

Studies on Phenoplasts by Pyrolysis Gas Chromatography

NASER SHARIFI and MOHAMMAD R. TIRGAN,
*Department of Chemistry, Faculty of Science,
Tehran University, Tehran, Iran*

Synopsis

A new technique of pyrolysis gas chromatography was used for the investigation of pyrolysis of phenol formaldehyde polycondensates and useful information about the nature of the chemical bonds and their relative strengths in these polycondensates were obtained. It was also found that by identifying only one of the pyrograms of a series of homologous compounds produced by the pyrolysis of polycondensates, all the pyrograms of the series were easily characterized and correspondingly the number of components in each series were identified.

INTRODUCTION

An investigation of the manner in which the chemical bonds of a phenoplast specimen are broken during consecutive pyrolysis allows the determination of the nature of the broken bonds, as well as their relative strengths. From the diagram of the variation of the pyrogram (chromatogram) peak area, corresponding to each component (compound), versus temperature, it is possible to identify the peaks representing homologous compounds possessing common functional groups. With the aid of such a diagram and the assignment of only one of the peaks, it is possible to identify all of the peaks belonging to the same group.

EXPERIMENTAL

Preparation of Resins

Resins were prepared from the condensation of phenol, any of the cresols (*o*-, *m*-, *p*-) or mixtures of *o*- and *p*-cresol of various proportions, with formaldehyde in a molar ratio of 2 to 1.6, using sulfuric acid as a catalyst. The products were purified of any traces of water, catalyst, and reactants.¹⁻⁵

GC Instrument

The pyrolysis products were identified by a GC instrument which operates with a flame ionization detector. The column used was 6 ft long, i.d. $\frac{1}{8}$ in., packed with a mixed phase of 10% DC/200 silicone oil and 5% DC/11 on Chromosorb W (60-80 mesh). The column was heated from 60° to

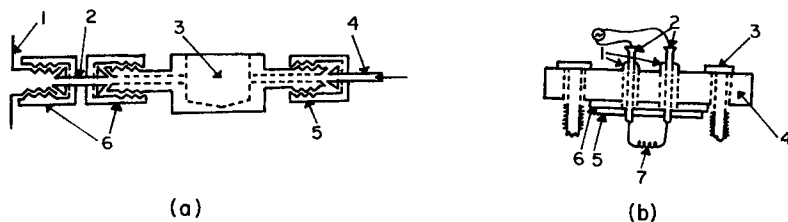


Fig. 1. (a) (1) Injector; (2) copper tubing; (3) pyrolysis chamber; (4) Teflon tubing for the carrier gas; (5) Teflon fittings; (6) joints. (b) (1) Teflon coating; (2) copper electrodes; (3) screws; (4) wooden body of the holder; (5) Teflon coating; (6) rubber sheet; (7) filament coil.

210° C by linear temperature programming. The injector temperature was set at 240°C. The carrier gas (N₂) was flowing at the rate of 22 ml/min; hydrogen was flowing at 25 ml/min. The chart speed was 38 cm/hr.

Pyrolysis System

The pyrolysis system⁶ used (similar to that of Reference 8) functioned via Ni-Cr coil filament (80 mm long, 0.5 mm in diameter). The coil resistance was 0.47 ohm, and its inner diameter was 2.8 mm, which was heated electrically. The pyrolysis temperature of the system was calibrated by using the melting points of 1-mg samples of pure inorganic salts, at different currents.^{7,8,9} The pyrolysis chamber,¹⁰ which was heated up to 200°C, was made of brass which is shown schematically in Figure 1a and 1b (bottom part is not shown).

RESULTS AND DISCUSSION

To avoid any trace of impurities, the coil filament was heated at 1000°C for 30 sec under nitrogen, and then cooled, and a sample of ≈ 4 mg was placed¹¹ inside the coil and heated for 15 sec at 200°C to remove impurities. Each sample was heated from 300° to 900°C at 100°C intervals for 15 sec, and the corresponding pyrograms (chromatogram) were obtained at each temperature. Figures 2 to 7 show such pyrograms. By plotting the area of each peak against the temperature, diagrams of the type shown in Figures 8 and 9 are obtained (the diagrams representing the pyrolysis of the phenol-formaldehyde resin at 300° and 400°C are not depicted).

