# THERMAL DEGRADATION OF POLY(GLYCIDYLMETHACRYLATE) AND COPOLYMERS OF GLYCIDYLMETHACRYLATE-METHYLMETHACRYLATE

**MUHAMMAD NAWAZ**

A dissertation submitted in partial fulfilment of the
requirement for the degree of

MASTER OF PHILOSOPHY
IN
ORGANIC CHEMISTRY

*DEPARTMENT OF CHEMISTRY*
*QUAID-I-AZAM UNIVERSITY*
*ISLAMABAD*
*"1 9 9 1"*

DEPARTMENT OF CHEMISTRY
Quaid-i-Azam University

This is to certify that this dissertation submitted by Mr. **Muhammad Nawaz** is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad as satisfying the dissertation requirements for the degree of **Master of Philosophy** in Organic Chemistry.

COMMITTEE

1. DR. MRS. SHAGUFTA ZULFIQAR ____________________
   Assistant Professor and
   Supervisor
   Department of Chemistry,
   Quaid-i-Azam University,
   Islamabad.

2. DR. MRS. MASHOODA HASAN ____________________
   Professor & Chairperson,
   Department of Chemistry,
   Quaid-i-Azam University,
   Islamabad.

3. EXTERNAL EXAMINER ____________________

DEDICATED

TO

MY

FAMILY

# CONTENTS

CHAPTER - I

CHAPTER - II

CHAPTER - III

CHAPTER - IV

# ACKNOWLEDGEMENTS

All praises for Allah and all my respects for his Holy Prophet (SAW).

I express a great pleasure and deep gratitude to my respected supervisor Dr. Mrs. Shagufta Zulfiqar, Assistant Professor, whose wise, inspirable guidance, vigilant sympathy, encouragement, and expertise in this field made me able to get the degree of Master of Philosophy. A note of keen appreciation also goes to Dr. M. Zulfiqar for his help during my research work.

I am grateful to Dr. Mrs. Mashooda Hasan, Professor and Chairperson, for providing all possible facilities. I am also thankful to Dr. Mrs. Roshan Ahmad for her help in IR spectroscopy.

Heartiest thanks to Mr. Khalid Masud, Ph.D. scholar, for his valuable suggestions and Moral support. Special gratitudes to my laboratory fellow Miss Anila for her kind behaviour. Thanks also due to Miss Asifa Piracha for her help in thermal degradation. Thanks to all my friends and well wishers for their help and cooperation.

**MUHAMMAD NAWAZ**

# ABSTRACT

The degradation behaviours of poly(glycidyl methacrylate), three glycidyl methacrylate-methyl methacrylate copolymers have been studied, and poly (methyl methacrylate) have been compared by using thermogravimetry and Thermal Volatilization Analysis (TVA) under vacuum, with programmed heating at 10°C/min. Volatile products have been separated by sub-ambient thermal volatilization analysis (SATVA) and identified by IR and mass spectroscopy. When poly(glycidyl methacrylate) decomposes thermally at temperatures upto 500°C, the major product is monomer due to depolymerization. Minor products arising from ester decomposition are acrolein, allyl alcohol, glicidol, carbon dioxide isobutene, propene, and carbonmonoxide. On degradation of copolymers, the major products are the two monomers, along with minor products arising from the ester decomposition as stated above. Copolymers also show, however, the formation of anhydride ring structures together with small amounts of methanol in volatile products. A mechanism which accounts for all the products has been formulated.

# CHAPTER - I

# INTRODUCTION

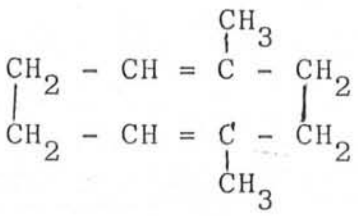
# INTRODUCTION

## Polymer Science ——— Past and Future

A polymer is a substance of high molecular weight which may occur in nature or be chemically synthesized and is characterized by the regular or irregular repitition of one or more types of chemical units. Natural polymers such as, wood, cotton, silk, wool, rubber and many other types of gums have been used for centuries in all kinds of practical applications, but their chemical composition and structures were unknown and they were believed to be made up of colloidal aggregates of small molecules. The first statement that these naturally occurring substances were polymeric in nature, was made in 1871 by Hasiwetz and Habermann[1].

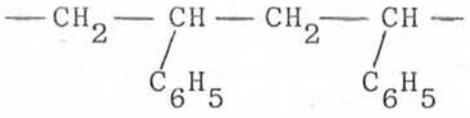
May polymeric substances were discovered by early organic chemists in an attempt to prepare new organic compounds, in high yields but they were discarded as oils, fat or undesirable residue. At that time no appropriate methods were available for the determination of molecular weight of high molecular weight substances. Cryoscopic and vapour density methods were less occurate in the high molecular weight range.

The inability of the investigators to account for the end groups was another barrier in determining the polymer structure. In 1905 the chain structure was rejected in favour of a cyclic dimer (I) since ozonlysis of natural rubber produced levulinic acid[2] and in 1914 the dimer structure was changed in favour of larger rings[3].



(I)

In 1920 staudinger[4] proposed chain formula for polystyrene (II) and polyoxymethylene (III).



(II)

$-CH_2-O-CH_2-O-$

(III)

In 1929 W.H. Carothers prepared polymeric molecules through known organic reactions and the properties of the products were then correlated with polymer structure[5].

Thus intensive fundamental studies by the workers like Stauinger, Carothers, Mark and Flory lead to much clear understanding of the process of polymerization and their nature and properties.

After 1940 successful extension amplification and refinement occurred in all directions specially, many new monomers, new catalytic systems and new polymerization techniques were developed. New techniques in polymerization are providing useful forms of polymers which had been prepared previously but were only low molecular weight forms with undesirable physical properties and were therefore cast aside. Polyformaldehyde is an excellent example of rediscovered polymer. Today it is possible to produce high polymers "Tailor made" for specific purposes or to suite special needs.

The impact of polymers on our present life is almost incalculable, products made from polymers——clothing made from synthetic fibers, polystyrene cups, fiberglass boats and water tanks, Nylon bearings, plastic shopping bags, polymer based paints, epoxy glue, polyurethane foams and cushions, silicon heart valves, teflon coated cook wares-----and this list is almost endless. Add to this artificial heart, heart valves, heart pumps, tissue adhesives, artificial skin, bones, joints, teath, contact lenses, artificial kidney and diffusion controlling membranes are all made from synthetic polymers. Rapid progress in the field of polymers, thus, reveals that coming age will be actually the "Polymer age".

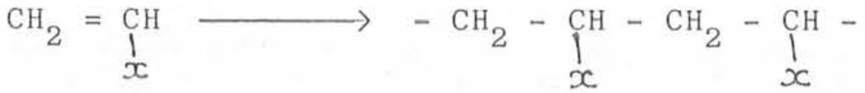
## Classification

In 1929 Carthers[6] divided polymers into two main groups.

(a) Condensation polymers: Polymers in which the molecular formula of the repeat unit lacks certain atoms present in the monomer from which it was formed for example formation of polyester.

$$x\,HO-R-OH + x\,HOOCRCOOH \longrightarrow HO|RCOORCOO|_{x}\!-H \quad + (2x-1)H_2O.$$

(b) Addition polymers: Polymers in which the repeat units have same composition as that of monomer.



$$CH_2 = \underset{x}{CH} \longrightarrow -CH_2-\underset{x}{CH}-CH_2-\underset{x}{CH}-$$

Flory[7] classified the polymers on the basis of the mechanism of polymerization as,

(a) Step polymerization: Mechanism of polymerization in which polymers are formed by the stepwise intermolecular condensation of reactive groups, with or without elimination of small molecules. Monomer disappears early and molecular weight rises near the completion of the reaction bifunctional monomers gives rise to linear chains. The monomers with functionality greater than two yield branched or crosslinked polymers.

(b) Chain polymerization: In chain polymerization polymers ordinarily result from chain reaction involving some sort of active centre, which is highly unstable usually transient and propagation occurs rapidly relative to initiation. Active centre may be free radical, anion, or cation, chain polymerization is further classified into,

(i) Free radical polymerization.

(ii) Ionic polymerization.

Free radical polymerization has three distinct steps.

(a) Initiation: It involves the decomposition of the initiator to yield a pair of the free radicals and then addition of this initiator molecular to the monomer.

$$I \longrightarrow 2R^{\cdot}$$

$$R^{\cdot} + M \longrightarrow M_1^{\cdot}$$

(b) Propagation: Successive addition of monomers to the radical formed is called propagation.

$$M_1^{\cdot} + M \longrightarrow M_2^{\cdot}$$

$$M_2^{\cdot} + M \longrightarrow M_3^{\cdot}$$

$$M_n^{\cdot} + M \longrightarrow Mn + 1$$

(c) Termination: It can occur by any of the three ways.

(i) Bimolecular coupling: Two growing chains can cuple as

$$M_x^\cdot + M_y^\cdot \longrightarrow M_{xy}$$

(ii) Disproportionation: Transfer of a free radical from one chain to the other is called disproportionation.

$$M_x^\cdot + M_y^\cdot \longrightarrow M_x + M_y$$

(iii) Chain transfer: Through transfer of a hydrogen free radical or other atom of the solvent to the growing chain.

$$M_x^\cdot + RSH \longrightarrow M_xH + RS^\cdot$$

When active centres initiating the chain reactions are ions, then mechanism is called ionic polymerization depending upon the charges, polymerization may be anionic or cationic. The charge carriers in cationic and anionic polymerizations are carbonium ions and carbanions respectively.

Stanford and Stepto[8] have, recently, revised the classification of polymers into random and sequential polymerization. The basis of their classification was statistical in nature. In the random type, polymerization proceeds through random intermolecular reaction of pairs of groups whereas, in sequential polymerization a polymer is formed by sequential addition of monomers to a growing polymer chain. The former type of polymerization resembles Flory's Step growth polymerization where like groups have equal reactivity.

The length of a polymer chain is specified by the number of repeat units in the chain. This is known as degree of polymerization (DP)[9]. The molecular weight of the polymer is the product of the molecular weight of the repeat unit and the degree of polymerization.

## Copolymerization:

Although polymerization of organic compounds has been known more than a century ago. But copolymerization (Simulataneous polymerization of two or more monomers) was not investigated until about 1911. when copolymers of olifines and diolifines were found to have rubbry properties.

In 1930's it was found that monomers differed markedly in their tendencies to enter into copolymers. In 1939 staudinger fractionated a vinylchloride vinyl acetate copolymer made from a mixture of equimolar quantities of each monomer, but the ratios of the two monomers in the copolymer were not equal instead they were 9:3, 7:3, 5:3, and 5:7. It was found that found that oxylic esters enter to copolymers faster than did the vinyl chloride.

Latter on it was found that monomers like Maleic anhydride and other monomers which homopolymerize with great difficulty were found to copolymerize redily with styrene and vinyl chloride.

Copolymers, thus can be classifed occording to the arrangement of the monomer units along the chain. According to this, there are four types of copolymers.

a) Random Copolymers.
b) Alternating Copolymers.
c) Block Copolymers.
d) Graft copolymers.

## Importance of Copolymerization:

Copolymers have been found to be more useful than homopolymers. Copolymers have more desirable properties both mechanical and chemical. Copolymers of MMA, for example, with acrylonitrile 1,3-butadiene and styrene all have valuable significance over PMMA. MMA-steyrene copolymer is more heat resisting and transparent than PMMA.

Copolymerization lowers the orystallinity, so valuable in the use of polymers like glass. Ethylene-butene (1-3%) is used in blown bottles due to its lower crystallinity.

Copolymerization enhanced the properties of the homopolymer without loss of other desirable properties. A number of copolymers of styrene with a minor amount of comonomers have enhanced heat and impact resistance without loosing other properties of the polystyrene.

Copolymers thus have more mechanical strength and elasticity than their respective homopolymers. Butadiene homopolymer has poor properties as length abrasion, resistance and solvent resistance but Butadiene-styrene copolymer (SBR), these properties are to a greater degree.

## Applications of Copolymers of Glycidyl Methacrylate:

Copolymers containing glycidyl methacrylate (GMA) as one of the monomers belong to the class of potential functional polymers. The high reactivity of the epoxy group to large varieties of the reagents provide novel routs to prepare numerous multifunctional polymers through chemical modifications of these polymers[10,11]. Thus the copolymers based on GMA have found extensive application as polymeric reagents, carriers for immobilization of enzymes and supports for affinity chromatography as well as in microelectronics research[12-16].

A polythiophenylene - $C_2H_4$ and Glycidyl methacrylate copolymer have elongation 25% and izod impact strength 4 Kg/cm as compared to 0 and 2 respectively forpolythiophenylene. Copolymers of methylmethacrylate, methacrylic aic and Glycidyl methacrylate has good adhesion and folding and blocking resistance. Copolymers of monomers with epoxy group and vinylchloride have good melt properties and film forming properties so has applications in plastics and plastic film forming industries. Ethylene and Glycidyl methacrylate copolymers has applications in blown bottles.

## Degradation of Polymers:

The term "Degradation" usually refers to the breaking of bonds in the backbone of polymer chain, thus changing the molecular weight and causing the deterioration of those properties[17] of polymers which make then useful commercially as rubber, plastics, and fibers.

Degradation usually takes place, due to the effect of high temperature, high energy radiations, bioactive materials and mechanical influences and accordingly it can be classified as.

1. Biodegradation.
2. Chemical degradation.
3. Physical degradation.

## 1. Biodegradation:

A series of natural processes resulting from the activities of microorganisims by which organic materials are converted to simpler compounds and finally to inorganic substances, ($CO_2$, $CH_4$, $H_2O$, $NO_3^{-1}$, $SO_2^{-2}$, $PO_4^{-3}$ etc) most of which are utilizable as nutrients by green plants is called biodegradation.

In nature two groups of organisms are responsible for biodegradation i.e. the heterotrophic bacteria and the fungi. Apart from the biodegradability of a compound many factors effects the rate of biodegradation in a given environment. The rate of bio-degradation depends initially on the interaction between the componds and the organism. The concentration of the degrading population. The compound concentration and the physicochemical parameters of the environment (temperature, pH, oxidation potential, salinity, nutrient. content, presence of toxic materiasls etc.).

Only polyethylene undergo biodegradation among the commerical packaging plastics but for the reasonable degree of biodegradation require the molecular weight of the sample should be low.

### 2. Chemical Degradation:

Chemical degradation is caused by the action of various chemical agents such as water, acids, amiens, alcohols, or oxygen etc. degradation by atmospheric oxygen and other oxidents is called oxidative degradation. When degradation is brought about by heat in the presence of oxygen that is Thermo-oxidative degradation.

The resistance of a polymer to oxidizing agents depends upon its structure and primarily on the presence of readily oxidizable groups and bonds in macromolecules.

### Physical Degradation:

Physical degradation can further be classified as:

(a) Mechanical Degradation: Structural changes of a polymer due to various kinds of mechanical processes is termed as mechanical degradation. Mechanical degradation may be brought about by, milling, shear, tensile stress, compression etc.

(b) Photo Degradation: Photodegradation occurs under the action of radiation during outdoor weathering and the resistance of a polymer to this type of degradation radiation of the wavelength of light, the condition of experiment and the nature of polymer.

(c) Thermal Degradation: Thermal degradation occurs at high temperature, when heat treatment of the polymer causes rupture of the chemical bonds, elimination of substituted elements, atoms or side chains depending upon the structure of the polymer and various types of defects in the polymer chain.

Various factors which determine the stability[18] of the polymer are; physical state of polymer, nature and intensity of energy, presence of impurities structure of the polymer and reactivity of the medium.

Thermal degradation has been broadly divided into[19],

(a) Chain scission reactions or depolymerization
(b) Non chain scission or substituent reactions.

Depolymerization process is characterized by breaking of the main polymer chain backbone, so that the ultimate products are monomer or closely related to it. In substituent reactions. Substituents on the backbone of the polymer chain are eleiminated or modified in such a way that the chemical nature of the repeating units is changed. A large variety of addition polymers depolymerize thermally, and detailed studies have shown quite distinct behaviour. Poly (ethylene) and poly(methylmethacrylate) are the two extremes.

Montrall and Simha[20] assumed that since there is a regular repeated pattern of bond strength throughout the polymer chain, Random chain scission is likely to occur. The early studies of thermal degradation of poly(ethylene)[21] showed that the degradation products are a continuous spectrum of hydrocarbon fragments as predicted by the above theory. But in later work[22] some discrepancies were found. According to the theory, the rate of bond scission should remain constant throughout the degradation, but Oak and Ri chards[22] found that it is decreased with time. This was explained by the presence of some weak linkages present in the chain due to traces of copolymerized oxygen.

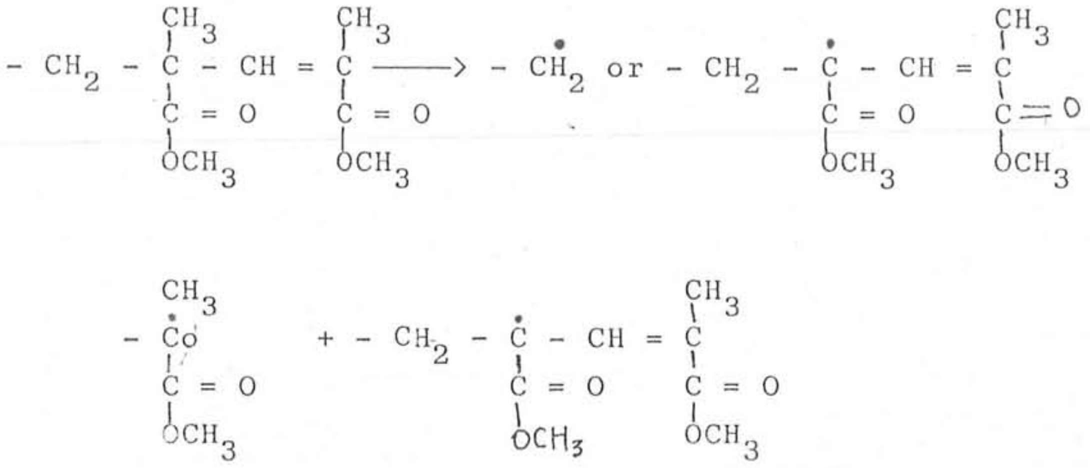
## Thermal Degradation of Polymethylmethacrylate:

Votinov and co-workers[23] were the first investigators to study the thermal degradation of poly(methyl methacrylate) in nitrogen atmosphere at 350°, 400°, and 450°C. They explained their results in terms of a random scission process of carbon-carbon bonds but such a process would have given a broad spectrum of molecular fragments. In the temperature range 150-500°C, the major product is monomer only. So this initial proposal was not considered applicable to poly(methyl methacrylate).

Change in the molecular weight of the residue formed during the thermal degradation of PMMA under vacuum at 160° and 200°C was determined by Grassie and Melville[24].

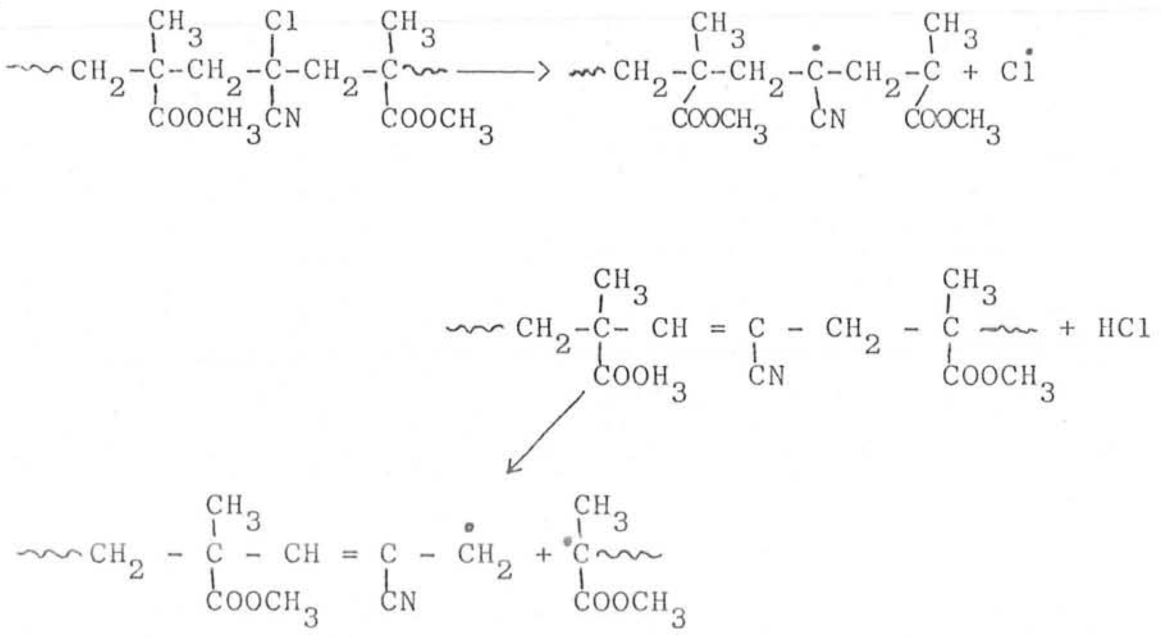
The rate of monomer production was determined and the molecular weight of the residues were determined. Monomer obtained was in quantitative yields. Thus a free radical chain end mechanism was proposed for the initial changes of such degradation. Grassie and Melville[25] interpreted the mechanism of thermal degradation of PMMA, as the formation of free radicals Via a random chain scission process, followed by unzipping to monomer. Grassie and Vance[26] showed that unstable chain ends are those with a double bond. The termination in the free radical polymerization has been shown by disproportion, so that half of the polymer chain has a double bond at one end. Madorsky[27] and Hart[28] measured the rate of volatilization of poly(methylmethacrylate) of defferent molecular weights at temperatures in the range of 240-270°C. Activation energy (33 Kcal/mole) obtained agreed well with that obtained by Grassie and Melville[24,25].

It has now been established that thermal decomposition of poly(methylmethacrylate) involves linkage of head to head type, but the majority of the proposals are based upon the repeat units derived from the head to tail polymerization of acrylic monomers. Following scheme shows the monomer production by the thermal decomposition of PMMA.



## Thermal Degradation of Copolymers of Methyl Methacrylate.

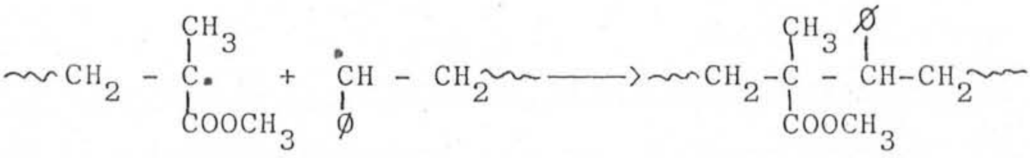
It is a well known fact that stability of a polymer may be profoundly effected by the presence of quite small proportions of comonomers. Sometimes the polymer is stablized, but in other cases, and perhaps more frequently destablization results. In either event. It has usually been possible to explain the phenomenon observed in terms of the way in which the comonomers interforce with the known degradation mechanism. No significant quantities of volatile products are formed from poly (methylmethacrylate) below 200°C. But in a copolymer of methyl methacrylate and 2-chloroacrylonitrile[41], however, volatile products methyl methacrylate, hydrogen chloride and traces of 2-chloroacrylonitrile appears even at 140°C. In this copolymer chain scission and the reaction products may be accounted for as follows, untill the best step when the radicals are apparently capable of dipolymerising to monomer.



