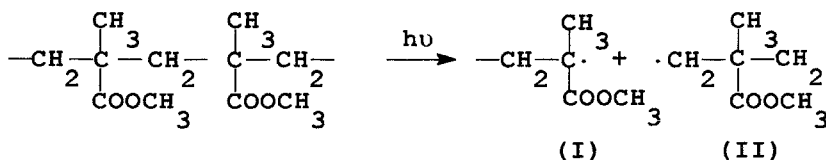
Fig.5 Normalized intrinsic viscosity $[\bar{\eta}]$ of PMMA (◐), BAPC (◼) and PMMA-BAPC blend of composition: 10:90 (Δ), 20:80 (⊠), 30:70 (O), 40:60 (□) and 50:50 (∇) as function of exposure time (h).

Exposure time (h)
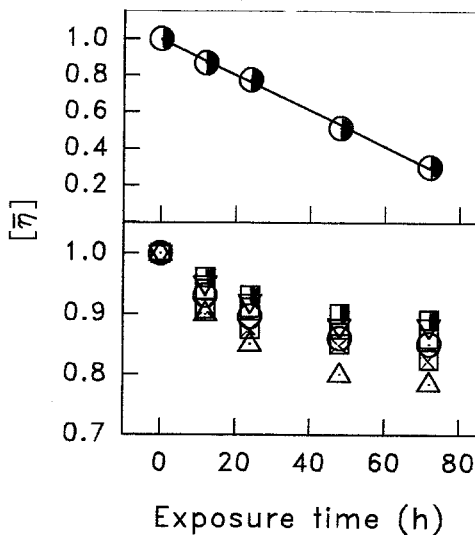
The reactions that have been postulated for the UV degradation of PMMA and BAPC (6) are indicated in schemes (A) and (B).
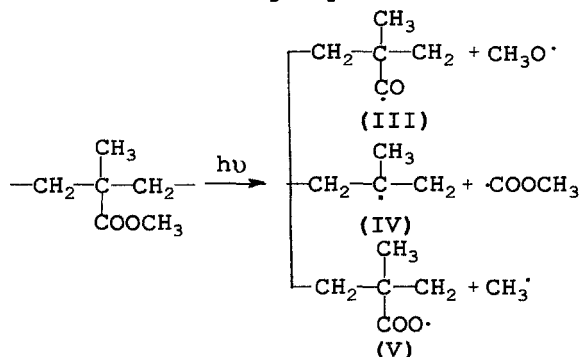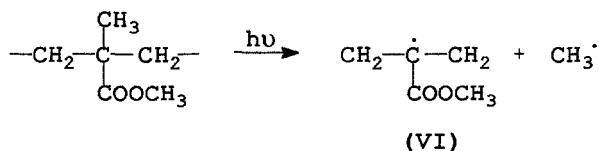
SCHEME A

Random homolysis of PMMA main chain

(I)   (II)

Radicals (I) and (II) may stabilize by disproportionation to give $\cdot COOCH_3$ radicals and polymer fragments with olefinic end group (2,5,8).
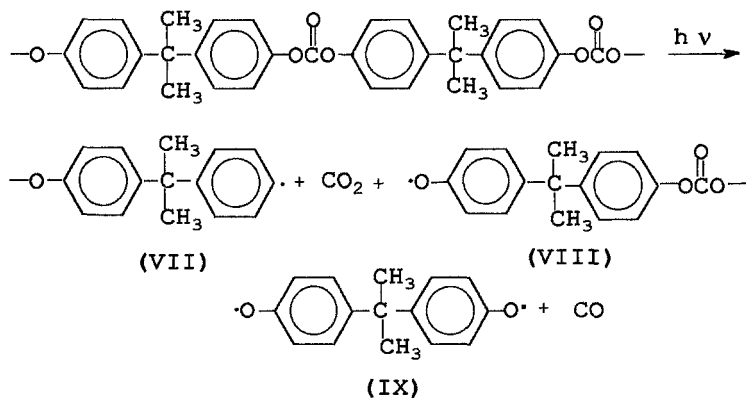
Photolysis of the ester side-group

$$-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- \quad \xrightarrow{h\upsilon}$$

$$-CH_2-\underset{\underset{\overset{|}{C}O}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 + CH_3O\cdot$$
(III)

$$-CH_2-\underset{}{\overset{\overset{CH_3}{|}}{\underset{\cdot}{C}}}-CH_2 + \cdot COOCH_3$$
(IV)

$$-CH_2-\underset{\underset{COO\cdot}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 + CH_3\cdot$$
(V)

The radical (III) by combination with a hydrogen atom leads to an aldehyde group on the polymer chain.

