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Joseph E. Clark
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STUDIES IN THE THERMAL STABILITY
OF POLY(METHYL METHACRYLATE)

BY
JOSEPH E. CLARK, M.S.

A Thesis
Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy at Assumption
University of Windsor

Windsor, Ontario
September, 1963
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ABSTRACT

A new technique was developed to allow kinetic studies of the rapid degradation of polymethylmethacrylate (PMMA) at elevated temperatures.

The apparatus consists essentially of an automatic recording quartz spoon gauge. For studies of PMMA pyrolysis, a polymer film was deposited on the inside walls of the spoon gauge, and after evacuating and sealing off the gauge it was immersed in a hot liquid metal bath in such a way that the deflection of the gauge pointer was measured by a Statham Transducer, whose electrical output signal was electrically recorded. Thus, the pressure of the volatile products of PMMA degradation was rapidly recorded; temperature was simultaneously recorded on the other channel of the two-channel recorder via a calibrated thermocouple adjacent to the spoon gauge in the metal heating medium.

Significant advantages of the system are:

1) Very accurate measurements of volatile polymer degradation products are rapidly and continuously recorded.
2) Only small quantities of polymer are needed, i.e., 40 to 20 mg of PMMA, or even less.
3) Temperature equilibrium is achieved in less than 30 seconds, i.e., one-tenth the time required by previous investigators.
Useful data for PMMA degradation were obtained up to 400°C, which is a temperature about 100°C higher than that attained by previous workers not neglecting the initial parts of the reaction. The experimental results are readily converted by the ideal gas equation into moles of gas produced as a function of time. The derivative of the curve was plotted against percentage degradation; the resulting rate versus conversion plot confirmed that two processes occur in PMMA degradation. Less than 50% of high molecular weight PMMA degraded by the initial rapid reaction.

The activation energy and frequency factor for the rapid reaction are found to be 26 kcal/mole and about $10^9$, respectively. For the slow reaction, the values are 49.5 kcal/mole and about $10^{16}$.

The effect of short kinetic chain length on degradation of long polymer chains is considered, and a rationale is developed to explain why less than 50% of the PMMA samples degraded rapidly. Structure of the polymer resulting from various polymerization mechanisms is shown to be very important in determining the thermal stability of PMMA. The structure of the unsaturated chain-end probably has considerable influence on the degradation mechanisms.

A study of the reactivity of the postulated unsaturated chain-ends showed them to be difficult to hydrogenate, even under moderately high pressures of hydrogen. These chain-ends were found to be slightly more susceptible to bromination than to hydrogenation.
To my wife
Madeleine
without whose
encouragement and understanding
this work would have been impossible.
ACKNOWLEDGEMENT

I wish to acknowledge with gratitude the direction of Dr. H. H. G. Jellinek who by his patience and guidance greatly enhanced the quality of this work.

Thanks are also due to Mr. Wolf Eberhart who fabricated the quartz spoon gauges used in this work, and to Messrs. Otto Brudy, Werner Grewe, and William Proby for construction, and assistance in the design, of the mechanical accessory apparatus.
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CHAPTER I

INTRODUCTION

To understand the reactions of any chemical substance we must have a reasonable knowledge of its structure. The structure of a polymer molecule is a permanent record of the reactions by which it was produced. Thus, knowledge of the polymer structure leads to knowledge of the reactions producing it, and knowledge of the polymerization steps gives knowledge of the final polymer structure. It was proposed, therefore, to carry out fundamental kinetic studies on the thermal degradation of vinyl polymers, since such investigations do not only yield information about the mechanism of breakdown of these long chain molecules but also give information about the stability of these polymers as a function of their structural features.

Numerous studies have been performed on the reactions of polymer molecules, particularly those reactions which result in degradation [1, 2]. Only recently, however, have quantitative experiments been done on the thermal degradation of polymers in temperature ranges above 300°C [3]. It was necessary to develop a new technique to allow accurate kinetic measurements to be made on the relatively rapid reactions which occur in this temperature range [4].
Polymethylmethacrylate was chosen as the prototype polymer since its pyrolysis is fairly well understood at lower temperatures.

In thermal degradation it is the physical agency of heat which causes reaction. Other physical means are ultraviolet light, ultrasonic waves, or mechanical agitation, as opposed to the chemical agencies causing oxidation, hydrolysis, and so forth. These forces may cause decomposition in two ways, which may be described kinetically as:

1) Random chain scission, and

ii) Depolymerization.

Random degradation consists of chain scission of bonds in the polymer chain, leaving a broad distribution of fragments that are usually larger than a monomer unit. It is characterized by a rapid decrease in molecular weight of the polymer sample undergoing breakdown.

Depolymerization consists of stepwise unzipping of the polymer chain by the successive release of monomer units; monomer is the predominant product of this process. It is analogous to addition polymerization, and is essentially its reversal (initiation, depopagation, chain transfer, and termination); it is characterized by a change in molecular weight of the remaining polymer that is either negligible or linear with the extent of degradation.

Either of these may begin at a chain-end or elsewhere in the chain, and they may occur separately or in combination,
so it is a prime purpose of kinetic investigations to discover which one, or both, is operating, and what factors influence the choice of mechanism.

**General Principles**

1. **Effect of Polymer Structure**

The results of thermal degradation research of the last two decades indicate that the heat stability of a polymer, the mechanism by which it breaks down, and the type and relative concentrations of the products depend chiefly on polymer structure. Some main generalizations for carbon-backbone polymers \( \langle 5, 6 \rangle \) are:

i) Tertiary carbon atoms weaken the adjacent C-C bonds in the chain (e.g., polymethylacrylate). Tertiary hydrogen atoms are naturally reactive, aiding transfer and reducing monomer formation.

ii) Abundance of main-chain hydrogen atoms induces random scission, and thus a wide size-distribution of products (e.g., polymethylene).

iii) Scarcity of main-chain hydrogen atoms induces stepwise depropagation, and thus monomer production (e.g., polymethylmethacrylate). Methylenic \( \beta \)-hydrogens are of much less importance than \( \alpha \)-hydrogens.

iv) The C-C bonds next but one to a double bond are weaker than normal C-C bonds (e.g., polystyrene) \( \langle 7 \rangle \).

v) Structural irregularities, such as peroxide or head-to-head linkages, constitute weak-links in the chain.
(e.g., polystyrene formed in the presence of oxygen) \cite{8, 9}.

The more stable the radicals formed during pyrolysis are, the more monomer production is enhanced. The stability of these macroradicals is predictable by the usual considerations of physical organic chemistry, resonance stabilization and steric hindrance being major factors.

Usually, the higher the temperature and pressure are, the greater is the fragmentation of volatile products.

It can be seen then, that bond cleavage may occur at any one, or a number of points, depending on the mechanism being followed. Scissions may occur in the backbone of the chain, between the carbons of the backbone and the side groups, within the pendant groups, and in numerous places in crosslinked polymers. Polymers tend to vaporize completely when only main-chain scission occurs; a stable, partially carbonized residue results from crosslinking and double-bond formation, due to scissions between the carbons of the backbone and the side groups; low molecular weight gases are usually given off when scissions occur within the pendant groups; a honeycombed solid consisting of carbonized residue is obtained from highly crosslinked polymers.

2. Experimental Approaches

It is usually possible to distinguish between the two extremes of the mechanisms by following the molecular weight of the residue as the reaction proceeds. If the molecular
weight of the residue of lower molecular weight linear polymers remains essentially unchanged during the degradation, then a depolymerization process is being followed, i.e., once a given chain begins to degrade, the entire chain unzips completely to monomer, leaving no stable residue to change the average molecular weight of the remainder. For very high molecular weight linear polymers, the molecular weight of the residue may be a linear function of the extent of reaction, because once a given macromolecule degrades, it may unzip to monomer, but not completely, since the kinetic chain length is not as long as the chain length of the polymer; this results in a stabilized residue of considerable molecular weight, which decreases the average molecular weight of the remainder. The kinetic chain length may be defined as the average number of monomer units produced from one chain.

The other mechanistic extreme, random degradation, is recognizable by the fact that the molecular weight of the residue drops drastically at a very small percentage of monomer produced.

An adjunct to the examination of residual molecular weights is the qualitative and quantitative examination of products of breakdown at moderate temperatures. If the volatiles consist of a large percentage of monomer then there is added evidence that depolymerization is occurring. On the other hand, if a variety of products having a wide molecular weight distribution are found then it is likely
that random chain scission has taken place. Direct gas chromatographic analysis of the volatiles is becoming increasingly more common as a method of separating and identifying products \cite{10, 11, 12, 13}, but the original method of pyrolyzing the polymer separately, then identifying the products on a gas chromatograph \cite{14} is also useful. An earlier method which still is useful is mass spectrometry \cite{15}. As might be expected, various types of light absorption spectroscopy are useful, particularly for studies of structural changes in the polymeric residue \cite{16}.

Neither of these methods alone (molecular weight change; product analysis) is sufficient to establish the entire degradation mechanism. Rate of monomer formation or rate of weight loss is often examined in fundamental degradation studies as an additional aid in deciphering the mechanism. Since quantitative pyrolysis studies are usually done "in vacuo" it is common practice to pump off the products as they are formed; collection of these products can yield data on the rate of monomer formation \cite{17}. The most common method for evaluating the thermal stability of a polymer is probably thermogravimetric analysis (TGA), in which the rate of weight loss is followed on a specially constructed balance \cite{6}. Differential thermal analysis (DTA) \cite{18, 19} is also finding increasing use in polymer stability studies \cite{20}.

Measuring changes in mechanical and electrical
properties during degradation of a polymer sample may be of help in both applied and theoretical studies.

In a complete study of a polymer, it is advantageous to make as many as possible of the above measurements. Combinations of these aforementioned approaches are feasible so that, once an apparatus has been set up, a maximum of information is obtained with a minimum of experimentation.

3. Mathematical Theories

A number of mathematical expressions may be derived to describe the overall degradation process. In the usual approach, assumptions are made as to polymer molecular weight distribution, points of initiation, mode of termination, kinetic chain length, and so forth. The fewer the assumptions that are made, the more complex becomes the mathematics; boundary conditions have to be taken into consideration for a rigorous derivation \(^{21}\). Boundary conditions consider the fact that the number-average kinetic chain length for depropagation depends on the polymer chain-length because of the finite size of the polymer chains. The best collection and correlation of the formal mathematical theories of degradation has been given in Jellinek's book \(^{1}\).

A different approach uses very general forms of general equations. The mathematical operations encountered in these cases become quite burdensome; for example, a high speed digital computer had to be used for evaluating molecular
weight distributions and averages for polymers undergoing random scission \cite{22}. Boyd \cite{23} has worked out the theoretical depolymerization kinetics for polymers with an initial "most probable" molecular weight distribution; this is considerably more complex than the same case with an assumed monodisperse polymer. Gordon \cite{24} has used a probability model theory to calculate the statistical kinetics of degradation. The latter author has recently summarized \cite{25} the newest advances in the theory of thermal degradation of heterodisperse polymers. These advances are based on:

1) use of an exponential molecular weight distribution;
2) use of differential equations that give relations between experimental variables;
3) statistical analysis of probability models as a technique complementary to the solution of systems of differential kinetic rate equations.

Degradation of Polymethylmethacrylate

The purpose of the present investigation was a study of the thermal degradation of polymethylmethacrylate (PMMA) at higher temperatures than those used by previous investigators, in order to gain a better understanding of the processes involved in its breakdown. Polyo-methylstyrene and PMMA are standard examples of polymers which degrade primarily to monomer \cite{26, 27} by depolymerization; PMMA has been studied more extensively, probably because of its
commercial importance and availability.

1. Structure of PMMA

In order to arrive at knowledge of the structure of PMMA it is well to consider the steps of its polymerization. The monomer may be polymerized by free radical or ionic addition polymerization. Stereospecific polymerization of this monomer is a recent achievement and degradation of the stereoregular polymers produced thereby have not been reported in the literature, although the importance of degradation studies of such tactic polymers has been pointed out. Radical polymerizations of methylmethaorylate (MMA) may be divided into the usual chain-reaction schemes of initiation, propagation, and termination; negligible transfer to monomer or polymer occurs in this purified bulk system without transfer agents.

With benzoyl peroxide as initiator, the initiation scheme is:

\[
\begin{align*}
&\text{INITIATION: } \phi-\text{COO}^- \text{ (or } \phi^-) + \text{CH}_2=\text{C} \rightarrow \phi-(\text{COO})\text{-CH}_2=\phi^- \\
&\text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

On moderate heating to 60°C, benzoyloxy radicals result from
a homolytic cleavage of the peroxide bond of the initiator. These radicals may subsequently decompose further to phenyl radicals and carbon dioxide or they may attack the monomer and initiate polymerization. The ratio of the rate constant for further decomposition ($k_2$) to the rate constant for attack on the monomer by benzoyloxy radicals ($k_3$) is 3.3 moles/liter at 60°C. At this temperature the measurements showed the maximum percentage of benzoyloxy groups in the polymer chain-ends to be 71%, for the polymerization in bulk. On performing the reaction at various concentrations of MMA in benzene, the results indicated a linear decrease in benzoyloxy-ends for the plot: $1/x$ versus $1/\text{MMA}$, where $x =$ the fraction of initiating radicals that are benzoyloxy. This reciprocal type of plot is necessary because the following relation derived from polymerization kinetics holds: $1/x = (k_2/k_3 \cdot \text{MMA}) + 1$. For 17.5% MMA, 35% benzoyloxy chain-ends were found. An independent measurement at 50% monomer in benzene, falls exactly on this line at 57% benzoyloxy-ends. Thus, as the concentration of MMA increases, the concentration of benzoyloxy-ends also increases, reaching a maximum at 71%. The catalyst residue becomes predominantly phenyl at higher temperatures.

Now let $F$ equal phenyl or benzoyloxy, then the propagation reaction is given by:
Propagation proceeds by rapid, successive addition of monomer units in a head-to-tail fashion with the configuration of the addition governed largely by experimental conditions. Normal PMMA prepared by radical polymerization at 50-100°C contains many syndiotactic sequences \[ \text{with placement becoming more random as polymerization temperature increases.} \]

The activation entropy is the same for isotactic and syndiotactic placement, but the latter requires an additional activation enthalpy of 0.70-0.85 kilocalories per mole \[ \text{[35, 39].} \]

Goode \[ \text{[29, 39], who was the first to prepare and characterize stereoregular PMMA, has shown that high-resolution infra-red spectroscopy gives a measure of the tacticity of the resulting polymer.} \]

An additional factor complicating the propagation process is that polymeric peroxides form if the polymerization of MMA is carried out in the presence of oxygen \[ \text{[36, 37].} \]

This can be avoided by degassing the reagents and carrying the polymerization out under nitrogen, in vacuum, or in the presence of an oxygen scavenger such as Wood's metal \[ \text{[38].} \]

Termination may occur in two ways:
Combination (C) occurs by head-to-head coupling of two growing chains and disproportionation (D) occurs by abstraction of hydrogen from the end of one growing chain by the radical end of another growing chain. It is not known from which site the hydrogen is abstracted although selective deuteration or tritiation of the monomer would seem to have possibilities of yielding such information. The exact structure of the unsaturated chain-end is discussed in Chapter IV.

The fact that PMMA terminates by combination and disproportionation is well established \( \text{(39)} \). However,
the relative proportions of these termination mechanisms at various temperatures is a subject of continuing disagreement [33, 40-46]. One certainty is that at higher temperatures disproportionation predominates over combination. The temperature at which combination becomes negligible is not known with certainty.

Before comparing some results and conclusions of various workers, it is well to state the four methods commonly used for arriving at data on the termination mechanism, since it will be seen that the mechanism followed is very important for the thermal stability of the resulting polymer. These methods are based on kinetics, end-group coupling, end-group analysis, and degradation. The principal weaknesses are indicated below.

1) The kinetic method consists of measuring the polymer molecular weight as a function of the initiator concentration. A plot of \(1/M_n\) versus the square-root of the initiator concentration yields a straight line, the slope of which is a function of the termination rate constants. If these are known, the fractions for disproportionation and combination can be calculated. Weaknesses here arise from inaccuracy of the molecular weight determinations, and the usual difficulties in estimating rate constants.

2) The coupling method is based on the use of an initiator with functional groups which are incorporated into the polymer as end-groups. These terminal groups can be linked together by a suitable bifunctional reagent. If
the average molecular weight after coupling increases to twice the original value then there was only one such end-group per molecule (100% disproportionation). Higher final molecular weights indicate more than one functional end-group per molecule. A great weakness here is the change of molecular weight distribution on coupling, and concomitant errors in molecular weight estimates.

iii) End-group analysis, joined with number-average molecular weight determinations, gives the number of end-groups per molecule. Disproportionation yields one, and combination yields two, end-groups per molecule. The most sensitive end-group assay is done with labelled initiators. Although this is probably the best method, a serious weakness arises in the treatment of the osmotic pressure data which yield the absolute molecular weights.

iv) Degradation rates indicate the fraction of a sample that degrades more rapidly than the remainder. It will be shown that terminal unsaturation in PMMA causes a weak link which breaks at moderate temperatures allowing that fraction of the sample to degrade readily. This is a sensitive method, but a weakness lies in the fact that the estimate of terminal unsaturation results from an extrapolation of rate measurements.

The errors inherent in each of these methods are of such significance that the final result should be considered no more than a reasonable estimate of the amount of disproportionation taking place. The data of each experimenter
usually appears self-consistent, but close analysis of the data and methods, and comparison with other data gives a broad spectrum of results. Table 1 summarizes the chief results for PMMA prepared at 60°C. Column 1 shows the method of preparation (Azo = Azobisisobutyronitrile and B.P. = Benzoyl Peroxide); all experimenters who studied solution polymerization at this temperature, chose benzene as solvent. Column 2 indicates the ratio of the rate constants for disproportionation ($k_d$) and combination ($k_c$), as given by the authors, except in the case of Reference 43 where the ratio was readily calculable from the authors' data. Column 3 gives the average number of initiator fragments per molecule obtained from radiochemical end-group analysis; the range of values is also indicated. Column 4a gives the percentage disproportionation as calculated from the ratio of the rate constants by the method described later in this Section. Column 4b gives the percentage disproportionation as taken from the point on Figure 1 corresponding to that number of initiator fragments per molecule.

