

Interaction of Poly(methyl Methacrylate) and Manganese Chloride

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SYNOPSIS

The thermal degradation of poly(methyl methacrylate) (PMMA), in the presence of manganese chloride has been studied by sealed tube reactions and thermogravimetric analysis coupled to FT-IR spectroscopy. From sealed tube reactions it was found that the degree of mixing of the $MnCl_2$ and PMMA has an important effect on monomer formation. In systems where the two components are simply poured together, the amount of monomer is about half that observed for the thermolysis of PMMA alone; when the two components are thoroughly mixed by dissolution in solvent, the monomer yield falls to zero. The TGA-FT-IR experiment on solvent mixed material does show the presence of monomer. In sealed tubes, monomer may not escape and must repolymerize, while in the TGA experiment the monomer is swept out before reaction may occur. Monomer production also commences at temperatures lower than those for degradation of PMMA alone. It is apparent that manganese chloride catalyzes both the degradation of polymer to monomer and the reoligomerization of this monomer. The gases that are produced include CO, CO₂, CH₃Cl, HCl, and CH₄. A mechanism is proposed to account for all of these products and a manganese ionomer is the final product of the reaction.

INTRODUCTION

The degradation of poly(methyl methacrylate) (PMMA) has been studied by many workers.¹⁻⁹ Radically polymerized material begins to decompose at a lower temperature than polymer prepared by an anionic route; regardless of the method of polymerization, the product is exclusively monomer and the products are little effected by an increase in temperature.^{10,11} Several workers have studied the activation energy for the degradation process¹⁰⁻¹⁵; each author has reported a different value for this activation energy due to the fact that two different degradation processes may occur in PMMA and the value recorded will depend upon the mix of these. The results depend very strongly on the history of the polymer.¹⁶

The effect of various additives on the degradation of PMMA has been studied by various workers.

McNeill examined the effect of silver acetate,¹⁷ ammonium polyphosphate,¹⁸ and zinc bromide^{19,20} on PMMA degradation. Silver acetate combined with PMMA leads to a severe destabilization of the polymer, apparently caused by diffusion of acetate radicals into the polymer chain, initiating chain scission. In the presence of ammonium polyphosphate, a second degradation process for PMMA becomes competitive with the normal depolymerization. This route leads to the formation of high boiling chain fractions and char, as well as such volatiles as carbon monoxide, carbon dioxide, dimethyl ether, and hydrocarbons. The combination of zinc bromide and PMMA appears to significantly retard depolymerization of the polymer. The initial product appears to be the formation of a zinc methacrylate salt.

In this laboratory, we have been concerned with developing an understanding of the thermal degradation of PMMA in the presence of various additives and using that understanding to develop efficacious flame retardants. We investigated the reaction of red phosphorus with PMMA and found that phosphorus will attack PMMA at a carbonyl site and

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leads to the formation of anhydrides and methyl, methoxy phosphonium ions.^{21,22} Since attack occurs at a carbonyl site, a reagent that would attack carbonyls, such as Wilkinson's catalyst, $\text{CIRh}(\text{PPh}_3)_3$, was a logical choice for investigation.²³ This reagent causes extensive charring of the polymer due to intermolecular anhydride formation. The reaction of Wilkinson's catalyst and PMMA proceeds by oxidative addition of the rhodium species into a carbon—oxygen bond of PMMA.^{24,25} An analysis of this reaction indicated that cobalt compounds may also be suitable flame retardants.²⁶

The above investigations have established that one may identify the course of a reaction between a polymer and an additive and thus identify other putative retardants for the polymer. The success with the cobalt compounds suggests that simple transition metal compounds may react with PMMA, and that these reactions may be useful in retarding the degradation of PMMA. This paper presents the results of the reaction of PMMA and MnCl_2 .

