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Thermal Degradation of Polymers. III: Mass Spectrometric Thermal Analysis of Condensation Polymers

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GENERAL DISCUSSION

Mass spectrometric thermal analysis (MTA), the determination of total ion current as a function of time and temperature, has been employed for investigation of pyrolytic reactions (*1*). In combination with differential thermal analysis (*1b*) it has proved to be very useful for distinguishing between energy changes caused by phase transformations and those caused by decomposition reactions. Determination of total ion current alone is not particularly informative in most cases of polymer degradation, when several products may be formed simultaneously or sequentially. We have modified the usual procedure by repeatedly scanning spectra, as the temperature is raised on a linear program, and then plotting peak height as a function of temperature. MTA determinations conducted in this way have been helpful in several polymer investigations currently in progress in our laboratory. The alternative method, recording of a characteristic peak for each product on an individual channel of the Bendix Time-of-Flight mass spectrometer, was rejected as less reliable and more cumbersome when the number of products exceeds the number of channels on the instrument.

For qualitative analysis of polymers it is not necessary to know the products of the reaction, since identification can be based on temperatures and relative heights at the maximum of several of the more prominent fragments, once these have been established for

known materials. Additional information about the degradation chemistry can be secured if one chooses peaks characteristic of specific products.

Since the Knudsen cell inlet system and the mass spectrometer are being evacuated continuously, the pressure in the vicinity of the ionizing filament is dependent on the rate of production of the effusing gases. Peak height is therefore proportional to the rate of production of a given species. For competitive first-order reactions the amount of each product is proportional to its rate of production, so that the composition of the product mixture at a particular temperature may be derived from a single spectrum. Further, since peak height is proportional to the rate at each temperature, a semilogarithmic graph of the peak height versus reciprocal absolute temperature (Arrhenius plot) will give a straight line with a slope of E_a/R over a range in which the amount of polymer (or of a functional group) does not change significantly. At heating rates of 15 to 50°C/min it is possible to obtain linear plots over a 50-to-200°C temperature increment, the increment varying inversely as the activation energy (E_a). In this way activation energies for reactions leading to each product can be obtained easily. A composite activation energy comparable to that derived from thermogravimetric analysis or isothermal kinetic studies can be obtained by taking a weighted average of the individual activation energies. Furthermore, from areas under graphs of rate of formation versus time, the relative yield of each volatile product can be determined. Unfortunately, identification of products of polymer degradation from the mass spectrum of an unfractionated effluent cannot always be considered reliable, unless confirmation is secured by other analytical methods, such as gas chromatography.

EXPERIMENTAL

Descriptions of the thermogravimetric analysis techniques and apparatus (2) and of the MTA method (3) have been reported. Most experiments were conducted with the Knudsen cell inlet of a Bendix Time-of-Flight mass spectrometer. Small polymer samples (2 to 15 mg) were placed in a tungsten crucible; the system was evacuated; then they were heated at a linear rate. Spectra were determined at 1-min intervals. The thermocouple had been welded to a support rod 3 mm below the crucible and had been calibrated