Photolysis of methyl group

$$-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- \quad \xrightarrow{h\upsilon} \quad CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{\cdot}{}}{C}}-CH_2 + CH_3\cdot$$
(VI)

SCHEME B

Random homolytic main-chain scission of BAPC (6)

(VII)   (VIII)

(IX)

Phenolic products are formed by the attack of radical (VII) on an adjacent chain, and radical (X) may eventually leads to gel.

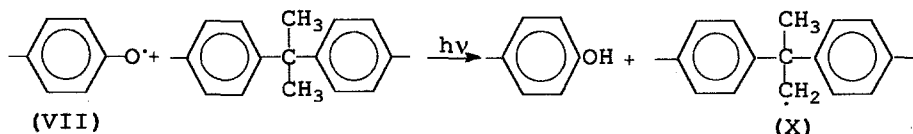(VII)   (X)

Photo-induced Fries rearrangment

phenyl salicylate group
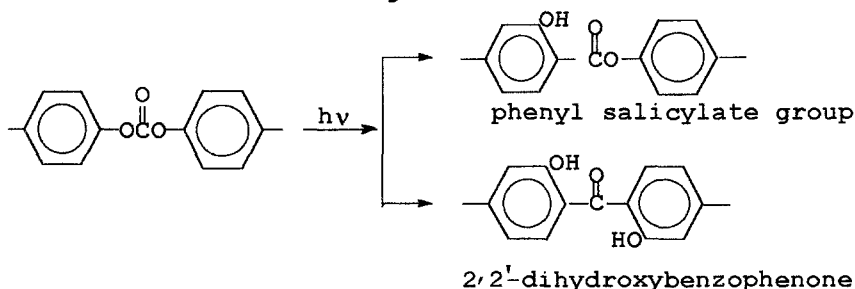
2,2'-dihydroxybenzophenone

Photo-induced Fries rearrangement (6-8) produces phenyl salicylate and 2,2'-dihydroxybenzophenone groups. These products which contain groups of higher molar absorptivity (9) may be responsible for UV filtering of the blend which retards the photodegradation of the PMMA.

Conclusions

Because PMMA is transparent to UV light, main chain scission of PMMA may take place in vacuum. In the case of BAPC this occurs mainly at the surface due to its high absorption coefficient. Fries rearrangment in BAPC produces products that leads to self photo-stabilization. Due to this effect, the photodegradation of PMMA is greatly reduced by blending with as little as 10% of BAPC. These results are in good agreement with the photolysis of PMMA, BAPC and PMMA-BAPC blends under nitrogen at ambient temperature.

Acknowledgments

References

1. Rincón G. A, Krestonosich S, and Contreras R. J (1988)
   Actas del I Simposio Latinoamericano de Polímeros II: 785
2. Osawa Z. and Fukuda Y (1991) Polym Deg. & Stab. 32: 285

3. Fukuda Y. and Osawa Z (1991) Polym Deg. & Stab. 34: 75
4. Salomon O. F and Ciuta I. Z (1962) J Apply Polym Sci 6: 683
5. Moore J. E (1981) Photodegradation and photostabilization of coatings (Ed. Pappas S.P & Winslow F.H.) 151: 97
6. Rånby B. and Rabek J. F (1975) Photodegradation, Photo-oxidation and Photostabilization of polymers, John Wiley & sons Ltd 156-159 and 227-230
7. Mullen P. A and Searle N. Z (1970) J Appl Polym Sci 11: 765
8. Fox R. B, Isaacs L, Stokes S. J (1963) Polym Sci Part A. 1: 1079
9. Guillet J. E, Merle-Aubry L, Holden D. A and Merle Y. (1980) Macromolecules 13: 1138