The Oxidative Thermal Degradation of Poly(Methyl Acrylate)*

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Received April 5, 1971

The degradation of thin films of poly(methyl acrylate) has been studied under 300 mmHg pressure of oxygen in the temperature range 180—250°C. Crosslinking and chain scission occur. Carboxyl, hydroxyl and γ-lactone structures are formed on the polymeric residue. Carbon dioxide comprises *ca.* 52% of the total evolved volatiles which also include methanol, water and methyl formate. The overall activation energy for volatile formation (weight loss) is 9.8 kcal. Possible oxidation mechanisms are considered and it is concluded that the oxyradical $-CH_2-\overset{\overset{O\cdot}{|}}{\underset{\underset{CO_2CH_3}{|}}{C}}-CH_2-$ plays an important part.

In recent years several papers have been published on the photolytic [1] and vacuum thermal degradation [2] of some of the polyacrylates. Poly(methyl acrylate) (PMA) has received most attention but so far there have been no reports of the effects of oxygen on the pyrolysis of this polymer although the oxidative thermal degradation of poly(ethyl acrylate) (PEA) has been studied in some detail [3, 4]. In this paper we report the results of a study of the degradation of PMA in the temperature range 180—250°C under 300 mmHg pressure of oxygen.

Experimental

PMA was prepared in benzene solution (50/50 v/v) at 70°C using benzoyl peroxide (6.5×10^{-4} mole l^{-1}) as initiator. Conversion of monomer to polymer was 20% and the polymer was purified by precipitation. Films, approx. 0.1 mm in thickness (0.1 g), were cast from benzene solution on to a glass degradation tray which was then placed inside a cylindrical glass vessel. After continuous pumping on the high vacuum line for 24 hours pure oxygen was admitted to a pressure of 300 mmHg. The sealed vessel was then heated for the required time in a fluidized sand bath in which the temperature was controlled to within ± 1°C.

The products of degradation are conveniently divided into three fractions as shown in Table 1.

* Presented at the IUPAC Conference on Chemical Transformation of Polymers. Bratislava, June 22—24, 1971.

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Table 1

Products of oxidative thermal degradation of PMA at 210–250°C

Fraction number	Nature	Yield (% by wt. of total volatilized)
I	polymer	residue
II	low polymer	~ 1.5 (~ 90)[a]
III	condensible volatiles	
	CO_2	~ 52 (4.8)
	methanol, water, methyl formate, others	~ 46.5[b]

a) Figures in brackets denote yield from vacuum thermal degradation [5].
b) By difference.

Separation of Fractions I, II, and III was achieved by attaching the degradation vessel to the vacuum line at room temperature and pumping slowly through a cold trap at −196°C. In this manner Fraction III condensed in the cold trap, Fraction II remained adhering to the walls of the vessel and Fraction I remained in the glass tray. Any permanent gases were lost by this procedure. The CO_2 in Fraction III was measured as described previously using a fixed-volume manometer [5], the other components being held as liquids in a side arm at −76°C. The mixture of volatile liquids which made up the remainder of Fraction III was examined by gas–liquid chromatography.

The soluble portion of the polymeric residue was determined by benzene extraction as before [6]. Infrared spectra of this sol fraction were recorded with a Perkin–Elmer 237 Spectrophotometer using films cast on sodium chloride discs and n.m.r. spectra with a Varian NMR Spectrometer model A60, using deuterochloroform as solvent.

Results

Products of degradation

The products of degradation averaged over 0–20% volatilization in the temperature range 210–250°C are summarized in Table 1. It is probable that the degradation temperature affects the relative yields of these products but this feature has not yet been investigated.

Any permanent gases were below detectable limits but may have been present in small amounts which were greatly diluted by the oxygen atmosphere. The amount of CO_2 was found by calibration of the constant-volume manometer. At least two other low-boiling liquids were present in Fraction III. These have not been positively identified but were not monomer, methyl methacrylate, methyl acetate, formic acid, formaldehyde, acetaldehyde, acetic acid, methyl propionate, acrolein or benzene (residual solvent).

The relative quantities of these volatile products of degradation contrast with the yields from vacuum degradation. CO_2 is the main product of oxidative degradation while low polymer is the main product under vacuum conditions. The small yield of low polymer under oxidation conditions is partly due to the lower temperatures employed

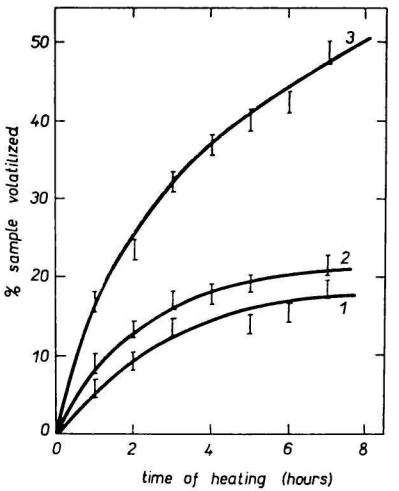


Fig. 1. Volatilization, as a percent of initial sample weight, *vs.* heating time at various temperatures.
1. 180°C; *2.* 210°C; *3.* 250°C.