EXPERIMENTAL

Materials

The majority of chemicals used in this study were acquired from Aldrich Chemical Co. Solvents were purchased from EM Scientific or Aldrich. TGA work was carried out using a Perkin-Elmer TGA-7. TGA-FT-IR work was performed on an Omnitherm horizontal balance Instrument interfaced to a Digilab FTS-60 FT-IR spectrometer with a heating rate of $10^\circ\text{C}/\text{min}$ and a flow rate of $50\text{ cc}/\text{min}$ argon. Proton NMR spectra were obtained on a Varian EM360; ^{13}C NMR spectra were obtained on a JEOL FX60Q or a GE QE300. FT-IR spectra were obtained on an Analect FX 6200 Spectrometer. Gas-phase infrared spectra were identified by comparison with spectra of authentic compounds.²⁷ A Hewlett-Packard 5890 gas chromatograph with a Hewlett-Packard 5970 mass selective detector was used for GC-MS work. Viscosity measurements were performed with an Ubbelohde viscometer.²⁸ Limiting oxygen index measurements were carried out on a home-built apparatus.^{24,29} Powder pattern X-ray diffraction measurements used a GE BR1 Goniometer, a GE XRD 5F Source (chromium radiation), and a Diano XRD 8000 detector.

Sealed Tube Reactions

These reactions were carried out in vessels of about 180 mL volume. The reactants were added to the

tube and the tube was then thoroughly evacuated for at least 2 h on a high vacuum line. The tube was sealed off from the vacuum line, placed in a muffle furnace, and heated for 2 h at the desired temperature. At the end of the heating period, the tube was carefully removed from the oven and placed in liquid nitrogen. **Caution:** *Vessels have been known to explode upon removal from the oven. Care must be exercised.* Some vessels were equipped with break seals, which were reattached to the vacuum line and the gases quantitated by pressure-volume-temperature measurements. The gases were identified by IR and GC-MS. The tube was then opened and the products were scrapped out and extracted with chloroform or acetone. This permitted the separation into two fractions. The chloroform-soluble fraction was typically analyzed by IR, NMR, and, where appropriate, GC-MS. The chloroform insoluble fraction was then treated with water or methanol to remove the soluble unreacted MnCl_2 . The residue was subjected to infrared spectroscopy and, frequently, to powder pattern determination. The reported recoveries are an average of several determinations and frequently their sum is more than that of starting materials. Typical recovery values may be considered accurate to about 10%. For gases, the inaccuracy is the result of traces of other compounds present with a major component. For the nonvolatile fractions, it is not possible to quantitatively remove all materials from the vessel.

Thermolysis of PMMA

A 1.0-g sample of PMMA was introduced into a break seal vessel and heated to 400°C for 2 h. The noncondensable gas was 0.5 mmol CO with a trace of CH_4 . Condensable gases consisted of CO_2 and monomeric methyl methacrylate. These were weighed together and then the carbon dioxide was allowed to evaporate and the amount of monomer was determined. The identity was confirmed by IR. There was 0.06 g CO_2 and 0.56 g monomer. After removal of the vessel from the line, the nonvolatile products (0.36 g) were completely soluble in chloroform. The infrared spectrum of these products showed only the presence of polymer. Viscosity measurements indicated that the molecular weight had decreased.

Thermolysis of PMMA- MnCl_2 Mixtures

A 1.0-g sample of PMMA and 1.0 g anhydrous MnCl_2 were combined in a standard vessel and heated to 400°C . The vessel was opened on the high vacuum

line and 0.5 mmol gas was found. Infrared spectroscopy showed the presence of CO and traces of methane. The condensable gas consisted of carbon dioxide and monomeric methyl methacrylate with traces of methyl chloride and methanol. All gases were weighed together, 0.67 g, then the more volatile gases were allowed to escape and 0.30 g monomer were found. After the vessel was removed from the vacuum line, the contents were slurried with chloroform and filtered. The chloroform soluble fraction had a mass of 0.18 g. The infrared spectra showed the presence of ester and anhydride. The insoluble fraction has a mass of 0.85 g, which was slurried with methanol to dissolve the excess MnCl_2 . The resulting material showed the presence of MnO_2 by powder pattern and IR showed an organic salt.

In another experiment, the same amounts of MnCl_2 and PMMA were thoroughly ground in a mortar and pestle and thermolyzed under identical conditions. The total yield of gases was greatly reduced; 0.37 g chloroform-soluble fraction and 1.36 g chloroform-insoluble fraction were obtained. The IR spectra were identical to those obtained in the unmixed case.

In a third experiment, 5.0 g PMMA and 5.0 g MnCl_2 were dissolved in an acetone/methanol mixture, and the solvent was evaporated on a rotary evaporator. A 2.0-g sample of the blend was thermolyzed under identical conditions; 0.02 g monomer, 0.23 g CO_2 , and 0.08 g CO were recovered. The chloroform-soluble fraction had a mass of 0.23 g, while the insoluble comprised 1.8 g.

Viscosity measurements were carried out on the soluble fraction. The specific viscosity for a solution of CHCl_3 -soluble material at a concentration of 0.0020 g/mL was 0.012; a PMMA solution at an identical concentration gave a specific viscosity of 0.067.

Thermolysis of MnCl_2 and Monomer

A 1.0-g sample of MnCl_2 and 0.55 g monomer were combined in a standard vessel equipped with a break-seal and heated to 350°C. After removal from the oven, the vessel was reattached to the vacuum line and the break-seal opened. The amount of monomer recovered was 0.18 g.

Limiting Oxygen Index Measurements

The LOI was measured as previously described, using bottom ignition. The samples were prepared by casting films from solvent mixed MnCl_2 /PMMA in a 1 : 1 mass ratio. The results are presented in Table I.

Table I

% Oxygen	Observation
14	Extinguishes
16	Extinguishes
19	Extinguishes
20	Extinguishes
22	Burns and extinguishes
24	Burns and extinguishes
26	Burns to char

Thermolysis of MnCl_2 and dimethylglutamate (DMG)

A 1.0-mL sample of DMG (6.8 mmol) and 0.85 g MnCl_2 (6.8 mmol) were combined in a standard vessel and heated to 400°C. The vessel was reattached to the high vacuum line and opened. The noncondensable gases (0.3 mmol) consisted of carbon monoxide with a trace of methane. The condensable gases were CO_2 with traces of methyl chloride and methanol (0.40 g). The vessel was opened and slurried with chloroform and filtered. The chloroform soluble fraction, 0.32 g, was analyzed by IR and GC-MS. The results were very irreproducible; some compounds were strong in one reaction and virtually absent in other reactions. The only product that could be identified with certainty was methyl glutarate. Great care was taken to determine if any glutaric acid was produced; this was never a product of any reaction at any temperature. The chloroform-insoluble fraction, 1.15 g, contained three components: unreacted MnCl_2 , manganese glutarate, and MnO_2 . The unreacted manganese chloride, 0.10 g, was separated by dissolution in methanol and filtration. The residue was dissolved in a large amount of water, filtered, and evaporated. The insoluble residue, 0.13 g, was identified as MnO_2 by powder pattern. The soluble fraction, 0.92 g, was subjected to elemental analysis.

ANAL: Calcd: $\text{MnC}_5\text{H}_6\text{O}_4 \cdot \text{H}_2\text{O}$, 29.56%; C, 27.09%; Mn, 3.94%; H, 0% Cl. Found: C, 28.41%; Mn, 27.36%; H, 3.84%; Cl, 3.33%.

An aqueous solution of this compound was passed through an ion exchange column in the sodium form. The solution was evaporated, and IR and NMR spectra were obtained. The spectra were identical with an authentic sample of sodium glutarate. When the identical reaction was performed at 425°C, the amount of MnO_2 increased, while that of manganese glutarate decreased.

Preparation of Manganese Glutarate

A 5.0-g sample of glutaric acid (3.8 mmol) was dissolved in water and treated with 3.0 g NaOH (7.6 mmol). The solution was evaporated to give sodium glutarate. Equimolar amounts of MnCl_2 and sodium glutarate were mixed in water and manganese glutarate precipitated from the solution. This was filtered and dried at 110°C.

Thermolysis of Manganese Glutarate

A 1.0-g sample of manganese glutarate was placed in a standard vessel and heated to 425°C for 2 h. Upon reattachment to the vacuum line, no noncondensable or condensable gases could be found. The vessel was then opened and the contents slurried with acetone, filtered, and the acetone solution evaporated. The mass of insolubles was 0.60 g, while 0.35 g solubles were recovered. The solubles consisted of some water and organic compounds that were not further identified. The insolubles were slurried with 50 mL 3 M H_2SO_4 to dissolve the excess manganese glutarate and then filtered. The acid insoluble had a mass of 0.19 g and was identified as MnO_2 by powder pattern.

RESULTS AND DISCUSSION

This investigation was initiated because it was observed that the combination of PMMA and MnCl_2 leads to a decreased yield of monomer with the formation of anhydrides. The burning of any plastic material requires that there be some decomposition to generate fuel; in the case of PMMA, that fuel is monomer. Thus, any additive that will reduce monomer formation will have some flame retardant activity. It should be noted that this is a study of fuel generation that does not involve oxygen and thus the investigations are carried out in either sealed tube reactions under vacuum or by thermogravimetric analysis (TGA) in an inert atmosphere.

The degree of mixing between the manganese chloride and the polymer is of great importance in monomer formation. When bulk MnCl_2 and PMMA are simply poured together and heated under vacuum to 400°C, the monomer yield is less (30–35%) than that observed for PMMA alone (50–70%). It should be noted that these sealed tube reactions do not yield 100% monomer as normally observed for PMMA degradation, probably due to the reoligomerization of the monomer. More intimate mixing of the reactants leads to decreased monomer yield. When the

two are ground in a mortar and pestle, monomer yield is reduced; when the two components are mixed in solution and then evaporated to give solids, the monomer yield is essentially nil.

In addition to monomer, other gaseous products that are observed in this reaction include methane, carbon monoxide, carbon dioxide, methanol, methyl chloride, and HCl. With the exception of CO and CO_2 , these are present in quite small amounts. The nonvolatile products may be subdivided on the basis of solubility in chloroform. The infrared spectrum of the soluble fraction shows the presence of anhydride and ester. The insoluble portion is the largest mass fraction, and contains manganese dioxide and an organic manganese salt.

The molecular weight of the chloroform-soluble fraction was investigated by viscosity measurements and was found to be about 10% that of the starting polymer. One must construe from this that a significant fraction of the polymer does react to form monomer and that this is then repolymerized to yield relatively low-molecular-weight oligomer. Presumably, MnCl_2 catalyzes this reoligomerization. In TGA experiments, it will be shown that monomer is formed and is able to immediately escape from the system. In sealed tube reactions, product monomer may not escape and is available for further reaction. The intimate mixing that may be achieved by solvent mixing of the polymer and additive must produce a relatively efficient catalyst for reoligomerization.

The combination of MnCl_2 and PMMA causes a decreased yield of monomer, the formation of relatively low-molecular-weight oligomers that contain anhydrides and esters, the evolution of several gases, and the formation of an insoluble product. These sealed tube reactions permit the detection and quantitation of each of these species. It is not, however, possible to determine the order in which these species are formed. Such time evolution data may be very useful in establishing at which time reactions occur so that one may begin to sketch a mechanism for this reaction. To accomplish this goal, the combination of thermogravimetric analysis and Fourier transform infrared spectroscopy (TGA-FT-IR) has been utilized.^{30,31}

A sample of solvent mixed MnCl_2 -PMMA was investigated by TGA-FT-IR. The TGA curves for PMMA are shown in Figure 1(a). Kashiwagi et al.³² showed that there is a direct correlation between the TGA curve and the method of preparation, presence of weak links, and end groups. From this curve, the material used in this study is anionically polymerized with no irregular structures. Figure 1(b)

