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APPROACHES TO FLAME-RESISTANT POLYMERIC MATERIALS

Final Report

March 1975

by

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ABSTRACT

Four research and development areas are suggested for further exploration in the quest of more flame-resistant polymeric materials. It is suggested that improvements in phenolphthalein polycarbonate processability may be gained through linear free energy relationship correlations. Looped functionality in the backbone of a polymer leads to both--improved thermal resistance and increased solubility. Because of this unique characteristic, such polymers deserve special attention in higher flame-resistance applications. It is further suggested that the guidelines used in the pyrolytic carbon production constitute a good starting point also for the development of improved flame-resistant materials.

Numerous organic reactions requiring high temperatures and the techniques of protected functionality and latent functionality constitute the third area for exploration. Finally, some well-known organic reactions are suggested for the formation of polymers that have not been made before.

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I. INTRODUCTION

The objective of this study was to review pertinent literature to define options available for making polymeric materials more flame-resistant. As a result of this effort, the following research and development areas are suggested for further exploration:

1. Looped functionality polymers;
2. Structure-pyrolytic reaction correlations;
3. High temperature reactions;
4. New polymer-forming reactions.

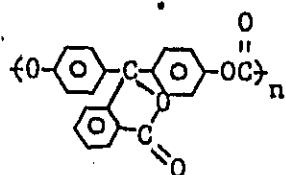
The areas listed are in the order of priorities for obtaining practicable results in the shortest time possible, if the No. 1 area were explored first and then the others in sequence. Because of the time limitations of this effort, none of the areas were explored in detail; however, sufficient background and key references have been given so that subsequent development of any area could be done with a minimum of delay. Of course, the areas No. 3 and No. 4 are based on classical organic chemistry; it is not the quantity of references but rather the imagination of the investigator that would set the limits upon the number and variety of new and fascinating molecules which may be designed for the synthesis of new polymers or controlled crosslinking reactions in synthesized polymers. The synthetic polymer chemistry is only as varied and limitless as the organic chemistry is:

One of the significant conclusions in the work of Parker, Fohlen, and Sawko¹ was that enhanced flame resistance can be imparted to a polymer material if it is provided with functional groups that furnish crosslinking sites by thermochemical reactions at the decomposition temperatures.

This is one of the most significant recent developments in the field of flame-resistant polymeric materials and needs to be vigorously explored.

II. LOOPED FUNCTIONALITY POLYMERS

In recent years polymers with cyclic functional side groups--looped functionality--have been increasingly investigated. Phenolphthalein polycarbonate:



is one example of such polymers. A review on looped functionality polymers (cardo polymers) has been recently written.² The presence of looped functionality in the backbone of a chain confers enhanced thermal stability and solubility properties upon such polymers in general.

There are many ways of increasing thermal resistance in polymers: by introducing aromatic rings in the backbone, by increasing intermolecular interaction (hydrogen bonding, polar groups) by polar crystallization, by introducing chemical crosslinks, or by preparing stereoregular polymers. Better solubility of a polymer may be achieved by preparing amorphous materials, by decreasing the rigidity of the backbone, by introducing various polar groups that show affinity for the solvent, and by introducing dissimilar groups in the backbone. Comparison of the two sets of factors will show that usually the improvement of thermal resistance of a polymer will lead to impairment of its

solubility characteristics and vice versa. However, a singular exception to the above is the introduction of looped functionality in the backbone of a polymer in that this leads to both--improved thermal resistance and increased solubility. A rationale for this is given in the above mentioned review article.² Because of this unique characteristic of such polymers, they deserve a special attention in high flame-resistance applications.

1. Phenolphthalein Polycarbonates

From the work of Parker, Fohlen, and Sawko,¹ it is obvious that phenolphthalein polycarbonate offers substantial advantages in fuel fire burn-through, laser resistance, and exposure to high-temperature operating environments over state-of-the-art materials. However, one problem remains with this material. Because of its very high glass transition temperature (278°C), its very high decomposition temperature (425°C), and the fact that the polymer does not melt or flow but softens, it is deduced that a considerable branching and/or crosslinking due to ester interchange with the lactone ring is taking place already at temperatures below the glass transition temperature. This then complicates the processing techniques of phenolphthalein polycarbonate. The following rationale and suggestions are offered for obviating this problem.

