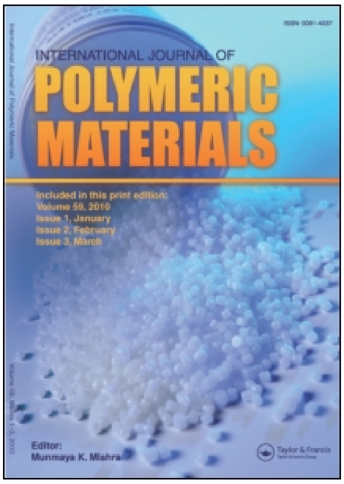

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# Products of Thermal Degradation in Polymer Systems Based on Methyl Methacrylate

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# Products of Thermal Degradation in Polymer Systems Based on Methyl Methacrylate

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The effects of γ-irradiation, copolymerisation and the presence of various additives on the nature of the degradation products from polymer systems based on methyl methacrylate are reviewed. The ways in which the normal pattern of degradation of poly(methyl methacrylate) to give near quantitative yields of monomer is modified are examined and patterns of behaviour established. The types of system in which the greatest changes in behaviour may be expected are identified.

KEY WORDS Thermal degradation, methyl methacrylate

## INTRODUCTION

Poly(methyl methacrylate) (PMMA) is one of the few polymers which can give almost quantitative yields of monomer when thermally degraded. When comonomer units are present in the chain, however, or when additives are present in the polymer, not all the MMA repeat units in the chain are necessarily converted into monomer. In some cases, the yield of MMA may be substantially less than expected simply on the basis of polymer or copolymer composition. One consequence of this is that analysis of MMA copolymers by pyrolysis-gas chromatography, using the monomer peak as a measure, could be very unreliable. The thermal degradation of many MMA-based systems has now been studied in depth and it is the purpose of this presentation to review the various behaviour patterns which have been established and show why the original MMA repeat units in the chain may in some cases degrade to products other than monomer. On this basis, it should be possible to predict likely decomposition routes for other MMA-based systems.

## THERMAL DEGRADATION OF PURE PMMA

The thermal stability of a pure PMMA sample is very dependent upon the conditions of polymerisation, as illustrated in Figure 1 for programmed heating at 10°C/min. The data in this and some of the subsequent diagrams have been obtained by the thermal volatilisation analysis (TVA) technique.[1,2] PMMA prepared by the anionic route degrades in a single stage. For the normal free radical route, however,

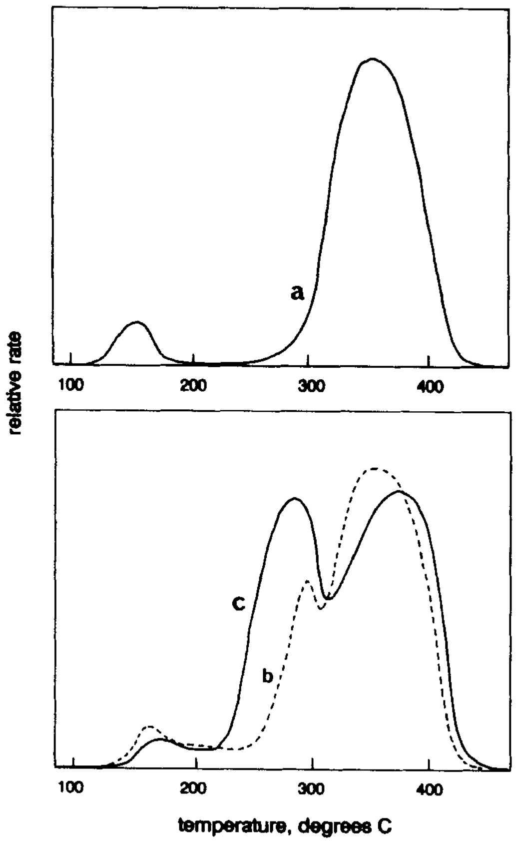
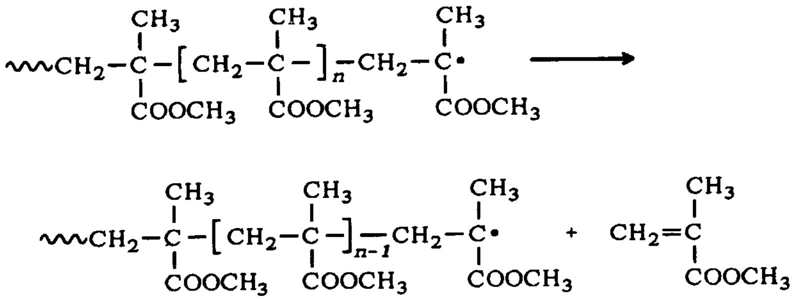


FIGURE 1 TVA traces for (a) PMMA, high molecular weight, prepared by anionic route, (b) PMMA, high molecular weight, and (c) PMMA, low molecular weight, prepared by free radical route. Continuous evacuation, heating rate 10°C/min. Volatilisation below 200°C is due to volatile material released when the polymer softens.

