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A COMPARATIVE STUDY OF ROLES PLAYED BY ALUMINUM TRIBROMIDE AND ALUMINUM ACETYLACETONATE ON THE THERMAL DEGRADATION OF PMMA BY SIMULTANEOUS THERMOANALYTICAL TECHNIQUES

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Blends of poly(methyl methacrylate) (PMMA) were prepared with aluminum tribromide ($AlBr_3$) and aluminum acetylacetonate ($Al(acac)_3$)in definite ratios. Thermal studies (TG-DTG-DTA) of polymer and blends with both additives were carried out in inert atmosphere to investigate the mode of degradation and the effects of stability/destability on either component. The addition of compounds in polymer resulted early decompositions. The intermediates formed during decomposition were also identified. The possible explanation of the thermal degradation reactions is advanced on the basis of results gathered. The apparent activation energy (E_o) and order of reaction (n) of the pyrolitic reactions were determined by Horowitz and Metzger method from the corresponding TG curves.

Keywords:: PMMA, $AlBr_3$, $Al(acac)_3$, Thermal degradation, Thermoanalytical characterization, IR spectroscopy, Comparative study

1. Introduction

Numerous publications have appeared on the thermal degradation of vinyl polymers in the past few decades due to their commercial importance [1-3]. Poly(methyl methacrylate) (PMMA), a vinyl polymer, has received a lot of attention owing to its widespread applications [4-7]. For instance, it has found use as intraocular lenses (IOLs) in which additives are incorporated to act as UV absorbers [8]. Various techniques have been employed by many researchers to study the different aspects of PMMA degradation [9-12]. It is well-understood that free radical generation causes the unzipping of PMMA chains to quantitative yield of monomers. The initiation step is believed to be next to double bonds at chain ends which are considered as weak links. At higher temperatures, random backbone chain scission also starts [13]. When polymers are heated in the presence of additives to high temperatures, formation of volatile liquid products and color changes take place. In case of methacrylate polymers/copolymers, the decomposition and stability relate to their structure, type of ester group, molecular weight and stereoregularity. The thermal degradation of PMMA with various additives (metal halides and other salts) was the subject of several publications [4,5, 14-17].

In a previous communication [18], we investigated the effect of aluminum ethoxide on the degradation of allyl methacrylate-methyl methacrylate (AMA-MMA) copolymers. It was observed that despite initial destabilization of the system, the stable residue from the decomposition of additive provided stabilization to the system in different temperature zones. Interestingly enough, certain products showed higher yield and a few new products were also noticed, which were absent when the components of the system were degraded alone. Physical and chemical interactions were noted due to change in the mode of degradation.

In continuation of our on-going work on thermal studies of polymeric/copolymeric systems in the presence of various additives, the current investigation describes the comparison of the

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effect of two additives, viz., aluminum tribromide ($AlBr_3$) and aluminum acetylacetonate ($Al(acac)_3$) on the pyrolysis of PMMA. Though one system, i.e., aluminum acetylacetonate and PMMA was prepared by intimate mixing of the components and the other (aluminum tribromide and PMMA) was used as film (cast from common solvent), yet the thermal studies furnished interesting results. IR spectroscopy was employed alongwith TG-DTG-DTA (under nitrogen) to identify the degradation products. Activation energy and order of reaction were determined by Horowitz and Metzger method [19].

2. Experimental

2.1 Materials

Methyl methacrylate monomer (MMA) was procured from Merck (Germany). It was washed with 5% aqueous NaOH to remove the inhibitor. It was again washed with distilled water and dried over anhydrous calcium chloride for 24 hours [20]. Finally it was distilled prior to use. Only middle portion was selected for polymerization. The initiator, 2, 2'-azobisisobutyronitrile (AIBN-supplied by Merck) was purified by recrystallization from absolute ethanol. The crystals were dried under a vacuum and stored in refrigerator (black paper wrapped around bottle). The additive, aluminum tribromide anhydrous (Aldrich-Sigma), was of analytical grade with 99% purity and was used without further purification. Aluminum acetylacetonate was prepared in the laboratory. All solvents were distilled twice before use.