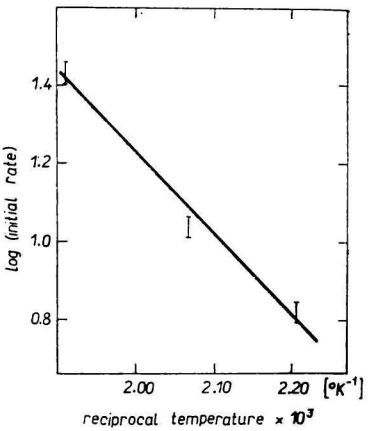


Fig. 2. Arrhenius plot of initial rates from Fig. 1.

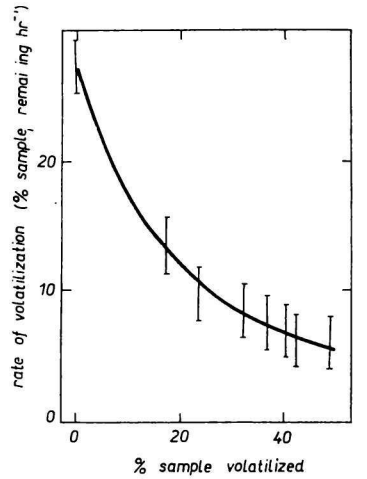


Fig. 3. Rate of volatilization (percent wt. of sample remaining per hour) *vs.* extent of volatilization.

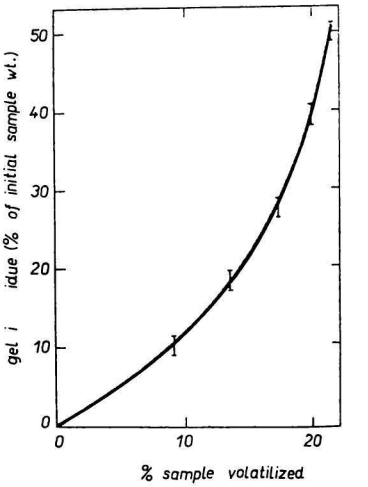


Fig. 4. Amount of gel (percent of initial sample wt.) as a function of sample volatilized at 210°C.

and to the effects of the oxygen pressure which limits vapourization of all but the most volatile species.

Total amounts of volatiles, as a percentage of the initial sample weight, *vs.* heating time are shown in Fig. 1. An Arrhenius plot (Fig. 2) from the initial rates obtained from Fig. 1 gives an activation energy for volatilization of 9.8 ± 2.0 kcal^{-1} compared with 35 kcal for vacuum degradation [2]. Fig. 3 shows the rate of volatilization, as percent weight of sample remaining per hour, *vs.* extent of volatilization. The exponential decrease in rate indicates that this is not an autocatalytic process.

The polymeric residue

The polymeric residue, Fraction I, changes from colourless through yellow to dark brown as oxidation progresses. The proportion of insoluble gel increases (Fig. 4) while the molecular weight of the soluble fraction of the residue falls sharply. Crosslinking and chain scission therefore occur as in vacuum degradation. Gel formation, however, is much more rapid in the presence of oxygen than under vacuum. Indeed the crosslinking reaction appears to be particularly sensitive to the presence of small amounts of oxygen. It has already been reported that PMA samples aged in air show an enhanced tendency to form gel on subsequent thermal degradation under vacuum [6]. As part of the present

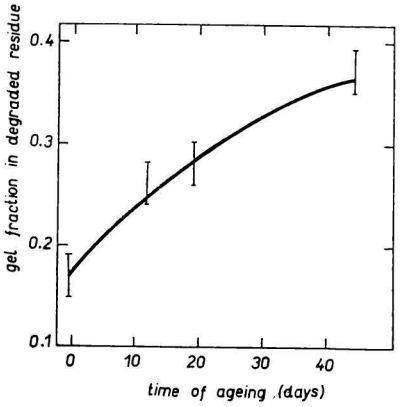


Fig. 5. Effect of ageing time at 60°C in air on gel fraction formed in subsequent vacuum thermal degradation at 210°C for 50 hours.

work some experiments on the effects of accelerated ageing were conducted by maintaining PMA samples in air at 60°C for up to 42 days. This treatment had no discernible effect on the i.r., n.m.r. or visible spectra, or on the solubility or molecular weight. Fig. 5 shows, however, that gel formation in these samples on subsequent vacuum thermal degradation at 210°C for 50 hours increases markedly with time of ageing. This ageing effect is probably caused by a small amount of oxidation.

