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Effect of additions of metals and their derivatives upon the thermal degradation of polymers

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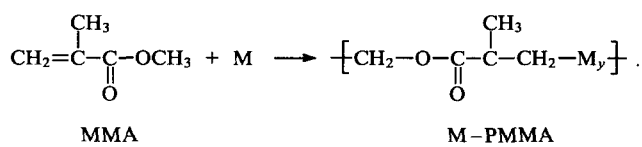
Abstract. The effect of additions of metals and of their halides and acetylacetonates on the thermal degradation of polymers [mainly, poly(methyl methacrylate)] has been studied by various physicochemical methods (thermogravimetry, NMR, IR, and UV spectroscopy, X-ray structural analysis, DSC, etc.). The results are analysed in terms of the use of these additives in polymers as ecologically clean retardants. The bibliography includes 40 references.

I. Introduction

The study of the pyrolysis of polymers with formation of gaseous combustible thermal degradation products is important from the point of view of the protection of polymer materials from contact with flames. Nonmetallic compounds containing chlorine, bromine, phosphorus, boron, and sulphur have previously been used[1,2] as additives in order to protect the polymers from combustion. The study of the effect of metals and their compounds on the thermal degradation of polymers was stimulated by the current search for retardants in which the currently used toxic additives[3,4] are replaced by other materials.

II. Effect of metals on the thermal degradation of polymers

Cardenas and Retamal[5] studied the effects of the metals Au, Cu, Ga, In, Ge, Sn, Sb, and Bi (when dispersed in methyl methacrylate MMA) on the polymers (PMMA) produced by the polymerisation of MMA in the presence of azo-isobutyronitrile. The following reaction was proposed[5–8] for the synthesis of polymers containing a metal previously dispersed in the monomer:



MMA M–PMMA

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The polymer samples contained only 2% of the metal; the molecular mass of the polymers was $(2.7-5) \times 10^5$ (see Ref. 8).

The thermogravimetric curves obtained in the study of the polymer samples are shown in Fig. 1. The temperatures of the onset of decomposition (T_d) of these polymers are given in Table 1. The highest T_d values are found for Au–PMMA and Bi–PMMA.

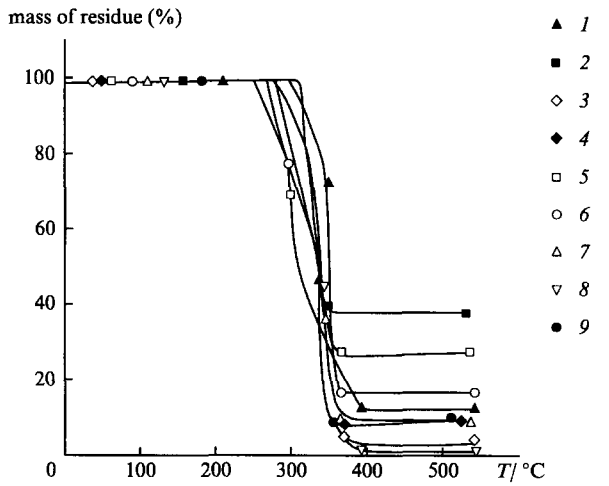


Figure 1. Thermogravimetric curves for the dissociation of M–PMMA compositions containing Bi (*1*), Sn (*2*), Au (*3*), Pd (*4*), Cu (*5*), Ge (*6*), Ga (*7*), In (*8*), and Sb (*9*) at a heating rate of 10 °C min^{-1}.

Table 1. Kinetic parameters for metal polymethacrylates.

Polymer	Z/s^{-1}	E_a/kJ mol^{-1}	T_d/°C
Au–PMMA	2.6×10^4	99.3	300
Bi–PÛÛÀ	2.3×10^2	78.9	325
In–PÛÛÀ	1.4×10^2	74.2	275
Cu–PÛÛÀ	2.4×10^2	70.6	240
Ge–PÛÛÀ	4.8×10^1	64.1	225
Sb–PÛÛÀ	2.5×10^1	63.9	275
Pd–PÛÛÀ	1.5×10^1	61.5	250
Sn–PÛÛÀ	1.4×10^1	61.0	250
Ga–PÛÛÀ	4.3	51.5	200

By analysis of the kinetic data on the loss of mass of the samples in an inert medium it was found that the metal polymers dissociate by a zero-order reaction whose activation energies (E_a) and pre-exponential factors (Z) are given in Table 1. It follows from these results that the activation energy depends on the nature of the metal. In particular, Au–PMMA is a very stable system, just as gold is stable towards oxidation. On the other hand gallium is an easily oxidised metal, and in the Ga–PMMA system we observe the lowest values of the activation energy and of the incipient decomposition temperature.

Systems containing rhodium and cobalt were studied in detail by Wilkie and coworkers,[9–12] who reported a continuing study of the effect of metals on the thermal degradation of polymers aimed at the possibility of using these compounds as retardants of the combustion of polymers.

The aim of this review is to discuss some other recently reported studies of the mechanism of the effect of metal compounds on the thermal degradation of polymers in the case of the halides of chromium and magnesium.

III. Thermal degradation of polymers in the presence of metal halides

Beer et al.[12] studied the effects of Cr(III) in anhydrous salts and crystal hydrates on the oxidation of PMMA. The prepared compositions of these materials were placed in glass tubes which were evacuated and sealed. The tubes were then heated for 2 h at predetermined temperatures. The IR spectra of the uncondensed reaction products detected 6% of methane and carbon monoxide from the starting material. The condensed gases amounted to 44% of the sample (mainly the monomer, CO_2, HCl, and water). The fraction soluble in chloroform was 13%. The IR spectra of this fraction showed the presence of carbonyl and carboxyl products.

In the pyrolysis of pure PMMA the products contain many oligomers, but if the reaction is carried out in the presence of $CrCl_3$ no oligomers are detected.

The fraction insoluble in chloroform contained 36% of the initial sample. The IR spectrum in this case suggests the presence of anhydrides with absorption bands at 1800, 1760, and 1150 cm^{-1}. An X-ray analysis of the solid residue showed the presence of CrOCl and CrO_3.

The chromium crystal hydrate $CrCl_3 \cdot 6H_2O$ is a mixture of the three isomers $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$, which behave in different ways during thermolysis.[13] At temperatures below 100 °C the first and the third isomer evolve only water, whereas the second isomer evolves only HCl. Since the sample of chromium chloride used in this work evolved both HCl and H_2O at temperatures below 100 °C it must have been a mixture of hydrated isomers. Between 200 and 300 °C all these isomers form chromium hydroxide chloride $Cr(OH)Cl_2$. At higher temperatures chromium oxide chloride CrOCl is formed. At these high temperatures the anhydrous chromium chloride $CrCl_3$ can lose a chlorine atom and give the chloride $CrCl_2$ (see Gmelin's Handbook[14]). It follows that the system contains several chemical compounds of chromium, and it is difficult to establish which of these actively influences the degradation of the polymer.

The results of a thermogravimetric analysis[12] of a mixture of PMMA and $CrCl_3 \cdot 6H_2O$ (taken in a mass ratio of 1 : 1) are shown in Fig. 2. As can be seen, the decomposition of the polymer becomes marked at ~250 °C, above which the rate of the reaction increases rapidly, though 22% of the sample is lost below it. The reaction products include water, HCl, and the monomer. Water and HCl are formed by the thermolysis of aqueous $CrCl_3$: anhydrous $CrCl_3$ produces only HCl, and the monomer is formed by the depolymerisation of the PMMA.