2.2. Preparation of poly(methyl methacrylate) (PMMA)

The homopolymer was synthesized by free radical polymerization with AIBN as initiator by reported method [7]. The setup used for the preparation of PMMA is shown in Fig. 1. The purified monomer was degassed on high vacuum line and distilled into another dilatometer which contained the initiator (solution composition 0.7% w/v). The dilatometer was sealed under vacuum and polymerization was carried out to 5% conversion at 60 °C in a water bath. The mixture was then added to 100 mL of toluene and the polymer was precipitated from 1 L of methanol. The polymer was purified by several re-precipitations and dried under vacuum at 50 °C for 24 hours. The molecular weight was found 120000.

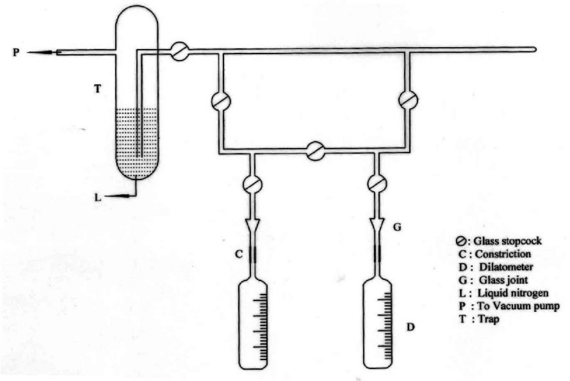

Figure 1. The vacuum line for the preparation of homopolymer.

2.3. Preparation of aluminum acetylacetonate [$Al(acac)_3$]

Aluminum acetylacetonate was prepared by already reported method [21]. An ammoniacal solution of acetylacetone (6g) in water was added to an aqueous solution of aluminum sulfate (6g). The white crystalline precipitate was filtered and washed with a little acetone. It was recrystallized in chloroform from acetone and after drying it in vacuum oven, it was kept in desiccator for future use. Its synthesis was confirmed by IR spectroscopy and XRD. This additive melted at 195°C (rather it sublimed) whereas reported melting point is 192-194°C (sublimes at 140°C at 10 mmHg).

2.4. Polymer-additive blends

(i) PMMA-$AlBr_3$ blend was prepared as film cast from a common solvent of two materials in acetone as the percent composition of 90:10 (this was arbitrarily selected keeping in view the dominance of PMMA). Both polymer and additive were dissolved separately in acetone and left overnight for complete dissolution. The solutions were then mixed in a 50 mL Pyrex conical flask which was stoppered properly. The solution was kept as such for 24 hours for thorough mixing. The resulting solution was poured onto a stainless steel boat coated with high density polythene sheet. The evaporation of solvent was allowed in dark open place and then dried in an oven at 40 °C for 36 hours. The film was transparent on the sheet indicating compatibility and uniform dispersion of the two components of the blend into each other. The film was stored in a desiccator for further use.

(ii) PMMA-$Al(acac)_3$ blend was prepared by mixing the polymer-additive powders completely in agate mortar for 5 minutes.

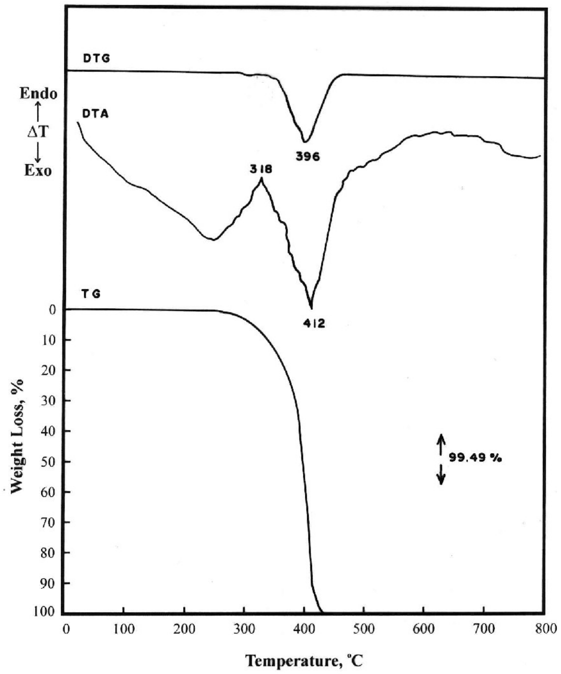

Figure 2. Thermoanalytical (TG, DTG and DTA) curves of PMMA in nitrogen atmosphere.

