

Thermal Degradation of Phenolic Resins. V

G. S. LEARMONTH and D. P. SEARLE, *University of Aston in Birmingham, England*

Synopsis

The effect of varying the nature of crosslinks in phenolic resins has been studied with the use of resins made from phenol, *p*-cresol, and bisphenol A. Thermal analysis showed that the methylene bridge was stronger under nonoxidative conditions than the isopropylidene linkage. The result is somewhat affected by the degree of crosslinking.

Introduction

We have previously reported the effect of high temperature on phenolic resins and reviewed the work of previous authors.¹ We have found that thermogravimetric analysis (TGA) readily gives consistent results with phenolic resins, but is less sensitive than differential thermal analysis (DTA), which is, however, more subject to procedural variations. We have also reported the use of isothermal vacuum pyrolysis (IVP) in studying the production of carbon by pyrolysis of related resins.²

It is known that phenolic resins degrade in three recognizable steps: postcuring, thermal re-forming, and ring-stripping.³ The first stage obviously is controlled by the proportion of unreacting (methylol) groups present; the last stage, by the elemental composition of the polymer entering it. The course of the middle stage depends on the formation of free radicals by thermal fission (homolytic) processes. A radical so formed may abstract hydrogen from the polymer, becoming saturated, and will then enter the volatile fraction resulting from the pyrolysis. On the other hand, a radical may react with another to become part of a condensed ring structure and then part of the carbon residue in the last stage of pyrolysis.

We are concerned with manipulating the middle stage of the pyrolysis to obtain a higher proportion of carbon under nonoxidative conditions. The present work involved predetermination of the position and nature of some crosslinks by the use of bisphenol A, which has a central isopropylidene bridge and four free ring positions placed ortho to the phenolic hydroxyl group. At the same time we tried to vary the distance between such linkages by the interpolation of *p*-cresol in the resin network.

Conley and Bieron showed⁴ that under oxidative conditions bisphenol A-formaldehyde resins degraded at half the speed of phenol resins, because of protection of the central linkage by the geminal methyl groups. They also showed that the normal mode of degradation of phenolic resins is thermo-

oxidative even in an inert atmosphere. For these reasons we believed that the pyrolysis of bisphenol resins under nitrogen would give a higher yield of carbon than is achieved with phenol resins. The use of bisphenol should give fragments during pyrolysis large enough to give a relatively long residence time in the pyrolysis zone with consequent retention of a higher proportion of the carbon in the original resin.

It is known^{4,5} that the properties of phenol-formaldehyde networks are highly affected by the extent to which the crosslinking reaction has occurred. Hence all our resins were cured by a rigorous procedure intended to ensure comparable crosslink density except when this was intentionally varied.

The degradative processes were followed by TGA measurements and in some cases by isothermal vacuum pyrolysis.

Experimental

The conditions of experimentation are given in Table I.

TABLE I

Resin No.	Phenol, g	37% aq. formalin, g.	4 <i>N</i> aq. NaOH, ml	Reactants, molar ratio
I	phenol, 94.0	102.5	20	1:1.25
II	phenol, 94.0	164.0	20	1:2.0
III	bisphenol, 114.0	61.5	100	1:1.50
IV	bisphenol, 114.0	123.0	100	1:1.30
V	bisphenol: 57.0			
	<i>p</i> -cresol: 54.0	164.0	60	1:2:8
VI	bisphenol: 22.8			
	<i>p</i> -cresol: 86.5	164.0	36	1:8:20

If curing is complete, the phenol-formaldehyde (1:1.25) and bisphenol-formaldehyde (1:1.50) resins have the same crosslink density.

Samples for analysis were prepared by curing all the resins under the same conditions. To avoid difficulties due to different reactivities of the various resins used a very long curing time was given (Table II), and it was assumed that even slowly reacting resins would be fully crosslinked by this procedure. In addition, to the same end, samples were powdered to pass 100-mesh B S and to be retained on 150-mesh before postcuring. A nitrogen atmosphere was maintained over the resins throughout curing.

The equipment used for both TGA and IVP was the thermobalance Mk I made by Linseis (Selb, Bavaria). The procedures used do not call for detailed comment, and the following main conditions were used (Table III).

TABLE II

	Successive time and temperature conditions		
Cure cycle	80°C, 2 hr	100°C, 2 hr	120°C, 2 hr
Postcure cycle		180°C, 24 hr	

TABLE III

TGA	Rate of heating, 5°C/min or 10°C/min Sample weight, 0.100 g
IVP	Temperature, 500°C or 900°C Sample weight, 0.050 g

To avoid loss by "spattering" during analysis⁶ samples were contained in either a small cylindrical silica crucible with a tight-fitting sintered silica lid or a silica spoon covered by platinum foil.