Even though these authors generally considered chain transfer to benzene to be negligible for their calculations, the results show a definite decrease in disproportionation with increasing concentration of benzene. The notable exception to this generalization of neglecting transfer is the study by Grassie and Vance [47] in which degradation evidence for the nature of termination and transfer to
# Table 1

Data on the termination mechanism of PMMA polymerization at 60°C

<table>
<thead>
<tr>
<th>PMMA Preparation</th>
<th>( \frac{k_p}{k_i} )</th>
<th>Initiator Fragments per Polymer Molecule (Average and Range)</th>
<th>( % )</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk, Azo</td>
<td>5.75</td>
<td>1.08 (0.99 to 1.15)</td>
<td>85%</td>
<td>91%</td>
<td>End-Analysis</td>
</tr>
<tr>
<td>Bulk, Azo (a)</td>
<td>2.04 (b)</td>
<td>-</td>
<td>67%</td>
<td>-</td>
<td>Kinetic</td>
</tr>
<tr>
<td>50% Benzene, B.P.</td>
<td>-</td>
<td>1.27 (1.26 to 1.30)</td>
<td>-</td>
<td>72%</td>
<td>End-Analysis</td>
</tr>
<tr>
<td>50% Benzene, Azo</td>
<td>-</td>
<td>1.06 (1.16 to 1.33)</td>
<td>-</td>
<td>72%</td>
<td>End-Analysis</td>
</tr>
<tr>
<td>80% Benzene (c)</td>
<td>0.75</td>
<td>1.60 (1.50 to 1.70)</td>
<td>42%</td>
<td>40%</td>
<td>Kinetic and End-Analysis</td>
</tr>
<tr>
<td>80% Benzene (c)</td>
<td>0.75</td>
<td>1.61 (1.48 to 1.71)</td>
<td>42%</td>
<td>39%</td>
<td>Kinetic and End-Analysis</td>
</tr>
<tr>
<td>90% Benzene, B.P.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>42%(f)</td>
<td>Degradation</td>
</tr>
</tbody>
</table>

* See text for Methods of Calculation.

a) Inhibited with various thiols.
b) Calculated from authors' experimental results, using \( k_p = 315 \), according to Reference 40.
c) Polymerized to 12% conversion.
d) There was an approximately linear decrease of initiator fragments per molecule versus \( k_p \).
e) Polymerized to 35% conversion.
f) By extrapolation from degradation rate curves.
benzene was given. They showed that the rate of degradation of PMMA was decreased by chain transfer during preparation in benzene. Thus, it is apparent that appreciable transfer to solvent does occur. The incorporation of C-14-radioactivity into the polymer during preparation in C-14-labelled benzene should give conclusive evidence on this point.

The curve in Figure 1 has been calculated for the theoretical number of initiator fragments per molecule at various percentages of disproportionation. An average of 1 initiator fragment per molecule is assumed for 100% disproportionation; 2 initiator fragments per molecule are assumed for 100% combination. An implicit assumption is that disproportionation and combination are the only processes by which chains are terminating. The percentage of a sample with unsaturated ends may also be read directly from this graph. The percentages of disproportionation in Column 4b of Table 1 were taken from the points on this curve corresponding to the experimental number of fragments per molecule, in Column B.

The percentages of disproportionation in Column 4a of Table 1 were calculated from the rate constant ratio in Column A. The values were calculated from the three simultaneous equations corresponding to the following assumptions:

1) All polymeric products (three species) result from disproportionation and/or combination: \( U + S + C = 100\% \).
Fig. 1. Theoretical relation of disproportionation to end-group.

% Disproportionation vs. % Unsaturated ends.

Initiator fragments/molecule.
ii) The percentages of the two products of disproportionation are equal: \( U = S \).

iii) The ratio of the percentage of products from disproportionation and combination is given by the ratio of the rate constants: \( (U + S)/C = k_d/k_c \).

\( U \) is the percentage of polymer with unsaturated chain-ends arising from disproportionation. \( S \) is the percentage of polymer with saturated chain-ends arising from disproportionation, and \( C \) is the percentage of polymer arising from combination. Transfer is assumed to be absent; disproportionation and combination are considered to be the only modes of termination.

An estimate of the increase of disproportionation with temperature may be obtained from the data of Schulz et al.\(^{45}\), although the absolute values are certainly open to question. Table 2 gives these estimates obtained using the rate constant ratios of these authors in the calculation which was explained above.

### TABLE 2

**The Increase of Percentage Disproportionation with Temperature.**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( k_d/k_c ) (^{45})</th>
<th>% Disproportionation</th>
</tr>
</thead>
<tbody>
<tr>
<td>40°C</td>
<td>0.49</td>
<td>33.5%</td>
</tr>
<tr>
<td>60°C</td>
<td>0.75</td>
<td>43.0%</td>
</tr>
<tr>
<td>80°C</td>
<td>1.27</td>
<td>56.0%</td>
</tr>
</tbody>
</table>
In review, it is seen that the structure of PMMA is affected considerably by variations in initiation, propagation, transfer, and termination. Temperature and impurities also have significant effects, either directly or indirectly.

2. Previous Degradation Experiments

The thermal degradation of PMMA has been the subject of a number of investigations. Pyrolysis studies on polymers are usually done with the sample as a solid film. The two primary reasons for this are first, the heat conductivity of polymers is quite low [48], and second, that the thinner the layer of polymer is the less likely it becomes that diffusion of products is rate-controlling. Likewise, working in vacuum aids diffusion of small-molecule products out of the film, and the complication of reactions with atmospheric oxygen is removed.

Jellinek [1] and Grassie [2] have both summarized the early work on PMMA pyrolysis, the former giving a more satisfactory quantitative interpretation of data. On heating PMMA to the range of 200-400°C, depolymerization takes place by initiation at weak links (such as the unsaturated chain-ends) followed by rapid unzipping of thousands of monomer units. This process may terminate by combination or disproportionation of the remaining low molecular weight radicals depending on the kinetic chain length. The products consist of almost 100% monomer, thus the process is
essentially the reverse of addition polymerization.

However, this comparatively straightforward explanation is complicated by two facts:

1) the kinetic chain length (E) may be less than the polymer chain length (P).

2) only up to 50% of the chains degrade by chain-end initiation at the unsaturated ends.

The effect of short kinetic chain length may be seen from the results of Grassie and Melville at 220°C (Figure 2) and Brockhaus and Jenckel at 300°C (Figure 3). The molecular weight of the remaining polymer is unchanged up to high conversions to monomer, for molecular weights approaching 50,000. But increasing deviation from this linear behavior is observed for molecular weights up to about one-half million; in such a high molecular weight range, a linear decrease takes place.

Jellinek obtained further information by plotting Grassie's initial rates of monomer production at 220°C as a function of reciprocal number-average molecular weight (Figure 4). This shows the initial rate to be essentially independent of molecular weight up to about 250,000; at this point, the rate becomes proportional to some function of molecular weight, i.e., \(1/M_0\) or \((1/M_0)^{1/2}\). The point of intersection of the straight-line extrapolations is a measure of the kinetic chain length; the value of the number-average molecular weight \(M_n\) from this plot is about 250,000, or 2500 monomer units released per initiated chain.
Degradation to monomer, per cent

Fig. 2  Molecular weight of the residual polymer in the thermal degradation of polymethyl methacrylate. The initial molecular weight for each experiment is indicated. Melville and Grassie. [*49*]

% THERMAL DECOMPOSITION

Fig. 3  DECREASE OF MOLECULAR WEIGHT WITH % THERMAL DECOMPOSITION

( BROCKHAUS AND JENCKEL, 17 )

% Degradation to monomer

Fig. 4  Theoretical reaction curves for possible polymethyl methacrylate depolymerization mechanisms. [*54*]

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These results can be interpreted well in the light of present understanding of degradation mechanisms. Generally, three possible cases may be considered:

i) One involatile stable residue remains after some degradation process: \( E < P_0 \); End Initiation.

ii) No residue results: \( E > P_0 \).

iii) More than one stable residue results: \( E < P_0 \); Random Process.

Kinetic chain length is \( E \), and initial polymer chain length is \( P_0 \).

These possibilities are shown graphically in Figure 5. The straight-line "i" fits the PMMA results with very high molecular weights, i.e., a given chain may begin to degrade from the end but the kinetic chain is not long enough to complete the process, leaving one stabilized residue. The straight-line "ii" fits the findings for low molecular weight PMMA, i.e., once a chain is initiated it decomposes completely to monomer, leaving negligible residue. Results for intermediate original molecular weights approach line "i" as these increase. This medium length chain mechanism is complicated by the existence of a molecular weight distribution in the polymer sample; shorter chains of the distribution degrade completely but longer chains only incompletely.

This interpretation is confirmed by Figure 4 which gives a measure of the kinetic chain length as 2500 monomer units. Furthermore, this plot yields the rate constant at...
Fig. 5: Initial rates of monomer formation for polymethylmethacrylates as a function of their reciprocal number average molecular weight (0.2 g., 220°C.).
220°C for the initiation reaction:

\[
\frac{dM_1}{dt} = k_{1d} \cdot m_0 = \text{ml/sec}
\]

or,

\[
k_{1d} = 6.12 \times 10^{-5} \text{ sec}^{-1}
\]

where \(\frac{dM_1}{dt}\) is the rate of monomer formation with time, \(k_{1d}\) is the rate constant for initiation of degradation, and \(m_0\) is the total number of monomer units contained in the original polymer sample. This same value for \(k_{1d}\) results if \(E\) is chosen as 1670, for the case in which \(E > P_0\) with first order termination (but this termination process is still unconfirmed):

\[
\frac{dM_1}{dt} = k_{1d} \cdot m_0 \cdot \left(\frac{E}{P_0}\right)
\]

The general nature of the degradation was thus understood, but it remained for further experiments to show at which chain-end the initial scission takes place. Brockhaus and Jenokel \(^{17}\) have shown conclusively that up to 50% of their PMMA samples (benzoyl peroxide initiated in bulk at 80°C) degrades rapidly to monomer and this less stable portion contains terminal double bonds. It was concluded that these double bonds constitute weak links and allow chain-end initiation. The method used by these workers for showing that the unsaturated end-groups react faster was oxidation with \(\text{KMnO}_4\) of partly pyrolyzed PMMA.
Their results for various molecular weight samples are shown in Figure 6. The difficulty of the measurements of such small concentrations of unsaturation is emphasized by the spread of the points through which the straight-lines are drawn. Further measurements of this nature would be helpful since it appears from these results that the percentage of unsaturated ends may decrease with increasing molecular weight.

That chain-end initiation was taking place had already been suggested by others, but their conclusions were based on much less evidence. Jellinek \cite{1} deduced, using Grassie and Melville's degradation data for a low molecular weight sample, that about 50% of the chains have such weak links. This was supported by Grassie's results, that PMMA prepared by photoinitiation, degrades twice as fast as the peroxide-produced polymer, because the photopolymer has twice as many susceptible ends (later shown to be unsaturated ends). In 1953, Grassie and Vance \cite{47} postulated that the unsaturated end is the cause for the low activation energy by showing that the rate of degradation of PMMA is decreased by chain transfer, during polymerization, to benzene solvent. Brockhaus and Jenckel \cite{17} found a reduced rate with a cyclohexane-transferred polymer.

Grassie and Melville's quantitative results \cite{49} are in fair agreement with the later results by Brockhaus and Jenckel \cite{17}. These and other results are given in Table 3.
Fig. 6 Dependence of the theoretical ester concentration on percentage thermal decomposition, for various polymerizates $P_v$ = viscosity-average chain length (Brockhaus and Jenckel, 17)
# TABLE 3

**OVERALL ACTIVATION ENERGIES FOR PYROLYSIS OF PMMA**

<table>
<thead>
<tr>
<th>Activation Energy (Kcal/mole)</th>
<th>Molecular Weight</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_A$</td>
<td>$E_B$</td>
<td>$M_V = 40,000$</td>
</tr>
<tr>
<td>27</td>
<td>44</td>
<td>$M_n = 150,000$</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>$M_n = 179,000$</td>
</tr>
<tr>
<td>31</td>
<td>42</td>
<td>$M_V = 425,000$</td>
</tr>
<tr>
<td>27</td>
<td>49</td>
<td>$M_n = 5,100,000$</td>
</tr>
<tr>
<td>-</td>
<td>52</td>
<td></td>
</tr>
</tbody>
</table>

Molecular Weight Reference:
- $M_V$ refers to the viscosity-average molecular weight.
- $M_n$ refers to the number-average molecular weight.

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Thus, at least two separate depolymerization mechanisms occur during PMMA pyrolysis:

1) Up to half of the chains contain terminal unsaturation, formed by disproportionation-termination. These are weak links at which an process begins and proceeds to run off very many monomer units. If the polymer chain has a degree of polymerization greater than the kinetic chain length, the polymer radicals become stabilized by disproportionation or combination.

ii) The remaining chains contain saturated ends and degrade more slowly, with a higher energy of activation. If polymerization had terminated solely by disproportionation, then the non-catalyst saturated ends have an isobutyrate-type structure (see Chapter IV). It has not been shown conclusively whether these chains degrade via random or chain-end initiation although Brockhaus and Jenckel have concluded from their results that the process is random; in either case an unzippering of monomer follows. If some combination occurred during polymerization, then all ends of these chains contain catalyst fragments. The sterically hindered bond formed by combination probably constitutes a weak link.

As was mentioned previously, the products of PMMA pyrolysis at lower temperatures are almost exclusively monomer. The substantial amount of analytical data on this and other degradations has been very recently reviewed. It is not surprising, however, that recent studies above
$500^\circ C \left[50\right]$ show products other than monomer: CO, CH$_4$, C$_2$H$_6$, CO$_2$, C$_2$H$_4$, and C$_2$H$_2$. The percentages of the last three increase at the expense of the others as the temperature approaches $1000^\circ C$. Figure 7 shows that the fraction of monomer in the products decreases to an apparent minimum of approximately 20% at extreme temperatures. It has yet to be determined whether the small product molecules come directly from scission of polymer main-and-side-chains or from decomposition of the monomer.

The apparatus used for this study consisted of a hollow "Teflon" block equipped with a platinum heating coil. This machined block was fitted into the inlet of a gas chromatograph and "fired" by passing a calibrated current through the platinum resistance wire. A polymer sample coated on the wire is thus thermally degraded and the gaseous products swept into the gas chromatograph by helium carrier gas. Chromatographic retention times and peak areas serve to assess the products.

This method has been used primarily for analytical purposes so far, and no kinetic data or mechanistic interpretations of the results have been published. However, it has recently been shown [51] that sample thickness is important with such a heating method, since the rate becomes independent of thickness only below about $2.5 \times 10^{-6}$ centimeter. Grassie [49] had noted that maximum thickness with his method was approximately 0.03 centimeter.
Figure 7. The Effect of Degradation Temperature on the Amount of Methyl Methacrylate Monomer in the Pyrolyzate. (Lehmann, Forzati, and Brauer, 1950)
3. Mathematical and Quantitative Interpretations

a) Theoretical Approach

In the last few years, a highly theoretical approach to polymer degradation has been developing. Since PMMA has been studied extensively by experiment, comparisons of theoretical and experimental results have been made. The most notable work in this connection has been done by Gordon [24], who calculated the statistical kinetics of the degradation of PMMA.

Consideration is made of the three types of chain-ends possible in radical-polymerized PMMA: unsaturated ends, single-bond ends with catalyst fragments, and single-bond ends without catalyst fragments. The first is most reactive to unzip, the second less reactive, and the third is unreactive. Allowance is made for the facts that:

i) the proportions of each vary during degradation,

ii) the kinetic chain length changes with reaction progress, and

iii) disproportionation of radicals may occur.

The theoretical results agree quantitatively with the data of Brockhaus and Jenckel [17], up to 50% conversion. Above 50% conversion, agreement is qualitative, the deviations being attributed to side reactions. Gordon shows that Brockhaus and Jenckel's rate theory is the limiting case for his theory, considering long chains. It is further shown that Brockhaus and Jenckel's data agree well
with the data of Madorsky and Straus \cite{52} at 240-270°C, but both differ from Cowley and Melville \cite{53} at 192.5°C, in that the termination step shows almost no activation energy (i.e., gel effect is absent).

Arrhenius plots of Gordon's results indicate unimolecular initiation at the unsaturated ends with activation energy of 29.6 ± 4.4 kilocalories/mole and pre-exponential factor of $10^{9.0} ± 1.5$/second. No activation energies were obtained for the other possible reactions.

Less detailed consideration of PMMA degradation in the light of such theories has been mentioned in other papers \cite{25,30}.

b) Equilibrium Approach

Another comparison of approaches to degradation is possible by considering the propagation-depropagation equilibrium. The activation energy for depropagation is comparatively high (ca. 10-30 kcal/mole) for most addition polymerizations but the depropagation rate may become appreciable at higher temperatures \cite{54}. The temperature at which the rates of propagation and depropagation are equal is the "Ceiling Temperature", which may be defined as the temperature above which the formation of high polymer is impossible, at a given monomer concentration. This explains why many an attempted polymer synthesis fails: the reaction is carried out at too high a temperature.

It is possible to show the existence of an "Equilibrium Monomer Concentration", $M_0$, which is the concentration of
monomer coexisting with polymer under equilibrium conditions at a given temperature \( T \).

\[
K_e = \frac{\frac{1}{M_x} + \frac{1}{M_{x+1}}}{\frac{1}{M_x} + \frac{1}{M_{x+1}} + \frac{1}{M_e}} = \frac{k_p}{k_d}
\]

where \( K_e \) is the propagation-depropagation equilibrium constant, \( M_x \) and \( M_{x+1} \) represent polymer molecules of chain length \( x \) and \( x+1 \), \( M_e \) is the equilibrium monomer concentration, and \( k_p \) and \( k_d \) are the rate constants for propagation and depropagation, respectively. Measurement of this concentration of monomer has recently been accomplished for the styrene-polystyrene equilibrium \( /55/ \), and less recently for MMA-PMMA \( /57, 58/ \). Rate constants for propagation, \( k_p \), have been measured by numerous workers \( /43, 45, 59, 60, 61, 62/ \), and are summarized in Table 4. Rate constants at other temperatures may be calculated (with caution) by substituting the resulting activation energy and frequency factor into the Arrhenius equation. The corresponding values of \( K_e \) and \( k_p \) then lead directly to a value of \( k_d \).

Another value of the rate constant may be obtained from photodegradation studies (\( k_d = 378 \text{ sec}^{-1} \) at 158°C).

Comparing the rate constants obtained from these two methods (equilibrium approach; photodegradation) should give independent confirmation of the kinetics. No such comparison has yet been published. Unfortunately, the choice of various values from the available data gives a
**TABLE 4**

**PROPAGATION RATE CONSTANTS FOR PMMA**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( kp ) (1/mole-sec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>42</td>
<td>( 60 )</td>
</tr>
<tr>
<td>24</td>
<td>310</td>
<td>( 62 )</td>
</tr>
<tr>
<td>24</td>
<td>513</td>
<td>( 61 )</td>
</tr>
<tr>
<td>30</td>
<td>251</td>
<td>( 45 )</td>
</tr>
<tr>
<td>30</td>
<td>286</td>
<td>( 59 )</td>
</tr>
<tr>
<td>50</td>
<td>410</td>
<td>( 45 )</td>
</tr>
<tr>
<td>50</td>
<td>580</td>
<td>( 62 )</td>
</tr>
<tr>
<td>60</td>
<td>515</td>
<td>( 45 )</td>
</tr>
<tr>
<td>60</td>
<td>573</td>
<td>( 43 )</td>
</tr>
<tr>
<td>60</td>
<td>734</td>
<td>( 59 )</td>
</tr>
<tr>
<td>70</td>
<td>640</td>
<td>( 45 )</td>
</tr>
<tr>
<td>80</td>
<td>800</td>
<td>( 45 )</td>
</tr>
</tbody>
</table>
range of values of \( k_d \) via the equilibrium calculation; by judiciously choosing values from the available data the two values of \( k_d \) may be brought within about 20\% of agreement or the values may differ by a factor of ten.