2.5. *Analytical techniques*

2.5.1. *Thermal analysis*

Thermoanalytical (TG-DTA-DTG) studies of solid samples were performed under inert atmosphere using NETZSCH Simultaneous Thermal Analyzer STA-409 with a temperature programmed furnace. Samples were contained in an alumina crucible Al 203 (8 mm dia x 10 mm depth) with central base recess. The crucible was then adjusted on palladium-ruthenium crucible support platform which gave a proportional signal to the recorder and computer interface to plot the weight-loss of sample against the temperature. The heating rate was kept at 10^{o}C/min. All the experiments were conducted in the temperature range of ambient to 800^{o}C. The evolved products were identified on weight-loss curve coupled with DTA results-basis.

2.5.2. *Infrared spectroscopy*

The IR spectra of polymer, additives, polymer-additive blend and residues (obtained after heating the blend at 300, 400 and 500^{o}C) were recorded on PYE UNICAM infrared spectrophotometer in the range 4000-400 cm^{-1} as KBr discs.

2.5.3. *Activation energy and order of reaction*

The activation energy (E_o) and order of reaction (n) of polymer and blend were calculated using Horowitz and Metzger method [19] from TG curves. A plot of ln ln Wo/Wt (where Wo = initial weight of material and Wt= weight of material at temperature T) against θ (θ = T-Ts) resulted in a straight line. The activation energy was determined from its slope which was equal to E_o/RTs^2 (where R = gas constant and Ts = temperature (from DTG peak) at which maximum weight-loss occurs). Order of reaction was calculated by using the relation between reaction order and concentration at maximum slope.

3. Results and Discussion

3.1. *Thermal analysis*

(i) Thermal analysis of PMMA is an extensively studied area both in air and under nitrogen. It undergoes one-step degradation and monomer is yielded quantitatively with no residue at the end. Our investigations (Fig. 2) confirm this thermal behavior of PMMA. It starts losing weight around 250^{o}C and the single stage decomposition terminates around 440^{o}C. Two DTA peaks at 318 and 412^{o}C and a DTG peak (for maximum weight-loss in the only step of pyrolysis) at 396^{o}C corroborate the well-established thermal degradation of PMMA. The degradation begins near the chain ends (next to double bonds—DTA peak at 318^{o}C) and the unzipping of chains furnishes monomers. Random backbone scission (DTA peak at 412^{o}C) also contributes towards the production of monomers at some later stage.

(ii) Thermal behavior of aluminum tribromide has not been studied, though the corresponding salt with chlorine was blended with polystyrene to investigate the catalytic effect [2]. TG of $AlBr_3$ (Fig. 3) shows a two-step degradation (under nitrogen) starting to decompose at 70^{o}C. The first small portion of weight-loss (about 5-6%) is attributed to the elimination of absorbed moisture. The main stage of splitting commences at 108^{o}C and ends at 223^{o}C exhibiting an overall weight loss of ~76%. This part of decomposition is marked by the evolution of Br (nascent), Br_2 and $Br^{\cdot}$. A DTG peak at 215^{o}C gives the temperature of maximum weight-loss for this stage. The last stage of degradation reveals a very slow loss of weight over a temperature range of 223-800^{o}C. Upto 660^{o}C, the weight-loss is only 6-7% which may be attributed to the loss of bromine (either in atomic or radical form). At 660^{o}C, aluminum metal starts melting and shows a weight-loss of 2.5% due to its evaporation. Three DTA peaks (95, 375 and 588 ^{o}C) give the energy changes for the degradation reactions taking place in different temperatures zones. The residue which is almost 9% of the original weight is assigned to aluminum metal.