Most of the mass (62%) is lost between 250 and 500 °C. In this case the volatile products include the monomer, carbon oxides, an unidentified organic acid, and traces of methane. The monomer is

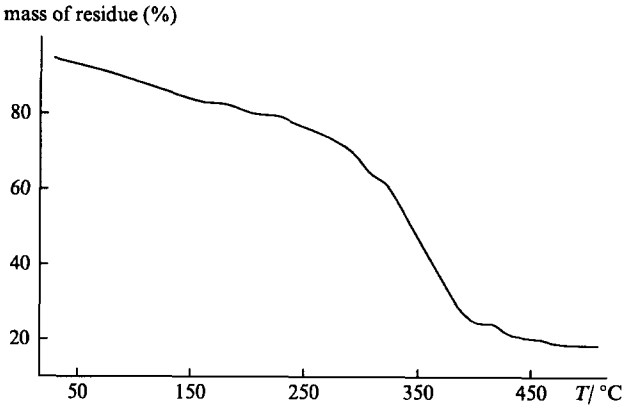


Figure 2. Thermogravimetric curve for a 1 : 1 mixture of aqueous $CrCl_3$: PMMA at a heating rate of 20 °C min^{-1}.

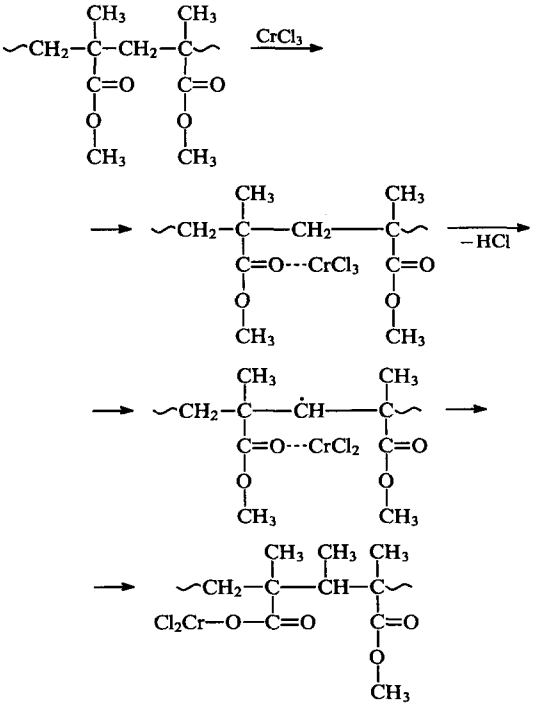
the main product of the decomposition at 430 °C. Above this temperature the relative amount of monomer decreases, and the amount of carbon oxides and of the organic acid increases.

In the decomposition of mixtures containing aqueous chromium salts evolution of HCl takes place at 150 °C as a result of the decomposition of aqueous $CrCl_3$, and again at temperatures above 450 °C. In compositions containing anhydrous chromium chloride HCl begins to be evolved at 430 °C and continues to be formed up to 500 °C.

The solid residue beyond 500 °C contains 16% of the initial mass of the sample. However, if the whole of the water had been evolved from the hydrated $CrCl_3$ and the whole of the PMMA had depolymerised the fraction of $CrCl_3$ in the solid residue would have been 30% of the initial mass of the sample, and if $CrCl_2$ and CrOCl had been formed the solid residue would have been 23% and 20% respectively. The finding that, in reality, the solid residue amounts to 16% shows that none of these compounds can be (in the pure form) the final product of the reaction.

These results have been explained[12] in terms of Scheme 1. Most probably the $CrCl_3$ is coordinated at the carbonyl group of PMMA. This postulate has been confirmed independently.[15–17]

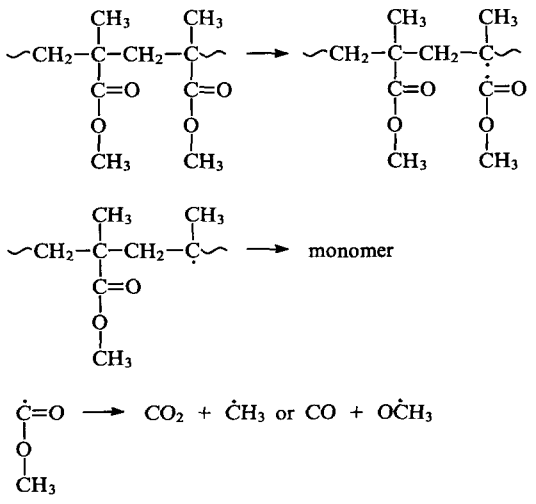
Scheme 1



We know that $CrCl_3$, when heated, splits off a chlorine atom [14] which then removes a hydrogen from the main chain of the PMMA, forming a polymeric radical. This scheme is confirmed by the presence of HCl among the reaction products.

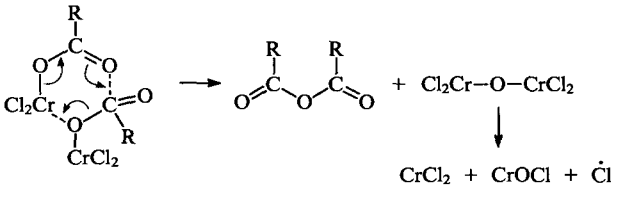
Manring and coworkers [18–21] have attributed the presence of CO, CO_2, and CH_4 among the decomposition products of PMMA to the removal of carbomethoxy groups from the main chain of the polymer, accompanied by the formation of an unstable carbomethoxy radical which then decomposes, giving CO and $CH_3\dot{O}$ or CO_2 and $\dot{C}H_3$ (Scheme 2).

Scheme 2



Scheme 2 is confirmed by the detection by NMR of unsaturated oligomers among the reaction products. All the gaseous products are also formed by Scheme 2. The presence among the solid products of chromium anhydride and chromium oxides is ascribed to processes described by Scheme 3. The atomic chlorine removes a hydrogen atom from the PMMA chain, generating polymeric radicals which can decompose or become cross-linked.

Scheme 3



Thus in the pyrolysis of compositions consisting of chromium chloride and PMMA the most important reactions are: (1) the coordination of the chromium chloride at the carbonyl group of PMMA with subsequent elimination of a chlorine atom; (2) the removal by the chlorine atom of a hydrogen atom from the PMMA; (3) the corresponding migration of the methyl ether to the main chain of the PMMA, leading to the formation of a chromium carboxylate salt; (4) the dissociation of this salt to the anhydrides; (5) the stabilisation of the polymer by the chromium carboxylate or through the cross-linking of the polymeric radicals formed in the preceding stage. The interaction of the chromium chloride with the PMMA does not affect the formation of the monomer, and therefore it seems unlikely that $CrCl_3$ may act as an inflammation retarder.

Wilkie et al. [22] studied the thermal degradation of PMMA–$MnCl_2$ (anhydrous) mixtures by standard methods. The more volatile reaction products contained carbon monoxide and traces of methane. The condensable gas consisted of carbon dioxide, the monomer, and traces of methyl chloride and methanol. The IR spectrum of the fraction soluble in chloroform [23] showed the presence of ether and an anhydride. The insoluble products were washed free from $MnCl_2$ with methanol, which left a fraction consisting of MnO_2 and an organic salt. It should be noted that the proportion of the monomer in the thermal degradation products of PMMA in the presence of anhydrous $MnCl_2$ decreases as compared with pure PMMA, and depends on the method of preparation of the system. [24] Thus, in samples prepared by simple mixing of PMMA and $MnCl_2$ the yield of monomer after vacuum heat treatment (400 °C, 2 h) was 30%–35%, whereas pure PMMA under the same conditions produced 50%–70% of the monomer. With compositions prepared from solutions of $MnCl_2$ and PMMA in an acetone–methanol mixture, followed by removal of the solvents, thermal decomposition does not usually produce any monomer.