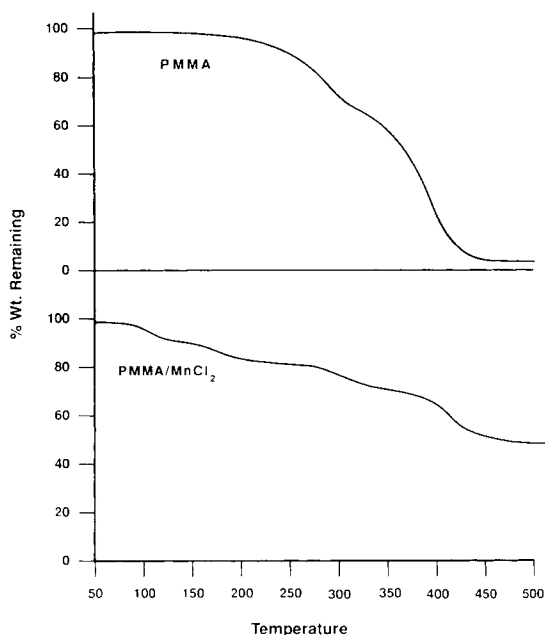


Figure 1 Thermogravimetric analysis curve for PMMA (top) and a 1 : 1 blend of PMMA-MnCl₂, run under an inert atmosphere at a scan rate of 20°C/min.

shows the TGA curve for the MnCl₂-PMMA blend. The degradation can be separated into five distinct temperature regions; each will be discussed separately and the gases that evolve identified.

In the first region, 100–145°C, 7.5% of the sample volatilizes. The only material that is present in the FT-IR spectrum is water. Even though anhydrous MnCl₂ was used in these investigations, some water is picked up by the salt and is fairly easily lost.

An additional 9.5% of the sample volatilizes between 145 and 215°C. It is evident from the IR spectrum that this is due to monomer evolution. Note that in pure PMMA monomer evolution does not begin until higher temperature, and in sealed tube reactions no monomer is produced. This apparent contradiction is due to the difference between the two experiments. In the sealed tube reactions, all gases are retained within the vessel and monomer may participate in further reaction. In the TGA-FT-IR experiment, the gases are swept out of the chamber by argon and thus may not further react. The manganese chloride must catalyze the reoligomerization of the monomer in the sealed tube reaction, and, since monomer formation begins at such a low temperature, it must also catalyze the depolymerization reaction. An experiment has been performed in which monomer and MnCl₂ were combined and heated to 350°C. Significant oligomerization of monomer occurs under these conditions.

The third region of weight loss, 215–345°C, is characterized by the continued formation of monomer, as well as the appearance of methyl chloride and methanol (10.5% is lost in this region). The spectrum of the gases evolved at 303°C is shown in Figure 2. The carbonyl absorption for monomer is evident in the 1700–1800 cm⁻¹ region; in addition, one may also see methanol at 1034 cm⁻¹ and methyl chloride at 733 cm⁻¹. Since the only source of chlorine is the MnCl₂, the presence of CH₃Cl indicates that a reaction between MnCl₂ and PMMA has occurred. The formation of both methyl chloride and methanol must involve the methyl ester functionality of the PMMA.

Between 345 and 455°C, an additional 19% of the sample volatilizes. In this region, the gases are identified as CO₂, CO, CH₄, HCl, and an aliphatic acid.

The final region of weight loss, 455–630°C, accounts for 5% of the sample and is identified as HCl by infrared spectroscopy. A representative spectrum at 565°C is shown in Figure 3.

A total of 51.5% of the sample has volatilized by 630°C, leaving 48.5% nonvolatile residue. Since the charge is a 1 : 1 mixture by mass of the components, one might conclude that all the PMMA has volatilized, leaving the MnCl₂ behind. This is not the case since chlorine is observed among the volatile products and the infrared spectrum of the residue show the presence of organics, notably in the C-H region and the carbonyl region. The residue consists of two fractions: recovered MnCl₂ and some new insoluble organic manganese compound.

Scheme 1 presents an interpretation of the reaction and delineates a pathway whereby all of the products may arise. MnCl₂ facilitates the initial cleavage of carbon-oxygen bonds, producing methoxy and methyl radicals, as well as carbonyl radicals and carboxyl radicals, along the polymer chain.