The blend (PMMA:$AlBr_3$, 90:10%) degraded in two steps (Fig. 4). The first stage, which started at 50^{o}C and proceeded to 190^{o}C, showed weight-loss of 21%. This portion of pyrolysis is attributed to the degradation of additive ($AlBr_3$). It is noteworthy that $AlBr_3$ commenced to decompose at 70 ^{o}C when heated alone. It is also interesting to note that more weight-loss is observed for this stage of degradation than the overall percentage of additive in the blend. It is believed that although additive begins to disintegrate earlier than the temperature at which it started to decompose alone, it causes polymer to lose weight at an early temperature. Likewise, in the presence of polymer, additive (due to interaction with polymer pendant groups) showed an early splitting. This shows destabilization of additive and polymer in this part of heating. However, it certainly gives an indication of interaction between the two components of the system. Formation of nascent bromine (Br) and generation of bromine free radicals (Br) are believed to be the cause of destabilization of polymer. Two peaks of DTG (121and 170^{o}C) and three DTA peaks (131, 148 and 181^{o}C) are found for this stage of pyrolysis. The second stage starts immediately after the completion of first stage (190^{o}C) and exhibits a weight-loss of 76%. The decrease in weight of the degrading blend is very slow from 190^{o}C to 360^{o}C as if the splitting is being hindered due to the interaction of degrading species (formation of new links/bonds which prevent quick weight-loss cannot be excluded in this zone). Alternatively, the degrading system becomes stabilized in this region. However, around 360^{o}C the energy content overpowers the holding forces (binding forces) and the system exhibits a rapid weight-loss. The degradation process completes at 440^{o}C with the elimination of a number of products including those which were absent when the components of the blend were pyrolyzed alone. For the slower portion of degradation of the final step, two DTA peaks (288 and 335^{o}C) are observed which give the energy changes occurring due to the interaction of blended components. For the faster portion of the final degradation step, one DTA peak (400^{o}C) and one DTG peak (395^{o}C) appear. The residue is only 3.56 % of the original weight of the blend and is

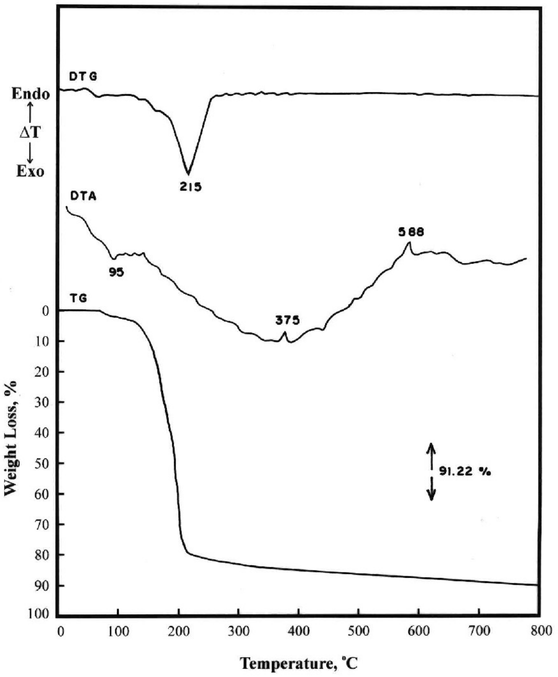

Figure 3. Thermoanalytical (TG, DTG and DTA) curves of aluminium tribromide in nitrogen atmosphere.

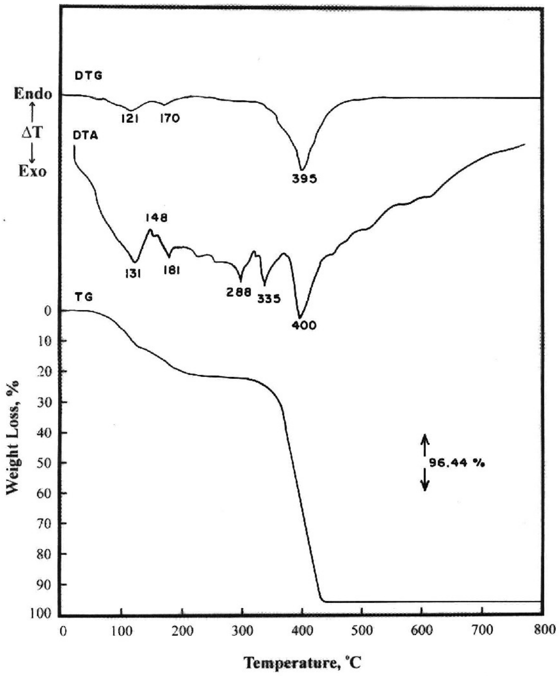

Figure 4. Thermoanalytical (TG, DTG and DTA) curves of PMMA-$AlBr_3$ blend in nitrogen atmosphere.

identified as aluminum attached with oxygen and carbon, pure aluminum metal and char [22].