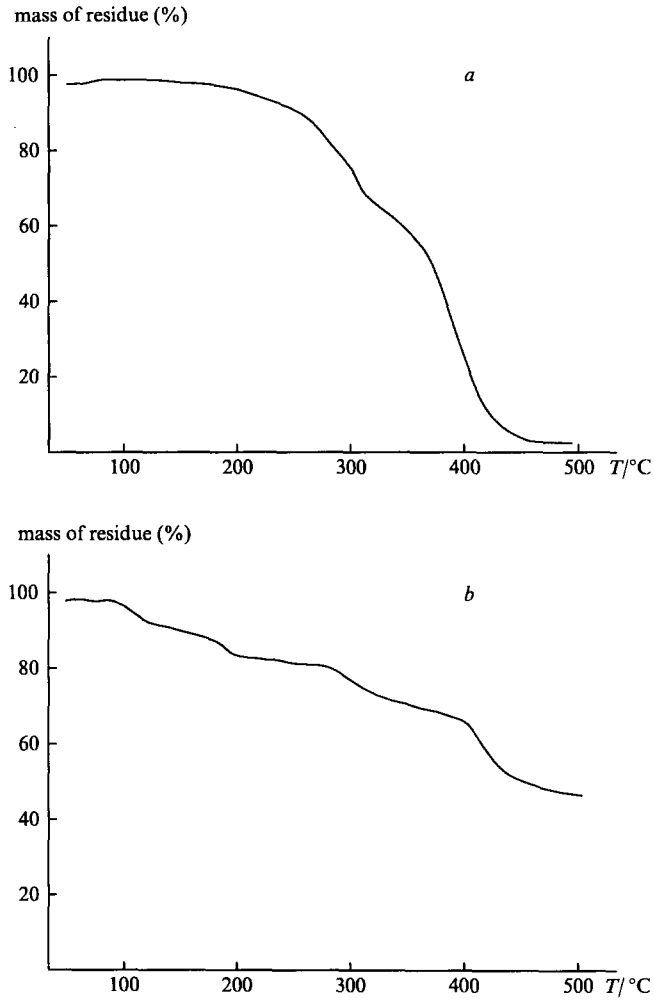


Figure 3. Thermogravimetric curves: (*a*) PMMA, (*b*) PMMA : $MnCl_2$ (1 : 1); heating rate 20 °C min^{-1}.

The molecular mass of the fraction dissolved in chloroform was 10% of that of the initial polymer. [25] It follows that the greater part of the polymer decomposes to the monomer, and the latter repolymerises with formation of a low-molecular oligomer; this reoligomerisation is probably catalysed by $MnCl_2$. By using thermogravimetric analysis methods it was confirmed that the monomer is formed and then slowly consumed. The TGA curves of $MnCl_2$–PMMA mixtures prepared from solutions are shown in Fig. 3. It can be seen from Fig. 3*b* that the breakdown of this composition is characterised by five temperature regions.

Between 100 and 145 °C 7.5% of the composition is gasified. The Fourier transform IR spectra of the gaseous products show that this loss is mainly water introduced into the system with the salt and easily removed. A further 9.5% of the composition is gasified between 145 and 215 °C: the IR spectra show that in this regime the monomer is evolved. In the case of pure PMMA the evolution of the monomer begins at higher temperatures.

The third plateau of the weight-loss curve is found at 215 to 345 °C. It is characterised by the evolution of the monomer and by the formation of methyl chloride and methanol. The formation of methyl chloride is evidence of the interaction between $MnCl_2$ and PMMA, involving the ester group of the latter.

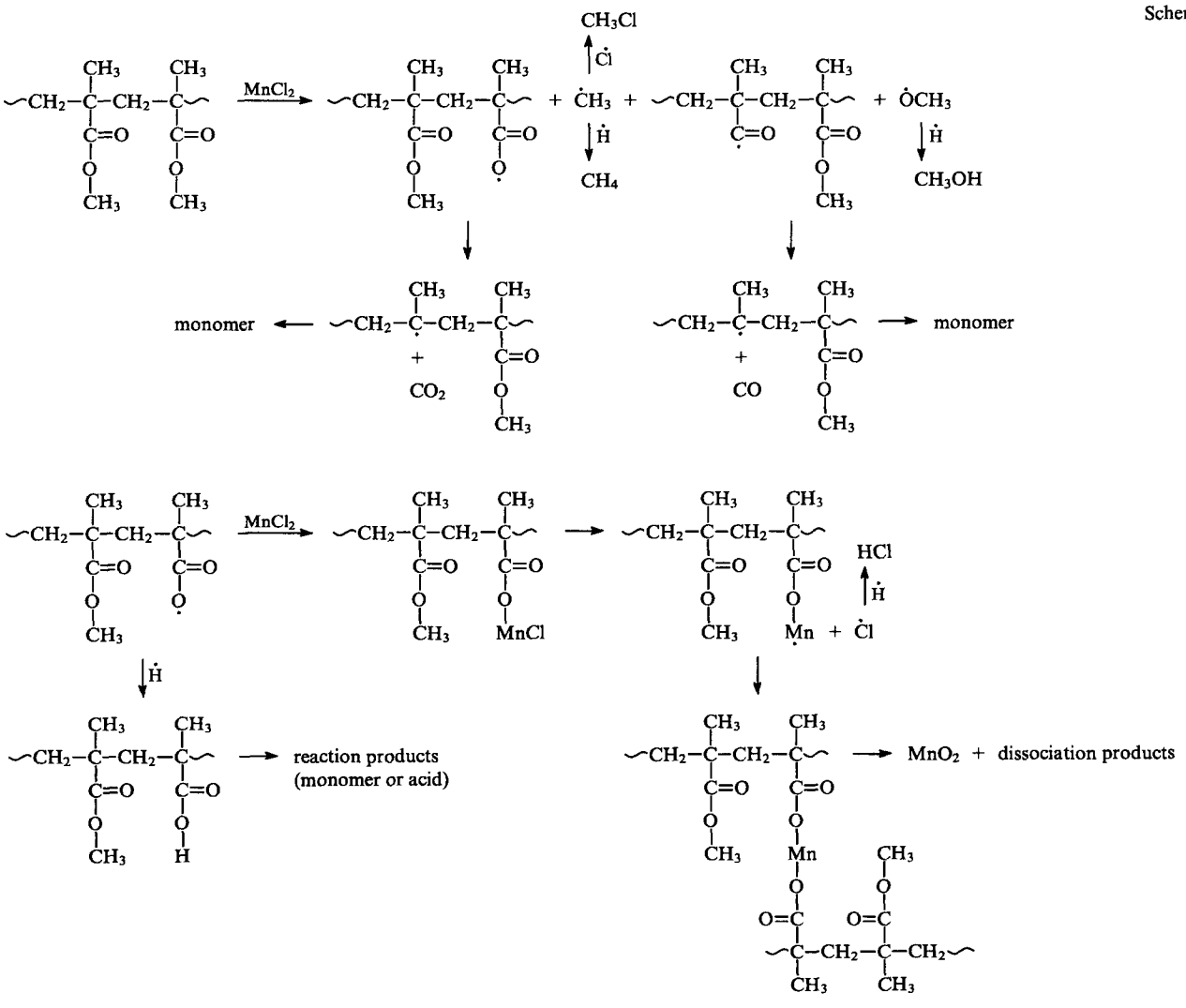
A further 19% of the composition is dissociated between 345 and 455 °C. CO_2, CO, CH_4, HCl, and an aliphatic acid were identified among the gaseous products.

