The Interaction of Poly(methyl methacrylate) and Chromium Chloride: Transfer of Methyl Groups from the Ester to the Main Chain

RUDOLFO SCOTT BEER,[1] CHARLES A. WILKIE,[1,*] and MARTIN L. MITTLEMAN[2]

[1]Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233; and [2]BP America Research, 4440 Warrensville Center Road, Cleveland, Ohio 44128

SYNOPSIS

The interaction of transition-metal halides with poly(methyl methacrylate) (PMMA) has been studied in the past and methyl halides are always observed as a product of the reaction. When $CrCl_3$ is used as an additive for PMMA, only traces of methyl-containing products are seen and these only at quite high temperatures. The principal volatile products consist of carbon dioxide, carbon monoxide, and monomer, while the nonvolatile residue contains a multitude of methylene and methine carbons. A mechanism is invoked by which the ester methyl is transferred to the polymer backbone in a concerted process.

INTRODUCTION

The degradation of poly(methyl methacrylate) (PMMA) has been studied by many workers[1-9] who have found that its mode of degradation depends upon the preparation procedure. Radically polymerized PMMA begins to degrade at a much lower temperature due to the presence of head-to-head linkages and other "weak-links" in the polymer.[10-12] Polymer that has been prepared by an anionic route has much fewer "weak-links" and does not degrade as easily. Regardless of the preparation method, there is general consensus that PMMA produces exclusively monomer upon degradation.

The effect of additives upon PMMA degradation has also been investigated. McNeill and McGuiness examined the effect of silver acetate,[13] ammonium polyphosphate,[14] and zinc and cobalt bromides[15,16] upon PMMA degradation. The first of these causes a destabilization of the polymer and an increased degradation rate, whereas the metal bromides appear to slow the degradation process. The initial step with these metal bromides appears to be the formation of some complex between the metal ion and the ox-

ygens of the polymer, leading ultimately to the formation of an ionomer.

In this laboratory, we have been systematically investigating the interaction of a variety of additives with PMMA with the goal of developing some mechanistic understanding of this interaction. By understanding the chemistry involved when a polymer and an additive interact, one can then expand that understanding to prevent the degradation of the polymer. Since monomer is the only product observed during thermal degradation of pure PMMA, if an additive that reduces the amount of monomer formed and increases the amount of char that is produced during degradation, it must have a significant flame-retarding effect. Char is a desirable product because it will thermally insulate the degrading polymer and prevent further degradation.

In this laboratory, we have examined the effects of red phosphorus[17,18] and Wilkinson's catalyst,[19,20] $ClRh(PPh_3)_3$, on PMMA and have discovered that in both cases cross-linking of the polymer occurs with the concomitant formation of char. Our investigations have indicated that other transition-metal compounds may also have an effect on the degradation. We have previously reported that two cobalt compounds, $K_4Co(CN)_6$ and $HCo[P(OPh)_3]_4$, inhibit the degradation of PMMA.[21] Related to the work of McNeill and McGuiness noted above is an

investigation on the effect of manganese chloride on PMMA degradation.[22] This additive appears to act much like zinc bromide in that an initial coordination of the metal ion causes some degree of stabilization. Manganese chloride, unlike zinc bromide, appears to function as a catalyst for the depolymerization of the polymer at low temperatures. In previous work, the transition metal has always been in the 2^+ oxidation state; in this paper, we report the investigation of the reaction between PMMA and a metal in a higher oxidation state, chromium (III) chloride, both in the anhydrous and hydrated form.

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. Proton NMR spectra were obtained on a Varian EM360; ^{13}C NMR spectra were obtained on a GE 300Ω. FTIR spectra were obtained on an Analect FX 6200 spectrometer. Gas-phase IR spectra were identified by comparison with spectra of authentic compounds.[23] A Hewlett-Packard 5890 gas chromatograph with a Hewlett-Packard 5970 mass selective detector was used for GC–MS work. Limiting oxygen index measurements were carried out on a home-built apparatus.[19,24] Powder pattern X-ray diffraction measurements were obtained with a GE BR1 Goniometer, a GE XRD 5F source (chromium radiation), and a Diano XRD 8000 detector. TGA/IR work was performed on an Omnitherm horizontal balance Instrument interfaced to a Digilab FTS-60 FTIR spectrometer with a heating rate of 10°C/min and a flow rate of 50 cc/min of argon.[25,26]

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.