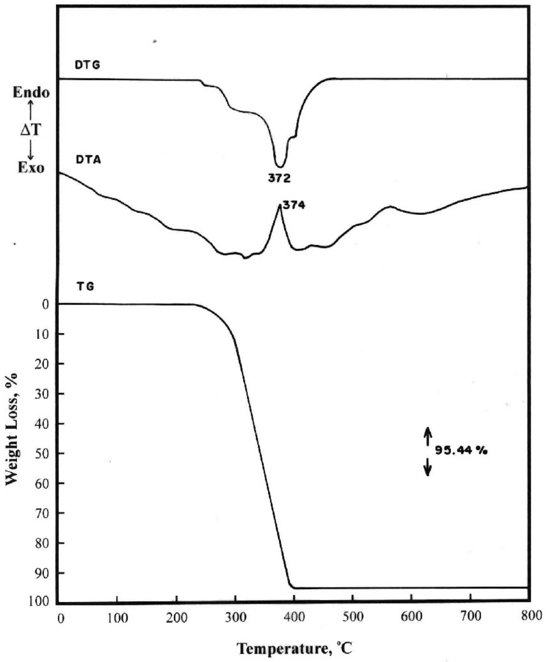

Figure 5. Thermoanalytical (TG, DTG and DTA) curves of PMMA-Al(acac)$_3$ blend in nitrogen atmosphere.

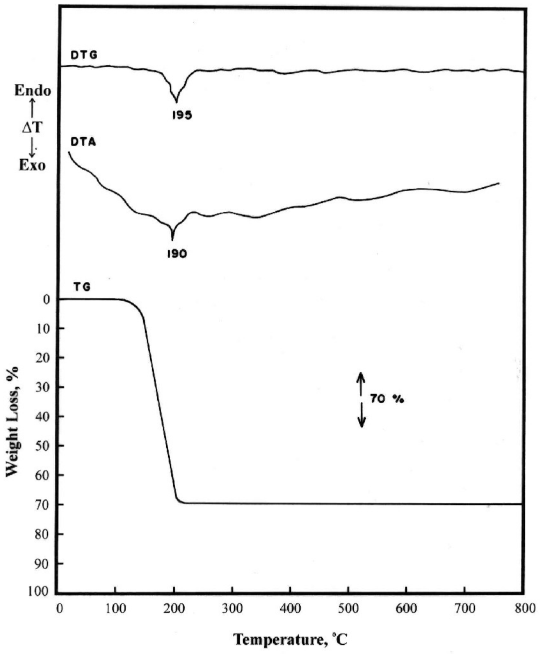

Figure 6. Thermoanalytical (TG, DTG and DTA) curves of aluminum acetylacetonate in nitrogen atmosphere.

(iii) In case of PMMA-Al(acac)$_3$, blend was prepared (PMMA:Al(acac)$_3$ 90:10 (percentage)) as intimate mixture of powders. The system appears to be destabilized in the early part of degradation. PMMA alone started to lose weight around 250^{o}C whereas blend (Fig.5) and additive (Fig.6) showed the first signs of weight-loss at 234 and 112^{o}C, respectively. The polymer stabilized the additive (additive's degradation/sublimation was prevented by the presence of polymer—interaction from the very early stage is established) while the additive destabilized the polymer by 16 ^{o}C. Single stage degradation is evident for individual components and blends. Two DTA peaks are observed for PMMA and one each for the additive and blend (Table 1). Only PMMA leaves no residue at the end of degradation; additive gives 30% around 200^{o}C (termination of degradation) and blend provides 4.56% around 400^{o}C (completion of degradation). The evidence of interaction—physical as well as chemical—comes from the identification of degradation products and residues.

3.2. *IR spectra*

(i) IR spectrum of the pure additive shows typical stretchings for $AlBr_3$. As additive absorbs moisture so a broad band in the region 3600-3000 cm^{-1} confirms the presence of H_2O. The other peaks at 1603, 1089, 676, 580, 478 cm^{-1} arise due to Al-Br bond.

The bands in the region 1725-1735 cm^{-1} give the presence of ester linkages for PMMA. The absence of peaks in the region 1630-1640 cm^{-1} clearly indicates the polymeric form of the compound and absence of monomeric C=C double bonds. The saturated C-H stretchings appear around 3000 cm^{-1}.

The IR spectrum of the blend—film was produced with the percentage ratio of PMMA to $AlBr_3$, 90:10—gives characteristic peaks for PMMA with displaced positions. This may be attributed to the presence of additive alongwith the physical interactions the additive may have developed with the polymer. For instance, the peaks for ester linkages of PMMA appear now at lower frequencies, i. e., around 1716 cm^{-1}. Likewise, Al-Br stretchings either seem suppressed or appear at higher frequencies. Peaks at 1616, 686, 593 cm^{-1} clearly reveal the interaction between PMMA and $AlBr_3$ [23]. The film cast by common solvent was transparent which confirmed the compatibility of the components and mixing at molecular level.