Monomer

A number of comonomers whose hompolymers do not depolymerize to monomer are capable of blocking monomer-producing depolymerization. For example a small amount of copolymerized ethyl acrylate have been used industrially to stabilize poly(methyl methacylate) towards depolymerisation. Depolymerization proceeds through methylmethacrylate units from the point of initiation but acrylate units cannot be liberated so that the terminal acrylate radicals are instead deactivated[42].

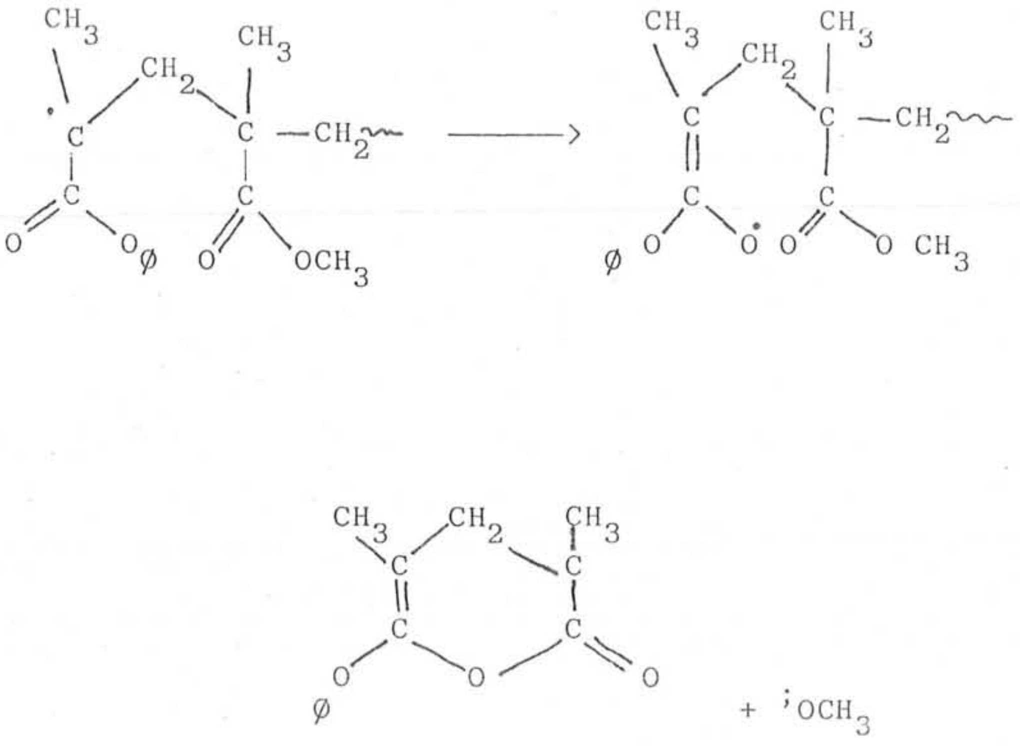
In poly(methylmethacrylate) termination occurs by disproportionation so that about half of the polymer chains contain unsaturated chain ends. But when styrene is copolymerised with MMA. The termination occurs between unlike radicals.



$$\sim CH_2 - \underset{COOCH_3}{\overset{CH_3}{C^{\bullet}}} + \underset{\phi}{\overset{\bullet}{C}H} - CH_2\sim \longrightarrow \sim CH_2 - \underset{COOCH_3}{\overset{CH_3}{C}} - \overset{\phi}{C}H - CH_2\sim$$

Thus due to this "cross termination" number of unsaturated chain ends decreases considerably, through which initiation readily starts. So the initial rate of depolymerization of the 1/4 styrene/MMA copolymer degraded at 300°C is roughly half to that of pure PMMA degraded at 260°C.

S. Zulfiqar, M. Zulfiqar, Tasneem Kausar and I.C. Mcneil in a recent paper[43] studied the thermal degradation of copolymers of methyl methacrylate and phenyl methacrylate and observed an increase in the stability of methyl methacrylate homopolymer. This increased stability has been atributed to the formation of anhydride rings during thermal degradation, as shown below.



Thus a comonomer may make a homopolymer stable or unstable. A comonomer may have an unstable structure which can induce a new kind of degradation reaction as in the effect of 2-chloroacrylonitrile and poly (methyl methacrylate). Stability of a homopolymer may be due to the formation of anhydride rings as in PMA/MMA copolymer.

## Non-Scission or Substituent Reactions:

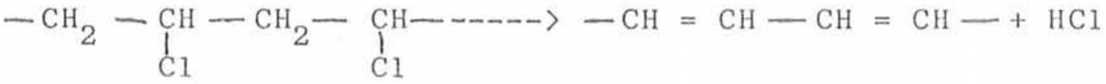
The essential main chain scission features of a polymer remains as such, substituents, however can modify these reactions. These reactions occurs at relatively lower temperature than those reactions at which main chain bonds are broken. Substituent reactions which may occur along with the main chain scission processes are of three types.

(a) Elimination reactions.

(b) Cyclization reactions.

(c) Ester decomposition.

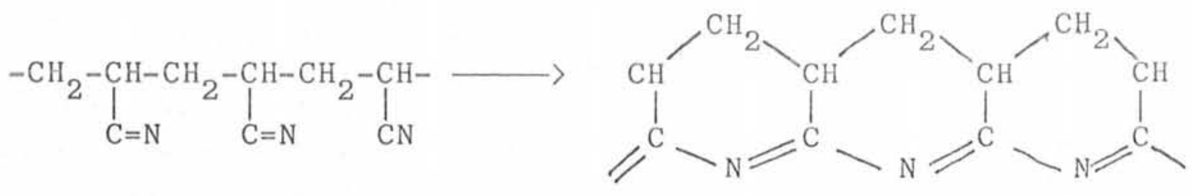
Poly (vinyl chloride) is an example of elimination reaction. In PVC a conjugated polymer chain is produced by the elimination of hydrogen chloride.



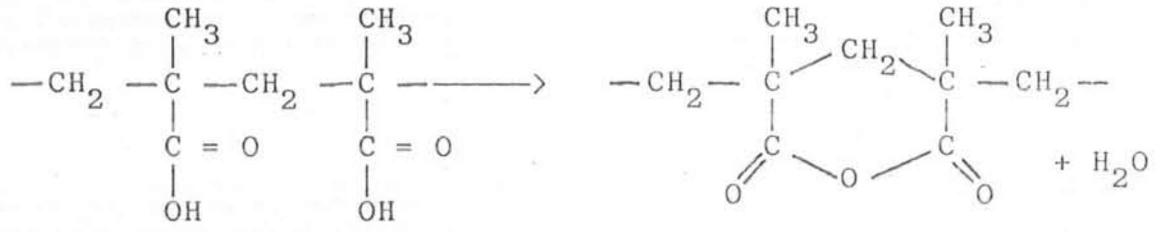
$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}\text{------}\rangle\; -CH=CH-CH=CH-+HCl$$

Similar reactions are known for other substituents as, OH, Br, $-O-CO-CH_3$. Different theories have been put forwarded that the elimination of HCl is respectively ionic[29], molecular[30], or Radical[31]. It is now clear that degradation of PVC may be accounted for, qualitatively in terms of the radical mechanism, although there is no general mechanism for its interpretation.

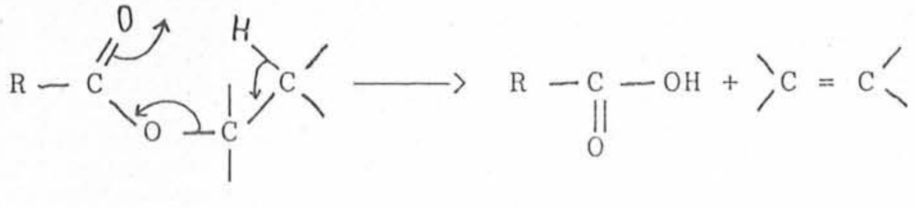
In type (B) the side groups undergo reactions to give a cyclic polymer structure. Heat induces a rearrangement in the chemical structure of certain polymers, without simultaneous evolution of volatile materials. Poly acrylonitrile[32,33] is an example of such a cyclization reaction,



Cyclization may also occur with the elimination of small molecules, as in poly (methacrylic acid)[34] and in poly(N-methacrylamide) 3[5].



Ester decomposition may also occur by the heat effect. Thus ester decomposition into acid and olifin is known to proceed by a molecular mechanism, which is facilitated by a six-membered ring, as shown.



Number of β-Hydrogen atoms and the inductive effect of the substituents on the alkyl group[36,37] explain the ease with which this reaction will occur.

whatever the reaction may be, the substituent reactions lead to the formation of products which are structurally different to the original polymer structure. The final product in such reactions, at temperature above 500°C is usually a carbonaceous residue, often akin to graphite[38]. Such reactions, since form conjugated unsturated structures, so often lead to the colouration of the residue. Substituent reactions often take place at lower temperatures than those at which depolymerization commence. Such reactions if allowed to proceed will, thus, inhibit any potential depolymerization process. Formation of such structure which do not permit depropagation, thus inhibit depolymerization reactions.

# CHAPTER - II

# EXPERIMENTAL TECHNIQUES

## EXPERIMENTAL TECHNIQUES

Characterization and thermal degradation of the polymers and copolymers have been studied using different techniques e.g. IR, NMR, GPC, DTA, TG, TVA, and SATVA. Thermal volatilization analysis (TVA) and sub-ambient thermal volatilization analysis (SATVA) is now a well established techniques in the field of thermal analysis . A brief description of all these techniques is given below.

(a) **Infra-red Spectrophotometry**: Infrared spectrophotometry is a standard method for analysis of compounds and particularly of groups of atoms in organic compounds. It involves irrediating the sample under test with infrared radiations programmed through the range (5000-650 $cm^{-1}$). The response of the sample is monitored against a reference beam and the difference signal at the detector is plotted as the 'infrared spectrum'.

Each polymer has its own characteristic infra red spectrum and this provides a very accurate means of analysis. Infra red spectroscopy may be carried out quantitativly in which case any significant change on reaction may be observed. This, of course, is especially useful in this work, where a different spectrum would be expected for the prepolymer and the cyclized polymer.

(b) **Dilution Viscometry**: This technique of molecular weight determination can be used to determine the viscosity average molecular weight (Mv) which is between the number and the average values and can be correlated exactly with either, although it always tends to be near the weight average value.

It can however be used to determine absolute Mv value when two constants K and $\alpha$ in the Mark Houwink equation are known.

$$|\eta|_{c=o} = k\ |\bar{M}v)^{\alpha}$$

$|\eta|_{c=o}$ = Instrinsic viscosity at infinite dilution.

k, $\alpha$ = constants determined by other methods.

For this series of polymers and copolymers k and values could not be easily determined due to solubility restrictions and the polymers could be compared in terms of their respective $|\eta|_{c=o}$ values.

Value of instrinsic viscosity at zero concentration was determined using a computer programme during molecular weight calculations in GPC.

Briefly the relations are as:

$$\text{Relative viscosity } \eta_r = \frac{\text{Time soln}}{\text{Time solv.}} = \frac{\eta\text{ soln}}{\eta\text{ solv.}}$$

$$\left(\frac{\log\eta_r}{C}\right)\text{ at } = |\eta_c| \quad C = \text{Concentration.}$$

This is determined from a plot of $\frac{\log \eta_r}{C}$ vs. C, also $\eta_{sp} = \eta_r - 1$ and $\left|\frac{\eta_{sp}}{C}\right|$ at $_{c\,=\,o}$ = $|\eta_o|$. This can be determined from a plot of $\frac{\eta_{sp}}{C}$ vs. C and the results should be identical in theory.

(c) **Gel Permeation Chromatography (GPC):** GPC has now become a well established technique for the determination of the molecular weight of macromolecules, and for molecular weight distribution. The techniques involves the elution of the very dilute solution of the polymer ($10^{-2}$-$10^{-4}$ g $cm^{-3}$) through the column usually of polystyrene. The molecular weight of the polymer chains is computed using a detector, and then feeding the data to a computer. Most commonly columns with pore sizes $10^2$, $10^3$, $10^4$, $10^5$ $A^o$ are used.

Instrument was run under the following conditions.

| | |
|---|---|
| Flow rate | 1 $cm^3$ $min^{-1}$. |
| Injection volume | 20 $\mu$l. |
| Sample concentration | 5 x $10^{-3}$g $cm^{-3}$ |
| Solvent | THF |
| Calibration | with polystyrene |

(d) **Differential Thermal Analysis (DTA):** Differential thermal analysis (DTA) is a techniques in which temperature differences between a sample material and an inert reference material (glass beeds or alumina) are recorded with respect to temperature or time as the material is heated at a uniform rate. Thus any heat changes, exothermic (evolution of heat with respect to reference material) or endothermic (absroption of heat) associated) with a chemical reaction (evaluation of water of crystallization) or a change of nature of state of sample (glass transition) are recorded.

In such studies it is necessary to record the following variables, rate of heating, atmosphere, and changes in temperature and temperature scale. Quantitative estimation of heats of reaction are obtainable in theory from ideal experiments using known sample weight and controlled procedural variables, but are however difficult to obtain in practice.

**(e) Thermogravimetric Analysis (T.G.):** Two thermogravimetric techniques have been developed to characterize polymer degradation reactions involving weight loss.

(i) Isothermal weight loss: Where the change in weight of a sample is recorded as a function of time at a particular temperature.

(ii) Dynamic weight loss: In which the weight change is recorded as a function of both time and temperature whilst the sample is heated at a constant rate.

Fundamentally the analysis may be conducted under a range of experimental conditions to obtain information on polymer degradation and residue production in various atmospheres and the different rates of heating. Dudley has reviewed the kinetic data from thermogravimetric analysis studies on polymer materials. It is possible to obtain a value for activation energy (E) from the kinetic data, and this value of E may be used as a measure of the thermal stability of polymers.

(f) **Thermal volatilization Analysis (TVA)**: In TVA[39] degradation is carried out under high vacuum conditions and the pressure exerted by the volatile products is measured continuously by a Pirani gauge. The volatile products pass to a cold trap and the response of the pirani gauge is measured and plotted as a function of the oven temperature. The pirani response is a measure of the rate of volatilization of the sample.

Basic TVA layout is shown in the figure.2.1.A glass tube usually 20 cm. long and 4.5 cm. diameter with flat bottom over which the sample is placed, is heated in the oven. Top of the tube is cooled by a water jacket (usually referred as cold Ring, (CR) Heating is carried out with a linear temperature programmer Sample can be heated upto $500^{o}C$ at the rates from 1 to $40^{o}C\ min^{-1}$. Oven temperature is recorded using a chromelalumel thermocouple.

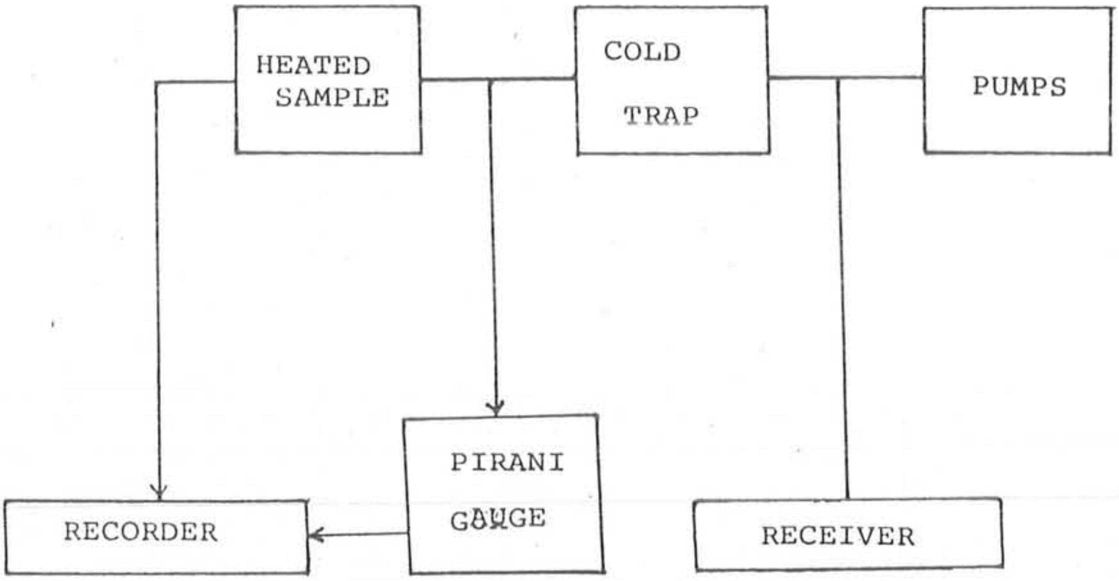


Fig. 2.1

Schematic layout of basic TVA apparatus.

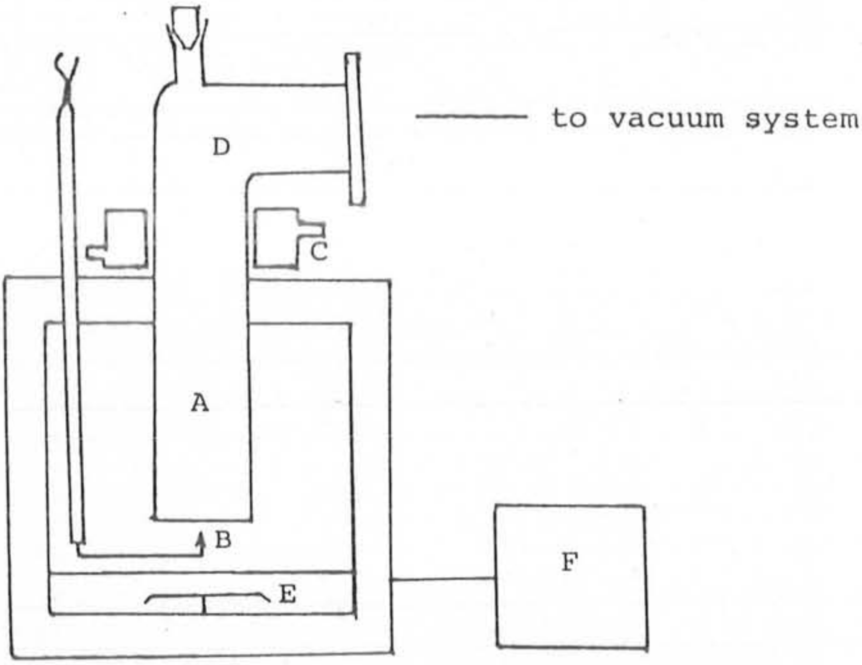


Fig. 2.2

oven arrangement for TVA
A Degradation tube
B Chromel-alumel thermocouple
C Cooling jacket
D Removable socket joint
E Oven fan
F Temperature programmer

Collection of products of TVA. In TVA degradation products are of two types.

(a) The Residue (remaining at the base of the tube after heating).

(b) Volatile products. These can be of three types.

(i) Cold Ring Fraction CRF: Products which are not volatile at room temperature but volatile at the temperature of degradation.

(ii) Condensibel products: Products which are not volatile at the cold traps temperature but at the temperature of degradation.

(iii) Non Condensible products: Products volatile even at liquid nitrogen temperature ($-196^{o}C$).

All the products can be identified using IR spectroscopy. Residue can be subjected to IR spectroscopy for the nature of the functional groups present.

CRF can be removed, using a suitable solvent, usually chloroform or dichloromethan and solution spectra can be recorded.

Non-condensible products e.g. methane, carbonmonoxide, can be identified by using a closed system which consists

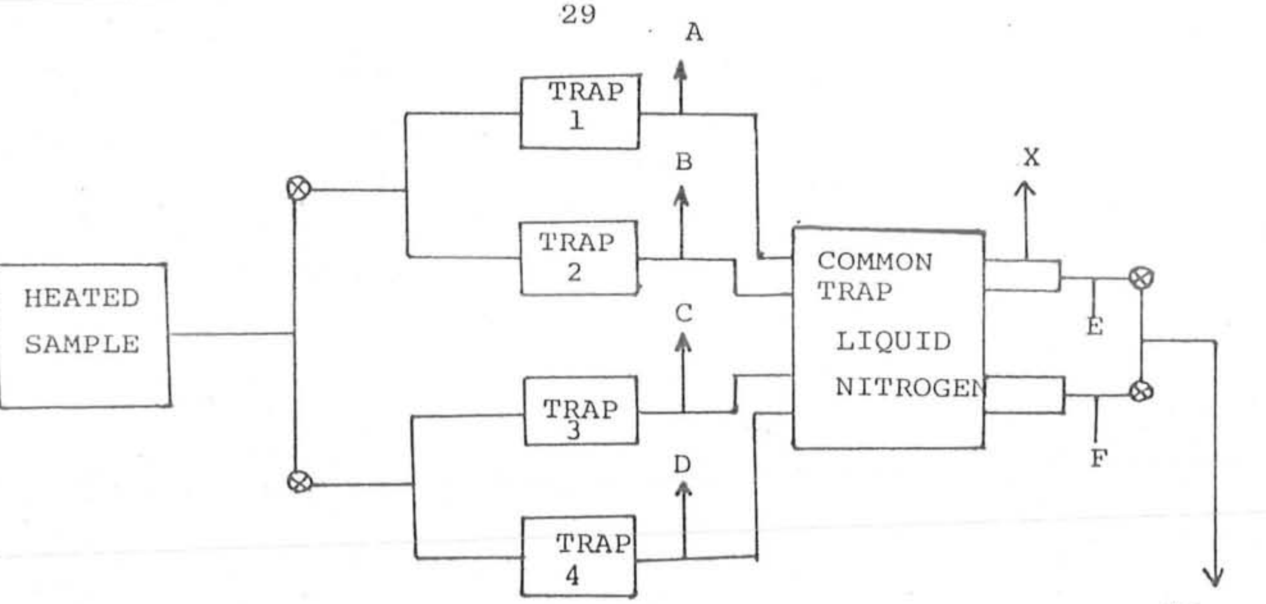
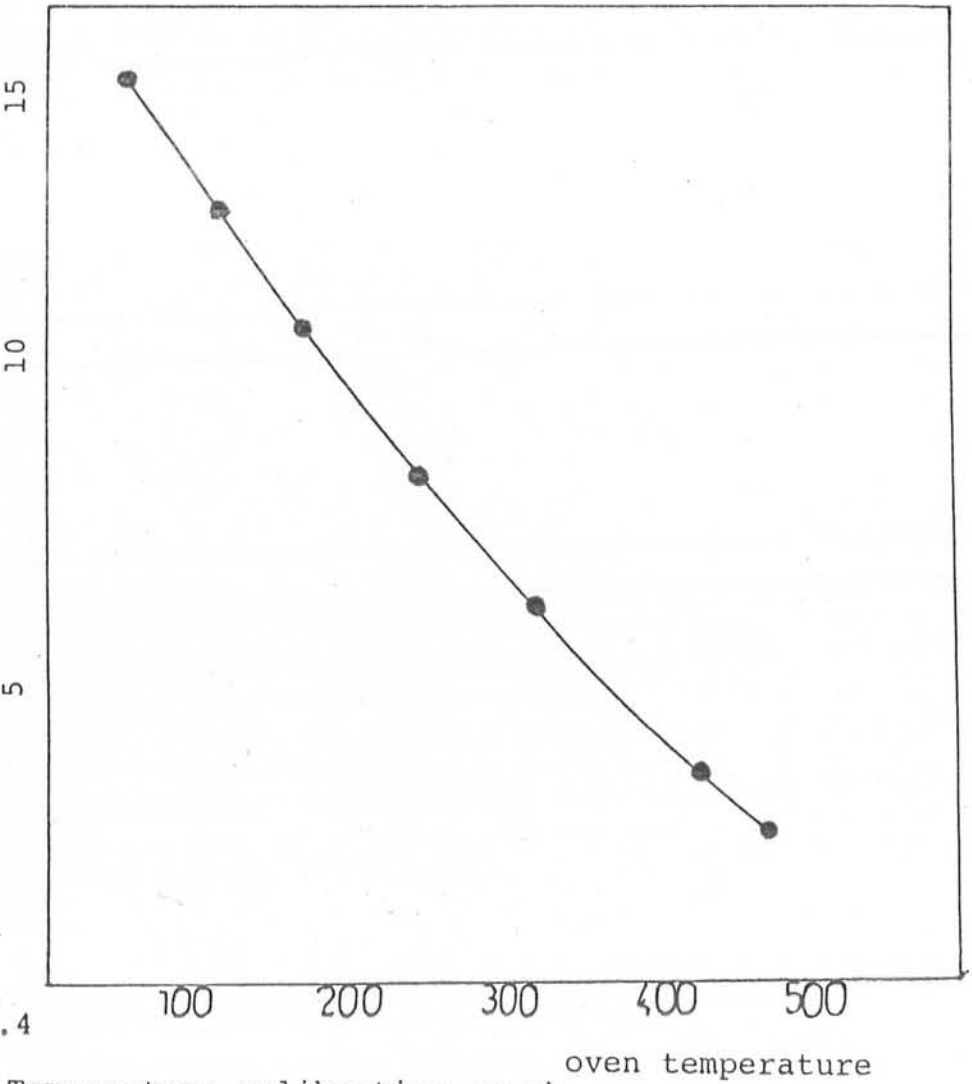


Fig. 2.3

Normal working temperature (°C): 0,-45,-78-100
A,B,C,D,are Pirani gauge heads
E,F, are sample receiving tubes as IR gas cell.