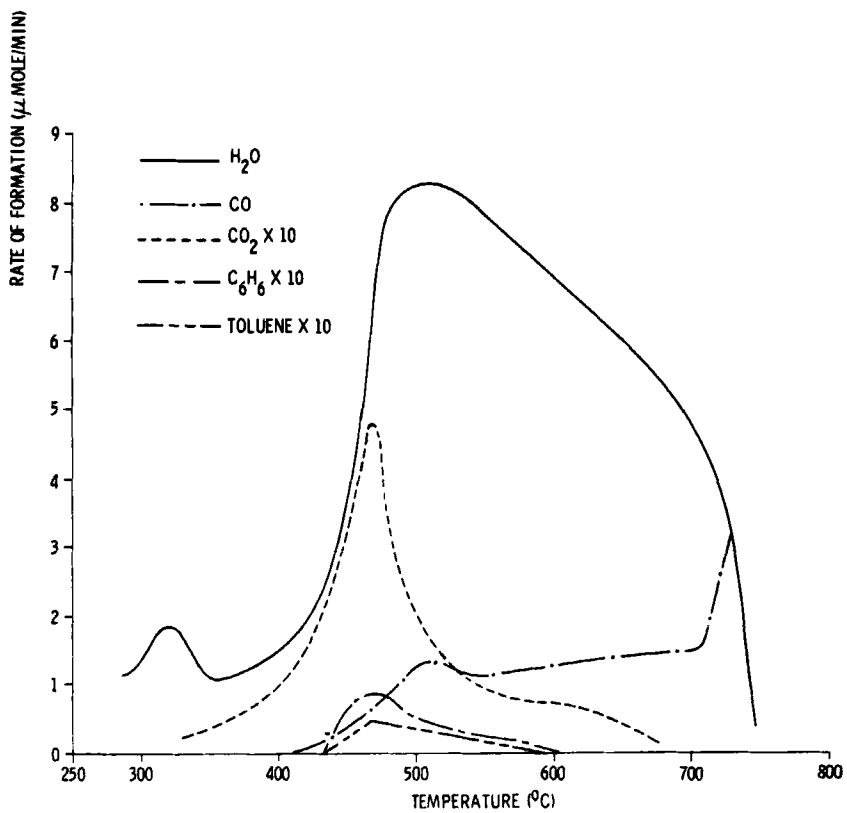
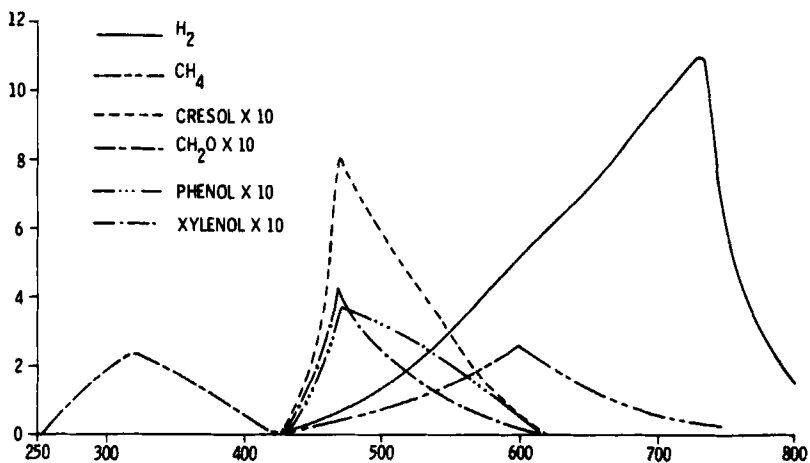


FIG. 1. Mass spectrometric thermal analysis of phenol-formaldehyde polycondensate.

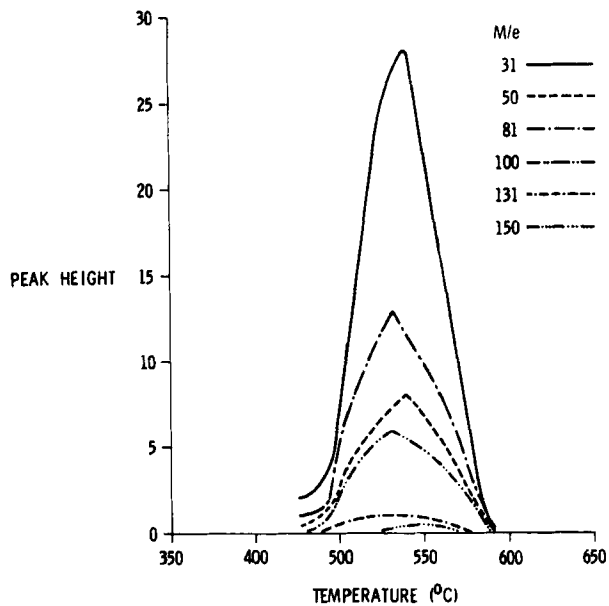


FIG. 2. Mass spectrometric thermal analysis of polytetrafluoroethylene.

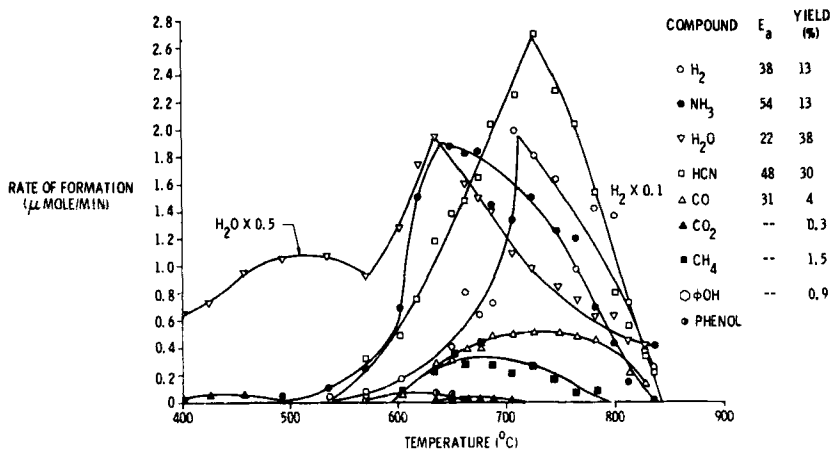


FIG. 3. Mass spectrometric thermal analysis of polybenzimidazole.

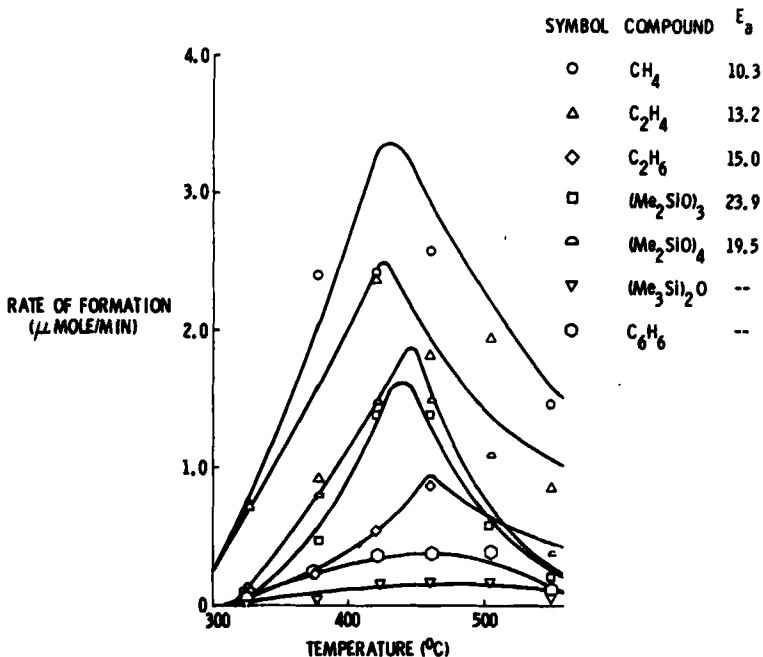


FIG. 4. Mass spectrometric thermal analysis of silicone.

against a thermocouple in the bottom of the crucible at each heating rate. Experimental details are summarized in Table 1.

KINETIC APPLICATIONS

MTA is particularly valuable for the investigation of kinetics when thermogravimetric techniques are inadequate. Thus, determination of kinetic data from thermogravimetry for a high-temperature polymer having a high residual char presents a formidable problem. The "active fraction" depends on the weight fraction after complete reaction, but in a typical case, the aromatic polybenzimidazoles, weight loss is not complete even at 1000°C. The problem is compounded if the polymers are incompletely cured or hygroscopic and resistant to drying, so that the initial weight is also uncertain. The average activation energy for decomposition of poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole varies from 29 to 41 kcal, as compared to the very low value of 18 determined

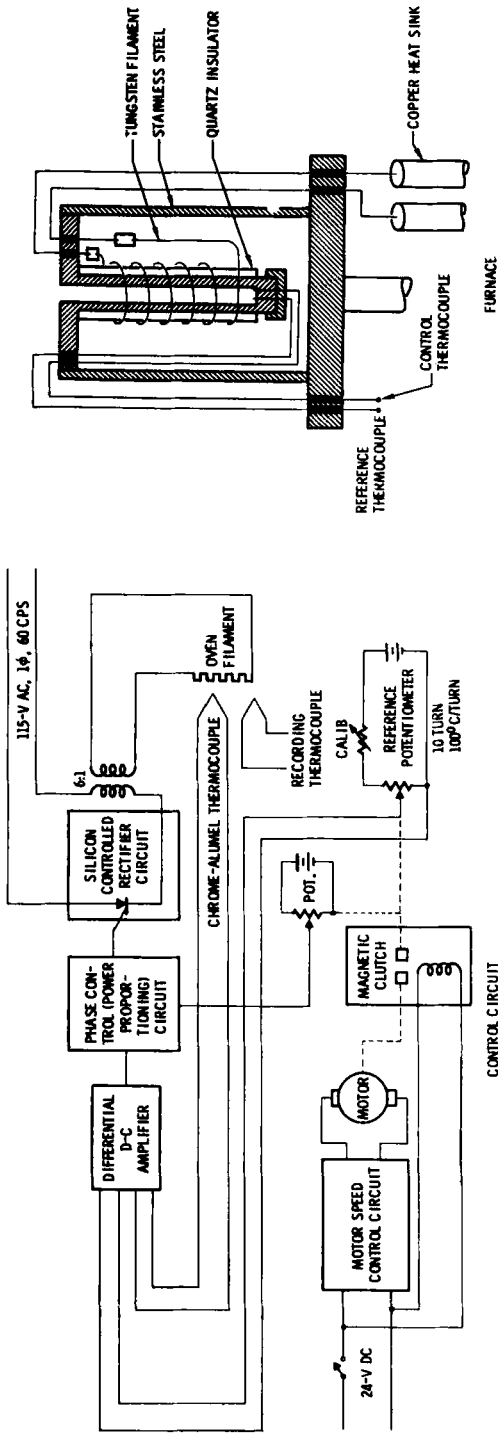


FIG. 5. Modified Knudsen cell.

TABLE I
Experimental Details of MTA

Polymer	Form	Weight, mg	Heating rate, °C/min	Fig. no.
Phenolic	Powder	14.9	29	1
Polytetrafluoroethylene	Chips	12.7	14.5	2
Polytetrafluoroethylene ^a	Chips	3.5	1200	
Polybenzimidazole ^b	Powder	15.5	20	3
Silicone ^c	Filings	11.9	28	4

^a With modified Knudsen cell (Fig. 5).

^b Poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole.

^c General Electric RTV 655.

from thermogravimetry up to 720°C. The MTA-derived activation energy is generally within experimental error of the 44 ± 11 kcal determined from isothermal mass spectrometric kinetic studies or the value of 34 kcal determined by thermogravimetry in the 720-to-900°C region. Phenolic resins also have an activation energy that is markedly dependent on temperature (3); see Fig. 6. This behavior is a result of the formation of the various products in more than one temperature range via processes having different activation energies. Temperature-dependent values will be obtained when average activation energies are calculated from the equation

$$E_a = \Sigma(E_p \times M_p \times R_p) / \Sigma(M_p \times R_p)$$

where E_p = activation energy for formation of a product, M_p = molecular weight of the product, and R_p = relative molar rate of formation of the product.

The opposite behavior is shown by the silicone resin, which has multiple pathways for decomposition proceeding simultaneously. Disregarding the contribution of silane and silica products (which could not be included in the MTA), an activation energy of 19 kcal would be derived. Since homolytic processes having activation energies approximately equal to the silicon-oxygen bond energy of 127 kcal or the silicon-carbon bond energy of 85 kcal (4) are probably responsible for formation of silanes and silica, the activation energy may actually be quite close to the value of 43.5 kcal determined thermogravimetrically. This apparent lack of agreement demonstrates the need for inclusion of all major products

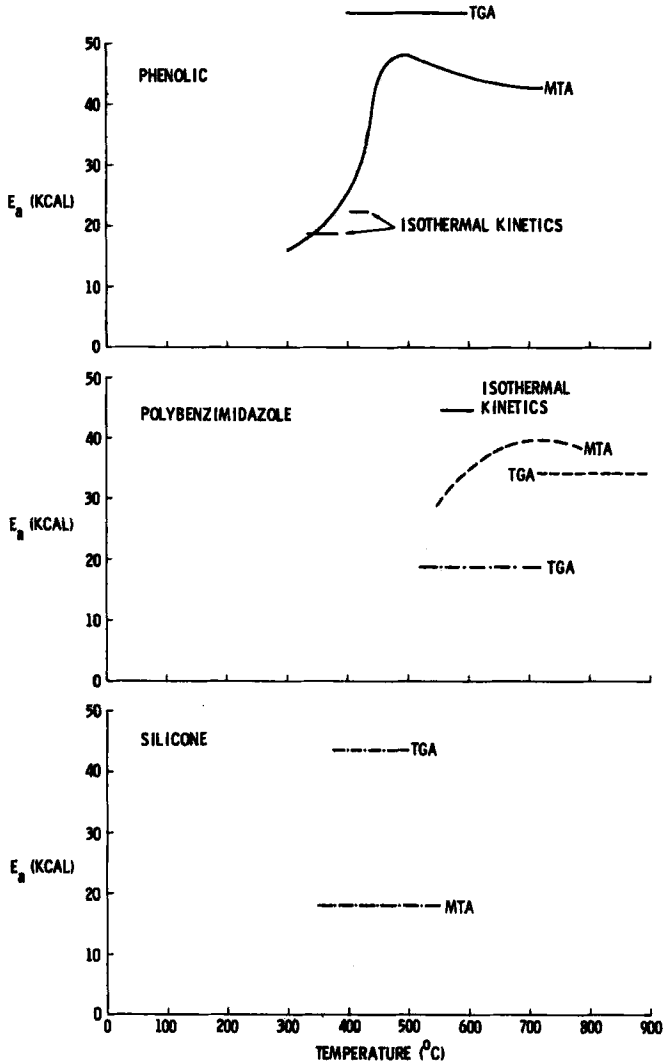


FIG. 6. Temperature dependence of average activation energy.

in the MTA, if it is to be used for a meaningful calculation of activation energy.

High heating rates lead to severe propulsive (5) and aerodynamic (6) forces, which prevent use of a balance for determination of degradation rates. The fast response of the time-of-flight mass spec-

trometer permits its use as a detection device for thermal analysis at high heating rates.

Operation in the high vacuum of the mass spectrometer causes decomposition to occur at somewhat lower temperatures. Comparison with thermal analyses performed at higher pressures is possible by using the fact that a semilogarithmic plot of pressure versus temperature of maximum rate (TGA inflection, DTA maximum or minimum, MTA maximum) is linear (Fig. 7). No theoretical explanation of this relationship is apparent; it must therefore be treated as an empirical correlation which should be verified before application to polymer systems other than silicones and polytetrafluoroethylene. It is possible that changes in pressure are partly responsible for the discrepancy in the silicone activation energy. At atmospheric pressure in the TGA experiments loss of marginally volatile pyrolysis or recombination products may be delayed until higher temperatures, causing an artificially high activation energy value to be derived.

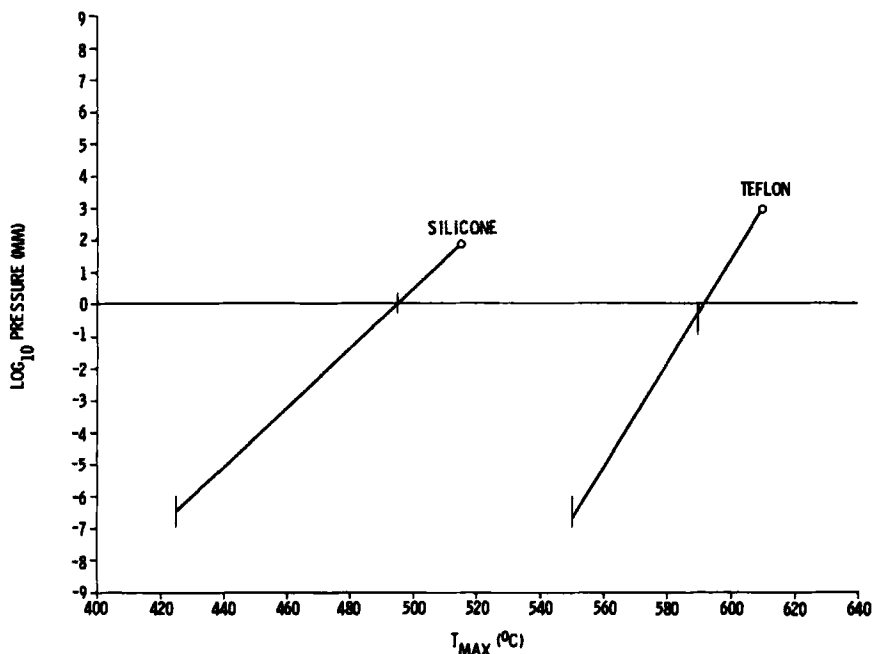


FIG. 7. Effect of pressure on temperature of maximum rate.

APPLICATION TO DETERMINATION OF DEGRADATION MECHANISMS

Three types of datum useful in the determination of degradation mechanisms can be generated conveniently by means of MTA: (1) temperature range(s) at which each product is formed, (2) activation energies for processes leading to each product, and (3) qualitative and quantitative analyses without complications due to presence of recombination products (because of the low pressures involved).

The examples presented below demonstrate the use of MTA for the determination of polymer decomposition mechanisms.

Polybenzimidazoles (7)

A tentative mechanism (Fig. 8) for degradation of poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole has been proposed, based principally on the mass spectrometric thermal analysis. The principal decomposition products are hydrogen cyanide, ammonia, water, and hydrogen; in lesser amounts are carbon monoxide, carbon dioxide, phenol, and methane. Activation energies for formation of the major products range from 26 to 54 kcal mole⁻¹, which is lower than the energy required for homolytic scission of any of the bonds in the polybenzimidazole structure. Since oxygen-containing products are formed and there is water present even in the cured polymer, hydrolytic ring opening (step I) to an amide is postulated as the likely slow step in the reaction. Subsequent homolytic degradation of the amide tautomers leads to the various products.

At 550 to 62°C (step II) stepwise processes leading to *o*-aminophenyl radicals, benzonitrile structures, and hydroxyl radicals (water precursor) can be written. The degradation of benzonitrile to hydrogen cyanide has been reported (8). Coupling of two *o*-aminophenyl radicals gives a 2,2'-diaminobiphenyl structure, which degrades with loss of ammonia to carbazole or anthracene structures (9).

Degradation of polyamides of aromatic acids can give carbon monoxide (10). The suggested scheme for the 600-to-800°C temperature range (step III) involves elimination of carbon monoxide, leaving phenyl and *o*-aminophenylamine radicals. Coupling of these would lead to a carbon-nitrogen residue with a ladder polymer

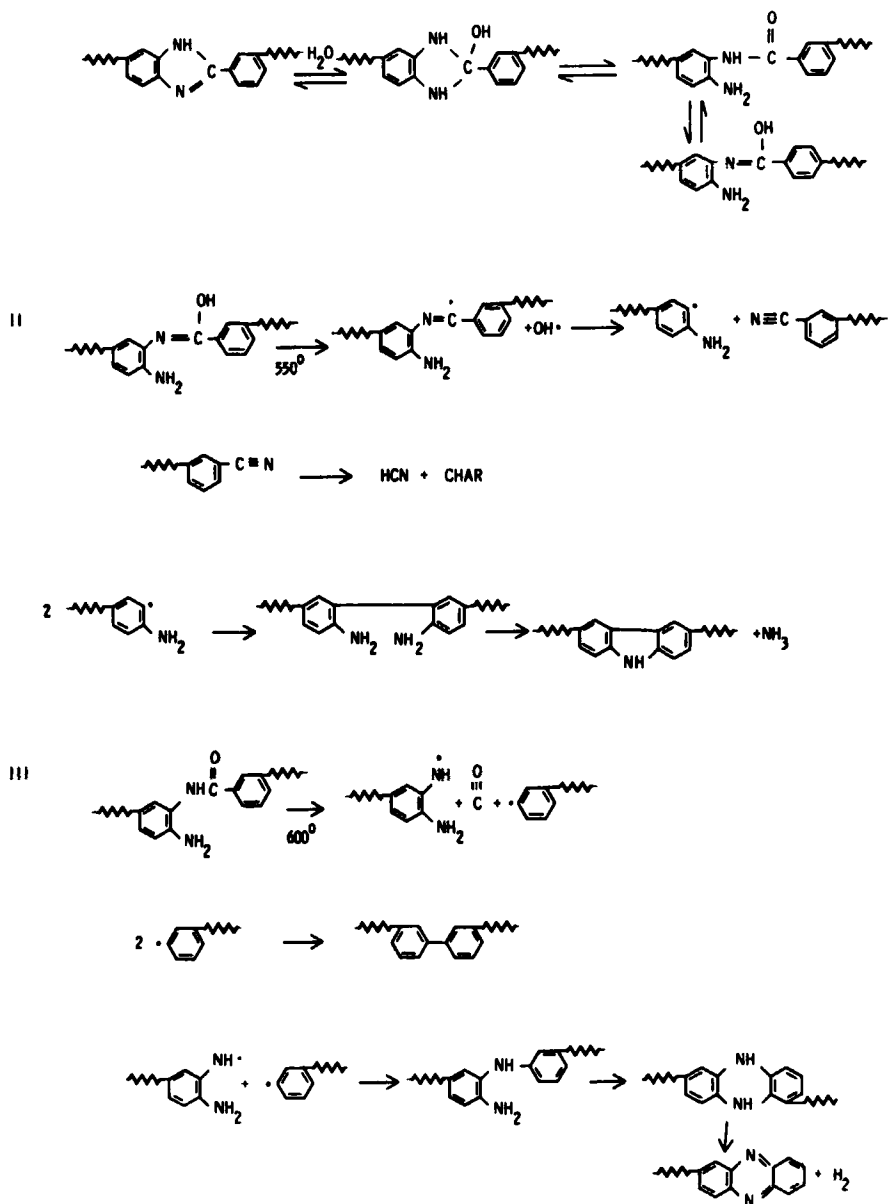


FIG. 8. Postulated mechanisms for thermal degradation of poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole.

structure. Hydrogen must be formed by dehydrogenation of piperazine structures (step III) or by cross-linking of adjacent chains to a graphitic structure.

Silicones

The General Electric 655 silicone elastomer used in this investigation is a dimethylsiloxane polymer with some phenyl and vinyl substituents. From gas chromatographic analysis it was known that oligomeric dimethylsiloxanes, hydrocarbons (methane, ethylene, benzene, etc.), and methylsilanes were the principal groups of volatile products, along with a residue of silica. Since more than thirty-five compounds were identified in the gas chromatogram, a complete MTA was impossible, but characteristic m/e numbers for the principal products were chosen as the basis of the MTA work. Degradation to all products occurred in the range of 375 to 525°C. As might be expected, the activation energies for hydrocarbon products fell into a narrow range, while the siloxane activation energies were somewhat higher. No determination of the silanes was possible, since their principal peaks, $(\text{CH}_3)_3\text{Si}^+$ (m/e 73), are also major peaks of such species as hexamethylcyclotrisiloxane. The oxygen material balance requires that silanes and silica be formed in equivalent amounts. It is therefore necessary to propose three simultaneous processes to account for the degradation products: (1) equilibration to volatile cyclic siloxanes, (2) carbon-silicon cleavage, giving hydrocarbon moieties, and (3) silicon-oxygen cleavage, giving dialkylsilane moieties. These are shown in Fig. 9. Although no evidence of a free-radical mechanism leading to hydrocarbon products was obtained, and in spite of the fact that activation energies are much too low, such a mechanism is as shown in Fig. 9, Step II, since it is difficult to propose a satisfactory alternative. The presence of residual curing agents in the polymer could account for a homolytic process with low activation energy.

Phenolics (3)

A detailed mechanism of the thermal-oxidative degradation of a resole has been proposed by Jackson and Conley (11). Mass spectrometric thermal analysis of the same resin generally confirmed the mechanism. Three distinct stages were observed: (1)

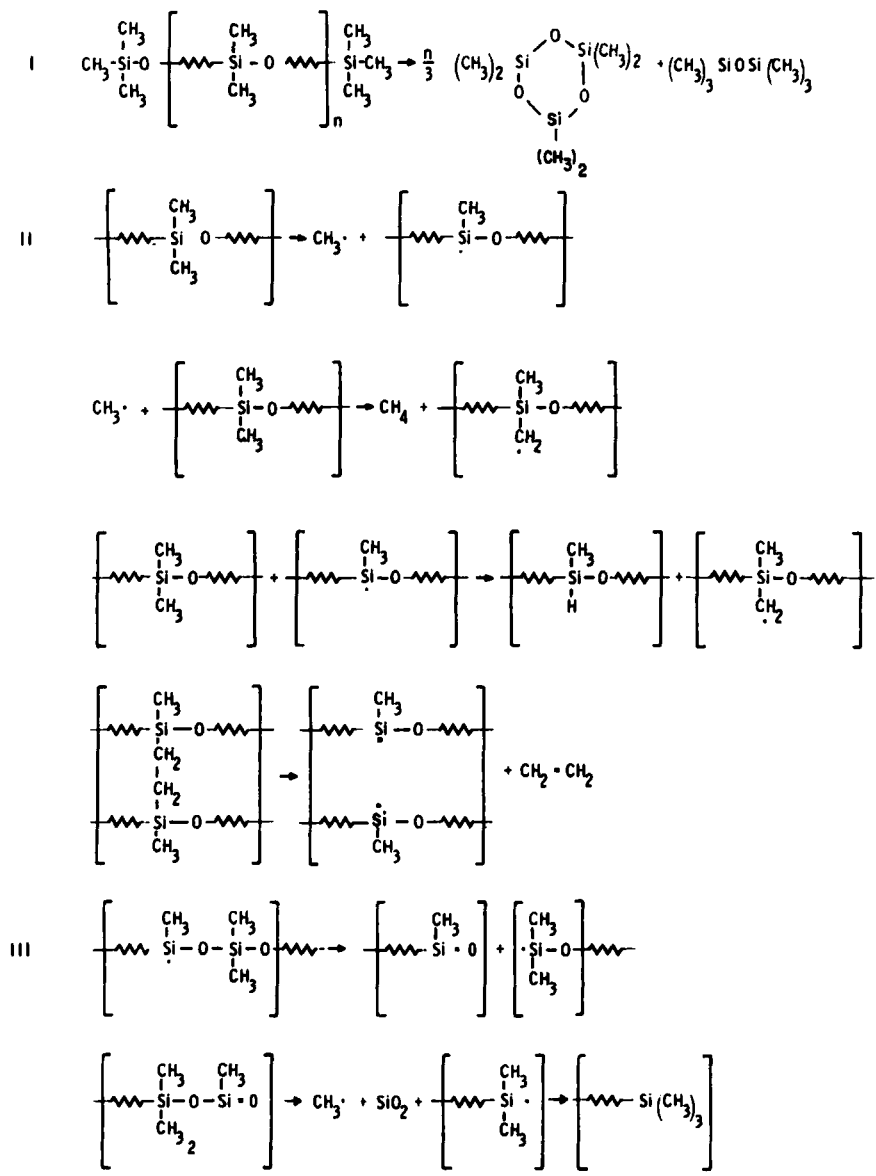


FIG. 9. Proposed routes of silicone degradation.

a low-temperature postcuring and oxidative degradation, giving formaldehyde and water, (2) general degradation at 450 to 600°C to oxidation products such as carbon monoxide, carbon dioxide, and water, with low activation energies, comparable to those measured for the low-temperature oxidation (12) or to phenol and its homologues with high activation energies, suggesting thermally induced homolytic scission, and (3) a high-temperature char-forming stage, in which hydrogen and additional carbon monoxide are liberated.

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