The challenge of space-age technology demands a concerted research effort to better understand and successfully design new polymeric materials that can perform reliably under the most extreme conditions. Impressive advances have already been made on such biological materials as proteins, nucleic acids, and other bio-polymers on which life itself depends. In this paper we review some important areas of polymer research and describe APL study of the thermal stability of a new, experimental, dielectric material. By means of thermogravimetry, thermal degradation profiles in air and vacuum were obtained, and from these were calculated rates and activation energies. By such means we can assess the potentialities of polymeric materials.

Some Fundamental Concepts of Polymer Chemistry

A polymer is composed of large molecules that are formed by the repetitive combination of small structural units (monomers) and held together in long chains by covalent bonds. The number of such repeating units in a chain is called the degree of polymerization. The molecular weight of a polymer is the product of the molecular weight of the individual repeating units and the degree of polymerization.

There are essentially three types of polymers:
POLYMERIC MATERIALS
S. D. Bruck

linear polymers, in which the structural units are connected in a linear sequence to form long chains; branched polymers, in which the structural units are hooked together to form branches; and cross-linked polymers in which the polymer chains are interlinked to form either three-dimensional networks or two-dimensional ladder-like structures. Cross-linked polymers may be synthesized directly or may be produced by post-modification reactions caused by radiation or chemical treatment. Vulcanized rubber is a practical example of a cross-linked polymer in which the polysulfide cross-links are introduced by chemical treatment of an initially linear structure.

These three structural types of polymers may be classified into two broad classes: condensation and addition polymers. In the former the repeating unit of the polymer chain lacks certain atoms that are present in the original monomers, as, for example, if water is eliminated during the reaction:

\[
\begin{align*}
\text{HO-C-(R)_n-C-OH} + \text{H}_2\text{N-(R')_y-NH}_2 & \rightarrow \\
\left(\text{C-(R)_n-C-NH-(R')_y-NH}\right)_n + \text{nH}_2\text{O}.
\end{align*}
\]

In addition polymerization no loss of a small molecule takes place. For example, vinyl compounds polymerize as follows:

\[
\begin{align*}
n \text{-CH}_2\text{-CH} & \rightarrow \left(\text{-CH}_2\text{-CH-CH}_2\text{-CH}_2\text{-CH}\right)_n.
\end{align*}
\]

Historical Review

As early as 1861 Thomas Graham recognized that the rate of diffusion of certain materials in solution is slow and that molecules of these substances are unable to migrate through semipermeable membranes. During the early years of this century, chemists, especially Wolfgang Oswald, advanced the concept of colloids. Colloid particles were visualized as clusters of small molecules held together by intermolecular "secondary valence" forces. From this there gradually grew the concept of a polymer molecule as being composed of small structural units held together in long chains by covalent bonds. The macromolecular theory of polymeric materials is mainly due to Staudinger's work, beginning in 1920. For his contributions he was awarded a Nobel prize in 1953. Although the oldest commercial synthetic plastic was Baekeland's "Bakelite" (a phenolformaldehyde polymer), followed by polystyrene in Germany around 1930, the real rise of synthetic polymeric materials did not begin until about ten years later. In 1929 Wallace Hume Carothers began a series of chemical investigations aimed at the synthesis of polymers. In the late 1930's Carothers' efforts and leadership led to the development of many polyamides and polyesters, of which the nylon are the best known popular examples. Following Carothers' initial work, W. Kuhn in Germany did theoretical work in which the first application of statistical methods to the molecular weight distribution of de-
graded cellulose was elaborated. In 1934 E. Guth, H. Mark, and W. Kuhn studied the configurations of long polymer chains. These theoretical efforts lead the way to the solution of important problems such as rubber elasticity and high viscosity of polymers.

**Thermal Stability of Polymers**

The thermal degradation of addition polymers depends largely on free-radical-initiated chain reactions. Condensation polymers, on the other hand, may be influenced by traces of moisture and acidic catalysts present in the material, which promote hydrolytic breakdown, thus:

\[
\begin{align*}
\text{O} & \quad \quad \text{O} \\
\text{R} - \text{C} &= \text{H}_2 \text{N} - \text{R'} + \text{H}_2 \text{O} \\
\rightarrow & \quad \quad \rightarrow -\text{R} - \text{C} - \text{OH} + \text{H}_2 \text{N} - \text{R}'.
\end{align*}
\]

According to Simha and Wall, free-radical-initiated chain reactions involve the elementary steps of initiation, depropagation, intermolecular or intramolecular transfer, and termination. The initiation step may be brought about by thermal, radiative, or chemical means, and this primary attack may occur at random, or at weak points in the polymer chain. Unlike gas-phase reactions where depropagation is favored, the solid-phase degradation of polymers seems to proceed by intermolecular transfer with the production of little or no monomer (starting material).