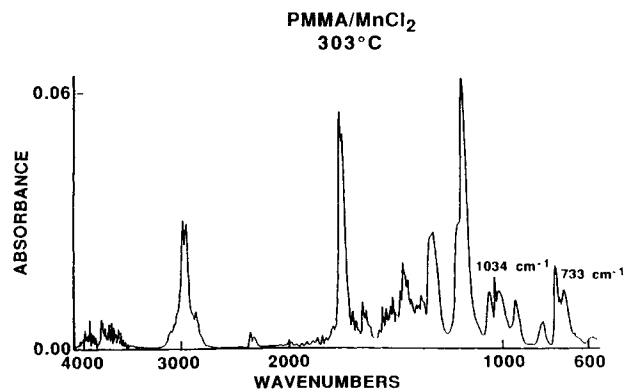


Figure 2 Representative FT-IR spectrum of gas evolved at 303°C.

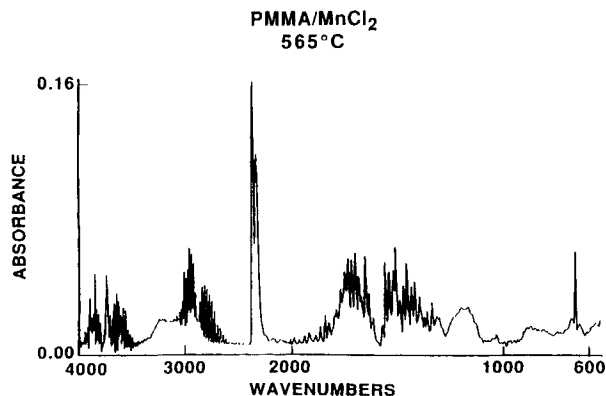


Figure 3 Representative FT-IR spectrum of gas evolved at 565°C.

These methoxy and methyl radicals may abstract protons and give methanol and methane, respectively. The methyl radical may also combine with a chlorine radical and produce methyl chloride. The carbonyl radical may decarbonylate, giving CO and a tertiary radical, while the carboxyl radical can decarboxylate, giving CO₂ and the same tertiary radical. These tertiary radicals will lead to PMMA degradation products, predominately monomer with some other smaller fractions. Since much more CO₂ is produced than CO, the loss of methyl radical must occur more often than the loss of methoxy radical. This carboxyl radical has an alternate pathway open: It may interact with the MnCl₂, producing an MnCl salt and a chlorine radical. This chlorine radical may combine with any other radical produced in the reaction to give products; methyl chloride, noted above, is one of those products. The manganese chloride salt of PMMA may lose a chlorine radical and produce a manganese radical on the PMMA chain. The combination of this manganese radical with a second carboxyl radical gives the manganese ionomer of PMMA. This manganese ionomer may thermally decompose to produce MnO₂ and other degradation products. An aliphatic acid is also produced in the reaction. This may arise from the abstraction of a hydrogen by the carboxyl radical and subsequent depolymerization, giving monomeric methacrylic acid as well as other degradation products.

From the TGA-FT-IR data, the first reaction must be depolymerization to give monomer. At a somewhat higher temperature, MnCl₂ catalyzes the loss of methyl and methoxy radicals with the formation of carbonyl and carboxyl radicals. These may then react and give CO, CO₂, and the manganese ionomer.

