Thermal and photolytic degradation of plates of poly(methyl methacrylate) containing monomer

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Specimens of 1.5 mm thick absorber-free poly(methyl methacrylate) (PMMA) containing ~0.6% monomer but no absorber have been photolytically degraded in air at 50°, 85° and 115°C and thermally degraded in air at 115° and 125°C. Specimens were exposed to a simulated solar spectral range. Degradation was followed by gel permeation chromatographic determinations of molecular weight as a function of depth in the specimens. The results show increased photodegradation at the plate faces (back and front) over that occurring in the centres, and a rapidly attained constant amount of degradation for thermal degradation. Degradation mechanisms are proposed. The thermal degradation is ascribed to weak links and unspent initiator. Photolytic initiation is ascribed, at least in part, to degradation of the ester group by wavelengths in the range 300 to 330 nm. The effect of oxygen is to convert alkyl radicals into peroxyl radicals, some of which form alkoxyl radicals which tne undergo β-scission to give in-chain ruptures. Where the oxygen concentration is low, monomer changes non-tertiary alkyl radical sinto tertiary radicals by addition to the monomer double bond. After their peroxidation by molecular oxygen, tertiary radicals react with one another to give alkoxyl radicals and subsequent chain scission rather than undergoing the Russell termination reaction with no chain scission characteristic of non-tertiary peroxyl radicals. The effect of temperature is mostly to decrease the importance of the cage effect and to allow the initial radicals formed to diffuse away from one another. The products of photo-oxidation absorb the shorter (300 to 330 nm) radiation significantly and progressively shield the remainder of the plate as degradation proceeds.

(Keywords: poly(methyl methacrylate); photo-oxidation; thermal degradation; solar photolysis; molecular weight degradation; mechanism)

INTRODUCTION

Polymers are candidates for glazing materials in active solar collectors because of their light weight, low cost and good strength. However, they must have acceptable durability, i.e. the length of time before at least one of their important properties, such as high solar transmittance, good resistance to mechanical shock and sufficiently high softening point, falls below an acceptable level.

To detect the early stages of degradation, to identify the underlying causes and to relate degradation to durability in poly(methyl methacrylate) (PMMA), we have measured degradation as a function of depth, temperature and irradiance level. PMMA was selected for study because of its long history of satisfactory use in outdoor environments and because of possible uses in solar applications. The results have been interpreted in terms of degradation mechanisms and influence on the mechanical properties.

EXPERIMENTAL

The PMMA specimens were cut from a commercially available sheet of PMMA*. Each specimen was 3.7 cm long by 1.8 cm wide by 0.15 cm thick. According to the manufacturer, this material contains no u.v. absorber but does contain ~0.6% monomer. Specimens were aged either thermally in an oven at 115° and 125°C or thermally and photolytically at three temperatures (50°, 85° or 115°C) and three irradiance levels (24 cm, 30 cm or 37 cm from the light source). Specimens at 115°C were exposed at all three irradiance levels. Specimens at 50° and 85°C were exposed only at the 30 cm irradiance level. The total doses received by the specimens were essentially equivalent.

The exposure cells used for photolytic exposures were independently heated. After the 3 h required to reach thermal equilibrium had elapsed, the cells could be maintained within ±2°C of the required temperature for long periods of time. During exposure, the specimens were firmly held against a copper platform inserted into the exposure cell. Cowley and Melville[1] reported that copper

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* UVT PMMA, made by Rohm and Haas Inc. Identification is made solely to define experimental materials used and not to endorse a particular product.

does not catalyse the thermal or photolytic degradation of PMMA. The maximum reflectance from the copper plate was only 8%, so any additional photolysis from this effect can be neglected.

Photolytic degradation was initiated using 6500 W xenon arc radiation filtered through borosilicate filters and water to give a spectral distribution approximating that of the solar spectrum. The intensity of the xenon arc was monitored continuously at 320 nm and automatically adjusted to the initial irradiance level.

Molecular weight measurements were made on bulk specimens, and on 50 to 75 μm thick slices planed parallel to the exposed face of the specimens using a milling machine. Specimens were dissolved in tetrahydrofuran at a concentration of 10 mg in 20 ml. The solution was filtered through a 0.47 μm filter prior to injecting it into a gel permeation chromatograph (g.p.c.). The columns, pump chamber and injector of the g.p.c. were maintained at 30°C. The g.p.c. columns were standardized against polystyrene samples. Two sets of columns were used, one with a molecular weight range of 2×10^3 to 6×10^6, and a second with a range of 2×10^3 to 13×10^6. The standard refractive index detector provided with the g.p.c. was used. Collection and processing of the g.p.c. data were greatly facilitated by a series of programs written by J. D. Barnes and F. L. McCrackin of NBS. Mark–Houwink param-

eters for the universal calibration method[2] were taken from ref. 3 for polystyrene at 30°C, and from ref. 4 for PMMA at 25°C. The value given for PMMA in ASTM D3593-80[5] is misquoted from ref. 4.

Infra-red, ultra-violet and fluorescence spectra were taken only after exposed specimens had been stored in the laboratory for over six months, and hence these spectra do not include contributions from time-dependent unstable states[6].
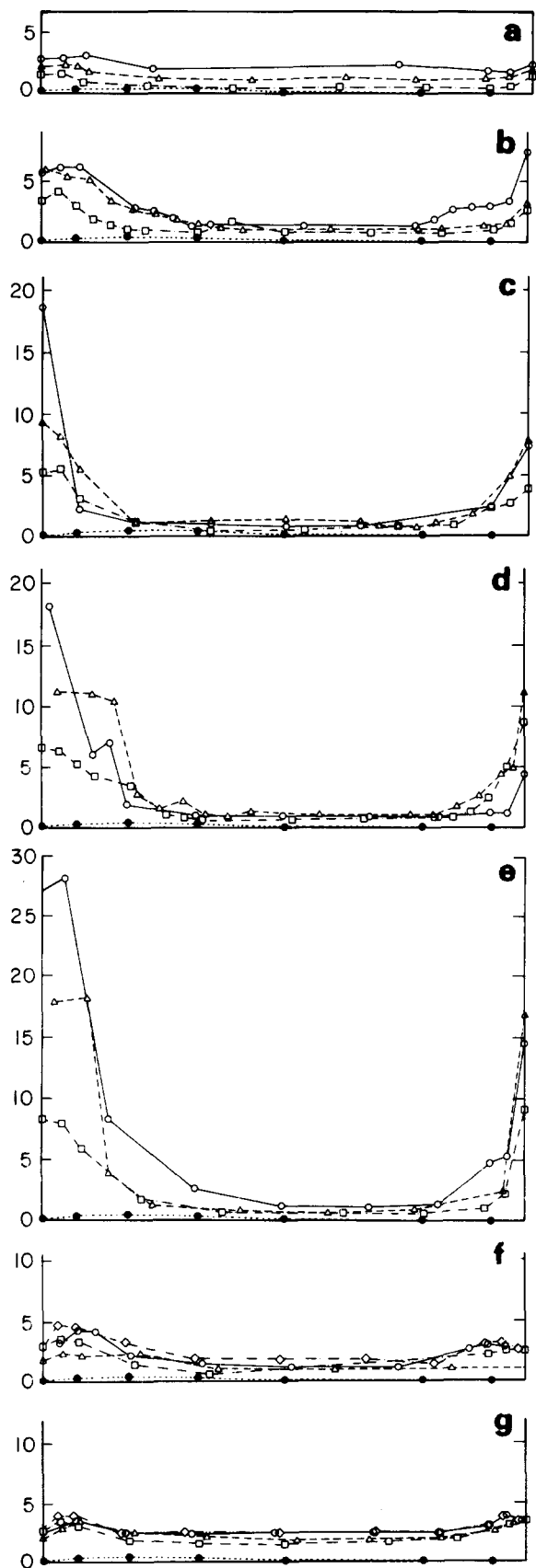
RESULTS