The degradation of polymers is governed by the dissociation energies of the bonds in the chain. In gas-phase degradation the free radicals that are formed as the result of bond rupture are able to combine freely (activation energy of this recombination being near zero); in the condensed phase, as in solid polymers, the free radicals must overcome an additional energy barrier due to the viscous medium in which they find themselves. This is the so-called "cage effect" and is responsible for the higher activation energies needed for bond rupture in polymers than are usually observed for gas-phase reactions.

During the degradation of polymeric materials, two processes can take place: scission (rupture) of the bonds and cross-linking. Polymers in which the "backbone" undergoes mainly scission usually vaporize completely if heated (pyrolyzed) for prolonged periods. As a consequence the molecular weight of the material gradually decreases and its strength becomes zero. This is not so in the case of those polymers in which the formation of cross-links is promoted by pyrolysis. These materials become stabilized because of the formation of a rigid, insoluble network that exhibits increased toughness and does not melt. Both scission and cross-linking are free-radical processes and are initiated by the abstraction of hydrogen atoms from the polymer chain. The incorporation of aromatic rings into the polymer chain, however, tends to increase the resistance of the system to free-radical attack because of the much higher energy required for the removal of a hydrogen atom from a benzene ring.

The thermal stability of a polymer can also be increased by the complete or partial replacement of the hydrogen atoms by fluorine atoms as in Teflon and Viton. Another approach to increased thermal stability is the synthesis of polymers composed of such inorganic elements as titanium, aluminum, phosphorous, and boron. For example, the polymer polysiloxane,

\[
\begin{align*}
\left( \text{R} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{O} \right)_n,
\end{align*}
\]

is composed of silicon-oxygen links, whereas the polymer,

\[
\begin{align*}
\left( \text{R} - \text{Si} - \text{O} - \text{Al} - \text{O} - \text{Si} - \text{O} - \text{Al} - \text{O} \right)_n,
\end{align*}
\]

has additional aluminum atoms in the chain.

Thermally stable boron and silicon containing polymers with carborane (C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) groups having the following structure have recently been reported:

\[
\begin{align*}
\left( \text{C}_3 \text{H}_7 - \text{C}_3 \text{H}_7 - \text{Si} - \text{O} - \text{Si} - \text{O} \right)_n
\end{align*}
\]

In the above polymer the spherical nucleus of ten boron atoms is bridged by two carbon atoms. These

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carborane-silicon polymers are stable above 400°C and are fusible and soluble in organic solvents, which are important practical considerations in assessing their ultimate industrial usefulness.

Lately it has been recognized that linear and random network polymers do not exhaust the range of possibilities of molecular architecture and that non-random network polymers can be made, which exhibit superior thermal stability.

Among the naturally occurring substances, probably the best known ordered network is asbestos:

Among organic polymers that have at least some ordering in a double-chain arrangement is "Black Orlon," obtained by catalytic heating of the polyacrylonitrile fiber, "Orlon,"* in the presence of a controlled quantity of oxygen. A possible mechanism of this reaction may be the following:

In addition to its high thermal stability (it may be heated with an oxygen torch without decomposition), the above "pyro-polymer" exhibits high electric conductivity. This phenomenon will be discussed below.

At least two other important discoveries have very recently been made concerning ordered polymer systems. In one group of inorganic coordination polymers reported by Block et al.,4 beryllium, chromium, zinc, and other metal atoms are linked together by pairs of diphenylphosphinate groups, forming a double-chain metallophosphinate polymer:

In the case of the beryllium compound, no loss of weight was observed when it was heated up to 530°C. Another example of a synthetic, ordered, network polymer having high thermal stability has recently been reported by Brown et al.5

In this diagram the atoms of oxygen connected by heavy bonds are above the surface on which the network is visualized, whereas the broken bonds are below the surface. These polymers contain phenylsilsequioxane units joined together in such a way as to give a ladder-like, stereo-regular (ordered) linear network structure. It has been reported that these materials could withstand intimate contact with a white-hot wire without degradation.