A further 5% of the composition is decomposed in the region of 455–600 °C with formation of HCl.

The overall result is that up to 600 °C 51.5% of the composition is gasified, leaving a 48.5% residue of involatile products. Since the ratio of PMMA to $MnCl_2$ in the initial composition is 1:1 it might be thought that the whole of the PMMA is gasified and the residue consists of $MnCl_2$. However, an analysis of the thermal degradation products does not confirm this assumption: firstly, because the IR spectrum of the solid residue shows the presence of organic substances (hydrocarbon and carbonyl groups), and secondly because the solid residue is found to contain a new, insoluble organomanganese compound in addition to $MnCl_2$.

Wilkie et al.[22] proposed the following scheme to account for the degradation of the PMMA–$MnCl_2$ compositions (Scheme 4). The manganese chloride initiates the breaking of the carbonyl bonds in PMMA, giving methoxy and methyl radicals. These radicals can abstract a proton, giving methanol and methane respectively. The methyl radical can also recombine with a chlorine radical, forming methyl chloride. The carbonyl radical can be further converted into carbon monoxide and a tertiary radical, and the carboxyl radical can produce carbon dioxide and the same tertiary radical. These tertiary radicals initiate the decomposition of PMMA with preferential formation of the monomer and other low-molecular products. Since the decomposition products contain more CO_2 than CO it follows that the methyl radicals are consumed faster than the methoxy radicals. The carboxyl radical can react in various directions. Firstly it can interact with $MnCl_2$, giving MnCl and Cl˙. The latter can recombine with any other radical, giving different products. Methyl chloride mentioned above is one of these products; the manganese chloride salt of PMMA can split off a chlorine radical and form a manganese radical attached to the PMMA chain. The recombination of this radical with the carboxyl radical gives the manganese monomer of PMMA. This monomer can dissociate thermally, giving MnO_2 and other products. This reaction also produces an aliphatic acid, which can also be formed during the abstraction of hydrogen by a carboxylic radical, followed by depolymerisation, to give monomeric methacrylic acid and other dissociation products.

Scheme 4



The limiting oxygen index (OI) for the PMMA – $MnCl_2$ system shows that manganese chloride has some flame-retardant properties.[26] Thus, as compared with pure PMMA, whose OI is 14, the OI of a PMMA – $MnCl_2$ composition (1 : 1 ratio) increases to 25. This increase in the OI is convincing evidence of the effectiveness of $MnCl_2$ as an additive.

These results differ from those reported by McNeill and McGuiness[15,16] for the $ZnBr_2$ – PMMA system. The gaseous products are the same for the two systems, but different reaction paths were proposed in the two cases. Whereas in the presence of $ZnBr_2$, methyl bromide appears at 160 °C, in the $MnCl_2$ system methyl chloride is formed at temperatures above 220 °C; furthermore, in the $MnCl_2$ system the monomer appears at temperatures well below those observed in pure PMMA. In both cases the reaction product is the metal salt of methacrylic acid.

When the common features of these two reactions are examined it seems very likely that all the main processes are the same in the two cases. Wilkie et al.[22] conclude that $MnCl_2$ plays a dual role in the system. On the one hand it accelerates the initial depolymerisation of PMMA, and thus assists its combustion, but on the other hand it also markedly increases the amount of incombustible reaction products.

Kochneva et al.[27] studied the effect of $ZnCl_2$ on the thermal stability of polymethacrylates and polyacrylates. These polymers were found to decompose by different mechanisms. The polymethacrylates are almost completely depolymerised, whereas the polyacrylates are degraded by breakdown of the ester groups.

The loss of mass of PMMA and polymethacrylate (PMA) after 2 h at 300 °C in a vacuum is shown in Fig. 4 as a function of the concentration of $ZnCl_2$. Increasing the concentration of $ZnCl_2$ lowers the degree of decomposition for PMMA (curve *1*) and increases it for PMA (curve *2*). The decomposition products of these polymers in the presence of $ZnCl_2$ are listed in Tables 2 – 5.[27]

In the decomposition of PMMA in the presence of $ZnCl_2$ the yield of monomer decreases, which suggests a depolymerisation process, whereas the yields of alcohol, of chain breakdown products, and of CO_2 increase (Table 2). Similar effects have been observed in poly(n-butyl methacrylate) (PBMA) (Table 3).

In the thermal degradation of PMA (Table 4) the yields of alcohol and CO_2 rapidly increase after even small additions of $ZnCl_2$. A similar effect is found in poly(n-butyl acrylate) (PBA) (Table 5).

Alkyl chlorides were determined qualitatively in the thermal degradation products of the polymethacrylic and the polyacrylic ester in the presence of $ZnCl_2$. On the basis of these results Kochneva et al.[27] suggested that CH_3Cl is formed mainly by the reaction of $ZnCl_2$ with the carbonyl group of the ester.

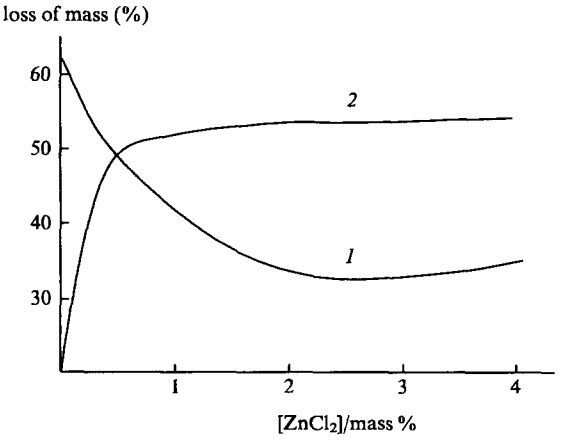


Figure 4. Mass loss curves for PMMA and PMA as a function of concentration of $ZnCl_2$. (*1*) PMMA, (*2*) PMA.

Table 2. Main products of the thermal degradation of PMMA in the presence of $ZnCl_2$ (mass % of the initial mass of polymer).

Products and degree of thermal degradation	[$ZnCl_2$] / mass %				
	0	0.05	0.5	2	10
Degree of degradation	60.7	55.6	44.8	30.0	25.0
Solid residue	39.3	44.4	55.2	70.0	75.0
MMA	60.2	54.0	43.0	25.3	11.5
CH_3OH	0.40	0.34	0.40	0.90	2.60
H_2O	0	0	0	0	3.10
CH_3Cl	0	0.03	0.28	1.29	2.64
CO_2	0	0.12	0.15	0.25	0.20
Other products (CO, CH_4, C_3H_6)	0	0.020	0.03	0.11	1.14

Table 3. Main products of the thermal degradation of PBMA in the presence of $ZnCl_2$ (mass % of the initial mass of polymer).