Table 1. Comparative TG, DTG and DTA data for additives, polymer and polymer-additive blends

Additive/polymer/blend composition (w/w %)	TG (^{o}C)			DTG (^{o}C)			DTA (^{o}C)	
	T_i	T_{50}	T_{100}	I	II	III	Peaks	Thermal effect
$AlBr_3$	70	200	--	215	--	--	95 375 588	Exo Endo Endo
$Al(acac)_3$	112	185	--	195	--	--	190	Exo
PMMA	250	390	440	396			318 412	Endo Exo
PMMA-$AlBr_3$ (90:10)	50	390	--	121	170	395	131 148 181 288 335 400	Exo Endo Exo Exo Exo Exo
PMMA-$Al(acac)_3$ (90:10)	234	345	--	372	--	--	374	Endo

Endo = Endothermic
Exo = Exothermic
T_i = Temperature corresponding to the start of weight loss.
T_{50} = Temperature at which 50% weight loss is observed.
T_{100} = Temperature for 100% weight loss.

For gaining conclusive evidence regarding the products' identification, the blend was heated at 300, 400 and 500 ^{o}C for a minute and the residues were collected. IR spectra of residues were taken as KBr discs. The IR spectra of residues helped in identifying the nature of intermediates at different temperatures.

The IR spectra of the blend (90% PMMA:10% $AlBr_3$) and residue of this blend after heating at 300 ^{o}C are not showing much difference thereby revealing that after the initial low-temperature decomposition of additive (it is believed that Br^-, Br, Br_2, HBr, CH_4, CO, CO_2, CH_3Br, CH_3OH and certain other smaller molecules evolve as the temperature rises to 300^{o}C) which also causes a minor degradation of polymer; the system is intact with aluminum forming bonds with ester oxygen of several chains, thus, stabilizing the blend in this temperature zone. The amount of moisture appears to have diminished which may be attributed to its complete elimination by 300^{o}C and then reabsorbance by the undegraded $AlBr_3$ in the residue. TG curve is in agreement with IR findings as rate of mass loss is slow around 300^{o}C. The products are either larger fractions of slightly degraded polymer, i. e., tetramers, pentamers, etc. or oligomers bonded to aluminum through ester oxygen or oligomers with bromine that replaces the $–CH_3$ group other than ester $–CH_3$. The production of methanol seems to arise due to the involvement of another interaction, i. e., Al…O=C<.

The IR of residue (when the blend was heated at 400^{o}C) was markedly different from that which was recorded for the residue when the blend was heated at 300^{o}C. As the major and quick (sharp fall in TG traces, Fig. 4) weight-loss is observed in this region (300 to 400^{o}C), the products seem to be those which are expected prior to completion of degradation process, i. e., undegraded portion of polymer end chains, Al-O linked with smaller carbon moieties, absence of ester linkages, etc. However, some C-H stretchings of $–CH_3$ and $-CH_2-$ can still be observed (3749, 3675, 3648 cm^{-1}) [22,23]. The bromine content has almost vanished. Few bromine atoms are believed to be still bonded to aluminum which, in turn, appears to have developed true bonds with oxygen of ester linkages.

The heating of blend to 500^{o}C was carried out to study the nature of residue only. The degradation of the blend completed around 440^{o}C (Fig. 4). The IR spectrum of the residue gives evidence for Al-O-C linkages (940-1200 cm^{-1}), C-C bonds (1300-800 cm^{-1} which may be ascribed to char) and Al-C linkages (400-900 cm^{-1} that may be attributed to Al_4C_3) [22]. The presence of aluminum metal cannot be excluded on visual inspection-basis.

The IR investigations of residues at 300, 400 and 500^{o}C helped monitor the progress of degradation. These studies furnished enough evidence which suggests that apart from earlier low-temperature degradation, the blend appears stable around 300^{o}C (the nature of products found at this temperature is a convincing clue). In the region around 400^{o}C, the energy content is so high that the bonds between Al and O (both ester as well as carbonyl) cannot block the unzipping process of main chain scission. The presence of Al-O and Al-C linkages in residue at 500^{o}C indicates the role played by aluminum of the additive in modifying the overall degradation mechanism of polymer. Bromine (free radicals) was thought to initiate the early decomposition of the MMA units. In later part of the degradation, it is Al which interacts with disintegrating polymer, thus, modifying the pattern of pyrolysis and mode of production of degradation products.

