

(Figure 4) and the 2-foot 0.5% Carbowax column (Figure 5).

Preliminary quantitative studies indicate a relatively high conversion of amino acid to derivative. Further studies on the reproducibility of the method, and recovery of C^{14} -amino acid derivatives under various conditions are in progress. Although further work is required before the present procedure can be applied to the complete quantitative analysis of protein hydrolyzates, the method in its present form is applicable to less difficult analytical problems. For example, it is possible to analyze hydrolyzates of small peptides eluted from paper chromatograms, to detect impurities in commercial samples of amino acids (alloisoleucine in isoleu-

cine, allothreonine in threonine, glycine in β -alanine, hydroxyproline in proline, etc.), and to identify the minute amounts of amino acids present in preparations of soluble ribonucleic acids.

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Analysis of Pyrolyzates of Polystyrene and Poly(methyl Methacrylate) by Gas Chromatography

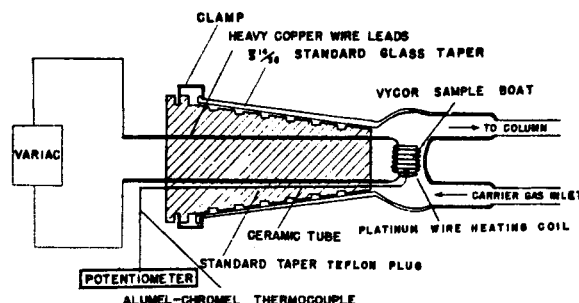
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► Analysis of the composition of the pyrolyzates of polystyrene and poly(methyl methacrylate) degraded at temperatures ranging from 400° to 1100° C. was accomplished by gas chromatography. Styrene monomer is the major product in the degradation of polystyrene below 700° C. Poly(methyl methacrylate), below 450° C., depolymerizes nearly exclusively to monomer. Gaseous and liquid products are formed at higher temperatures. Although the results are dependent on the specific conditions employed in the pyrolysis, this rapid method is applicable to the degradation studies of other polymers and shows the relative importance of various pyrolytic reactions over a wide range of temperatures. The procedure also gives valuable information about the structure of polymers and can be used for the determination of polymer constituents.

THE RECENT INTEREST in developing polymers that are heat stable at high temperatures has made it desirable to obtain more information on the degradation reactions and mechanisms of polymers. A great number of papers have described the thermal behavior of polymers at moderately high temperatures—that is, in the 200° to 500° C. range (2, 5). However, relatively little information (8) is available on the reactions occurring at higher temperatures.

Figure 1. Pyrolysis chamber



Gas chromatographic techniques that have been employed in the identification of polymers (1, 3, 4, 9) and quantitative determination of the composition of copolymers (6, 11) also offer a rapid means for the analyses of volatile pyrolyzates which so far have only been made by time-consuming separations or mass spectrometric methods.

This investigation deals with the study of the volatile pyrolysis products of polystyrene and poly(methyl methacrylate) obtained on degradation of these polymers at temperatures ranging from 425° to 1125° C.

EXPERIMENTAL

Reagents. The polystyrene was a thermally polymerized sample of number average molecular weight 233,000. The poly(methyl methacrylate) was a suspension polymer. Reagent grade liquids and compressed gases were used as standards for the identification of pyrolysis products.

Apparatus and Procedure. A chromatograph with a redesigned inlet system differing from that previously described (11) was used. Figure 1 shows the experimental setup employed to pyrolyze the polymeric material. In order to expose the specimen to a uniform temperature, to avoid spattering on decomposition, and to determine quantitatively the amount of residue left, the 2- to 3-mg. sample was placed in a weighed high-silica (Vycor) glass boat (3-mm. outside diameter, 4-mm. height). This material was chosen to avoid the occurrence of degradation reactions that may be catalyzed by the boat. The boat was surrounded by a 34-gage platinum heating coil having a total resistance of about 0.2 ohm. The ends of the coil were silver-soldered to two copper wire leads connected to a series of variable transformers by which the temperature of the boat could be regulated. The pyrolysis temperature was measured by placing a Chromel-Alumel thermocouple (gage No. 42 wire) in a small indentation in the

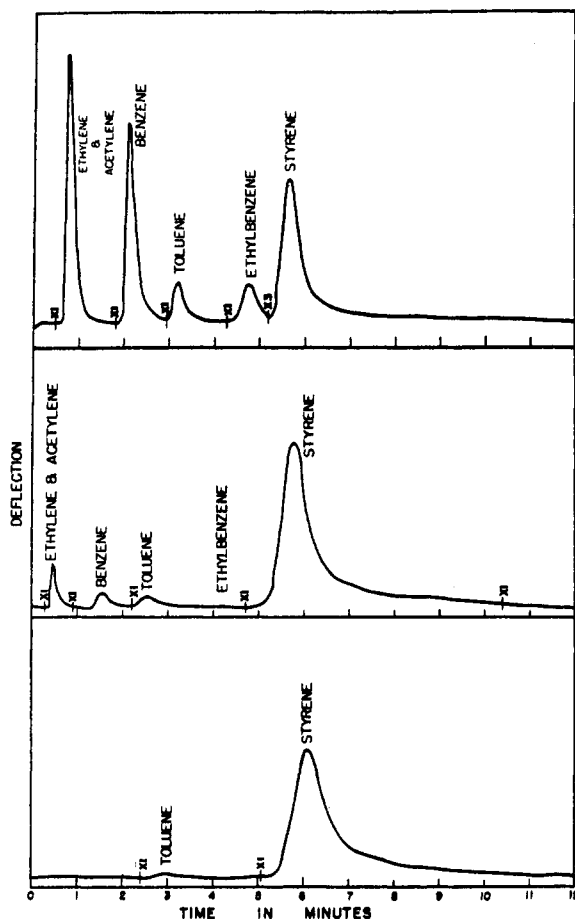


Figure 2. Chromatograms of pyrolysis products of polystyrene

Column, Apiezon L; col. temp., 140° C.; flow rate, 60 ml./min.
Pyrolysis temp., ° C.
Top. 1025 Middle. 825 Bottom. 425
(Attenuation scale indicated by numbers in figure)

bottom of the boat. This thermocouple was calibrated against a second thermocouple placed with the sample inside the boat. During the actual pyrolysis runs this second thermocouple was removed from the boat to prevent any catalytic effects on the polymer degradation due to the metals of this thermocouple. Measurements of the pyrolysis temperature were considered to be accurate within 10° C.

The copper wire leads were sealed into a standard taper (14/35) polytetrafluoroethylene plug which was inserted into a female glass joint. This

joint was connected to the metal inlet system of the chromatograph by two glass-to-metal seals.

After flushing the apparatus with helium for at least 3 minutes an electric current was passed through the heating coil. The voltage of the transformers was preset to heat the boat to the desired temperature which was reached within 15 seconds at 425° to 825° C. and within 3 to 5 seconds at the higher temperatures; the temperature was maintained for 20 to 30 seconds at 425° to 825° C. and for 5 to 10 seconds at 825° to 1125° C. The helium passing over the sample carried away the vaporized products into the column. The column material and temperature were varied until chromatograms with sharp peaks that did not overlap and suitable retention times were obtained. A summary of the experimental conditions including the column materials and temperatures as well as the carrier gas flow rate and pressure is given in Table I. The column was considered to be purged of the more volatile pyrolytic products when no further peaks on the chromatogram were obtained for at least 10 minutes. The boat was removed from the chromatograph, cooled, and weighed to de-

Table I. Operating Conditions

Column length, 6 feet
Bore (I.D.), 1/16 inch
Column materials, 30% (wt.) Apiezon L, Chlorowax 70, and dinonyl phthalate on ground firebrick 30-60 mesh; silica gel 30-200 mesh
Carrier gas, helium
Flow rate, 20, 60 ml./min.
Pressure head, 20 p.s.i.
Column temperatures, 100°, 120°, 128°, or 140° C.
Sample quantity, 2 to 3 mg.

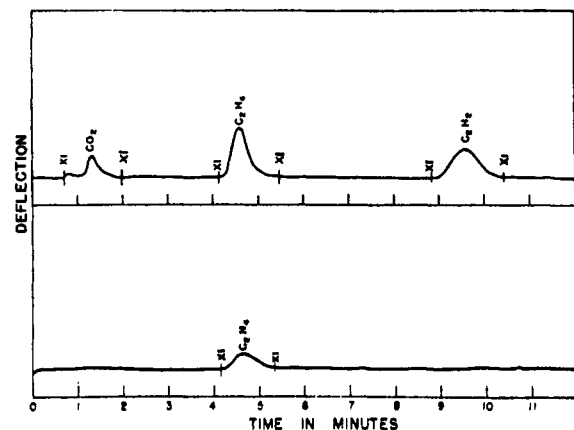


Figure 3. Chromatograms of gaseous pyrolysis products of polystyrene

Column, silica gel; col. temp., 100° C.; flow rate, 60 ml./min.
Pyrolysis temp., ° C.
Top. 1025 Bottom. 825
(Attenuation scale indicated by numbers in figure)

termine the presence of any nonvolatile residue.

A series of known amounts of monomers was also introduced into the column. The peak areas of the resulting chromatograms served as standard curves for the determination of the amounts of product present in the pyrolyzates and for determining the amounts of volatiles retained in the column.

RESULTS

Polystyrene. Typical chromatograms obtained on pyrolyzing polystyrene at 425°, 825°, and 1025° C. are shown in Figure 2. At 425° C. only styrene monomer is eluted from the column; degradation at 825° C. produces a number of identifiable products. Reactions leading to these products are even more important at a temperature of 1025° C. Identification of the compounds from the various peaks was made by comparing their retention times with those obtained from chromatograms of known compounds.

The composition was not altered appreciably on increasing the temperature from 1025° to 1125° C. as evidenced by the nearly identical chromatograms for the pyrolyzates. On heating the boat above 1025° C. the polymer was probably flash-pyrolyzed completely before the boat reached this temperature. The initial peak for the gaseous products could not be resolved by columns containing hydrocarbon high-vacuum grease (Apiezon L) or chlorinated paraffin wax on ground firebrick (Chlorowax 70). Chromatograms with a silica gel column showed the presence of ethylene, acetylene, and some carbon dioxide (Figure 3).

Results of the analyses at various pyrolysis temperatures are shown in Table II. Duplicate runs usually agreed

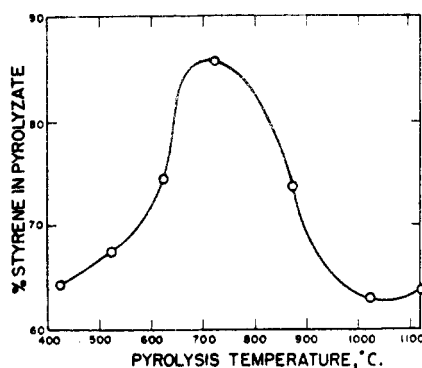


Figure 4. Effect of degradation temperature on amount of styrene monomer in pyrolyzates

within 1%. Substitution of an Apiezon L for the Chlorowax 70 column gave chromatograms with peaks at different retention times, but did not change appreciably the results of the chromatographic analyses. The Apiezon L column, however, separated the ethylbenzene-toluene single peak obtained with Chlorowax 70. In all degradations at temperatures above 350° C. no residue was found on reweighing the boat after cooling. However, at 425° C., 35.7% of the volatile material is retained in the column. Based on the results of previous studies (7, 10), this is mainly styrene dimer. The quantity of material retained in the column decreases with the pyrolysis temperature and amounts to only 4.3% at 1025° C.

Percentage of styrene monomer in the pyrolyzate vs. pyrolysis temperature is shown in Figure 4. At 425° C., 64.3% monomer is present in the pyrolyzate. The monomer content increases on raising the degradation temperature and reaches a maximum around 725° C. Reactions leading to the formation of ethylbenzene, toluene, benzene, ethylene, and acetylene occur at higher temperatures and the percentage of styrene in the pyrolyzate decreases.

Variations of the flow rate of the carrier gas between 45 and 75 ml. per minute did not alter the composition of the degradation products. At lower flow rates (less than 45 ml. per minute) the primary products were not immediately carried away from the hot zone and secondary reactions probably took place. Thus, the percentage of benzene was increased more than twofold in the pyrolysis at 1025° C. when the flow rate was reduced from 60 to 10 ml. per minute.

Comparison of the chromatographic results with mass spectrometric analyses of polystyrene degraded in a helium atmosphere by Madorsky and Straus (8) indicates that consistently larger quantities of monomer are obtained by the chromatographic procedure. The high flow rate of the carrier

Table II. Composition, Weight Per Cent, of Pyrolyzates of Polystyrene
[Average of two or more analyses. Column: 30% (wt.) Chlorowax 70 on ground firebrick, 30–60 mesh (except where indicated otherwise); col. temp., 140° C.]

Product	Pyrolysis Temperature, ° Centigrade						
	425	525	625	725	825	1025	1125
Carbon dioxide	Trace ^a	Trace ^a	Trace ^a
Ethylene	Trace ^a	4.1 ^a	6.9 ^a	6.8 ^a
Acetylene	Trace ^a	4.1 ^a	6.9 ^a	6.8 ^a
Benzene	Trace	8.1	13.4	12.0 ^b
Toluene	Trace ^a	Trace ^a	Trace ^a	0.9 ^a	2.5 ^a	5.6 ^a	5.8 ^a
Ethylbenzene	3.7 ^b	...
Styrene	64.3	67.5	74.4	83.9	73.7	63.8	64.3
Material retained in column	35.7	32.5	25.6	14.4	7.5	4.3	3.3

^a Column: silica gel 30–200 mesh; col. temp., 100° C. Values obtained by resolving total percentage of gaseous products with Chlorowax 70 and Apiezon L column, respectively.

^b Column: 30% (wt.) Apiezon L on ground firebrick, 30–60 mesh; col. temp., 140° C.

^c Weight per cent of toluene and ethylbenzene.

Table III. Composition, Weight Per Cent, of Pyrolysis Products of Poly(methyl Methacrylate)

[Column: 30% (wt.) dinonyl phthalate on ground firebrick 30–60 mesh; col. temp., 128° C.]

Product	Pyrolysis Temperature, ° Centigrade						
	425	525	625	725	825	875	1025 ^a
Gaseous components	Trace	3.6	4.2	18.2	60.3	73.6	76.3
Methanol	Trace	Trace	Trace	Trace	Trace
Ethanol	Trace	Trace	0.6	0.5	0.4
Methyl acrylate	...	Trace	Trace	Trace	Trace	Trace	Trace
Methyl propionate	Trace	Trace	0.4	0.5	0.7	0.2	0.3
Methyl isobutyrate	Trace	Trace	0.4	0.5	0.8	2.5	3.0
Methyl methacrylate	99.4	96.2	94.7	80.6	37.4	23.2	19.9
Residue	Nil	Nil	Nil	Nil	Nil	Nil	Nil

^a Column temperature, 100° C.

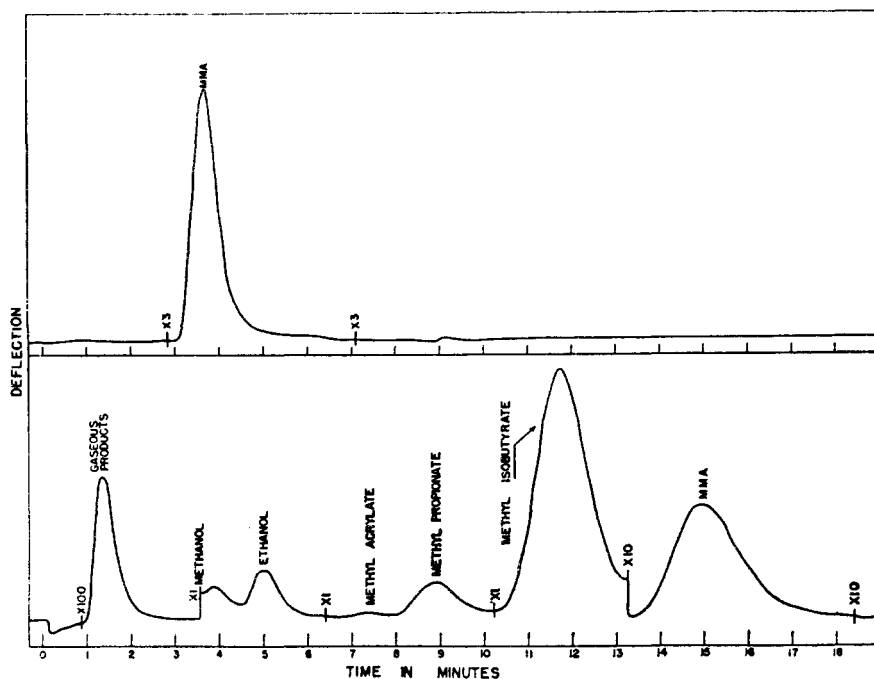


Figure 5. Chromatograms of pyrolysis products of poly(methyl methacrylate)

Column, dinonyl phthalate
Top. Pyrolysis temp., 425° C.; col. temp., 128° C.; He flow rate, 60 ml./min.
Bottom. Pyrolysis temp., 1025° C.; col. temp., 100° C.; He flow rate, 20 ml./min.
(Attenuation scale indicated by numbers in figure)

Table IV. Composition, Weight Per Cent, of Gaseous Pyrolyzates of Poly(methyl Methacrylate)

(Column: silica gel, 30-200 mesh; col. temp., 100° C.)

Product	Pyrolysis Temp., ° C.*	
	825	1025
Methane + carbon monoxide	47.9	12.4
Ethane	8.4	2.2
Carbon dioxide	18.5	42.6
Ethylene	12.6	24.9
Acetylene	12.6	17.9

* At 425° C., only trace values were found.

Table V. Elementary Composition of Polymer and Degradation Products

(Pyrolysis temperature, 1025° C.)

	C, %	H, %	O, %
Polystyrene			
Polymer	92.2	7.8	...
Pyrolysis products	91.8	8.2	Trace
Poly(methyl methacrylate)			
Polymer	60.0	8.0	32.0
Pyrolysis products	59.4	7.4	33.2

gas rapidly sweeps the primary reaction products from the hot zone into the chromatographic column. On the other hand, the pyrolysis chamber used by Madorsky and Straus is quite large, and the primary products are kept at the elevated temperature for a considerable time period, during which they can undergo secondary decompositions.

Poly(methyl Methacrylate). Chromatograms obtained from pyrolyzing poly(methyl methacrylate) at 425° and 1025° C. using a dinonyl phthalate column are shown in Figure 5. Monomer is formed nearly exclusively at 425° C., whereas a number of compounds are detected at 1025° C. No volatile products are retained in the column. The gaseous products which appear as a single peak on the chromatograms are separated and identified with a silica gel-packed column, with the exception of methane and carbon monoxide, which give overlapping peaks. Tables III and IV give the composition of the pyrolyzates at degradation temperatures from 425° to 1025° C. (Values listed are the result of two analyses.) Figure 6 shows the percentage of monomer product as a function of degradation temperature. At 425° C. the product contains 99.4% monomer. The percentage of methyl methacrylate monomer in the pyrolyzate decreases to about 20% at 875° C. and remains constant at higher temperatures. Gaseous products predominate at 825° C. and above. On raising the temperature from 825° C. to 1025° C. the percentage of carbon dioxide, ethylene, and acetylene in the gaseous mixture increases, whereas the percent-

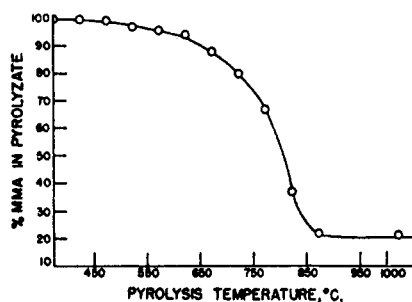


Figure 6. Effect of degradation temperature on amount of methyl methacrylate monomer in pyrolyzate

age of methane, ethane, and carbon monoxide is lowered.

DISCUSSION

Products obtained on pyrolysis of polystyrene and poly(methyl methacrylate) between 425° and 1025° C. can be analyzed readily by chromatographic techniques. Table V shows the comparison of the percentages of carbon, hydrogen, and oxygen in the polymer sample and in the products of the pyrolysis. The nearly identical percentages of carbon, hydrogen, and oxygen obtained for the pyrolysis products and those calculated for the original polymer indicate that any volatile materials retained in the column, such as is observed on degradation of polystyrene, are mainly polymer fragments.

The chromatograph employed a filament-type katharometer for measuring the thermal conductivity of the effluent gas. Corrections for variations of the thermal conductivities of the vaporized liquid components of the pyrolysis mixture appear unnecessary. Results accurate within 1% were obtained for synthetic mixtures having the same composition as the liquid pyrolyzates. This error is of the same order as that for the reproducibility of duplicate determinations of the composition of the pyrolyzate. In degradations in which the percentages of gaseous products are large and their conductivity values at the operating temperature of the detector are available, corrections for variations of the conductivities are recommended.

At temperatures below 350° C. degradation is still occurring after the retention times of the pyrolysis products. Hence, the chromatogram will show tailing peaks which make it difficult to determine quantitatively the composition of the pyrolyzate.

Similar to other techniques that are based on the behavior of polymers on heating, the results are dependent on the experimental conditions employed in the degradation. Analyses of the decomposition products of polystyrene show that faster carrier gas flow rates

and therefore more rapid removal of the products from the hot reaction zone produce increased proportions of monomer. Since the reactions do not proceed to equilibrium, their extent depends on the initial reaction temperature and is influenced by the rate of cooling of the products. The latter variable is influenced by the temperature and rate of flow of the carrier gas as well as by the geometry and thermal properties of the pyrolysis vessel.

It is not possible to state the complex reactions which lead to the products observed without detailed kinetic studies. Inspection of Tables II, III, and IV shows that reaction products other than the respective monomers are found in increasing amounts as the temperature of the pyrolysis is increased. The C_6H_5 —C bond of styrene and the bonds adjacent to the $C=C$ in methyl methacrylate monomer are probably most susceptible to cleavage. The resulting radicals may undergo a variety of reactions such as disproportionation, further cleavage of bonds, or recombination with other fragments. Free radicals formed on scission of the C_6H_5 —C bond will yield benzene and acetylene. Some of the acetylene as well as some of the remaining styrene may react with hydrogen, another possible product, to form ethylene and ethylbenzene. Secondary decomposition reactions of methyl methacrylate are even more complex and much work remains to be done to clarify the intermediate steps.

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