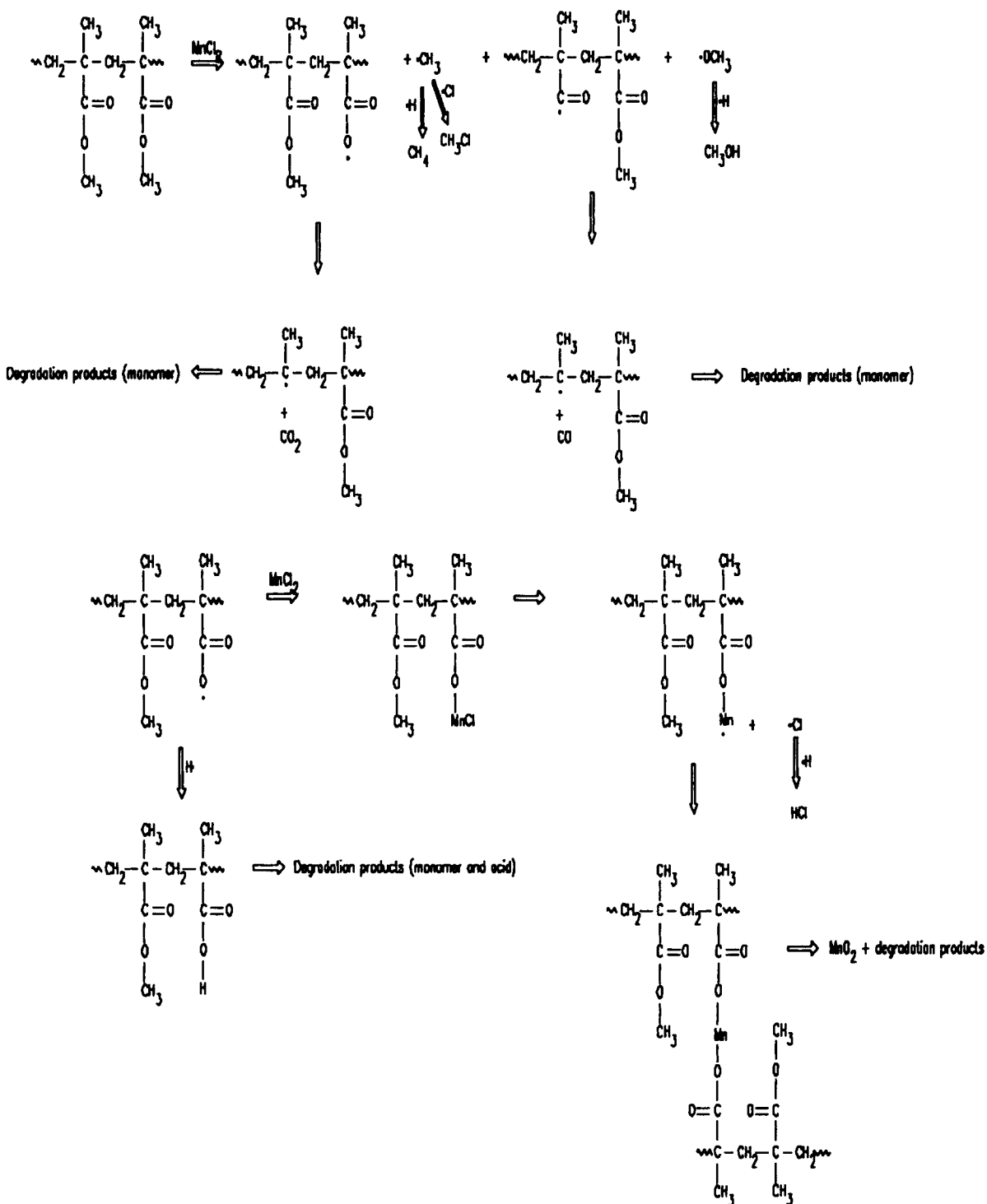
Anhydride is also noted as a product of the reaction. Both intra- and intermolecular anhydride formation may occur, as shown in Scheme 2.

The limiting oxygen index of the mixture of PMMA and manganese chloride has been investigated and indicates some efficacy for MnCl₂ as a flame retardant. At a 1 : 1 mass ratio the LOI, bottom ignition,²⁹ has increased from about 14 for pure PMMA to around 25 for the blend of MnCl₂ and PMMA. This loading is well beyond any value that might have commercial significance. It nonetheless shows that this additive has an effect.

To validate this reaction pathway, the reaction between MnCl₂ and dimethylglutarate (DMG) has been examined. DMG is recovered unchanged upon heating to 400°C in a sealed tube. When DMG is heated in the presence of MnCl₂ a variety of products are produced. The volatile products include CO₂, CO, CH₄, CH₃Cl, and CH₃OH. These products are all observed in the reaction of MnCl₂ with PMMA and presumably arise by the same pathway as noted above. The chloroform-insoluble, nonvolatile products include MnO₂, manganese glutarate, and unreacted manganese chloride. Note that the manganese glutarate is analogous to the manganese ionomeric form of PMMA produced in the PMMA reaction. The MnO₂ must arise from the degradation of manganese glutarate and produces as a by-product carbonyl radicals. The amount of MnO₂ increases as the temperature is raised. The thermolysis of pure manganese glutarate produces MnO₂, as well as some unidentified organic fragments.