Two series of curves can be distinguished in these diagrams: (a) those related to the phenolic components, whose maximums occur around 600–620°C, and (b) those belonging to aromatics with their characteristic maximums centering around 720–730°C. A tailed curve with a maximum located at higher temperatures can as well be seen, which belongs to small volatile hydrocarbons.

With regard to the first series, phenol, the major product of pyrolysis, appears initially at $\approx 500^\circ\text{C}$, and the amount *o*- and *p*-cresol and other phenols are negligible. As the temperature is raised, other phenols start to appear. In general, the amount of phenols, which are products of methyl-

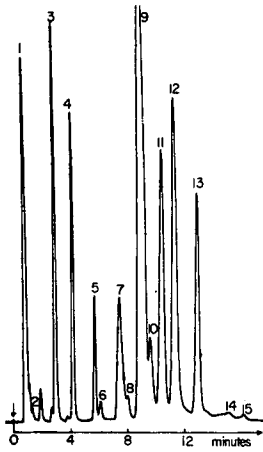


Fig. 2. Pyrogram of *o*-cresol-formaldehyde (acid catalyst).

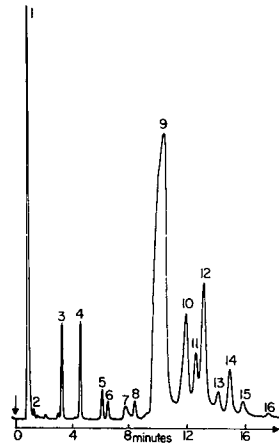


Fig. 3. Pyrogram of *m*-cresol-formaldehyde polycondensate (acid catalyst).

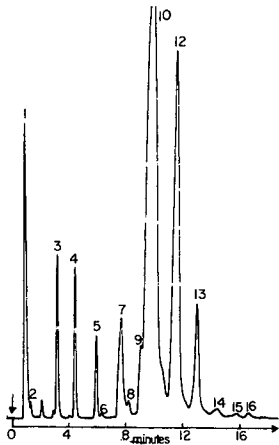


Fig. 4. Pyrogram of *p*-cresol-formaldehyde polycondensate (acid catalyst).

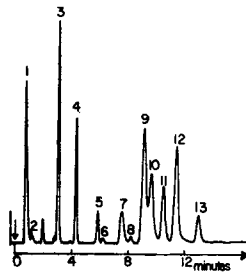


Fig. 5. Pyrogram of *o*-cresol, *p*-cresol (75:25)-formaldehyde polycondensate (acid catalyst).

ene bond cleavage, passes through a maximum and then drops rapidly as the thermal degradation proceeds gradually.

At 550°C, aromatics and other small hydrocarbons start to appear, their thermal degradation going through a maximum with increase in temperature. Production of aromatics involves the separation of —OH groups from the aromatic rings besides the cleavage of the methylene bridges. Their maximum, therefore, could be attributed to the rupture of the Ar—OH bond.

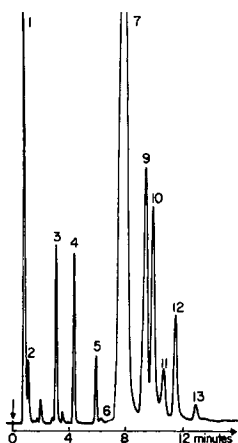


Fig. 6. Pyrogram of phenol-formaldehyde polycondensate (basic catalyst).

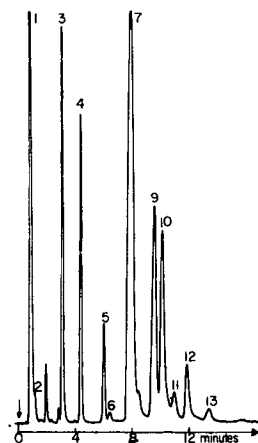


Fig. 7. Pyrogram of Bakelite (basic).