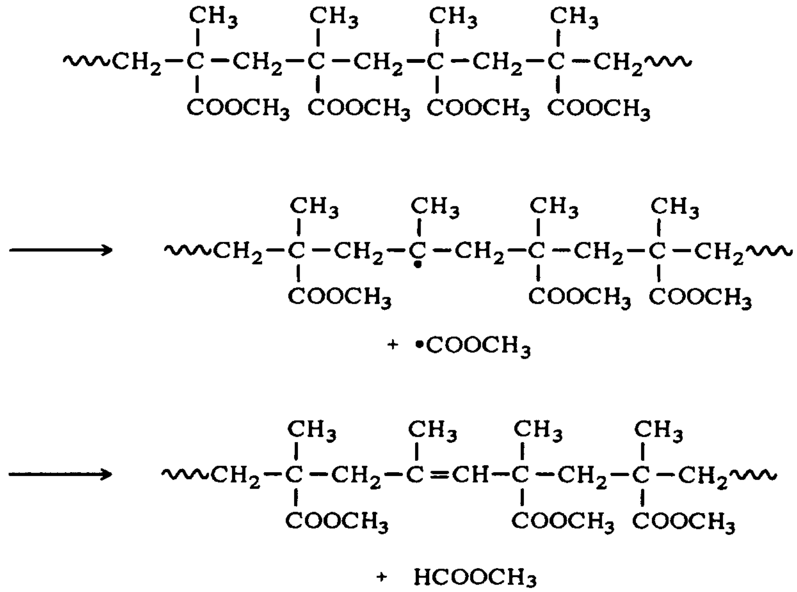
the polymer shows two stages of breakdown, the relative importance of which depends upon the initial molecular weight.[3] Nevertheless, in each of the three situations illustrated, the sole product of thermal degradation is monomer, apart from traces of carbon dioxide.

The mechanism of degradation of pure PMMA provides the basis for understanding the reasons for differences in behaviour of MMA units in other MMA-based systems. The degradation is initiated by chain scission, which can occur in all samples by random scission at temperatures (during programmed heating) above about 300°C. In polymers made by the free radical route, chain scission can occur initially at lower temperatures adjacent to the unsaturated chain ends which are present in about half the chains as a consequence of disproportionation as the main termination process in the polymerisation. Whether chain scission occurs at random or at the unsaturated chain ends, the consequence is depropagation ("unzipping") of the chain (Scheme I).

A feature of this mechanism which is crucial in importance both in respect of



SCHEME I



SCHEME II

the influence of molecular weight on degradation behaviour and to situations in MMA-based systems other than pure PMMA is that in the pure polymer the average zip length of the monomer-producing depropagation, once the radical is formed, is of the other of 200 monomer units.

## THERMAL DEGRADATION OF γ-IRRADIATED PMMA

The effect of subjecting pure PMMA to doses of γ-irradiation between 10 and 300 kGy on the subsequent thermal degradation behaviour has recently been investigated in our labortory.[4] Irradiation causes scission of a few of the ester side groups to give methyl formate, leaving a double bond in the polymer backbone at the elimination site (Scheme II). When the irradiated polymer is thermally degraded, monomer remains almost the sole product, but there is an increase in the amount of carbon dioxide formed and other trace products are methane, isobutene, methyl formate and benzene. It is also observed that the end-initiated depropagation to monomer is progressively eliminated with increasing radiation dose.

The main effect of irradiation, as with many other MMA-based systems discussed subsequently, is to introduce "blocking groups" at which, apparently, the depropagation stops if the temperature is below 300°C, so explaining the reduction in end-initiated formation of monomer. At higher temperatures, however, the chains can still produce monomer by random scission initiation. In view of the appearance of methyl formate and benzene as trace products, it is likely that the double bonds introduced as in Scheme II activate the adjoining monomer unit for side group scission at higher temperatures, enabling short conjugated sequences to develop which are the source of benzene.

## THERMAL DEGRADATION OF MMA COPOLYMERS

The emphasis, in the discussion which follows, is on copolymers in which MMA is the predominant monomer unit present in the chains. MMA copolymers show a very wide range of thermal degradation behaviour, which can, however, be explained on the basis of four basic types.

### Unrestricted Depolymerisation

This "ideal" situation is relatively uncommon in MMA copolymers. Its occurrence would imply the ability of the depropagation process to pass through a monomer unit other than MMA without hindrance. This type of behaviour probably arises in some systems in which the comonomer is also a methacrylate ester which degrades to monomer without ester side group decomposition, e.g., the ethyl and some of the higher *n*-alkyl esters. Although poly(phenyl methacrylate) degrades entirely to monomer, MMA-PMA copolymers show a more complex degradation pattern than unrestricted depolymerisation.[5] Although copolymers of styrene and MMA with relatively low styrene contents give the two monomers as predominant products, indicating the likelihood that unzipping proceeds through the styrene comonomer units, the end-initiated type of depolymerisation at around 300°C is prevented by the styrene units.[3]

### Blocked Depolymerisation

Many comonomers will prevent the end-initiated depropagation at moderate degradation temperatures, either directly or as a consequence of inter-unit reaction as considered below. The very long zip length in PMMA is reduced to the average length from an unsaturated end to the first co-monomer unit. The case of styrene has already been noted. Acrylates such as the ethyl ester are used to stabilise the PMMA chain because of this property. The effect of increasing amounts of methyl acrylate on the stability of the PMMA chain is illustrated in Figure 2.[3] Provided there is no inter-unit cyclisation, however, and considering copolymers with MMA content much more than 50 mole %, this type of behaviour will still lead to expected MMA yields at higher temperatures.