Only one chloroform-soluble product can be identified, methyl glutarate, analogous to the aliphatic acid produced in the PMMA reaction. There are a variety of other chloroform-soluble products that appear in this reaction; however, every reaction shows different amounts of these products. A product that seems quite abundant in one reaction may be almost totally absent in the next. These products must be the result of radical coupling reactions, and the diversity must be due to the nonspecificity of these reactions: Whatever radical is encountered first will be the reaction partner and the products will be quite diverse.

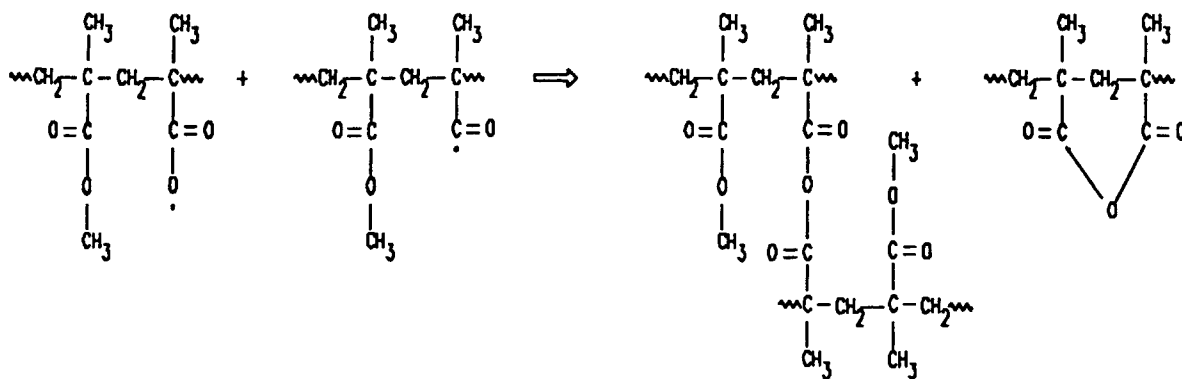
This work must be contrasted to the investigation of the ZnBr₂-PMMA system by McNeill and McGuiness.^{19,20} The gaseous products observed are identical for both additives; however, the order of appearance for these is not the same. With ZnBr₂, the initial product that is formed is methyl bromide, released at 160°C; the analogous methyl chloride is not formed with the manganese salt until temper-



Scheme 1

atures above 220°C are reached. The initial reaction observed with $MnCl_2$ is the formation of monomer; indeed, this occurs at temperatures well below that

where monomer is formed in pure PMMA. On the other hand, with $ZnBr_2$, the initial reaction is elimination of methyl bromide with formation of the zinc



Scheme 2

salt of methacrylic acid. In both cases, the product of the reaction is a metal salt of methacrylic acid. In this work, this has been categorized as an ionomer to indicate the stability expected for this species. Considering the great similarity between these two reactions, it seems very likely that the reactions are quite similar; the only likely difference is in the interpretation of the results.

CONCLUSION

There are both advantages and disadvantages to the use of manganese chloride as a flame retardant for PMMA. On the one hand, MnCl_2 promotes an initial depolymerization of the polymer and thus promotes burning. On the other hand, a nonvolatile ionic species is ultimately produced. Unfortunately, there is sufficient degradation of the polymer to generate burnable materials so this species is not an adequate flame retardant. The purpose of this investigation was not to establish MnCl_2 as a flame retardant for PMMA; rather, it was to understand the course of the reaction and then to use that understanding as a basis for further investigations. These results permit a clear understanding of the reaction between PMMA and MnCl_2 . Future work must concentrate on discovering methods of promoting ionomer formation while preventing monomer formation.

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