2.4

Temperature calibration graph.

of are IR gas cell and cold traps to condense less volatile substances. Such a system has been described and explained by McNeill .

## (g) Sub-Ambient Thermal Volatilization Analysis (SATVA):

The mixture of the volatile products obtained by TVA can be separated by SATVA.

SATVA is non-destructuive so that, unless the products interact. Repeat experiments are possible from the same starting material. Separation of the products depends on, how much, the products differ in volatility. Strong Hydrogen bonding effect may also hinder separation.

Briefly, the total condensible degradation products obtained in TVA are collected in a tube surrounded by an outer tube containing glass beeds, instead of p-xylene as reported previously[40], frozen to -196°C. The frozen glass beeds are allowed to warm up using laboratory conditions, whilst the inner product tube is contineously evacuted. The pressure of the gasses evolved is measured by a pirani gauge and contineously recorded. Different peaks are obtained, each peak referring to evolved degradation products, which can be collected for subsequent identification and analysis.

# CHAPTER - III

# EXPERIMENTAL

## Experimental:

**Materials and Methods**: Selected monomers MMA and GMA for synthesis of homopolymers and copolymers are available commercially. Monomers used for the purpose were Glycidyl methacrylate (GMA) and Methyl methacrylate (MMA). pracipitation and purification was carried out with solvents as methanol, chloroform acetone and diethylether.

**Purification of Solvents:** Solvents were purified and dried by treatment with calcium chloride for 24 hours. In order to remove small traces of water all the solvents were treated with ground calcium hydride for 12 hours, and then distilled.

**Distillation of Monomers**: Monomers GMA and MMA both were dried by calcium hydride for 12 hrs. They were then purified by vacuum distillation. The procedure is as:

Monomers were taken separately into two necked, 50 ml, round bottom flasks, one of the neck was fitted with thermometer and other with a distillation head, a condenser and a multiple receiver. One arm of the receiver was attached to vacuum pump and the other was fitted into a receiving flask.

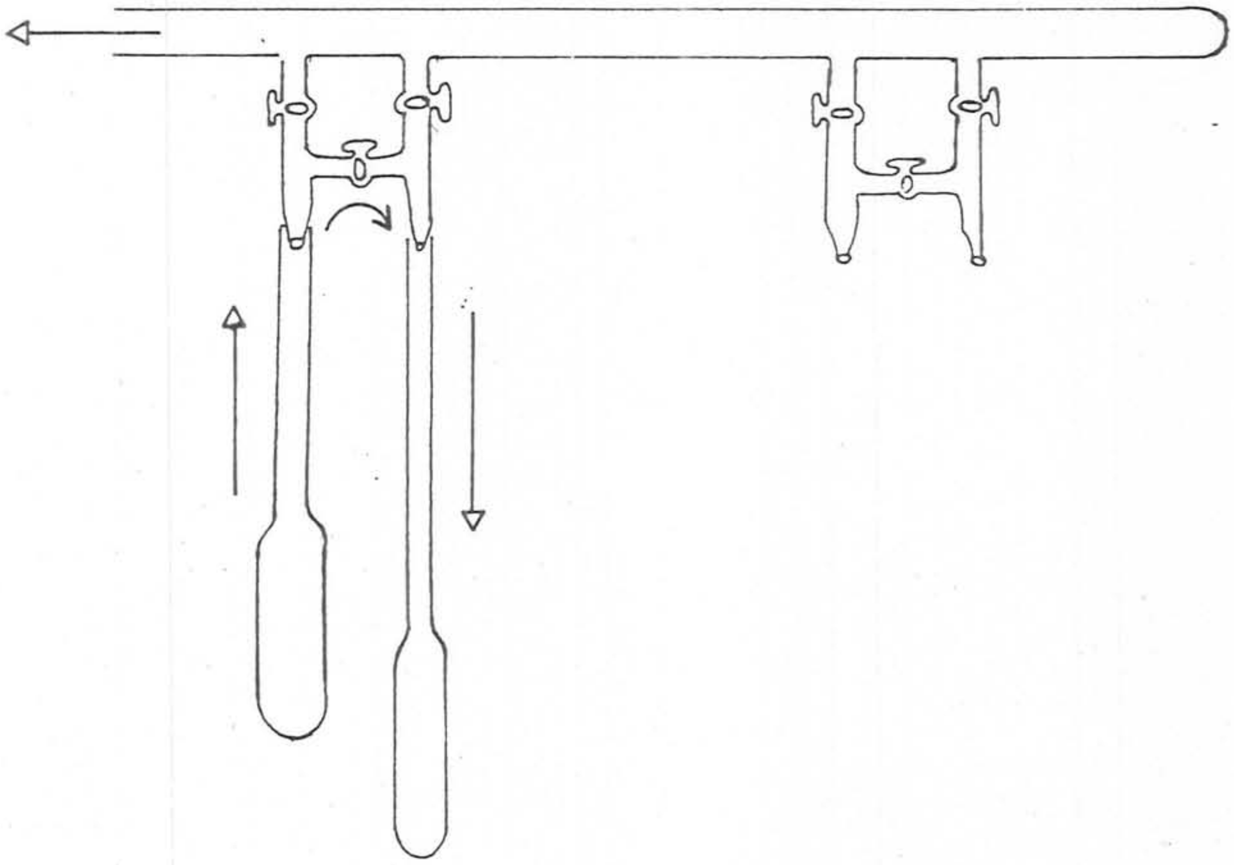
Distillation was carried out under reduced pressure, first few ml were discarded and pure monomers were seperately collected. Under the conditions of the distillation, GMA was distilled at 80-85°C and MMA was distilled at 45-48°C.

**Initiator for Polymerization**: Synthesis was carried out by free radical polymerization. Initiator was $\alpha, \bar{\alpha}$-Azoisobutyronitril (AIBN). The concentration of initiator in each case of polymerization was 0.5% w/v. Initiator was introduced into the dilatometer before the introduction of monomers.

**Purification of Initiator**: Initiator was purified by recrystallization from ethylalcohol. AIBN was allowed to dissolve in ethylalcohol at a slightly higher temperature, and then allowed to cool slowly. Pure crystals of AIBN were separated by filtration and then dried.

**Introduction of Monomers into Dillatometer**: GMA was introduced directly into the dilatometer because its boiling point was very high. MMA was introduced from reservoir into the dilatometer by vacuum distillation on vacuum line. In case of copolymers, calculated amounts of the monomers were introduced into the dilatometer containing 0.5% w/v AIBN.

**Composition of Copoolymers**: Selected monomers for copolymerization were GMA and MMA. Different compositions of the two monomers in copolymers were:

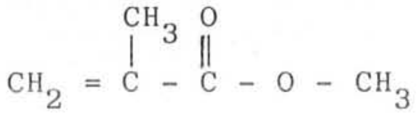


Apparatus for the introduction of monomer into the Dilatometer.

| Copolymer No | GMA % | MMA % |
|---|---|---|
| 1 | 100 | 0 |
| 2 | 90 | 10 |
| 3 | 50 | 50 |
| 4 | 10 | 90 |
| 5 | 0 | 100 |

**Structure of the Monomers:**

(i) Methyl Methacrylate (MMA).

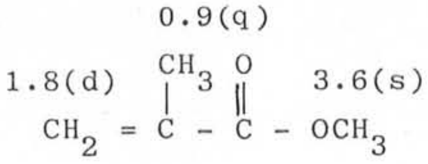


$CH_2 = C(CH_3) - C(=O) - O - CH_3$

IR Spectra gives the following characteristic peaks.

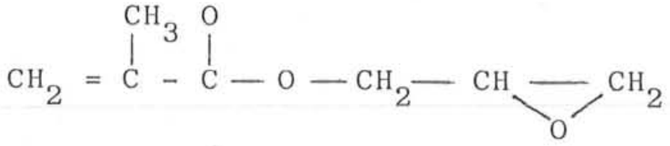
| | |
|---|---|
| 3004<br>2956 $Cm^{-1}$ | C - H. Str. Vib. |
| 1728 $Cm^{-1}$ | C = O Ester, Str. Vib. |
| 1644 $Cm^{-1}$ | C = C Str. Vib. |
| 1161 $Cm^{-1}$ | C - O - C Str. Vib. |

NMR



$CH_2 = C(CH_3) - C(=O) - OCH_3$

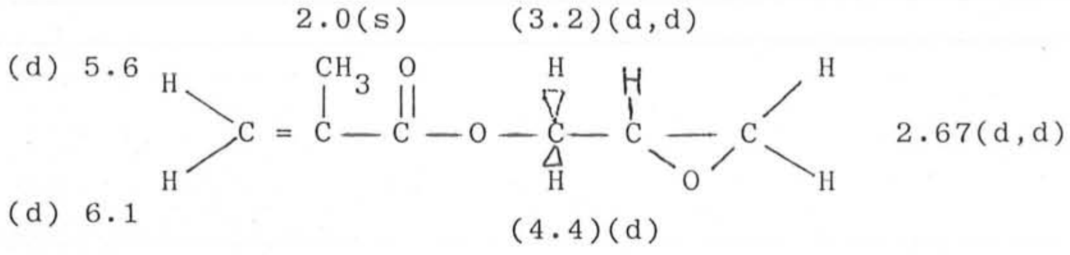
(ii) Glycidyl Methacrylate (GMA).



IR Spectra shows the following peaks.

| | |
|---|---|
| 3004<br>2962 $Cm^{-1}$ | C - H Str. Vib. |
| 1725 $Cm^{-1}$ | C = O Str. Vib. |
| 1641 $Cm^{-1}$ | C = C Str. Vib. |
| 909, 843 $Cm^{-1}$ | Peaks characteristic of epoxide ring. |

NMR.

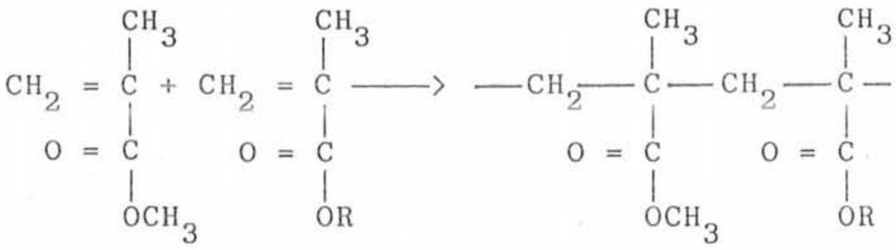


## Polymerization:

The two monomers were copolymerized in the dilatometer which were sealed under vacuum, after the introduction of the initiator and the monomers. Polymerization was carried out in a thermostat at 60°C ± 0°C. It was necessary to encase the dilatometer in a shield as a precaution against explosion. Polymerization was indicated by the increase in viscosity of the contents in dilatometer.

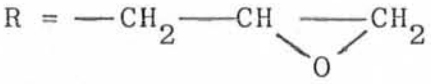
The process was quenched by pouring the contents in a beaker containing methanol. Pracipitation was done by constant stirring. Polymers were pracipitated as white hard solid masses.

Process of copolymerization can be represented as.



$$CH_2=C(CH_3)COOCH_3 + CH_2=C(CH_3)COOR \longrightarrow -CH_2-C(CH_3)(COOCH_3)-CH_2-C(CH_3)(COOR)-$$

Where



$$R = -CH_2-CH-CH_2 \text{ (with O bridging CH and CH}_2\text{)}$$

## Purification of Homopolymers and Copolymers:

After pracipitation homopolymers and copolymers were purified. The products were dissolved in acetone to remove impurities. Repracipitation was performed in methanol. Purified homopolymers and copolymers were white in colour. Purification was performed again. Products were dried in vacuum at ambient temperature for 24 hours to remove all traces of solvents. Dried products were ground into fine powder.

## Table -

**Polymerization DATA**

Volume of dilatometer = 40 ml

Temperature of polymerization = $60.0 \pm 0^{\circ}C$

Initiator concentration = 0.5 % w/v

| Sample No. | MMA % | GMA % | $M_1$ | $M_2$ | Time (minutes) |
|---|---|---|---|---|---|
| 1 | 0 | 100 | - | - | 25 |
| 2 | 10 | 90 | | | 35 |
| 3 | 50 | 50 | 0.5520 | 0.4479 | 50 |
| 4 | 90 | 10 | 0.9177 | 0.0822 | 70 |
| 5 | 100 | 0 | - | - | 90 |

$M_1$ = Mole freaction of MMA.

$M_2$ = Mole fraction of GMA.

## Experimental Notes:

(1) GMA used for polymerization and copolymerization was from E. Merck. All the other solvents used were also from the same company.

(2) IR Spectra of polymers and copolymers were recorded on a Hitachi 270-50 Data processor, spectrophotometer. Polymers and copolymers were examined as KBr disks.

(3) DTA and TG were recorded on a Simulataneous Thermal Analyser STA 429 using Alumina as reference in air atmosphere.

(4) GPC was carried out using THF as solvent with a flow rate of 1 $cm^3$ $min^{-1}$. Calibration was done with polystyrene.

(5) GPC program applies the following formulae,

a) $MN = \frac{\sum Hi}{\sum (Hi/Mi)} x \; QF$

b) $MW = \frac{\sum (Hi \; x \; Mi)}{\sum Hi} \; x \; QF$

c) $MZ = \frac{\sum (Hi \; x \; Mi^2)}{\sum (Hi \; x \; Mi)} \; x \; QF.$

d) $MV = \left| \frac{\sum HiMi^{\alpha}}{\sum Hi} \right|^{\frac{1}{\alpha}} \; x \; QF.$

e) $I.Visc = K \; x \; (Mv)^{\alpha}$

Where

Hi = Height

Mi = Molecular weight or Molecular chain length

QF = "Q-Factor", Molecular weight per Molecular chain length.

$\alpha$,K = Constants of the Mark-Houwink Viscosity formula

# CHAPTER - IV

# RESULTS AND DISCUSSIONS

## CHARACTERIZATION AND THERMAL ANALYSIS

Homopolymers and copolymers were characterized by different available techniques, IR, GPC, and dilution viscometery.

Spectroscopic Studies IR.: Ir Spectra of the monomers MMA and GMA showed characteristic carbonyl absorption peaks at 1730 $cm^{-1}$. GMA shows two absorption peaks at 843 and 909 $cm^{-1}$, which are characteristic of epoxy group. A peak characteristic of C=C is present at 1630 $cm^{-1}$. The homopolymer PGMA shows all the characistic bands except 1630 which is of C=C, the absence of this peaks confirms that polymerization has occurred, two bands at 909 and 843 $cm^{-1}$ confirms the presence of epoxy group in homopolymer. PMMA shows all characteristic bands except for double bond at 1640 $cm^{-1}$, again confirming the polymerization.

IR spectra of the copolymers (90%, 50%, 10% GMA) are shown in the figs 4.1 . Two absorption peaks at 909 and 843 $cm^{-1}$ confirms the presence of epoxy group, showing that GMA has been incorporated in the polymer chain. All the copolymers shows strong bands at 1730-1740 $cm^{-1}$ for carbonyl absorption and strong bands at 1400-1150 $cm^{-1}$ due to C-O streching vibrations.

Molecular Weight: Molecular weight averages are defined according to the equation.

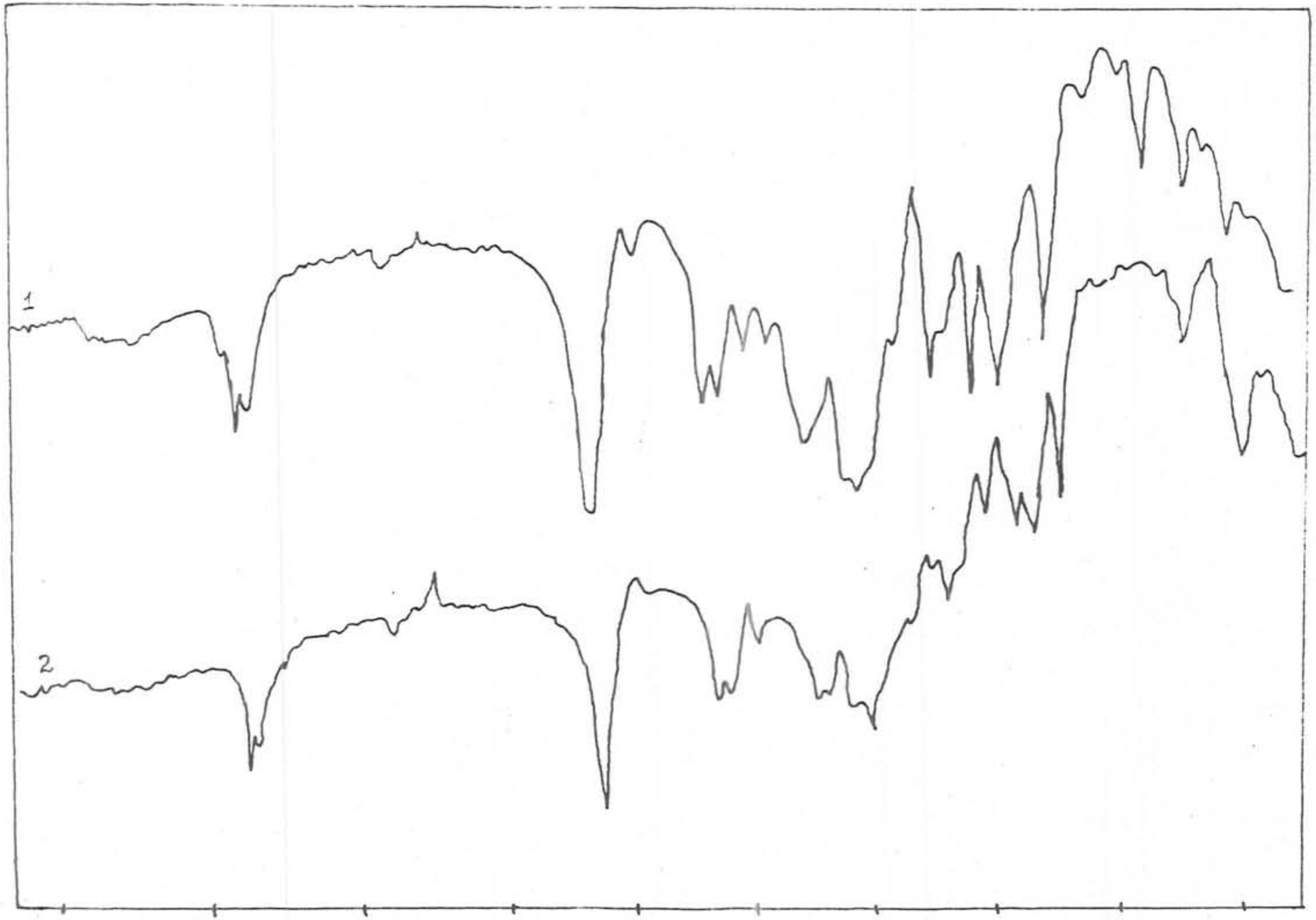


Fig. 4.1. IR Spectra of Copolymers.
1.90% GMA : 10% MMA
2.10% GMA : 90% MMA

$$M_K = \sum iNiMi^k / \sum iNiMi^{k-1}$$

Where:

Ni = Number of the molecules.

Mi = Molecular weight of molecules.

In this equation when,

k = 1, equation gives number average molecular weight Mn.

k = 2, equation gives weight average molecular weight Mw.

These equations can thus be represented as Mn = iNiMi and Mw = iWiMi respectively where Ni and Wi are the number and weight average fractions of molecules of molecular weight Mi. Other molecular weight averages can also be defined but special significance of Mn and Mw are that they can be determined by the commonly used absolute molecular weight methods.

Molecular weights of homopolymers and copolymers were determined by GPC using a computer programme. Molecular weights are given in the table.4.1.In case of hompolymer PGMA the molecular weight is 78627 as compared to PMMA with molecular weight 251675. Low molecular weight of PGMA shows that epoxy group in GMA prevents the formation of the longer chains and termination occurs. Epoxy group

## Table - 4.1

Molecular Weights of Homopolymers and Copolymers

| GMA | MMA | Mn | Mw | Mz | Mv |
|---|---|---|---|---|---|
| 100 % | 0 % | 78627 | 494610 | 940804 | 494610 |
| 90 % | 10 % | 264930 | 635119 | 977787 | 635119 |
| 50 % | 50 % | 269555 | 416476 | 577309 | 416476 |
| 10 % | 90 % | 365999 | 588821 | 774023 | 588821 |
| 0 % | 100 % | 251675 | 448837 | 699446 | 448837 |

thus causes some stability to the free radical. PGMA thus contains more unsaturated chain ends groups but PMMA with higher molecular weight indicates less unsaturated chain ends.

Molecular Weight Distribution: The polymers are characterized best by the molar mass distribution. Most polymers contain a broad distribution of molecular weight species as a result of either the random nature of initiation, termination and transfer processes in chain-growth polymerization reaction ofthe random interaction of the species of all sizes which often occur in step growth polymerization.

The index of heterogeneity of the molecular weight distribution of a polymer is usually given by the ratio. Mw/Mn. The molecular weight distribution in a step growth polymerization reaction in which all functional groups have equal probability of reacting, has been termed the most probable distribution. In the present case the homopolymers as well as the copolymers have Mw/Mn = 2 (approximately). This type of distribution also occurs in a number of other processes, such as in the random scission of an infinite molecular weight polymer chain.

Viscometry: The values of instrinsic viscosity at zero concentration was determined using a computer program in GPC. The Mark-Houwink equation;

## Table - 4.2

### Molecular Weight Distribution

| GMA | MMA | Mw/Mn |
|---|---|---|
| 100 % | 0 % | 2.29 |
| 90 % | 10 % | 2.39 |
| 50 % | 50 % | 1.54 |
| 10 % | 90 % | 1.60 |
| 0 % | 100 % | 1.78 |

$$|\eta|_{c=o} = k(Mv)^{\alpha}$$

where $|\eta|_{c=o}$ is the instrinsic viscosity at infinite dilution.