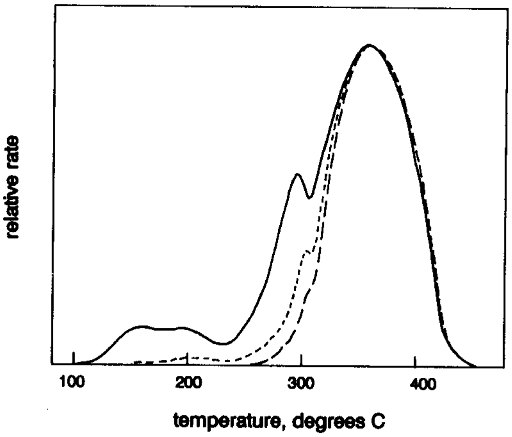


FIGURE 2 TVA traces for high molecular weight PMMA (radical route)——and 26/1 ---- and 8/1---copolymers (MMA/methyl acrylate) of comparable molecular wt. Volatilisation below 200°C is due to volatile material released when the polymer softens.

## Chain Scission

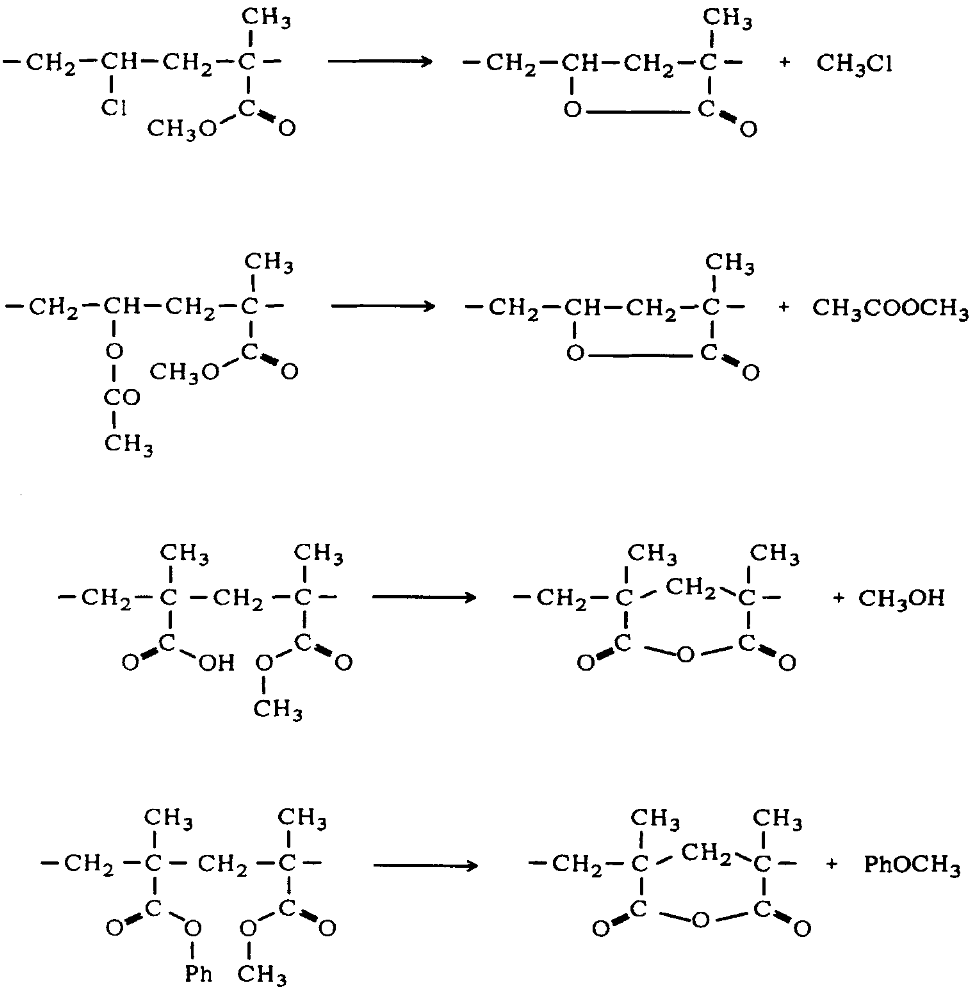
When copolymers of MMA with small amounts of acrylonitrile[6] or α-chloroacrylonitrile[7] are heated, the first effect is chain scission. In the first case, chain scission leads to molecules and unzipping does not immediately follow, but in the latter case, the terminal macroradicals formed on chain scission unzip to monomer at abnormally low temperatures. In these cases, yields of MMA on thermal degradation are essentially as expected from the composition.

## Intramolecular Cyclisation

Many cases have now been documented in which the first reaction to occur in the MMA copolymer as the temperature is gradually increased is a cyclisation involving an MMA unit and the adjoining comonomer unit. Because suitable pairs of reactive functional groups are held in proximity without the need for collision to occur, such reactions can take place at temperatures significantly, even considerably, lower than those required to bring about homolysis in the backbone or side groups. These systems are of particular importance because they inevitably lead to the conversion of some of the original MMA units into products other than monomer.