These were reattached to the vacuum line and the gases quantitated by pressure–volume–temperature measurements and identified by IR and GC–MS. The tube was then opened and the products were scraped out and extracted with chloroform or acetone to separate them into two fractions. The chloroform-soluble fraction was typically analyzed by IR, NMR, and, where appropriate, GC–MS. The chloroform insoluble fraction was characterized by IR spectroscopy and X-ray powder pattern determination. Reported recoveries are an average of several determinations and, frequently, their sum is more than that of starting materials. Typical recovery values are accurate to about 10%. For gaseous products, the inaccuracy results from traces of other compounds present with the major components. For the nonvolatile fractions, errors are incurred in attempting to remove all of the products from the reaction vessel.

Thermolysis of PMMA and Hydrous Chromium Chloride

A typical reaction was carried out by charging 2.0 g of a blend of PMMA and hydrous chromium chloride to a reaction vessel. The blend was prepared by combining acetone solutions containing equal weights of the two components and removing the acetone on a rotary evaporator. Pressure–volume–temperature measurements and IR spectra of the noncondensable gaseous products indicate that approximately 6% of the charge has been converted to methane and carbon monoxide. The condensable gases represent about 44% of the starting charge and consist of monomer, CO_2, HCl, and water. The carbon dioxide was separated by standard vacuum line techniques and found to be about 14% of the gas.

The chloroform-soluble fraction is a brown viscous material that is about 13% of the mixture. Sodium fusion indicates the presence of chloride, whereas a spot test for chromium shows its absence. The IR spectrum indicates the presence of carbonyl and carboxylate moieties. The ^{1}H-NMR spectrum of this fraction shows three broad regions of overlapping peaks; these are between 0.9 and 1.8 ppm, 2.0 and 3.0 ppm, and 6.5 and 8.0 ppm. The ^{13}C-NMR spectrum shows a broad band of peaks between 10 and 60 ppm with a second band between 110 and 150 ppm.

The chloroform insoluble fraction was 36% of the starting materials. Its IR spectrum shows the presence of anhydrides with absorptions at 1800, 1760, and 1150 cm^{-1}. These anhydrides could be easily

cleaved by the addition of water, and absorptions attributable to carboxylic acid are then observed. An X-ray powder pattern shows the presence of CrOCl and CrO_3. A quantitative sodium fusion demonstrated the presence of 0.05 g of chlorine— 13% of the chlorine present in the starting material.

Thermolysis of PMMA and Anhydrous Chromium Chloride

A 1.0 g sample was prepared by grinding anhydrous $CrCl_3$ with PMMA. This mixture was heated at 400°C for 2 h. The only difference in this reaction and that with hydrous $CrCl_3$ was that water was not produced in this reaction.

Thermolysis of Heptadecane and CrCl$_3$

A mixture of 0.5 mL of heptadecane and 0.5 g anhydrous $CrCl_3$ was thermolyzed at 350°C for 1 h. The IR spectrum of the gaseous products showed a typical HCl pattern as well as weak absorption near 1650 cm^{-1}. The nonvolatile components also showed absorptions near 1650 cm^{-1}.

Preparation and Thermolysis of Chromium Chloride Salt of Poly(methacrylic acid)

When aqueous solutions of poly(methacrylic acid) and hydrous chromium chloride were combined, a precipitate of the chromium chloride salt was formed.[27] This precipitate was filtered and dried under vacuum. The exact composition of this salt is unknown but it was shown to contain both chromium and chlorine. A 0.5 g sample was thermolyzed at 350°C for 1.5 h. The presence of anhydride in the residue was confirmed by absorptions in the infrared spectrum near 1805, 1760, and 1100 cm^{-1}.