Methane, the predominant species among the small hydrocarbons, has its maximum of production at a temperature higher than those of aromatics. The charred residue which remains after each test reveals the breaking of C—H bonds and the transfer of hydrogen and its adoption by the free radicals produced during the pyrolysis process.

CONCLUSIONS

With diagrams of the type represented in Figures 8 and 9 and a knowledge of only the curve of one of the phenols and one of the aromatics, it is possible to identify all the respective peaks in the diagram. This can be accomplished by determining the series of curves on the diagram to which the pyrogram peaks belong. It is also possible to explore the nature of the broken bonds during the pyrolysis, as well as the appropriate temperatures of the bond cleavage, which allows one to compare their relative strengths. An investigation of the resin obtained from a mixture of *o*- and *p*-cresol (in a proportion of 75 to 25) and formaldehyde, as shown in Figure 9, supported our predictions.

From the number of the curves related to each series, one can find the number of homologous compounds. For instance, all the pyrolysis products whose maximums fall on the left side of the diagram (Figs. 8 and 9) and are located in the same thermal range represent the phenolic compound, while those on the right with their maximums in another region represent aromatics.

With application of the gas chromatograph-mass spectrometer (GC-MS) and with the aid of such diagrams, each constituent of the pyrogram, isomers, and their molecular structure can be identified (GC-NMR is helpful for the isomer identification).

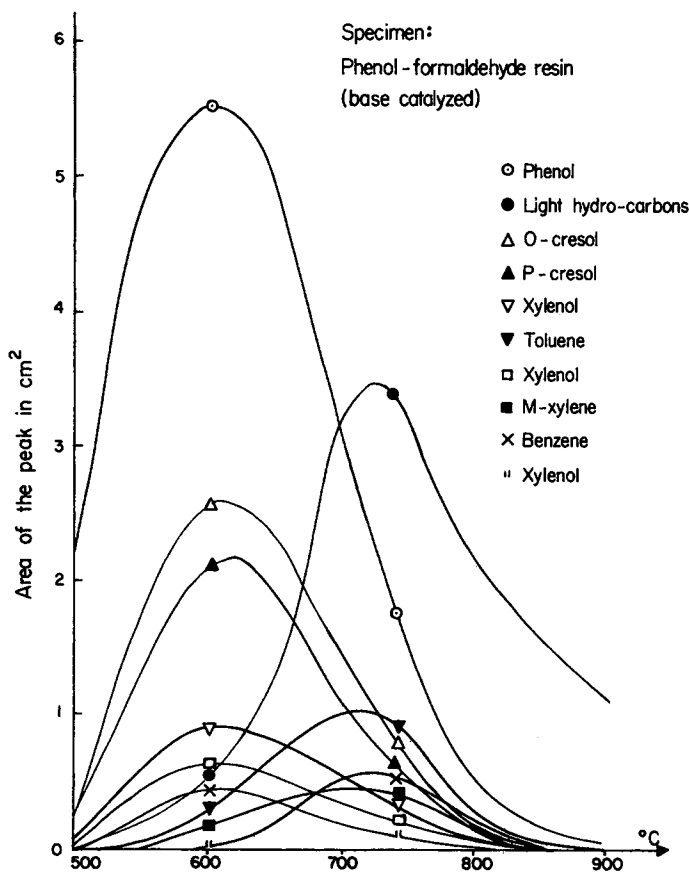


Fig. 8.

Infrared spectroscopy does not seem to be a promising method for the analysis of the pyrolysis products, because in combined GC-IR equipment, phenolic OH may be determined only under certain limited conditions (due to lack of knowledge about the presence or the absence of hydrogen bonding and the shift of the absorption band as a result of neighboring groups, which are even more complicated in phenolic compounds). On the other hand, the above diagram, as noted, yields the total number of phenols as well as aromatics.

The diagrams of *o*- and *p*-cresol-formaldehyde resin, as depicted in Figure 9, consist of two series of curves: (1) those whose maximums are in the range of 450–470°C; and (2) those whose maximums are in the 590–610°C region. By comparing the respective diagrams of the phenol-formaldehyde resin with those of *o*- and *p*-cresol-formaldehyde resin, it is found that the corresponding maxima of the latter are located about 140°C below those of the former, which simply reflects their structural differences, i.e., the presence of methyl groups (instead of methylene bridges in the three-dimensional network of phenol formaldehyde) which results in a linear polymer;

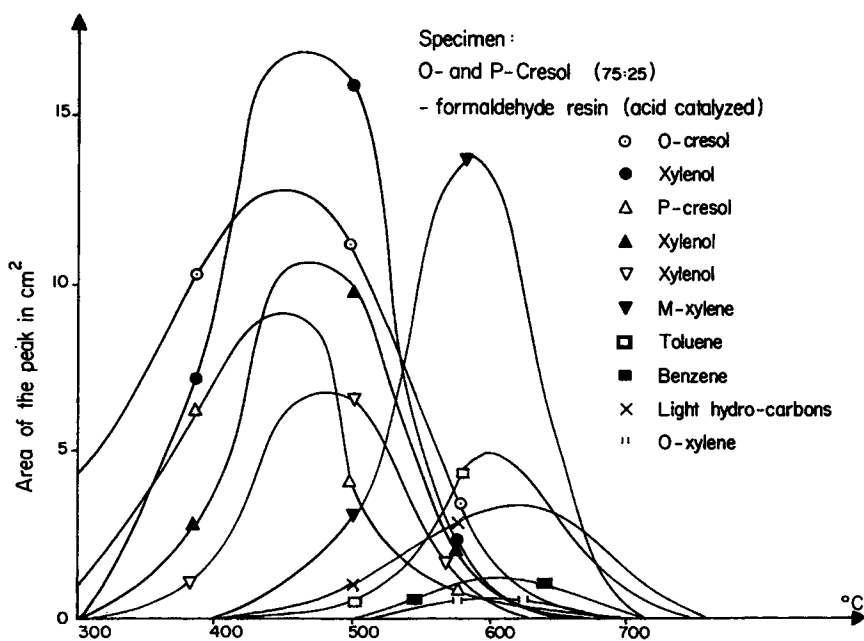


Fig. 9.

lack of molecular orientation due to the absence of symmetry in the cresol units in the polymer chain; and finally, most important of all, the inductive effect of methyl groups which causes the formation of more stable free radicals compared to those formed from the cleavage of the methylene groups in the phenol-formaldehyde resin, which in turn results in faster degradation of the *o*- and *p*-cresol formaldehyde resin. Besides, the decrease in the phenol content and the increase in the phenolic derivative contents in the pyrolysis product of the *o*- and *p*-cresol-formaldehyde resin supports the notion that the Ar—CH₃ bond is stronger than methylene bonds.

References

1. H. Staudinger and A. Steinhoffer, *Ann.*, **517**, 35 (1935).
2. F. Midgley and A. L. Henne, *J. Amer. Chem. Soc.*, **51**, 1215 (1929).
3. W. H. T. Davison, S. Slaney, and A. L. Wragg, *Chem. Ind.*, 1956 (1954).
4. J. Haslam and A. R. Jeffs, *J. Appl. Chem.*, **7**, 24-1957).
5. G. F. Dalelio, *Experimental Plastics and Synthetic Resins*, Wiley, New York, 1960.
6. M. R. Tirgan and N. Sharifi Sandjani, M.S. Thesis Dept. of Chemistry, Faculty of Science, Tehran University, 1969.
7. J. Zulaica and G. Guichon, *Bull. Soc. Chim. France*, 1343 (1966).
8. C. J. Karr, J. R. Comberati, and P. A. Estep, *Fuel*, **42**, 211 (1963).
9. W. M. Barbour, *J. Gas Chromatogr.*, **3**, 228 (1965).
10. W. Simon and H. Giacobbo, *Chem.-Ing.-Tech.*, **37**, 709 (1965).
11. C. C. Luce, E. F. Humphrey, L. V. Guild, H. H. Noirish, J. Coull, and W. W. Castor, *Anal. Chem.*, **36**, 482 (1964).
12. G. Guichon and J. Henniker, *Brit. Plast.*, **37**, 74 (1969).

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