Examples of comonomers which lead to intramolecular cyclisation with adjoining MMA units are vinyl chloride,[8] vinylidene chloride, methacrylic acid,[9] acrylic acid, vinyl acetate[10] and phenyl methacrylate.[5] Four of the cyclisation reactions involved are shown in Scheme III. Some acrylate and methacrylate ester comonomers can result in similar reaction at somewhat higher temperatures since the corresponding acid comonomer is left in the chain following scission to alkene in the side group.

The effect may be discussed taking vinylidene chloride (VDC) as an example. The TVA curve for a copolymer with 1:4 VDC:MMA molar ratio is illustrated in Figure 3 and shows a two-stage decomposition. The first stage, starting below 200°C, gives products which are volatile at −100°C, identified as methyl chloride and hydrogen chloride. At the second stage, several products of different volatilities



SCHEME III

are present, including a gas shown to be CO by bleeding the products through an on-line quadrupole mass spectrometer. In this investigation,[11] the condensable gas and volatile liquid fraction was subjected to separation on the basis of volatility by the subambient TVA (SATVA) technique.[12] The SATVA curve (Figure 4) shows clearly the presence in the products of heating the copolymer to 500°C of HCl, $CO_2$, $CH_3Cl$ (the major product at some compositions), MMA and a liquid of lower volatility. Infrared spectra were also obtained for the tar-wax (cold ring) fraction and the polymer residue after partial degradation. The most significant feature is the appearance of lactone C=O absorption, particularly evident in copolymer heated to the end of the first stage of decomposition indicated in Figure 3. The CO and $CO_2$ result from fragmentation at higher temperatures of these lactone rings. The low volatility product in the SATVA trace is a dimer with a

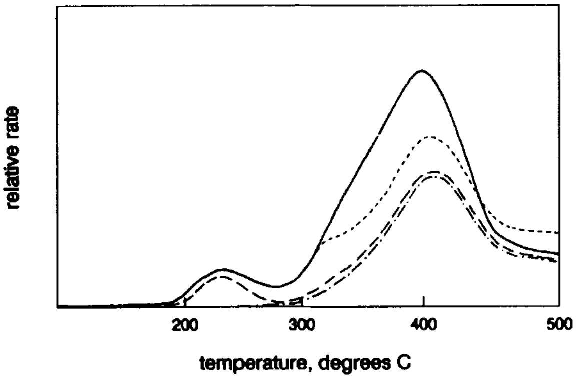


FIGURE 3 Differential condensation TVA data for MMA-vinylidene chloride copolymer with 20 mole % vinylidene chloride. Continuous evacuation, heating rate 10°C/min. Key to differential condensation traces: ——0 and −45°C, ---- −75°C, --- −100°C, -·-·- −196°C.

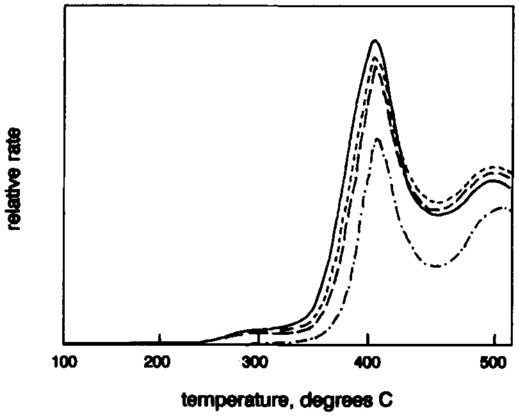
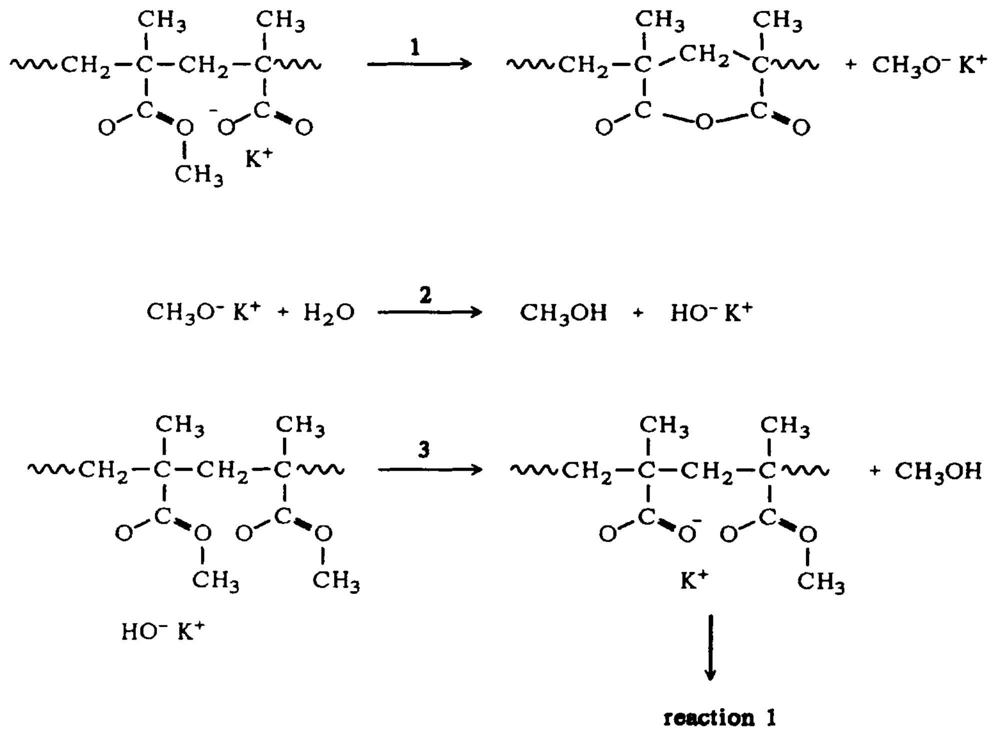