Results

The results of the experimentation are given in Table IV. See also Figures 1 to 4.

Discussion

The results of these experiments are quite clear qualitatively. Both the thermograms (TGA) and the residual carbon (IVP) measurements show

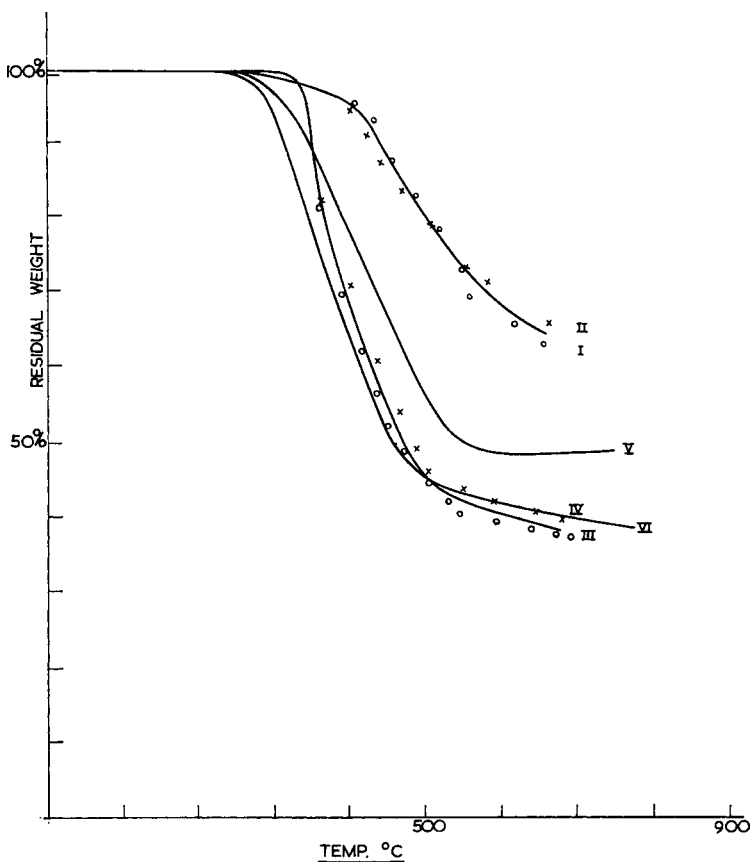


Fig. 1. Thermogravimetric analysis of Resins I-VI: heating rate, 50°C/min.

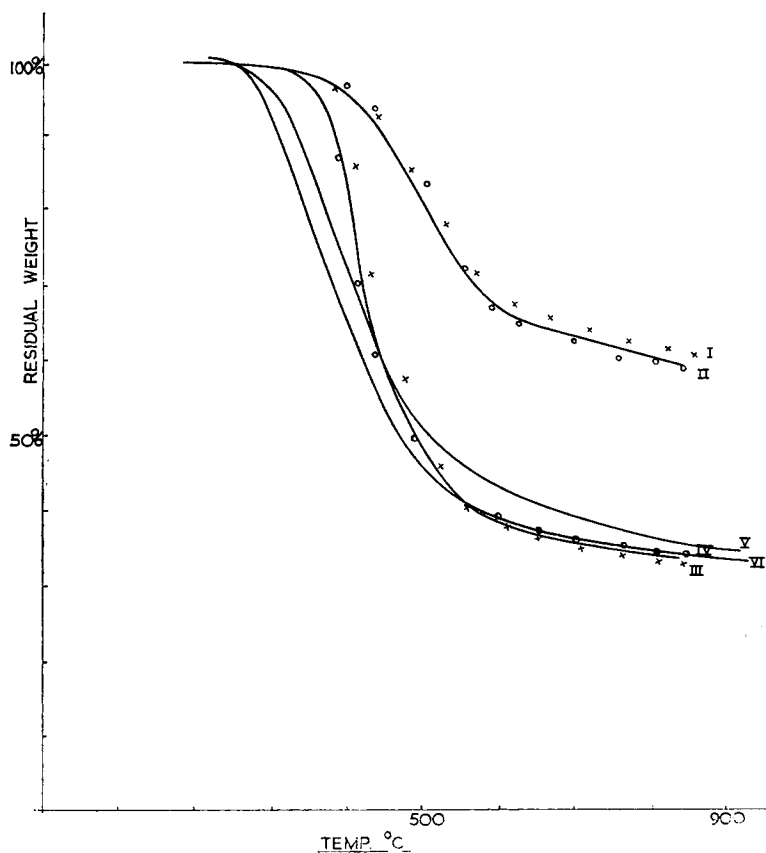


Fig. 2. Thermogravimetric analysis of Resins I-VI: heating rate, 10°C/min.

that the phenol resins give a much higher yield of residual carbon than any which contain bisphenol. The activation energies derived from the TGA suggest that this is due to decrease in overall stability: that is, under the conditions used the isopropylidene linkage is less stable than the methylene bridge.