Products and degree of thermal degradation	[$ZnCl_2$] / mass %		
	0	0.5	2
Degree of degradation	56.5	58.0	33.0
Solid residue	43.5	42.0	67.0
BMA	49.0	43.5	23.0
n-C_4H_9OH	4.0	7.5	6.4
H_2O	0.25	0.39	0.60
CO_2	0.17	0.24	0.20
C_4H_9Cl	0	0.14	0.35
C_4H_8	1.0	0.9	0.6
Other products (H_2, CH_4, C_3H_6, CO)	0.1	0.9	0.6

Table 4. Main products of the thermal degradation of PMA in the presence of $ZnCl_2$ (mass % of initial mass of polymer).

Products and degree of thermal degradation	[$ZnCl_2$] / mass %				
	0	0.05	0.5	2	10
Degree of degradation	15.6	32.0	47.0	43.5	49.0
Solid residue	84.4	68.0	53.0	56.5	51.0
CH_3OH	2.6	13.6	20.4	16.6	17.6
MMA	Trace	0.2	0.3	0.3	0.4
H_2O	0.1	0.2	0.3	0.35	1.0
CO_2	0.3	1.1	5.0	7.0	7.7
CH_3Cl	0	0.04	0.3	1.1	5.1
Other products (H_2, CH_4, CO)	0	Trace	0.3	0.4	1.1

Table 5. Main products of the thermal degradation of PBA in the presence of $ZnCl_2$ (mass % of the initial mass of polymer).

Products and degree of thermal degradation	[$ZnCl_2$] / mass %			
	0	0.05	0.5	2
Degree of degradation	21.8	14.3	20.6	20.2
Solid residue	78.2	85.7	79.4	79.8
n-C_4H_9OH	9.0	10.0	16.0	15.5
H_2O 0.4	0.2	0.3	0.5	
BMA	Trace	Trace	Trace	Trace
CO_2	0.8	0.8	0.8	1.2
C_4H_8	1.4	1.3	1.0	1.5
C_4H_9Cl	0	Trace	0.1	0.3
Other products (H_2, CH_4, CO)	0.1	0.1	0.1	0.2

Table 6. Formation of alkyl chlorides (mass %) as a function of the concentration of $ZnCl_2$ during the thermal degradation of polymethacrylates and polyacrylates (300 °C, vacuum, 2 h).

$[ZnCl_2]$/ mass %	CH_3Cl		C_4H_9Cl	
	PMMA	PMA	PBMA	PBA
0.05	0.03	0.04	0.03	0.03
0.5	0.3	0.4	0.1	0.1
2	1.3	1.2	0.4	0.3
10	2.6	5.1	–	–

Table 6 shows the effect of the concentration of $ZnCl_2$ on the yield of alkyl chlorides during the thermal breakdown of polymethacrylates and polyacrylates after 2 h at 300 °C *in vacuo*.

It follows from the data in Table 6 that the rate of formation of alkyl chlorides decreases with increasing length of the hydrocarbon radical in the ester group. Zinc chloride has similar effects on the formation of the insoluble fraction in the thermal degradation of PMMA and PMA, and therefore the authors suggest that reticular cross-linking of the polymer takes place mainly through the interaction of the ester groups with $ZnCl_2$. The contribution of this reaction is not large, but it is neverthe-less significant in compositions including large quantities of zinc chloride.

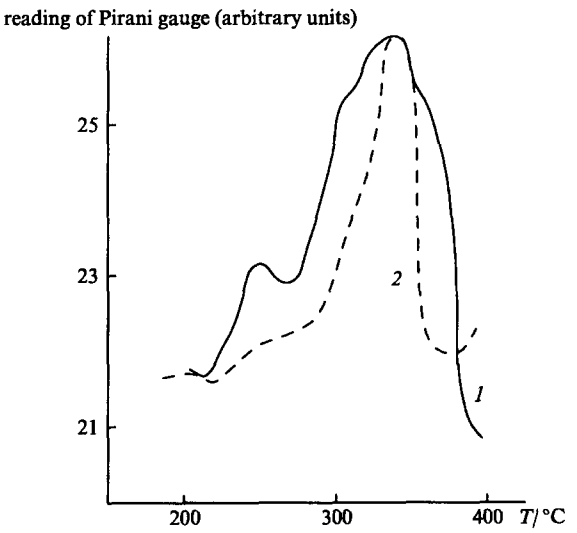
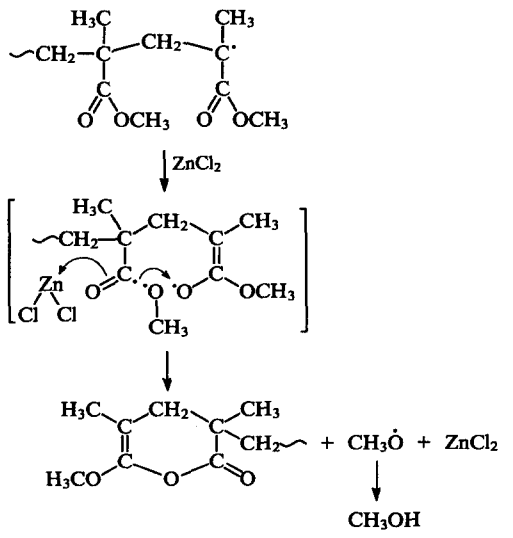


Figure 5. Thermovolumetric curves: (*1*) PMMA; (*2*) PMMA + 2 mass % $ZnCl_2$.

Scheme 5



A thermovolumetric analysis [28] of the thermal degradation of PMMA showed that $ZnCl_2$ when present in the system suppresses the formation of the monomer by removing the unsaturated end groups (note the disappearance of the characteristic monomer peak at 250 °C in Fig. 5).

The formation of a complex between $ZnCl_2$ and the end groups of the macroradicals leads to the evolution of alcohol and inhibits the depolymerisation. This process is described [27] by Scheme 5.

The IR spectrum of samples of PMMA dissociating in the presence of $ZnCl_2$ includes an absorption band at 1760 cm^{-1} corresponding to γ,δ-unsaturated lactones.

IV. Effect of metal acetylacetonates on the thermal degradation of polymers

Metal acetylacetonates are of interest because they are used as polymerisation indicators, accelerators, and antioxidants for polyolefins. As a result it has been suggested [29–33] that these compounds could act as flame retardants and suppress the formation of smoke in various polymers.

McNeill and Liggat [34] studied the effect of cobalt(III) acetylacetonate on the thermal degradation of PMMA, and concluded that this effect is responsible for the formation of an acetylacetonato complex of cobalt with the ester groups of PMMA.

Very different compositions were studied: from 1 part of $Co(acac)_3$ per 400 monomer units to 1 part per 10 monomer units.

The thermal degradation was studied by the thermovolumetric analysis method, [35, 36] which allows four fractions of products to be studied: (1) uncondensable gases, (2) condensable gases and volatile liquids, (3) solid fractions (resins, waxes, etc.), (4) the residue at any stage in the decomposition.