Decreases in molecular weights were observed for all thermally/photolytically and thermally aged specimens (*Figure 1*). The molecular weight distributions of the bulk samples remained unimodal during thermal/photolytic degradation at 50° and 85°C, but became bimodal during thermal/photolytic degradation at 115°C. The molecular weight distributions of the thermally aged specimens remained unimodal.

The profiles of the number of bonds broken per original molecule are shown as a function of depth in the plate in *Figure 2*. The number of bonds broken, N, per original molecule is defined as:
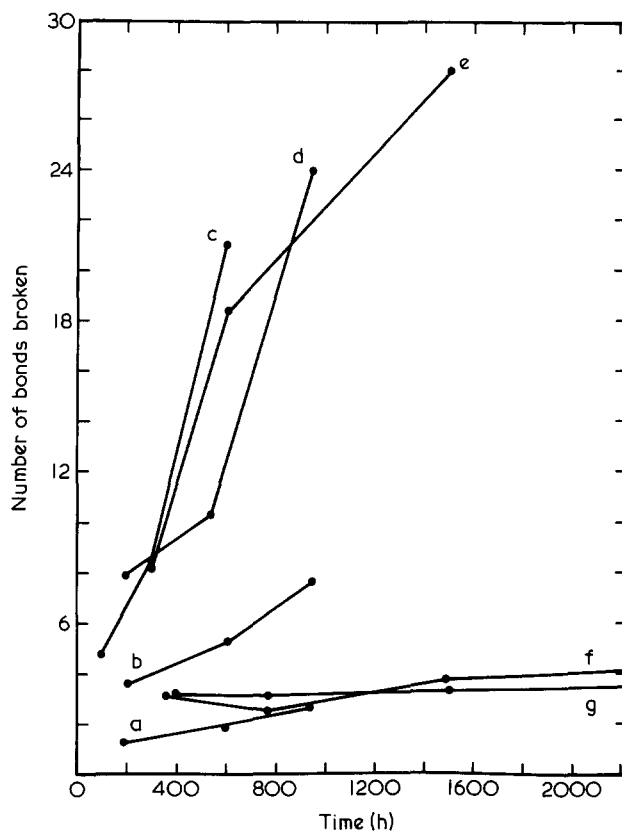
$$N = M_0/M_t - 1$$
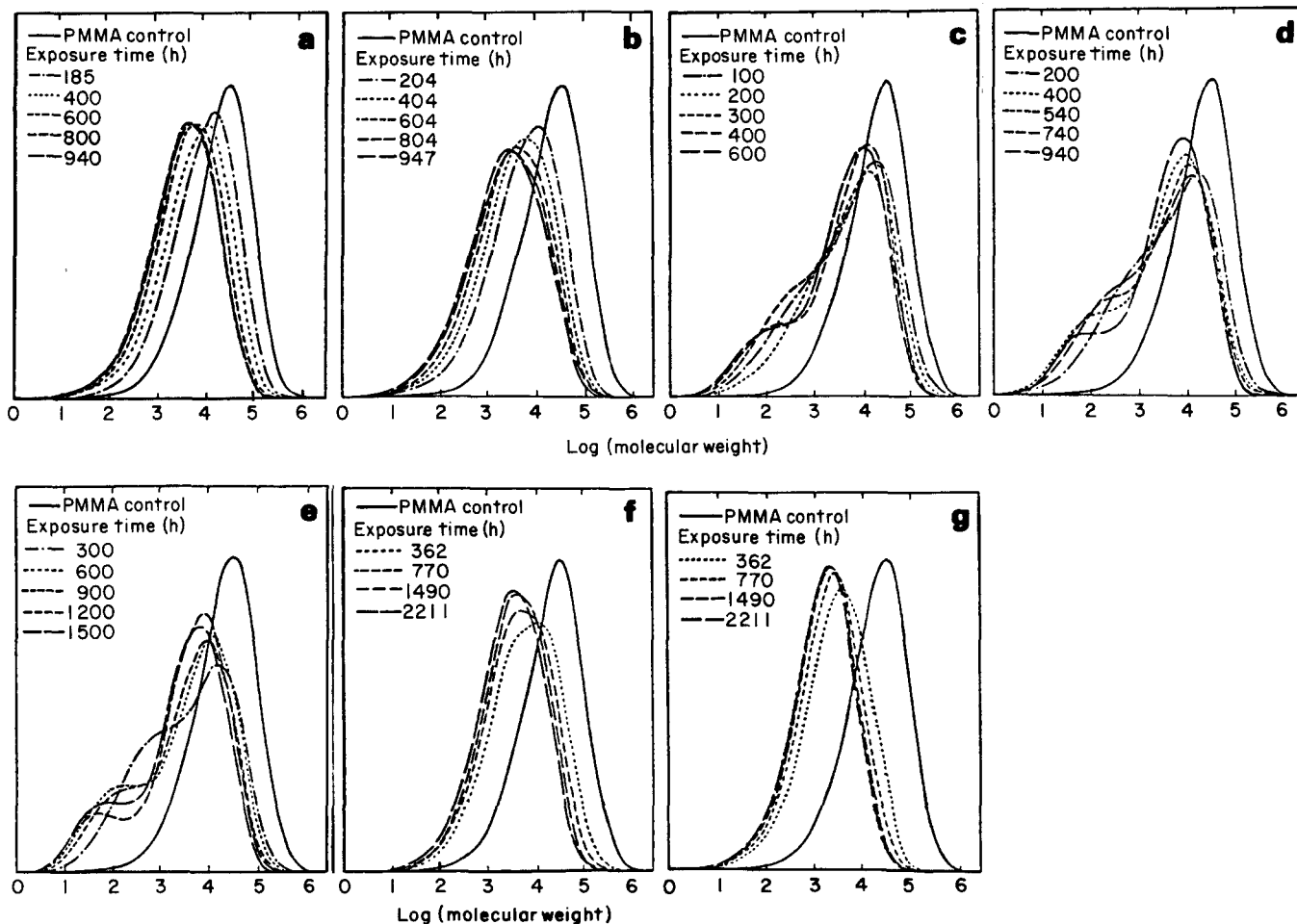
Figure 1 Molecular weight distributions of bulk specimens of aged PMMA: (a) exposed at 50°C, 30 cm from arc; (b) exposed at 85°C, 30 cm from arc; (c) exposed at 115°C, 24 cm from arc; (d) exposed at 115°C, 30 cm from arc; (e) exposed at 115°C, 37 cm from arc; (f) aged in oven at 115°C; (g) aged in oven at 125°C