K, $\alpha$ are constants which can be determined by other methods. Viscosity of the polymer depends upon its molecular weight but also on the nature of the monomer. High molecular weight polymer have high viscosities. Results obtained are given in the table.4.3.Interesting point to note is that PMMA ($M_N$ = 251675) has I. Vis. of 448 but PGMA ($M_N$ = 78627) has I. Vis. of 494 which shows that nature of the monomer effects the viscosity of a polymer.

It is interesting to note that 90% GMA ($M_N$ = 264930) and 50% GMA ($M_N$ = 269555) have I. Viscosity of 635 and 416 respectively. This showing that A copolymer with higher content of GMA has high viscosity although both have almost same Mv values.

Thermogravimetry: A single stage degradation is evident from the curve for PMMA leaving very small amount of residue about 3.3% of the original weight at 450°C, as a result of complete depolymerization of the polymer to monomer. For PGMA two stages of breakdown are apparent from the TG curve, initial 7.0% weight loss may be due to solvent and moisture absorbed. Subsequent weight loss 73.4% is due to depolymerization. This weight loss is unzipping

## Table -4.3

| MMA | GMA | I. Viscosity |
|---|---|---|
| 0 % | 100 % | 494 |
| 10 % | 90 % | 635 |
| 50 % | 50 % | 416 |
| 90 % | 10 % | 588 |
| 100 % | 0 % | 448 |

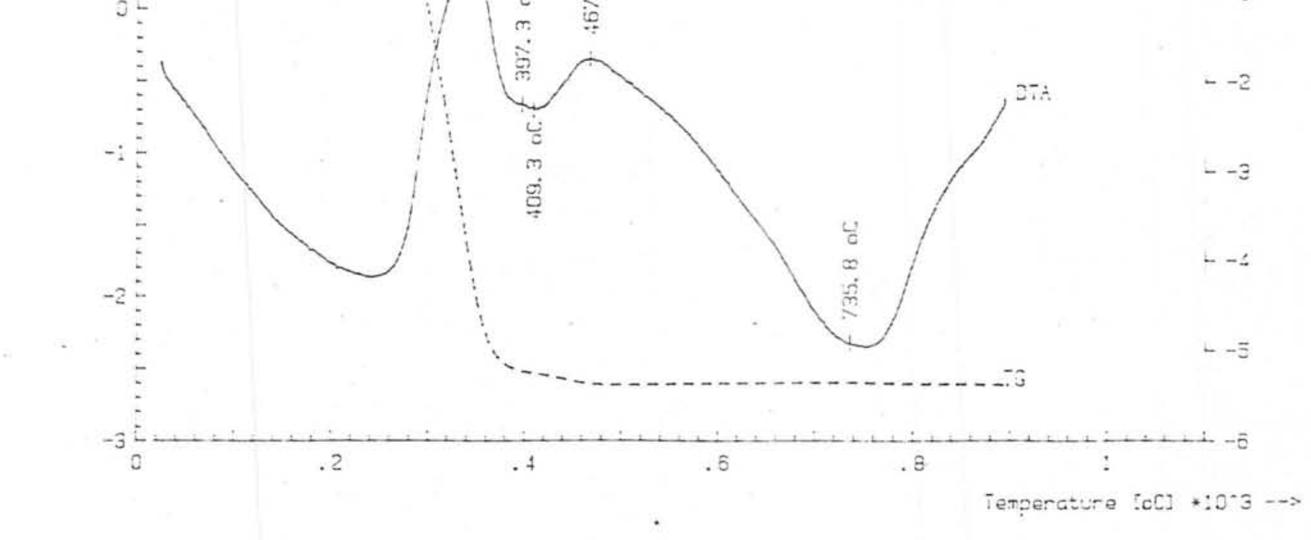


Fig. 4.2. TG, DTA of Homopolymer PMMA

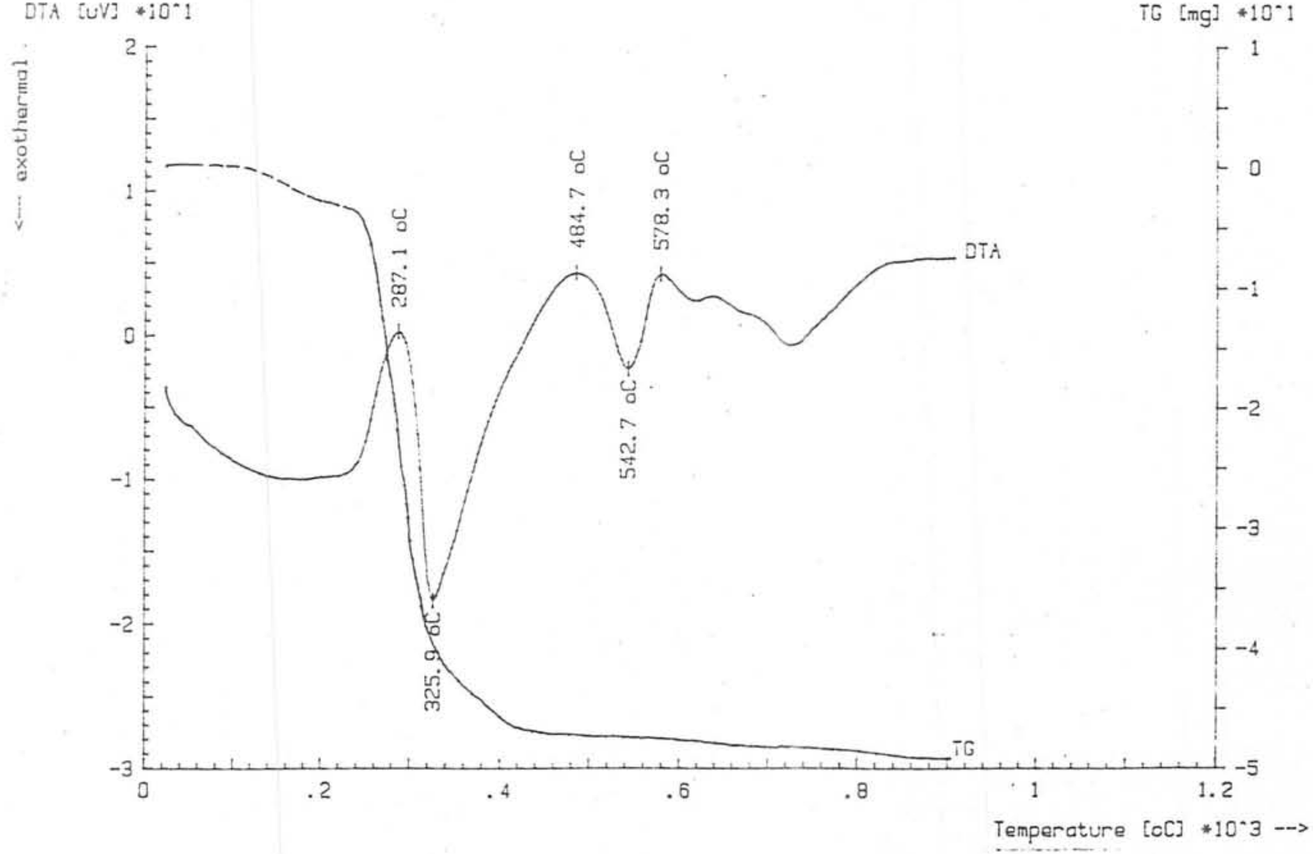


Fig. 4.3. TG, DTA thermogram of Homopolymer PGMA.

## **Table – 4.4**

TG DATA of Homopolymers and Copolymers

| MMA | GMA | Weight Loss | Residue at 450°C |
|---|---|---|---|
| 0 % | 100 % | 94.8 % | 5.2 % |
| 10 % | 90 % | 93.9 % | 6.1 % |
| 50 % | 50 % | 97.2 % | 2.8 % |
| 90 % | 10 % | 93.5 % | 6.5 % |
| 100 % | 0 % | 96.7 % | 3.3 % |

of the polymer from the unsaturated chain ends, and the final weight loss about 18.4% is due to random degradation of the polymer leaving ultimately 5.5% residue at 450°C. Low molecular weight of PGMA (78627), reveals that the extent of weight loss in the first region of degradation is consistent with the presence of large number of unsaturated chain ends.

TG Curves for various copolymers are shown in the fig 4.4-.6.TG curves of PMMA and PGMA shows that depolymerization is completed at about 400°C. So the TG curves and weight loss of copolymers can be compared with the PMMA and PGMA at 400°C. Residue left at 400°C for copolymers is 6.1%, 2.8%, and 6.5% for 90%, 50% and 10% GMA respectively.

Differential Thermal Analysis (DTA): DTA Curves for homopolymers PMMA and PGMA are shown in the fig 4.2-4.6 . The DTA of PMMA shows a broad endotherm at 350°C making the first endotherm at 312°C. It indicates an initial depolymerization and random chain scission. DTA Curve for PGMA is quite different from PMMA. It shows the first endotherm at 287°C and a broad endotherm at 484°C. Broad endotherm at 484°C indicates the increase in temperature of depolymerization.

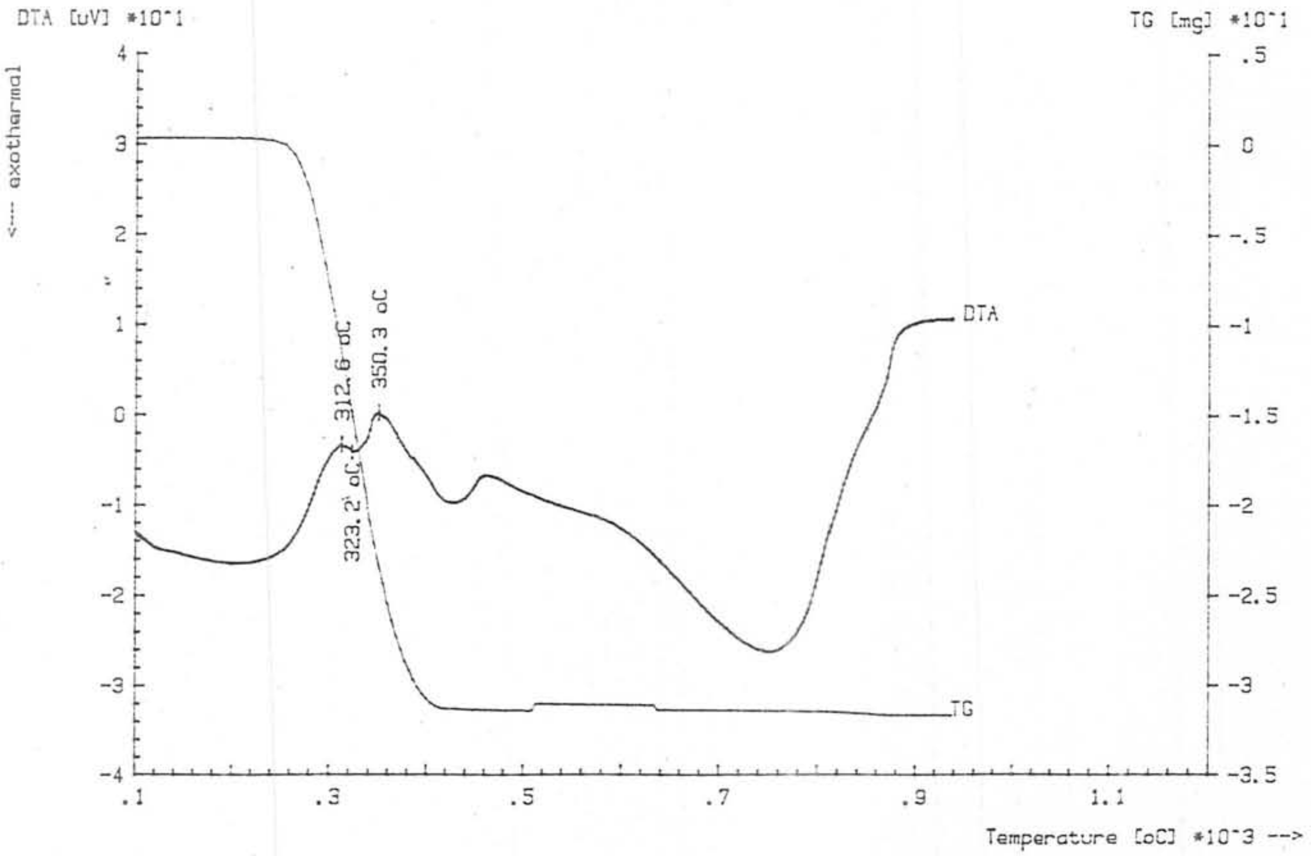


Fig. 4.4. TG, DTA of Copolymer (GMA 10% MMA 90%)

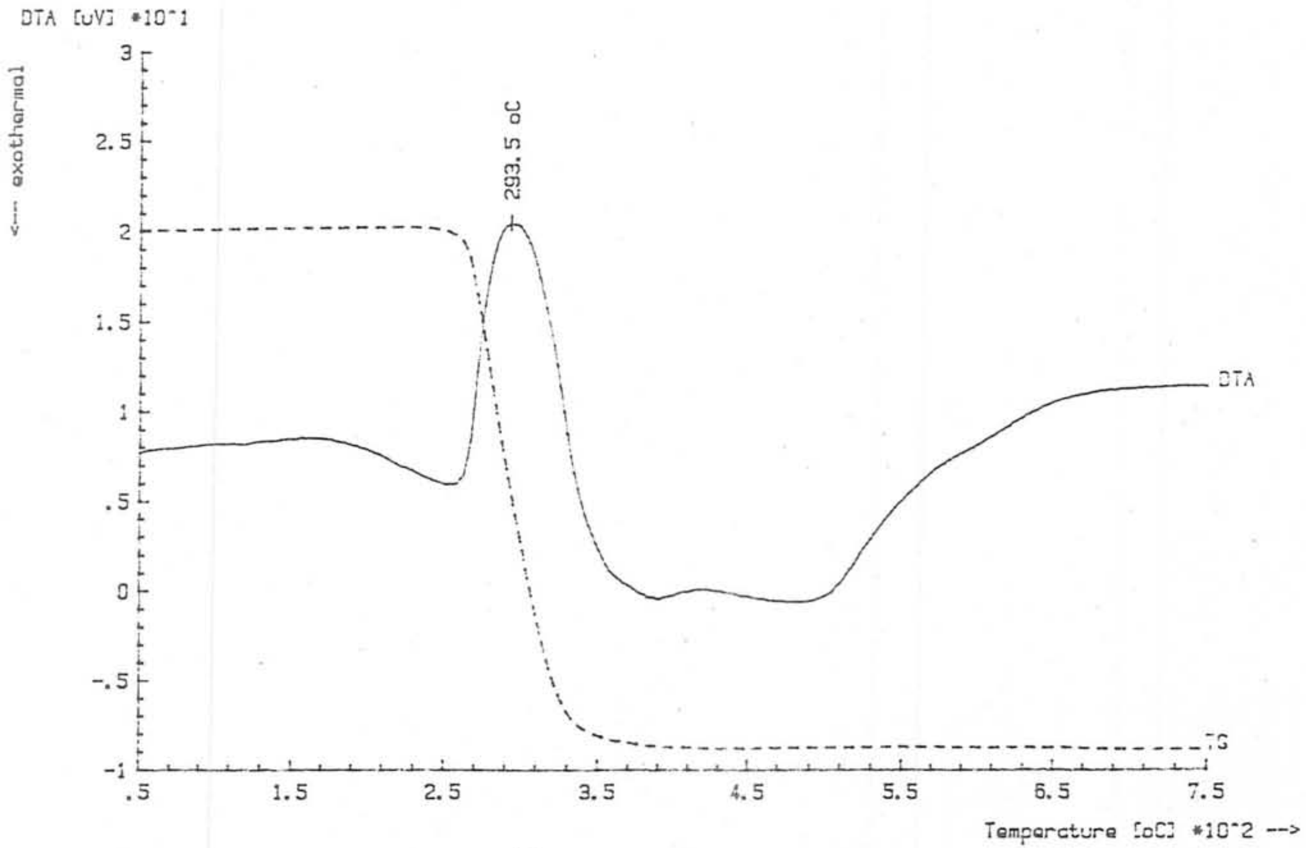


Fig. 4.5. TG, DTA of Copolymer (GMA 50% MMA 50%)

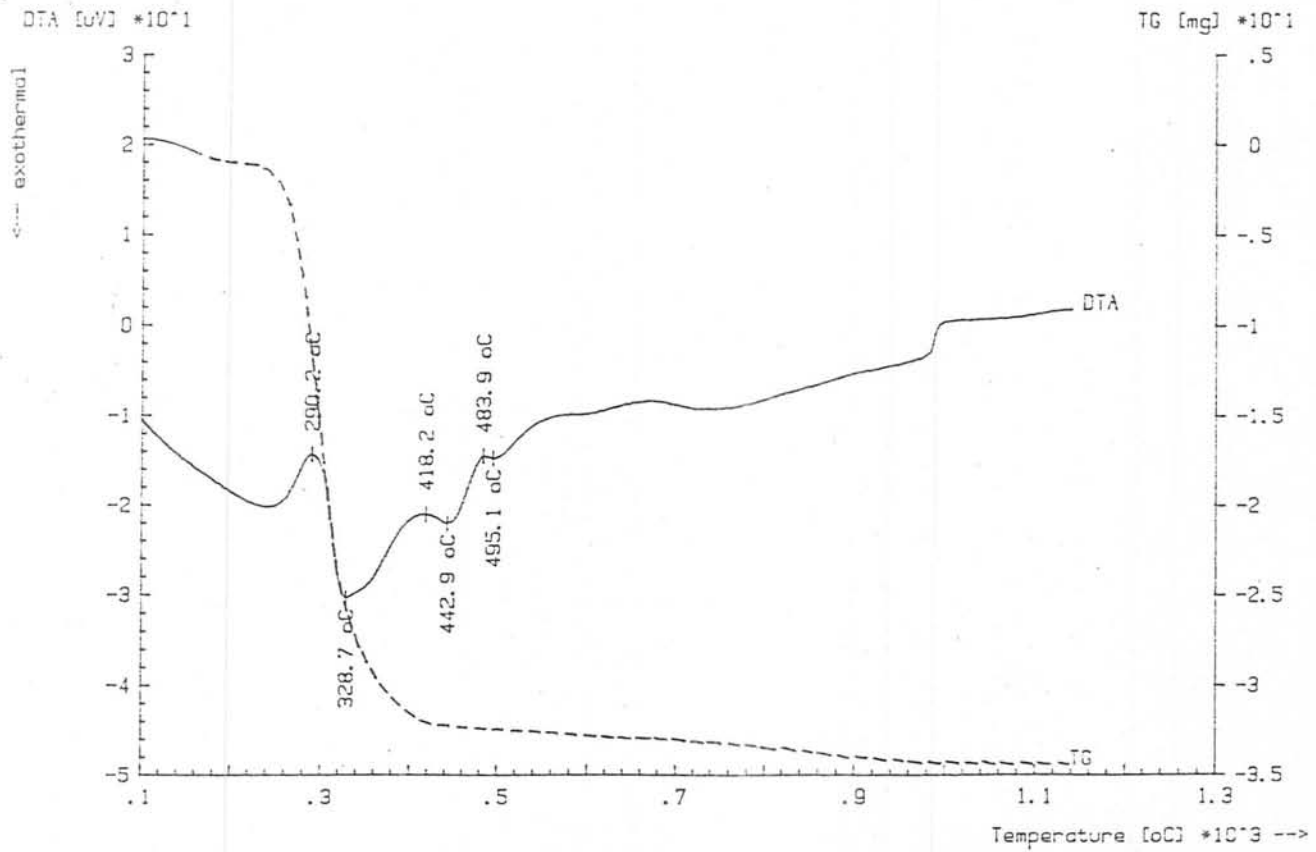


Fig. 4.6. TG, DTA of Copolymer GMA 90% MMA 10%)

## Table -4.5

### DTA Endotherms for Polymers

| MMA | GMA | First Endotherm | Second Endothrm |
|---|---|---|---|
| 0 % | 100 % | 287°C | 484°C |
| 10 % | 90 % | 290°C | 418°C |
| 50 % | 50 % | 293°C | |
| 90 % | 10 % | 342°C | 467°C |
| 100 % | 0 % | 312°C | 350°C |

DTA curves for the copolymers are shown in the fig. 4.2-2.6. Copolymer having 10% GMA show major endotherm at 342$^{O}$C while having 10% MMA shows endotherm at 290$^{O}$C, thus both copolymers showing some stability as compared to hompolymer. The copolymer having 50% GMA however shos a broad endotherm at 293$^{O}$C

Endothermic reactions evident in both homopolymers correspond to an initial depolymerization. For PGMA the first endotherm at 287$^{O}$C may represent the monomer formation from chain ends with a second broad endotherm at 484$^{O}$C, which is most probably due to random chain scission.

PMMA However shows a broad endotherm at 350$^{O}$C along with a small endotherm around 312$^{O}$C. This may be due to lesser number of unsaturated chain ends. (Molecular weight 251675 as compared to 78627 for PGMA).

Mass Spectral Analysis: Homopolymer PGMA and the copolymers were degraded thermally in a glass tube and mass spectra of the evolved products were recorded. A 100 mg sample was taken in a glass tube fitted with a stopcock. The solvent free sample was degraded by heating it upto 500°C under vacuum in a closed system. The evolved products were fed to a Mass Spectrum Analyser, attached with a computer. The results obtained are shown in the tables along with the SATVA results.

Thermal Volatilization Aanalysis (TVA): Fig.4.7-8 and illustrate the TVA curves for 60 to 65 mg powder samples of PMMA and PGMA. The homopolymer samples were heated to 500°C at the rate of 10°C/min under the normal conditions of TVA. The curve shown in fig. 4.8 is typical of PMMA sample, moderately high molecular weight as reported previously[46,47].

The TVA trace of PMMA indicates the two different modes of degradation. Volatilization began around 200°C and limiting rate of the first peak volatiled product upto 0.6 mv is observed at -75°C trace. The region upto 340°C is characteristic of MMA in TVA system. The rate of volatilization increases upto 250°C and then falls to a minimum. At this temperature the rate of volatilization again begins to increase and reaches its maximum rate T(max) at 360°C.