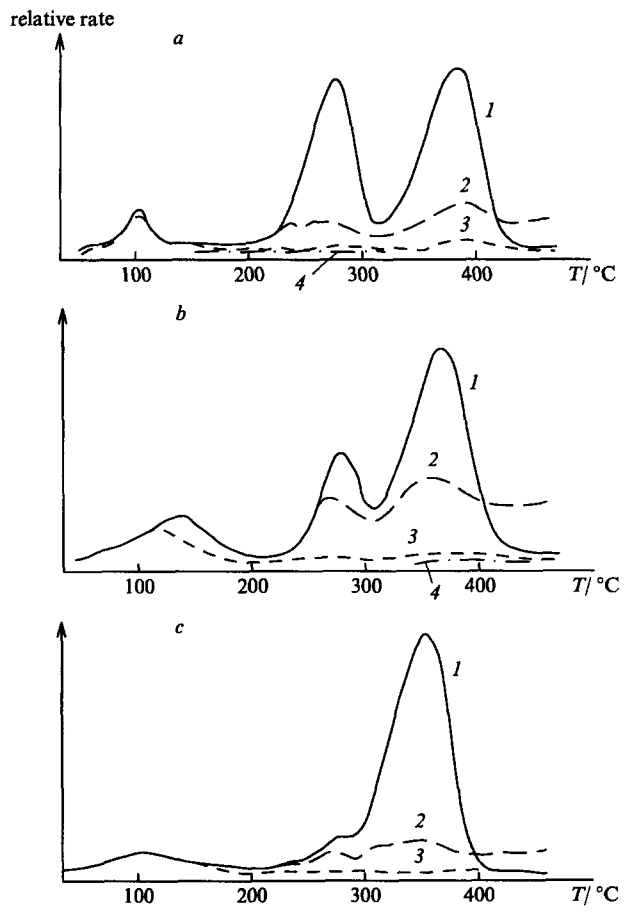
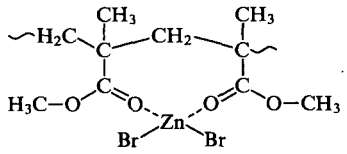


Figure 6. Thermovolumetric curves (vacuum, 10 °C min^{-1}). $\overline{M}_n$ = 2 × 10^4 (*a*), 1.5 × 10^5 (*b*), 10^6 (*c*); *T*/°C = 0 (*1*), 75 (*2*), 100 (*3*), 196 (*4*).

Fig. 6 shows the thermovolumetric curves for PMMA samples of different molecular mass: we observe two peaks, corresponding to two stages in the decomposition (initiation at the end groups and random initiation respectively).

The rate of degradation of PMMA is strongly influenced by the presence of complexing agents such as metal halides or acetylacetonates. For example, in the presence of $ZnBr_2$ the main decomposition products are methyl bromide and methanol, and the yield of monomer is negligibly small.[37,38] This is due to the formation of a complex having the following structure:



It could be expected that stable metal acetates will interact with the ester groups of PMMA, and that this process will be reflected in the stability and dissociation mechanism of the polymer.

The thermal degradation of $Co(acac)_3$ at 210 °C takes place by the scheme

$$Co(acac)_3 \longrightarrow Co(acac)_2 + acac^{\cdot};$$

$$acac^{\cdot} \xrightarrow{H^+} Hacac.$$

The UV spectra of PMMA films with additions of $Co(acac)_3$ show that in this case the $Co(acac)_3$ does not contribute to complex formation with the PMMA at the ester groups, whereas the UV spectra of PMMA films with additions of $Co(acac)_2$ indicate the formation of these complexes.

It follows that during the degradation of the composition $Co(acac)_3$–PMMA the $Co(acac)_3$ first changes into $Co(acac)_2$, which then forms a complex with the PMMA.

The four stages in the breakdown of the composition $Co(acac)_3$–PMMA are shown diagrammatically in Fig. 7.[34]

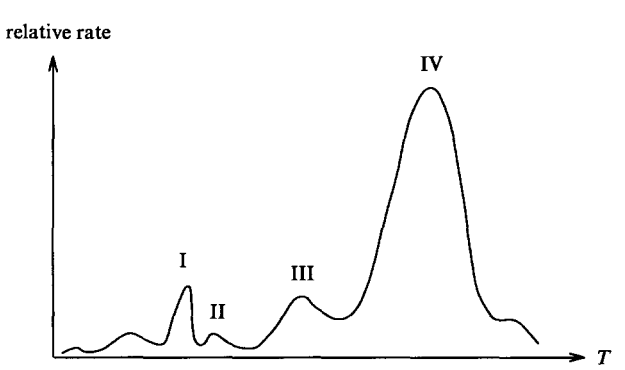


Figure 7. Schematic diagram of the decomposition of a $Co(acac)_3$–PMMA mixture, based on an analysis of the thermovolumetric curves.

Stage I: $T_{max} \approx 135$ °C. The height of the peak is inversely proportional to the molecular mass of the polymer, and is independent of the concentration of $Co(acac)_3$. The main decomposition product in this stage is the monomer. It is assumed that depolymerisation initiated at the ends of the molecule takes place in stage I, so that the $Co(acac)_3$ forms a complex with the unsaturated end groups (on average, one unsaturated end group per 400 monomer units in a sample of low molecular mass).

Stage II: $T_{max} \approx 190$ °C. The height of the peak is proportional to the molecular mass of the polymer and to the concentration of $Co(acac)_3$. The only exceptions to this rule are samples with a high molecular mass of the polymer and a high concentration of $Co(acac)_3$. The main decomposition product in this stage (as in the previous stage) is the monomer. In addition, gaseous acetylacetone and methanol are formed towards the end of stage II (above 200 °C). At high concentrations of $Co(acac)_3$ traces of an uncondensable gas are formed. The authors note that in this stage the chain length for the reaction is greater.

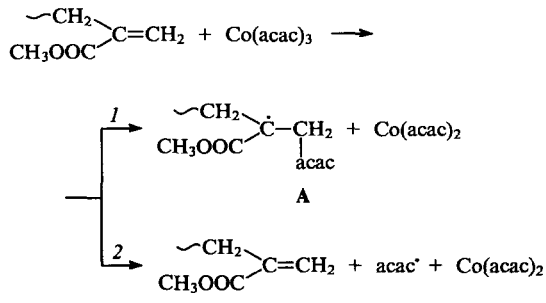
Stage III: $T_{max} \approx 270$ °C. The height of the peak decreases in all the compositions with respect to the peak height for pure PMMA, irrespective of the concentration of $Co(acac)_3$. As a rule the monomer is formed in this stage. The main process is depolymerisation, initiated at the end groups. Unsaturated end groups are nevertheless present, or can be formed in stage I. The chain length of the reaction decreases.

Stage IV: $T_{max} = 360-380$ °C. This peak is characterised by the formation of uncondensable gases. The authors attribute this to a decrease in the length of the reaction chain and to the development of new reactions accompanying the depolymerisation reaction. In addition to the monomer the following gaseous products are formed towards the end of this stage: acetylacetone, methanol, carbon oxides, keten, methyl acetate, acyclic anhydride, isobutene (traces), and dimethyl ether (traces).

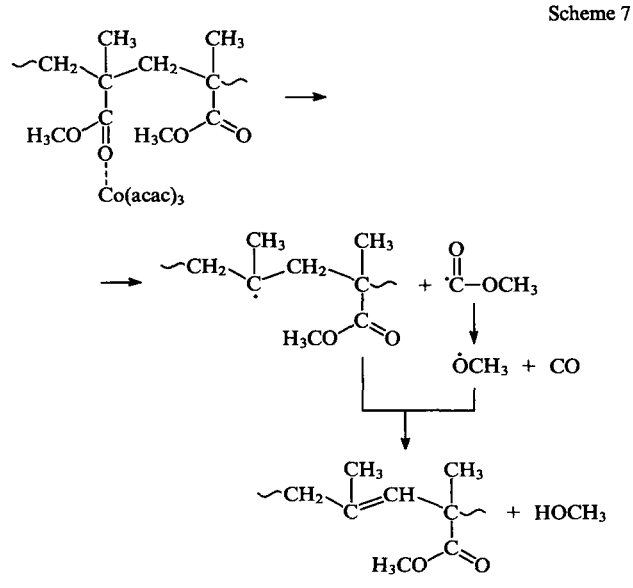
The IR and UV spectra of films of PMMA compositions containing $Co(acac)_3$, heat treated at temperatures up to 500 °C, have also been studied. The results were used to produce the following interpretation of the dissociation mechanism of these compositions.