Figure 3 Number of bonds broken per original molecule near plate surface in aged PMMA: (a) exposed at 50°C, 30 cm from arc; (b) exposed at 85°C, 30 cm from arc; (c) exposed at 115°C, 24 cm from arc; (d) exposed at 115°C, 30 cm from arc; (e) exposed at 115°C, 37 cm from arc; (f) aged in oven at 115°C; (g) aged in oven at 125°C
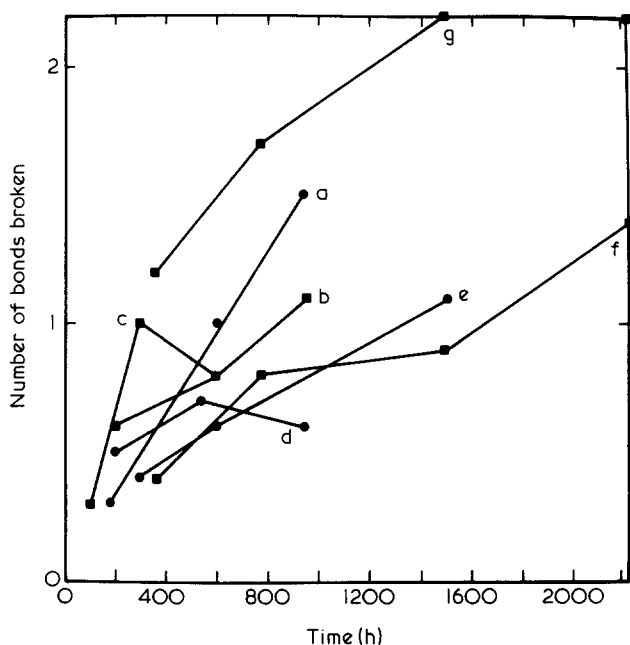

Figure 2 Number of bonds broken per original molecule as a function of depth in plate for aged PMMA: (a) exposed at 50°C, 30 cm from arc, □ 185 h, △ 600 h, ○ 940 h, ● control; (b) exposed at 85°C, 30 cm from arc, □ 204 h, △ 604 h, ○ 947 h, ● control; (d) exposed at 115°C, 30 cm from arc, □ 200 h, △ 540 h, ○ 940 h, ● control; (e) exposed at 115°C, 37 cm from arc, □ 300 h, △ 600 h, ○ 1500 h, ● control; (f) aged in oven at 115°C, □ 362 h, △ 770 h, ○ 1490 h, ◇ 2211 h, ● control; (g) aged in oven at 125°C, □ 362 h, △ 770 h, ○ 1490 h, ◇ 2211 h, ● control

where M_0 and M_t are the number average molecular weights of the unexposed specimens and specimens exposed for time t, respectively. M_0 is the average molecular weight of 24 specimens and was determined to be 385 000. The shape of the curve representing the number of bonds broken per original molecule as a function of plate depth appears to be U-shaped for all exposure conditions, with more damage to a plate occurring near the surfaces than in the centre. These curves are approximately symmetrical for the 50°C thermally/photolytically aged specimens and for the two thermally aged specimens (see *Figures 2a, f* and *g*) but are asymmetrical for the 85° and the 115°C thermally/ photolytically aged specimens. The degree of asymmetry increases both with increasing temperature and with exposure time. Also, for specimens exposed to the same total dose, the curve shapes are more asymmetrical for specimens exposed for longer periods of time (compare *Figures 2c, d* and *e*).

In *Figures 3* and *4*, the numbers of bond scissions per original molecule, as given in *Figure 2*, are plotted as a function of time for the face and centre slices, respectively. For thermally aged specimens, the degradation at the face was initially rapid (*Figure 3*), and then stopped after about four bond scissions per original molecule had occurred. For the centre slices of thermally aged specimens, the rate of thermal degradation appears to be more temperature dependent (*Figure 4*). At 125°C, degradation stops at just over two bond scissions per original molecule. At 115°C, degradation appears to be linear with time. Perhaps a limiting number of bond

Figure 4 Number of bonds broken per original molecule near plate centre in aged PMMA: (a) exposed at 50°C, 30 cm from arc; (b) exposed at 85°C, 30 cm from atc; (c) exposed at 115°C, 24 cm from arc; (d) exposed at 115°C, 30 cm from arc; (e) exposed at 115°C, 37 cm from arc; (f) aged in oven at 115°C; (g) aged in oven at 125°C

scissions per original molecule would eventually have been reached at 115°C.

For the thermally/photolytically aged specimens, the number of bond scissions per original molecule in the face slices (*Figure 3*) is temperature dependent and appears to increase linearly with time. In the centres of the thermally/photolytically degraded specimens (*Figure 4*), the rate of degradation does not seem to increase with increasing temperature.

Infra-red and ultra-violet absorption spectra and fluorescence excitation spectra were measured for representative specimens. These results will be incorporated into the discussion.

DISCUSSION

Photolytic degradation of PMMA in the absence of oxygen has been studied by many workers, and well characterized by Gupta *et al.*[7]. Photo-oxidative degradation of PMMA has support in the literature[8-10], although there are reports[11-14] which concluded that oxygen may have no effect or even a retarding effect on the photodegradation of PMMA. Our experimental results indicate as detailed below that both photo-oxidation and non-photo-oxidation processes cause degradation in commercial PMMA and that monomer increases the efficiency of the photo-oxidation. First, because in air there are far more chain scissions under illumination than in the oven at the same temperature, the photolytic processes appear to be more important than the purely thermal processes under these conditions.

Secondly, in addition to evidence given in the references cited above, evidence for the role of oxygen comes from infra-red analysis that we have conducted on both bulk and sliced materials. As can be seen from *Figure 5a*, increased absorption occurs in the region 3600 to 3000 cm^{-1} for the aged bulk material. The difference

spectrum between an outer slice and a centre slice (*Figure 5b*) shows increased absorption bands at ~ 3510 cm^{-1} and ~ 3300 cm^{-1} for the edge slice. These regions correspond best to non-hydrogen-bonded and hydrogen-bonded –OH groups, respectively (see subsection on Degradation of PMMA . . .). The increase in absorption is consistent with oxygen diffusion into the plate having an important effect.

The case where the depth at which a given amount of damage occurs in a plate increases as a linear function of the square root of time has been considered by many authors, including Camk[15] and Wilson[16]. Depths for two amounts of damage in *Figures 2b, c, d* and *e* are plotted in *Figure 6* against the square root of time. The implication from these figures is that degradation is diffusion controlled at both 85° and 115°C, but not at 50°C where degradation is linear with time. That Fick's law appears to be obeyed above and below the glass transition temperature indicates[17,18] that the active diffusing species is small, like oxygen, as opposed to larger species such as monomer.