TABLE IV

Resin No.	Thermogravimetric analysis			Isothermal vacuum pyrolysis, resid. C yield, %	
	Resid. C yield, %		E_A^a	500°C	900°C
	5°C/min	10°C/min			
I	60	60	15.0	72	62
II	60	60	17.9	71	58
III	38	35	12.8	36	32
IV	40	35	11.9	40	34
V	46	40	10.3	45	34
VI	36	35	8.8	39	31

^a Procedural activation energy.

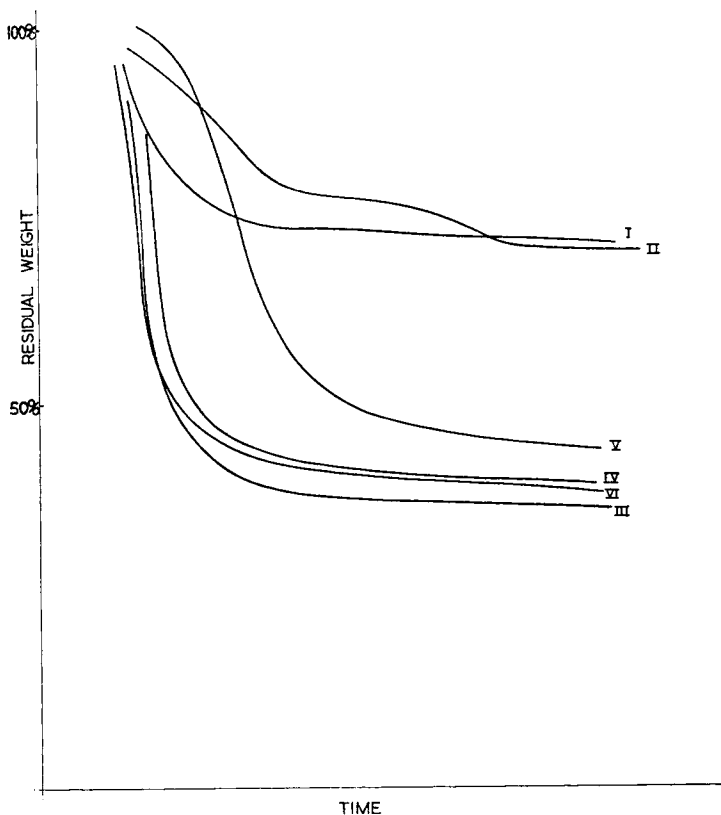
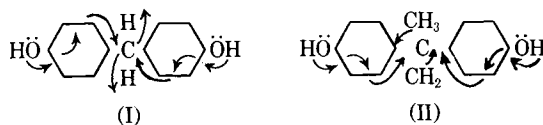
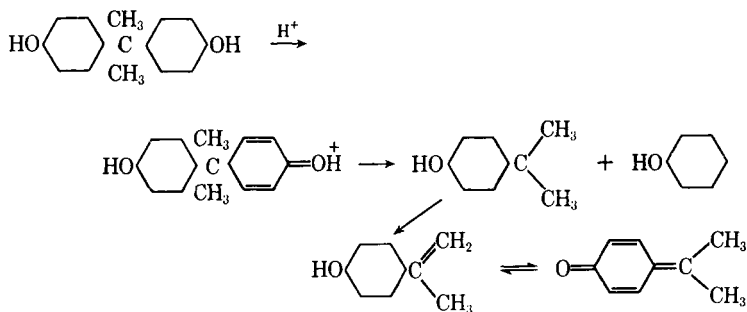


Fig. 3. Isothermal vacuum pyrolysis at 500°C.



It is known that oxidation fission of the methylene bridges takes place; however, the thermal homolytic fission of the aromatic and aliphatic carbons is less favored by the characteristic bisphenol structure. In structure (II) the inductive effect of the geminal methyl groups and the mesomeric effect of the phenolic nuclei are in an opposite sense. This will lead to an increase in the bond length between aromatic and aliphatic carbon, with a concomitant decrease in bond energy. Thus, the thermal homolytic fission of this particular bond will be favored in structure (II) relative to structure (I).

Bisphenol A-formaldehyde polycondensates may also undergo thermal degradation by a heterolytic process. At elevated temperatures bisphenol A is itself unstable in the presence of acidic catalysts and will undergo heterolytic cleavage as follows:



Thus, phenolic compounds formed by homolytic fission during the thermal degradation of the polycondensate possibly act as acidic catalysts and cause further heterolytic cleavage of the isopropylidene linkages in the resin structure.