Experiments under Inert Gas Flow

To better characterize the solid products obtained in the TGA/IR study, a series of experiments was performed in which the blends of the chromium compound and polymer were thermolyzed in a two-legged vessel under nitrogen flow. A 1.0 g sample of the blend was charged to one leg of the vessel, and this was placed in a fluidized sand bath that could be heated up to 500°C; the second leg of the vessel was cooled in a suitable cold bath in order to condense the volatile products. The nonvolatile residue recovered when the sample was heated between 270 and 400°C showed anhydride absorptions in the IR. When the sample was heated above 400°C, these

anhydride absorptions diminished in intensity and were completely absent when the thermolysis temperature was above 440°C. As the anhydride absorption diminished, carboxylic acid bands grew in intensity. Elemental analysis of the residue obtained by thermolysis at 500°C found 16.78% carbon, 1.77% hydrogen, 7.10% chlorine, and 43.43% chromium.

RESULTS

The degradation of PMMA in the presence of chromium chloride has been studied both by sealed-tube reactions, TGA/IR, and reactions under inert gas flow. Sealed-tube reactions keep all evolved gases within the tube, thus some of the primary degradation products may undergo further reaction before they may be analyzed. In a TGA/IR experiment, the gases are immediately swept from the heated zone and identified by IR spectroscopy. Because of this inherent difference, results from the two experiments may show some variation. Thermolysis experiments under an inert gas flow simulate the TGA/IR studies very closely and they also permit the identification of the residue that is produced at any given temperature.

Thermal Stability of Chromium Chloride (CrCl$_3$)

Hydrous chromium chloride, $CrCl_3 \cdot 6H_2O$, exists as a variety of coordination isomers: $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$. Each of these shows slightly different behavior upon thermolysis.[28] Below 100°C, the first and third isomers lose only water, while the second isomer loses only HCl. Since the chromium chloride used in this study loses both HCl and H_2O below 100°C, it is apparently a mixture of hydration isomers. Between 200 and 300°C, each of these isomers will produce chromium hydroxy dichloride, $Cr(OH)Cl_2$. At higher temperatures, chromium oxychloride, CrOCl, is obtained. At elevated temperatures, anhydrous chromium chloride can lose a chlorine atom and produce chromium(II) chloride, $CrCl_2$.[29] Thus, there may be several species present in this reaction system and it is difficult to identify those actually involved.

Reactions of Chromium Chloride and PMMA

Sealed-tube Reaction

Since both hydrous chromium chloride and PMMA are soluble in acetone, it is possible to prepare a

well-mixed blend by combining solutions of each component and then evaporating the solvent. For anhydrous chromium chloride, the blend was prepared by simple grinding of the components. There are three components that can be isolated from a reaction mixture: volatiles, a soluble fraction, and an insoluble fraction. Each of these will be discussed in turn.

Volatile Fraction

The volatiles are separable on a high-vacuum line by the use of standard techniques and can be identified by IR spectroscopy. For a 1 : 1 blend by mass of PMMA and hydrous chromium chloride, the volatile products are 50% of the starting material. The species that may be identified include HCl, CO_2, CO, methyl methacrylate, and acetone. Acetone is attributable to residual solvent from the blending process. HCl is produced by both hydrous and anhydrous chromium chloride. Its evolution from a hydrous chromium chloride blend is not unexpected. However, HCl evolution in the anhydrous case implies some reaction between the components. Monomer, carbon monoxide, and carbon dioxide are always observed as PMMA degradation products in sealed-tube reactions where the products are contained. However, degradation under flowing conditions yields exclusively monomer. Quantitation of the CO_2 in the sealed-tube reactions shows that at least 75% of the starting material has been decarboxylated. This is unexpectedly high considering that when PMMA is thermally degraded alone or in the presence of other additives that have been studied in this laboratory the amount of CO_2 produced has been much less.

Soluble Fraction

Approximately 13% of the initial weight of the hydrous blend was found to be chloroform soluble. When PMMA is pyrolyzed alone in sealed tubes, substantial amounts of oligomers are produced. When PMMA is mixed with $CrCl_3$, simple oligomeric products are not found. The ^1H-NMR spectrum of PMMA shows a singlet at 3.6 ppm attributable to the methoxy protons. In the spectrum of the reaction product, this singlet is absent and there are no methyl ester groups. This same loss of methyl esters has been observed in the reaction of PMMA with zinc[15,16] and manganese salts.[22] However, in these studies, methyl halide is evolved and a zinc or manganese ionomer produced. There are no methyl-containing gases produced in the reaction of PMMA with hydrous or anhydrous chromium chloride. The

proton NMR spectrum of the chloroform soluble fraction contains many overlapping bands from about 0.6 to 3.0 ppm, indicative of a large number of methyl, methylene, and methine hydrogens. There is also a very broad band due to olefinic hydrogens between 6 to 8 ppm and a few peaks between 3 and 4 ppm attributable to hydrogens adjacent to carbonyl or chlorine substituents. Thus, the ^1H spectrum indicates the presence of oligomeric products containing double bonds as well as methyl, methylene, and methine hydrogens. When $MnCl_2$ is used as an additive for PMMA, the NMR spectrum of the chloroform soluble fraction does not show these broad bands attributable to methylene and methine hydrogens. These new resonances imply some unique reaction of this chromium additive.

The ^{13}C-NMR spectrum of the chloroform soluble fraction confirms the observation from the proton spectrum. There are numerous peaks between 10 and 50 ppm as well as some in the double-bond region. A qualitative bromine absorption test confirmed the presence of double bonds. Carbonyl peaks are of very low intensity, suggesting a large amount of decarboxylation, in agreement with the large amount of CO_2 measured in the gas-phase products. There are also a few ^{13}C peaks between 60 and 70 ppm, probably adjacent to an electronegative substituent, which correlate to the proton signals between 3 and 4 ppm.

The most prominent feature in the infrared spectrum of this fraction is the very broad carbonyl absorption, spanning the region from 1700 to 1780 cm^{-1} with its maximum intensity at 1704 cm^{-1} and shoulders at 1731 and 1770 cm^{-1}.

Chloroform Insoluble Fraction

This fraction is not only insoluble in chloroform but it also did not dissolve in any common laboratory solvents, including acetone, water, ethyl acetate, carbon tetrachloride, and tetrahydrofuran. Its infrared spectrum indicates the presence of anhydride groups with absorptions at 1805, 1770, and 1016 cm^{-1}. Peaks at 1540 and 1420 cm^{-1} indicate carboxylate salts. Identical absorptions are observed when a salt is prepared from chromium chloride and poly(methacrylic acid). Skupinska et al.[27] have shown that some chromium carboxylate salts are stable above 500°C.

TGA/IR Studies

The TGA trace for a 1 : 1 mixture by mass of $PMMA/CrCl_3 \cdot 6H_2O$ is shown in Figure 1. A rela-
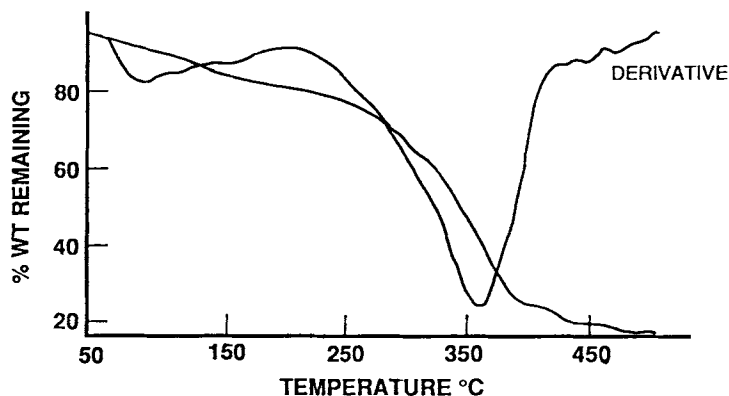
TGA OF PMMA/CrCl₃·6H₂O

temperature region	products	IR absorption (cm⁻¹)	% wt. loss
30-215°C	acetone	1738	22%
	H₂O	3500	
	HCl	2800	
	MMA	1749	
270-500°C	MMA	1749	62%
	HCl	2800	
	CO₂	2361	
	CH₄	3016	
	CO	2123	
	RCOOH	1755	

Figure 1   TGA curve for a 1 : 1 by mass blend of hydrous CrCl₃/PMMA. The heating rate is 20°C/min. The table identifies the weight loss and the gases that are evolved.

tively gradual weight loss occurs until a temperature of about 250°C; above this temperature, degradation occurs more rapidly. Approximately 22% of the sample is lost up to 250°C. Acetone, water, HCl, and monomer evolution are detected. Loss of acetone is simply residual solvent from the preparation of the blend. Water and HCl result from thermolysis of the hydrous CrCl₃. When anhydrous CrCl₃ is used, water is absent but HCl is still observed. Monomer results from the depolymerization of PMMA. Up to 250°C degradation of the individual components occurs with no apparent interaction between them.

An additional 62% weight loss occurs between 250 and 500°C. The evolved gases consist of monomer, carbon dioxide, carbon monoxide, an unidentified organic acid, and a trace of methane. The IR spectrum of the gases evolved at 411°C is shown in Figure 2. Carbon dioxide appears between 2300 and 2400 cm⁻¹, CO appears near 2100 cm⁻¹, and monomer is evidenced by the carbonyl vibration at 1749 cm⁻¹ and the carbon–carbon double-bond frequency

near 1650 cm⁻¹. Monomer is the principal component evolved until about 430°C. Above this temperature, the bands attributable to monomer become less intense and bands due to CO₂, CO, and an aliphatic acid are more intense. For the hydrous chro-
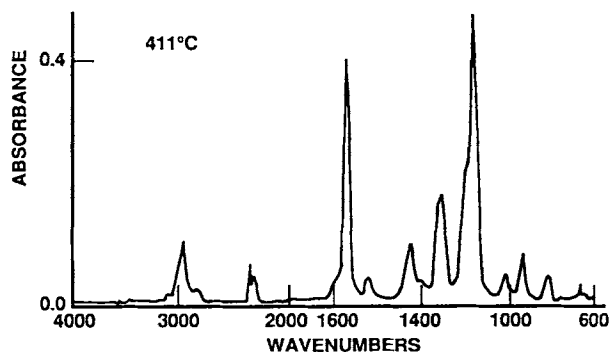

Figure 2   IR spectrum of the gases that are evolved from a 1 : 1 by mass blend of anhydrous CrCl₃/PMMA.

mium compound, HCl evolution is evident at 150°C, from degradation of the hydrous $CrCl_3$, and again above 450°C. With the anhydrous $CrCl_3$, HCl evolution commences at 430°C and it continues until the highest temperature used in this study: 500°C.

The nonvolatile residue that remains at 500°C represents 16% of the starting mass. If all the water was evolved from the hydrated $CrCl_3$ and all the PMMA was depolymerized, $CrCl_3$ would be left as a residue representing 30% of the starting mass. If the product were $CrCl_2$, then the residual mass would be 23%; CrOCl would leave 20% residue. A recovery of only 16% indicates that none of these are, themselves, final reaction products.

Examination of a residue analogous to that left in the TGA/IR study was accomplished by heating a quantity of the material in a sand bath under a nitrogen purge, to the same final temperature. A two-legged vessel was used for this purpose: The first leg was charged with the reactants and the second was cooled with a dry ice/acetone bath. Residues were recovered at several final pyrolysis temperatures and analyzed by NMR and IR spectroscopies. An infrared spectrum of the residue obtained when the blend of PMMA/chromium chloride is heated to 260°C begins to show anhydride absorptions. The formation of anhydride occurs concomitant with the evolution of CO_2 and CO in the TGA/IR experiment. Anhydride is present in residues heated to about 450°C. Above this temperature, most carbonyl absorptions disappear, leaving only an unresolved carboxylate salt peak near 1550 cm^{-1}.

The residue recovered at 300°C was extracted with chloroform and the chloroform soluble fraction was analyzed by ^{13}C-NMR spectroscopy. This spectrum confirms the presence of methyl, methylene, and methine carbons as well as mono- and disubstituted olefinic carbons. The residue obtained by heating to 500°C was 19% of the starting charge, while in the TGA study, approximately 16% remained at 500°C. This slight difference between the two reactions may be attributed to the different amounts, and depths, of material present in the two reactions. This residue was found to contain chromium, chlorine, carbon, hydrogen, and oxygen. It was determined that about 19% of the chromium, 94% of the chlorine, 84% of the oxygen, 84% of the hydrogen, and 93% of the carbon have been volatilized in this reaction. The IR spectrum of the residue shows an absorption at 1650 cm^{-1} that may be attributable to a carboxylate salt. The product is undoubtedly a mixture of components: CrO_3 and CrOCl have been identified by the X-ray powder pattern.

DISCUSSION

An interaction between PMMA and chromium chloride is unlikely below a temperature of about 260°C. The products below this temperature are only those expected for the independent degradation of the individual components. Scheme 1 delineates a pathway for the initial interaction of chromium chloride with PMMA.

The first step is probably coordination of $CrCl_3$ to the carbonyl of the PMMA. The work of McNeill and McGuiness on $ZnBr_2$ (Refs. 15 and 16) and our own work on $MnCl_2$ (Ref. 22) have both suggested an initial coordination to the carbonyl. It is known that $CrCl_3$ can thermally lose a chlorine atom,[29] and this reaction should be accelerated by the additional coordination to the carbonyl. The liberated chlorine atom may remove a hydrogen atom from the main chain of the PMMA, leaving a radical site on the PMMA chain. The presence of HCl suggests that this reaction occurs rather easily. The reaction between heptadecane and $CrCl_3$ also produces HCl and this provides further evidence in support of this reaction. The reaction is formulated as a radical process, but there are other pathways by which this reaction may occur: Hydrogen abstraction from a methyl would form a primary radical, while abstraction from a methylene generates a more stable secondary radical. If a primary radical is formed initially, it would rearrange to form the more stable secondary radical. This secondary radical is formed in the immediate vicinity of the ester methyl group. Transfer of this methyl group to the main chain will complete the formation of a chromium carboxylate salt. Proof for this step comes from the observation of methine protons (and carbons) along the main chain and an abundance of methyl resonances in the NMR spectra. When $MnCl_2$ or $ZnBr_2$ are used as additives, volatile methyl-containing products are obtained by reaction of the ester methyl moieties. The difference between these is the stability of the manganese and zinc salts vs. the instability of the chromium salt. In the chromium system, a chlorine atom may be easily lost, leading to hydrogen abstraction, whereas in the manganese or zinc system, no halogen is lost. With zinc and manganese, salt formation occurs by the loss of a methyl radical rather than transfer of the methyl to the main chain. Since PMMA should be completely evolved by 390°C, the evolution of monomer at higher temperatures indicates that some stabilization of the polymer has occurred, possibly by cross-linking. Degradation of these cross-links at higher temperatures would account for the evolution of monomer.
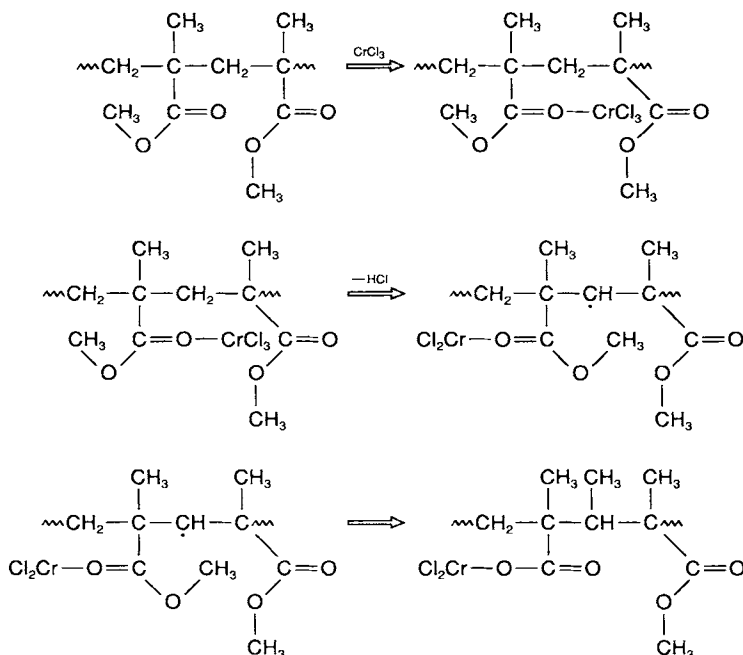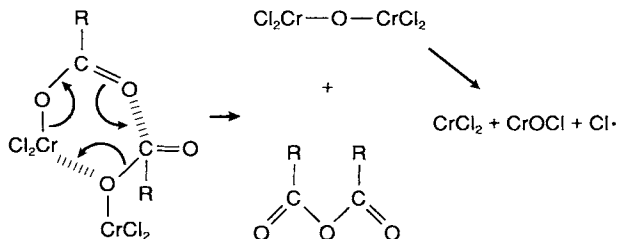
Scheme 1

The formation of CO, CO_2, and CH_4 from PMMA degradation have been explained by Manring[30-33] as arising from the cleavage of the carbomethoxy from the main chain of the polymer generating a unstable carbomethoxy radical that can decompose to generate CO and a methoxy radical or CO_2 and a methyl radical. This is illustrated in Scheme 2. The formation of olefins has been noted in this reaction by carbon NMR spectroscopy. The origin of these olefinic bands is believed to be due to the degradation of the polymer to produce unsaturated oligomers of PMMA.

All volatile products have been accounted for by the above mechanism; however, the formation of
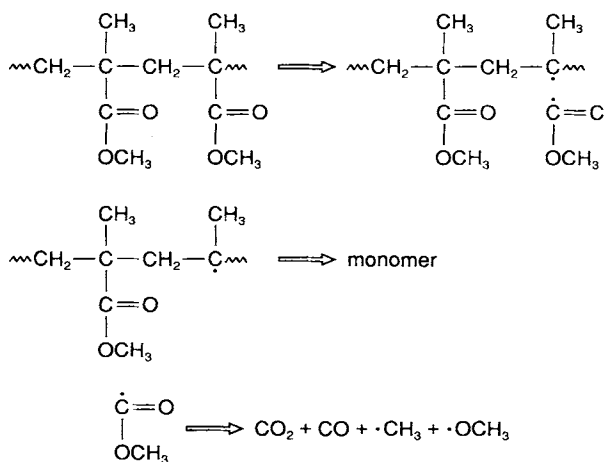
anhydride and chromium oxides are as yet not explained. As noted above, the pyrolysis of a chromium carboxylate salt generates anhydrides. The interaction of two chromium carboxylate salts may produce anhydride with the elimination of chromium oxides. This last step is entirely analogous to the results of the zinc bromide system; McNeill and McGuiness attributed the formation of zinc oxide to the decomposition of zinc carboxylate with the formation of anhydride. A possible scheme wherein this reaction may occur is shown in Scheme 3. This process involves the interaction of two chromium carboxylate salts with the formation of anhydrides, CrOCl, CrO_3, and a chlorine atom. The generation of the chlorine atom implies that another hydrogen atom may be abstracted from the PMMA chain, generating main-chain radicals that may degrade or cross-link. It is of interest to note that anhydride groups are detected even at 270°C. Since this is the last step in the mechanistic pathway, this implies that all of the steps must occur almost simulta-

Scheme 2

Scheme 3

neously. Following initial hydrogen abstraction by a chlorine atom, the subsequent steps of methyl migration, reaction with a chromium salt, and the degradation of that salt must immediately occur.

The formation of a carboxylic acid has been noted in other studies. This acid is thought to arise from the abstraction of a hydrogen atom by the carboxyl radical. A similar path is likely in this reaction. At relatively high temperatures, the evolution of methane is noted. This may be associated with the degradation of some of the remaining ester functionalities or it may come from some other source.

CONCLUSION

A variety of reactions occurs when a blend of chromium chloride and PMMA is pyrolyzed. The most important reactions seem to be (1) the coordination of chromium chloride to the carbonyl of PMMA and subsequent loss of a chlorine atom; (2) abstraction of a hydrogen atom from PMMA by this chlorine atom; (3) a concerted migration of the methyl ester to the main chain of the PMMA, leading to the formation of a chromium carboxylate salt; (4) degradation of the chromium carboxylate salt to give anhydrides; and (5) stabilization of the polymer from the chromium carboxylate formed in the previous step or stabilization by cross-linking of main-chain radicals formed in the previous step. The interaction of chromium chloride and PMMA does not offer any significant reduction in the formation of monomer and, thus, it is unlikely that it can effectively function as a flame retardant. The purpose of this investigation is to further understand possible reactions that may occur between a polymeric matrix and an additive to facilitate the design of an effective flame retardant.

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