1. At low temperatures (100 °C) the monomer is thought to be formed by the dissociation of the complex between $Co(acac)_3$ and the unsaturated end groups in the polymer (Scheme 6).

Scheme 6



Scheme 7



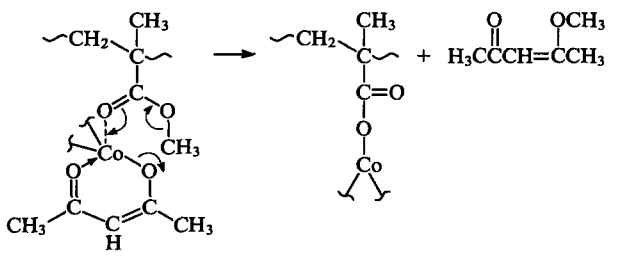
In the depolymerisation of the radical A by path *1* not all the unsaturated end groups can be removed when the part of the chain being broken down in the polymer molecule is shorter than the same molecule (a short length of the part being broken down probably corresponds to temperatures close to the glass transition temperature of the polymer).

During depolymerisation by path *2* the unsaturated end groups are not used, and the depolymerisation is initiated by attack on the chain by the acac radical.

2. The thermal degradation of $Co(acac)_3$ produces $Co(acac)_2$ and acac radicals. Complex formation of $Co(acac)_2$ with the ester groups accelerates the reactions of these groups and the formation of CH_3OH, CO, and double bonds in the main chain of the polymer (Scheme 7).

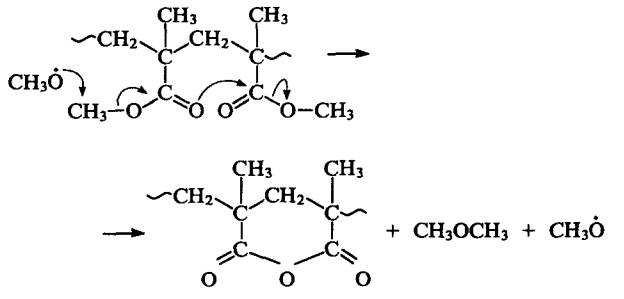
The complex can also decompose to a cobalt carboxylate structure (Scheme 8).

Scheme 8



3. The CH_3O radicals can also attack some ester groups, forming anhydride rings (Scheme 9).

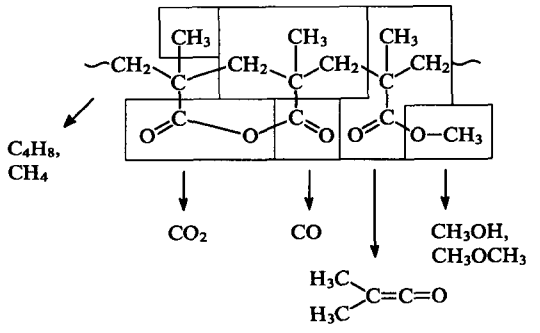
Scheme 9



4. The presence of these rings in the chain decreases the chain length and stabilises the polymer in the high-temperature region.

5. The fragmentation of the modified polymer structures gives mainly monomers, and small quantities of other products characteristic of these structures (Scheme 10).

Scheme 10



McNeill and Liggat[39] carried out a similar study for the PMMA–$Mn(acac)_3$ system, using the procedure of Wilkie et al.[22] The DSC curve for $Mn(acac)_3$ (Fig. 8) shows a characteristic combination of endothermic and exothermic peaks at 170, 175, and 257, 260 °C. The peaks at 170 and 175 °C are assigned to the homolytic breaking of the single bond between the ligand and Mn in $Mn(acac)_3$, with formation of acetylacetone and the bischelate,[40] whereas the peaks at 257 and 260 °C (and at higher temperatures) correspond to the breakdown of the bischelate.

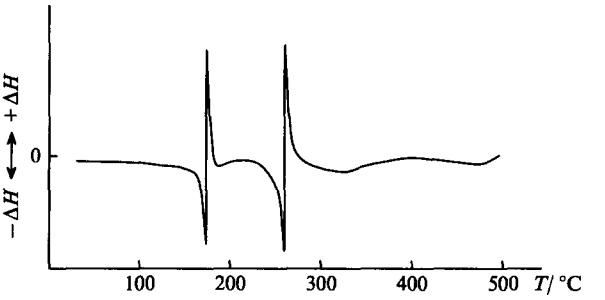


Figure 8. DSC curve for $Mn(acac)_3$ (nitrogen, 10 K min^{-1}).

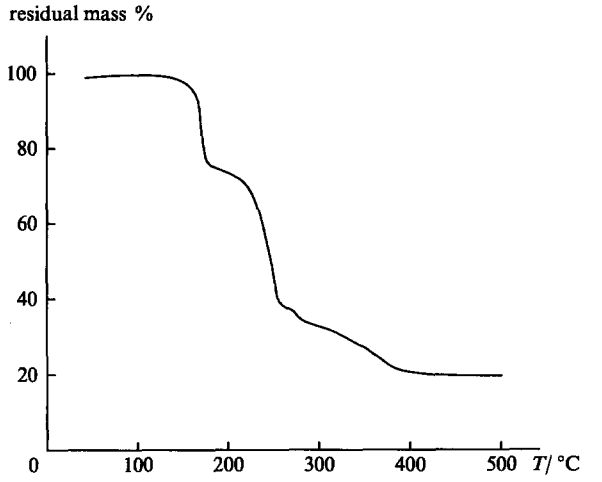
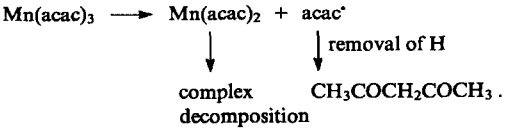


Figure 9. Thermogravimetric curve for $Mn(acac)_3$ (rate of decomposition 10 K min^{-1}).

The data from the thermogravimetric curve (Fig. 9) are fully consistent with the above conclusions, since the initial weight loss (24%) corresponds to the removal of one acac group. The next loss of mass has a more complex explanation: it is assumed that radicals can be formed in this stage, and that the final reaction product is the metal oxide. Hence the thermal degradation of $Mn(acac)_3$ can be represented as follows:



This mechanism is similar to the mechanism of the dissociation of $Co(acac)_3$, and therefore it was assumed that the thermal degradation of the PMMA system with a Mn(III) salt has a similar nature.

Table 7. Comparison of the thermal stability of PMMA and of its compositions with $Mn(acac)_3$.

	PMMA of high molecular mass			PMMA of intermediate molecular mass		
	PMMA	50:1 [a]	10:1 [a]	PMMA	50:1 [a]	10:1 [a]
T_d/ °C	210	130	125	220	130	130
T_{max} of the main decomposition / °C	350	365	400	360	365	400

[a] Number of monomer units per molecule of $Mn(acac)_3$.