The overall activation energy for photo-oxidation in the edge slices may be calculated from the number of bonds broken at the maximum exposure time, and is ~ 10 kcal mol^{-1} over the range 50° to 115°C. It is independent of the glass transition temperature, which is 103°C for these specimens. This activation energy is close to that found by Stannett and Williams[17] for the diffusion of oxygen in poly(ethyl methacrylate) (7.6 kcal mol^{-1}). Stannett and Williams also found that the activation energy for the diffusion of oxygen was insensitive to the glass transition temperature in poly(ethyl methacrylate),
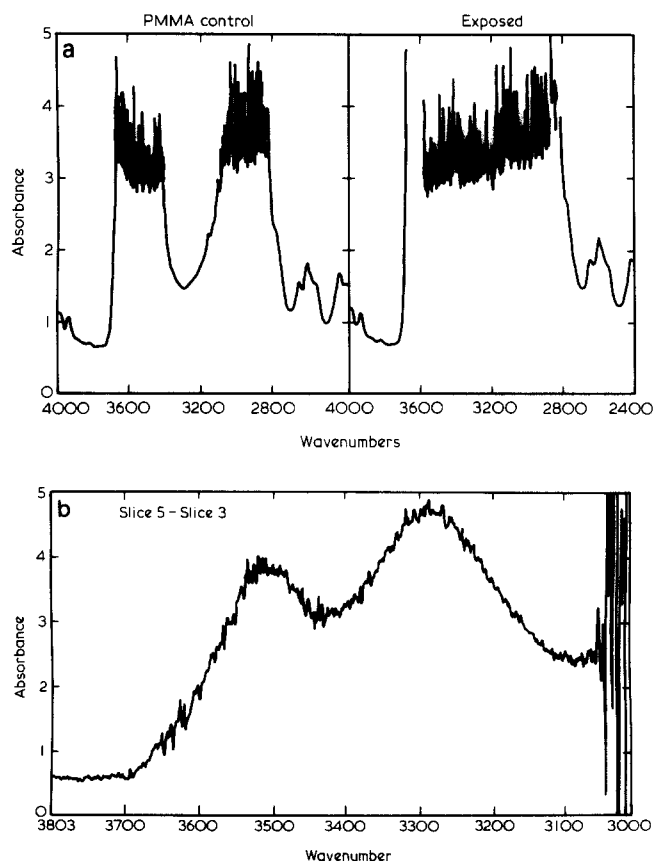
Figure 5 Infra-red difference spectra for (a) aged and non-aged plates of PMMA and (b) outer slice and inner slice for aged PMMA
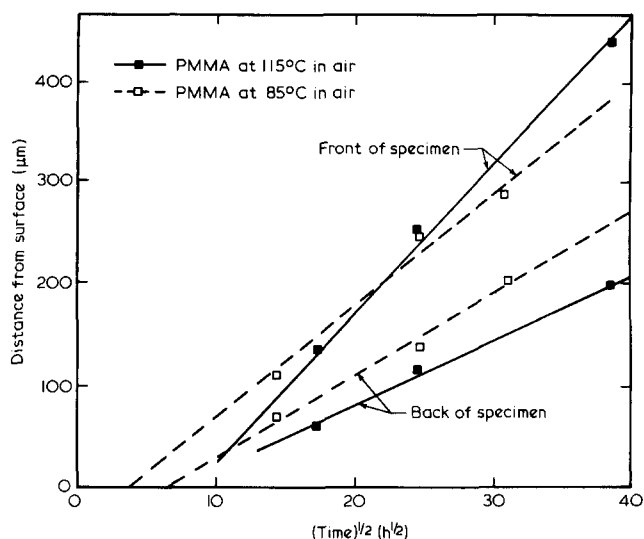
Figure 6 Test of diffusion control of damage in aged PMMA

and explained this insensitivity as being due to the diffusing molecule being small compared with the holes comprising the free volume in the polymer. This reasoning implicates oxygen as the controlling diffusing species in the photolytic degradation of PMMA.

Limiting effects of oxygen diffusion

Figure 1 shows molecular weight distributions for the bulk samples after degradation at various temperatures. From the variation of bonds broken with depth in the sample, *Figure 2*, we know that the smallest molecular weights in *Figure 1* are associated with material near the specimen surfaces and the largest molecular weights with material near the centre of the plates. The initial jump in degradation is equal at 85° and 115°C and is probably due to the availability of oxygen throughout the plate at the beginning of the experiment and the existence of weak links, peroxides and groups added to control the polymerization process during manufacture. The differences in molecular weight distribution show that, over the longer times, less degradation is taking place in the specimen centres at 115°C than at 85°C. The reason that less damage occurs in the centre of the 115°C specimen is that all of the available oxygen diffusing into the plate is used up near the surfaces of the specimen.

The damage in the 115°C specimens exposed at three different irradiance levels is shown in *Figures 1* to *4*. The doses at the maximum times at each of these irradiance levels are approximately the same. Damage is not exactly dose dependent, because the longer the exposure at 115°C, the greater the damage occurring to the edge slices. This is a consequence of the process being limited by the diffusion of oxygen rather than the initiation of free radicals.

Initiation of degradation in PMMA

PMMA is known to degrade at wavelengths greater than 300 nm[8,9,19], where the absorbing units in PMMA are the ester groups (for wavelengths near 300 nm, ref. 19), and perhaps carbonyl groups[20,21] and/or peroxide derivatives formed if the polymerizing radicals come into contact with air during and at the end of the polymerization reaction. Peroxide linkages decompose thermally above 40°C[22-25] and under the conditions used here are probably only important in the initial stages of heating.

The role of carbonyl groups is not clear, but such oxidation products of methyl methacrylate as methyl pyruvate are not photochemically active[26,27]. Decomposition of the ester group undoubtedly plays a role in the initiation of degradation.

Reactions of radicals in PMMA in the absence of oxygen and the absence of monomer

Decomposition of the ester group by 254 nm radiation involves the three reactions[7]:
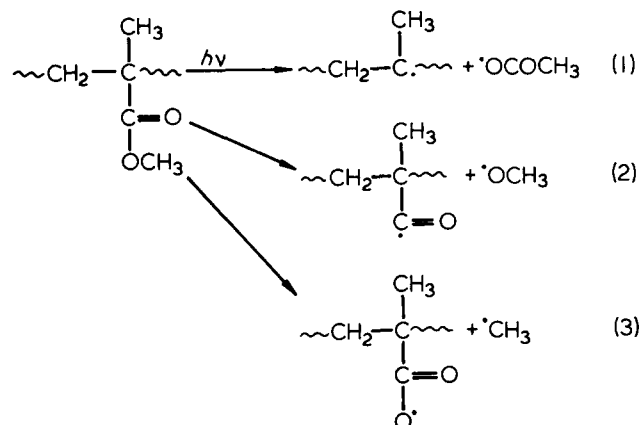

The same reactions are probably induced at wavelengths greater than 300 nm, but with much smaller efficiency. To some extent, these radicals then eliminate either CO or CO_2, as appropriate, to give the corresponding alkyl radicals, i.e.
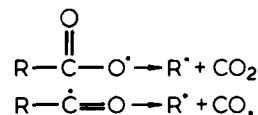

At 254 nm every absorbed photon results in degradation of the ester group[7], with reaction (1) being the most important process. However, the quantum yield for chain scission is only 0.05[7,11], and arises from a β-scission step, i.e.
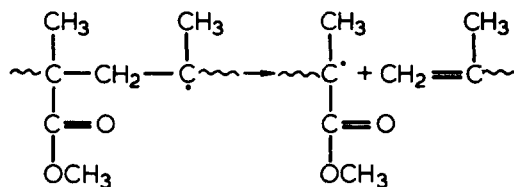
This step is in competition with radical-removing disproportion reactions such as
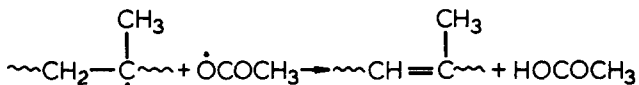
which are most rapid when the two radicals are held in close proximity by the cage effect of the glassy matrix. If the small radical escapes from the cage, it can abstract hydrogen to give a secondary alkyl radical, viz.
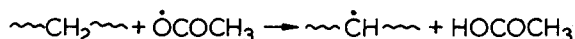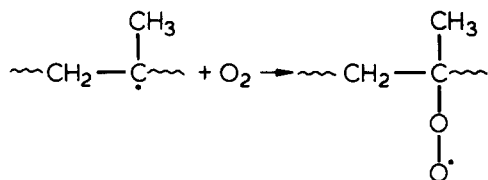

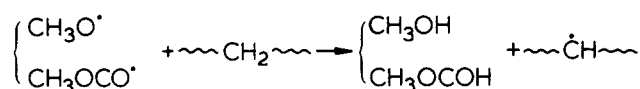which may undergo β-scission or, when mobile enough to encounter another radical, enter into disproportionation.

Degradation of PMMA in the presence of oxygen

When oxygen is available, the above reactions are superseded by the well-known rapid reactions of alkyl
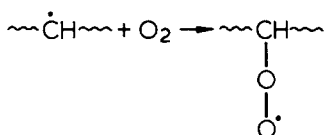
radicals with oxygen to give peroxyl radicals, e.g.

$$\sim\text{CH}_2-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\sim + \text{O}_2 \longrightarrow \sim\text{CH}_2-\underset{\underset{\underset{\underset{\text{O}^\bullet}{|}}{\text{O}}}{\underset{|}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}}}{}\sim$$

Tertiary peroxyl radicals are not very reactive, and will not abstract hydrogen from the –CH$_2$– and –CH$_3$ groups in PMMA to any significant extent. Mostly they will interact with other peroxyl radicals. The small radicals formed in the decomposition of the ester group can abstract hydrogen from the –CH$_2$– groups in the PMMA backbone, or, if alkyl, also add to oxygen. If oxygen is available, secondary alkyl radicals formed in this way will rapidly add oxygen to give secondary peroxyl radicals. The steps are
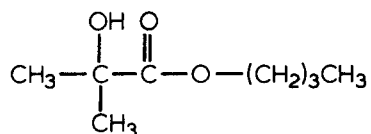
$$\left\{\begin{array}{l}\text{CH}_3\text{O}^\bullet\\\text{CH}_3\text{OCO}^\bullet\end{array}\right. +\sim\text{CH}_2\sim \longrightarrow \left\{\begin{array}{l}\text{CH}_3\text{OH}\\\text{CH}_3\text{OCOH}\end{array}\right. +\sim\overset{\bullet}{\text{CH}}\sim$$

and

$$\sim\overset{\bullet}{\text{CH}}\sim + \text{O}_2 \longrightarrow \sim\underset{\underset{\underset{\text{O}^\bullet}{|}}{\overset{\overset{\text{O}}{|}}{\text{CH}}}}{}\sim$$

Also, the $\text{CH}_3^\bullet$ radical will peroxidize, e.g.

$$\text{CH}_3^\bullet + \text{O}_2 \longrightarrow \text{CH}_3\text{—O—O}^\bullet$$
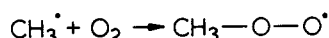
Interactions between peroxyl radicals are then inevitable. When at least one of the peroxyl radicals is not tertiary, two peroxy radicals can terminate in a Russell-type interaction to give an alcohol, a ketone or aldehyde, and no chain scission, viz.
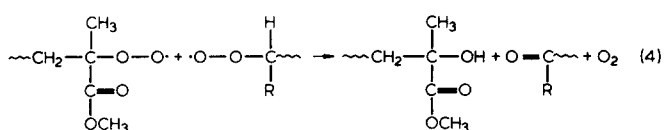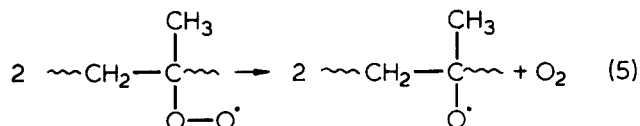
where R = hydrogen or backbone. The appearance of the –OH group in equation (4) can be monitored via its infrared spectrum. The –OH absorption for the analogous compound butyl-2-methyl-lactate,

$$\text{CH}_3-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{OH}}{|}}{\text{C}}}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}-(\text{CH}_2)_3\text{CH}_3$$

is in the region 3550 to 3530 cm^{-1} for free –OH and from ~3530 to ~3200 cm^{-1} for hydrogen-bonded –OH groups. Absorptions in these regions are present in our specimens of photo-oxidized PMMA (*Figure 5*). We note also that hydroperoxides are known[28,29] to absorb at 3560 to 3510 cm^{-1} for free –OOH groups and 3470 to 3380 cm^{-1} for hydrogen-bonded groups. Because there are in principle no tertiary carbon atoms to provide hydrogen abstractible by tertiary peroxyl radicals, and
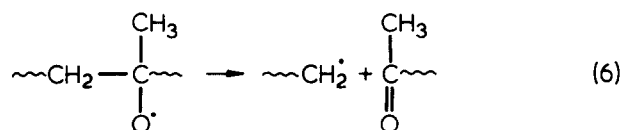
nearly all non-tertiary peroxyl radicals will terminate in the Russell reaction rather than abstract hydrogen, it is probable that hydroperoxides do not form to any appreciable extent in this system. Chemical tests for hydroperoxides will be performed soon.

When both peroxyl radicals are tertiary, a non-terminating interaction occurs to give alkoxy radicals, e.g.

$$2 \sim\text{CH}_2-\underset{\underset{\underset{\text{O—O}^\bullet}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}}{}\sim \longrightarrow 2 \sim\text{CH}_2-\underset{\underset{\underset{\text{O}^\bullet}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}}{}\sim + \text{O}_2 \quad (5)$$

This type of reaction has also been found to occur to some extent for secondary peroxyl radicals[30].

Alkoxyl radicals are very reactive and if sufficiently long-lived can abstract hydrogen from many organic groups. However, a very important competing reaction is β-scission, viz.

$$\sim\text{CH}_2-\underset{\underset{\underset{\text{O}^\bullet}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}}{}\sim \longrightarrow \sim\text{CH}_2^\bullet + \underset{\underset{\underset{\text{O}}{\|}}{}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\sim \quad (6)$$

and it is probably through this reaction that the presence of oxygen greatly increases the damage to PMMA. The primary alkyl radical formed in this step will rapidly peroxidize, and these and most secondary peroxyl radicals will undergo Russell-type termination with some other peroxyl radical.

At temperatures below (say) 40°C, a possible termination mechanism is the formation of peroxide links by combination of pairs of tertiary alkoxyl radicals formed by mutual interaction of pairs of tertiary peroxyl radicals. This mode of termination is unimportant at the temperature of our experiments, because such peroxide links are known to be unstable at 40°C. In a glassy matrix such as PMMA, radicals on chains are relatively immobile, and termination reactions will be predominantly between radicals generated in the same initiation step, or their descendents or oxygenated derivatives, or, less frequently, with a radical derived from some low-molecular-weight impurity.

Possibility of oxygen entering into initiation step

Other possibilities for the role of oxygen have been proposed. Tomlinson *et al.*[26] attributed increases in the refractive index of PMMA made with preoxidized monomer and irradiated with 325 nm and 365 nm radiation to crosslinking following decomposition of the peroxide groups in the material. A weak shoulder between 300 and 400 nm in the u.v. absorption spectrum was found to be dependent on the degree of irradiation. Bowden *et al.*[27] extended this work to show that two of the oxidation products, methyl pyruvate and a copolymer of methyl methacrylate and oxygen, were much less active in the photochemical reaction than a compound thought to be a monomeric peroxide derivative of methyl methacrylate. This last material was destroyed slowly at 40°C and quickly at 100°C and would seem not to exist under the conditions of our experiments. No evidence of cross-linking in PMMA was found in their work. Density increases in irradiated specimens, which were the object of the investigation, were believed to arise from the

polymerization of residual monomer (usually 0.5 to 2% in commercial PMMA).

A mechanism for photodegradation of PMMA using a xenon arc was proposed by Panke and Wunderlich[9]. They combined the findings of Shlyapintokh and Goldberg[31] that monomer sensitizes PMMA to u.v. degradation, of Bowden *et al.*[27] that the presence of a monomeric methyl methacrylate peroxide sensitizes PMMA to photolytically initiated oxidation, and Kearn's proposal[32] that oxygen that adds to double bonds is in singlet oxygen form. Thus, in Panke and Wunderlich's mechanism, a photoexcited monomer molecule transfers energy to oxygen to produce singlet oxygen, which then adds to the double bond in the monomer. The resultant radical then attacks the polymer chains in an unspecified way.

The work of Gardner and Epstein[33] shows that quenching of excited states in PMMA by small molecules occurs, and also suggests that a charge-transfer mechanism may take place. This also is a possible mode of interaction for molecular oxygen. We found that fluorescence develops as the photodegradation of PMMA proceeds. A typical example for a sample photodegraded at 30 cm from the light source and at 115°C is shown in *Figure 7*. Maximum excitation occurs at ~ 375 nm, as has been found by other workers. Grassie and Torrance[34] attributed this phenomenon to conjugated unsaturation

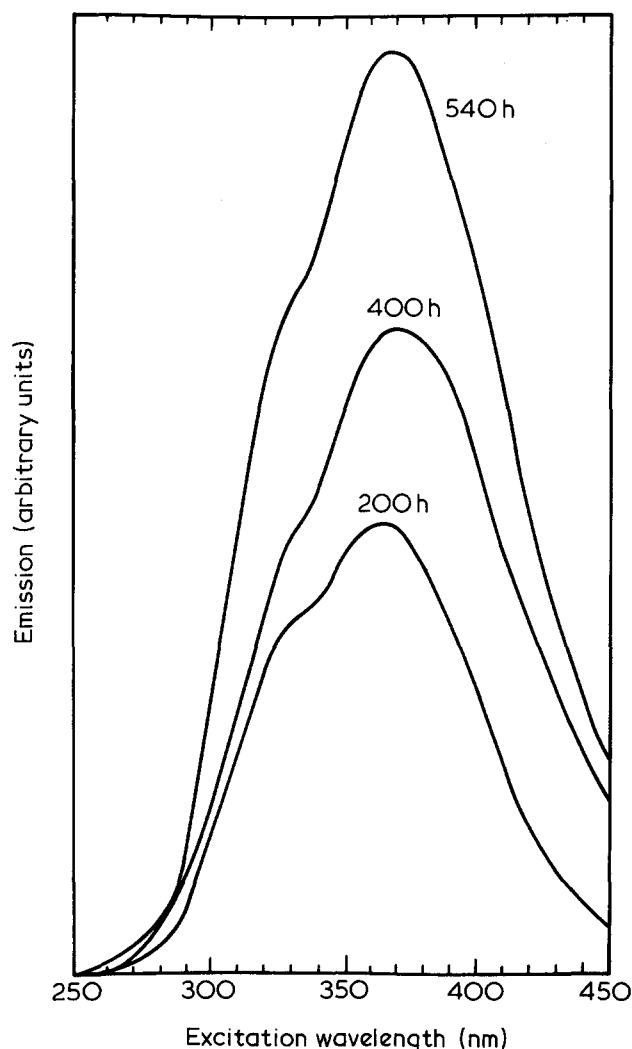Figure 7 Excitation spectrum for fluorescent emission at 480 nm in aged PMMA

but more likely possibilities are α-diketones with tertiary carbons α to each carbonyl group[35,36] and α,β unsaturated aldehydes[37]. Both species undergo $n \rightarrow \pi^*$ transitions near 380 nm.

One possibility in which oxygen can enter into the initiation step is for molecular oxygen in the triplet form to be converted into singlet oxygen by quenching excited chromophores which have crossed over into the triplet form from the excited singlet form. If the Panke and Wunderlich mechanism plays a significant role in the photodegradation of PMMA, it could be because of a phosphorescence component of the fluorescence which develops with degradation. Many papers have been published which study quenching of phosphorescent species introduced into PMMA, and this technique has also been used to study the diffusion of oxygen in PMMA. Singlet oxygen has been implicated in polymer degradation and adds (although with some difficulty) to double bonds. This mechanism could be a source of the new –OH absorption (as hydroperoxide) observed in the infra-red spectrum.

The excitation spectrum shown in *Figure 7* also has considerable implications with regard to the broad spectral range (250 to >450 nm) in which u.v. absorbers must provide protection if the fluorescence is important in initiating the photodegradation of PMMA. We therefore searched for a phosphorescence component of the fluorescence. The fluorescence exhibited by our degraded PMMA specimens has a lifetime of 900 ± 50 ps (R. Kavanaugh and D. King, NBS, private communication). No longer-term luminescence process up to a lifetime of 1 ms was found at 25°C in degraded PMMA specimens which had been pumped at < 1 μmHg pressure for ~ 1 week, and within these limits there is no indication of the existence of a process which could be quenched by molecular oxygen to give singlet oxygen. At this stage, significant initiation by singlet oxygen in the photodegradation of PMMA is not indicated.

*Evidence for the effect of monomer on radicals produced in degrading PMMA*

In *Figure 2*, many of the profiles appear to have a lower or equal amount of damage for the first few edge slices (e.g. see *Figures 2b, d* and *e*). One explanation for this is that monomer sensitizes PMMA to oxidative degradation but diffuses so slowly that its concentration falls significantly near the specimen surface (partly by evaporation) compared with its concentration in the interior of the specimen.

Possibilities for the effect of monomer include absorption of the incident photons and subsequent degradation of the ester group, as found for PMMA itself. However, although monomer has a higher absorptivity than ultrapure PMMA, it absorbs less than slightly oxygenated PMMA[38], and is present in less than 0.6% concentration.

The sensitivity effect[31] of monomer on the degradation rate may be to convert primary and secondary alkyl radicals into tertiary alkyl radicals by addition to the monomer double bond in regions where the concentration of oxygen is sufficiently low. This would significantly affect the lifetime of the radicals and the reaction path with oxygen.

Evidence for the effect on the lifetime and on the identity of the radicals formed comes from several

electron spin resonance (e.s.r.) investigations. Free radicals associated with random, homolytic main chain scission as produced in mechanical degradation of PMMA include the tertiary alkyl type A

(A)   (B)   (C)
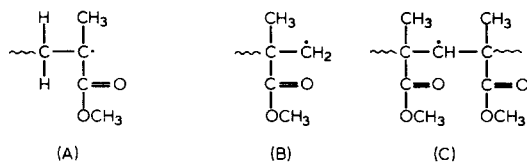
which is known to give the 5 + 4 line spectrum in electron spin resonance studies[39-41] and the radicals B and C which have been identified in PMMA milled at 77K[42]. A and B are direct results of chain scission. C arises from hydrogen abstraction by B and its formation shows that the primary alkyl radicals are very reactive. Production of these radicals can be initiated by a variety of degradation sources including ionizing radiation[43], mechanical fracture[44] and bulk polymerization[41].

Bullock and Sutcliffe report[41] that under the conditions of their experiment they did not observe radical B with electron spin resonance, indicating that it has a very short half-life. This is consistent with the findings of Tabata *et al.*[42], who showed that B abstracts hydrogen from PMMA to give C in the absence of oxygen. The half-life of radical A is approximately 20 h at room temperature, but is greatly reduced with increased temperature. This indicates the greatly increased mobility of the polymer strands at the higher temperature. Symons[45] reported a half-life between 4 and 5 min at 110°C, while Michel *et al.*[39] found no detectable amounts of free radical after exposing specimens to 110°C for 30 min. Tabata *et al.*[42] found a 50% decrease in the number of radicals on passing PMMA through the glass transition temperature.

When monomer is present in the plate, the amount of free radical A produced is directly proportional to the amount of monomer present[39]. Also far more radicals are produced in the presence of monomer than in its absence when PMMA is irradiated with radiation > 300 nm[46]. These findings are consistent with radicals such as B and C adding to monomer to give the more stable tertiary radical A, as in the scheme given by Bullock and Sutcliffe[41], viz.

(B)   (A)   (7)
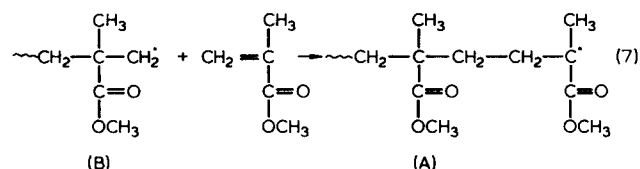
Radicals B and C can presumably also add to unsaturated chain ends formed in disproportionation reactions during polymerization, but this reaction will be less important than that with monomer because the chain ends will be much less mobile than monomer.

Termination of these types of radical in PMMA in the absence of oxygen can occur by disproportionation if one of the radicals has an available hydrogen atom, i.e.
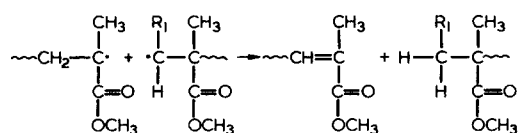
where R_1 = H or backbone. This type of reaction can also readily take place when the radicals produced in reaction (1) are held in close proximity by the cage effect. Combination of radicals is another possible mode of termination.

In the presence of abundant oxygen, peroxyl radicals will be formed. Where oxygen is limited in supply, and monomer is available, more than 50% of the alkyl radicals may well be tertiary. Thus after peroxidation there will not be enough primary and secondary peroxyl radicals to remove all tertiary peroxyl radicals by the Russell termination reaction, equation (4). Since peroxyl radical termination requires that at least one of the two radicals be non-tertiary, termination of the excess of tertiary radicals produced in the presence of monomer and oxygen is only possible after some primary radicals have been generated by chain scission through β-scission of tertiary alkoxyl radicals. As monomer is lost from the surface, the concentration of radicals of type A formed in reaction (7) will decrease. As the concentration of A radicals is reduced, correspondingly more B and C radicals will be available for the sequence of peroxidation and termination, which will remove all types of radicals, and consequently reduction in plate damage on the surface will occur.

Changing effect of cage with temperature

It is obvious from *Figures 1* and *2* that more degradation occurs at higher temperatures and that the parts of the specimen accessible to oxygen degrade more extensively than the interior of the specimen. The U-shaped curves of bonds broken become more U-shaped with temperature. Diffusion coefficients increase with temperature, so increases in temperature would tend to even out the oxygen concentration in the specimen, other things being equal, and give curves for the bonds broken which are less U-shaped at higher temperatures than at lower temperatures. The obvious explanation for the increase in U-shape with increasing temperature is that the consumption of oxygen increases faster than its diffusion. We ascribe the increase in oxygen consumption to decreases in the efficiency of the cage effect. Further work will be carried out to see if thermal decomposition of photo-oxidation products also plays a significant role in initiation.

Gupta *et al.*[7] and Fox *et al.*[11] determined that the quantum yield of scissions in PMMA in the absence of oxygen is ~0.05. It is obvious from the increased degradation near the edge compared with the degradation at the centre of the plate in *Figure 2* that the presence of oxygen produces more scissions than occur when oxygen is not present. For the radicals to react with oxygen, the radicals must escape from their cage or oxygen must enter the cage. Dan and Guillet[47] showed that the quantum yield of chain scission increases with temperature for copolymers of methyl methacrylate and methyl vinyl ketone degrading by the Norrish II reaction, and that, although the glass transition temperature of these polymers is 102°C, there is a discontinuity near 70°C. This is similar to our findings that damage becomes diffusion-controlled between 50° and 85°C. They assigned their results to increases in polymer mobility because the mode of degradation they assigned to their material requires a particular orientation in neighbouring segments of the polymer chain. A similar indication of increasing radical mobility with increasing temperature is given by the

shortening of radical lifetime with increasing temperature, as described in the previous subsection.

For the case of glassy polymers, the activation energy of diffusion of small molecules has been related to the movement of a segment of a polymer molecule chain to connect momentarily two parts of the free volume of the polymer and allow diffusant molecules to pass. The activation energy has been related to the molecular diameter of the diffusant raised to the 1.6 power[17,18,48,49]. The opening of the cage also requires the movement of a polymer segment and is conceptually like diffusion.

From the work of Gupta et al.[7], we see that in 70% of the cases the radicals produced (with 254 nm radiation) are the in-chain radical $\sim\!C(CH_3)\!\sim$ and the methyl formate radical (equation (1)). Both these are much larger than oxygen; hence, the activation energy for opening of the cage must be significantly greater than the activation energy for the diffusion of oxygen. If this is so, the rate of escape of such radicals from their cages will increase more with increasing temperature than will the diffusion of oxygen into the plate. Where there is an ample supply of oxygen, oxygen will be able to diffuse into the cage, with a rate that increases relatively slowly with temperature. Where there is a limited supply of oxygen, the effective concentration of oxygen at a given depth in the sample will decrease with increasing temperature because the rate of consumption (which depends on the inefficiency of the cage effect in holding together the radicals produced in the initiation step) will be more temperature-dependent than the replenishment of the oxygen by diffusion. In the absence of oxygen, chain scission will be infrequent, with quantum yield $\sim\!0.05$.

Shielding effect by photo-oxidation products

It is known from the Beer–Lambert law that photons are absorbed almost uniformly through the plate when the transparency of a material is high. For short exposure times, the profiles of bonds broken in our PMMA specimens are relatively symmetrical as expected. With increasing degradation, however, the transparency of the plate in the ultra-violet region decreases significantly, especially for the shorter wavelengths (*Figure 8*). Similar decreases have been previously reported[11,50]. Since fewer photons arrive at the side remote from the illumination as the transmission through the plate decreases, the remote side degrades photolytically at a slower rate than the side nearer the light source, and the profile of bonds broken becomes asymmetric. The loss in transmission probably results from the formation of oxidation products.

Photo-oxidation and mechanical properties

Mechanical properties of PMMA can be related to molecular weight, as shown by Kusy and Turner[51] and Berry[52], and are expected to be quite susceptible to surface degradation. The most degraded of our samples had molecular weights of 12 000 near the plate face. This is well into the brittle part of the relationship given in Figure 5 of Kusy and Turner, and is consistent with our findings that the outer surfaces of these specimens were difficult to plane because attempts to cut off a layer produced a fine powder, whereas planing the central portions of all specimens was relatively easy. Thus sufficiently degraded PMMA acquires a layered structure, although the optical properties remain good. The outer layer(s) become brittle, while the inside portion remains
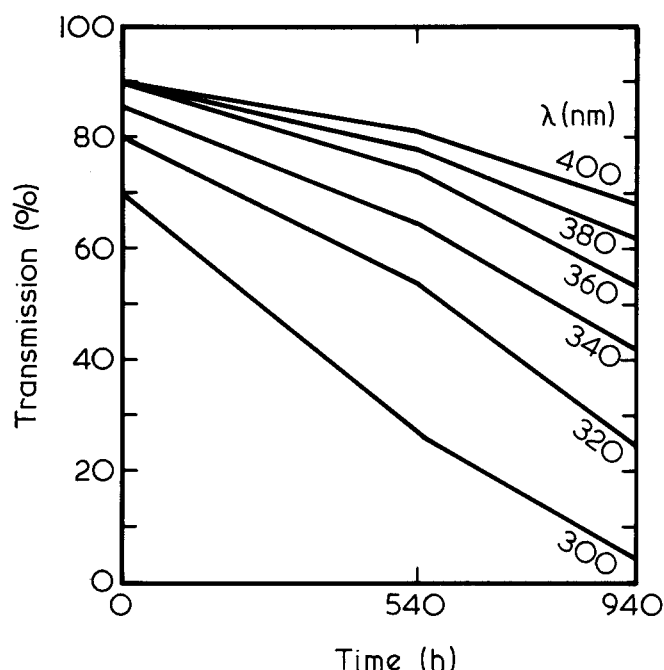

Figure 8 Change of transmissivity with ageing for various wavelengths in PMMA exposed at 115°C, 30 cm from arc

plastic. This weakens the material, as has been shown for polystyrene in ref. 53. Flexural stress applied to the plate produces cracks in the brittle phase, and at the end of the cracks subjects the plastic phase to stress concentrations which propagate the fracture process in the brittle mode, as can be seen by examining fracture planes under the microscope.

SUMMARY

One of the major differences between the conditions in the earlier investigations and the conditions used here is that 254 nm radiation was used in most of the earlier studies. This radiation is absorbed by the ester group of methyl methacrylate with unit efficiency and causes significant chain scission (quantum yield 0.05) in the polymer even in the absence of oxygen. Oxygen will have a significant effect only at low rates of initiation, where its concentration can remain at a significant level. The rate of initiation for a given flux is much higher at 254 nm than at wavelengths above 300 nm. Also, the samples of PMMA used in these earlier studies contained very little monomer, and it is reasonable to suppose that in the presence of oxygen the Russell termination reaction occurred to a far greater extent than did the generation of scission-inducing tertiary alkoxy radicals, described above under the 'effect of monomer'.

In principle, PMMA has little chromophore activity in the u.v.–visible region of sunlight (>295 nm), although the tail of the intense u.v. absorption of the ester group near 240 nm extends a little past 300 nm. The low activity of chromophores is one reason for the good stability of PMMA outdoors. Attack on the ester group is not very efficient for radiation with wavelengths longer than $\sim\!300$ nm, because the absorptivity at these wavelengths is very much lower than at 240 nm, and under these conditions the effect of oxygen in producing chain scissions becomes important. The fact that oxygen must diffuse into the specimens limits the degradation to the

surface at high rates of initiation (high levels of irradiance or moderate irradiance levels and high temperatures). When oxygen plays a dominant role, the degradation rate increases greatly with temperature because of the decreasing efficiency of the cate effect. The role of oxygen is to produce chain scissions via β-scission of alkoxy radicals on the chain. As photo-oxidation proceeds, the products of photo-oxidation absorb the damaging wavelengths and shield the material behind the leading edge. A phosphorescence component of fluorescence which develops in photo-oxidizing PMMA has not yet been found. Such a component, if it exists, could be quenched by oxygen to give singlet oxygen which could add to double bonds in the material and could act as an initiator of photodegradation. The fluorescence is excited by wavelengths in the range 250 to 450 nm. Wavelengths above 390 nm are not significantly absorbed by the absorbers most commonly used in PMMA.

ACKNOWLEDGEMENTS

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