(ii) In case of PMMA-Al(acac)$_3$, blend, IR spectroscopy reveals the formation of acetone, acetylacetone and methyl methacrylate in case of blend whereas the evolution of gases, i. e., methane, carbon monoxide, carbon dioxide, dimethyl ketene, and ethylene appears to have occurred as a logical course of degradation. PMMA rendered only monomer while additive either partially sublimed or degraded with the evolution of carbon monoxide and acetylacetone. Residue was Al_2O_3 for additive whereas it was Al_2O_3 and char for blend. The stable residue from the decomposition of additive not only acted as heat sink in different temperature zones of blend pyrolysis but also changed the nature of degradation products through chemical interaction.

Table 2. Activation energies and order of reaction for PMMA and PMMA-additive blends

Sample	E_o (KCal/mol)	Order of reaction (n)
PMMA	138.9	3/2
PMMA-AlBr$_3$ (90:10)	41.4	½
PMMA-Al(acac)$_3$ (90:10)	25.1	½

Activation energy and order of reaction are tabulated in Table 2 for polymer, additives and blends and the plots of ln ln Wo/Wt versus θ are reproduced in Figs. 7-9 for polymer and blends. Further research work in this direction employing some other analytical techniques to substantiate the degradation mechanism is underway.

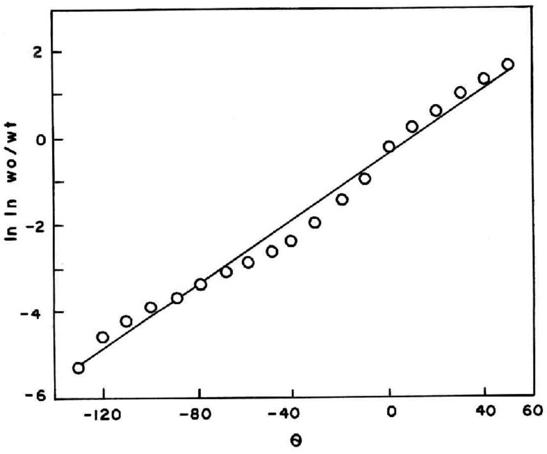

Figure 7. Determination of activation energy of thermally degraded of PMMA.

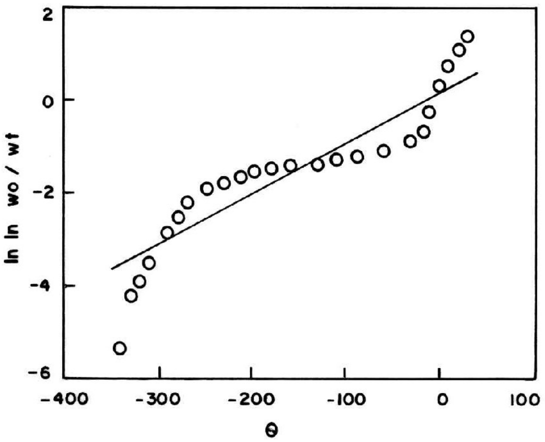

Figure 8. Determination of activation energy of thermally degraded of PMMA-AlBr$_3$ blend.

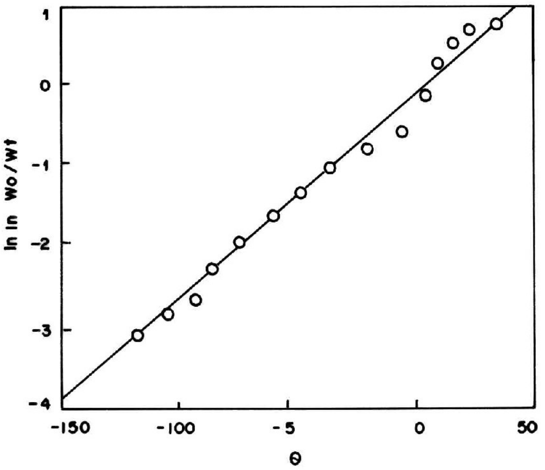

Figure 9. Determination of activation energy of thermally degraded of PMMA-Al(acac)$_3$ blend.

Acknowledgements

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