In Table 7 we show results on the thermal stability of PMMA – $Mn(acac)_3$ compositions. It can be seen that pure PMMA is not gasified at temperatures up to 210 °C when heated at 10 °C min^{-1}. In the compositions with $Mn(acac)_3$ the decomposition of PMMA begins at 125 °C. The data in Table 7 show that although under these conditions the temperature of the onset of degradation in PMMA is lowered, the onset of the main process is moved to higher temperatures. From this point of view $Mn(acac)_3$ behaves like $Co(acac)_3$ in compositions with PMMA.

The dissociation diagram as a function of temperature for the composition PMMA – $Mn(acac)_3$ is shown schematically in Fig. 10. Three main dissociation stages can be identified. In stage I two overlapping processes at 150 – 160 °C are associated with the formation of acetylacetone and a small quantity of the monomer. These products are formed through the dissociation of $Mn(acac)_3$, initiated by the depolymerisation of the polymer produced by attack from the acac radicals and by the corresponding rupture of the chain with formation of a macroradical which can disproportionate as far as the monomer.

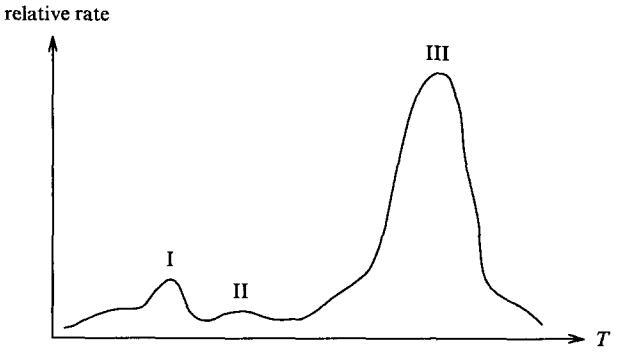


Figure 10. Schematic decomposition diagram for a $Mn(acac)_3$ – PMMA mixture.

In stage II acetone and carbon dioxide are formed. This process is ascribed to the breakdown of the $Mn(acac)_2$ produced in the preceding phase. The breakdown of the complex at the bond between $Mn(acac)_2$ and the ester side groups is accompanied by the formation of carboxylate structures which suppress the breaking of the PMMA chain in stage III.

The mechanism of the processes taking place during the thermal degradation of the PMMA – $Mn(acac)_3$ system has been treated like the corresponding mechanism for the PMMA – $Co(acac)_3$ system, discussed in detail in this review. It is stressed that the ability of $Mn(acac)_3$ to form complexes at the ester groups is not reflected, in general, by the mechanism of the thermal degradation processes of the system. This conclusion is again confirmed by the important role played by $Co(acac)_2$ and $Mn(acac)_2$ in the thermal degradation of PMMA compositions containing these salts.

References

1. C F Cullis, M M Hirschler *The Combustion of Organic Polymers* (Oxford: Oxford University Press, 1981)
2. M M Hirschler, in *Developments in Polymer Stabilisation* Vol. 5 (Ed. G Scott) (London: Applied Science Publishers, 1981) p. 107
3. R M Aseeva, G E Zaikov *Makromol. Chem. Makromol. Symp.* **74** 335 (1993)
4. R M Aseeva, G E Zaikov *Combustion of Polymer Materials* (New York: Hanser, 1981)
5. G-T Cardenas, C-C Retamal *Thermochim. Acta* **176** 233 (1991)
6. G-T Cardenas, K Klabunde, E Dale *Langmuir* **3** 986 (1987)
7. G-T Cardenas, K Klabunde, E Dale *Proc. Opt. Eng., SPEI* **821** 206 (1987)
8. G-T Cardenas, C-C Retamal *XVIII Jornadas Chilenas de Quimica, Nov. 1989*. Santiago (Chile) p. 350
9. S J Sirdesai, C A Wilkie *J. Appl. Polym. Sci.* **37** 863 (1989)
10. S J Sirdesai, C A Wilkie *J. Appl. Polym. Sci.* **37** 1595 (1989)
11. C A Wilkie, S J Sirdesai, T Suebsaeng, P Chang *Fire Safety J.* **15** 297 (1989)
12. R S Beer, C A Wilkie, M L Mittleman *J. Appl. Polym. Sci.* **46** 1095 (1992)
13. D Kiraly, K Zalatnai, M T Beck *J. Inorg. Nucl. Chem.* **11** 1 (1959)
14. L Gmelin, in *Gmelins Handbuch der Anorganischen Chemie* (Berlin: Verlag Chemie, 1962) p. 208
15. I C McNeill, R C McGuiness *Polym. Degrad. Stabil.* **9** 1 (1984)
16. I C McNeill, R C McGuiness *Polym. Degrad. Stabil.* **9** 2 (1984)
17. C A Wilkie, J W Pettigrew, C E Brown *J. Polym. Sci., Polym. Lett.* **19** 409 (1981)
18. L E Manring *Macromolecules* **21** 528 (1988)
19. L E Manring *Macromolecules* **22** 2673 (1989)
20. L E Manring, D Y Sogah, G M Cohen *Macromolecules* **22** 4652 (1989)
21. L E Manring *Macromolecules* **24** 3304 (1991)
22. C A Wilkie, J T Leone, M L Mittleman *J. Appl. Polym. Sci.* **42** 1133 (1991)
23. R H Pierson, A N Fletcher, E S Gantz *Anal. Chem.* **28** 1218 (1956)
24. T Kashiwagi, A Inaba, J E Brown, K Hatada, T Kitayama, E Masuda *Macromolecules* **19** 2160 (1986)
25. H R Allcock, F W Lampe, in *Contemporary Polymer Science* (Englewood Cliffs, NJ: Prentice-Hall, 1981) p. 378
26. D E Stuetz, A H Diedwardo, F Zitomer, B P Barnes *J. Polym. Sci., Polym. Chem. Ed.* **13** 585 (1975)
27. L S Kochneva, N A Kopylova, L M Terman, Yu D Semchikov *Eur. Polym. J.* **15** 575 (1979)
28. S L Madorsky *Thermal Degradation of Organic Polymers* (New York: Wiley, 1964)
29. E M Arnett, M A Mendelsohn *J. Am. Chem. Soc.* **84** 3821, 3824 (1962)
30. T Otsu, N Minimii, Y Nishikawa *J. Macromol. Sci., Chem.* **A2** 983 (1968)
31. H S Laver, in *Developments in Polymer Stabilisation* Vol. 1 (Ed. G Scott) (London: Applied Science Publishers, 1977) p. 167
32. M U Amin, G Scott *Eur. Polym. J.* **10** 1019 (1974)
33. N J Kroenke *J. Appl. Polym. Sci.* **26** 1167 (1981)
34. I C McNeill, J J Liggat *Polym. Degrad. Stabil.* **29** 93 (1990)
35. I C McNeill *Eur. Polym. J.* **3** 409 (1967)
36. I C McNeill *Eur. Polym. J.* **6** 373 (1970)
37. I C McNeill, R C McGuiness *Polym. Degrad. Stabil.* **9** 167 (1984)
38. I C McNeill, R C McGuiness *Polym. Degrad. Stabil.* **9** 209 (1984)
39. I C McNeill, J J Liggat *Polym. Degrad. Stabil.* **37** 25 (1992)
40. I Yoshida, H Kobayashi, K Ueno *Bull. Chem. Soc. Jpn.* **47** 2203 (1974)