

## Thermal Stability of Model Compounds Related to Thermostable Polymers by Pyrolysis-Gas Chromatography

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### Synopsis

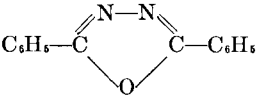
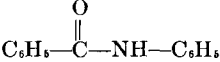
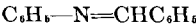
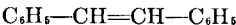
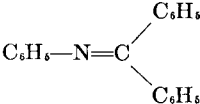
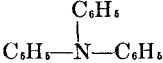
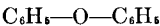
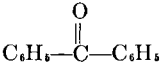

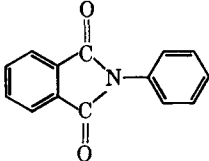
Thermal stabilities of eighteen model compounds related structurally to thermostable polymer systems were determined accurately by pyrolysis-gas chromatography. This approach offers distinct advantages over previously used indirect methods which measure parameters other than actual starting material remaining undecomposed. Both the oxadiazole ring and the aromatic amide link were found to have poor thermal stabilities in comparison with other compounds studied. Since polymers based on these two features have been shown to be valuable for use in air at 200–400°C., the data suggest that oxidation resistance rather than the ultimate in pure thermal resistance should be sought in all-purpose thermostable materials.

### Introduction

Considerable data exist in the literature concerning the thermal stabilities of various compounds and polymers. Most of the methods which have been used to determine these stabilities were indirect. For example, the isoteniscope method employed by Johns and co-workers<sup>1,2</sup> measures the changes in vapor pressure over the sample being tested at elevated temperatures. The increase in vapor pressure is, of course, dependent upon the number of fragments produced during decomposition and, since this may vary from two to scores, interpretation of the results may not be straightforward. In addition, the isoteniscope method tells nothing about what is occurring during decomposition. Thermogravimetric analysis (TGA) has been used extensively as a measure of the thermostability of polymers. However, this method is not applicable to model compounds since only volatility would be measured.

Johns and co-workers<sup>1,2</sup> made use of four different methods to investigate the relative stabilities of organic compounds. However, we have observed that the most minute change in conditions greatly affects the observed stability. Therefore, if meaningful conclusions are to be drawn as to relative thermostabilities of a large number of substances, it is necessary that data be compared from experiments conducted under identical conditions.

TABLE I<sup>a</sup>  
Model Compounds Related to Thermostable Polymer Systems  
in Increasing Order of Thermal Stability

Compound	Structure	Pyrolysis temp., °C.	Pyrolysis, %
2,5-Diphenyloxadiazole		750	100 <sup>b</sup>
Benzanilide		"	72
Benzylidene aniline		"	55
Stilbene		"	45
Benzhydrylidene aniline		"	42
Triphenylamine		"	14
Diphenyl ether		870	83
Benzophenone		"	72
Diphenylamine		"	54
N-Phenylphthalimide		"	52

(continued)

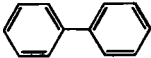
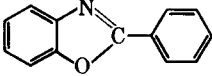
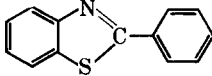
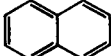


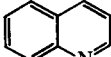
### Discussion

A pyrolysis-gas chromatography method has been developed to measure directly thermostability of volatilizable model compounds under identical conditions. Furthermore, the volatile fragments can also be isolated and identified. By this method a weighed sample is volatilized in a pyrolysis zone and the pyrolyzate vapors together with unpyrolyzed samples are swept by means of a helium flow into a temperature-programmed gas chromatograph equipped with a Disc integrator.

Comparison of the peak area due to starting material remaining unpyrolyzed at a given temperature with the peak area due to an unpyrolyzed reference sample provides the data necessary to obtain a measure of thermostability.

Two methods of evaluating data from pyrolysis-gas chromatography studies were used. In the first of these, per cent decompositions were determined at a series of temperatures, and from Arrhenius plots of the data,

TABLE I (continued)

Compound	Structure	Pyrolysis temp., °C.	Pyrolysis, %
Diphenylmethane	$C_6H_5-CH_2-C_6H_5$	"	38
Biphenyl		"	35
2-Phenylbenzoxazole		"	29
2-Phenylbenzothiazole		"	29
Naphthalene		"	29
Pyridine		"	6
Benzene		"	5
Quinoline		"	0

<sup>a</sup> 3,4,5-Triphenyl-1,2,4-triazole is completely destroyed at 750°C. However, rearrangement rather than fragmentation appears to account for the occurrence. No data for 2-phenylbenzimidazole are reported as a sample affording a single peak in the gas chromatograph could not be prepared. Liquids were measured with a Hamilton micro-liter syringe and the samples were chilled by Dry Ice packed around the storage chamber of the pyrolysis accessory until ready for thermolysis.

<sup>b</sup> 100% decomposition doubtlessly occurs at even lower temperatures.

the temperatures required for 50% decomposition of several compounds were obtained. It is possible, however, to determine relative thermal stabilities much more simply by comparing per cent pyrolysis of a number of compounds at a given standard temperature. The temperature resistance in the gas phase in inert medium of 18 model compounds related to thermostable polymer structures were determined in this way. (Table I). Because of the range of thermal stabilities encountered, it was necessary to employ two standard temperatures, 750 and 870°C. From the quantity of unpyrolyzed starting material present in the pyrolysis unit off-gases, the per cent decomposition was calculated, and the relative thermal stability of the compound in question was determined. All values listed for a given compound were confirmed by two or more determinations which agreed within 3%. Identity of pyrolysis products can be ascertained, if desired, by appropriate analysis of the eluates.

