Combined Pyrolysis and Radiochemical Gas Chromatography for Studying the Thermal Degradation of Epoxide Resins and Polyimides. II. Degradation of Polyimides.

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Synopsis

The thermal degradation of aromatic polyimides in nitrogen at 700°C was studied using pyrolysis gas chromatography, infrared spectroscopy, and radiochemical techniques. Degradation mechanisms were postulated to account for the breakdown products found and to explain variations in the ratio of carbon monoxide to carbon dioxide.

INTRODUCTION

The Thermal Degradation of Aromatic Polyimides in Nitrogen

Aromatic polyimides (Fig. 1) have been well publicized as "high temperature polymers,"[1-5] and although their behavior at high temperatures has been studied[1-10] the mechanism of their thermal degradation still needs further clarification.

A number of workers have carried out thermogravimetric analyses on polyimides in air and in various inert atmospheres.[1-3, 6-10] Bruck[7] and Heacock and Berr[2] have collected and identified volatile degradation products, and Bruck has also investigated the nature of the "tar" and the "char" which are formed on pyrolysis in inert atmospheres.[7,8] As a result of these studies, it is known that aromatic polyimides begin to break down between 450° and 500°C in air and between 500° and 600°C in inert atmospheres, depending on the nature of R (Fig. 1) and on the purity of the cured polymer.

The major degradation products recorded at temperatures of 500°–600°C are carbon monoxide and carbon dioxide, but the ratio of these gases varies with pyrolysis methods and the sample purity. In addition, hydrogen, methane, ammonia, water, hydrogen cyanide, and benzene are formed, and there is evidence for phenol and benzonitrile in very small quantities.

Little effort has been made to establish the mechanism of the formation of these products, but some suggestions have been put forward. Bruck[7] suggests that carbon monoxide is evolved as a result of primary cleavage of
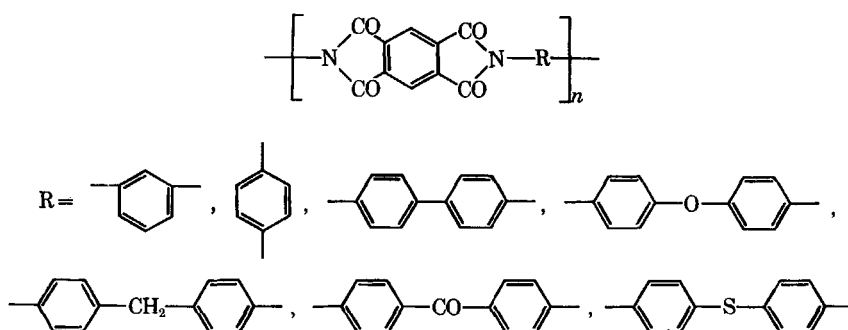
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Fig. 1. Aromatic polyimides.

carbonyl carbon–nitrogen bonds followed by cleavage of aromatic–carbonyl carbon bonds. He also suggests that carbon dioxide is formed by elimination from polyamic acid remaining as impurity in the polyimide.
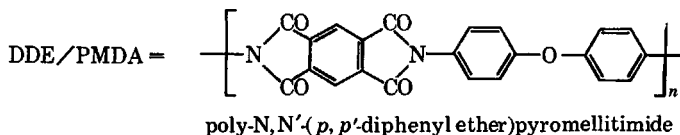
The quantities of carbon dioxide found seem too large to be accounted for in this way, however, and it seems likely that carbon dioxide is also eliminated from imide groupings. In fact, Cotter and Dine-Hart[11] found that carbon dioxide is a major breakdown product when aromatic imides are subjected to electron impact. Since it has been established that strong similarities often exist between the thermal breakdown of molecules and breakdown brought about by electron impact in the mass spectrometer,[13–15] the work of Cotter and Dine-Hart[11] may be taken as strong evidence for the evolution of carbon dioxide from imide groupings in polyimides at high temperatures.
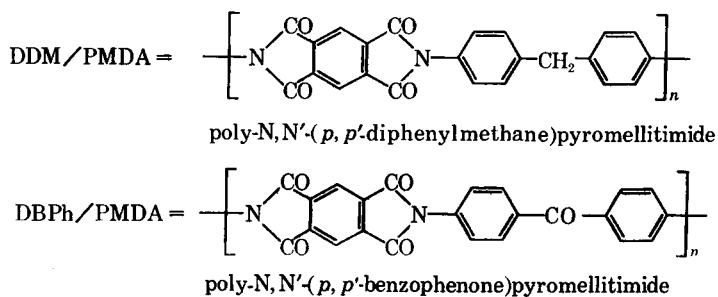
EXPERIMENTAL

This paper describes work using hot-wire pyrolysis followed by gas chromatography as the method of analyzing the degradation of polyimide film. The methods were those described for the degradation of epoxide resins in part I of this series and essentially involved a scintillation counter in the gas stream to detect radioactive breakdown products produced by the degradation of ^{14}C-labelled polyimides. By this means the exact origin of breakdown products in the original molecule could be assessed.

Materials

The three different polyimides used in this work were supplied by Wright and Dine-Hart of the Royal Aircraft Establishment, Farnborough, Great Britain, in film form. The samples are referred to as DDE/PMDA, DDM/PMDA, and DBPh/PMDA:

poly-N,N'-(p, p'-diphenyl ether)pyromellitimide

DDM/PMDA =

poly-N,N'-(p, p'-diphenylmethane)pyromellitimide

DBPh/PMDA =

poly-N,N'-(p, p'-benzophenone)pyromellitimide

A sample of DDE/PMDA was prepared in these laboratories using pyromellitic dianhydride (PMDA) which was ^{14}C-labelled at the carbonyl groups; this sample is referred to as DDE/PMDA*.

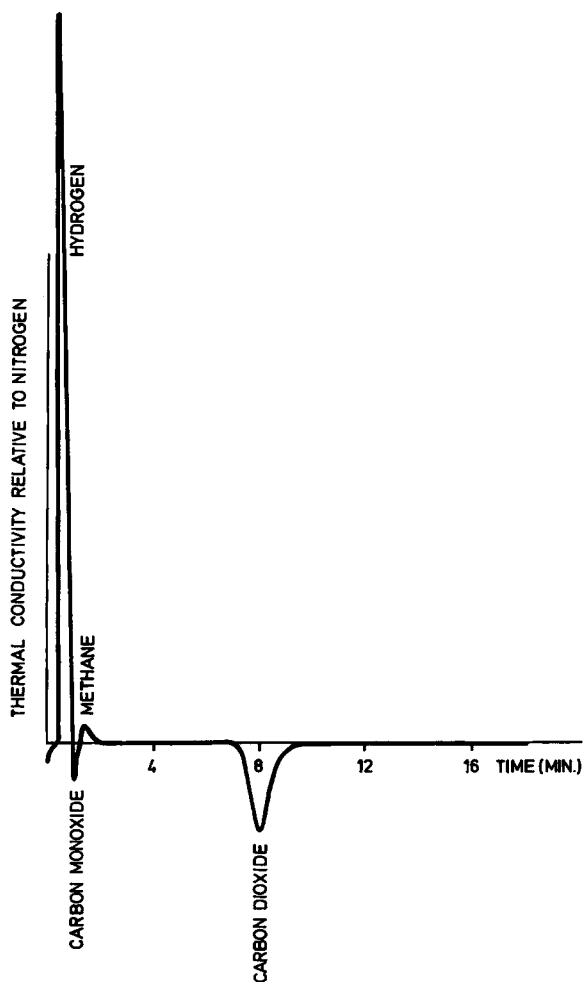Fig. 2. Gaseous degradation products of DDE/PMDA: column, silica gel; oven temp 50°C, pyrolysis temp 700°C, carrier gas N_2, 40 ml/min.

Experimental details for the preparation of these materials are reported in the literature.[15] The sample of ^{14}C-labelled PMDA was prepared by Yarsley Research Laboratories, Chessington, Surrey, Great Britain.

RESULTS

Polyimide samples were pyrolyzed on an electrically heated nichrome filament in a stream of nitrogen which was also the carrier gas for the gas chromatograph. A fixed pyrolysis temperature of 700°C was used, except when the effect of pyrolysis temperature on the relative quantities of volatile degradation products was being studied. The sample size was varied between 5 and 30 mg, with no apparent change in the relative amounts of the pyrolysis products. A variety of columns, oven temperatures, and carrier gas flow rates were used for separating pyrolysis products. Typical programs are shown in Figures 2–4 together with the column details and operating conditions.

Separated degradation products were identified by their retention times and by infrared spectroscopy, where possible. The ^{14}C-labelled CO and CO_2 evolved from DDE/PMDA* were detected and estimated using a flow-through scintillation counter and integrator connected to the exit port of the gas chromatograph (see Figure 6).
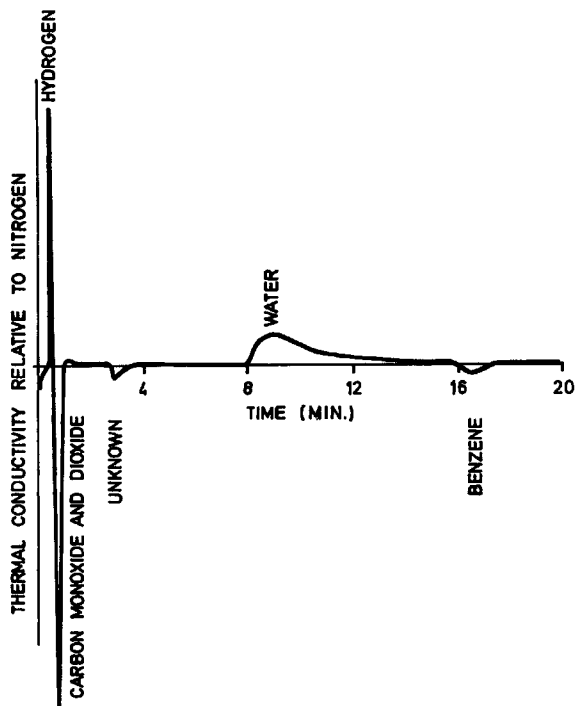

Fig. 3. Low-boiling degradation products of DDE/PMDA: column, 7,8-benzoquino-line/60–80 mesh Chromosorb P, 15/85; oven temp 50°C, pyrolysis temp 700°C, carrier gas N_2, 40 ml/min.
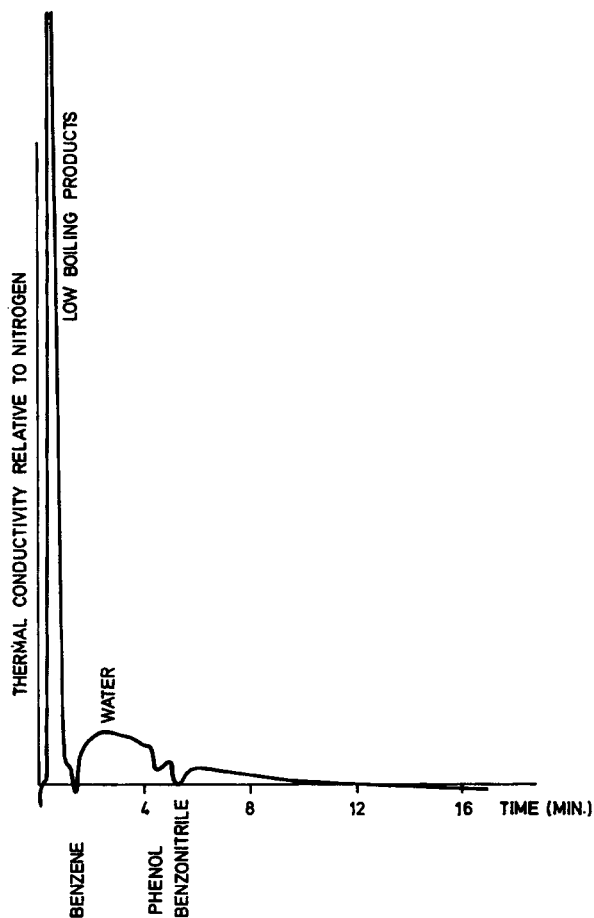
Fig. 4. Higher-boiling degradation products of DDE/PMDA: column, Apiezon L/60–80 mesh Chromosorb P, 10/90; oven temp 150°C, pyrolysis temp 700°C, carrier gas N₂, 40 ml/min.

Volatile Degradation Products

The volatile degradation products identified by us for the three polyimides are listed in Table I. Possible mechanisms for their formation are suggested at the end of this paper.

High-Boiling Degradation Products

The high-boiling degradation products or tars which condensed on the walls of the pyrolysis tube were dissolved in acetone and transferred to an agate mortar. The acetone was evaporated and the tars were ground with dried KBr and pressed into discs for infrared analysis. The IR spectra of these tars suggest that the tars consist largely of short fragments of polyimide chains, probably with N—H, —NH₂, or —C≡N endgroups. The
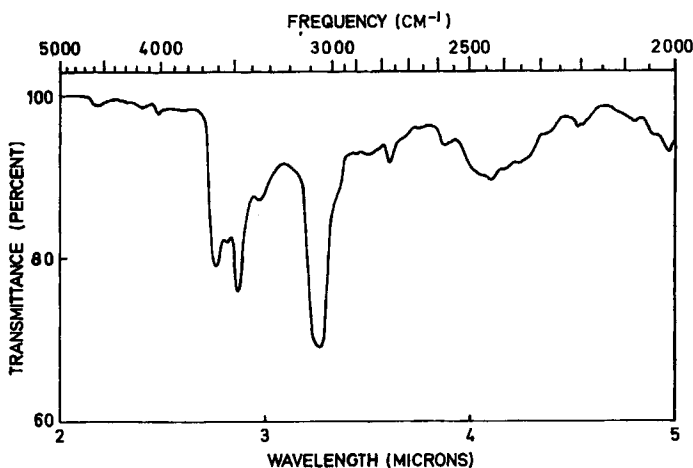
Fig. 5. Infrared spectrum of DDE/PMDA between 2 and 5 μ.

characteristic imide absorptions at 1780 cm^{-1} and 720 cm^{-1} are still discernible in all three tar spectra. The principal absorptions of DDE/PMDA at 1725, 1500, 1375, and 1230 cm^{-1} are still present in the DDE/PMDA tar, and similarly the principal absorptions of the other tars correspond to absorptions of the original polymers. All three tars have an absorption band at 3350 cm^{-1} which corresponds to the N—H stretching frequency and suggests N—H or possibly —NH$_2$ endgroups. This peak is much smaller in the spectra of the original polymers and should not be confused with the O—H bands at 3450 and 3600 cm^{-1}, which are discussed later. The tars also have an absorption at 2250 cm^{-1} which may be due to —C≡N endgroups.

TABLE I
Volatile Degradation Products of Aromatic Polyimides

DDE/PMDA	DDM/PMDA	DBPh/PMDA
Hydrogen	Hydrogen	Hydrogen
Carbon monoxide	Carbon monoxide	Carbon monoxide
Methane	Methane	Methane
Carbon dioxide	Carbon dioxide	Carbon dioxide
Unknown	Unknown	Unknown
(HCN?)	(HCN?)	(HCN?)
Water	Water	Water
Benzene	Benzene	Benzene
Phenol	Toluene	Benzonitrile
Benzonitrile	Benzonitrile	

Solid Residues or Chars

The nature of the solid residue that remained on the pyrolyzer wire after pyrolysis was studied by weighing, elemental analysis, and infrared spectroscopy.
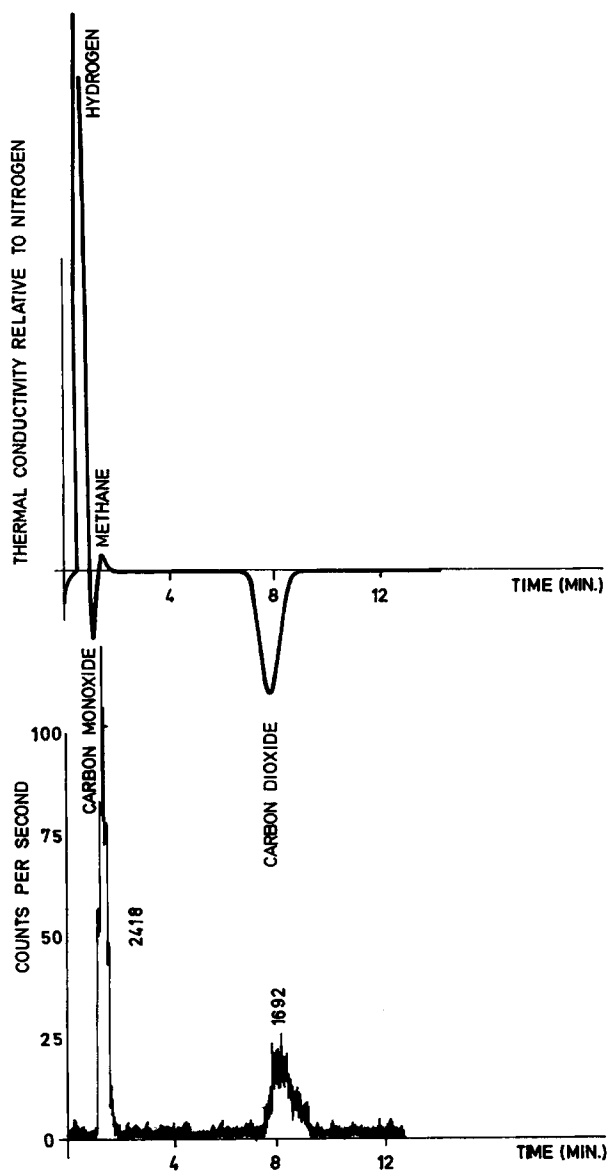
Fig. 6. Pyrogram and "radiopyrogram" for DDE/PMDA*: column, silicon gel; pyrolysis temp 700°C, oven temp 50°C, carrier gas N_2, 40 ml/min.

Approximate weight loss experiments showed that the polyimides all lost about 40% weight on complete pyrolysis at 700°C in nitrogen. A typical elemental analysis for a DDE/PMDA char gave C, 78.8%; H, 2.79%; N, 5.87%; O (by difference), 11.54%. The original DDE/PMDA requires C, 69.1%; H, 2.62%; N, 7.33%; O, 20.94%.

The elemental analyses of the chars were consistent with the loss of large quantities of CO and CO_2 and also indicated a considerable loss of nitrogen. The quantities of benzonitrile detected among the volatile products were not sufficient to account for this loss, and since the predominant odor of the volatiles was that of a cyanide, it seems likely that some nitrogen was lost as HCN although the latter was not positively identified in this work.

DISCUSSION

In any discussion of the degradation of polyimides one must consider that, depending on the curing sequence, there is a varying proportion of uncyclized material, as indicated below:
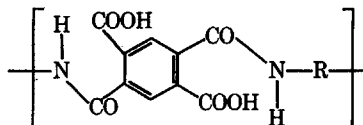

Attempts have been made to estimate the number of uncyclized units by consideration of the infrared spectra of cured polyimide films. NH (stretching) and carboxylic OH (stretching) vibrations are at 3350 and 3600 cm^{-1}, respectively (Fig. 5). Dine-Hart[16] has estimated that, based on the intensity of the —N—H band and assuming the polymer has no terminal NH_2 groups, there is one uncyclized ring per nine polymer repeat units. Calculations based on the intensity of the carboxyl OH band suggest one uncyclized ring per eight polymer units.[16] Uncyclized rings may be expected to make a special contribution to the degradation reactions of polyimides.

As has been stated, CO and CO_2 are the major products of pyrolysis of polyimides; the ratio CO/CO_2 appears to vary with pyrolysis conditions and purity. In the present work the CO/CO_2 ratio was found to vary with pyrolysis temperature. Samples of polymer, previously dried at 300°C, pyrolyzed at 600°C, gave a CO/CO_2 ratio of 1.66, but pyrolyzed at 700°C they gave a ratio of 1.42. The effect of water vapor on the CO/CO_2 ratio is not entirely clear, but there is some suggestion that this may be affected by the moisture content of the film.

In view of the large amounts of CO_2 generated, it is reasonable that CO_2 cannot originate in the uncyclized units alone.

Polyamic acid units may be expected either to dehydrate or decarboxylate on heating (I), but when water is present it is possible that hydrolytic scission, followed by decarboxylation, will occur (II):
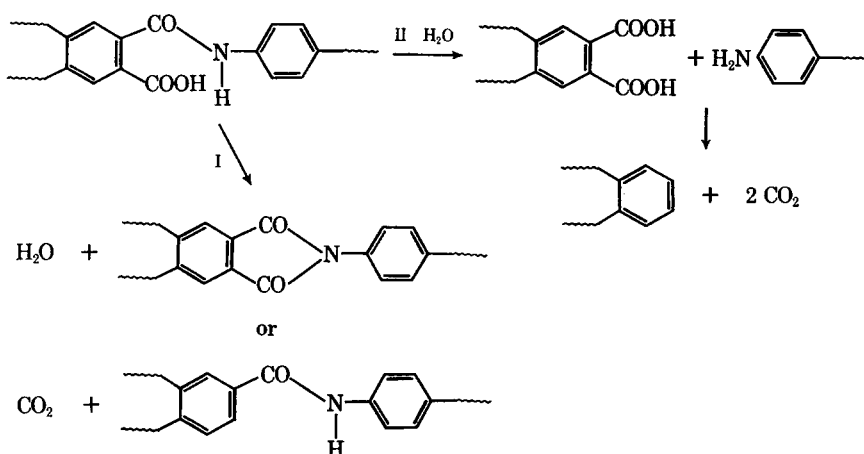
Analysis of the chars indicated a high percentage of the carbonyl groups were lost on pyrolysis, so that it must be concluded that imide rings, as opposed to polyamic acid groups, yield both CO and CO_2 when low CO/CO_2 ratios are recorded.

The following degradation reactions are suggested to explain the findings of our own work and that of others:
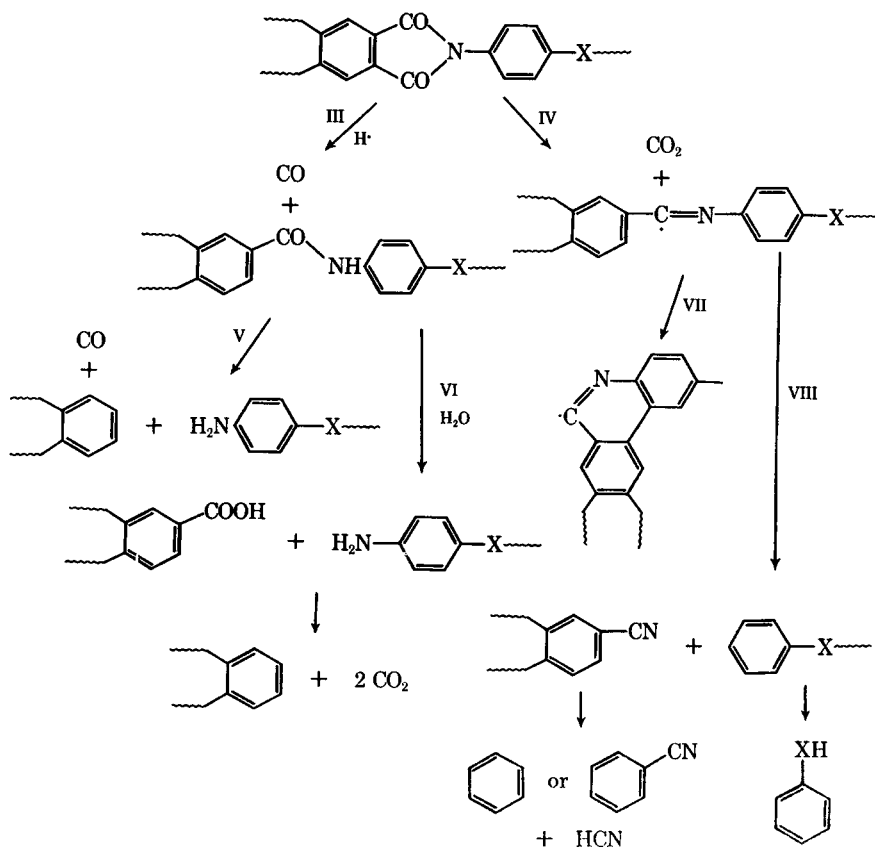
The variation in CO/CO_2 ratio with pyrolysis temperature is accounted for if the relative contributions of reactions III and IV vary with temperature. The only degradation products found, but not accounted for, are hydrogen and methane. Hydrogen is stripped from aromatic nuclei at temperatures above 600°C, but the formation of methane is not easily explained.

References

1. J. Idris Jones, F. W. Ochynski, and F. A. Rackley, *Chem. Ind.* (London), 1686 (1962).

2. J. F. Heacock and C. E. Berr, *SPE Trans.* Vol. 2, 105, April (1965).

3. J. H. Freeman, L. W. Frost, M. Bower, and E. J. Traynor, *S. P. E. Trans.* Vol. 2, 75, April (1965).

4. T. J. Aponyi, *Mod. Plast.*, Vol. 45, 151, Oct. (1967).

5. N. W. Tood, F. A. Wolff, R. S. Mellouk, and F. E. Sdhweitzer, *Machine Design,* Vol. 36, 228, April (1964).

6. S. D. Bruck, *Polymer,* **5,** 435 (1964).

7. S. D. Bruck, *Polymer,* **6,** 49 (1965).

8. S. D. Bruck, *Polymer,* **6,** 319 (1965).

9. S. Nishizaki and A. Fukami, *Kogyo Kagaku Zasshi,* **67,** 474 (1964).

10. S. Nishizaki and A. Fukami, *Kogyo Kagaku Zasshi,* **68,** 1756 (1965).

11. J. L. Cotter and R. A. Dine-Hart, *R. A. E. (Farnborough) Technical Report No. 66254,* Aug., 1966.

12. F. W. McLafferty, *Mass Spectrometry of Organic Ions,* Academic Press, London, 1963, p. 311.

13. E. K. Fields and S. Meyerson, *Chem. Comm.,* 474 (1965).

14. J. L. Cotter and S. J. Knight, *Chem. Comm.,* (1966), p. 336.

15. R. A. Dine-Hart and W. W. Wright, *J. Appl. Polym. Sci.,* **11,** 609 (1967).

16. R. A. Dine-Hart, Private Communication.