It may be concluded that the results of the equilibrium calculation are at least compatible with the results of degradation studies. The true value of \( k_d \) will have to be decided by further study.
CHAPTER II

PRELIMINARY STUDIES

A number of avenues for quantitative study presented themselves. It was decided to undertake experiments in a static system in vacuum, in order to avoid, at least initially, some of the problems inherent in flow systems. To this end, a vacuum rack of standard design was constructed, to attain vacuum of at least $10^{-5}$ mm mercury. To the vacuum rack could be sealed, via a ground glass joint, the Bourdon spoon-type reaction vessel shown in Figure 8. The initial spoon pyrex vessels were replaced later by quartz vessels.

After depositing a polymer film sample on its inside walls, the reaction vessel was evacuated and sealed off. It was then set in a clamp attached to an 0.5-inch steel plate imbedded in a sturdy concrete table. An air furnace, having been preheated to the desired temperature, was rapidly lowered over the vessel. The ensuing thermal degradation of the sample was followed by recording the pressure change in the reaction vessel as measured by the deflection of the spoon gauge pointer.
Fig. 8. Pressure Measuring Apparatus

(Shown at actual size)

R - Recorder
T - Transducer

Enlarged Side View of Bourdon Gauge
Prototype Apparatus

1. Vacuum System

The source of high vacuum was a two-stage mercury diffusion pump backed by a Duo-Seal Rotary Vacuum Pump (W. M. Welch Mfg. Co., Chicago, Illinois). To prevent oil or mercury vapor from entering the system, a liquid air trap was interposed before the main body of the system which consisted of a row of 10/19 outer ground glass joints to which spoon gauges could be joined for evacuation. All joints were lubricated regularly with High Vacuum Silicone Stopcock Grease (Dow-Corning Corporation, Midland, Michigan).

Degree of vacuum was read on a tipping McLeod Gauge; this indicated a "sticking vacuum" (ca. $10^{-5}$ mm mercury, or better) whenever an experiment was carried out.

2. Reaction Vessel

The basic purpose of the reaction vessel was to contain a polymer sample and measure the pressure of its volatiles produced on degradation. A good review of many Bourdon and spoon gauges is given by Partington \(^64\). One of the earliest references to a gauge of this type is by Bodenstein and Dux in 1913 \(^65\), and consequently it is sometimes known as a Bodenstein gauge. Its use as a differential manometer, or in the spiral form is also fairly common. Its principle of operation is that the curved surfaces distort to relieve the strains caused by the applied force (pressure).
A number of modifications of the basic spoon gauge were experimented with. All of these early modifications were blown from pyrex glass. The design factors found which significantly altered sensitivity, were spoon curvature, volume, length and width, and their ratio.

To magnify the basic deflection of the spoon, a pointer was attached to its tip. Solid rod was found to constitute the most satisfactory pointer.

Originally, only one support rod was connected to the vessel. Because of uneven heat effects the position of the spoon was found to change slightly, and this resulted in false pressure readings. Adding symmetrical supports on both sides eliminated this problem, and adding a cross-brace between them made the delicate instrument much more sturdy. Again, solid rod was found to be most satisfactory, hollow tubing being more fragile and susceptible to uneven heat effects.

The body of the spoon gauge was about 3 inches long, and constructed from 11 mm outside diameter (1 mm wall) tubing. The 28 cm pointer was made of 3 mm-diameter rod. Seven mm-diameter rod was used for the 50 cm supports. Average volume of the spoon gauge vessels was about 15 milliliters.

Finally, the entire piece was made of quartz (General Electric Co., Willoughby, Ohio). Tubing was clear quartz, type 204; rod was clear quartz, type 201. Although the glassblowing fabrication was extremely difficult, the
added temperature resistance, insensitivity to heat effects, and increased thermal conductivity resulted in an excellent instrument.

3. Stable Supports

Solid screw clamps were machined from aluminum to hold the support rods of the reaction vessel. These were mounted on an adjustable aluminum plate.

The latter plate was firmly bolted to a ½-inch steel plate imbedded in a sturdy concrete table (ca. 2 ft. x 2 ft.) which was specially constructed for this work as a vibration-free foundation. Vibration was further minimized by placing the heavy concrete base on "Isomodal" rubber pads, of heavy rubber with perpendicular molded grids on its opposite sides. This was necessary because of the fact that the very sensitive spoon gauges picked up vibrations in the building caused by machinery, personnel, and outside agencies. A more detailed description will be given later, when the improved apparatus will be discussed.

4. Air Furnace

a) Construction

As the original source of heat, an air furnace was constructed. A quartz tube, 3 inches in diameter and 2 feet long, was wound on the outside with Chromel-A Resistance Ribbon (Hoskins Mfg. Company, Detroit, Michigan). The ribbon was one-sixteenth inch wide and 0.016 inch thick,
giving a resistance of 0.538 ohms per foot. The windings were cemented in place with Sauereisen High Temperature Acid-Proof Cement, Number 31 (E. H. Sargent and Co., Detroit, Michigan). To obtain an even temperature profile throughout the furnace, the resistance wire was wound in sections with increasing number of turns per inch as the end of the tube was approached. For example, the central 4 inches had 2 turns per inch, the next 4 inches had 4 turns per inch, the next had 6 turns per inch. Each section was tapped to a variable resistance so that the resistance (and the resulting temperature) of each section could be varied somewhat by varying this external resistance. Total resistance of a typical furnace was about 35 ohms.

This wound quartz tube was centered in a box with a frame of three-quarter inch angle-iron and sides of asbestos board. Similar ends, but with centered 3-inch holes, were fitted and the box filled with fine aluminum oxide sand for insulation. All seams were sealed with asbestos cement.

A 6-inch section constant in temperature to within one-half degree Centigrade was obtained in the quartz tube.

b) Support

The furnace was supported by a large 2-inch angle iron frame, into which was built a stainless steel guiding track system. Since the total furnace weight was about 150 pounds it was counterweighted by lead ballast
attached to a pulley system to facilitate operation.

Thus the furnace could be easily and rapidly lowered over the reaction vessel which was clamped in place on the concrete table. The furnace was hung from 1000-pound-tested stainless steel cable; this passed over two pulleys to the controlling counterweighted handle.

After 6 months of use the steel cable suddenly broke, causing destruction of the air furnace. Failure of the cable was probably due to repeated flexing over the pulleys.

c) Temperature Control

Accurate and reproducible temperature control was obtained by use of a Sunvic Platinum Resistance Thermometer Controller, Type RT-2 (Sunvic Controls Ltd., London, England). The circuitry is shown in Figure 9, where E is the voltage supply through a Variac, B is the thermal cycling unit of the controller, and it may be considered as a by-pass for R₁, the "increment resistance". The furnace is R₂. Precise proportional temperature control was thus obtained so that the temperature did not vary by more than a few tenths of a degree over a period of days.

5. Detecting and Recording System

a) Detecting Transducer

The reaction vessel pointer was placed so as to deflect the probe of a Statham Strain Gauge Transducer, Model G 10E-0.3-350 (Statham Instruments Inc., Hato Rey, Puerto Rico). The transducer translated the pointer
Fig. 9 Temperature Control and Recording Circuit

A - Cycling Unit of Controller (Sunvic)
C-T - Chromel-Alumel Thermocouple
E - Input Voltage from Variac
P-T - Platinum Resistance Thermometer (Sunvic)
R - Sanborn Recorder
R₁ - Increment Resistance (11.4 ohms)
R₂ - Furnace (ca. 30 ohms)
deflection of the reaction vessel into an exact electrical analog, and this electrical impulse was fed into the recorder described below.

Strain gauges and transducers are very convenient instruments for translating physical changes (load, torque, pressure, vibration, displacement, etc.) into electrical signals. "Their application is limited only by the user's imagination" [66]. The type used in this study was an unbonded strain gauge in which the strain sensitive resistance wire elements are arranged in the form of a Wheatstone Bridge. Moving the transducer probe changes the resistance (length and cross-section) of the bridge elements, and so the bridge becomes unbalanced. The amount of unbalance is the output signal.

This transducer had a range of ±0.3 ounce with a sensitivity of 11.54 millivolts per ounce. Its range of displacement was 0.015 inch (0.038 cm). This temperature-compensated gauge has a linear response and the non-linearity plus hysteresis effect of the gauge was less than ±1% of a bridge voltage which could be A.C. or D.C., but not in excess of 9 volts.

b) Recorder

Two quantities were recorded: pressure (transducer deflection) and temperature (thermocouple voltage).

The latter was measured by a calibrated Chromel-P/Alumel thermocouple (28 gauge wire) with the reference
couple in an ice bath. The output voltage of the thermo-
couple could either be read directly on a potentiometer or recorded continuously. The measuring thermocouple itself was situated in a thin quartz sheath in the heating medium.

Pressure was measured by means of transducer deflection caused by the spoon gauge pointer.

These electrical signals were recorded on a Sanborn two-channel recorder, Model 150 (Sanborn Company, Waltham, Massachusetts). To activate the transducer, Sanborn Carrier Preamplifier Model 150-1100, with zero suppression, was chosen for its excellent rapid frequency response. It supplied a D.C. excitation voltage of 4.5 volts, 2400 cycles per second, to the bridge of the transducer. The carrier preamplifier input impedance of 2400 ohms was well matched to the transducer impedance of 258 ohms. Drift was found to be negligible.

On the other recorder channel, the voltage from the thermocouple was recorded with Sanborn Low Level Preamplifier Model 150-1500, with zero suppression. This preamplifier had a maximum sensitivity of 10 microvolts per division, i.e., temperature could be read to better than ± 0.05°C on the recorder.

Preliminary Results

It was first necessary to test the apparatus just described. It was found that well-shielded and grounded
wire was necessary for all connections, since the detecting and recording system was extremely sensitive to stray signals.

Therefore, shielded wire was used for all electrical connections from the transducer and thermocouple to the recorder; it was also necessary to electrically shield in the same way all connections of the temperature controller. In addition, the furnace, its supports, and all metal accessory equipment had to be well grounded. Having minimized electrical and mechanical interference, it was possible to attempt introductory experiments.

1. Linear Response and Calibration

Linear response of the transducer and recorder were confirmed by pressing the transducer probe against a firmly anchored metal rod. Mounting the transducer on a plate movable by a precision micrometer allowed exact deflections to be measured and recorded. Linearity was confirmed exactly (see Figures 10a and 10b).

It was then necessary to show linear response to pressure by the spoon gauge. Known pressures of helium were introduced into the gauge, and it was sealed off. The measured and calculated (by the Ideal Gas Equation) pressures agreed within 2% at all temperatures to which the gas was heated: 250, 300, and 500°C.

The reaction vessels were individually calibrated by introducing air of known pressure and recording the
FIG. 10a

TYPICAL VESSEL CALIBRATION CURVE

TRANSUDER DEFLECTION (INCHES X 10^3)

PRESSURE (cm·MERCURY)
response. A typical calibration curve is shown in Figure 10. Table 5 gives the calibration values of each spoon gauge used. This calibration gave the same results whether it was done with the vessel in the bath at elevated temperatures, or outside the bath at room temperature, if the results were converted to the same temperature for either case.

Volume of the vessels also had to be known accurately. The volumes were obtained by filling the spoons with mercury, then weighing that amount of mercury. Handbook values of mercury density yielded the exact volumes. The thin tubing holding the ground glass joint on each vessel was calibrated as 0.205 milliliter per centimeter length; the small correction of this added volume was made in each experiment, by measuring the length of tubing that remained on the vessel after it was sealed off under vacuum.

2. Temperature Equilibrium

With the air furnace, the rate at which the desired temperature was attained was measured with a thermocouple. The couple was placed inside a well in the reaction vessel, and the furnace lowered to begin heating. Temperature equilibrium was attained within 5 minutes.

Alternatively, the calculated pressure of a known amount of helium gas was attained in about 4 minutes.

This rather long heating time was one of the major disadvantages of this heating system; however, approximately the same amount of time was needed with the apparatus of
Fig. 10b
CALIBRATION CURVES FOR SPOON GAUGES

REACTION VESSEL
12
14
16
18

PRESSURE (CM. Hg)

CHART DEFLECTION (CM.)
<table>
<thead>
<tr>
<th>Number</th>
<th>Sensitivity*</th>
<th>Sensibility*</th>
<th>Initial Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.135</td>
<td>370.</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.060</td>
<td>333.</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.134</td>
<td>372.</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>0.150</td>
<td>333.</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.800</td>
<td>62.5</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>6.60</td>
<td>7.57</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>4.00</td>
<td>12.5</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>1.90</td>
<td>26.3</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>2.80</td>
<td>17.8</td>
<td>13.0</td>
</tr>
<tr>
<td>10</td>
<td>2.50</td>
<td>21.7</td>
<td>15.15</td>
</tr>
<tr>
<td>11</td>
<td>5.61</td>
<td>8.90</td>
<td>16.45</td>
</tr>
<tr>
<td>12</td>
<td>1.95</td>
<td>25.5</td>
<td>13.77</td>
</tr>
<tr>
<td>13</td>
<td>2.38</td>
<td>21.0</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>1.47</td>
<td>34.0</td>
<td>12.86</td>
</tr>
<tr>
<td>15</td>
<td>4.36</td>
<td>11.47</td>
<td>16.95</td>
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<td>12.80</td>
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<td>3.98</td>
<td>12.56</td>
<td>13.03</td>
</tr>
<tr>
<td>18</td>
<td>3.12</td>
<td>16.0</td>
<td>16.67</td>
</tr>
<tr>
<td>19</td>
<td>2.09</td>
<td>23.9</td>
<td>14.22</td>
</tr>
<tr>
<td>20</td>
<td>3.45</td>
<td>14.49</td>
<td>17.91</td>
</tr>
<tr>
<td>21</td>
<td>4.28</td>
<td>11.68</td>
<td>15.98</td>
</tr>
<tr>
<td>22</td>
<td>4.56</td>
<td>10.96</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>4.86</td>
<td>10.28</td>
<td>17.02</td>
</tr>
<tr>
<td>24</td>
<td>2.65</td>
<td>18.87</td>
<td>13.81</td>
</tr>
<tr>
<td>25</td>
<td>2.09</td>
<td>23.9</td>
<td>12.04</td>
</tr>
<tr>
<td>26</td>
<td>2.83</td>
<td>17.66</td>
<td>-</td>
</tr>
<tr>
<td>27</td>
<td>1.10</td>
<td>45.4</td>
<td>12.21</td>
</tr>
<tr>
<td>28</td>
<td>2.65</td>
<td>18.87</td>
<td>15.16</td>
</tr>
<tr>
<td>29</td>
<td>1.42</td>
<td>35.21</td>
<td>14.10</td>
</tr>
</tbody>
</table>

*Sensitivity is given in cm of recorded chart deflection per cm of mercury pressure. Chart deflections are given at 1 X Attenuation. The higher this value, the more sensitive the spoon gauge.

+Sensibility is given in cm of mercury pressure per cm of recorded chart deflection. Chart deflections are given at 50 X Attenuation. These values were used directly in calculation of moles of product, as explained in the text.
Madorsky and also that of Brockhaus and Jenckel.

3. Monomer Stability

As a prelude to polymer decomposition studies, the thermal stability of the monomer was investigated briefly. No decomposition of the monomer was observed after 60 hours at 308°C; the calculated pressure was maintained during this duration. Likewise, gas chromatographic analysis indicated only monomer.

Furthermore, no decomposition was detected after 15 hours at about 500°C.

4. Initial Polymer Studies

The pressure expected from complete decomposition of PMMA into monomer was calculated by the Ideal Gas Equation. Higher pressures are obtained from more polymer, higher temperatures, and smaller spoon volumes. Since the spoon gauge volumes were about 15 ml and the 300-400°C range was chosen for study, the amount of polymer to give 1 atmosphere pressure was less than 100 milligrams. Table 6 shows the calculated pressures obtained from 1 milligram of polymer at various temperatures, assuming 100% degradation to monomer.

For the initial studies, an unpurified commercial sample of PMMA (Chemstrand Corporation, Decatur, Alabama) was used. The degradation was found to be incomplete after 100 hours at 310°C; gas chromatography of the pyrolyzate showed monomer, 1% ethane, and a trace of hydrogen. The
TABLE 6

THEORETICAL PRESSURE FROM 1 MG. PMMA
(ASSUMING VESSEL VOLUME OF 12.5 ml)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>300°K = 27°C</td>
<td>1.50 cm. Hg.</td>
</tr>
<tr>
<td>400°K = 127°C</td>
<td>1.98 &quot; &quot;</td>
</tr>
<tr>
<td>500°K = 227°C</td>
<td>2.48 &quot; &quot;</td>
</tr>
<tr>
<td>600°K = 327°C</td>
<td>2.98 &quot; &quot;</td>
</tr>
<tr>
<td>700°K = 427°C</td>
<td>3.48 &quot; &quot;</td>
</tr>
<tr>
<td>800°K = 527°C</td>
<td>3.96 &quot; &quot;</td>
</tr>
<tr>
<td>900°K = 627°C</td>
<td>4.46 &quot; &quot;</td>
</tr>
</tbody>
</table>
latter two products probably resulted from pyrolysis of impurities in the sample. Degradation was apparently incomplete at 310°C, even after 100 hours.

Occasional gas chromatographic analyses were done throughout these experiments. The reaction vessel was immersed in liquid air, and the volatiles pumped off by inserting the end of the vessel into vacuum tubing connected to the gas sampling system of chromatograph. In both cases, a black residue partly insoluble in acetone was formed.

In carrying out these preliminary experiments on the polymer, irregularities were observed in the rate curves. These deviations in degradation rate were caused by diffusion control of product evolution; using thin polymer films formed by evaporation from solution solved this difficulty. The following method of sample preparation was developed: Two percent weight/volume acetone solution of the polymer was prepared. A 1 ml aliquot of this solution contains 20 mg of PMMA, so if a 10 mg sample was desired 0.5 ml was added to the spoon gauge from a volumetric pipet; 1 ml gave 20 mg, 2 ml gave 40 mg, and so forth. From the surface area covered by this amount of polymer, the average film thickness so obtained from 20 mg was calculated to be about 0.002 inches (0.005 cm); 40 mg yields 0.003 inch (0.007 cm). The most uniform films were formed when the solvent was slowly evaporated over about 24 hours by immersing the vessel in a 50°C water bath. To remove any final
traces of solvent, the film was baked out at 65°C for 24 hours on the high vacuum rack.
CHAPTER III

KINETICS OF PMMA DEGRADATION

Apparatus

1. Improved Heating Medium

Development of the prototype apparatus has been described in Chapter II. Because of the slow heating time of the air furnace it was desirable to develop a more rapid heating method. Since liquid baths should give better heat contact and heat transfer to the vessel, baths useful to high temperatures were investigated. A review of high temperature heating media has just recently appeared [64]. Most of the common commerical fluids have a maximum useful temperature range about 250-350°C, e.g., Uoon Lubricants (polyglycols of Union Carbide Company), Thermol (chlorinated biphenyls of Monsanto Company), Dowtherm-A (diphenyl-diphenyl oxide of Dow Chemical Company), and silicones (Dow-Corning Company).

Molten salt mixtures and liquid metal baths seemed to hold most promise, so these were tried. Various HTS (Heat Transfer Salt) mixtures are known, one of the most common and most stable being 14.5% sodium nitrate-46.8% potassium nitrate-38.6% sodium nitrite. These attacked

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the silicon dioxide of the quartz vessel to form silicates; because of this the vessels weakened and broke easily.

Liquid metal baths were the next alternative. A major drawback of this type is that the vapors are often toxic; however, the bath was set up in a well-ventilated area, and the concentration of metal vapor was minimized. Plumber's solder (50% lead-50% tin) was chosen since it was readily available and inexpensive. The bath container was built from 3-inch-diameter, 10-inch length, iron pipe with cap, coated with Sauereisen Number 31 cement. Chromel-A resistance ribbon (0.538 ohms per foot) was then wrapped around this coated pipe and connected to the temperature controller as before.

To obtain an even temperature profile, the ribbon was wound onto the cement-coated pipe on a lathe, with a continual decrease in windings per inch from bottom to top; the bottom inch had four turns per inch and the top inch had one turn per inch.

Resistance of the furnace at room temperature was 26 ohms. This furnace core was encased in an 8-inch diameter sheet-metal cylinder containing aluminum oxide insulation. Temperature profile of the bath did not vary more than ±1°C over the center six inches, and the temperature remained constant within a few tenths of a degree for several weeks.

With the liquid metal bath complete, temperature
equilibrium was achieved within one minute; furthermore, the measured temperature is within 10% of the desired temperature in less than 30 seconds. Figure 11 shows the attainment of temperature equilibrium as measured by a thermocouple in various positions inside the spoon gauge.

An additional measure of the rapid temperature equilibration is that measured amounts of monomer attain the calculated pressure in less than 10 seconds.

It is likely that a thin polymer film inside the vessel reaches temperature equilibrium between these times of ten and thirty seconds.

2. Redesigned Detector Equipment

To accommodate the liquid metal bath, it was necessary to redesign the arrangement of accessory equipment. Instead of the furnace being movable, the transducer and spoon gauge clamps had to be movable. The arrangement in Figure 12 was found satisfactory.

The accessory equipment mounted on a movable steel plate supported above the bath included the transducer and clamps for the reaction vessel. The steel plate was supported by the vibration-free concrete table previously described. The machined aluminum screw clamps for the support rods of the spoon gauge were movable and adjustable in all directions to facilitate alignment of the vessel over the metal bath. As before, the spoon gauge pointer deflected the transducer probe, and the resulting electrical signal
Fig. 11
ATTAINMENT OF TEMPERATURE EQUILIBRIUM AT 350°C

- ○ THERMOCOUPLE NOT TOUCHING WALLS OF REACTION VESSEL
- × THERMOCOUPLE TOUCHING WALLS OF REACTION VESSEL
Fig. 12a

Apparatus for the study of polymer degradation

1. Quartz spoon gauge
2. Statham transducer
3. Micrometer
4. Furnace
5. Safety lock

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was continuously recorded.

Two types of support locks have been used in this redesigned equipment. The earlier type, shown as B in Figure 12, used an Allen wrench to tighten a bolt against the movable bar, the friction between the bar and bolt serving to hold the support in place. A later type used a perfectly counterbalanced support, so that no positive lock was required since the counterweight and the support were perfectly balanced.

Reagents

1. Monomer and Miscellaneous

All of the solvents and precipitants used in these experiments were of analytical reagent grade: acetone, methanol, benzene, and chloroform.

Methyl methacrylate monomer was supplied with compliments of Rohm and Haas Company, West Hill, Ontario. It contained 0.006% hydroquinone to inhibit polymerization. The following purification scheme \(\text{\textsuperscript{68}}\) was performed before use for any purpose:

The monomer was washed at least three times with one-fifth its volume 5% NaOH-20% NaCl solution, to remove inhibitor. It was then dried over anhydrous sodium sulfate and stored at \(-20^\circ\text{C}\) for a day or two until used.
2. Polymer

a) Commercial Sample

For the preliminary studies, a commercial sample of small PMMA chips (Chemstrand Corporation, Decatur, Alabama) was used. Polymerization details were not known, although it was presumably formed by the usual free radical process of polymerization in bulk at 60°C and "finished off" at 120°C. The intrinsic viscosity in chloroform was 3.84 deciliters per gram.

b) Polymerized in 50% Benzene-PMMA I

Monomer was used after purification as described above. Into a 3-neck round bottom flask were added 0.50 gm benzoyl peroxide, 60 gm benzene, and 70 gm monomer. This was heated with stirring at reflux temperature (80°C) for 3 hours. A very viscous solution was obtained and this was dissolved in 750 ml benzene by slight warming. The solution was precipitated into twice its volume of methanol, and a flocculant, somewhat sticky mass of PMMA was obtained. The polymer was dissolved in 1 liter of acetone, and precipitated dropwise into twice its volume of distilled water. Thirty-five grams (50% conversion) of fine white polymer was obtained after drying to constant weight. The intrinsic viscosity in chloroform was 0.50 deciliters per gram.

c) Bulk Polymerization to 75% Conversion-PMMA II

The previously purified monomer was distilled under reduced pressure of nitrogen, and the middle fraction
collected for use. Into a 250 ml, 1-neck round bottom flask were added 0.50 gm benzoyl peroxide and 100 gm monomer. Nitrogen was bubbled through for 5 minutes, then the flask was loosely stoppered and heated for 30 minutes at 80°C in a thermostated water bath. This very viscous mass was allowed to stand at room temperature overnight, then it was dissolved in an equal volume of acetone and precipitated by pouring slowly into twice its volume of methanol. Seventy-five grams (75% conversion) of fine white polymer was obtained after drying to constant weight. The intrinsic viscosity in chloroform was 0.98 deciliters per gram.

d) Bulk Polymerization to 5% Conversion—PMMA III

The previously purified monomer was distilled under reduced pressure of nitrogen, and the middle fraction collected for use. Into a 250 ml, 1-neck round bottom flask were added 0.50 gm benzoyl peroxide and 100 gm monomer. This was degassed by successive freezing and thawing under vacuum, then the flask was sealed off with a hand torch. Polymerization was carried out for 30 minutes at 60°C, then the flask was broken open and the slightly viscous solution poured into methanol. The polymer was filtered off and dissolved in 250 ml acetone and precipitated dropwise into ten times its volume of methanol. Five grams (5% conversion) of fine white polymer was obtained after drying to constant weight. The intrinsic viscosity in chloroform was 2.01 deciliters per gram.
e) Bulk Polymerization to 5% Conversion-PMMA IV

The previously purified monomer was distilled under reduced pressure of nitrogen, and the middle fraction collected for use. Since a large volume of monomer was to be polymerized, to avoid viscosity and local heat effects the polymerization was carried out in a vessel consisting of six 100 ml test tubes sealed in tandem to a main tube; the main tube contained a T-piece for access. Into this container were added 2.00 gm benzoyl peroxide and 400 gm monomer. This was degassed by successive freezing and thawing under vacuum, then the container was sealed off with a hand torch. Polymerization was carried out for 30 minutes at 60°C, then the container was broken open and the slightly viscous solution poured into five times its volume of methanol. The polymer was dissolved in 2.51 acetone and precipitated dropwise in batches from ten times its volume of methanol. Twenty grams (5% conversion) of fine white polymer was obtained after drying to constant weight. The intrinsic viscosity in chloroform was 2.28 deciliters per gram.

f) Fractionation of PMMA IV

The polymer formed by bulk polymerization at 60°C to 5% conversion-PMMA IV- was fractionated by the stepwise addition of methanol to an acetone solution; the lower, concentrated solution which settled out after each addition was collected. The method of Hall [69] was followed closely.
The vessel described in the latter reference was used, but without passage of nitrogen during fractionation. This was a 5 liter 3-neck round bottom flask in which a pear-shaped blister had been blown in the bottom. The blister terminated in a good-fitting 2 mm bore stopcock. Stirring was provided by a glass propeller-type stirrer operating through a one-hole cork stopper, and arranged so that it could be raised or lowered. The burette for non-solvent addition was fitted with a long tip to enable the non-solvent to be directed towards the stirrer shaft.

The entire apparatus was immersed in a 30-gallon water bath thermostated to 0.1°C at 25°C.

Fifteen grams of PMMA IV were dissolved in 1.5 liters acetone (ca. 1% solution) in the fractionation flask, and allowed to reach the bath temperature. Precipitation of each fraction was accomplished as follows: Methanol was added slowly into the vortex to the point of turbidity. An auxiliary bath heater was then turned on, and the bath temperature raised to about 35°C so that turbidity disappeared. It was then allowed to cool to 25°C overnight, allowing the polymer-rich phase to settle into the blister. If the precipitate was too small (or too large) a milliliter or so of non-solvent (or solvent) was added; in either case the heating and cooling cycle had to be repeated.

The fractions were isolated by raising the vessel out of the bath and venting the polymer-rich phase into a small container via the stopcock. The vessel was then replaced.
in the bath and the fractionation cycle continued.

Each viscous fraction was diluted to about 2% in acetone and the polymer isolated by total precipitation with ten times its volume of methanol. The solid polymer was washed, dried and weighed; the supernatent liquid was returned to the fractionation vessel.

Successive fractions were withdrawn until most of the polymer was removed as evidenced by the fact that no more polymer was precipitated by methanol addition. The lowest molecular weight species were recovered as the final fraction (F 9) by evaporating the final acetone-methanol solution to dryness under vacuum at room temperature.

The total yield was 14.33 gm polymer, indicating only 4% polymer loss. Characterization of the fractions is given in a following section.

g) Stereoregular Polymers

Two samples of stereoregular PMMA were received from Dr. H. E. Goode (Rohm and Haas Research Laboratories, Bristol, Pa.): syndiotactic PMMA and isotactic PMMA. Both were prepared by stereospecific anionic polymerization.

3. Polymer Characterization

a) Infra-Red Spectra

The infra-red spectra of all 5 polymers and 9 fractions described in the previous section were taken on a Beckman IR-5. Samples were pressed into discs of 2 milligrams polymer and 400 milligrams potassium bromide. No significant
differences were seen between any of the samples, except the isotactic PMMA which had a singlet (instead of a doublet as for the atactic) in the 7.7 to 8.3 micron range, as expected \( \text{[70]} \). Spectra are shown in Figures 13 to 23.

The observed spectra agree with present knowledge of the structure of PMMA, insofar as existing correlations of group frequencies can be applied. The outstanding features of the absorption spectra \( \text{[71]} \) are as follows (absorption bands are given in microns):

i) Comparable strength of the absorption peaks at 3.37 and 3.40 indicating the absence of long chains of \( \text{CH}_2 \) groups.

ii) Strong \( \text{C} = \text{C} \) absorption at 5.77.

iii) Strong absorption in the 8-9 region due to the \( \text{C-O-C} \) stretching mode.

The following assignments have also been made:

\[
\begin{align*}
6.66-7.41 \mu & : \text{alpha-methyl deformation vibrations} \\
7.69-8.33 \mu & : \text{C-O-C-O} \text{ stretching} \\
10.0-14.3 \mu & : \text{methyl and methylene rocking and skeletal vibrations.}
\end{align*}
\]

b) Viscosity Measurements

As a measure of the molecular weights of the samples, intrinsic viscosities were measured and viscosity-average molecular weights \( (M_v) \) were calculated. Measurements were done in chloroform solution in a water bath thermostated to \( 25.0 \pm 0.03^\circ \text{C} \). An Ubbelohde dilution viscometer was used:
flow time of 2 ml of chloroform was 82.81 seconds; all dilutions were made with the same 2,3 and 5 ml pipettes. Flows were timed with a stopwatch reading to 0.01 second, and were reproducible to within 0.1 percent. Solutions used were drawn into the pipette through a sintered glass filter, to prevent false readings due to dust.

Figures 24 and 25 and Table 7 give the results for unfractionated polymers. Figure 26 and Table 8 give the results for the fractions of PMMA IV. Figure 27 shows the integral and differential weight distribution for PMMA IV constructed from this data.

Intrinsic viscosities were obtained by the double extrapolation to zero concentration of \( \eta_{sp}/c \) and \( \ln \eta/\eta_{sp} \).

Viscosity-average molecular weights were calculated by the equation of Meyerhoff and Schulz \( \sqrt[\gamma]{72} \), which was confirmed by Bischoff and Desreux \( \sqrt[\gamma]{73} \):

\[
\sqrt{\eta} = (4.85 \times 10^{-5}) M_v^{0.80}
\]

Intrinsic viscosity is given in deciliters per gram. The relation is valid over the molecular weight range of 80,000 to 1,400,000.

From the viscosity data on the fractions, a check on efficiency of fractionation is possible by computing:

\[
\sum \sqrt{\eta}_F W_F
\]

where \( \sqrt{\eta}_F \) and \( W_F \) are the intrinsic viscosity and weight fractions of the \( F \)th fraction. This sum of products is
FIG. 25

VISCOSITY RESULTS FOR PMMA I, II, III, IV

\[ \frac{3}{C} \]

\[ C \text{ (gm/100 ml)} \]
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### TABLE 7

**INTRINSIC VISCOSITIES FOR UNFRACTIONATED PMMA SAMPLES**

<table>
<thead>
<tr>
<th>Chemstrand</th>
<th>( \eta^* ) (dl/gm)</th>
<th>( M_v^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA - I</td>
<td>0.50</td>
<td>104,000</td>
</tr>
<tr>
<td>PMMA - II</td>
<td>0.98</td>
<td>241,000</td>
</tr>
<tr>
<td>PMMA - III</td>
<td>2.01</td>
<td>591,000</td>
</tr>
<tr>
<td>PMMA - IV</td>
<td>2.28</td>
<td>691,000</td>
</tr>
</tbody>
</table>

\( \eta^* \) calculated by \( \sqrt{3} \eta^* = (4.85 \times 10^{-5}) M_v^{0.80} \), according to \( \sqrt{73} \eta^* \).
<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight</th>
<th>$\sqrt{3J_F}$ dl/gm</th>
<th>$\eta_v$</th>
<th>Weight Fraction ($w_F$)</th>
<th>$\sqrt{3J_F}w_F$</th>
<th>Cumulative Weight Fraction</th>
<th>Corrected* Cumulative Weight Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>F 1</td>
<td>1.4163</td>
<td>3.91</td>
<td>1,360,000</td>
<td>0.099</td>
<td>0.387</td>
<td>1.000</td>
<td>0.951</td>
</tr>
<tr>
<td>F 2</td>
<td>1.9425</td>
<td>2.97</td>
<td>963,000</td>
<td>0.135</td>
<td>0.401</td>
<td>0.901</td>
<td>0.833</td>
</tr>
<tr>
<td>F 3</td>
<td>2.1354</td>
<td>2.72</td>
<td>863,000</td>
<td>0.149</td>
<td>0.405</td>
<td>0.766</td>
<td>0.691</td>
</tr>
<tr>
<td>F 4</td>
<td>1.3601</td>
<td>2.40</td>
<td>737,500</td>
<td>0.095</td>
<td>0.228</td>
<td>0.617</td>
<td>0.569</td>
</tr>
<tr>
<td>F 5</td>
<td>1.9441</td>
<td>2.22</td>
<td>669,000</td>
<td>0.136</td>
<td>0.302</td>
<td>0.522</td>
<td>0.454</td>
</tr>
<tr>
<td>F 6</td>
<td>1.5438</td>
<td>1.86</td>
<td>536,000</td>
<td>0.108</td>
<td>0.201</td>
<td>0.386</td>
<td>0.332</td>
</tr>
<tr>
<td>F 7</td>
<td>2.8122</td>
<td>1.29</td>
<td>339,500</td>
<td>0.196</td>
<td>0.253</td>
<td>0.278</td>
<td>0.180</td>
</tr>
<tr>
<td>F 8</td>
<td>0.4060</td>
<td>0.88</td>
<td>210,500</td>
<td>0.028</td>
<td>0.025</td>
<td>0.082</td>
<td>0.081</td>
</tr>
<tr>
<td>F 9</td>
<td>0.7692</td>
<td>0.53</td>
<td>111,500</td>
<td>0.054</td>
<td>0.029</td>
<td>0.054</td>
<td>0.027</td>
</tr>
</tbody>
</table>

*Calculated by the method of Hall [69].
found to be 2.23, compared to the intrinsic viscosity of unfractionated PMMA IV of 2.28. Two conclusions may be drawn from these values:

1) There was no significant loss of low molecular weight material during fractionation procedure, since the value of 2.23 is not higher than the value of 2.28.

ii) No degradation occurred during fractionation since the intrinsic viscosity calculated by summation is not significantly below the initial value.

Experimental Procedure

The new technique that has been developed for studying polymer degradation reactions consists essentially of an automatic recording quartz spoon gauge.

A thin film (ca. 0.005 cm) of PMMA was formed in the reaction vessel by 50°C evaporation of the solvent from a 2% w/v solution of the polymer in acetone. Residual solvent was baked out of the film at 65°C at about 10^-6 mm mercury vacuum, then the vessel was sealed off with a hand torch. The two symmetrical support rods of the gauge were inserted into the clamp arrangement shown in Figure 12. Contact was made with the transducer and the assembly was rapidly lowered so that the spoon gauge was immersed in a heated thermostated 50% lead-50% tin bath. Temperature equilibrium was reached within 30 seconds.

Polymer degradation to monomer in the spoon gauge caused a pressure increase and concomitant pointer
deflection of the gauge. The pointer deflection was transmitted via the transducer to a two-channel Sanborn recorder. The chart of the recorder could be run at various speeds (0.25, 0.5, 2.5, 5, 10, 25, 50, 100 mm/sec.) to suit the rate of the reaction. Spoon gauges of various sensitivities were used after being calibrated by introducing air of known pressures into the vessel and recording the resulting deflections. The signal from a thermocouple adjacent to the reaction vessel was given on the second channel of the recorder.

Thus, both pressure and temperature of the degrading sample were recorded continuously and simultaneously.

**Experimental Results**

Tabulation of conditions employed to degrade each polymer sample is given in Table 9. The results are given in Figures 28 to 40 as moles of gas produced as a function of time. The assumption that only monomer is produced is not quite correct because the residual polymer became progressively darker (yellow to brown) as temperature increased and at 400°C a small amount of carbonized residue was also seen. This may explain the observation that usually somewhat more than the theoretical amount of moles of monomer was found on complete degradation. It is also possible that there is some strongly bound residual solvent in the polymer. However, gas chromatographic analysis of various samples detected only very small amounts of products other than
TABLE 9

CONDITIONS OF SAMPLE DEGRADATION
(* = 20 mg; + = 40 mg)

<table>
<thead>
<tr>
<th>Isotactic</th>
<th>Syndiotactic</th>
<th>PMMA I</th>
<th>PMMA II</th>
<th>PMMA III</th>
<th>PMMA IV</th>
<th>F1</th>
<th>F5</th>
<th>F9</th>
</tr>
</thead>
<tbody>
<tr>
<td>275°C</td>
<td></td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300°C</td>
<td>+</td>
<td></td>
<td>+</td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325°C</td>
<td></td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>350°C</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>375°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig 29a
350°C 20 mg of PMMA

Fig 29b
350°C 20 mg of PMMA
Fig. 30
300°C 20 mg PMMA III
EXPERIMENT NO
83 ○
27 ●
30 ●
32 ○

TIME (HOURS)
Fig. 32a
300 °C
I - 20 mg. PMMA III
II - 40 mg. PMMA III

Fig. 32b
300 °C
I - 20 mg. PMMA III
II - 40 mg. PMMA III
Fig. 33
328°C
20 mg. OF PMMA III

TIMEx (HOURS)

S = 10^8 (MOLES)
Fig. 34
380 °C
20 mg. PMMA III
**Fig. 35**

375°C

20 mg. PMMA III

**Fig. 36**

400°C

20 mg. PMMA III

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Fig. 37
500 °C
I - 20 mg. PMMA
II - 40 mg. PMMA
FIG 36a
350°C 20 mg of F1, F5, F9

FIG 36b
350°C 20 mg of F1, F5, F9

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Fig 39a:
380°C 20 mg of isotactic and syndiotactic PMMA

Fig 39b:
380°C 20 mg of isotactic and syndiotactic PMMA
Moles of gas produced was calculated by the Ideal Gas equation using the spoon gauge calibrations of pressure and volume, and the measured temperature.

\[ n = \frac{PV}{RT} = \frac{\text{Measured chart} \times \text{Pressure cal.}}{\text{Gas constant}} \times \frac{\text{Volume cal.}}{\text{Temperature}} \]

\[ = \frac{(\text{cm chart} \times \text{cm Hg/cm chart}) \times (\text{ml})}{(\text{ml} \times \text{cm Hg/mole-degree}) \times (\text{degrees Absolute})} \]

In the cases in which three or more identical degradation experiments were done, the value of the moles of gas produced (\( \overline{n} \)) is an average value. Standard deviation (S) of the average was calculated by the usual formula \( S \approx \sqrt{\frac{(n_x - \overline{n})^2}{X-1}} \):

where \( n_x1, n_x2, n_x3, \ldots \) are the values of \( n \) for each experiment, \( \overline{n} \) is the average value of the \( n_x \)'s, and \( X \) is the total number of such measurements averaged in the calculation.

In the cases in which only two degradation experiments were performed, the average value of \( n \) was calculated, but standard deviations were not since their significance would be questionable.

Experiments were not used in the average if their values of \( n \) were outside the range of twice the standard
deviation from the average.

Standard deviations are shown as vertical lines in the Figures.

1. Degradation of PMMA I, II, III, IV at 350°C

Figure 28 compares the results of degradation of PMMA I, II, III-samples polymerized in 50% benzene at 80°C, in bulk to 75% conversion at 60°C, and in bulk to 5% conversion at 60°C, respectively. Rate versus conversion curves are shown in Figure 41.

Figure 29 compares the degradation results of PMMA III and IV-samples polymerized in bulk to 5% conversion at 60°C resulting in somewhat different molecular weights: \( M_w = 591,000 \) and 691,500 respectively. Rate-conversion curves are given in Figure 42.

Table 10 gives representative data from which these figures were drawn.

2. Degradation of PMMA III at 275-400°C

Figures 30 to 36 show the degradation results of PMMA III-a sample polymerized in bulk at 60°C to 5% conversion at 275, 300, 325, 350, 375, and 400°C. Figure 37 compares the percentage of theoretical conversion to monomer, of 20 mg and 40 mg of this polymer at 300°C. Rate-conversion curves are given in Figures 43 to 48.

Table 11 gives representative data from which these curves were produced.
<table>
<thead>
<tr>
<th>PMMA I (1 run)</th>
<th>PMMA II (1 run)</th>
<th>PMMA III (a) (5 runs)</th>
<th>PMMA IV (3 runs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>Arithmetic Mean X10^5</td>
<td>Arithmetic Mean X10^5</td>
<td>Arithmetic Mean X10^5</td>
</tr>
<tr>
<td>30 sec.</td>
<td>6.56</td>
<td>6.42</td>
<td>4.28</td>
</tr>
<tr>
<td>1 min.</td>
<td>7.83</td>
<td>7.61</td>
<td>5.50</td>
</tr>
<tr>
<td>3 &quot;</td>
<td>9.82</td>
<td>9.87</td>
<td>8.55</td>
</tr>
<tr>
<td>5 &quot;</td>
<td>11.04</td>
<td>11.27</td>
<td>10.79</td>
</tr>
<tr>
<td>10 &quot;</td>
<td>13.16</td>
<td>13.49</td>
<td>13.96</td>
</tr>
<tr>
<td>20 &quot;</td>
<td>15.67</td>
<td>15.59</td>
<td>16.20</td>
</tr>
<tr>
<td>40 &quot;</td>
<td>18.00</td>
<td>17.21</td>
<td>18.01</td>
</tr>
<tr>
<td>1 hr.</td>
<td>19.10</td>
<td>17.91</td>
<td>18.71</td>
</tr>
<tr>
<td>2 &quot;</td>
<td>20.64</td>
<td>18.88</td>
<td>19.44</td>
</tr>
<tr>
<td>3 &quot;</td>
<td>21.36</td>
<td>19.26</td>
<td>19.68</td>
</tr>
<tr>
<td>5 &quot;</td>
<td>22.16</td>
<td>19.80</td>
<td>19.98</td>
</tr>
</tbody>
</table>

(a) Including 1 run up to 10 min., 1 up to 2 hr., and 2 up to 3 hr.
### TABLE 11

Arithmetic mean values of gas moles produced and standard deviations at various times and temperatures (20-mg films)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>Arithmetic mean X10^6</th>
<th>Standard deviation X10^6</th>
</tr>
</thead>
<tbody>
<tr>
<td>300°C</td>
<td>30 sec</td>
<td>2.9 ± 0.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>3.8 ± 0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 min</td>
<td>4.7 ± 0.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>6.6 ± 0.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 hr</td>
<td>7.5 ± 0.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 min</td>
<td>9.5 ± 0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 min</td>
<td>11.3 ± 0.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15 min</td>
<td>13.9 ± 0.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 sec</td>
<td>4.50 ± 0.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>6.0 ± 0.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 min</td>
<td>8.6 ± 0.61</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>10.8 ± 0.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 min</td>
<td>11.8 ± 0.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 min</td>
<td>14.3 ± 0.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 min</td>
<td>16.5 ± 0.49</td>
<td></td>
</tr>
<tr>
<td>350°C</td>
<td>30 sec</td>
<td>4.3 ± 1.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>5.5 ± 0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 min</td>
<td>8.6 ± 1.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>10.8 ± 0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 min</td>
<td>14.0 ± 1.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 min</td>
<td>18.0 ± 1.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 min</td>
<td>18.7 ± 1.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 min</td>
<td>19.6 ± 0.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90 min</td>
<td>21.0 ± 0.45</td>
<td></td>
</tr>
<tr>
<td>375°C</td>
<td>30 sec</td>
<td>8.6 ± 1.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>12.4 ± 1.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 min</td>
<td>14.4 ± 1.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>16.0 ± 1.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 min</td>
<td>18.8 ± 1.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15 min</td>
<td>21.0 ± 0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 min</td>
<td>27.5 ± 0.80</td>
<td></td>
</tr>
<tr>
<td>400°C</td>
<td>30 sec</td>
<td>12.8 ± 2.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 min</td>
<td>15.1 ± 2.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 min</td>
<td>16.7 ± 2.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70 min</td>
<td>18.5 ± 1.97</td>
<td></td>
</tr>
</tbody>
</table>

**275°C**

(4 Runs)

<table>
<thead>
<tr>
<th>Time</th>
<th>Arithmetic mean X10^5</th>
<th>Standard deviation X10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 sec</td>
<td>1.89 ± 0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>1 min</td>
<td>2.19 ± 0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>2 min</td>
<td>2.70 ± 0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>5 min</td>
<td>3.63 ± 0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>10 min</td>
<td>4.91 ± 1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>1 hr</td>
<td>5.28 ± 1.02</td>
<td>1.02</td>
</tr>
<tr>
<td>3 hr</td>
<td>6.08 ± 0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>6 hr</td>
<td>7.04 ± 0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>15 hr</td>
<td>8.75 ± 0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>20 hr</td>
<td>9.37 ± 0.83</td>
<td>0.83</td>
</tr>
</tbody>
</table>
FIG. 46
350°C
20 mg PMMA III

\( \frac{d\bar{n}}{dt} \times 10^5 \text{ MOLE/MINUTE} \)

% DEGRADATION

\( \bar{n} \times 10^5 \text{ (MOLES)} \)

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FIG. 48
400°C
20 mg OF PMMA III
3. Degradation of PMMA IV and its Fractions at 350°C

The results of degradation of PMMA IV—a sample polymerized in bulk to 5% conversion at 60°C, and some of its fractions are presented in Figure 38. The fractions—F 1, F 5, and F 9—have viscosity-average molecular weights of 1,360,000, 669,000, and 111,500, respectively. Rate versus conversion curves are given in Figure 49.

Table 12 contains representative data from which these curves were drawn.

4. Degradation of Steroregular PMMA

Figures 39 and 50 compare the degradation and rate-conversion curves for single experiments on Isotactic and Syndiotactic PMMA.

Figures 40 and 51 compare the degradation results of equal weights of Syndiotactic PMMA and PMMA III at 300°C.

5. Degradation of Hydrogenated PMMA

Hydrogenation of terminal unsaturation in PMMA was attempted as described in Chapter IV.

Figures 59 and 63 compare the degradation results of the average of two hydrogenated samples of PMMA IV (H 5 and H 6) with the results on the original sample.

Figures 60 and 64 show the resemblance between un-hydrogenated F 9 and two hydrogenated samples of it (H 11 and H 12).

Figures 61 and 65 present the degradation curves for two attempts at hydrogenation of F 7 (H 10 and H 13).
<table>
<thead>
<tr>
<th>Time</th>
<th>Arithemetic Mean $\times 10^5$</th>
<th>Standard Deviation $\times 10^5$</th>
<th>F 1 (5 runs)</th>
<th>F 5 (6 runs)</th>
<th>F 9 (5 runs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 sec.</td>
<td>4.50</td>
<td>0.39</td>
<td>3.53</td>
<td>5.77</td>
<td>5.14</td>
</tr>
<tr>
<td>1 min.</td>
<td>7.62</td>
<td>0.10</td>
<td>6.39</td>
<td>9.06</td>
<td>8.12</td>
</tr>
<tr>
<td>5 &quot;</td>
<td>8.68</td>
<td>0.38</td>
<td>7.66</td>
<td>11.13</td>
<td>9.12</td>
</tr>
<tr>
<td>10 &quot;</td>
<td>11.41</td>
<td>0.87</td>
<td>10.59</td>
<td>14.28</td>
<td>11.66</td>
</tr>
<tr>
<td>20 &quot;</td>
<td>14.28</td>
<td>1.01</td>
<td>13.42</td>
<td>16.81</td>
<td>14.34</td>
</tr>
<tr>
<td>40 &quot;</td>
<td>17.03</td>
<td>1.00</td>
<td>16.01</td>
<td>19.41</td>
<td>16.43</td>
</tr>
<tr>
<td>1 hr.</td>
<td>18.47</td>
<td>1.07</td>
<td>17.33</td>
<td>20.42</td>
<td>17.62</td>
</tr>
<tr>
<td>2 &quot;</td>
<td>20.88</td>
<td>0.96</td>
<td>18.99</td>
<td>21.62</td>
<td>19.35</td>
</tr>
<tr>
<td>3 &quot;</td>
<td>22.03</td>
<td>1.08</td>
<td>19.55</td>
<td>22.25</td>
<td>20.26</td>
</tr>
<tr>
<td>5 &quot;</td>
<td>22.70</td>
<td>1.30</td>
<td>20.58</td>
<td>-</td>
<td>21.24</td>
</tr>
</tbody>
</table>

(1) Including 1 up to 2 hr. and 1 up to 3 hr.
(2) Including 1 up to 20 min. and 1 up to 30 min.
(3) Including 1 up to 2 hr.
FIG. 50a
300°C — 20 mg
SYNDIOTACTIC PMMA AND ISOTACTIC PMMA

% DEGRADATION

FIG. 50b
350°C 20 mg OF ISOTACTIC PMMA AND SYNDIOTACTIC PMMA

% DEGRADATION

$\frac{d[n]}{dt} \times 10^6$ (MOLES/ MIN.)

$$\pi \times 10^5$$ (MOLES)
6. Degradation of Brominated PMMA

Bromination of terminal unsaturation in PMMA was also attempted; these experiments are described in Chapter IV.

Figures 62 and 66 gives the results of degradation of the three such brominated samples (B 1, B 2, B 3).
CHAPTER IV

REACTIVITY OF THE UNSATURATED CHAIN-END

Theory

It has already been pointed out that up to 50% of a sample of polymethylmethacrylate (benzoyl peroxide initiated in bulk) may consist of macromolecules terminating in olefinic double bonds at one end. Although the exact structure of such a chain-end has not been proven conclusively, this part of the molecule should nevertheless undergo the normal reactions of unsaturated C=C double bonds.

The PMMA chain-end in question probably has a structure very similar to that of the monomer, viz.,

CHAIN-ENDS: \( \sim \text{C} = \text{O} \) or \( \sim \text{C} = \text{C} \)

\[ \text{II} \]

H \( \text{COOCH}_3 \)

H \( \text{COOCH}_3 \)

(I)

(II)

MONOMER:

\[ \text{II} \]

H \( \text{CH}_3 \)

\( \text{C} = \text{C} \)

H \( \text{COOCH}_3 \)

Significant difference in behavior may be brought about by
the fact that the polymer end-group may be an \( \alpha, \beta \)-disubstituted olefin, whereas the monomer is an \( \alpha \)-olefin. Thus some decrease in reactivity might be expected, due solely to steric shielding of the double bond by the adjacent disubstituted carbon atom. In addition, it is not known whether the polymeric group (P) on the \( \beta \)-carbon is cis or trans to the terminal ester group. Different reactivities would be predicted for each configuration:

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{P} & \quad \text{OOOCH}_3 \\
& \quad \text{(III)}
\end{align*}
\quad \begin{align*}
\text{P} & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{OOOCH}_3 \\
& \quad \text{(IV)}
\end{align*}
\]

Such cis-trans possibilities do not exist if the chain-end structure has the form (II).

The actual resulting structure of the chain-end depends primarily on the mechanism by which disproportionation occurs. The overall step involves termination by transfer of hydrogen to another polymer molecule to terminate it. Disproportionation may give a hydrogen radical:

\[
\begin{align*}
R-(\text{CH}_2-\text{CHY})_n-\text{CH} = \text{CHY} + \text{H}^+ \\
\text{H}^+ \quad R-(\text{CH}_2-\text{CHY})_n-\text{CH}_2-\text{CH}_2-\text{Y}
\end{align*}
\]

Marvel [75] deems it likely that this is only a special case of chain transfer in which one growing chain abstracts a hydrogen from another growing chain or polymer molecule. It is difficult to envisage such hydrogen abstraction from
the methylene group of the penultimate carbon atom of PMMA, because of steric hindrance from the methyl and carbomethoxy groups on both the attacking and the attacked chains. This leaves the energetically difficult task of hydrogen abstraction from the terminal methyl group.

Therefore, one is left in considerable doubt as to which mechanism predominates: formation of the preferred most stable species (I) (by methylene-hydrogen abstraction) or formation of a less stable, but sterically favored, species (II) (by methyl-hydrogen abstraction). If (II) is formed initially, formation of the skeletal, favored, and most highly alkylated double-bond (I) may come about by thermal rearrangement of (II) to (I).

Another perplexing problem is then seen to exist. If the skeletal double-bond (I) is the actual form, and bonds next but one to a double-bond are weak-links, then depolymerization is initiated by cleavage of 2 main-chain carbon atoms, and unless another such 3-carbon scission occurs, the bonds broken in the unzip of PMMA are not the same as those formed in the polymerization process.

There is one configurational aspect of the chain-end that can be predicted with reasonable confidence. This concerns the fact that there is a definite predominance of the syndiotactic form of polymethylmethacrylate when formed by free-radical processes [28].

In the Fisher projection, this may be shown as:
1. Acrylate and Methacrylate Reactions

With this understanding of the structure of the unsaturated chain-end, it is well to consider the reactions of the acrylic and methacrylic esters \( \text{I} \), since they serve well as model compounds for configuration (I), but not so well for configuration (II). The following information on these compounds is summarized from the preceding reference, unless otherwise noted.

These compounds react with a number of different types of active hydrogen reagents to form isobutyrate derivatives; they form adducts with dienes; they undergo many other types of condensation reactions involving either the double bond or the ester group, and sometimes both.

a) Active Hydrogen Compounds

Addition of such compounds usually occurs readily with acrylate esters to give \( \text{II} \)-substituted propionates. Such "carboxyethylation" occurs less readily with methacrylate esters, and they do not undergo all of the addition reactions that can be done with acrylate esters.

Hydrobromic acid adds almost quantitatively to both acrylates and methacrylates at 0-25°C to give the \( \text{II} \)-halogenated adduct. Although the reaction with HCl is
quantitative with acrylates, attempts to add HCl to methyl methacrylate at room temperature have failed completely. High temperatures and pressures of HCl achieve addition and some hydrolysis.

Primary and secondary alcohols add to the acrylates rather readily, but their addition to methacrylates is slow and inefficient. As the size of the alcohol increases, yields decrease.

Mercaptans add readily to acrylates and methacrylates—one of the few reactions where the methacrylates react as easily as the acrylates—to give high yields of sulfides. High yields of the $\mathcal{S}$-thio-adducts can be achieved by reaction of the esters with $\text{H}_2\text{S}$; the methacrylates require more severe reaction conditions. Sodium bisulfite adds easily to give the corresponding $\mathcal{S}$-sulfopropionates and $\mathcal{S}$-sulfoisobutyrates; the acrylate rate is 200 times greater than that for the methacrylate under the same conditions.

Other active hydrogen compounds that follow these same trends of reactivity are:

i) ammonia and amines;

ii) hydrazine and phenylhydrazine;

iii) nitroparaffins;

iv) active methylene compounds, such as esters, nitriles and ketones;

v) hydrogen cyanide and hydrazoic acid.
b) Diene Reactions

Acrylates and methacrylates react with dienes via the Diels-Alder reaction to form cycloaliphatic esters. Methyl acrylate and methyl methacrylate undergo 1, 4-addition with butadiene to form the tetra-hyrobenzoate adducts. Similar reactions have been observed with cyclopentadiene, substituted butadienes, and like compounds.

c) Miscellaneous Reactions

Various other reactions may take place. Methyl acrylate or methacrylate form the esters of 5-alkenoic acids when heated at 200-400° C, under the pressure developed by the reaction, with olefins such as propylene and butenes. Heating methyl methacrylate in a steel bomb at 225° C for 12 hours, the monomer remaining in the liquid phase, has been reported to yield a dimer of the structure:

\[
\begin{align*}
\text{CH}_3 \\
\text{H}_2\text{C} - \text{OH} - \text{COOCH}_3 \\
\text{H}_2\text{O} - \text{CH} - \text{COOCH}_3 \\
\text{CH}_3
\end{align*}
\]

The dimer was obtained in 60% yield (36% conversion), along with 24% yield (14% conversion) of trimer. Mercuric acetate adds to the double bond of methyl acrylate in methanol:

\[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{COOCH}_3 & \quad \text{Hg}\,(\text{oAc})_2 \quad \text{CH}_3\text{O-CH}_2-\text{OH} \quad \text{COOCH}_3 \cdot \\
\text{CH}_3\text{OH} & \quad \text{Hg(oAc)}
\end{align*}
\]
Potassium bromide and bromine convert this to the brominated derivative:

\[
\begin{align*}
\text{CH}_3\text{O} - \text{CH}_2 - \text{CH} - \text{COOCH}_3 & \xrightleftharpoons{\text{KBr}} \text{CH}_3\text{O} - \text{CH}_2 - \text{CH} - \text{COOCH}_3 + \text{Hg(oAc)} \\
& \xrightarrow{\text{Br}_2} \text{CH}_3\text{O} - \text{CH}_2 - \text{CH} - \text{COOCH}_3 + \text{Br}
\end{align*}
\]

Oxidation of ethyl acrylate with neutral KMnO\(_4\) yields ethyl glycerate in 65\% yield. The solution becomes strongly basic and MnO\(_2\) is formed.

As expected, halogens may be added to acrylates and methacrylates to give the dihalo-esters. Bromine adds quantitatively to methyl methacrylate at 10°C, but the addition of chlorine is more difficult; analogous results were mentioned for HOI and HBr earlier in this section. Methyl acrylate adds the hypobromous acid from cold bromine water in 80\% yield of the \(\alpha\)-bromopropionate.

2. Tiglate and Angelate Reactions

Good model compounds for the unsaturated chain-end are found in the tiglate and angelate esters (2-methyl-trans-crotonates and 2-methyl-cis-crotonates, respectively), i.e.,

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O} & \quad \text{COOR} \\
\text{H} & \quad \text{CH}_3
\end{align*}
\quad
\begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{COOR} \\
\text{CH}_3 & \quad \text{COOR}
\end{align*}
\]

(Tiglate) \quad \text{(Angelate)}

The literature (properties, syntheses, and reactions) on the
acids and their derivatives has been reviewed through 1953.

These esters, which have the isoprene carbon skeleton, isomerize readily from angelate to tiglate, but not from tiglate to angelate. With some exceptions, esterification simply reduces the reactivity of the original acids.

The following information on these compounds is summarized from the preceding reference, unless otherwise noted.

a) Addition Reactions

Various addition reactions of these acids and their esters have been studied. Hydrobromic acid adds readily to tiglic acid to give the 3-bromoderivative, but the reaction with angelic acid gives only the tiglic acid derivative. The reaction with HCl is not noted, but HI adds stereospecifically to both acids.

Addition reactions with alcohols, mercaptans, H₂S, and NaHSO₃ have not been published. Ethyl tiglate reacts with NaON to give, after saponification, meso-2, 3-dimethyl succinic acid mixed with some of dl-isomer.

b) Diene Reactions

Reactions with dienes are not to be found in the literature.

c) Miscellaneous Reactions

Both tiglic acid and esters are oxidized slower than the corresponding angelic acid and esters, by potassium dichromate in acetic acid. Oxidation by KMnO₄ in the cold
yield acetaldehyde, acetic acid and CO₂; mild oxidation by neutral permanganate gives the 2, 3-dihydroxy derivative.

Halogen addition to the acids and esters has been studied only with bromine, which adds stereospecifically. In carbon tetrachloride the results are often erratic since oxygen of the air inhibits the reaction. In acetic acid containing acetate ion, bromine addition is probably catalyzed by HBr. Likewise, lithium chloride or bromide catalyzes bromination.

3. Hydrogenation of Model Compounds

Since the polymer chain-end in question is believed to contain C-C unsaturation a look at hydrogenation of its model compounds is in order. The most straightforward reduction of this group is probably that mentioned by Brauer and Horowitz [77] for the reduction of methyl methacrylate to isobutyric acid with zinc dust and HCl, followed by hydrolysis.

A number of catalytic hydrogenations of α,β-unsaturated esters and acids have been reported, and these often include the acrylates, methacrylates, tiglates, and angelates [78]. Platinum and palladium catalysts have been used extensively in these studies, in both supported and unsupported forms. One of the earliest significant papers reports the catalytic hydrogenation of many α,β-unsaturated acids [78] including tiglic, angelic and crotonic. Catalysts such as Pt, Pt on carbon, Pd, Pd on carbon, or Pd on BaSO₄ were
successfully employed with water, acetic acid, acetone, toluene, or aniline. A later work by the same group describes reduction of angelic and tiglic acids in aqueous sodium carbonate solution with Pt or Pd; reduction is accomplished in ethanol with Pt on carbon or Pd on carbon.

Various tiglic and angelic esters (ethyl, n-butyl, isobutyl, and benzyl) were hydrogenated over Pt or Pd in ethanol. Another study by the same workers describes hydrogenation rates of angelic acid and its methyl ester to be greater than that of the corresponding tiglates; likewise, the crotonates hydrogenated faster than the α-methyl crotonates.

Another method of hydrogenation of such compounds is by reduction with hydrazine. Crotonic, tiglic and 1,4-dimethylaorylic acids were easily hydrogenated by the method used.

a) Physico-Chemical Aspects

The physico-chemical information on hydrogenation of olefins is sparse, most work having been done with ethylene and "great ignorance" existing in other cases. Hydrogenation of substituted olefins indicates that in many cases the products of cis addition are found to be predominant. The cis/trans ratio depends on hydrogen pressure and catalyst but not temperature. The cis/trans ratio is highest for Adams platinum, lower for Raney nickel, and lowest for supported palladium. Platinum and palladium metals are among
the most active for olefin hydrogenation, but different preparations give widely different activity. Rates decrease with increasing substitution of alkyl groups about the double bond; aryl substitution yields anomalous effects.

Catalytic hydrogenation is based on the activation of hydrogen at metallic and other surfaces, the activation process leading to the acquisition by the hydrogen of reactive properties similar to those of the gas in the nascent state. In modern practice, while reduction by nascent hydrogen has not completely disappeared, it has at any rate been relegated to a subordinate position not only because of the universality of the catalytic method but also due to the quantitative yields and relative freedom from side reactions which are usually associated with the latter method.

Kinetic investigations of catalytic reactions led Rideal to the view that a catalytic reaction may occur between one gas adsorbed in a primary chemisorbed layer on a catalyst, and a second gas admitted above it, either in a true van der Waal's layer or at gaps in the chemisorbed layer. The action of ordinary catalysts in hydrogenation is bound up with their power to activate hydrogen itself, apart from any adsorptive reaction between the substance hydrogenated and the catalyst or its adsorption complex. Molecular strain influences the stability and consequently the reactivity of substances adsorbed on the catalyst.

It is found in practice that the overall kinetics of
liquid-phase catalytic hydrogenation at a constant hydrogen pressure corresponds, according to the conditions, with two alternative types of reaction paths [86]. In the first instance, the reaction may be approximately of zero order, the rate of absorption of hydrogen remaining nearly constant until a stage in the neighborhood of saturation is reached, when the velocity decreases relatively rapidly and suddenly because of the deficiency in available supply of unsaturated substance. On the other hand, the conditions under which the hydrogenation is carried out may be such that the concentration of the unsaturated substance, and its disappearance by reaction, exercises an effective influence on the velocity from the start. This will give a continuously curved graph.

b) Effects of Variables

The velocity of hydrogenation is effected by temperature, pressure, solvent, agitation, structure, and catalyst [87,88,89].

i) Temperature - Since the distribution of the unsaturated substance between the free and adsorbed phases is adversely affected (from the adsorption side) by increasing the temperature, it is possible to produce conditions such that a hydrogenation which is linear at a lower temperature becomes curved as the temperature is raised.

ii) Pressure - Under many conditions, the rate of hydrogenation of liquids is approximately directly proportional
to the hydrogen pressure, but deviations from this simple relationship also occur. Direct variation occurs, provided, first, that the catalyst concentration is not too low, and, second, that the substance hydrogenated does not contain certain substituent groups. There is a recent tendency to employ much higher pressures, for instance, of the order of 100-300 atmospheres, with substances that can be hydrogenated only with difficulty.

iii) Solvent - In many cases it is convenient to treat a solution of substance rather than to hydrogenate the substance alone; accordingly, the use of organic solvents is common in hydrogenation processes. The reaction rate varies considerably with the solvent used. The concentration of dissolved hydrogen in the solvent is a function of the partial pressure of hydrogen in the gas phase and of the solubility coefficient. In addition, the rate of transport of the gas from the gas phase, through the solvent, to the catalytic surface varies with the viscosity and other factors (mechanical) which determine the rate of mixing.

iv) Agitation - In liquid phase hydrogenation, in which gaseous hydrogen is brought into intimate contact with the solution either by shaking or stirring, the reaction velocity in general increases with any increase in the degree of agitation. A more intensive agitation tends both to increase the gas-liquid interface, which is the means of entry of hydrogen into the solution, and also to facilitate
the mixing of this probably saturated surface layer with
the bulk of the solution, thus bringing the supply of dis-
solved hydrogen into contact with the catalyst. The exact
variation of reaction velocity with changing degrees of
agitation will, of course, vary from one hydrogenation
apparatus to another.

v) Structure - While the influence of the chemical
structure of the substance hydrogenated varies considerably
with the conditions of hydrogenation, certain regularities
exist which to some degree connect the structure of a com-
 pound with its ease of hydrogenation. In general, ethylenic
and, above all, acetylenic linkages hydrogenate far more
rapidly than either benzenoid or carbonyl groups. The ve-
locity decreases as the length of the ethylenic chain in-
creases. Acids usually hydrogenate more slowly than their
esters. With cis-trans isomers, the cis form generally
hydrogenates more readily.

vi) Catalyst - The selection of a catalyst and a method
of preparing it should not rest upon an exact method of com-
paring catalysts. A study of the behavior of catalysts
will show that it is apparently impossible to accurately
compare catalysts, except under conditions so completely
specified that the comparison is robbed of most of its
value.

It should be noted that there are various ways of pre-
paring catalysts and the method of preparation has an effect
on the extent of reduction and general activity of the
Hydrogenation of PMMA

This experimental work was an attempt to stabilize the proposed "weak-links" of the unsaturated chain-ends by hydrogenation of the double bonds. As a guide to the effectiveness of chosen conditions, hydrogenation of purified (see Chapter III) methylmethacrylate monomer was first carried out. Having thus chosen optimum conditions, hydrogenation of the polymer was attempted.

1. Apparatus and Chemicals

All monomer, solvents and catalysts were of analytical reagent grades. Monomer was washed free of inhibitor and purified as previously described (Chapter III). Platinum oxide-"Adams Catalyst"-(National Lead Company, New York) and 10% palladium on activated charcoal (Englehard Industries, New Jersey) were used for catalysts after saturating with hydrogen. Polymer preparation is described in Chapter III.

Apparatus used was of two types: atmospheric pressure and high pressure types. The atmospheric pressure type, as shown in Figure 52, consists essentially of a glass vacuum-pressure line to which are attached gas burets of various sizes, and in addition, a ground-glass outlet for a reaction flask. The solution of substance to be hydrogenated is added to the flask by a vent above the
FIG. 52
ATMOSPHERIC PRESSURE HYDROGENATION APPARATUS
ground-glass joint. Agitation was done with a magnetic stirrer.

The high pressure type consists of a "Parr Pressure Reaction Apparatus" (Parr Instrument Company, Moline, Illinois). This is composed essentially of a hydrogen inlet valve, steel buffer pressure chamber and pressure tubing connections to a reaction flask. The standard 500 ml pressure-tested flasks were replaced with a specially constructed heavy-wall 25 ml pear-shaped reaction flask; this could be firmly seated and clamped in place just as the standard flasks could be. Mechanical agitation was accomplished by pivoting the 7-inch flask back and forth at 4 sweeps per second.

Infra-red analyses were carried out on a Beokman IR-5. Monomer and methyl isobutyrate spectra were taken in chloroform and polymer spectra were taken in KBr pellets. Typical spectra are shown in Figures 54 to 58.

2. Hydrogenation Experiments

a) Atmospheric Pressure Experiments

Experiment H 1. - Monomer in the presence of zinc and acetic acid.

Amounts: 10 ml monomer; 12 ml glacial acetic acid; 10 ml distilled water; 6.5 gm zinc. No hydrogen atmosphere. When stirring of the turbid solution was stopped after 40 hours, 1% polymer was isolated but no significant hydrogenation occurred.
Experiment H 2. - Monomer in the presence of 10% palladium on charcoal in aqueous methanol.

Amounts: 1 ml monomer; 7 ml methanol; 7 ml water; 0.100 gm palladium on charcoal. Hydrogen pressure of 1 mm. After evacuating and flushing the catalyst three times with hydrogen, hydrogenation was carried out for 20 hours. The curved hydrogen uptake graph is shown in Figure 53. Hydrogen absorbed: Calculated = 230 ml; Found = 200 ml (82%). Infra-red analysis indicated little olefinic unsaturation remaining (using the 6.25 μ absorption band of C = C stretching (90°)).

Experiment H 3. - Monomer in the presence of 10% palladium on charcoal in chloroform.

Amounts: 2 ml monomer; 28 ml chloroform; 0.200 gm palladium on charcoal. Hydrogen pressure of 1 mm. After evacuating and flushing the catalyst four times with hydrogen, hydrogenation was carried out for 20 hours. The curved hydrogen uptake graph is shown in Figure 53. Hydrogen absorbed: Calculated = 460 ml; Found = 392 ml (85%). Infra-red analysis indicated negligible olefinic unsaturation remaining.

Experiment H 4. - Monomer in the presence of Adams Catalyst (reduced platinum oxide) in chloroform.

Amounts: 2 ml monomer; 28 ml chloroform; 0.200 gm platinum oxide. Hydrogen pressure of 5 mm. After evacuating and flushing the catalyst four times with hydrogen, hydrogenation was carried out for 90 minutes. The linear
hydrogen uptake curve is shown in Figure 53. Hydrogen absorbed: Calculated = 460 ml; Found = 464 ml (Quantitative). Infra-red spectrum was identical with that of the expected product, i.e., methyl isobutyrate.

**Experiments H 5 and H 6.** - Polymer in the presence of Adams Catalyst (reduced platinum oxide) in chloroform.

Amounts: 0.500 gm unfractionated polymer, PMMA-IV, (see Chapter III); 25 ml chloroform; 0.200 gm platinum oxide. Hydrogen pressure of 15 mm. After evacuating and flushing the catalyst four times with hydrogen, hydrogenation was carried out for 2 hours. A 50 ml volume increase was observed in this time. The polymer was precipitated, dried and degraded; no significant difference in degradation rate was observed (see Section 4). The infra-red spectrum of the product was the same as that of the original polymer.

Repeating this entire procedure (Experiment 6) yielded identical results, except that hydrogenation was carried out for 4 hours, and 100 ml volume increase was noted.

**Experiment H 7.** - Adams Catalyst (reduced platinum oxide) in chloroform.

Amounts: 25 ml chloroform; 0.200 gm platinum oxide. After evacuating and flushing the catalyst four times with hydrogen, chloroform alone was added, and normal hydrogenation procedure followed for 20 hours. A 100 ml volume increase was noted. Shaking the resulting chloroform with neutral distilled water yielded a water layer that was "strongly acid" as tested by pH paper, i.e., pH of about 3.
This probably indicates presence of HCl from a catalyzed reaction of hydrogen with chlorinated solvent.

Experiment H 8. - Adams Catalyst (reduced platinum oxide) in glacial acetic acid.

Amounts: 25 ml glacial acetic acid; 0.200 gm platinum oxide. After evacuating and flushing the catalyst four times with hydrogen, glacial acetic acid alone was added, and normal hydrogenation procedure followed for 20 hours. No volume change was observed. The pH of the resulting acetic acid was unchanged from that of the original.

Experiment H 9. - Monomer in the presence of Adams Catalyst (reduced platinum oxide) in glacial acetic acid.

Amounts: 2 ml monomer; 25 ml glacial acetic acid; 0.200 gm platinum oxide. Hydrogen pressure of 3 mm. After evacuating and flushing the catalyst four times with hydrogen, hydrogenation was carried out for 60 minutes. The linear hydrogen uptake graph is shown in Figure 53. Hydrogen absorbed: Calculated = 460 ml; Found = 455 ml (Quantitative). The infra-red spectrum was identical with that of the expected methyl isobutyrate.

Experiment H 10. - Polymer in the presence of Adams Catalyst (reduced platinum oxide) in glacial acetic acid.

Amounts: 0.500 gm fractionated polymer, PMMA-IV-F7 (see Chapter III); 25 ml glacial acetic acid; 0.200 gm platinum oxide. Hydrogen pressure of 5 mm. After evacuating and flushing the catalyst four times with hydrogen, hydrogenation was carried out for 115 hours. No volume
change was observed. The polymer was isolated, purified and degraded; no significant difference in degradation rate was noted (see Section 4). The infra-red spectrum of the product was identical with that of the original polymer.

b) High Pressure Experiments

Experiment H 11. - Polymer in the presence of Adams Catalyst (reduced platinum oxide) in glacial acetic acid.

Amounts: 0.250 gm fractionated polymer, PMMA-IV-F9 (see Chapter III); 25 ml glacial acetic acid; 0.200 gm platinum oxide. Hydrogen pressure of 5.3 atmospheres. All these substances were added to the reaction flask and the flask was seated securely in place. After flushing the apparatus with hydrogen for 5 minutes, it was sealed, and hydrogenation was carried out for 10 hours. No change was noted on the pressure gauge during this time. The polymer was isolated, purified and degraded; no significant difference in degradation rate was observed (see Section 4). The infra-red spectrum of the product was identical with that of the original polymer.

Experiment H 12. - Polymer in the presence of Adams Catalyst (reduced platinum oxide) in acidified glacial acetic acid.

Amounts: 0.130 gm fractionated polymer, PMMA-IV-F9 (see Chapter III); 25 ml glacial acetic acid through which about 1 ml dry HCl gas had been passed; 1.000 gm platinum
oxide. Hydrogen pressure of 5.6 atmospheres. All these substances were added to the reaction flask and the flask was seated in place. After flushing the apparatus with hydrogen for 5 minutes, it was sealed, and hydrogenation was carried out for 75 hours. No pressure change was seen. The polymer was isolated into a water-soluble fraction (ca. 30%) and a water-insoluble fraction (ca. 70%). The former was shown to be polymethacrylic acid by infra-red analysis; the degradation of the latter yielded slightly increased concentration of products and rates of formation (see Section 4).

Experiment H.13. - Polymer in the presence of Adams Catalyst (reduced platinum oxide) in dry acidified glacial acetic acid.

Amounts: 0.150 gm fractionated polymer, PMMA-IV-F7 (see Chapter III); 25 ml of dry glacial acetic acid through which about 1 ml HCl gas had been passed (drying achieved by prior addition of 5% acetic anhydride); 1.000 gm platinum oxide. Hydrogen pressure of 6.0 atmospheres. All these substances were added to the reaction flask and the flask was seated in place. After flushing the apparatus with hydrogen for 5 minutes, it was sealed, and hydrogenation was carried out for 75 hours. No pressure change was observed. The polymer was isolated into a water-soluble fraction (ca. 25%) and a water-insoluble fraction (ca. 75%). Degradation of the latter yielded slightly increased concentration of products and rates of formation (see Section 4).
Halogenation of PMMA

This experimental work was an attempt to reduce or eliminate the unsaturated chain-ends through bromination.