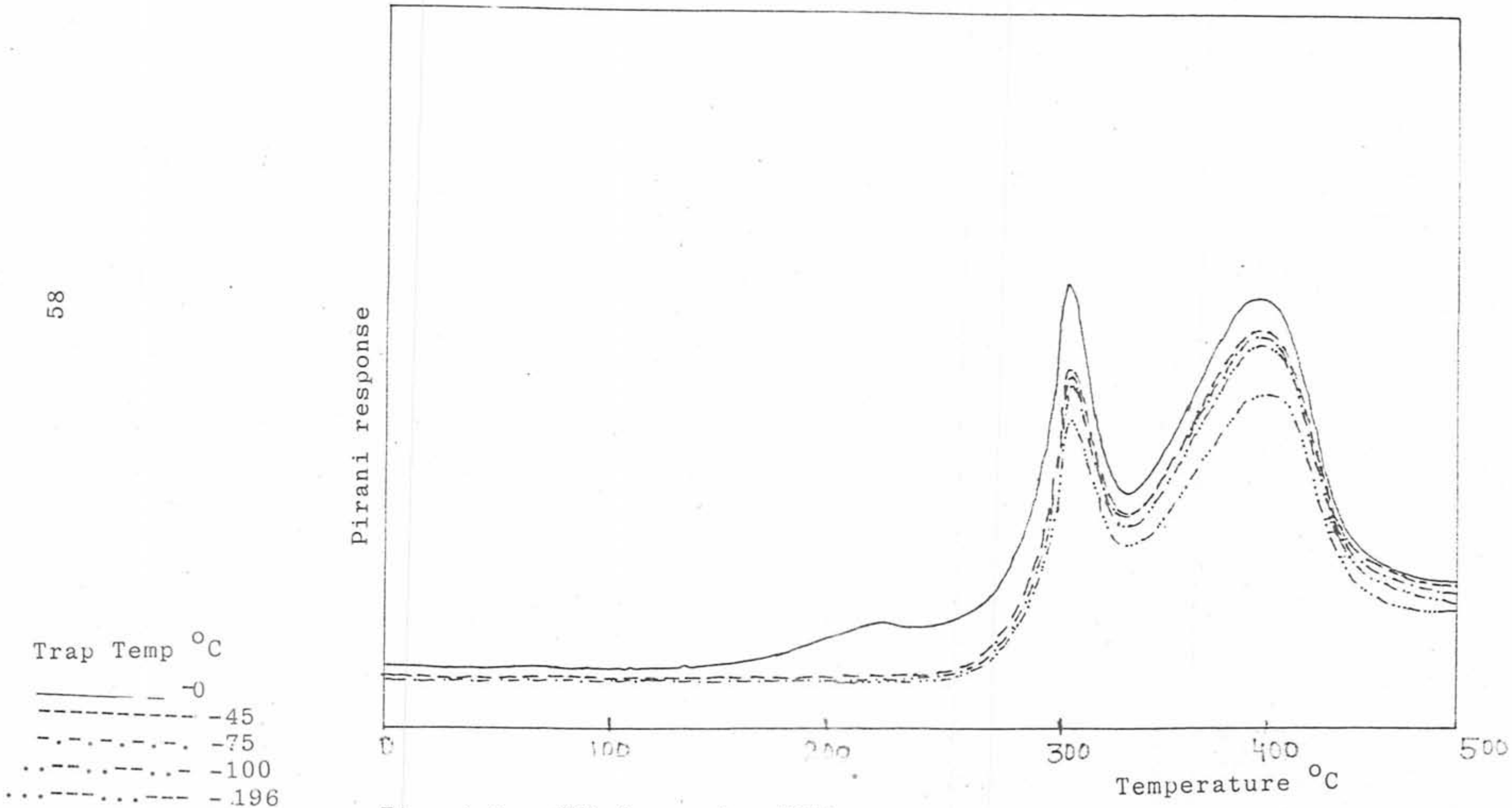


Fig. 4.7. TVA Curve for PGMA

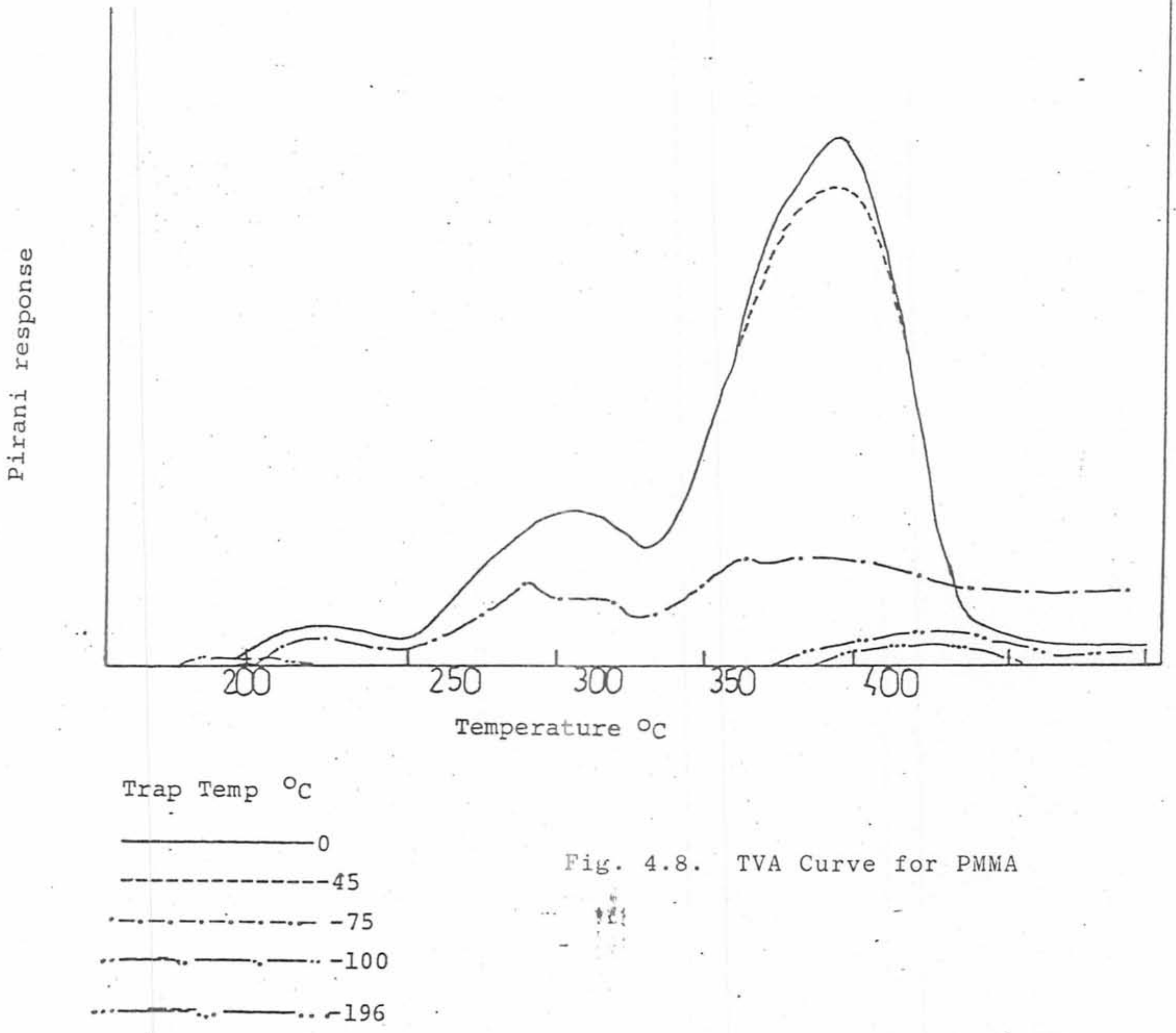


Fig. 4.8. TVA Curve for PMMA

The plateau in -75°C curve is again typical behaviour of the MMA monomer in TVA system and has been referred to limiting effect. It results from the low distillation of MMA from -75°C trap to liquid nitrogen trap. It seems that monomer is the only product of this polymer. The response at -100°C and -196°C suggests that there might be trace amount of low volatile products like $CO_2$, CO, and $CH_4$. Fig. 4.8 also shows that -100°C trace leaves the base line at the temperature of degradation at -100°C and returns to base line at 210°C. This may be due to evolution of solvent and pracipitant ($CHCl_3$, $CH_3COOH$, and $CH_3OH$)which were identified in the products from this region.

4.7

The TVA trace for PGMA reproduced in fig. shows that breakdown occurs in two main steps consistant with TG evidence. These steps produce similar amount of material. Volatilization began around 200°C, reaches to maximum at 313°C where the rate falls and again increases to yield second peak with T(max) 380°C. The most notable feature of TVA trace is the complexity of the products shown by the separation of various responses for different trap temperature. The -196°C trace shows the same general characteristics as the other above 250°C, indicating that high volatility products are formed throughout both main stages of decomposition. It is interesting that TVA trace of PGMA yields two peaks of comparable size with rate maxima at 313°C and 380°C. This seems consistant with the results reported for PMMA[46,47], in which the size of the first peak was found to increase with decrease in molecular weight of the polymer. Two peaks of similar size were observed when the mol. wt. $<$ zip length. Assuming termination of polymerization by disproportionation, there are two modes of initiation of unzipping to monomer; namely, at unsaturated chain ends, present in 50% of the macromolecules, and by random chain scission, respectively. The former reaction occurs in a lower temperature region.

TVA trace for three GMA-MMA copolymers are shown in fig.4.9-11. The characteristic of the trace is changing as GMA content of the copolymer increases. In all cases there are two regions of interest (1) The large peak (2) a small peak, from 200°C to the threshold of large peak. The copolymer with 50% GMA content, however, shows an additional small peak with T(max) at 245°C, starting from the base line. T(max) values for the large and small peaks are compared in the table for all the samples including the two homopolymers. It is obvious that the threshold temperature of PGMA is 180°C and as MMA content in the copolymer changes, the threshold temperature also changes.

Let us first examine the principle peak which is largest in all the copolymer systems. MMA monomer

Fig. 4.9. TVA Curve for Copolymer GMA 90 MMA 10.

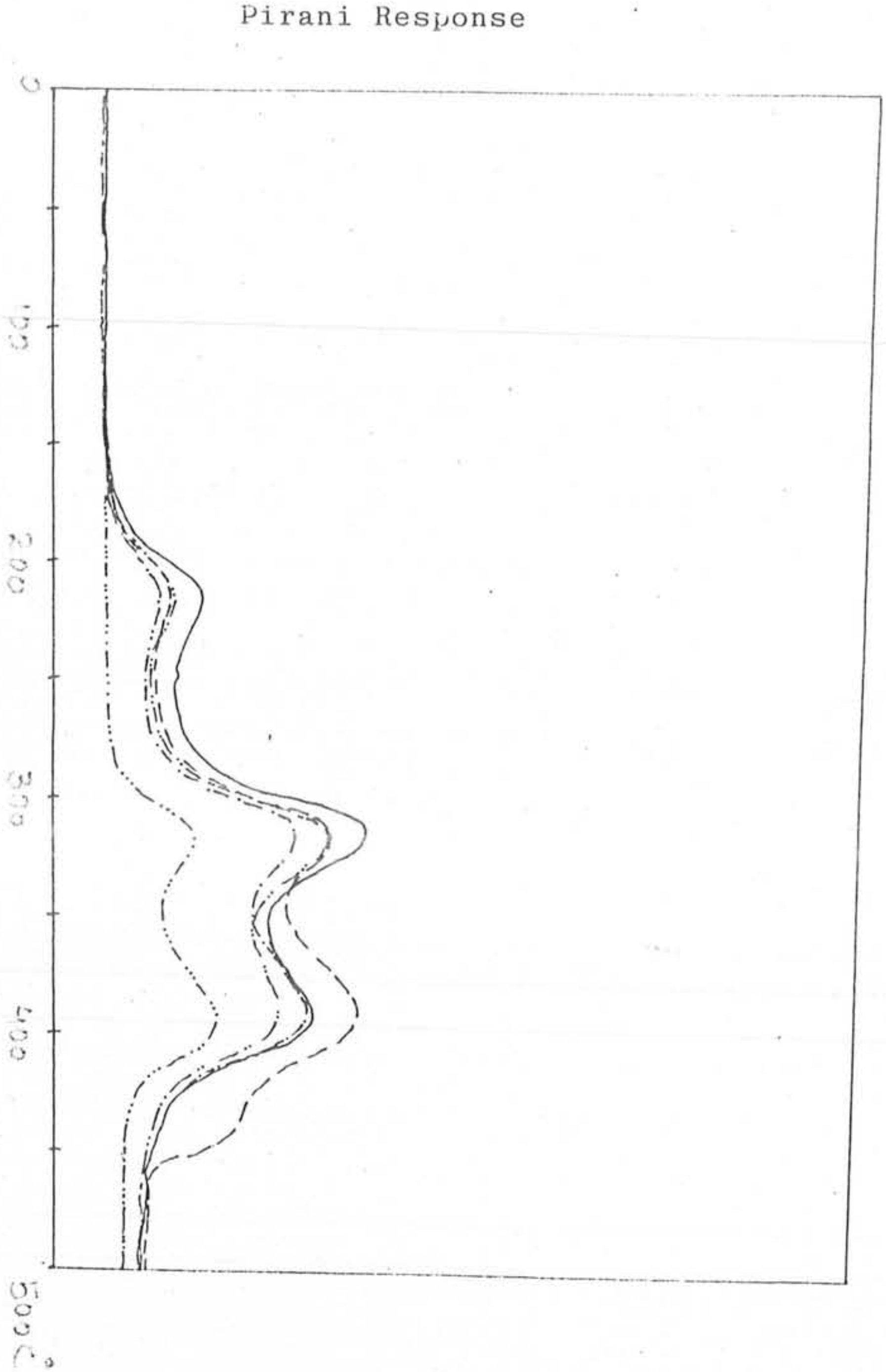


Fig. 4.10. TVA Curve for Copolymer (GMA 50% - MMA 50%)

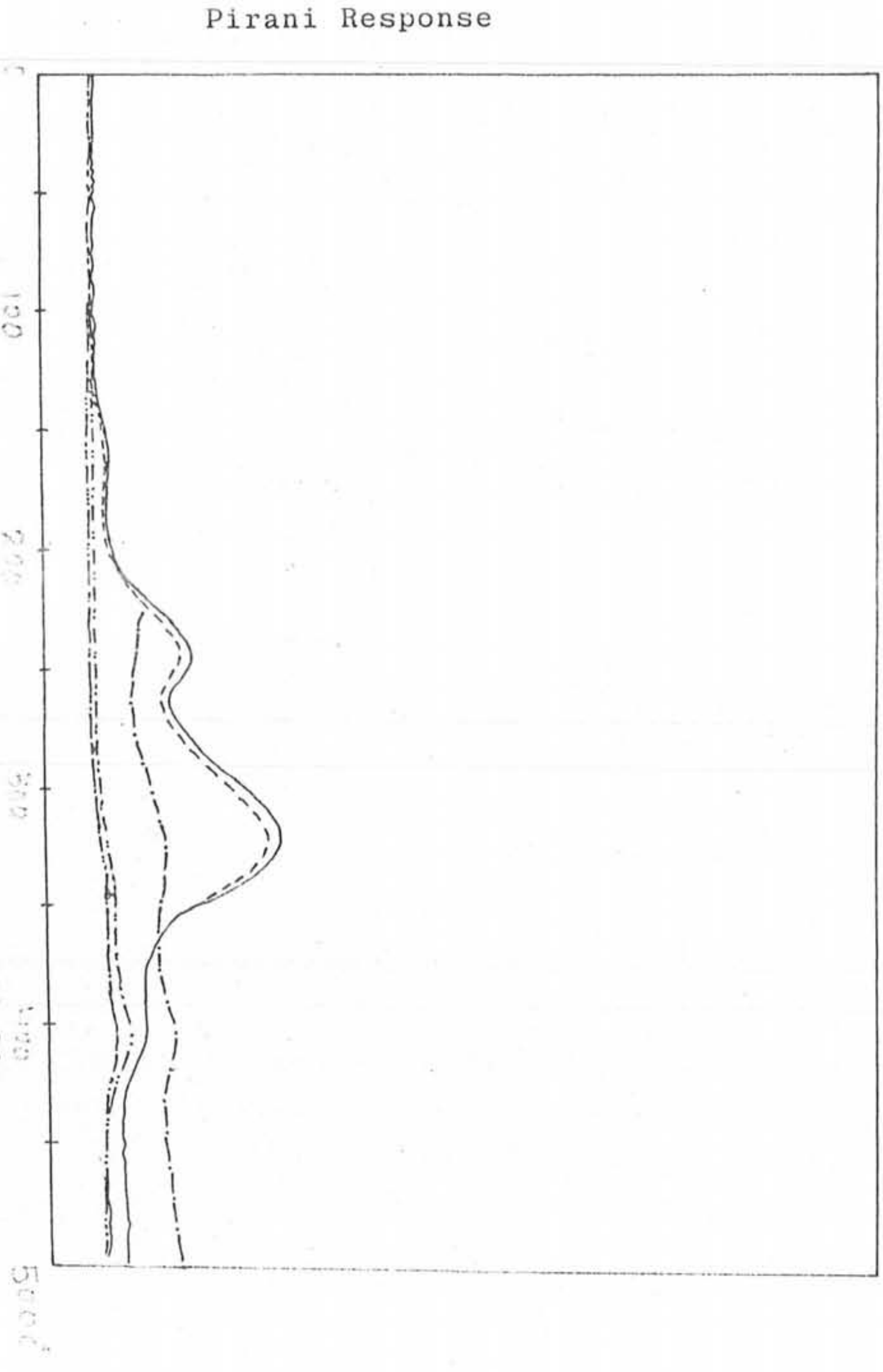


Fig. 4.11. TVA Curves for Copolymer GMA 10 - MMA 90

production as illustrated by the limiting rate effect at $-75^{o}$C trace and beyond the principle TVA peak, is apparent in homopolymer and copolymers having higher content of MMA monomer. The amount of MMA produced from copolymer 2(10% MMA) must therefore be considerably less than the copolymer 4 which contains 90% MMA, only if depolymerization was occurred as in PMMA homopolymer.

TVA Trace for 50% GMA copolymer shows a different pattern than the other two copolymers (10%, 90% GMA) volatilization starts around $200^{o}$C and three peaks are distinct, first smaller peak with rate maxima at $245^{o}$C. However the trace at $-196^{o}$C does not shows this peak. After $300^{o}$C this trace ($-196^{o}$C), shows the same general behaviour as all other traces (0, -45, -75, $-100^{o}$C). Two peaks of comparable size are evident with rate maxima at $345^{o}$C and $410^{o}$C. The most notable feature of TVA trace is the complexity of the products shown by the separation of the various responses for different trap temperatures. The $-196^{o}$C trace shows the same characteristic as the others above $300^{o}$C indicating that high volatility products are formed throughout decomposition.

<u>Sub-ambient Thermal Volatilization Analysis (SATVA)</u>: The condensable volatile products of degradation to $500^{o}$C under TVA conditions were separated by SATVA and characterized by IR spectroscopy. Typical traces obtained from

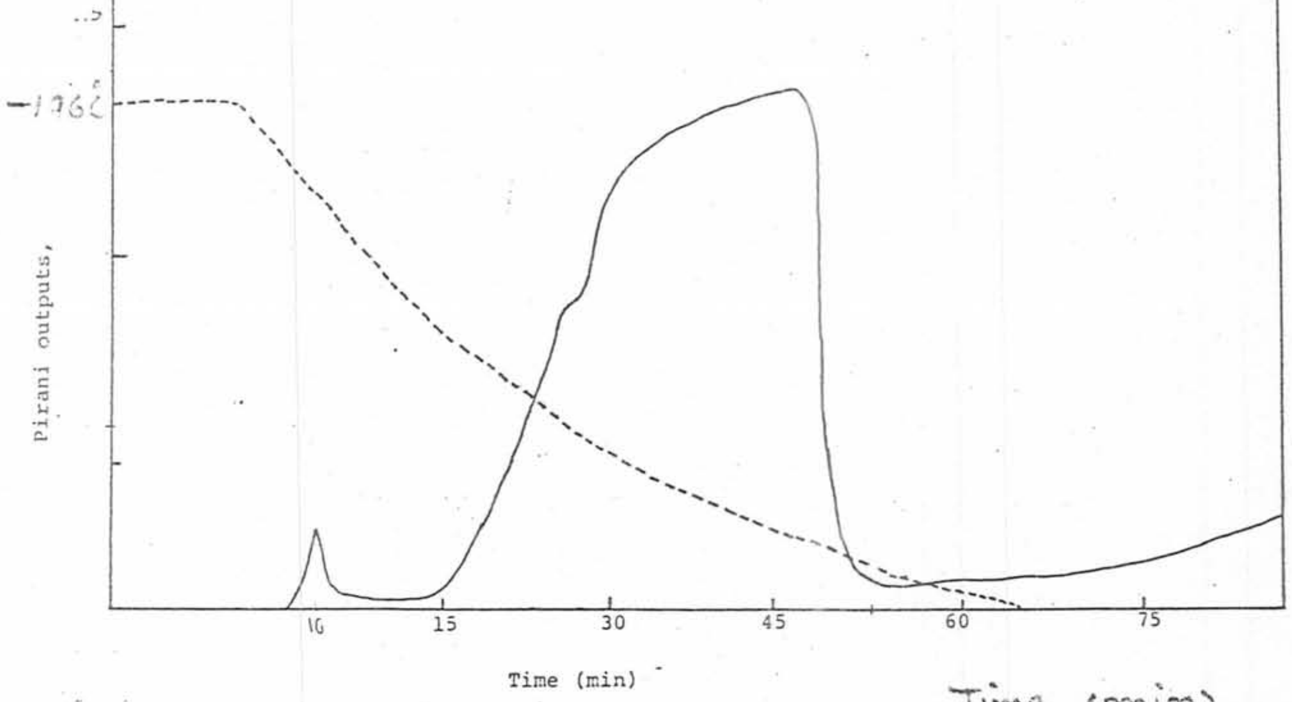


Fig. 4.13. SATVA Curve for PMMA.

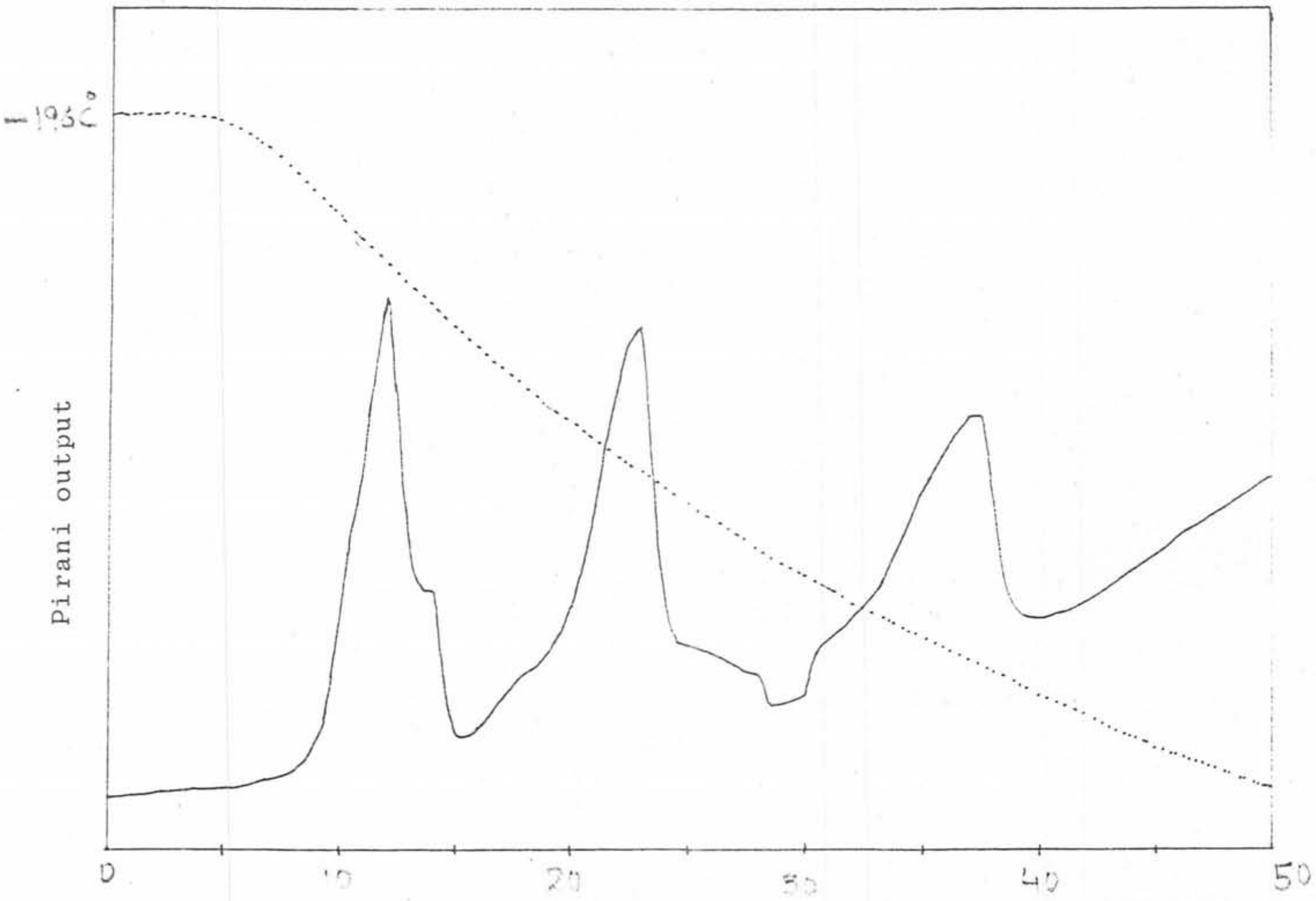


Fig. 4.12. SATVA Curve for PGMA.