### Experimental

The apparatus used in this study consisted essentially of a modified Perkin-Elmer pyrolysis accessory unit used in series with an F & M Model 500 dual column, temperature-programmed gas chromatograph equipped with a Disc integrator (Fig. 1).

To determine temperature accurately, a thermocouple used in conjunction with a temperature potentiometer was inserted into a thermocouple well which extended directly into the heated portion of the pyrolysis tube. Samples were contained in 15–20 mg. quartz microtubes rather than combustion boats to avoid the temperature drop encountered when the 0.5-g. boats were introduced into the small furnace. Sample tubes were introduced into the furnace with the aid of a hand-operated pusher inserted through a hole bored in the rubber seal which afforded more positive control than the magnet-controlled pusher provided with the equipment. A constant voltage transformer was employed to provide maximum furnace temperature stability.

Pyrolysis of samples was accomplished as follows. The entire apparatus was flushed with helium. After the furnace was heated to the desired standard temperature and allowed to equilibrate, the sample was pushed into the heated zone with the pusher. Volatilization and pyrolysis in the vapor state were almost instantaneous, and the vapors were swept by



Fig. 1. Modified Perkin-Elmer pyrolysis accessory unit.

helium flow (2 ml./sec.) through a heated (400°C.) glass connecting tube (quartz ball to Pyrex socket at pyrolysis end and glass-to-metal seal plus Swagelock at gas chromatograph end) into the temperature-programmed (11 or 21°C./min.) chromatograph. The chromatograph port was maintained at 400°C. to prevent condensation. The most suitable packing found for the chromatograph column was 3% SF-(silicone fluid) 1093 (a General Electric product) on 70/80 mesh acid washed, DMCS-treated Chromosorb G. A 7-ft. column with this packing is suitable for programming to at least 400°C. (dual column use) and affords good separation with elution at comparatively low temperatures.

The thermal stabilities of the model compounds were determined as follows. Accurately weighed samples ( $\pm 0.02$  mg.) approximately 3 mg. in size, were weighed into quartz microtubes. The peak size due to an unpyrolyzed sample was determined (duplicates within  $\pm 3\%$ ) by thrusting the microtubes into the heated zone maintained at 550°C. (sufficient to volatilize but not decompose the sample). The area of the resulting gas chromatogram peak was measured with the aid of a Disc integrator. The furnace temperature was then raised to one of the two standard values (750 or 870°C.) and duplicate samples pyrolyzed. The quantity of unpyrolyzed starting material was determined by measurement of peak areas (duplicates better than  $\pm 3\%$ ). These data were converted to per cent decomposition and are presented in Table I.

### Conclusions

Among the more significant data regarding the relative thermal stabilities of the model compounds are the following. (1) 2,5-Diphenyl-1,3,4-oxadiazole has the poorest thermal stability by far of all the compounds studied, yet certain oxadiazole-containing polymers have been shown to possess excellent long-term stability at moderate temperatures in air. (2) The aromatic amide link is the next poorest, yet aromatic polyamides have considerable utility in air at 200–400°C. (3) The phenyl ether link is poorer than benzophenone and much poorer than diphenylmethane or biphenyl. (4) The benzoxazole and benzothiazole rings are superior to the phthalimide structure.

These data suggest that for maximum utility of the polymeric product, oxidation resistance, rather than thermal resistance only, be designed into the structure, since the factors affecting each of these modes of failure are quite different.

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The technical assistance of Mr. G. K. Ragep is gratefully acknowledged.

### References

1. I. B. Johns, E. A. McElhill, and J. O. Smith, *Ind. Eng. Chem. Prod. Res. Devel.* **1**, 2 (1962).
2. I. B. Johns, E. A. McElhill, and J. O. Smith, *J. Chem. Eng. Data*, **7**, 277 (1962).

### Résumé

Les stabilités thermiques de 18 composés modèles liés structuralement à des systèmes polymériques thermostables ont été déterminées avec précision par chromatographie gaseuse sous pyrolyse. Cette approche présente divers avantages sur les méthodes indirectes préalablement utilisées et qui mesurent des paramètres autres que les actuels au départ de matériaux qui restaient non-décomposés. Le cycle oxadiazole et le lien amide-aromatique, ont été trouvés tous deux présentant la stabilité thermique la plus pauvre en comparaison avec les autres composés étudiés. Puisque ces polymères basés sur ces deux structures sont utilisables à l'air à 200-400°C, ces résultats suggèrent que la résistance à l'oxydation plutôt que la résistance ultime purement thermique doit être cherchée dans tous les matériaux thermostables à tout usage.

### Zusammenfassung

Die thermische Stabilität von achtzehn, strukturell mit thermostabilen Polymer-systemen verwandten Modellverbindungen wurde mittels Pyrolyse-Gaschromatographie genau bestimmt. Diese Bestimmung besitzt offenbar Vorteile gegenüber den früher benützten, indirekten Methoden, bei welchen andere Parameter als der unzer-setzte Anteil des tatsächlichen Ausgangsmaterials gemessen werden. Sowohl der Oxa-diazolring als auch die aromatische Amidbindung besass im Vergleich mit anderen un-tersuchten Verbindungen nur eine geringe thermische Stabilität. Da Polymere mit diesen beiden Gruppen sich als wertvoll zur Verwendung unter Luft bei 200°C bis 400°C erwiesen haben, sprachen die Ergebnisse dafür, dass bei thermostabilen Allzweck-Materialien nach Oxydationsbeständigkeit und nicht nach höchster rein thermischer Beständigkeit gestrebt werden sollte.

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