1. Apparatus and Chemicals

All reagents, solvents and catalysts were of analytical reagent grade. Polymer preparation is described in Chapter III.

A Burrell Wrist Action Shaker (Burrell Corp., Pittsburgh, Pa.) was used for agitation during the reactions.

Infra-red analyses were carried out on a Beckman IR-5. Polymer spectra were observed in KBr pellets.

2. Halogenation Experiments

Experiment B 1. - Polymer in the presence of bromine in chloroform.

Amounts: 0.500 gm fractionated polymer, PMMA-IV-F7 (see Chapter III); 25 ml chloroform; 0.30 ml bromine.

After dissolving the polymer in chloroform, bromine was added, and the flask shaken for 24 hours. No color change was observed during this time. The polymer was precipitated into methanol, then reprecipitated twice from acetone into ten times its volume of methanol. It was dried to constant weight under vacuum, then degraded. No significant decrease in degradation rate was observed. The infra-red spectrum of the product was the same as that of the original polymer.

Experiment B 2. - Polymer in the presence of bromine
in glacial acetic acid.

Amounts: 0.100 gm fractionated polymer, PMMA-IV-F7 (see Chapter III); 5 ml glacial acetic acid; 0.10 ml bromine. After dissolving the polymer in glacial acetic acid, bromine was added, and the flask shaken for 100 hours. No color change was seen. The polymer was precipitated into ten times its volume of methanol. It was dried to constant weight under vacuum, then degraded. No significant decrease in the degradation rate was noted. The infra-red spectrum of the product was the same as that of the original polymer.

Experiment B 3. - Polymer in the presence of bromine and mercuric acetate in glacial acetic acid.

Amounts: 0.150 gm fractionated polymer, PMMA-IV-F8 (see Chapter III); 5 ml glacial acetic acid; 0.10 ml bromine; 0.150 gm mercuric acetate. After dissolving the polymer in glacial acetic acid, mercuric acetate was added, then bromine. The flask was shaken for 120 hours. No color change was seen. The solution was filtered and the polymer was precipitated into methanol; it was then reprecipitated twice from acetone into ten times its volume of methanol. The polymer was dried to constant weight under vacuum, then degraded. No significant decrease in degradation rate was observed. The infra-red spectrum of the resulting polymer was the same as that of the original.
Degradation of the Halogenated and Hydrogenated Polymers

To determine the effect of halogenation or hydrogenation on the polymer stability, the resulting samples were thermally degraded at 350°C by the method described in Chapter III. For ease of comparison, all samples were prepared for degradation in the same way: 2% w/v solutions in acetone were prepared and 1 ml of the solution was evaporated to give thin films of \(2.0 \times 10^{-4}\) moles of polymer. All films were heated at 65°C under a vacuum of 10^{-5} mm mercury for 24 hours.

Table 14 gives the percentage of the polymer that degraded rapidly, as given by linear extrapolation of the initial rapid rate.

1. Hydrogenated Polymers

Figure 63 compares the degradation of the unfractionated polymers resulting from hydrogenation at atmospheric pressure in Experiments H 5 and H 6 with the untreated unfractionated polymer. There does not seem to be any significant difference in rate, but the extrapolated percentage of rapidly-degrading polymer is slightly decreased, compared to untreated PMMA IV.

Figure 65 shows the degradation rates for the fractionated polymer resulting from hydrogenation at atmospheric pressure in Experiment H 10. Although degradation of this untreated fraction was not performed, it would not be much
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different from that of the lower molecular weight fraction (F9) shown by the dotted line in Figure 65. No great difference is seen between the polymer from Experiment H 10 and the untreated lower molecular weight fraction; however, the apparent percentage of rapidly-degrading polymer is somewhat lower in the hydrogenated sample.

Figure 65 also indicates the rates of degradation for the fractionated polymer from a high pressure hydrogenation, H 13. An initial rapid jump to about 3.4 moles (17%) was noted on degrading this sample; it is very possible that this was due to some percentage of acid groups in the resulting polymer. The initial rate of degradation thereafter appears unchanged. The corrected extrapolated value of rapidly-degrading polymer is lower than the value for the untreated lower molecular weight fraction, F9; it is also lower than the estimated percentage for the fraction actually treated (F7).

Figure 64 gives degradation rates for the lowest molecular weight fraction (F9) for two samples hydrogenated under pressure (H 11 and H 12) compared to the untreated fraction. The three rates are very similar and the extrapolated values of unstable polymer are slightly lower than the original.

It should be noted that the total moles of products of Experiments H 12 and H 13 appear somewhat greater after long exposure to heat. The higher concentration of products is probably due to the presence of some poly(methacrylic
acid, or at least to some acid groups on the chain; these acid groups could arise from side reactions during the hydrogenation process.

2. Halogenated Polymers

Figure 66 shows the curves for degradation of fractionated polymers after bromination in Experiments B 1, B 2, and B 3. Although the rates are not greatly different from that of untreated F9, all three extrapolated values of rapidly-degrading polymer are lower than the 30% of F9, or the estimated percentages for the fractions actually treated (F7 and F8).
<table>
<thead>
<tr>
<th>Temperature</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>F1</th>
<th>F5</th>
<th>F9</th>
<th>Isotactic</th>
<th>Syndiotactic</th>
</tr>
</thead>
<tbody>
<tr>
<td>275°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td>300°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td>325°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td>350°C</td>
<td>38%</td>
<td>37%</td>
<td>27%</td>
<td>24%</td>
<td>20%</td>
<td>26%</td>
<td>30%</td>
<td>14%</td>
<td>18%</td>
</tr>
<tr>
<td>375°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HYDROGENATED</td>
<td>UNHYDROGENATED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>H 5, H 6</strong></td>
<td>25%</td>
<td>24% (IV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>H 10</strong></td>
<td>22%</td>
<td>ca.28% (F7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>H 11</strong></td>
<td>27%</td>
<td>30% (F9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>H 12</strong></td>
<td>25%</td>
<td>30% (F9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>H 13</strong></td>
<td>35% (18%\textsuperscript{a})</td>
<td>ca.28% (F7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>BROMINATED</th>
<th>UNBROMINATED</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B 1</strong></td>
<td>25%</td>
<td>ca.28% (F7)</td>
</tr>
<tr>
<td><strong>B 2</strong></td>
<td>15%</td>
<td>ca.28% (F7)</td>
</tr>
<tr>
<td><strong>B 3</strong></td>
<td>20%</td>
<td>ca.29% (F8)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}) This percentage arrived at by subtracting initial jump of 17%.
DISCUSSION OF RESULTS

In most PMMA samples studied to date, the rate of pyrolysis to monomer was found to decrease to negligible values at about 50% conversion, and the overall activation energy was found to rise from about 30 to 50 kcal/mole \(^\text{[17, 49]}\). It is commonly assumed that two distinct decomposition mechanisms may be operative: one, important at low conversion to monomer and the other, important at high conversion. From available data it has been deduced that the first reaction proceeds by chain-end initiation caused by terminal unsaturation, followed by a rapid unzipping of many monomer units. Primarily on the basis of small evidence of Brockhaus and Jenckel \(^\text{[17]}\), it has been postulated that the second reaction is randomly initiated, then rapid unzipping of monomer units follows. Chain transfer is probably negligible, and termination has been commonly assumed to be by disproportionation \(^\text{[91]}\).

Overall activation energies \((E_a)\) for PMMA degradation (see Table 3) are dependent on the method of polymer preparation. For peroxide or photoinitiated PMMA \(^\text{[17, 49]}\), end initiation appears to be the cause for the low \(E_a\)'s and random initiation for the high values. If the PMMA

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is prepared with hydrogen peroxide and ferrous ion, \( [\mathrm{Fe}^{2+}] \), a high \( E_a \) (48 Kcal/mole) is found for small chains and a low \( E_a \) (32 Kcal/mole) is found for long chains. Thus, small differences in PMMA structure cause considerable differences in the stability of the polymer.

**Technique**

In order to carry out the proposed quantitative studies performed in this work, it was necessary to conceive, develop, and construct a sensitive new apparatus for polymer degradation experiments. The technique which evolved consists essentially of an automatic recording quartz spoon gauge, which should be useful not only for polymer degradation studies but also for measurements of ceiling temperature, equilibrium monomer concentration and even non-polymeric reactions in which the partial pressure of a component changes. Principal advantages of the technique for this study are:

1) Temperature equilibrium is reached in less than 30 seconds, compared to at least 5 minutes required by previous investigators: Grassie and Melville \( [44] \), Madorsky \( [93] \), and Brockhaus and Jenckel \( [17] \).

2) Rapid, continuous, and accurate recording of results. Pressures could be read to \( \pm 1 \) mm mercury; that is, the moles of products could be computed within about one-half percent. These benefits accrue from coupling the rapid-response high-speed Sanborn recorder with the very pressure
sensitive spoon gauge and the accurate displacement-sensing Statham transducer.

iii) Useful kinetic results for PMMA degradation were obtained at 400°C, which is about 100°C higher than the temperature attained by previous investigators not neglecting the initial stages of reaction.

Unstable Percentage of PMMA

One of the most immediate conclusions that may be drawn from the data of these studies is confirmation of more than one degradation process taking place in PMMA. Less than half of any polymer sample pyrolyzed was found to degrade very rapidly (see Table 13). Previous authors have concluded that PMMA, prepared in bulk at high temperatures by benzoyl peroxide initiation, consists of chains of which 50% have double bonds at the ends and the other 50% have single bonds only. Kinetic, radiochemical, and degradation evidence for this conclusion was discussed in Chapter I.

1. PMMA III, IV, and Fractions

Two of the polymerizates used in this work were prepared in bulk at 60°C by benzoyl peroxide initiation: PMMA III and PMMA IV. The percentage of the rapidly-degrading portion of these unfractionated samples was about 25% in both cases (see Table 13). A comparatively simple explanation exists for this apparent disagreement with the 50%
estimate of the authors just mentioned. Lower molecular weight samples were used to obtain best previous estimates by degradation; linear extrapolation of their degradation rate versus percentage degradation curves indicated that 50% of the PMMA sample degraded rapidly. The principal results of various workers were as follows:

Brockhaus and Jenckel—B.P. in bulk at 80°C. \[17\].

\[M_v = 39,000; 52,000; 62,000; 96,000; 182,000; 426,000.\]

Grassie and Melville—B.P. in bulk at 60°C. \[44\].

\[M_n = 179,000.\]

This study—B.P. in bulk at 60°C.

\[M_v = 1,360,000; 691,500; 591,000; 111,500.\]

For the three lowest molecular weight samples of Brockhaus and Jenckel, the rate versus percentage degradation curves extrapolate linearly to within 1% of 50%. However, higher molecular weight samples yield the following linear extrapolations:

\[M_v = 96,000 \quad 45\%\]
\[M_v = 182,000 \quad 42\%\]
\[M_v = 426,000 \quad 30\%\]

The authors used a non-linear extrapolation of the initial rate (from rate versus conversion curves) to yield values of 50% for all samples, although their kinetic calculations did take into account the actual percentage of monomer resulting from chain-end initiation.

The rate versus percentage degradation curve of Grassie
and Melville has been extrapolated to 50% by Jellinek \cite{1}; if only the very initial part of the curve is used a value of 44% is obtained.

Figure 67 shows the relationship between molecular weight and the percentage of unstable polymer as determined by our linear extrapolations of thermal degradation rate measurements.

Comparison of this curve with the rate versus reciprocal molecular weight curve of Figure 5, shows that both yield an apparent measure of the kinetic chain length. Figure 67 appears to indicate that the kinetic chain length is about 2000 monomer units, in reasonable agreement with the estimate of 2500 from Figure 5.

Assuming that 50% of the chains initially contain weak-link terminal unsaturation, then degradation of this portion of the sample is initiated most rapidly. But if the polymer chain length is much larger than the kinetic chain length, the chains will not unzip completely; the radical chain-ends will stabilize by disproportionation or combination. If disproportionation occurs, then only 50% of the chains thus stabilized will contain further weak-link double bonds. More unzip would take place rapidly from these newly-formed unsaturated ends. Therefore, about 50% of the original unstable half of the chains would degrade rapidly, or, 25% of the overall sample.

This agrees well with the estimate herein of 25% for molecular weights of 691,500, 669,000 and 591,000 in Table 13.
DEPENDENCE OF % OF UNSTABLE PMMA ON MOLECULAR WEIGHT
The lowest molecular weight fraction, F9, \((M_v = 111,500)\) shows a higher unstable portion of 30%. This probably represents the effect of the distribution of chain-lengths in the fraction: shorter chains degrade completely (to give an estimate of 50%) and longer chains degrade incompletely and stabilize by disproportionation (to give an estimate of 25%). Similarly, for the long-chain samples of Brookhaus and Jenckel, the longer the polymer chain the more pronounced is the deviation from the degradation estimate of 50% unsaturated chains.

Madorsky also found that 22-24% of his PMMA polymerizate (B.P. initiated; molecular weight = 150,000) degraded rapidly at 240-250°C. Beyond these percentages a slightly less rapid reaction was almost completely stopped at 40 to 47%. However, as with all other investigators except Brookhaus and Jenckel, he attached little significance to the initial stage of the rapid reaction.

The highest molecular weight fraction, F1, \((M_v = 1,360,000)\) exhibits only 20% of unstable chains. The above scheme can explain this in one of two ways:

i) this fraction only contained 40% originally unsaturated chains, or,

ii) this fraction contained 50% unsaturated chains but on incomplete unzip, some chains did not stabilize by disproportionation; possibly, they were prevented from stabilizing by diffusion control.

It is of interest to compare the pyrolysis of another
very high molecular weight PMMA with our high molecular weight sample, Fl. Madorsky’s degradation rates for PMMA prepared at -30°C by storage for a year without initiator (Mn = 5,100,000) were essentially linear to 90-95% conversion. The predominant mode of termination under such conditions is combination, so probably no weak-link terminal unsaturation existed in this sample. The activation energy of 55 kcal/mole may well be a measure of the stability of the sterically hindered link resulting from termination-combination, or it may be a measure of stability of random links in the backbone of the chain.

2. PMMA I

It is probably fortuitous that the percentage of unstable polymer is about the same (37-38%) for PMMA I and PMMA II—benzoyl peroxide initiated samples prepared in 50% benzene at 80°C, and to high conversion in bulk at 60°C, respectively.

The benzene-transferred sample, PMMA I, is the lowest molecular weight sample prepared for this study: Mₜ = 104,000. The intermediate percentage (37%) of chains with unsaturated ends is the result of two competing effects, first, the quite low molecular weight of the sample (which favors complete unzip and an estimate of 50% unsaturation) and second, the decrease of unsaturated chain-ends because of some transfer to benzene (which favors an estimate of less than 50% unsaturation).
As a comparison, Grassie and Vance [47] have found that 29% of a sample prepared by benzoyl peroxide initiation in 50% benzene at 60°C ($M_n = 720,000$) degrades rapidly on pyrolysis. This estimate of 29% unsaturation is somewhat lower than our estimate of 37% for PMMA I. The polymerization of PMMA terminates by disproportionation at higher temperatures, and by combination at lower temperatures; therefore, at these authors' lower temperature of 60°C, less disproportionation occurred during their polymer preparation. This results in a lower percentage of terminal double bonds in the polymer; thus their lower estimate of unsaturation is to be expected not only because of the comparatively high molecular weight, but also because of decreased disproportionation.

Another of their polymerizates (prepared by benzoyl peroxide initiation in 90% benzene at 60°C; $M_n = 231,000$) showed 21% to degrade rapidly. Grassie and Vance explained their results solely on the basis of transfer to benzene, and did not consider the effect of molecular weight.

3. PMMA II

The sample polymerized to high-conversion in bulk at 60°C, PMMA II, has a viscosity-average molecular weight of 241,000. The intermediate percentage (38%) of chains with unsaturated ends compares well with our estimate of 42% for Brockhaus and Jenckel's sample of $M_v = 182,000$.

However, the 38% estimate is higher than the 30%
estimate for our lower molecular weight sample, F9 (M_v = 111,500). There are two possible explanations:

1) The estimate of unsaturation in F9 is erroneous; this is supported by the fact that the unsaturation percentage does not lie on the curve in Figure 67.

11) The thermal stability of PMMA II is changed due to some change in the termination mechanism at high percentages of polymerization, such as the "gel effect", which increases the propagation rate and decreases the termination rate at higher percentages of the PMMA bulk polymerization \[94\]. This effect involves an autoaccelerated increase in polymerization rate as the viscosity of the medium increases due to increased polymer concentration above 20\% \[95\]. An increase in molecular weight also occurs at these high conversions.

4. Stereoregular Polymers

The stereoregular PMMA samples would not be expected to exhibit two decomposition reactions since termination by disproportionation is highly unlikely during the polymerization via ionic chain-ends.

Therefore, a surprising result is the 15 ± 3% of both stereoregular polymers that degraded rapidly (see Table 13). No results have been published to date on the degradation of tactic polymethacrylates. The initial values obtained may be simply an indication of an exceptionally high percentage of entrapped solvents, or the values may indicate
some abnormalities in the polymer structures. It is highly improbable that such weak-links could arise from disproportionation or combination since either would involve intimate proximity of like-charged active ionic chain-ends. Likewise, the high percentage of oxygen necessary to form so many peroxide links would poison a normal ionic polymerization.

**Rates of Degradation**

Tables 15 and 16 give the rate constants for the rapid \( k_A \) and slow \( k_B \) degradation rates of PMMA samples. The rate constant at each percentage degradation is taken as the slope of the line at that point from the plot of \( \frac{dn}{dt} \) versus \( \bar{n} \), because Brookhaus and Jenkel [17] showed:

\[
\text{CHAIN-END INITIATION: } \lim_{t \to 0} \frac{d}{dn} \left( \frac{dn}{dt} \right) = -k_A
\]

\[
\text{RANDOM INITIATION: } \lim_{t \to \infty} \frac{d}{dn} \left( \frac{dn}{dt} \right) = -k_B
\]

However, as Gordon pointed out [24], these equations hold only for the case in which kinetic chain length is greater than polymer chain length. For longer polymer chains, \( P > E \), Gordon showed that the fraction \( f \) of unsaturated ends decays with first-order kinetics:
TABLE 15  
RATE CONSTANTS FOR THE FAST REACTION ($k_A$) AND THE SLOW REACTION ($k_B$)  
IN THE PYROLYSIS OF VARIOUS PMMA SAMPLES AT 350°C a.