PMMA and PGMA as illustrated in the figs. will be discussed separately. Poly(methylmethacrylate) SATVA curve for degradation products of PMMA (Fig. 4.13) shows three peaks. The first small peak with a rate maximum at about 10 minutes is CO and the second large peak with rate maximum at 35 minutes is of monomer MMA. A small shoulder on large peak is due to water. The third peak was not identified as the amount of this high boiling liquid, probably short chain fragments, is too small. Methyl methacrylate was the only product reported by other workers[48]. Results are summerized in the table 4.6. Poly(glycidyl methacrylate). SATVA curve for PGMA (fig. 4.12 ) shows four peaks. Ist peak with rate maximum at 10 minutes is, carbondioxide dimethylketene, propene and isobutene. 2nd peak (rate maximum 18.5 min.) is purely acrolein 3rd peak with rate maximum at 30 minutes is allylalcohol. Fourth peak starts increasing from 33 minutes and goes on increasing upto 45 minutes is due to very high boiling monomer GMA (B.P. 189°C) and Glycidol.

Copolymers: The SATVA curves for the volatile products of copolymers of GMA and MMA are illustrated in figs.

All spectra contain five peaks, although second peak appears as a small shoulder on the first peak. Results are summerised in the tables 4.2-10 . Size of the peaks changes as the copolymer composition changes. Lets discuss these peaks separately. Second peak which is not separable

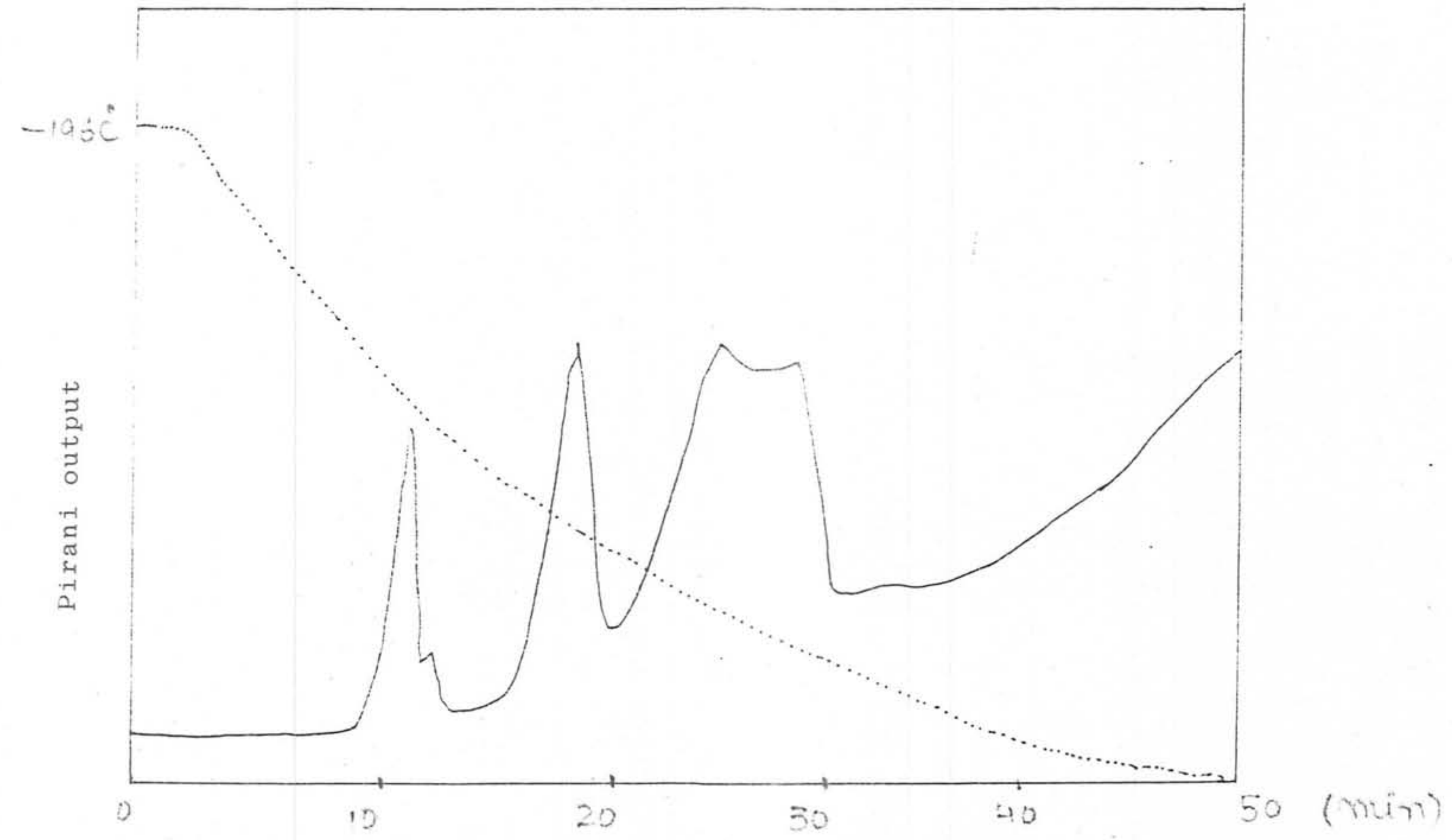


Fig. 4.14. SATVA Curve for Copolymer (GMA 90% - MMA 10%).

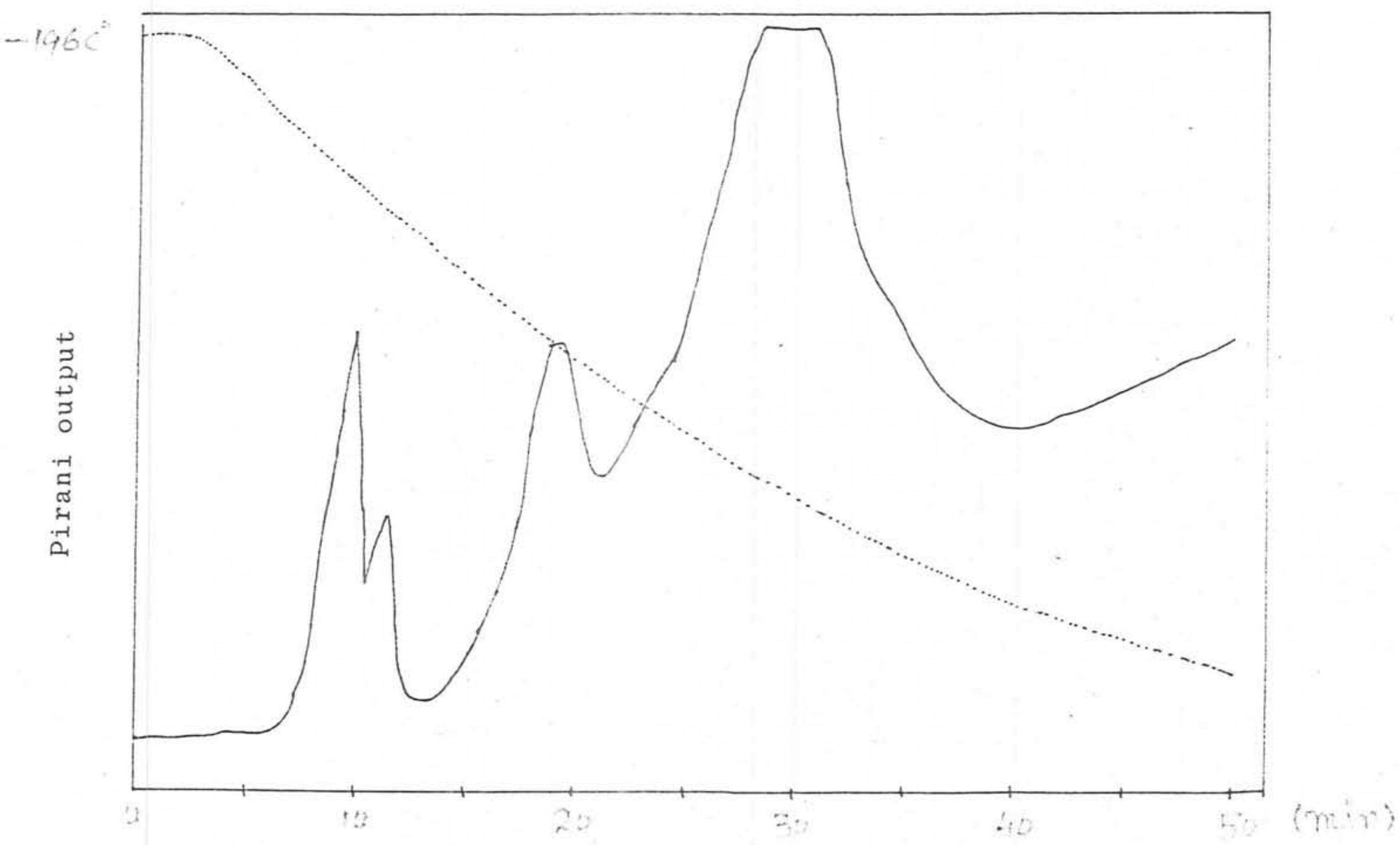


Fig. 4.15. SATVA Curve for Copolymer (GMA 50% - MMA 50%)

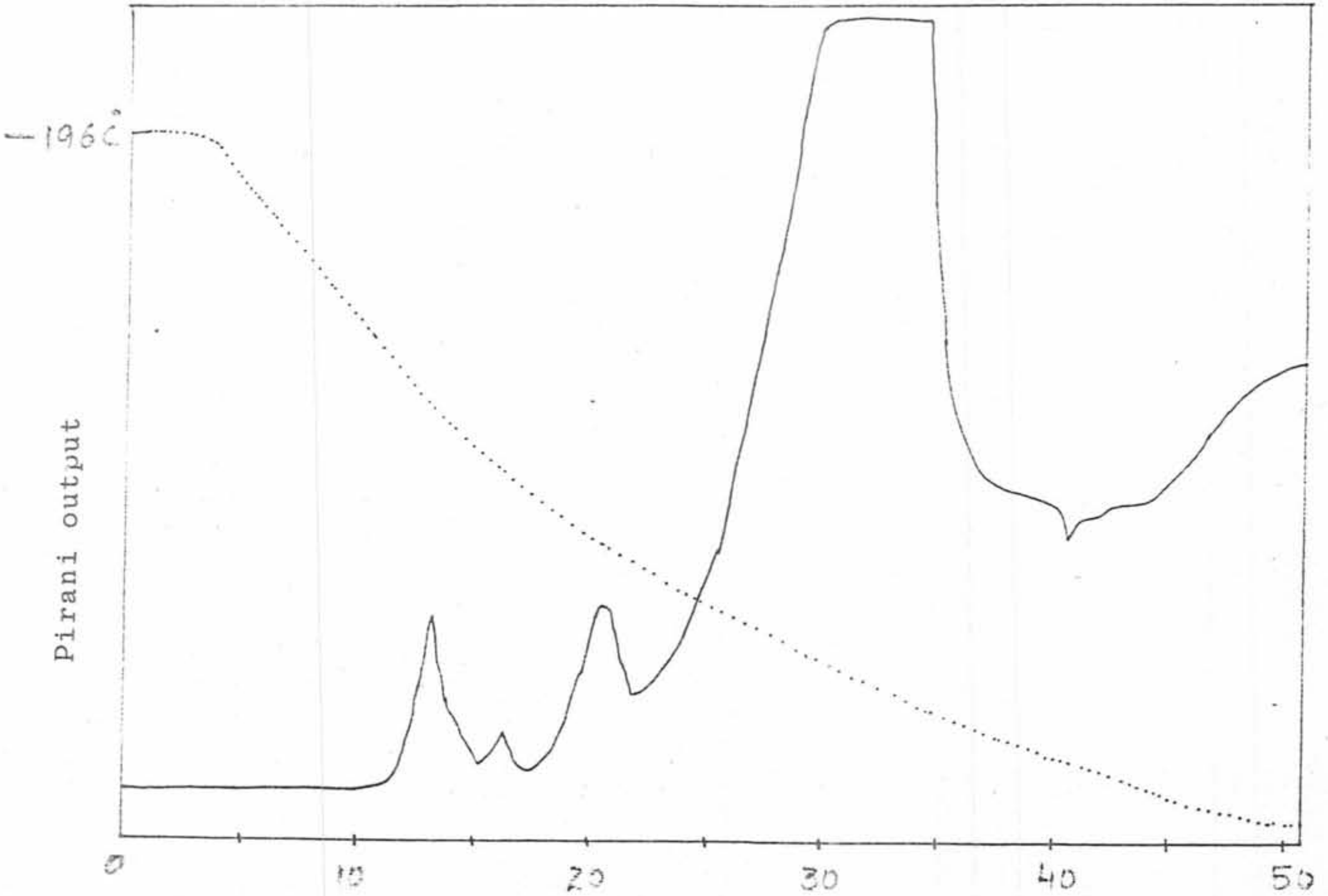


Fig. 4.16. SATVA Curve for Copolymer (GMA 10% - MMA 90%).

from the first peak actually appears as a shoulder of the first peak. So these two peaks will be discussed together. First and second peak contain a mixture of products, carbondioxide, propene, isobutene, and dimethyl ketene (dimethyl keten constitutes the second peak). Third peak with a rate maximum of about 20 minutes is of acrolein. Fourth peak (rate maximum at about 30 minutes) is due to monomer MMA and alkyl alcohol. Fifth peak, which is very broad, starts from 35 minutes is monomer GMA and Glycidol, that is high boiling materials. Results of SATVA along with relative mass peaks are summerized in the tables.

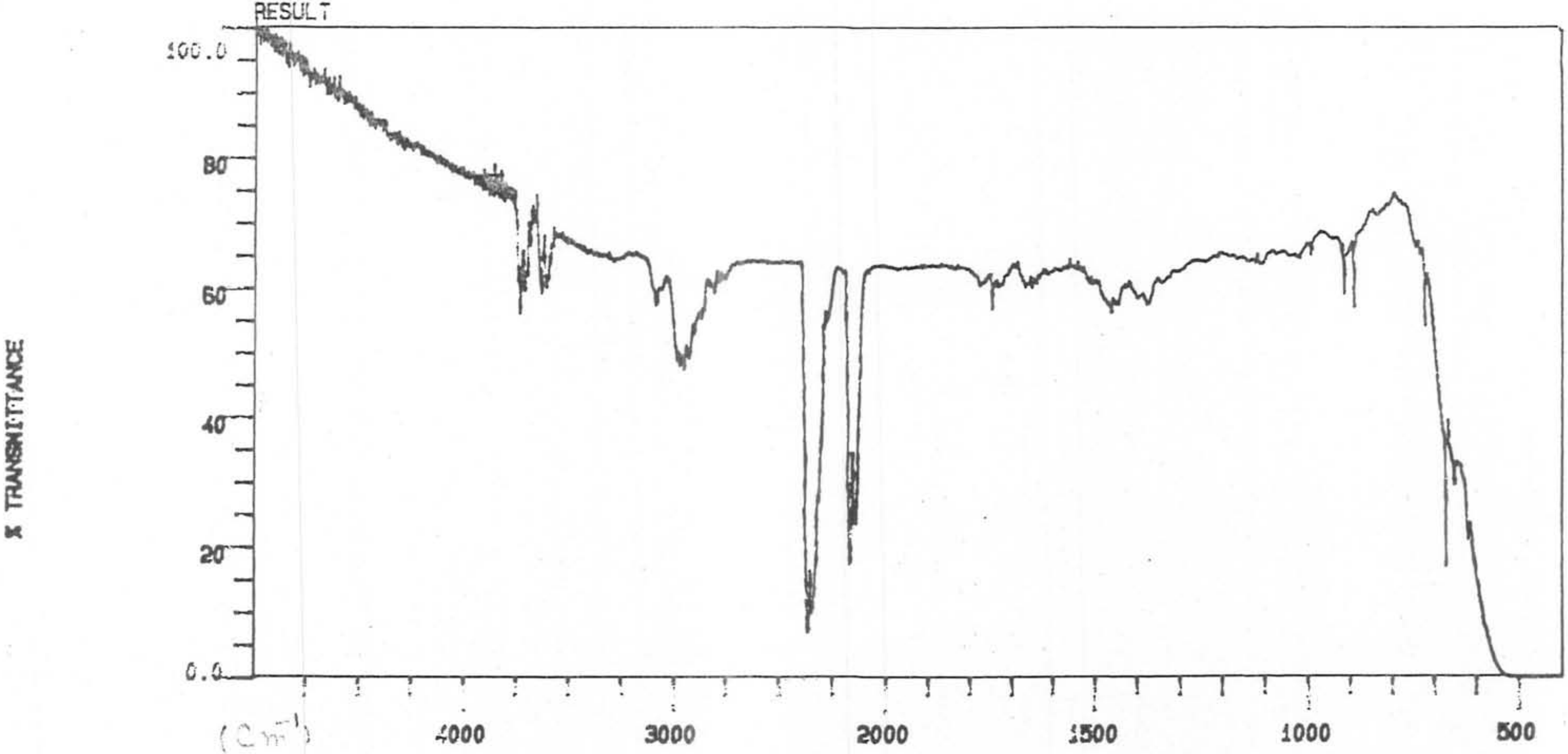


Fig. 4.17. FTIR-Peak Analysis (Peak 1) Copolymer (50:50)

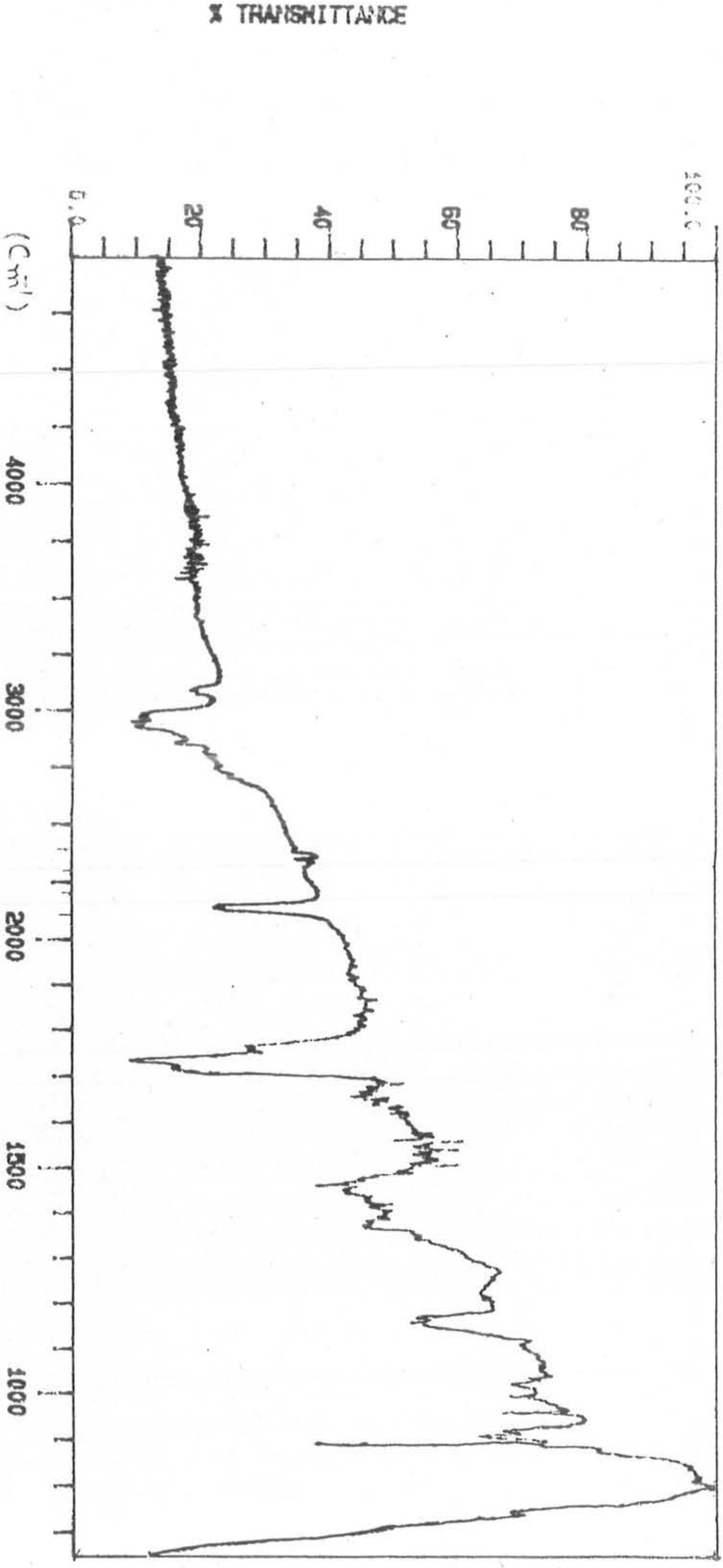


Fig. 4.18. FTIR Peak Analysis (Peak 2) Copolymer (50:50)