So-called "semi-ordered" network polymers have also been synthesized recently.6 In one case a partly oriented linear polyamide fiber was cross-linked with formaldehyde utilizing specific sites (amide nitrogens) in the amorphous regions of the polymer. In a related study, methylene sulfide and methylene disulfide cross-links were introduced at specific sites of the partially oriented polymer. Among the novel properties of these molecules

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were unexpected helical coiling and increased thermal and ultraviolet stabilities.

**Polymers with Conducting, Semiconducting, and Magnetic Properties**

An area of substantial importance in research deals with the synthesis and physico-chemical characterization of plastic materials having conducting, semiconducting, and magnetic properties. Interestingly, in many cases such materials are also characterized by high thermal stability.

The guiding force behind these efforts is the proper understanding of the electronic structure of polymer molecules and the application of quantum mechanics to the synthesis of new materials. A simplified description of some of these considerations may help to explain the problem.

If two \( p \)-orbitals overlap side by side, as seen in the illustration below, the resulting orbital is called a \( \pi \)-orbital. In conjugated (unsaturated) polymers, the carbon-carbon atoms are joined together by so-called \( \delta \)-bonds that result from the overlapping of two \( s \)-orbitals, an \( s \) and a \( p \)-orbital, or two \( p \)-orbitals (end-to-end). The \( \pi \)-orbitals are formed by the interaction of the remaining unpaired electrons, which are usually indicated by chemists as double bonds:

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} \\
\text{OVERLAP} & \quad \pi\text{-ORTBITAL} & \quad \delta\text{-BOND} & \quad \beta\text{-ORTBITAL} & \quad PATH\ OF\ MOBILE\ ELECTRONS
\end{align*}
\]

In a suitably conjugated double-bonded structure, an electronic disturbance at one of its ends may result in a redistribution of charge throughout the entire system by the action of the mobile \( \pi \)-electrons. Graphically, this may be represented as follows:

It is now possible, to a limited extent, to synthesize organic molecules or to pyrolyze (destructively heat) certain others so as to transform them into structures in which electronic conduction is possible. We have already stated that "Black Orlon" is an example of the latter type. Another is the pyrolysis product of divinylbenzene, which also exhibits semiconducting properties. A somewhat different approach to the synthesis of conducting and semiconducting polymers (as well as to the synthesis of polymers having high thermal stability) is the preparation of so-called metal-chelate polymers. For example, a conjugated polymer based on the blue pigment, phthalocyanine, and 1,2,4,5-tetra-cyanobenzene was found to exhibit conducting properties.

The synthesis of polymers having magnetic properties may also be of considerable importance. Paramagnetism is associated with the presence of either unpaired electrons or an incompletely filled electronic level. It is common to many of the transition and inner transition metals, to molecules containing an even number of electrons but unpaired electronic spin, and to many complex ions. It should be possible to prepare new polymeric materials in which either the polymer "backbone," or chains, or cross-links incorporate metals with paramagnetic characteristics.

**Biological Polymers**

Among naturally occurring macromolecules on which life processes depend are proteins, enzymes, hormones, and nucleic acids. Proteins are natural polymers of high molecular weight, consisting mainly of chains of \( \alpha \)-amino acids connected by peptide linkages. The peptide bonds are similar to those of synthetic polyamides formed by condensation polymerization:

\[
\begin{align*}
\text{NH}_2 & \quad \text{O} \\
\text{R}_1-\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{R}_2 \\
\text{H}& \quad \text{H} & \quad \text{O} \\
\text{Amino Acid (A)} & \quad \text{Amino Acid (B)} & \quad \text{H}_2\text{O} & \quad \text{R}_1-\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{R}_2
\end{align*}
\]

\(\uparrow\) Orbitals are sub-levels in which an electron may be located within the electron cloud surrounding the nucleus. The sub-levels (or orbitals) are identified as \( s \) (sharp), \( p \) (principal), \( d \) (diffused), or \( f \) (fundamental).


A great contribution toward our understanding of the structure of proteins is due to Pauling and Corey who, in 1951, determined on the basis of X-ray diffraction evidence that synthetic polypeptides made from \( \alpha \)-amino acid have a coiled, helical structure. The name \( \alpha \)-helix was applied to such systems. Hair, fingernails, and connective tissue (collagen) all have helical protein structures.