<table>
<thead>
<tr>
<th></th>
<th>$k_A$ (Min$^{-1}$)</th>
<th>$k_B$ (Min$^{-1}$)</th>
<th>40%</th>
<th>60%</th>
<th>80%</th>
<th>P&lt;sub&gt;v&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4.56</td>
<td>0.810</td>
<td>0.110</td>
<td>0.048</td>
<td></td>
<td>1040</td>
</tr>
<tr>
<td>II</td>
<td>4.55</td>
<td>0.810</td>
<td>0.110</td>
<td>0.052</td>
<td></td>
<td>2410</td>
</tr>
<tr>
<td>III</td>
<td>3.80</td>
<td>0.275</td>
<td>0.165</td>
<td>0.080</td>
<td></td>
<td>5910</td>
</tr>
<tr>
<td>IV</td>
<td>4.64</td>
<td>0.105</td>
<td>0.080</td>
<td>0.060</td>
<td></td>
<td>6915</td>
</tr>
<tr>
<td>F 1</td>
<td>4.02</td>
<td>0.100</td>
<td>0.065</td>
<td>0.035</td>
<td></td>
<td>13,600</td>
</tr>
<tr>
<td>F 5</td>
<td>4.16</td>
<td>0.100</td>
<td>0.065</td>
<td>0.035</td>
<td></td>
<td>11,600</td>
</tr>
<tr>
<td>F 9</td>
<td>4.08</td>
<td>0.100</td>
<td>0.065</td>
<td>0.035</td>
<td></td>
<td>5910</td>
</tr>
<tr>
<td>Isotactic</td>
<td>11.6</td>
<td>0.095</td>
<td>0.085</td>
<td>0.075</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syndiotactic</td>
<td>10.8</td>
<td>0.055</td>
<td>0.045</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H 5, H 6 (IV)</td>
<td>4.25</td>
<td>0.130</td>
<td>0.095</td>
<td>0.025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H 10 (F 7)</td>
<td>6.57</td>
<td>0.140</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H 11 (F 9)</td>
<td>6.00</td>
<td>0.200</td>
<td>0.075</td>
<td>0.040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H 12 (F 9)</td>
<td>4.50</td>
<td>0.200</td>
<td>0.070</td>
<td>0.040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H 13 (F 7)</td>
<td>6.30</td>
<td>0.565</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 1 (F 7)</td>
<td>6.50</td>
<td>0.115</td>
<td>0.070</td>
<td>0.045</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 2 (F 7)</td>
<td>6.80</td>
<td>0.115</td>
<td>0.070</td>
<td>0.045</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 3 (F 8)</td>
<td>10.70</td>
<td>0.115</td>
<td>0.070</td>
<td>0.045</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) At 300°C, for 40 mg Syndiotactic PMMA: $k_A = 5.20$  
$k_B = 0.020$
### TABLE 16

RATE CONSTANTS FOR THE FAST REACTION (k_A) AND THE SLOW REACTION (k_B) IN THE PYROLYSIS OF PMMA III AT VARIOUS TEMPERATURES *

<table>
<thead>
<tr>
<th>k measured at:</th>
<th>20%</th>
<th>40%</th>
<th>60%</th>
<th>80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>275°C</td>
<td>0.225</td>
<td>0.0015</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>300 (20 mg)</td>
<td>0.850</td>
<td>0.009</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>325 (40 mg)</td>
<td>0.750</td>
<td>0.008</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td>350</td>
<td>2.00</td>
<td>0.089</td>
<td>0.029</td>
<td>0.015</td>
</tr>
<tr>
<td>375</td>
<td>3.80</td>
<td>0.275</td>
<td>0.164</td>
<td>0.078</td>
</tr>
<tr>
<td>400</td>
<td>-</td>
<td>1.350</td>
<td>0.790</td>
<td>0.510</td>
</tr>
</tbody>
</table>

*Rate constants are given in units of Min⁻¹.*
An unusual kinetic equation also resulted from Gordon's derivation:

\[ \ln M = 2E_0f_0 \int \exp(-k_A t/4) - 1 \]  

(4)

The logarithmic mass decay implied by this equation is uncommon because \( \ln M \) instead of \( M \) decays exponentially with time. Thus, the process behaves like a first-order reaction in which the rate "constant", \( k_A \), itself decreases with time according to first order kinetics. In these latter equations, \( f \) = fraction of unsaturated chain-ends at time \( t \); \( f_0 \) = initial fraction of such ends; \( M \) = relative mass of polymer = \( n/n_0 \); \( E \) = initial kinetic chain length; \( P \) = polymer chain length. In deriving the latter equations, it was assumed that \( k_B = 0 \).

Therefore, it is significant in this case to speak of rate constants at specific percentages of degradation. Such rate constants, given in Tables 15 and 16, were obtained from the rate versus percentage degradation curves. To obtain the tangents at specific points, the tangentermometer described by Hochandel [96] was constructed and utilized.

1. The Rapid Reaction

Figure 68 shows an Arrhenius plot of the rate constant for the first reaction, \( k_A \) (at 20% degradation), versus reciprocal temperature for PMMA III from 275-400°C. This yields an activation energy for the rapid reaction of
FIG. 68
ARRHENIUS PLOT FOR PYROLYSIS OF PMMA III

TEMPERATURE °C

RATE CONSTANT (MINUTES⁻¹)

"Eₐ = 26 Kcal"

"Eₐ = 49.5 Kcal"

○ 20%  ● 40%  □ 60%  ▲ 80%
26 kcal/mole, in reasonable agreement with the values of 27 and 31 given in Table 3; also in agreement is $A_A \times 10^9$.

Table 15 presents the rate constants for the rapid reaction, $k_A$, for all samples degraded at 350°C; all these $k_A$ values could not be taken at the same percentage degradation, because in some cases the first reaction was almost completed by 20% degradation. Where this was the case, tangents were measured at 15%, or at 10%, if slopes at the higher percentages were not meaningful. The value of $k_A$ is approximately the same for all the peroxide-initiated samples, although the values for the fractions do seem to have slightly lower values. The $k_A$'s for the remaining three hydrogenated samples (H 10, H 11, H 13) and all three brominated samples (B 1, B 2, B 3) are significantly higher. The reason for this is not presently understood.

The $k_A$'s (at 10%) for both stereoregular samples are more than twice the values for the peroxide-initiated samples. Although an activation energy for the rapid reaction of about 10 kcal/mole can be calculated from $k_A$ at 300 and 350°C for the syndiotactic sample, further studies are necessary to obtain an exact value and to determine to what reaction this activation energy refers.

2. The Slow Reaction

Figure 68 presents an Arrhenius plot of the rate constants for the slow reaction, $k_B$, versus reciprocal temperature for PMMA III ($M_v = 591,000$) from 300-400°C. Using the Hochanadel tangentiometer [96], $k_B$ was taken as the
tangent to the rate versus percentage degradation curves at three points: 40%, 60%, and 80%. It should be noted that the rate constant thus measured decreases with increasing degradation.

The Arrhenius plot gives an activation energy for the slow reaction ($E_B$) of 49.5 kcal/mole; the activation energy is independent of percentage degradation over the range of 40 to 80%. This value is in reasonable agreement with the values of Brockhaus and Jenckel: $E_B = 44$ kcal/mole ($M_v = 37,000$) and $E_B = 49$ kcal/mole ($M_v = 426,000$).

The pre-exponential factor decreases with extent of degradation, as follows:

\[
\begin{align*}
40\% &: A_B^{40} = 4.9 \times 10^{16} \\
60\% &: A_B^{60} = 3.0 \times 10^{16} \\
80\% &: A_B^{80} = 1.4 \times 10^{16}
\end{align*}
\]

It has been stated $\text{[91, 17]}$ that for the slow reaction, the rate increases with molecular weight and then becomes constant at higher molecular weights. The results of this study do not confirm this postulate (see Table 17 for comparison of results).

Table 15 gives the rate constants for the slow reaction, $k_B$, for all samples degraded at 350°C; $k_B$ is approximately the same for all the peroxide-initiated samples, and the isotactic sample. The one value that appears
TABLE 17

COMPARISON OF RATE CONSTANTS FOR THE SLOW REACTION, $k_B$ ($\text{min}^{-1}$), BROCKHAUS AND JENCKEL [17] AND THIS STUDY.

<table>
<thead>
<tr>
<th>$P_y$</th>
<th>$k_B$ at 300°C</th>
<th>$k_B$ at 350°C</th>
<th>$P_y$</th>
<th>$k_B$* at 300°C</th>
<th>$k_B$* at 350°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4260</td>
<td>0.00143</td>
<td>0.0455</td>
<td>13,600</td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>1820</td>
<td>0.00138</td>
<td>-</td>
<td>6915</td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>960</td>
<td>0.00019</td>
<td>-</td>
<td>6760</td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>620</td>
<td>0.0006</td>
<td>-</td>
<td>5910</td>
<td>0.007</td>
<td>0.17</td>
</tr>
<tr>
<td>550</td>
<td>0.0006</td>
<td>-</td>
<td>2410</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>390</td>
<td>0.0004</td>
<td>0.0077</td>
<td>1115</td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1040</td>
<td></td>
<td>0.32</td>
</tr>
</tbody>
</table>

*Average of $k_B$ at 40, 60, and 80% in Tables 15 and 16
significantly different from the rest is \( k_p \) for syndiotactic PMMA, which is lower than the other \( k_p \)'s; the reason for this is not readily apparent. From \( k_p \) for the syndiotactic kcal/mole can be calculated; this is a low value, especially if initiation was a random process, therefore, further study is indicated.

3. Retardation of Rate

Brookhaus and Jenckel \([17\,7]\) showed that the degradation rate is retarded by increased pressure of monomer in the system. Slight rate retardation was observed in this work when the amount of sample was increased from 20 mg to 40 mg (see Figure 37). Whether this effect is due only to a diffusion process or also to a chemical reaction remains to be seen. In either case, no quantitative correlation of pressure with retardation appears presently possible.

4. Total Moles of Products

In agreement with the observation of Wall and co-workers \([97\,7]\) it has been noted that the total moles of product obtained from any given sample of PMMA is greater than the number calculated from 100% decomposition to monomer. Table 18 gives the average final moles of product at the indicated times of pyrolysis.

This is probably the combined result of the pyrolysis of small amounts of residual reagents in the polymer, end-group fragments and monomer breakdown products.
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Isotactic</th>
<th>Syndiotactic</th>
</tr>
</thead>
<tbody>
<tr>
<td>275°C</td>
<td>9.4-20 hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>14.015 hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>21.8-18 hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>22.4-6 hr</td>
<td>20.0-10 hr</td>
<td>20.1-7 hr</td>
<td>22.7-5 hr</td>
<td>20.1-5 hr</td>
<td>22.5-4 hr</td>
<td>21.1-7 hr</td>
</tr>
<tr>
<td>375</td>
<td></td>
<td></td>
<td>22.6-1 hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21.4-10 min</td>
<td></td>
</tr>
</tbody>
</table>
1. Model Compounds

Hydrogenation of the monomer was readily achieved by Adams Catalyst (reduced platinum oxide) or 10% palladium on charcoal, the former giving quantitative reduction in glacial acetic acid or chloroform. In the acid solvent, reduction was done in half the time required in chloroform. On the other hand, palladium on charcoal gave only 85% reduction in either aqueous methanol or chloroform and the time required was fifteen to twenty-five times longer. In accord with the results of Csuros, no polymer was formed with continual stirring and hydrogenation over the palladium catalyst. It is unfortunate that the tiglic and methyl esters were not available for hydrogenation, since these -substituted compounds probably provide better models for the sterically-hindered unsaturated chain-end.

2. Hydrogenation

Besides the difficulties in selecting a good catalyst, the problem of the best solvent is emphasized by the reaction encountered between the chlorinated solvent and the noble metal catalyst, liberating HCl. It is likely that a "good" solvent (in the polymer chemistry sense) serves better for hydrogenation of a polymer chain-end since the molecule is not coiled into a spherical shape and presents better opportunity for contact between a chain-end and an
active catalyst site.

To determine the success of attempts of hydrogenating the polymer, the most readily available method was degradation in the apparatus previously described. If the hypothesis that the unsaturated chain-end is the weak link at which degradation is initiated is correct, then removing this weak link by hydrogenation should provide a more heat-stable polymer. The resulting degradation curve would then differ from that of an unhydrogenated sample. In an analogous situation, hydrogenation of the residual double bonds in low-density polyethylene results in a polymer that is more stable to heat [99].

A brief consideration can be given to additional methods that might be used to determine whether hydrogenation had actually taken place.

1) Brockhaus and Jenckel [17] determined the number of double bonds in PMMA by oxidation with potassium permanganate. The slow reaction was followed by measuring the color change with a colorimeter; however, side reactions and incomplete oxidation complicate the accurate quantitative determination of double bonds.

2) Hydrogen uptake measurements are not possible for such polymer without an extremely sensitive manometer or great amounts of low molecular weight polymer. Our lowest molecular weight fraction had a viscosity-average molecular weight of about 100,000; for a monodisperse sample of such molecular weight, 0.1 gram can take up 0.003 milliliter of
Hydrogen if 50% of the molecules have unsaturated ends!

iii) Infra-red spectra of polyethylene show that olefinic absorption at 910 cm$^{-1}$ disappears when the polymer is hydrogenated. No assignment for such unsaturation in polymethylmethacrylate has been published, and this study did not show any difference in infra-red spectra of untreated or treated polymethylmethacrylate, probably because the concentration of the unsaturated group is so small that a high-resolution spectrophotometer is needed to detect the small absorption-band differences.

3. Bromination

Whitby attempted to determine the molecular weight of polystyrene by determining the number of double bonds present using bromine. The presence of double bonds was ascertained, but the analysis was too inaccurate for molecular weight determinations. Rate of bromine uptake decreased with increasing molecular weight of the polymer, so the double bonds become less reactive the higher the degree of polymerization. Some limited success might be expected by applying this approach to polymethylmethacrylate, and the brominations presented herein are a first step in that direction. The molecular weight of the fractions used in our study may well have been so high as to make the bromination rate prohibitively small.
4. Degradation of Treated PMMA

a) Hydrogenated PMMA

In every case of the polymer exposed to hydrogen, its degradation did not exhibit marked deviation from that of the unhydrogenated polymer. Table 14 shows that the percentage of rapidly-degrading polymer was slightly decreased by hydrogenation treatment in all cases, although complete disappearance of the rapid reaction was never achieved. In addition, Table 15 indicates that the rate of the rapid reaction usually increased somewhat; as expected, the rate of the slow reaction did not change.

In both cases where most stringent hydrogenation conditions were used (H 12 and H 13), some hydrolysis of the pendant ester groups apparently occurred. An unexpected result is that hydrolysis still seemingly took place even when the remaining 0.5% water in the glacial acetic acid had been taken up by acetic anhydride.

The fact that complete hydrogenation of the polymer apparently never took place even under the most severe conditions used might even lead to doubts of the existence of these terminal double bonds, at least in the polymer samples used in this study. However, terminal unsaturation still remains the best-supported explanation for all results on PMMA degradation reactions.

b) Brominated PMMA

The fact that the degradation curves for PMMA exposed
to bromination are not greatly different from the untreated low molecular weight samples does not rule out the possibility that some bromination occurred. Dehalogenation or dehydro-halogenation may have occurred readily. Gas chromatographic analysis of the volatile degradation products of these polymers indicated only a trace of carbon dioxide and possibly oxygen, in addition to monomer. Chromatographic analysis was performed on a Perkin-Elmer Vapor Fractometer, Model 154, with a silica gel column at 80°C.

Table 14 indicates that the percentage of rapidly-degrading polymer was decreased significantly in Experiments B 2 and B 3, while Experiment B 1 was not similarly successful. In addition, Table 15 shows the rate constant for the rapid reaction, $k_A$, increased considerably after bromination; unexpectedly, the rate constant for the slow reaction, $k_B$, even increased slightly.

Summary and Conclusions

In summary, it is seen that a useful new technique has been successfully developed and tested for polymer degradation studies. The apparatus consists of an automatic recording quartz spoon gauge. For studies of PMMA pyrolysis, a polymer film was deposited on the inside walls of the spoon gauge, and after evacuating and sealing off the gauge it was immersed in a hot liquid metal bath in such a way that the deflection of the gauge pointer was measured by a Statham transducer, whose electrical output
signal was continuously recorded. Thus, the pressure of the volatile products of PMMA degradation was rapidly recorded; temperature was measured by a calibrated thermocouple adjacent to the spoon gauge in the metal heating medium.

Significant advantages of the system are:

1) Very accurate measurements of volatile polymer degradation products are rapidly and continuously recorded.

ii) Only small quantities of polymers are needed, i.e., 40 to 20 mg of PMMA, or even less.

iii) Temperature equilibrium is achieved in less than 30 seconds, i.e., one-tenth the time required by previous investigators.

Useful data for PMMA degradation were obtained up to 400°C, which is a temperature about 100°C higher than that attained by previous workers not neglecting the initial parts of the reaction. The experimental results are readily converted by the ideal gas equation into moles of gas produced as a function of time. The derivative of the curve, i.e., the rate of degradation, was plotted against percentage degradation; the resulting rate versus conversion plot indicated that less than 50% of high molecular weight PMMA degrades rapidly.

The results were compared and contrasted with those of previous investigators, and the effect of short kinetic chain length on degradation of the long polymer chains was considered. Calculated activation energies for the rapid
and slow degradation reactions are in reasonable agreement with published data.

A study of the reactivity of the postulated unsaturated PMMA chain-ends showed that they are not readily hydrogenated, even under moderately high pressures of hydrogen. The unsaturated chain-ends were found to be slightly more susceptible to bromination than to hydrogenation.
APPENDIX

Jellinek [1] has derived the kinetic equations for various types of degradation. Some recent corrections should be observed [102, 103]. The equations applying to PMMA degradation are given on the following page.

Derivation of expressions to describe degradation is a lengthy process involving a good deal of mathematical and chemical intuition, and there are many expressions for various types of degradation. The expressions given here represent very well many of the experimental results for PMMA degradation.

Other approaches that have been used are the statistical [24] and the semi-empirical [23]; the full utility of these is yet to be realized.
1) Chain-End Initiation

\[ \frac{dM_1}{dt} = k_{id} \cdot m_o \]

\[ E > P_o : \]

\[ \frac{dM_1}{dt} = k_{id} \cdot E \cdot \frac{m_o}{P_o} \]

First Order Termination

Second Order Termination

\[ \frac{dM_1}{dt} = k_{dd} \cdot \frac{m_o}{P_o} \left( \frac{k_{id}}{k_{td}} \right)^n \]

ii) Random Initiation

\[ E > P_o : \]

\[ \frac{dM_1}{dt} = k_{id} \cdot (P_o - 1) \cdot m_o \]

\[ E < P_o : \] First Order Termination

\[ \frac{dM_1}{dt} = k_{id} \cdot E \cdot m_o \cdot \left( \frac{P_o - 1}{P_o} \right)^n k_{id} \cdot E \cdot m_o \]

Second Order Termination

\[ \frac{dM_1}{dt} = k_{dd} \cdot E \cdot m_o \cdot \frac{k_{id}}{k_{td}} \]

N. B. -- \[ E = \frac{k_{dd}}{k_{td}} \]

(for first order termination).

\[ M = \text{free monomer concentration.} \]

\[ m = \Sigma M \text{ in polymer sample} = \Sigma n_p \cdot P \]
LITERATURE CITED


(22) A. M. Kotliar, J. Polymer Sci., 62, 598 (1962).
(35) F. A. Bovey, J. Polymer Sci., 46, 59 (1960).


(52) S. L. Madorsky, J. Polymer Sci., 11, 491 (1953).


(84) Ibid., Chapter 5.


(86) Ibid., p. 629.


(99) K. M. Sinnott, Private communication.


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