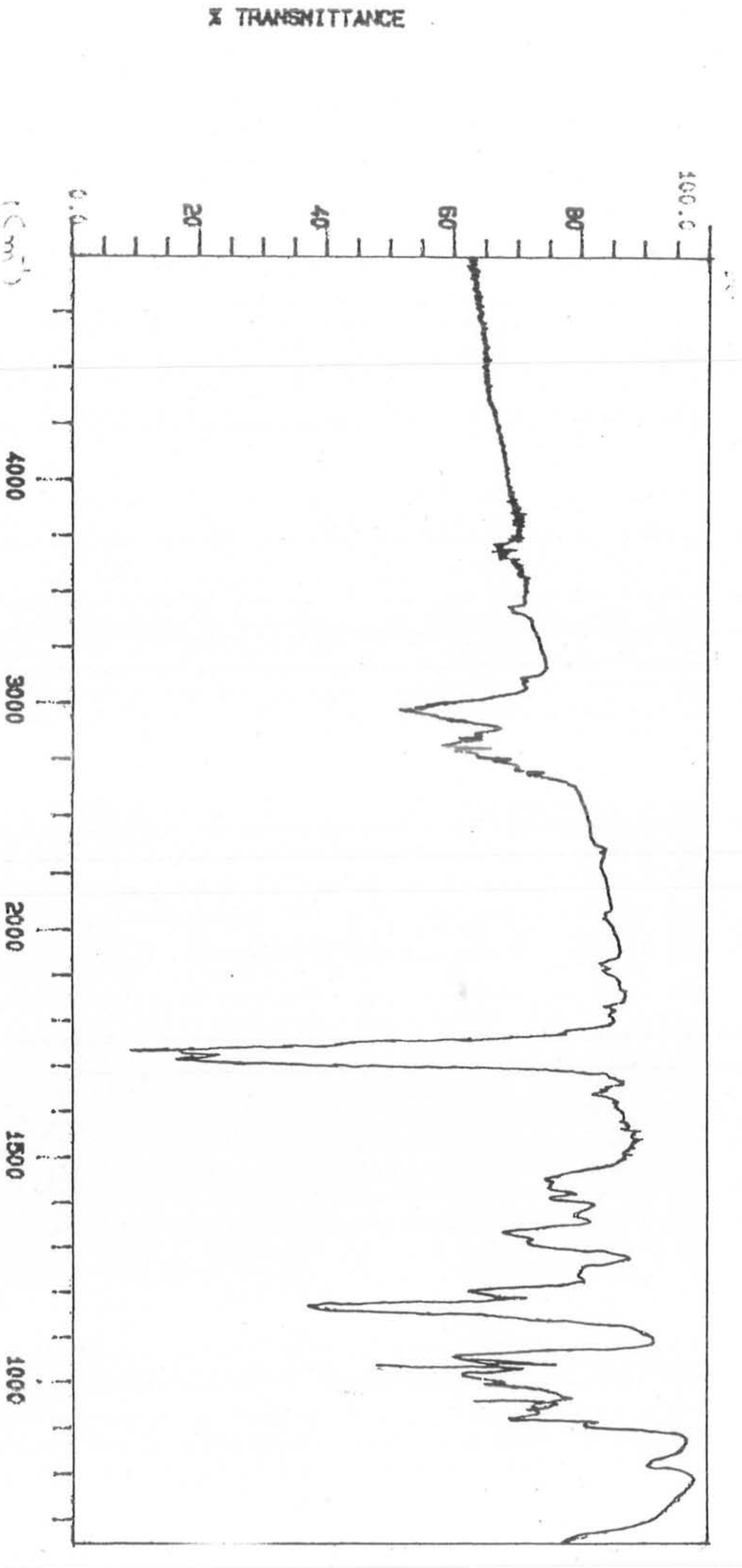


Fig. 4.19. FTIR-Peak Analysis (Peak 3) Copolymer (50:50)

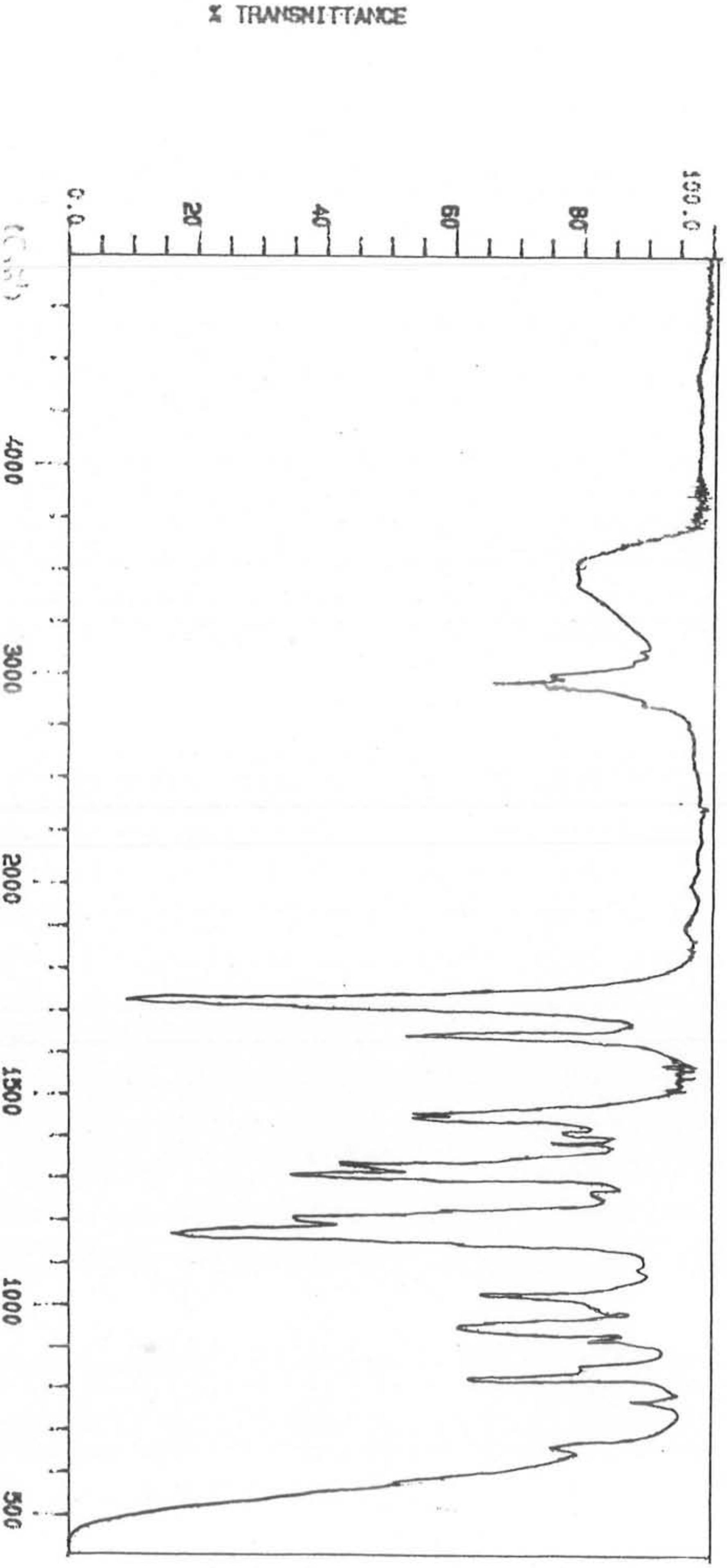


Fig. 4.20. FTIR-Peak Analysis (Peak 4) Copolymer (50:50)

## Table -4.6

### SATVA Peak Analysis (PMMA)

| Peak No. | Peak Time | IR (Cm$^{-}$) | Mass Peak | Products |
|---|---|---|---|---|
| 1 | 10 | 2300, 670 | - | Carbondioxide |
| 2 | 40 | 3200, 3400 | - | Water |
| | | 1030, 1020 | - | Methanol |
| | | 2945, 1720, 1644<br>1164, 981 | - | Methyl Methacrylate |

## Table - 4.7

### SATVA Peak Analysis (PGMA)

| Peak No. | Peak Time | IR ($Cm^{-1}$) | Mass Peak | Products |
|---|---|---|---|---|
| 1 | 10 | 2300, 670 | 44 | Carbondioxide |
| | | 2170, 2140 | 70 | Dimethyl Ketene |
| | | 3130-2940, 1670<br>990, 910 | 42 | Propene |
| | | 3090-2950,<br>1660, 890 | 56 | Isobutene |
| 2 | 18.5 | 3050-2750, 17107<br>1410, 1150, 1980,<br>920 | 56 | Acrolene |
| 3 | 30 | 3620, 3320,<br>30410, 2920, 1640,<br>1420, 1020, 990. | 58 | Allyl alcohol |
| 4 | 33+ | 3680, 3600,<br>3500, 2940,<br>1100, 950 | 74 | Celycidol |
| | | 2950, 2320,<br>1722, 1671,<br>945, 909 | 142 | Glycidyl Methacrylate |

## Table - 4.8

### SATVA Peak Analysis (90% GMA/10% MMA)

| Peak No. | Peak Time (Min.) | IR ($Cm^{-1}$) | Mass Peak | Products |
|---|---|---|---|---|
| 1 & 2 | 12.5 | 2310, 670 | 44 | Carbondioxide |
| | | 2170, 2140 | 70 | Dimethyl Ketene |
| | | 3080, 2950, 1640, 890 | 42 | Propene |
| | | - - | 56 | Isobutene |
| 3 | 20 | 2950, 2855 1710, 1410, 1160, 960, 920 | 56 | Acrolin |
| 4 | 26.5 | - - | 58 | Allyl Alcohol |
| | | 2920, 2859, 1730, 1640, 1455, 1257, 1197, 1167 | 100 | MMA |
| 5 | 34+ | 2950, 1722, 1671, 1257, 945, 909. | 142 | GMA |
| | | 3680-3500, 2940, 1100, 950 | 74 | Glycidol |

## Table – 4.9

### SATVA Peak Analysis (50% GMA/50% MMA)

| Peak No. | Peak Time | IR ($Cm^{-1}$) | Mass Peak | Products |
|---|---|---|---|---|
| 1 & 2 | 11 | 2300, 670 | 44 | Carbondioxide |
| | | 2170, 2140, | 70 | Dimethyl Ketene |
| | | 3080, 2950,<br>1640, 890 | 42 | Propene |
| | | - - | 56 | Isobutene |
| 3 | 19 | 3000-2700,<br>1710, 1410,<br>1160, 990, 920 | 56 | Acrolein |
| | | 1030 - 1012 | 32 | Methanol |
| 4 | 30 | 2980, 3600,<br>3300, 1640,<br>1410, 1020 | 58 | Allyl Alcohol |
| | | 2929,2850,1730,<br>1640,1455,1257,<br>1167. | 100 | MMA |
| 5 | 40+ | 3680-3500,2940<br>1100,950 | 74 | Glycidol |
| | | 2950,1722,1671<br>1455,1167,945,909 | 142 | GMA |

## Table - 4.10

### SATVA Peak Analysis (10% GMA/90% MMA)

| Peak No. | Peak Time (Min.) | IR ($Cm^{-1}$) | Mass Peak | Products |
|---|---|---|---|---|
| 1 & 2 | 13 | - - | 28 | Carbon monoxide |
| | | 2300, 670 | 44 | Carbon dioxide |
| | | - - | 42 | Propene |
| | | - - | 56 | Isobutene |
| 3 | 21 | 2920, 2860, 1710, 1460, 1160, 960 | 56 | Acrolein |
| | | 3600-3000, 2920, 2860 | | |
| 4 | 32.5 | 1640, 1460, 1150, 1030, 960 | 58 | Allylalcohol |
| | | 2962, 1740, 1644, 1443, 1164 | 100 | Methylmethacrylate |
| 5 | 41+ | 3620-3500, 2940, 1100, 950 | 74 | Glycidol |
| | | 2950, 1722, 1671, 1257, 1167, 945, 909 | 142 | GMA |

## Cold Ring Fraction (CRF):

The CRF which resulted from the degradation of PGMA and copolymer (50:50) by heating upto 500°C under TVA conditions were examined by ir spectroscopy. The ir spectrum of the Cold Ring Fraction was compared with that of the undegraded homopolymer (Fig. 4.21). In most respects these spectrum are similar, indicating that CRF consists essentially of short chain fragments of the polymer. CRF shows additional peaks, however, at 1640 $cm^{-1}$ which is typical of C=C, introduced into the polymer chain during the formation of short chain fragments.

In Fig. 4.22, the ir spectrum from the 50% GMA copolymer is compared with that of the undegraded copolymer. Spectra, are similar in most respects indicating that CRF again consists essentially of short chain fragments of copolymer. CRF shows additional peaks, however at 1020, and 1805 $cm^{-1}$, which are typical of six membered anhydride ring structure, previously reported in anhydro poly (methacrylic acid) by Grant and Grassie[49] and found also in glutaric anhydride[50]. The amount of CRF is greatest for 50% GMA copolymer.

## Analysis of the Residue:

The dark brown to black intractable residue which remains after heating to 500°C, for homopolymers and copoly-

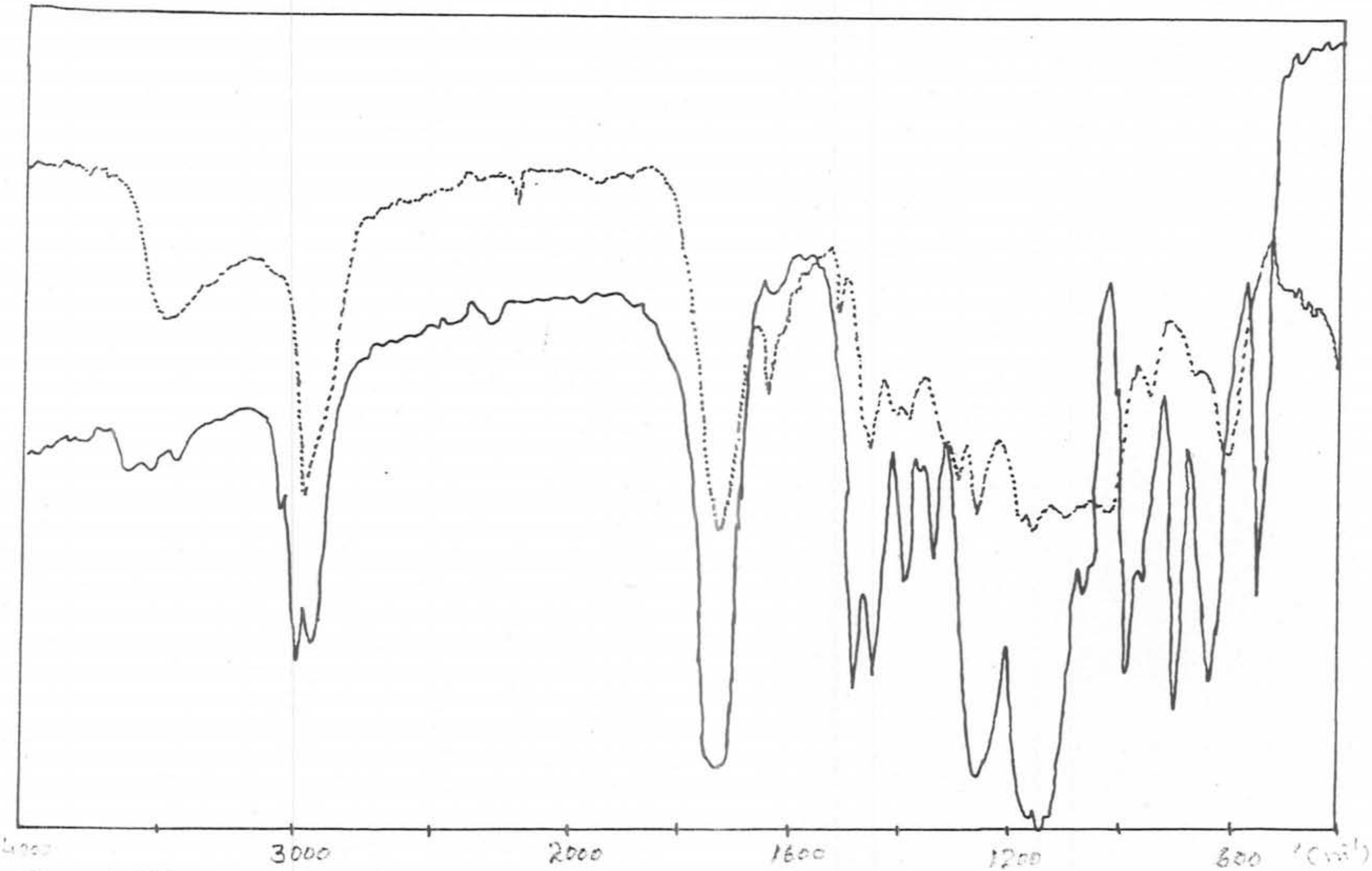


Fig. 4.21. PGMA. IR. - - - - -Cold Ring Fraction
——— Undegraded Polymer.

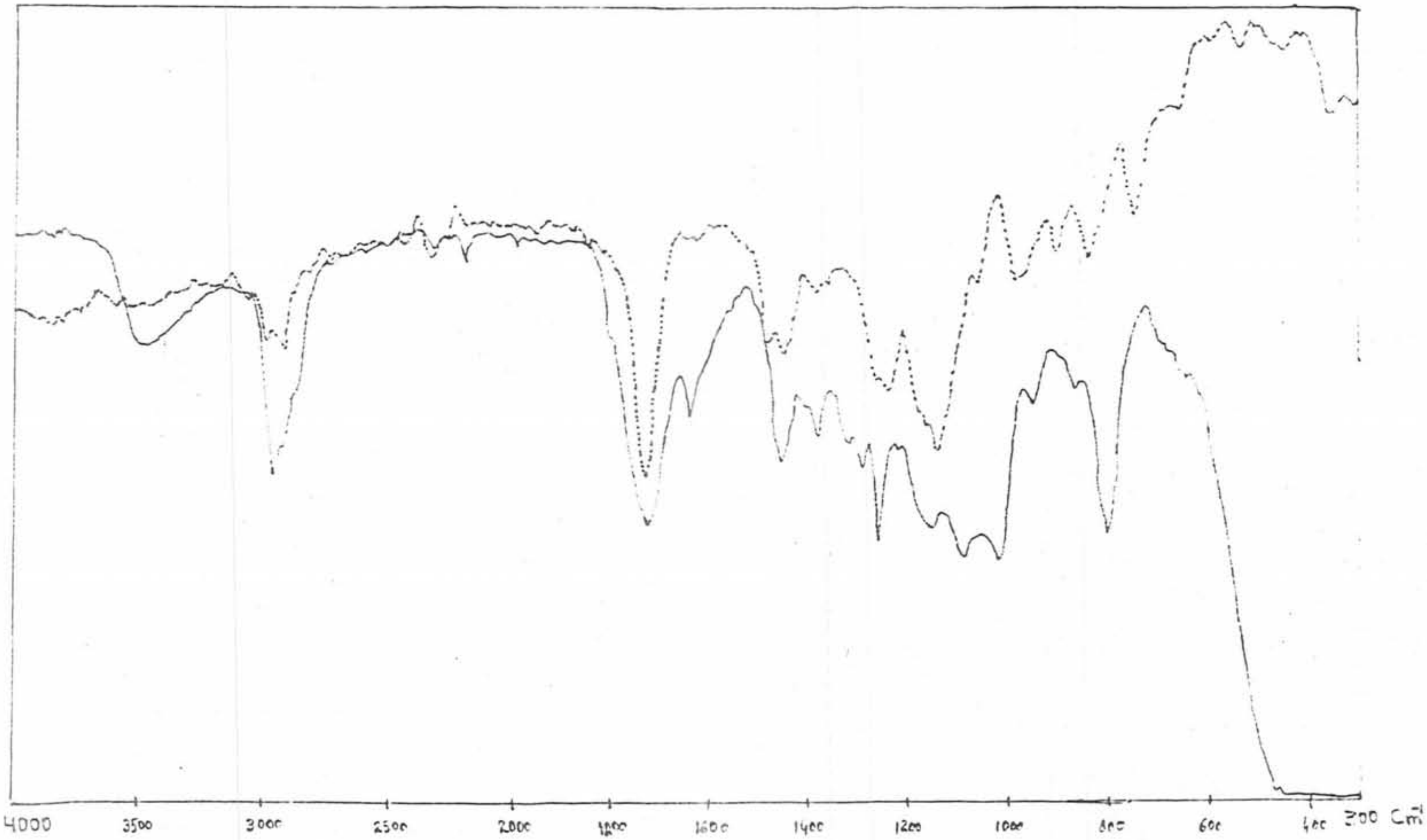


Fig. 4.22. Copolymer (50:50) IR.—Cold Ring Fraction

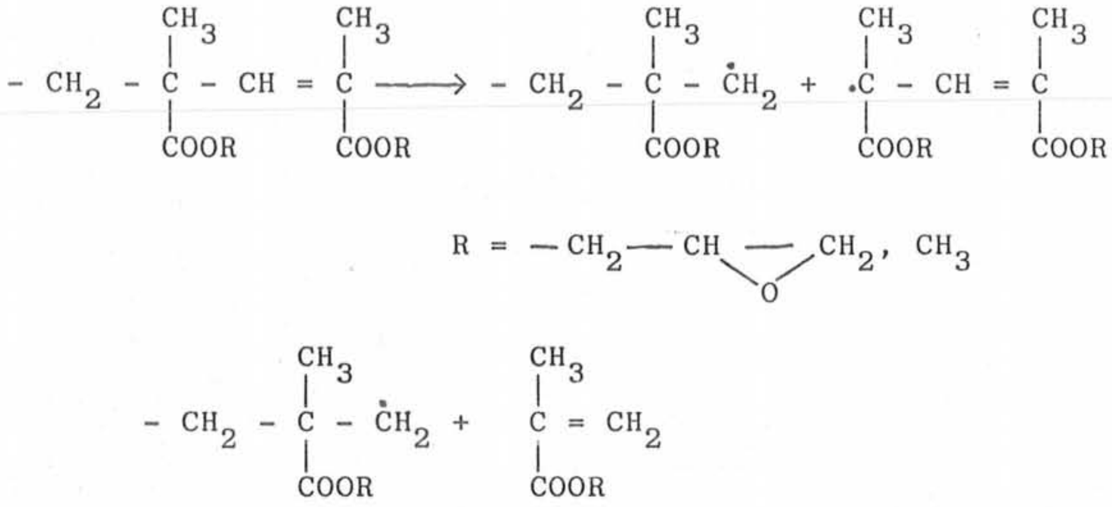
----------Undergraded Copolymer

mers, % by weight of the original polymer samples is shown in the Table

## Mechanism of Degradation:

Results obtained by TVA, SATVA, TG, and DTA, shows that the principal degradation product of PMMA is monomer only. PGMA however shows a different type of degradation. Many volatile products are obtained as, carbondioxide, dimethyl ketene, propene, isobutene, acrolein, allyl alcohol, and Glycidol other than the Glycidyl methacrylate monomer. Similarly copolymers shows both the monomers, GMA, MMA and other volatile products. The IR spectra of CRF of copolymer (50% GMA) shows that anhydride rings are also formed during thermal degradation of copolymer. A general mechanism which describes the depolymerization to monomers and evolution of all the volatiles is concluded here for PGMA and copolymers. TG and TVA data of PGMA shows that copolymer degrades in two stages, i.e. from unsaturated chain ends and by random chain scission.

(i) Monomer formation from unsaturated chain ends.