Conley and Bieron⁴ found that varying the ratio of phenol to formaldehyde in the resins had little effect on weight loss parameters obtained from

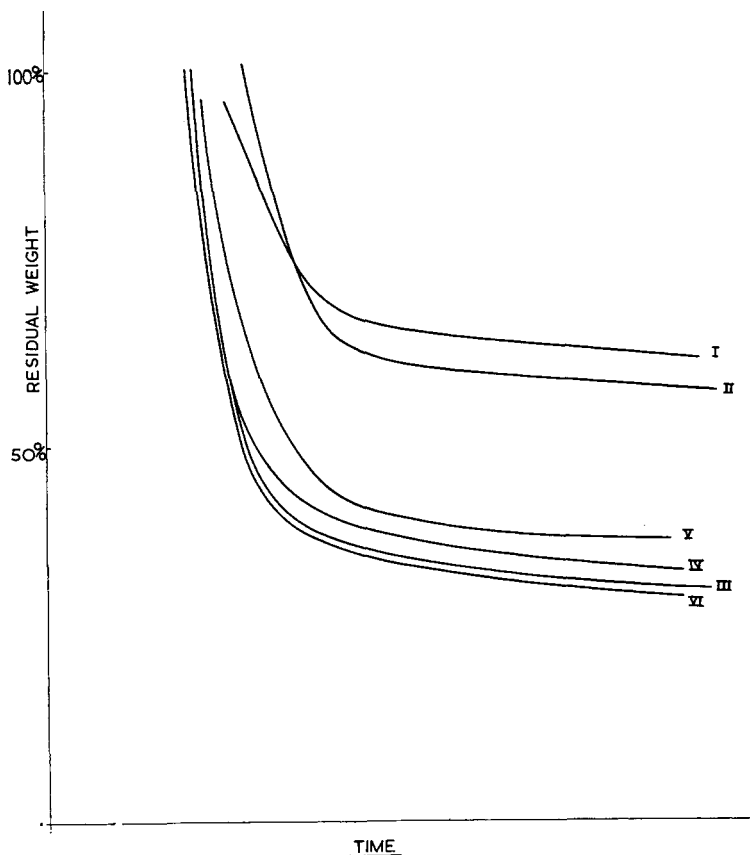


Fig. 4. Isothermal vacuum pyrolysis at 900°C.

TGA experiments. They therefore attributed the high thermal stability of phenol-based resins to the inherent stability of the dihydroxydiphenylmethane unit as a whole.

There are two anomalies in the TGA and IVP measurements of residual carbon. There is a slight difference between the results from phenol-formaldehyde resins with ratios of phenol to formaldehyde of 1:1.25 and 1:2.0, respectively. The activation energies calculated show a marked increase from 15.0 to 17.9. There is little difference between bisphenol resins with varying ratios, but those containing a small proportion of *p*-cresol consistently gave a higher carbon yield and apparently slower degradation than those from bisphenol alone. When the proportion of *p*-cresol was increased, the results resembled those from bisphenol alone. We would interpret both these results as indications of variation in the proportion of potential crosslinks actually achieved, owing to variation in steric factors.

Thus, phenol resins are known to crosslink easily in spite of having a short, stiff chain structure, but little is known about the true extent of crosslinking actually achieved, and it is likely that after a small amount of crosslinking the network is too stiff to allow further reactive groups to come into favorable positions for reaction. When bisphenol is used, steric hindrance is increased because of the larger and stiffer network unit and also its higher functionality. The introduction of *p*-cresol together with bisphenol may therefore give greatly increased steric freedom to the growing network and allow higher achievement of crosslinks. When high proportions of *p*-cresol are used, however, the density of crosslinking will decrease again because of low functionality of the cresol.

The activation energies quoted by us and others have limited useful meaning. As the overall reaction has three main, widely differing stages, an activation energy covering the whole is not likely to be interesting. Further the dynamic procedures used are highly affected by variations in procedure. We believe, therefore, that it will be necessary to examine the several stages by more rigorous isothermal techniques to make further analysis of the kinetics possible.

References

1. G. S. Learmonth and G. Nabi, in press.
2. G. S. Learmonth and P. D. Osborn, *J. Appl. Polymer Sci.*, in press.
3. D. W. van Krevelen, *Coal*, Elsevier, Amsterdam, 1964, p. 466.
4. R. T. Conley and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 171 (1963).
5. J. D. Flynt, *Plastics Technol.*, **2**, 577 (1956).
6. S. L. Madorsky, *Modern Plastics*, **38**, 134 (1961).

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