Two of the most thoroughly investigated proteins are hemoglobin and myoglobin, and both occur in association with a non-protein entity called the heme group. This heme group consists of a porphyrin ring having an iron atom in the middle to which the protein (globin) is attached in the following rather specific way:

\[
\begin{align*}
\text{R} & \quad \text{R} \\
\text{Fe}^+ & \quad \text{N} \\
\text{R} & \quad \text{R} \\
\text{N} & \quad \text{Fe}^+ \\
\text{R} & \quad \text{R}
\end{align*}
\]

The iron atom holds an oxygen molecule in a loose combination so that it can act as an oxygen carrier in the blood. Hemoglobin actually contains four heme groups, whereas myoglobin (which is responsible for the respiration of the muscle cells) contains only one. The structure of hemoglobin is not yet completely known although the X-ray diffraction work of M. F. Perutz in England contributed especially decisive information on this blood pigment. The structure of the related pigment, myoglobin, has recently been elucidated by Kendrew in England, for which he received a Nobel prize in 1961.

In both hemoglobin and myoglobin, the iron is in the ferrous (\( \text{Fe}^{2+} \)) state because the ferric (\( \text{Fe}^{3+} \)) iron cannot combine with molecular oxygen. In order to understand better the mode of operation of these materials and to elucidate the way in which the protein portion is attached to the heme group, synthetic models have been prepared.\(^9,10\) These synthetic models were remarkably able to combine with molecular oxygen (without the iron atom being oxidized to the ferric state) and supported the theory that the imidazole group of the protein might be involved in the heme-protein combination.

Another class of proteins, the enzymes, are specialized proteins designed to catalyze biological processes through the lowering of the activation energies of the reactions. The speeds of most enzymatic reactions are extremely fast (up to \( 10^{-12} \) sec) and could not be measured with satisfactory precision until, very recently, the so-called relaxation technique became available.\(^11,12\) The basic idea of this technique is that when a chemical reaction at equilibrium is perturbed for an extremely brief period, as by a pulsed change of temperature or pressure, the time-dependent behavior of the species near the equilibrium point can be characterized by a spectrum of relaxation times that are, in fact, reciprocal, first-order, rate constants.

Among proteins with hormone-type activity is insulin. The structure of this protein is now completely elucidated as the result of the work of Sanger in England. It has a molecular weight of 6000 and is composed of two polypeptide chains containing 21 and 30 amino acid units, respectively. The two chains are joined together by disulfide cross-links. A simplified structure may be written as follows:

\[
\begin{align*}
\text{Amino Acid No. 7} & \quad \text{Amino Acid No. 20} \\
\text{Chain 1} & \quad \text{Chain 2} \\
\text{CH}_2 & \quad \text{CH}_2 \\
S & \quad S \\
S & \quad S \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]

Significantly, if the disulfide cross-links are broken, insulin loses its biological activity.


Finally we come to two of the most exciting biological polymers, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Recent experiments with viruses and bacteria indicate that DNA and RNA are the carriers of genetic information. Nucleic acids are found in the nucleus of the cell and in the cytoplasm; they are basically sugar molecules (ribose and deoxyribose) polymerized by phosphate links. The sugar portion has substituent groups which are nitrogen bases, called purines and pyrimidines. In DNA the sugar component is deoxyribose, whereas in RNA it is ribose. Both DNA and RNA form double-stranded helices in which the chains run in opposite directions and are interconnected by base pairs.\textsuperscript{13-15} In order that DNA and RNA may carry the genetic information, a code must be used. This involves, in principle, the proper arrangement of the four bases of the nucleic acid molecule in such a way as to direct the synthesis of the protein by a highly specific arrangement of the latter's 20-odd amino-acid structural units. Although both DNA and RNA have double-stranded helical structures, they differ considerably from each other.\textsuperscript{16} The former has recently been implicated in the aging process.\textsuperscript{17}

\textbf{Investigations of the Thermal Stability of Polymers}

There are two well-known techniques for the study of the thermal stability of polymers: \textit{thermogravimetric analysis} (TGA), in which loss or gain of weight of a sample is studied as a function of temperature and time; and \textit{differential thermal analysis} (DTA), in which the various transitions and reactions that a polymer undergoes in controlled heating are studied. In brief, DTA consists of heating the sample, together with an inert material, in a furnace at a constant rate of heating, and recording the difference in temperature between


the sample and the inert material. If there is no reaction or transition, the temperature of the sample and the inert material will be the same. Since melting, decomposition, and dehydration are usually endothermic in nature, the temperature of the sample will lag behind that of the inert material. A typical thermograph may be illustrated as follows:

![Thermograph Illustration]

The first endotherm (A) represents the crystalline melting point of the polymer, the second endotherm (B) the decomposition point, and the flat (horizontal) portion of the curve between the two endotherms is indicative of the melt-stability of the material. By comparing the areas and locations of the endotherms (or exotherms) of various polymers, information can be derived about their relative thermal stability. This technique is also useful for the determination of the degree of cure (cross-linking) of various electrical encapsulating resins. The proper degree of cross-linking in these polymers is of great importance in insuring their proper mechanical strengths. This is important for reliable functioning of electrical components encapsulated in them, which subsequently may be exposed to extreme environments. Other applications of DTA include the determination of the heats of polymerization, glass-transition temperatures, and studying radiation effects.

Recently inaugurated research efforts at APL are aimed at study of the thermal stability of polymers. Information that may result from these and related investigations includes the determination of the rates of degradation in various environments, calculation of the activation energies of degradation, identification of the degradation products, and consequent formulation of a mechanism for the degradation. From these data, predictions may be made as to the useful life of the material in thermal and radiation environments.

The polymer chosen for our investigations was du Pont's promising new experimental "H"-film. This is chemically a poly(2,2'-bipyridyl-5,5'-dicarboxylic acid)imide, which is a condensation product of an aromatic dianhydride and an aromatic diamine. It has been reported to have exciting possibilities as an insulating material because of its excellent mechanical and electrical properties in the temperature range of $-40^\circ C$ to $+300^\circ C$.

The preparation of these polymers reportedly involves a two-step process, yielding a material with the following general structure:

\[ \text{Polymer Structure} \]

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where $X = -O-, \ SO_2, \ CH_2-, \ C=O, \ S$, or other groups.

**Instrumentation**—The thermogravimetric studies were carried out with a Cahn RG electrobalance, the operation of which is based on the null-balance principle (Fig. 1). The capacity of this instrument (sample plus container) is 0 to 1000 mg, with an ultimate precision of $2 \times 10^{-7}$ gm. In the present experiments, as the weight of the sample changes, the balance beam tends to deflect momentarily, thereby changing the amount of light reaching the phototube. The current of the phototube is amplified and passed through a coil mounted on the beam in a magnetic field. This action exerts a force, which restores the beam to its original position within $0.05 \text{ sec.}$

Because of this relatively constant position of the sample with respect to a thermocouple positioned below it, good temperature control is possible.

The balance mechanism was mounted within a special Pyrex vacuum housing equipped with O-ring joints for the connection of hangdown tubes. The glass housing was sealed to a vacuum system. For experiments carried out below $500^\circ \text{C}$, the hangdown tube was made of Pyrex glass, whereas for higher temperatures Vycor or quartz was used. A thermocouple was inserted into the hangdown tube so that its tip was immediately below the sample.

**Results**—The first series of thermogravimetric experiments was carried out in air at atmospheric pressure. Figure 2 illustrates the volatilization of the polymer as a function of time for various
temperatures. Zero time signifies the time at which thermal equilibrium was attained. As indicated, practically complete volatilization takes place in the temperature range of 468° to 485°C after 5 to 8 hr of heating. At 435°C the volatilization is much slower, and below 400°C the polymer shows practically no weight loss. In general, to obtain reliable data on rates from thermogravimetric experiments, one must choose conditions under which the rates of degradation are neither impracticably slow nor so fast that the polymer suffers excessive degradation during the heating-up period.

In Fig. 3 the rates of volatilization are plotted versus percent of volatilization. These rates were calculated from the volatilization-time curves with the aid of an electronic computer. The data in Fig. 3 indicate that distinct maxima were reached between approximately 55% and 65% volatilization.

Usually the activation energies for the degradation of polymers can be obtained from Arrhenius plots in which the extrapolated initial rates or maximum rates, or the rate constants (if known) of the reaction are plotted against the reciprocal of the absolute temperatures. Although some polymers like tetrafluoroethylene ("Teflon") follow a simple, first-order reaction, many others exhibit very complex rate patterns in which the rate constants cannot be readily obtained.