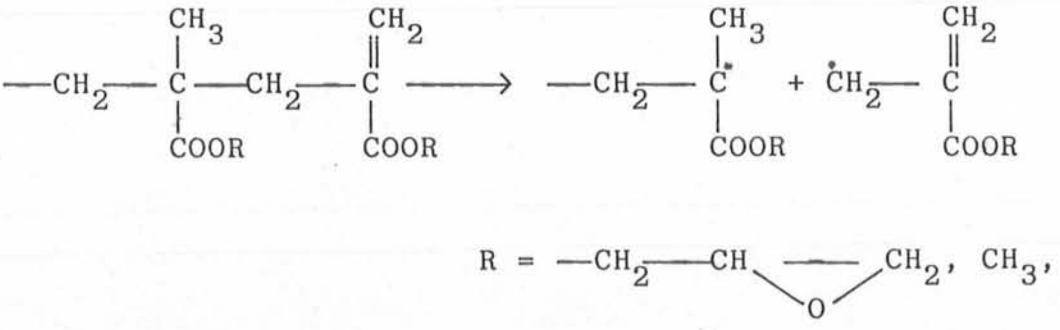


$$-CH_2-\underset{COOR}{\overset{CH_3}{C}}-CH=\underset{COOR}{\overset{CH_3}{C}} \longrightarrow -CH_2-\underset{COOR}{\overset{CH_3}{C}}-\dot{C}H_2 + \cdot\underset{COOR}{\overset{CH_3}{C}}-CH=\underset{COOR}{\overset{CH_3}{C}}$$

$$-CH_2-\underset{COOR}{\overset{CH_3}{C}}-\dot{C}H_2 + \underset{COOR}{\overset{CH_3}{C}}=CH_2$$

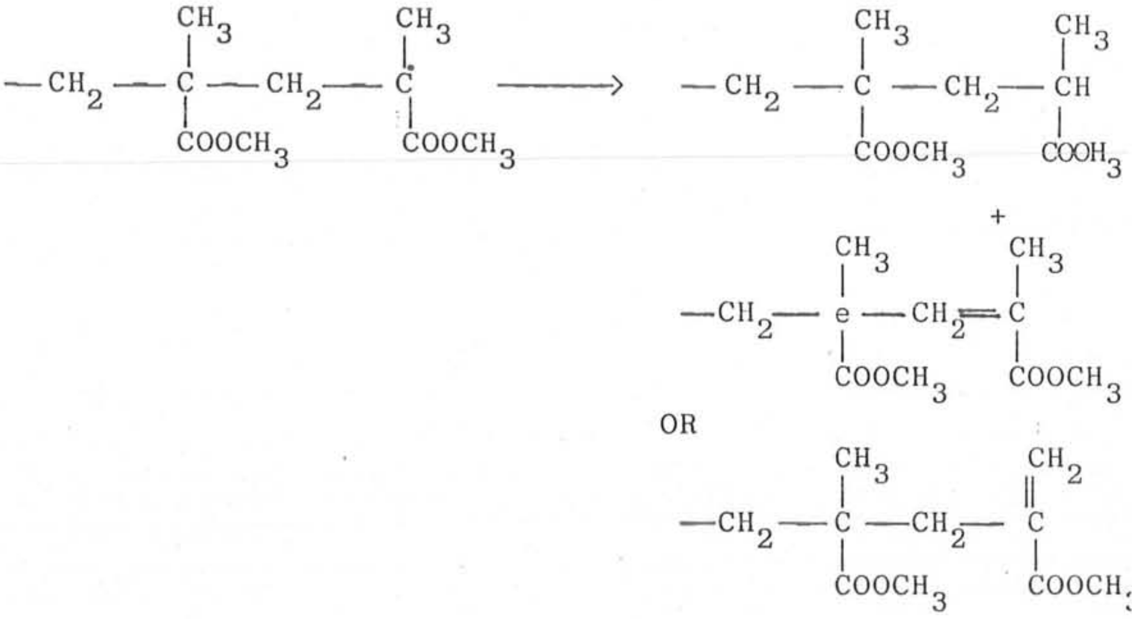
Monomer.

OR Monomer formation may be represented as:



$$-CH_2-\underset{COOR}{\overset{CH_3}{C}}-CH_2-\underset{COOR}{\overset{CH_2}{\overset{\|}{C}}} \longrightarrow -CH_2-\underset{COOR}{\overset{CH_3}{\dot{C}}} + \dot{C}H_2-\underset{COOR}{\overset{CH_2}{\overset{\|}{C}}}$$

One half of the polymer chains in PMMA contain unsaturated end groups, because it has been established that PMMA is terminated entirely by disproportionation, as shown.

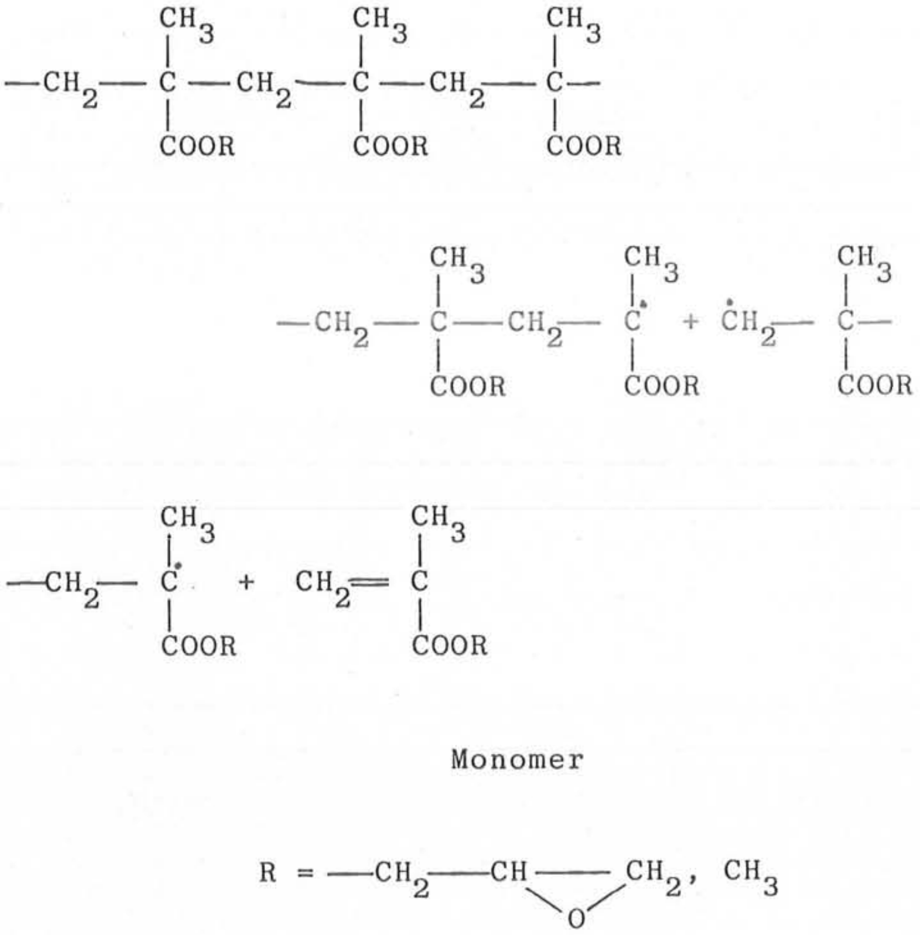


These allylic C-C, C-H, bonds have relatively less bond dissociation energy and homolytic cleavage can occur in such polymers. From the kinetic data activation energy has been calculated to be 48 Kcal/mole for initiation step of thermal decomposition. For allylic C-C bonds this is a reasonable amount of energy for dissociation.

The type of end initiation has also been shown by PGMA as revealed by TVA and TG Data. Molecular weight of PMMA is relatively high as compared to PGMA. This low molecular weight will cause an appreciable amount of degradation by end initiation.

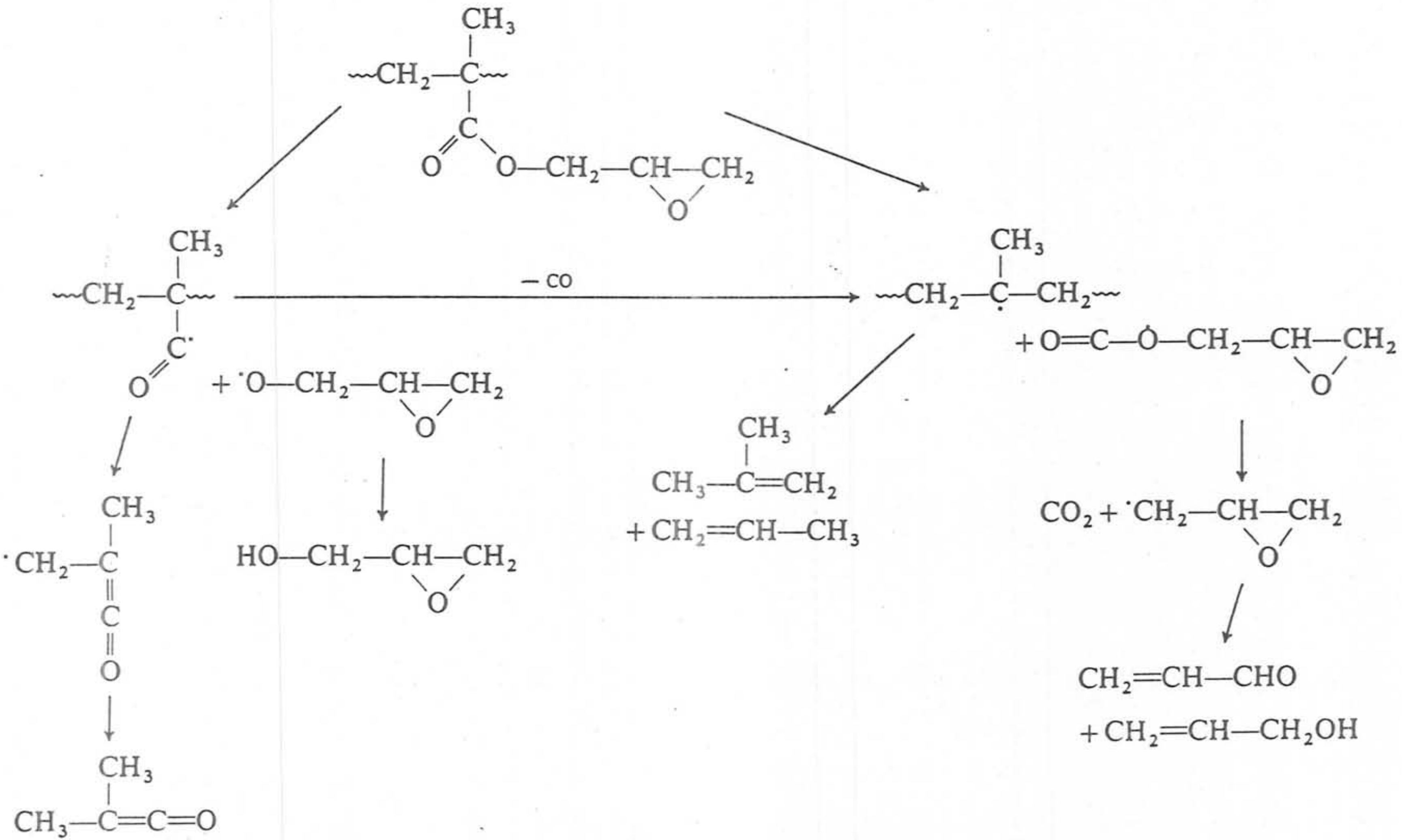
## (ii) Random Chain Scission:

Both TVA and TG data shows that degradation in the range of 300°C to 400°C is associated with initiation by random chain scission. The radicals thus produced, then depropagate, which is an exact reverse of propagation reaction in polymerization. This may be shown as



## (iii) Ester Decomposition:

The degradation products of copolymers are MMA and GMA which results by depolymerization reaction. SATVA


– CO
CH3–C(CH3)=CH2
+ CH2=CH–CH3
CO2 + ·CH2–CH–CH2 (O)
CH2=CH–CHO
+ CH2=CH–CH2OH
HO–CH2–CH–CH2 (O)
CH3–C(CH3)=C=O

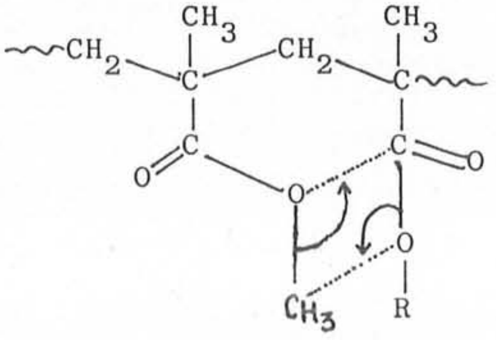
Scheme 1

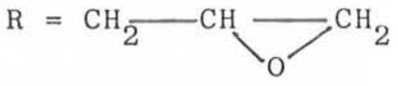
of PGMA and all the copolymers shows that except the major reaction which is depolymerization, the ester decomposition is also accounted which is the cause of volatile products, e.g. acrolein, allyl alcohol, carbondioxide, carbonmonoxide dimethyl ketene, isobutene, propene, and glycidol. Ester decomposition of PGMA is shown in the scheme I.

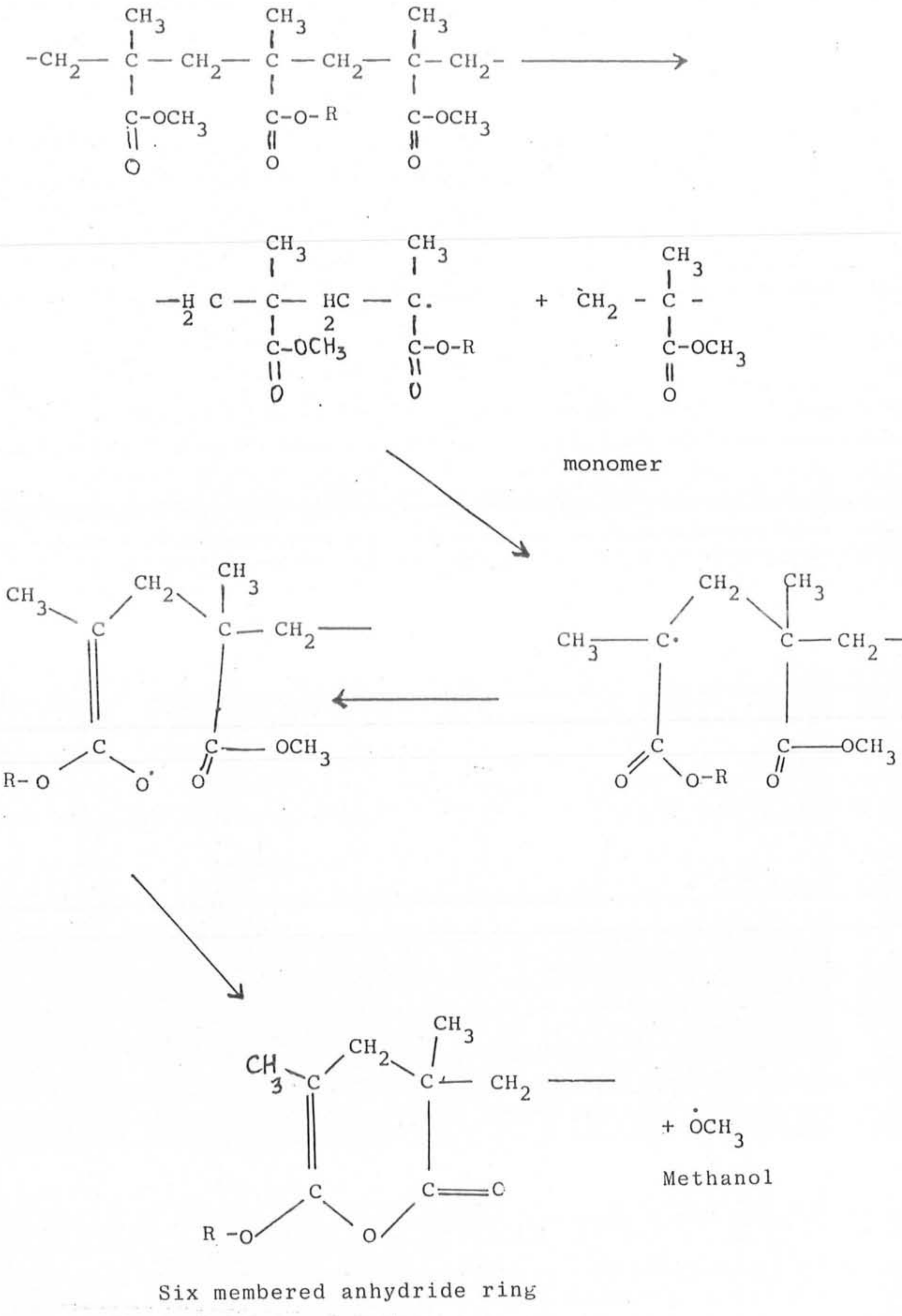
**Anhydride ring formation**:

the presence of methanol has been confirmed by FTIR of the degradation products of 50:50 copolymer, mass spectra also shows the presence of methanol. CRF of 50% GMA copolymer also shows peaks at 1020, 1805 cmy-$^{1}$ which are typical of anhydride rings. The production of $CH_3OH$ via anhydride can be explained according to the mechanism as shown on next page.

An alternative route, which explains the formation of six-membered anhydride rings, is through a concerted four-centre type transition state as shown below.






monomer
+ $\dot{O}CH_3$
Methanol
Six membered anhydride ring

Glycidyl methyl ether would be eliminated in this reaction, but has not been detected in the degradation products. Considering the volatility and ir spectrum of this material however, it is clear that it would be undetected in small concentration, since it has no characteristic ir absorptions. Further investigation by glc of the least volatile SATVA fraction in the copolymer degradation products is required to verify this.

## DISCUSSIONS

Polymerization data of the present study indicates that molecular weight of polymethyl methacrylate is higher than the poly (glycidyl methacrylate). This difference may be attributed to the more unsaturation in the latter. Intrinsic viscosity data shows that viscosity depends not only on the molecular weight but also on the groups present in the monomer. Epoxy compounds usually more viscous (Epoxy used as adhesives due to more viscosity). Thus PGMA although has lower molecular weight but has higher viscosity than PMMA. TVA and TG Data of homopolymers shows that PMMA depolymerizes essentially to monomer. PGMA however shows that two reactions occurs, first, Depolymerisation to monomer and second decomposition of ester group which leads to the volatile products shown before. Copolymers also shows degradation by above two reactions, comparing PGMA and copolymers with the behaviour of PMMA, It may be concluded that monomer formation occurs by two methods. In the lower range of temperature (upto 250$^{o}$C) monomer formation is due to initiation at unsaturated chain ends. In the higher range of temperature (300$^{o}$C to 400$^{o}$C)degradation of homopolymers and copolymers occurs by random chain scission. This is attributed to the low activation energy for allylic C-C bonds for initiation (48 Kcal/mole). At high temperature decomposition of repeat units involving side group scissions produce other minor products, observed during decomposition. Anhydride rings have been detected in the CRF of 50% GMA copolymer. The production of anhydride rings in a polymer chain initially containing MMA units has been shown in various previous studies to interfere with unzipping to monomer, which is unable to proceed beyond the ring structure[51,55]. The effect is that the end initiated depolymerization is suppressed and monomer production becomes dependent on many more initians by backbone scission, which require higher temperature. Stablization of the polymer towards monomer production is therefore observed; even low concentration of anhydride rings have a marked effect because the zip length in the depolymerization of pure PMMA is very large.

## REFERENCES:

1) H. Hesiwetz and Habermann Ann. Chem. Pharma. 159, 304, (1871).

2) C. Harries, Ber. 37, 2708 (1904)- 38, 1195, 3985 (1905).

3) C. Harries Ann. Ann. 406, 173, (1914).

4) H. Staudinger Ber. 53, 1073 (1920).

5) H. Mark and G.S. Whit by Eds. Collected papers of Wallace. Hume Carothers. Interscience Publishers, New York (1940).

6) W.H. Carothers, "Polymerization" Chemical Revs. 8, 353, (1931).

7) P.J. Flory, "Condensation Polymerization and Constition of Condensation Polymers", p. 221, New York (1949).

8) J.L. Stanford, and Stepto, J. Chem. Soc. Faraday Trans. I. 71, 1292, (1975).

9) V. Crescenz, et. al. Ric. Sci. Suppl. 29, 1424 (1959), 30, 1680, (1960), Chem. Abstract. 54, 4109, (1959).

10) Nishikubo, T; Saita, S. and Fuji, T; J. Polym. Sci. Part A Polym. Chem. 25, 1339, (1987).

11) Kalal, J; J. Polym. Sci. Polym. Symp. 62, 251 (1978).

12) Frechet, J.M. J; Bald, E. and Svec, F, React. Polym. 1, 21, (1985).

13) Lindsay, D. and Sherrington, D.C. React. Polym; 3, 327 (1985).

14) Dhal, P.K., Babu, G.N. Sudhakaran, S. and Borkar, P.S. Makromol. Chem., Rapid Commun; 6, 91 (1985).

15) Dhall P.K; Babu, G.N. Sudhakaran, S. and Borkar, P.S; J. Polym. Sci., Polym. Chem. Ed. 23, 319, (1985).

16) Thomson, L.F. You, L. and Doerrics, E.M; J. Electrochem. Soc; 126, 1703, (1979).

17) F.W. Billimeyer, Text book of Polymer Science, Sec. Edi. (1971).

18) M.B. Neiman, Aging and Stablization of Polymers, Consultant Bureau, New York, Ch. 6 (1965).

19) N. Grassie, Chemistry of Polymer Degradation Process, Butterworths, London, (1956).

20) E.M. Montroll and R. Simha, J. Chem. Phys. 8, 721, (1940).

21) L.A. Wall, J. Res. Nat. Bur. Stand. 41, 315, (1948).

22) W.G. Oaks and R.J. Richards, J. Chem. Soc. 2929, (1949).

23) A. Votinov, P. Kobeko, and F. Morei, J. Phy. Chem. (USSR) 16, 106, (1942).

24) N. Grassie and H.W. Melville, Proc. Roy. Soc. (London) Al 99, 24, (1949).

25) N. Grassie and H.W. Melville, Proc. Roy. Soc. (London) Al 99, 14, (1949).

26) N. Grassie and E. Vance, Tran. Faraday Soc; 49, 184, (1953).

27) S.L. Madoosky, J. Polym, Sci., 11, 49 (1953).

28) S.L. Madorsky, Thermal Degradation of Organic Polymer, Interscience, New York (1964).

29) G.C. Marks, J.L. Benton, and C.M. Thomas, S.C.I. Monograph No. 26, London (1967).

30) D. Druesdow and C.F. Gibbs, Nat. Bur. Standeric 525, 69 (1953).

31) R.R. Stromberg, S. Straus and B.G.A. Chhamer, J. Polym. Sci. 35, 355, (1959).

32) N. Grassie and J.N. Hay, J. Polym. Sci. 56, 189, (1960).

33) N. Grassie, and J.N. Hay, S.C.I. Monograph No. 13, London (1961).

34) P.H. Grant and N. Grassie Polym. I, 125 (1960).

35) S.E. Bresler, M.M. Koton, A.T. Osminskai, A.6. Prove. and M.N. Savilskaia Poly. Sci. (USSR) I, 393, (1960).

36) J.P.W. Houtman, J.V. Steenis and P.M. Heertjes Rec. Tranv. Chim. 65, 78, (1964).

37) A. Maccoll, J. Chem. Soc. 3398 (1958).

38) D. Dollimore and G.G. Hell, Carbon, 5, 65, (1967).

39) I.C. McNeill, J. Polym. Sci. A4, 2479 (1966).

40) I.C. McNeill, L. Ackerman, N.S. Gupta, M. Zulfiqar and S. Zulfiqar, J. Polym. Sci. Polym. Chem. Ed. 15, 2381 (1977).

41) N. Grassie and G. Scott, Polym. Deg. and Stabilization Ist Ed. (1985).

42) G.C. Cameron and D.R. Kane, Makromol. Chem. 75, 113, (1968).

43) S. Sulfiqar, M. Zulfiqar, T. Kausar, and I.C. Mcneil Polym. Degradation and Stability.

44) D.A. Skoog and D.M. West Principals of Instrumental Analysis See Ed.

45) D.B.V. parker, Polymer Chemistry Ist. Ed. 1974.

46) I.C. McNeill, Europ. Poly. J. 6, 373 (1970).

47) I.C. McNeill, Europ. Polym. J. 4, 21, (1968).

48) I.C. McNeill, L. Ackerman, J. Polym. Sci. 15, 2381, (1977).

49) P.H. Grant and N. Grassie. Polym. 1, 125, 1960.

50) H.M. Wassermann and H.E. Zimmermann J. Am. Chem. Soc. 72, 5787 (1950).

51) A. Jamicson and I.C. McNeill Europ. Polym. J. 10, 217 (1974).

52) A. Hamoudi and I.C. McNeill, Europ Polym. J. 14, 525 (1978).

53) I.C. McNeill and D. Neil Europ. Polym. J. 6, 569, (1970).

54) D.L. Gardner and I.C. McNeill Europ. Polym. J. 7, 603 (1971).

55) G. Camino, N. Grassie and I.C. McNeill. J. Polym. Sci. Polym. Chem. Ed. 16, 95, (1978).