FIGURE 4 Differential condensation TVA data for MMA-potassium methacrylate copolymer with 21 mole % potassium methacrylate. Continuous evacuation, heating rate 10°C/min. For key to differential condensation traces, see Figure 3.

lactone ring and an MMA unit. The MMA yield from a system such as this is clearly much lower than the MMA content of the copolymer.

Copolymers of MMA with some methacrylic acid (MAA) also provide an important case. It may be noted that some emulsion polymerisation recipes include MAA as a component and this will copolymerise to appear in low concentration in the PMMA chains. The presence of as little as 5 mole % of MAA will considerably suppress the end-initiated depropagation reaction, because anhydride rings formed as a result of the reaction shown in Scheme III act as blocking groups, greatly reducing the average zip length of the monomer-producing reaction. As a consequence of the cyclisation in this system, methanol appears as a significant volatile product of degradation.

A particularly interesting type of copolymer in relation to the products formed is that of MMA with the alkali metal salts of methacrylic acid.[13-16] These ionomers are more stable than PMMA and instead of degrading to monomer, a complex



SCHEME IV

mixture of products is formed. The relative amounts of MMA, methanol and cold ring fraction have been determined quantitatively and depend both upon the composition and the nature of the cation. The basic degradation process involves intramolecular cyclisation (Scheme IV).

The incorporation of 21 mole % potassium methacrylate (KMA) into the PMMA chain suppresses the end-initiated depolymerisation and moves the main decomposition peak upwards by about 20°C (Figure 4). Products of greater volatility than MMA, including non-condensable gas, begin to evolve at as low as 350°C. The KMA homopolymer is stable to about 400°C, so that these products are associated with inter-unit reaction. It would be expected that the maximum yield of the ultimate cyclisation by-product, methanol, would occur at equimolar ratio of MMA and KMA in the copolymers. In fact, that maximum occurs at about 20 mole % (Figure 5), and the methanol yield at copolymer compositions up to this maximum can be three or four times the expected amount, implying that at least one other route to methanol formation, involving uncyclised MMA units, exists. This has been explained by postulating that potassium methoxide, the initial cyclisation by-product, is hydrolysed by water retained by the hygroscopic copolymer to give potassium hydroxide and methanol. The hydroxide ion can then attack an ester group to generate a new KMA salt unit and methanol. Provided there is a sufficient excess of uncyclised MMA units, the process can be repeated until several times the predicted yield of methanol is observed.[16] Clearly, in this situation, the MMA yield is again considerably depleted.

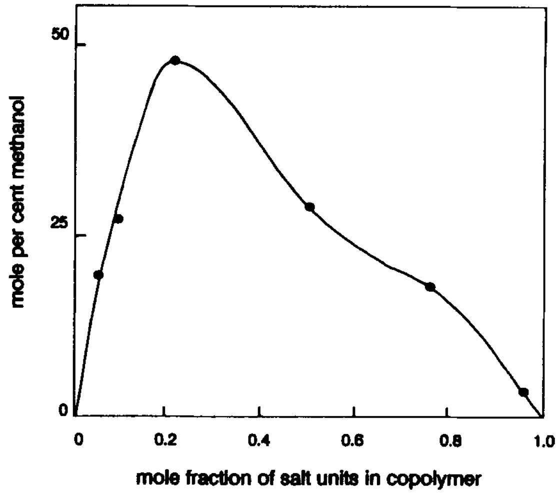


FIGURE 5 Comparison of methanol yield with copolymer composition for a series of copolymers of MMA and potassium methacrylate, degraded under TVA conditions to 500°C at 10°C/min.

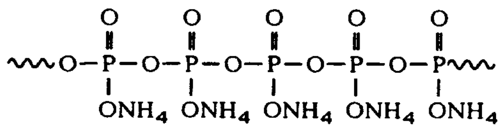
## THERMAL DEGRADATION OF PMMA CONTAINING ADDITIVES

Some additives have the effect of inducing depolymerisation in PMMA at lower temperatures than normal. In such situations, the MMA yield is not likely to be significantly reduced. In other cases, interaction between the additive and the polymer can result in structural change in the polymer backbone to give groups which not only stabilise the polymer by acting as blocking sites for the unzipping process, but also lead to a depletion of the MMA yield and the appearance of other products derived from the original MMA repeat unit. The most important PMMA additives are fire retardants, which are intended to modify the condensed phase reaction to reduce fuel (MMA) for burning or generate char. Several such systems have been examined in depth. Some other additive systems have been investigated which have been found to profoundly change the degradation behaviour of the polymer.