In view of the particular shapes of the curves in Fig. 3 (lack of apparent straight-line portions that can be extrapolated to 0% volatilization), the activation energy was calculated from maximum rates. According to the well-known Arrhenius equation, \( k = S e^{-(E/RT)} \), where \( k \) is the rate constant, \( S \) is the frequency factor, \( E \) is the activation energy, \( R \) is the gas constant, and \( T \) is the absolute temperature. By plotting the logarithm of maximum rates (here expressed in percent of the sample volatilized per minute) versus the reciprocal of the absolute temperature, a straight-line relationship was obtained, as illustrated in Fig. 4. The slope of this line gave an activation energy of 32 kcal/mole for the thermal degradation of "H"-film in air under laboratory atmospheric conditions.

The second series of experiments was conducted in vacuum (= 10^{-3} mm of Hg). Figure 5 shows the percent of volatilization as a function of time at various temperatures.

Figure 6 illustrates some of the data in which the rates are plotted versus percent of volatilization. As may be observed, there was very little weight loss beyond approximately 40% volatilization, in contrast to the thermal degradation in air where practically 100% volatilization was observed. Thermal degradation in vacuum leaves a brittle, dark-gray, carbonized residue that retains the general shape of the original sample. The infrared absorption spectrum of the original "H"-film.

![Fig. 6](image) Rates of thermal degradation of “H”-film polymer in vacuum at various temperatures.

![Fig. 7](image) Infrared spectra of undegraded “H”-film polymer (A), and carbonized residue (B).
film, and that of the carbonized residue remaining after vacuum pyrolysis at 639°C for 20 hr, are illustrated in Fig. 7. The infrared spectrum of the carbonized residue indicates practically no absorption bands as compared to the undegraded sample, thus confirming the carbonization process.

In order to calculate the activation energy, an Arrhenius type of curve was constructed by plotting the logarithm of the "apparent initial rates" versus the reciprocal of the absolute temperatures at which the degradations were carried out (Fig. 8). The "apparent initial rates" were obtained by extrapolating the straight-line parts of the rate curves to 0% volatilization. These "apparent initial rates" indicate what the actual initial rates would have been for the bulk of the polymer without the interference of complicating side reactions such as may arise from the degradation of impurities or low-molecular-weight species. These may well follow a separate mechanism of degradation from the bulk of the polymer itself. The activation energy for the degradation of the polymer in vacuum is 74 kcal/mole.

Discussion—The essentially total volatilization of the polymer during thermal degradation in air in contrast to its behavior in vacuum is most likely due to oxidative cleavage occurring at the imide bonds. The low activation energy calculated for degradation in air indicates such a process.

The thermal degradation of "H"-film in vacuum is somewhat similar to that of polytrivinylbenzene studied by Madorsky and Straus and by Winslow and associates. The rate-versus-volatilization curves (Fig. 6) strongly resemble those of polytrivinylbenzene in the early appearance of maxima, followed by straight-line (first-order) portions, and in the formation of carbonized residues amounting to approximately 43% to 50% of the original sample. It is important to note, however, that polytrivinylbenzene is highly cross-linked (unlike poly-pyromellitimide) since the monomer has three functional groups. In general, highly cross-linked polymers are, upon heating, converted to carbonized structures, whereas polymers in which the backbone undergoes primarily scission reactions tend to vaporize completely without leaving any appreciable residue.

The structure of the present polypyrromellitimide sample indicates stiff benzene rings that hinder chain mobility and rotation and hence exert a stabilizing influence, similar to cross-links. As a result, a carbonized residue forms upon vacuum pyrolysis. The fact that "H"-film has no melting point and no glass-transition temperature below 500°C substantiates this argument.

The exact mechanism of the degradation process in vacuum appears to be complicated by side reactions. Because of the insolubility of this material in any known solvent, fractionation and further purification were not carried out. Consequently one cannot make a conclusive statement as to whether the process follows a random, free-radical-initiated breakdown. For a purely random breakdown, Simha and Wall predicted, on theoretical grounds, the appearance of maxima in the rate-versus-volatilization curves at approximately 26% of vaporization. This has subsequently been found to be the case for many polymers, though not all. The thermal degradation of "H"-film in vacuum is apparently complicated by non-random processes that seem to have been characteristic also of polytrivinylbenzene and other polymers. In any case, the high activation energy of 74 kcal/mole for the thermal degradation in vacuum definitely suggests carbon-carbon scission. This high thermal stability, lack of a melting point, and unique mechanical and electrical properties offer an important challenge for further investigation.

References: