NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT
0708-20-07560

May 24, 1960

NBS REPORT
6853

Progress Report

on

ANALYSIS OF PYROLYZATES OF POLYMERS BY GAS CHROMATOGRAPHY

I. Pyrolysis of Polystyrene and Poly(methyl methacrylate) at 400 to 1100°C

by

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This work is a part of the dental research program conducted at the National Bureau of Standards in cooperation with the Council on Dental Research of the American Dental Association, the Army Dental Corps, the Dental Sciences Division of the School of Aviation Medicine, USAF, the Navy Dental Corps, and the Veterans Administration.

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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I. Pyrolysis of Polystyrene and Poly(methyl methacrylate) at 400 to 1100°C

Abstract

Pyrolyzates of polystyrene and poly(methyl methacrylate) were studied at temperatures from 400 to 1100°C using gas chromatographic techniques. A small Vycor boat surrounded by a platinum heating coil was placed in the inlet system of the chromatograph. The 2 to 3 mg sample was degraded at a constant temperature which was measured by means of a thermocouple placed in an indentation at the bottom of the boat. Helium carried the volatile products into the heated column of the chromatograph.

Analyses of the products could usually be accomplished with a reproducibility of better than 1%.

Polystyrene degrades to monomer below 700°C and poly(methyl methacrylate) behaves similarly below 450°C. At higher temperatures some gaseous and liquid secondary decomposition products are formed which were identified by their characteristic retention times.

The technique uses inexpensive equipment and is generally applicable for the study of the thermal

stability of polymers and their pyrolyzates. Results obtained are very helpful in identifying primary and secondary reaction products and in the elucidation of degradation mechanisms over wide temperature ranges. The procedure is also useful in the rapid characterization and quantitative estimation of the composition of complex copolymer systems.

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1. INTRODUCTION

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 [1,2]. However, relatively little information is available on the reactions occurring at higher temperatures.

The application of gas chromatographic techniques to the identification of polymers [3-5] and quantitative determination of the composition of copolymers [6-7] offers a rapid means for the analyses of volatile pyrolyzates. Until recently, such analyses could only be made by time consuming separations or mass spectrometric methods.

This investigation deals with the study of the pyrolysis products of polystyrene and poly(methyl methacrylate) obtained on degradation of these polymers at temperatures ranging from 400 to 1100°C.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

The polystyrene was a thermally polymerized sample of number average molecular weight 233,000. The poly(methyl methacrylate) was a Rohm and Haas No. 2 suspension polymer. Eastman reagent grade liquids and reagent grade Matheson compressed gases were used to identify pyrolysis products.

2.2 Apparatus

A Consolidated Electrodynamics Corp. type X-26-201 chromatograph with a redesigned inlet system differing from that previously described [6] was used. Figure 1 shows the experimental set-up that was employed to pyrolyze the polymeric material inside the chromatograph. A 2 to 3 mg sample was placed in a weighed Vycor glass boat [3 mm outside diameter, 4 mm height) that was surrounded by a 34 gauge platinum heating coil having a total resistance of about 0.2 ohms. 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 (gauge No. 42 wire) in a small indentation in the bottom of the boat. The measurement of the pyrolysis temperature was considered to be accurate within better than 10°C.

The copper wire leads were sealed into a standard taper (14/35) Teflon plug which was inserted into a female glass joint. This joint was connected to the metal inlet system by two glass-to-kovar seals.

After flushing the chromatograph with helium for 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 within 3 to 5 seconds. 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 are given in Table I. The column was considered to be purged of pyrolytic products when no further peaks on the chromatogram were obtained for 10 minutes. The boat was removed from the chromatograph, cooled and weighed to determine the presence of any non-

volatile residue.

3. RESULTS

3.1 Polystyrene

Typical chromatograms obtained on pyrolyzing polystyrene at 400°C, 800°C and 1000°C are shown in Figure 2. Whereas styrene monomer is the only product at 400°C, secondary products are formed at 800°C. These secondary reactions are even more important at a temperature of 1000°C. Identification of the compounds from the various peaks was made by comparing their retention times with those obtained from chromatograms of known compounds.

At temperatures above 1000°C the polymer was probably flash-pyrolyzed completely before the boat reached an equilibrium temperature. Hence, the composition was not altered appreciably on increasing the temperature from 1000° to 1100°C as evidenced by the nearly identical chromatograms for the pyrolyzates. The initial peak for the gaseous products could not be resolved by Apiezon L or Chlorowax 70 columns. Chromatograms with a silica gel column showed the presence of ethylene, acetylene and some carbon dioxide. The amount of each product in the pyrolyzate was calculated from the ratio of the area under the peak to the sum of the areas under all the

peaks. Results at various pyrolysis temperatures are shown in Table II. Duplicate runs usually agreed 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.

Percentage of styrene monomer in the pyrolyzate versus pyrolysis temperature is shown in Figure 4. Below 700°C the polyrolyzate was nearly all monomer under the experimental conditions employed. Secondary reactions leading to the formation of ethylbenzene, toluene, benzene, ethylene and acetylene occurred at higher temperatures.

Variations of the flow rate of the carrier gas between 45 ml/min and 75 ml/min did not alter the composition of the degradation products. At lower flow rates (less than 45 ml/min) the primary products were not immediately carried away from the hot zone and secondary reactions took place. Thus, the percentage of benzene (a secondary reaction product) was increased more than

twofold in the pyrolysis at 1000°C when the flow rate was reduced from 60 to 10 ml/min.

Comparison of the chromatographic results with mass spectrometric analyses of polystyrene degraded in a helium atmosphere by Modorsky and Strauss [8] indicates that consistently smaller quantities of secondary products are obtained by the chromatographic procedure. The high flow rate of the carrier gas rapidly sweeps the primary reaction products from the hot zone into the chromatographic column. The pyrolysis chamber used by Madorsky and Strauss on the other hand 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.

3.2 Poly(methyl methacrylate)

Chromatograms obtained from pyrolyzing poly(methyl methacrylate) at 400° and 1000°C using a dinonyl phthalate column are shown in Figure 5. Only monomer is formed at 400°C whereas a number of compounds are detected at 1000°C. The gaseous products which appear as a single peak on the chromatograms are separated and identified with a silica gel packed column (Figure 6). Tables III and IV give the composition of the pyrolyzates

at degradation temperatures from 400 to 1000°C. Figure 7 shows the percentage of monomer product as a function of degradation temperature. Below 400°C monomer is formed nearly exclusively. The percentage of methyl methacrylate monomer in the pyrolyzate decreases to about 20% at 850°C and remains constant at higher temperatures. Gaseous products predominate at 800°C and above. On raising the temperature from 800°C to 1000°C the quantities of carbon monoxide, methane and ethane decrease rapidly. Secondary reactions may partially convert these compounds to carbon dioxide and acetylene.

4. DISCUSSION

Products obtained on pyrolysis of polystyrene and poly(methyl methacrylate) between 400°C and 1000°C can be readily analyzed 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 satisfactory agreement of the material balance indicates that little if any of the products are retained in the column.

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. If 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 to improve the accuracy of the analyses. Substitution of ionization detectors for katharometers will eliminate these corrections since their response is solely dependent on the quantity of effluent.

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. To study degradation of these polymers below 350°C the material should be pyrolyzed in another apparatus and after collection, the pyrolyzate should be introduced into the chromatograph. The procedure is also limited by excessive depolymerization rates at elevated temperatures. Thus, the polymers investigated are degraded nearly instantaneously

above 1000°C whereas the equilibrium temperature of the boat is reached only after the sample is completely pyrolyzed.

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 produces increased proportions of monomer. It appears that even at the higher temperatures polystyrene and poly(methyl methacrylate) degradation is initiated at the chain ends and results in the formation of monomer. Since the secondary reactions do not proceed to equilibrium their extent depends on the initial reaction temperature and is also 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 the geometry and thermal properties of the pyrolysis vessel.

It is not possible to state the complex secondary reactions which lead to the products observed without detailed kinetic studies. Inspection of Tables II, III and IV shows that secondary reaction products were found in increasing amounts as the temperature of the pyrolysis was increased. Undoubtedly, the $C_6H_5 - C$ bond of styrene and the bonds adjacent to the $C = C$ in methyl methacrylate are most susceptible to chain scission.

The resulting free 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 will react with hydrogen, another 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.

5. SUMMARY

Analysis of the composition of the pyrolyzates of polystyrene and poly(methyl methacrylate) degraded at temperatures ranging from 400°C to 1100°C was accomplished by gas chromatography. The procedure in which the polymer is pyrolyzed inside the chromatograph and the vaporized components are carried directly into the column is rapid, uses relatively inexpensive equipment and is applicable to degradation studies of other polymers. Identity of the products was established from their retention times and the quantitative composition from the peak areas on the chromatograms. Below 700°C polystyrene degrades to monomer; poly(methyl methacrylate) shows a similar behavior below 450°C. Gaseous and liquid

products are formed at higher temperatures. The method is very useful for the identification of primary and secondary reaction products, aids in the investigation of the mechanisms of degradation 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 copolymers by comparison of the chromatograms of the pyrolysis products obtained at different degradation temperatures. The method can, therefore, be used for the rapid detection and determinations of polymers and constituents of copolymers.

6. REFERENCES

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TABLE I

Operational Conditions

Column length	6 ft
Bore (I. D.)	3/16 in.
Column materials	30% (wt) Apiezon L 30% (wt) Chlorowax 70 30% (wt) 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 - 3 mg

TABLE II

Composition of the Pyrolyzate of Polystyrene

Product^a	Pyrolysis Temperature, °C							
	400	500	600	700	850	1000	1000	1100
	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %
Carbon dioxide^b	-	-	-	-	-	Trace	Trace	-
Ethylene^b	-	-	-	Trace	4.4	7.2	7.0	7.0
Acetylene^b	-	-	-	Trace	4.4	7.2	7.0	7.0
Benzene	-	-	-	Trace	8.8	14.0	12.5^c	13.4
Toluene	-	-	-	1	2.7	5.8	2.8^c	6.1
Ethylbenzene	-	-	-				3.9^c	
Styrene	100	100	100	98	79.7	65.6	65.8^c	66.5
Residue	nil	nil	nil	nil	nil	nil	nil	nil

a. Average of two or more analyses. Column: 30% (wt) Chlorowax 70 on ground firebrick, (except where indicated otherwise) 30-60 mesh. Column temperature 140°C.

b. Column: Silica gel 30-200 mesh. Column temperature 100°C. Values were obtained by resolving the total percentage of gaseous products obtained with the Chlorowax 70 and Apiezon L column, respectively.

c. Column: 30% (wt) Apiezon L on ground firebrick, 30-60 mesh. Column temperature, 140°C.

TABLE III

Pyrolysis Products of Poly(methyl methacrylate)[a]

Column: 30% (wt) dinonyl phthalate on
ground firebrick 30-60 mesh

Product	Pyrolysis Temperature, °C					
	400	500	600	700	800	1000
	wt %	wt %	wt %	wt %	wt %	wt %
Gaseous components	Trace	3.6	4.2	18.2	60.3	76.3
Methanol	-	-	Trace	Trace	Trace	Trace
Ethanol	-	-	Trace	Trace	0.6	0.4
Methyl acrylate	-	Trace	Trace	Trace	Trace	Trace
Methyl propionate	Trace	Trace	0.4	0.5	0.7	0.3
Methyl isobutyrate	Trace	Trace	0.4	0.5	0.8	3.0
Methyl methacrylate	99.4	96.2	94.7	80.6	37.4	19.9
Residue	nil	nil	nil	nil	nil	nil

a. Average of two analyses.

TABLE IV

Composition of Gaseous Pyrolyzates of Poly(methyl methacrylate)[a]

Column: Silica gel, 30-200 mesh.
Column temperature, 100°C.

Product	Pyrolysis Temperature, °C		
	400	800	1000
	wt %	wt %	wt %
Methane	Trace	19.3	6.8
Carbon monoxide		28.6	5.6
Ethane		8.4	2.2
Carbon dioxide		18.5	42.6
Ethylene		12.6	24.9
Acetylene		12.6	17.9

a. Average of two analyses.

TABLE V

Elementary Composition of Polymer and Degradation products

Pyrolysis temperature: 1000°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

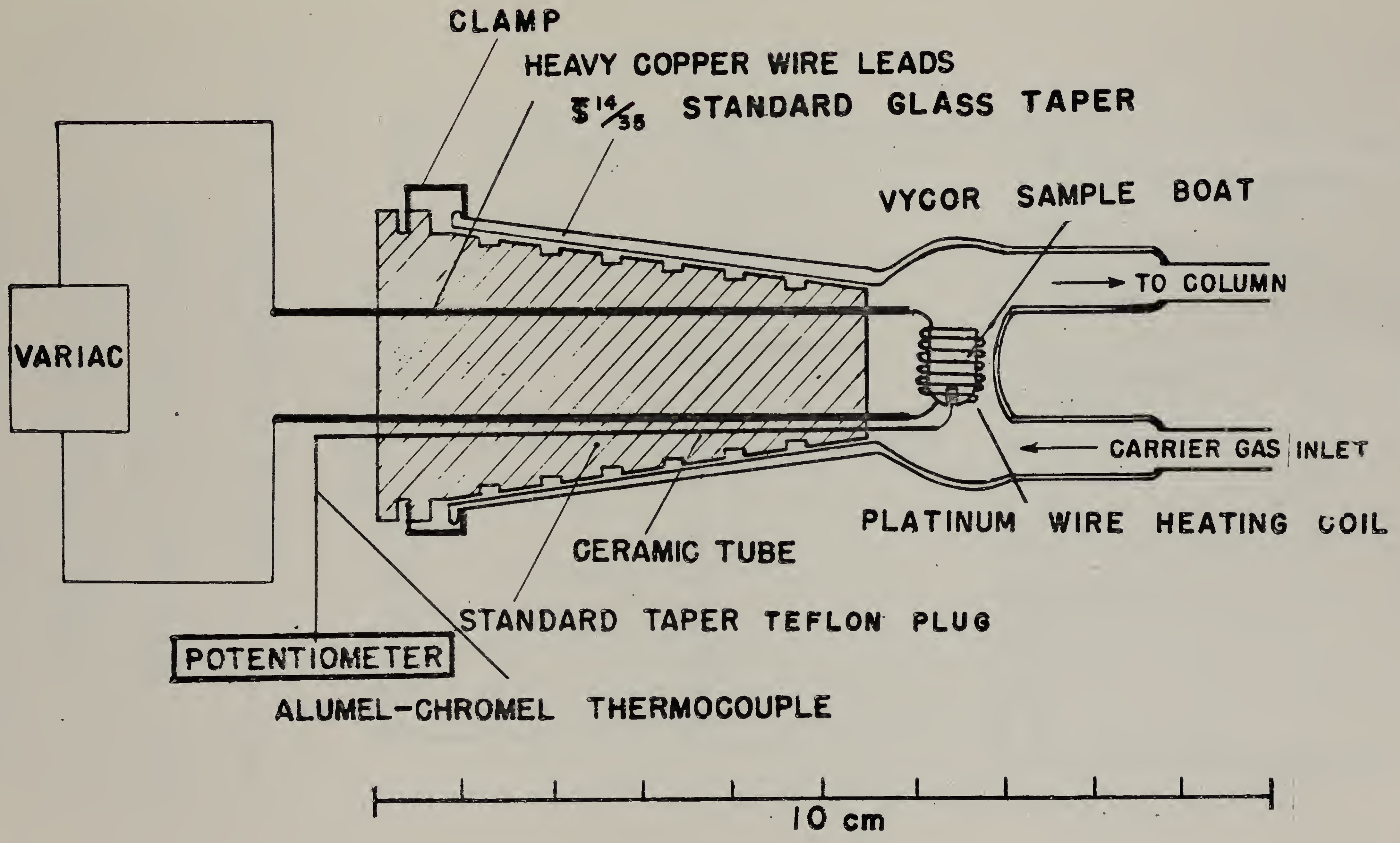

Figure 1. Pyrolysis Chamber

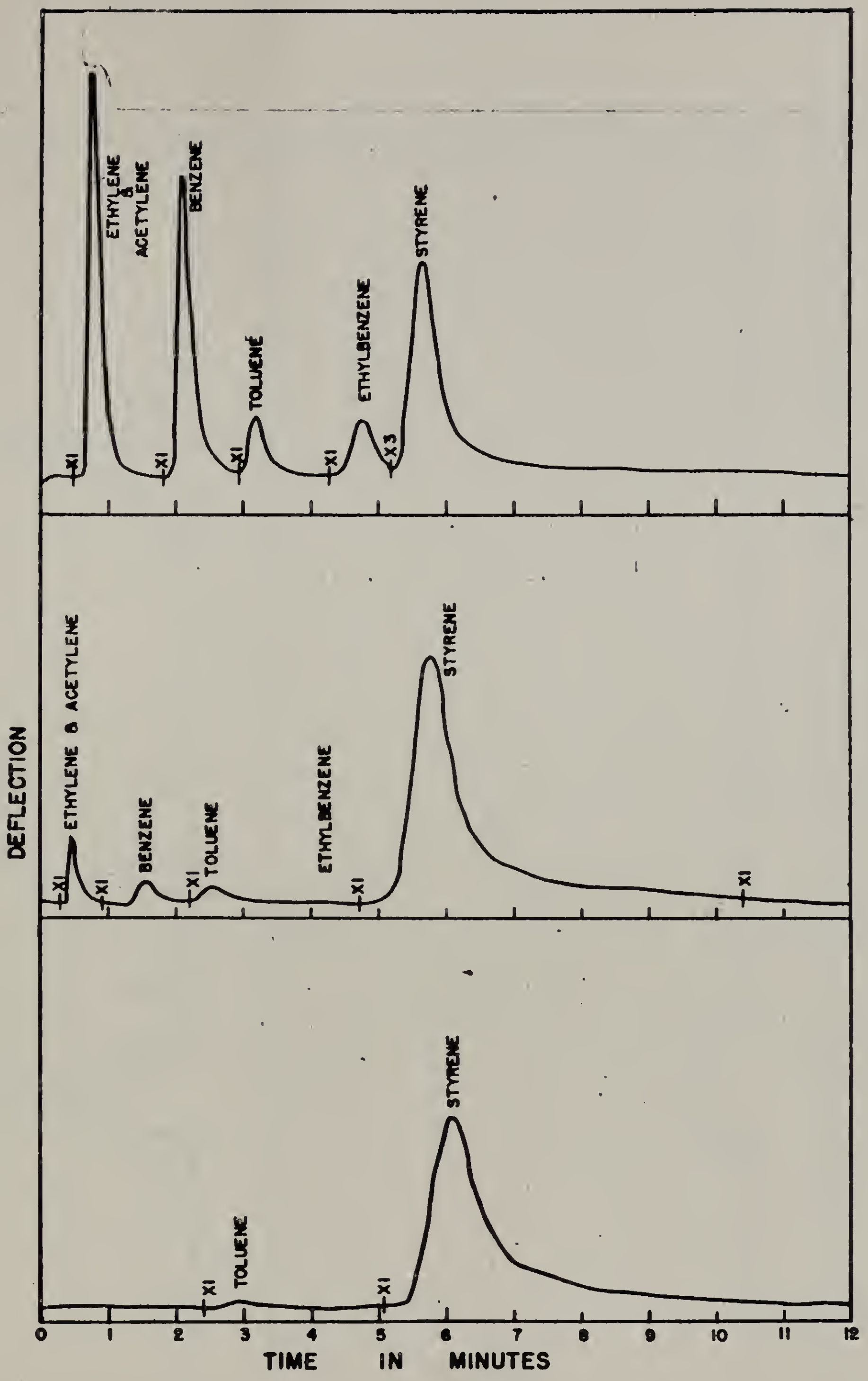

Figure 2. Chromatograms of the Pyrolysis Products of Polystyrene.

Column: Apiezon L. Column Temp: 140°C.
Flow Rate: 60 ml/min.

Top: Pyrolysis temp. 1000°C.
Middle: Pyrolysis temp: 800°C.
Bottom: Pyrolysis temp: 400°C.

(Change in scale is indicated by numbers on figure.)

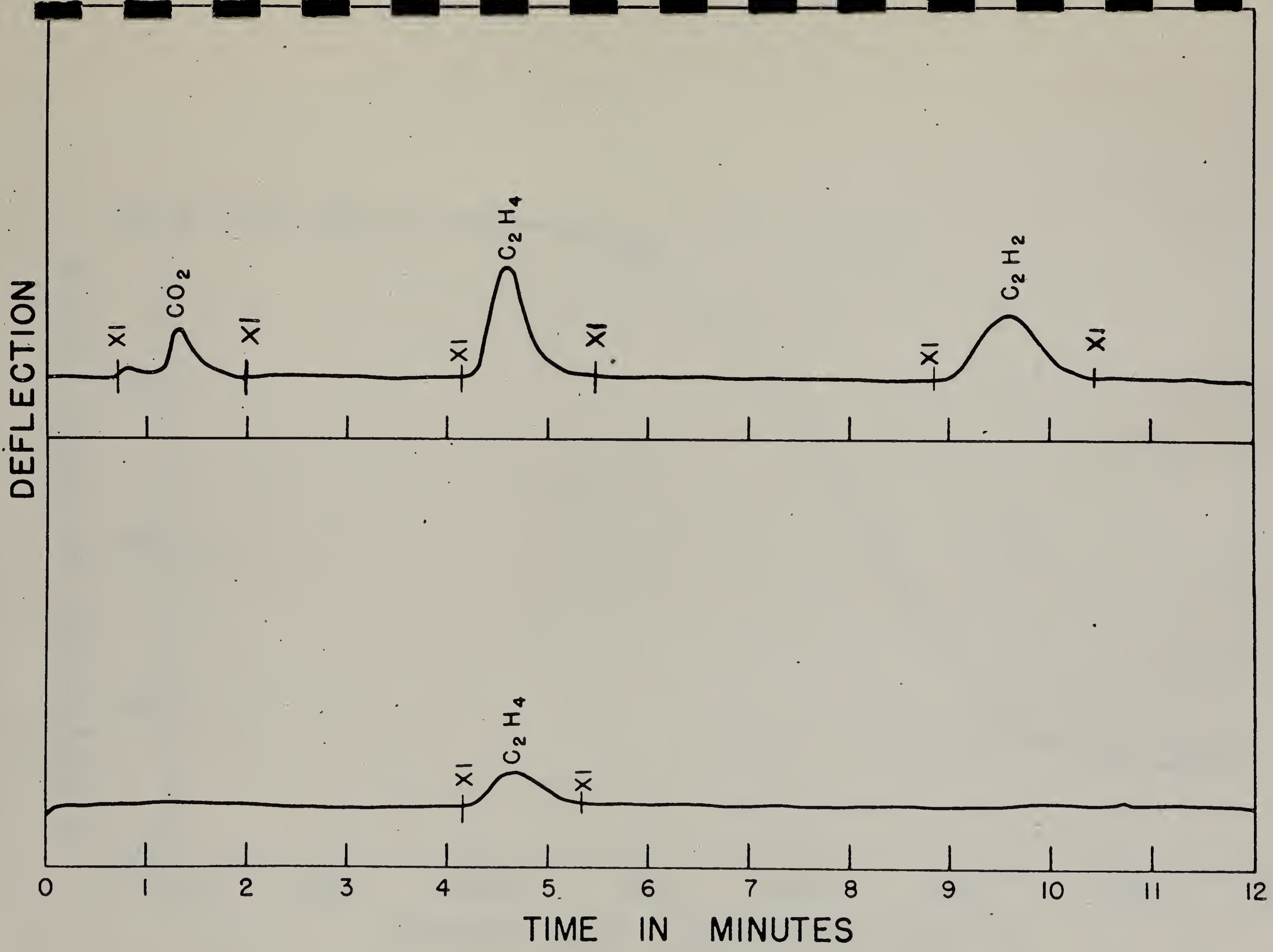

Figure 3. Chromatograms of the Gaseous Pyrolysis Products of Polystyrene.

Column: Silica gel Column Temp: 100°C
Flow rate: 60 ml/min.

Top: Pyrolysis temp: 1000°C
Bottom: Pyrolysis temp: 800°C.

([illegible] indicated by numbers on figure.)

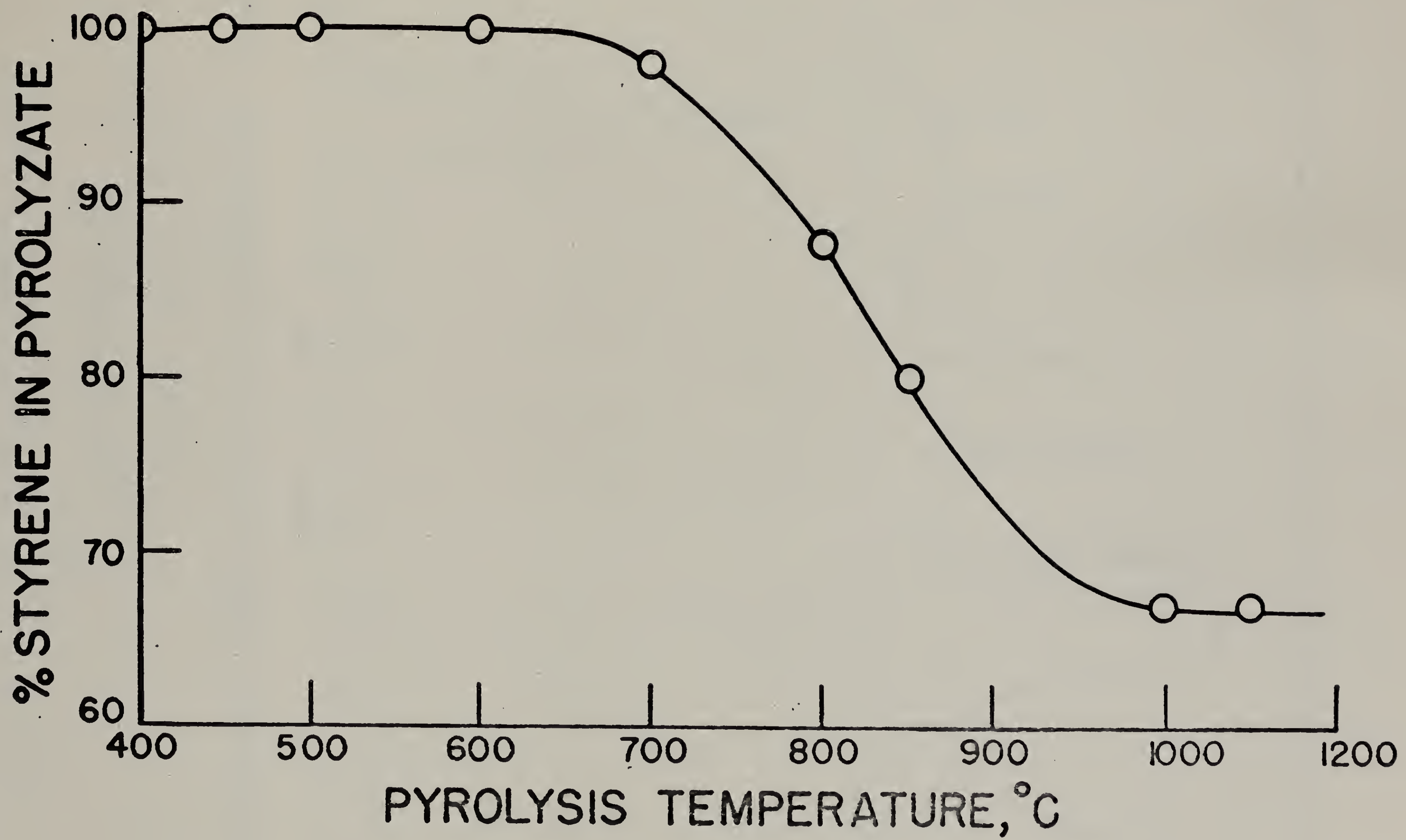

Figure 4. The Effect of Degradation Temperature on the Amount of Styrene Monomer in the Pyrolyzate.

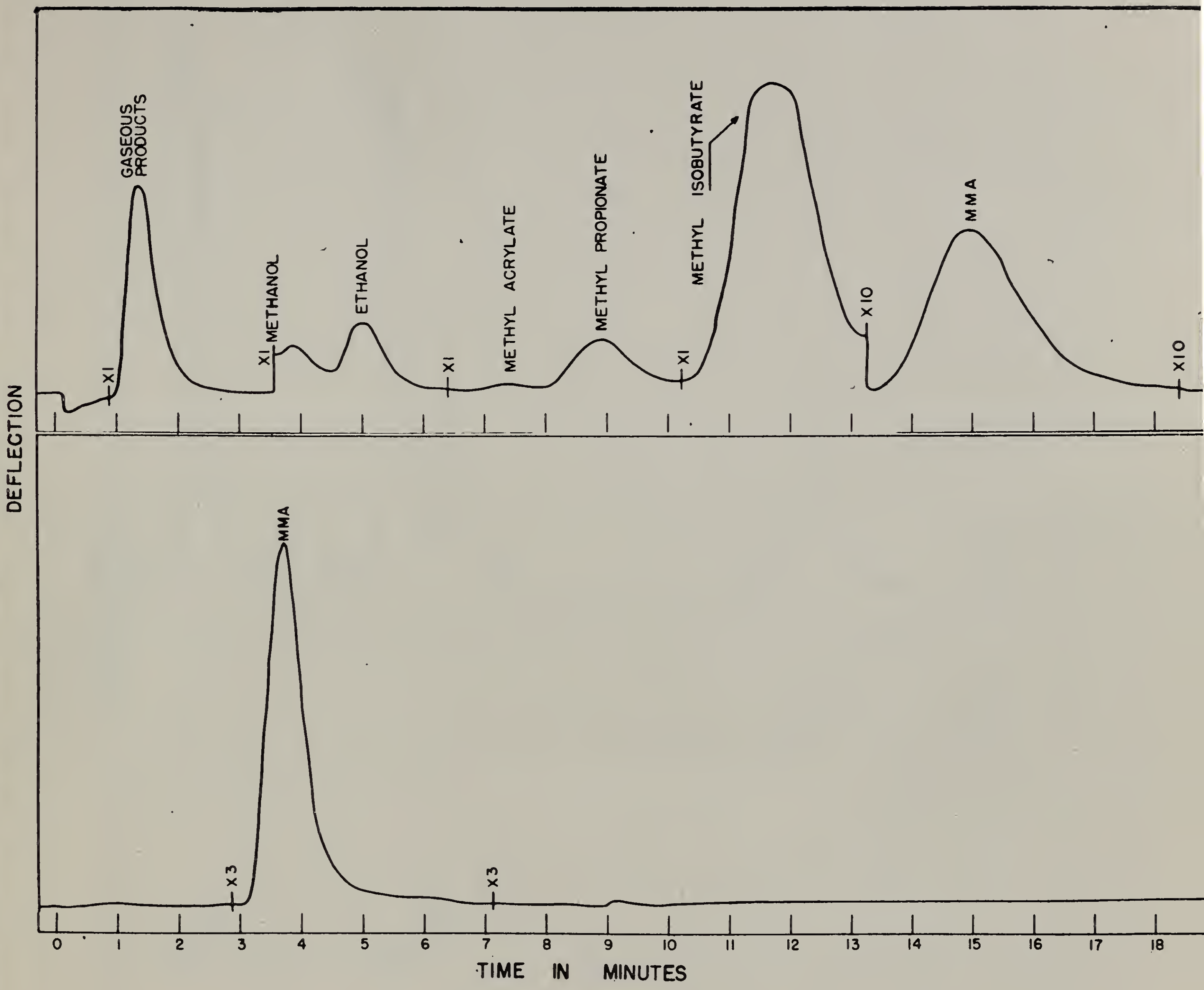

Figure 5. Chromatograms of the Pyrolysis Products of Poly(methyl methacrylate).

Column: Dinonyl phthalate.

Top: Pyrolysis temp: 1000°C.
Column temp: 100°C.
Helium flow rate: 20 ml/min.

Bottom: Pyrolysis temp: 400°C.
Column temp: 120°C.
Helium flow rate: 60 ml/min.

(Change in scale is indicated by numbers of figure.)

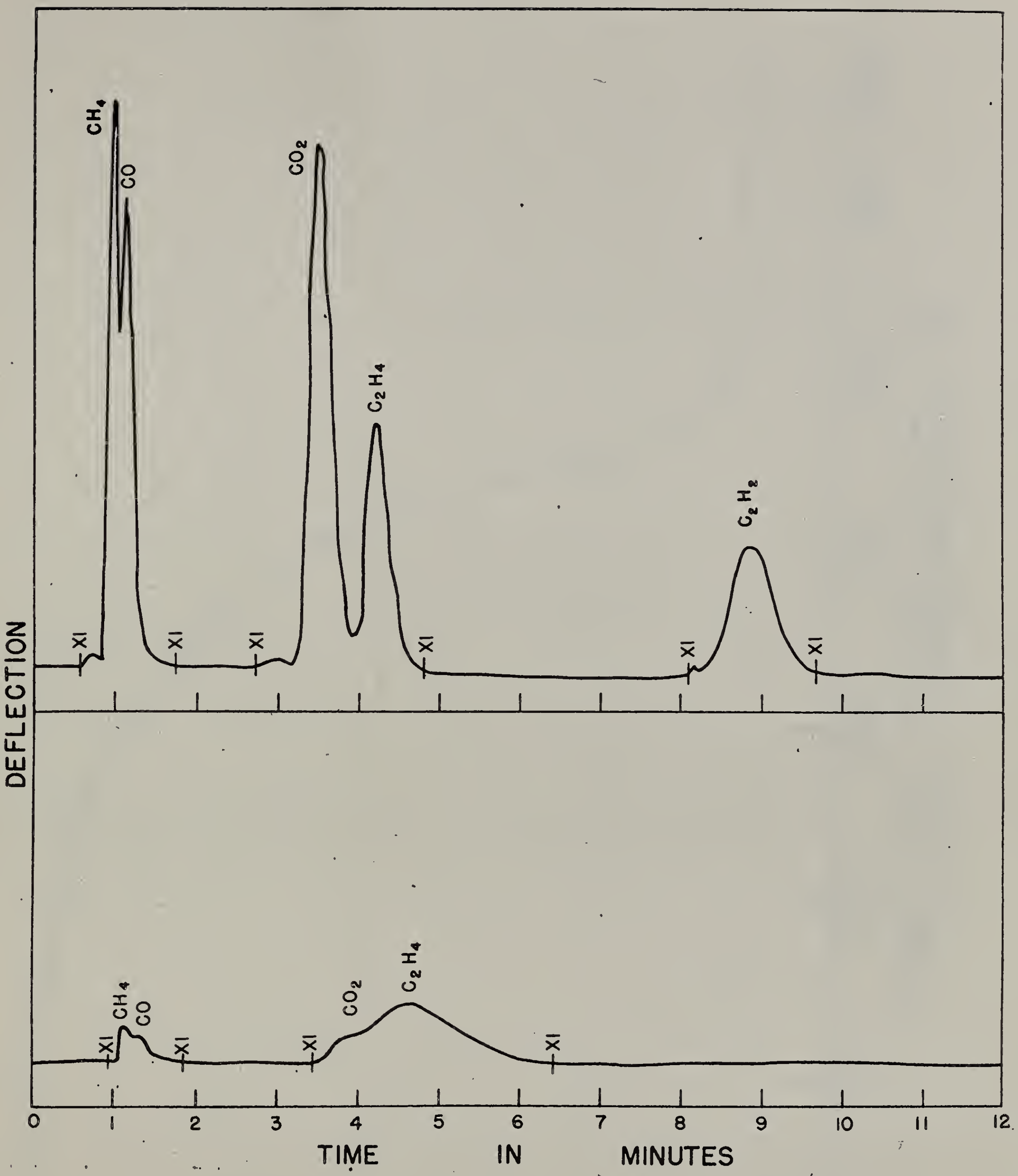

Figure 6. Chromatograms of the Gaseous Pyrolysis Products of Poly(methyl methacrylate).

Column: Silica gel. Column temp: 100°C.
Flow rate: 60 ml/min.

Top: Pyrolysis temp: 1000°C.
Bottom: Pyrolysis temp: 600°C.

(Change in scale is indicated by numbers in figure.)

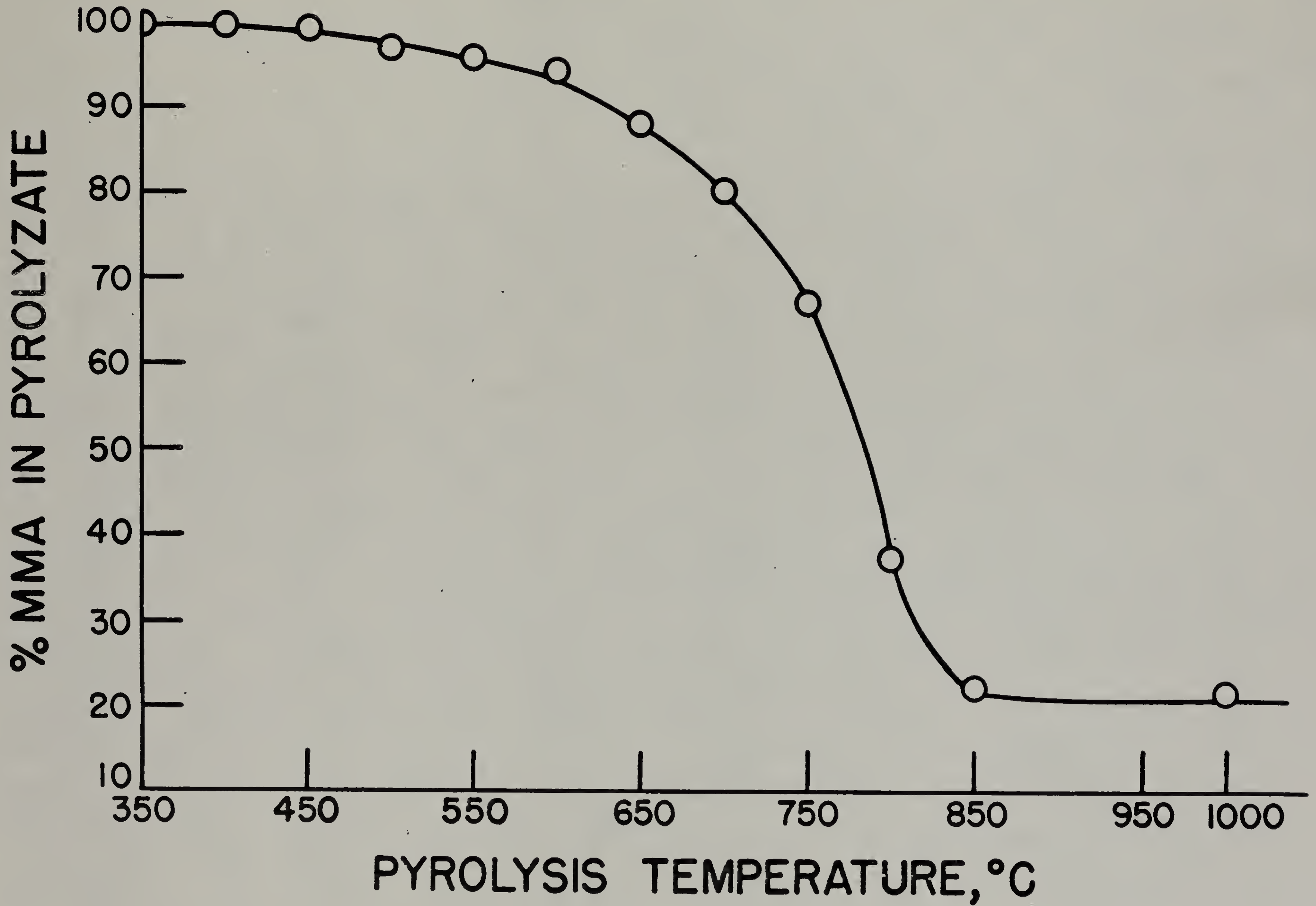

Figure 7. The Effect of Degradation Temperature on the Amount of Methyl Methacrylate Monomer in the Pyrolyzate.