The i.r. spectrum of the soluble fraction of PMA thermally oxidized at 250°C is shown in Fig. 6 along with that of the original polymer. The spectra below the range shown are identical. On oxidation new peaks are observed at 1790 and 1690 cm^{-1} along with a broad region of absorption from about 2900 to 3650 cm^{-1}. This broad region of absorption is characteristic of hydrogen-bonded hydroxyl groups, both of the alcohol (3650 – 3250 cm^{-1})

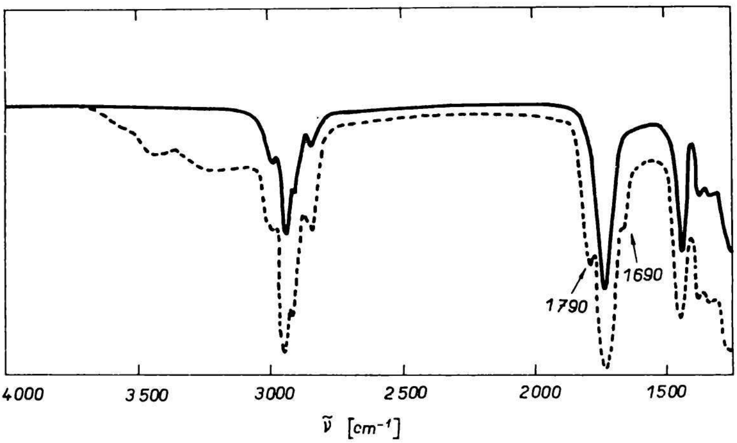


Fig. 6. Infrared spectra of undegraded (——) and sol fraction of oxidized (— —) PMA. Oxidation temperature 250°C.

and carboxyl (3300—2800 cm^{-1}) types [7]. The shoulder at 1690 cm^{-1} is characteristic of carbonyl groups in α:β-unsaturated carboxylic acids while the peak at 1790 cm^{-1} could be due to γ-lactone structures.

The n.m.r. spectrum of the sol fraction also shows evidence of hydroxyl protons in a broad absorption between 5.0 and 5.8 τ which disappears after a D_2O shake. There is no evidence in the n.m.r. spectrum of Fraction I of the unsaturated end structure

$$CH_2{=}C{-}$$
$$\quad | $$
$$CO_2CH_3$$

which appears during vacuum degradation [2].

Satisfactory spectra of the insoluble portion of Fraction I were not obtained. The colouration in Fraction I after oxidation, however, is associated mainly with this insoluble portion but was not attributed to any specific chromophore.

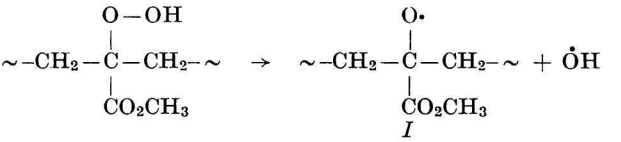
The i.r. spectrum of Fraction II is similar to that of Fraction I but contains an additional peak at 1630 cm^{-1} which is probably due to unsaturation within the low polymer backbone.

Discussion

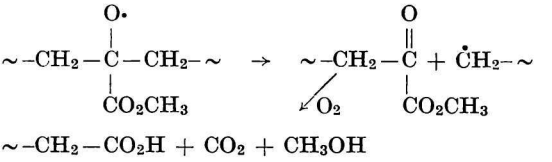
The activation energy for the overall volatilization process (9.8 kcal) is considerably lower than the figure 50.9 kcal reported for the oxidative thermal degradation of PEA over a similar temperature range [3]. We are unable to account completely for this unexpected discrepancy but it is worth noting that in the present experiments the changes in sample weight were obtained directly whereas *Conley* and *Valint* [3] estimated the amount of polymer in the residue from the carbon—hydrogen stretching frequencies in the i.r. spectra. Due to the complexities of the degradation reactions the two methods of calculating the rate of decomposition of the polymers are not necessarily equivalent. The two sets of results also differ in that Conley and Valint found no evidence of hydroxyl

groups in thermally oxidized PEA. Their results, however, are at variance in this respect with the observations of *Steele* and *Jacobs* [4] whose findings are largely in accord with ours. Despite these differences the following reactions for PMA oxidation are basically similar to those proposed for PEA.