### PMMA with Fire Retardants

One of the materials commonly used as a fire retardant in PMMA is ammonium polyphosphate (APP) (**I**). When APP is heated it loses ammonia and water to produce an ultraphosphate (**II**) and then polyphosphoric acid. As the temperature is further raised, the polyphosphoric acid fragments to give smaller phosphoric acid type species. When a mixture of APP and PMMA is degraded, the polymer is stabilised, less monomer is formed and several other products appear, notably methanol.[17] Unlike the situation with pure PMMA, there is some char formation. The additive operates by reducing fuel, raising the temperature needed to generate fuel and impeding heat transfer through char formation.

When the IR spectrum of the partially-degraded PMMA in an APP-PMMA mixture is examined, it is found to show absorption bands at 1025, 1760 and 1805



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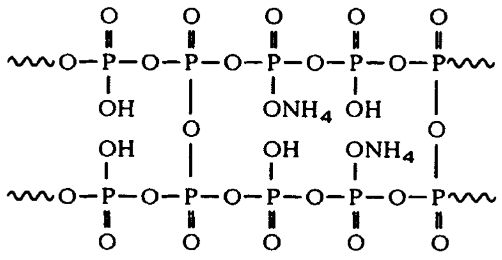
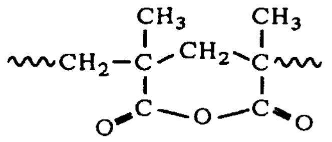
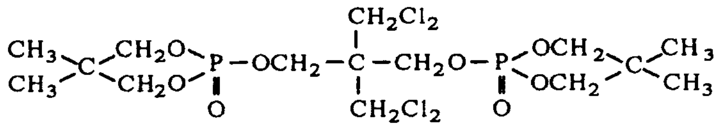
(I)



(II)



(III)



(IV)

STRUCTURES (I)-(IV)

$cm^{-1}$ characteristic of the six-membered cyclic anhydride (**III**). This is believed to be produced in the polymer as a result of interaction of the smaller phosphoric acid species with ester side groups. As has already been noted, this ring structure blocks unzipping to monomer: it is also the source of char at higher temperatures.

Red phosphorus has also been found to act as a fire retardant in PMMA and this has also been attributed to formation of cyclic anhydride structures in the backbone.[18]

One of the problems with many fire retardant additives is poor compatibility with the polymer. This is the situation in the two cases above. Some modern commercial fire retardants are designed to be more compatible with the polymer,

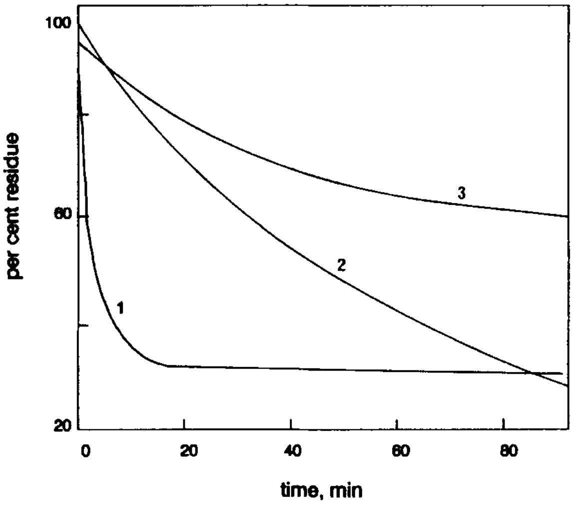


FIGURE 6 Thermogravimetric curves for (1) Sandoflam 5085, (2) PMMA, high molecular weight, (3) blend of PMMA with 15% by weight of Sandoflam 5085. Dynamic nitrogen, isothermal heating at 300°C.

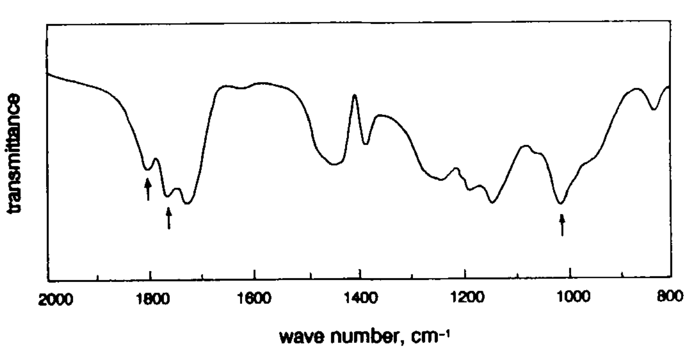


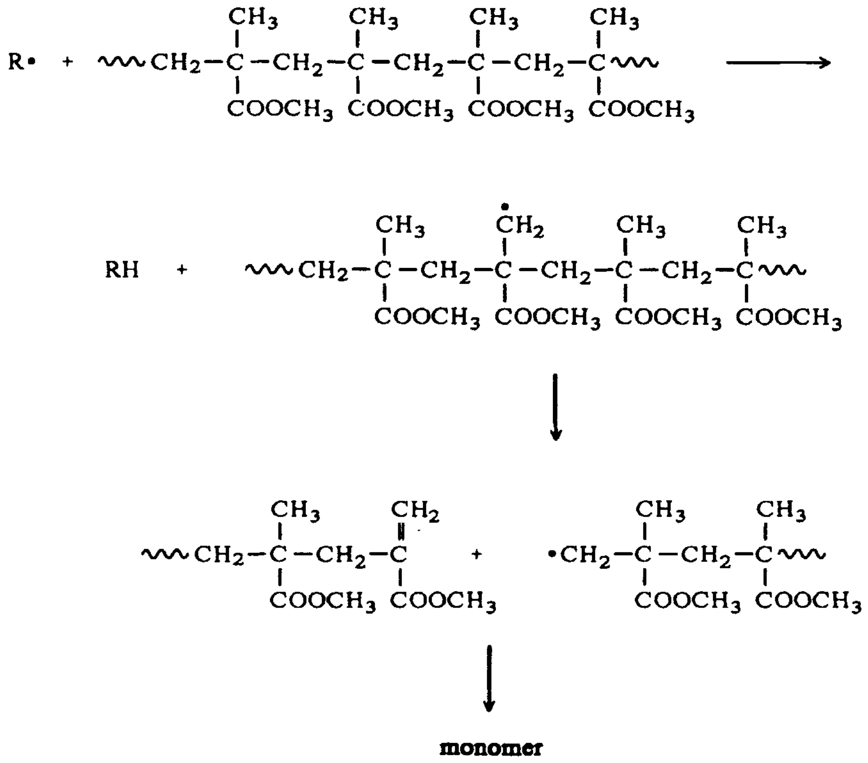
FIGURE 7 Infrared spectrum of PMMA residue after heating with 15% by weight of Sandoflam 5085 in air at 320°C for 15 min. Characteristic absorptions of the cyclic anhydride structure (**III**) are indicated by arrows.

a feature which would also be expected to improve effectiveness when a condensed phase interaction is involved. One such is Sandoflam 5085 (**IV**). Despite its complex structure, this compound acts ultimately in the same way as APP, but also has a second mode of action. In Figure 6 is shown the thermogravimetric (TG) behaviour of PMMA, the additive and a blend with 15% of additive. The stabilisation of the PMMA, reducing available fuel for burning, is clearly evident. The IR spectrum of PMMA extracted from the residue after partial degradation (Figure 7) shows clear evidence for the presence of the cyclic anhydride structure. On heating, Sandoflam 5085 breaks down to give a phosphoric acid, isoprene, carbon dioxide, 4-chloro-2-methyl-pentene-1, 2-methylbutanal and hydrogen chloride.[19] The phosphoric acid can interact effectively with PMMA, because of good initial compatibility of polymer and additive, to produce the anhydride; so too can hydrogen chloride[20] but in this case its role is likely to be minimal (trace amount); the other halogen-containing product, however, is likely to have a significant role in flame quenching.

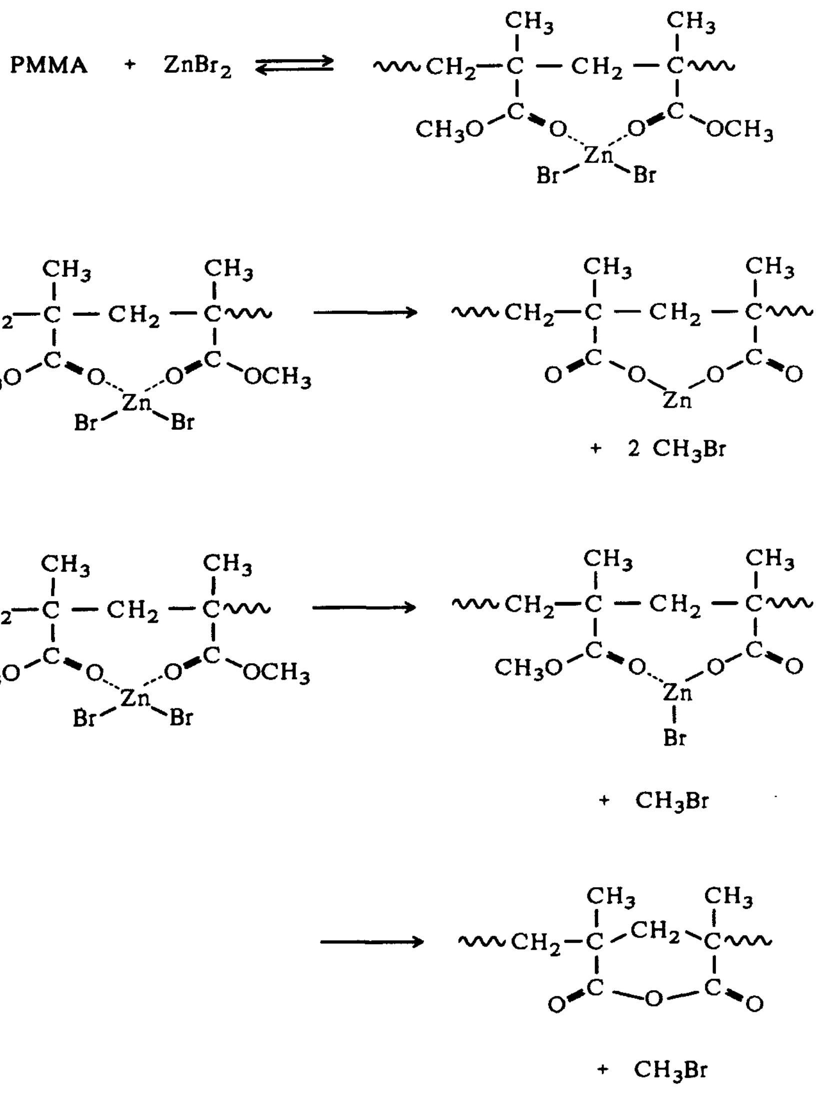
### PMMA with Other Additives

Additives which can act as sources of free radicals at relatively low temperatures have been found to induce decomposition to monomer in PMMA at lower temperatures than for the polymer alone. This behaviour has been observed in some polyblend systems,[21] but the present discussion is limited to low molecular weight additives.

Blends of PMMA with silver acetate have been found to give MMA in the temperature region of decomposition of silver acetate, the rate of monomer evolution being quite rapid at 200°C, whereas under similar programmed heating conditions, MMA begins to be evolved from the polymer a little below 300°C. This has been explained[22] in terms of migration of acetate radicals, intermediates in the formation of acetic acid from silver acetate, into the PMMA, where they abstract hydrogen atoms. This leads to chain scission according to Scheme V, producing the normal PMMA radical chain end which can depropagate in this temperature region. In this blend system, however, MMA monomer remains the sole product originating from the polymer.



SCHEME V



SCHEME VI

Metal acetylacetonates find use in some polymers as smoke suppressants; they have also found use as polymerisation initiators and have been reported to show pro- and antioxidant effects. The possible modification of the degradation behaviour in PMMA through complexing of the chelate with the ester side groups has been investigated in the cases of low concentrations of cobalt (III) acetylacetonate[23] and manganese (III) acetylacetonate.[14] Even very small concentrations of the acetylacetonate (acac) salt have a major effect on PMMA decomposition. The degradation behaviour is quite complex, but there are two main features. Thermal decomposition of the acac salt to give the corresponding bis-chelate and an acac radical leads to radical attack on the PMMA in the same way as in Scheme V, so

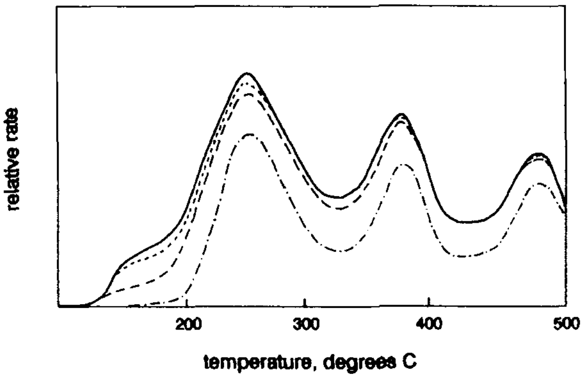


FIGURE 8 Differential condensation TVA data for a blend of PMMA and zinc bromide in 2:1 molar ratio of MMA units to zinc bromide. Continuous evacuation, heating rate 10°C/min. For key to differential condensation TVA traces, see Figure 3.

that low temperature evolution of monomer is observed. Complexing of the bischelate with the ester side groups, however, has a stabilising effect resulting from the formation of blocking groups for the unzipping reaction, including anhydride rings and metal carboxylate side groups. The main decomposition of the polymer is therefore shifted upwards in temperature region and some products other than monomer (which remains the main product at the acac concentrations employed), notably methanol and carbon dioxide, are observed.

Some Lewis acid additives have been shown to alter profoundly the pathway of PMMA decomposition, as a result of complex formation with the ester side group. The effect of zinc bromide has been studied in some detail.[25-27] Other additives which behave similarly are cobalt bromide,[25] and zinc chloride.[28,29] When zinc bromide is present, MMA yields are greatly reduced and methyl bromide appears as a volatile degradation product. The product composition depends on the ratio of PMMA to zinc bromide; even small amounts of zinc bromide have a major effect on the mechanism of decomposition, but at 2:1 molar ratio of MMA units to zinc bromide the major volatile products of heating to 500°C are carbon dioxide, carbon monoxide, methyl bromide and methanol. Seven other minor products were identified, one of these being MMA. The three main reactions involved in the degradation, shown in Scheme VI, result in the alteration of the normal degradation route of PMMA: a number of secondary and other reactions are responsible for the range of observed products.

The considerable adverse effect on the stability of the polymer is illustrated in Figure 8, which may be compared with the corresponding behaviour of the polymer alone in Figure 1b; the great difference in product composition is also apparent from the TVA traces. Even at much lower zinc bromide concentrations, the yield of MMA is much reduced because some methyl bromide is produced, and the salt and anhydride ring structures formed act as blocking groups for unzipping to monomer.

## CONCLUSIONS

The simple reverse polymerisation mechanism which operates when pure PMMA is thermally degraded and results in MMA as the sole decomposition product can be considerably modified when comonomer units are present in the PMMA chain, even in quite small amount. Various additives also can greatly influence the pattern of degradation. The biggest effects can be traced to (a) presence or formation of structures which interfere with the unzipping to monomer as blocking groups, reducing zip length (stabilisation), (b) radical sources inducing degradation to monomer at abnormally low temperatures (destabilisation), (c) intramolecular cyclisation (destabilisation, non-monomer products important) and (d) complex formation with the polymer (destabilisation, complex behaviour and range of products, sometimes with little monomer).

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