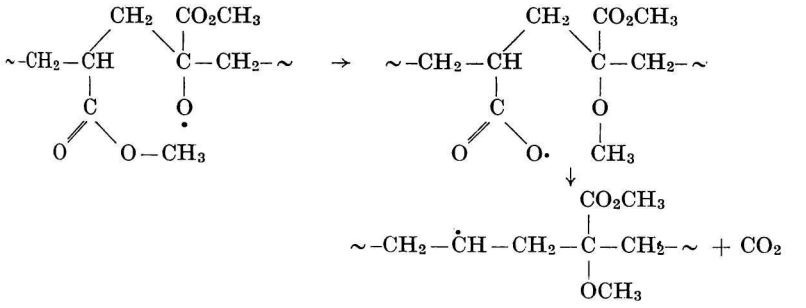
The products of degradation and the spectral changes observed in Fractions I and II can be accounted for by assuming that degradation involves the initial formation of hydroperoxides on the polymer backbone. The ageing experiments indicate that these hydroperoxides are stable at least up to 60°C but decompose on subsequent heating. It is probable that the initial site of attack is the tertiary carbon atom and that the resulting hydroperoxide decomposes as shown below. The possibility of some oxygen attack at the methylenic carbon atom, as appears to occur in polyacrylonitrile [8], cannot be wholly discounted.



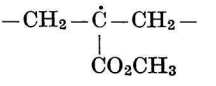
The oxypolymer radical *I* can undergo chain scission



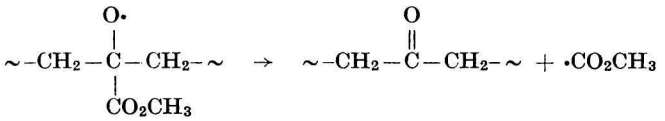
and, as suggested by *Conley* and *Valint* for PEA [3], the α-keto-ester would be further oxidized to yield CO_2, alcohol and a carboxylic acid group on the polymer chain. Further decarboxylation of the acid would increase the yield of CO_2 which could also be formed in the reaction



This mechanism is analogous to that proposed for CO_2 formation in vacuum thermal degradation in which the oxypolymer radical is replaced by the tertiary radical

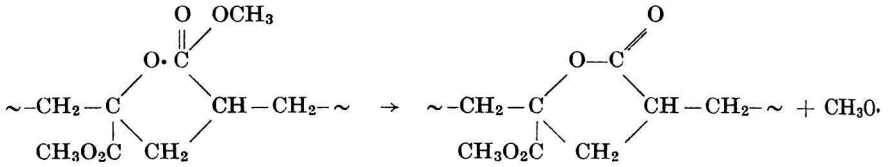


The radical *I* could also expel a methyl formyl radical

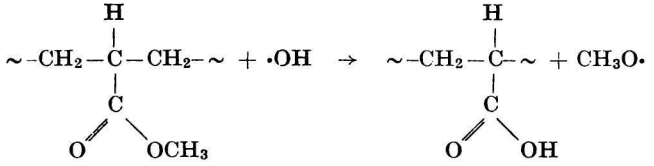


thus accounting for the formation of methyl formate and the general broadening of the carbonyl region in the i.r. spectrum of the polymer residue.

Other routes to methanol formation are the elimination reaction

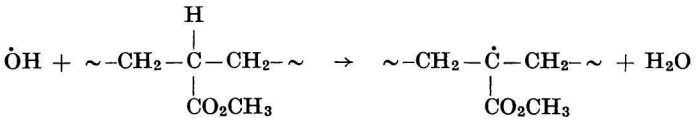


and the displacement reaction



The former leads to γ-lactone and the latter to carboxyl formation. The presence of both functions on the degraded polymer is supported by the spectroscopic evidence.

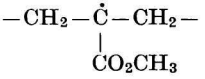
Water is most likely to be formed in hydrogen abstraction by the •OH radical, for example



Further abstraction or loss of an adjacent methylene proton would lead to backbone unsaturation. Alcohol hydroxyl groups on the polymer could be formed by hydrogen abstraction by the oxyradical *I* or by addition reactions of the •OH radical.

Gel formation would result from intermolecular combination and addition reactions of macroradicals as proposed in vacuum degradation [5]. The occurrence of crosslinking reactions changes both the physical and chemical properties of the polymer, and is probably responsible for the non-autocatalytic nature of the volatilization processes.

Thus, the primary formation of the hydroxyl radical and the oxyradical *I* can account qualitatively for most of the features of the degradation. It can be seen that the oxyradical is likely to play an analogous role in oxidative degradation to the radical



in vacuum thermal degradation.

Acknowledgements. F. D. Gratefully acknowledges the award of a studentship from the Science Research Council.

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