Different measurements allow us to observe different things, and some phenomena are easier to see with certain types of measurements than with others. Thus, for example, the effect of para substitution in the phenyls of tetraphenylporphyrins is readily seen in chemical reactivity experiments, less readily seen in ESR measurements, and barely detectable in mass spectroscopy, and IR and NMR spectroscopy.³ A change of a few tenths of an angstrom

in a structural bond can produce a change of tens of kilocalories in the observed bond energies.⁴ Similarly, a change of a few kilocalories/mole in a reactivity process can result in a change of a couple of orders of magnitude in the rate of that process. Thus, in going from the molecular structure of phenolphthalein polycarbonate to understanding its high temperature reactivity, one may have to be prepared to look very carefully for small but meaningful differences of some measured molecular structure parameter.

Many different types of strategies can be adopted to successfully pursue the goal of developing improved flame-resistant materials. One such strategy is based on molecular structural interrelationships with the reactivity tendencies of the material. As far as the phenolphthalein polycarbonate problem is concerned, it is presumably the phenolphthalein portion of the molecule that is of primary concern to us. The potential of the phenolphthalein molecule as a model compound in studying the structure reactivity relationships is enormous. This is so because of the very large number of closely controlled variations of the basic phenolphthalein molecule that can be prepared with a wide range of chemical reactivities and physical properties.

Hammett^{5,6} was one of the first to propose a general quantitative relation between the nature of the substituent, R, and the reactivity



of the side chain X. This relation is known as the Hammett equation [the Hammett linear free energy relationship] and is widely applied in the form

$$\log \frac{k}{k^0} = \sigma \rho$$

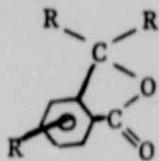
Here k and k^0 are rate or equilibrium constants for reactions of the substituted and the unsubstituted compounds, respectively; σ is the substituted constant, which depends solely on the nature and position of the substituent R; and ρ is the reaction constant, which depends on the reaction, the conditions under which it takes place, and the nature of the side chain X.

The σ value has been associated with the effect of the substituent on the charge density of the carbon atom which bears the side-chain reaction center. Both inductive and resonance interactions of the substituent with the benzene ring are reflected in σ values. The interest in σ value correlations follows several different lines.

In particular, with regard to the phenolphthalein polycarbonate problem, we feel that if there are effects other than polar that may contribute to those observed, the empirically predicted polar effect may enable the approximate evaluation of these effects. It may even be possible to study unambiguously and in near-quantitative terms the other effects of molecular structure on the polycarbonate reactivity at high temperatures, and thus presumably also its charring tendency.

Finally, two other items should be mentioned. Theoretically the Hammett relationship, in terms of substituent polar effects, required that the free radical reactions were not correlatable. However, later careful investigations have shown that there are major electronic changes in the transition states of radical reactions leading to a dependence upon polar effects because of considerable resonance stabilization effects.⁷

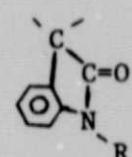
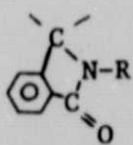
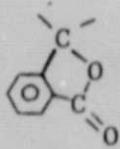
Apparently the Hammett relationship is applicable to more complex substrates in which the reacting side chain or substituent is attached to the benzene ring in two positions, e.g., reactions of substituted phthalides.⁸⁻¹²



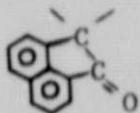
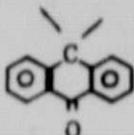
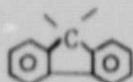
Both the opening of the lactone ring as well as its closing (lactonization)¹³ follow the Hammett relationship. Thus, our proposal is that the phenolphthalein polycarbonate should be amenable to a linear free-energy relationship correlation with its reactivity and hence processability as well as its charring tendency.

2. Other Looped Functionality Polymers

Another purely empirical approach to varying the reactivity of the looped functionality is through the variation of its chemical constitution. Polymers with the following looped functionalities have all been synthesized:²



where R = H, ϕ , alkyl

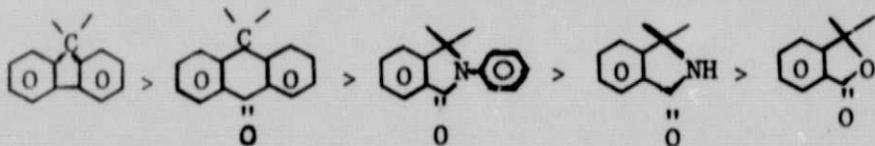


Thus, as a first task, their evaluation for crosslinking tendencies by thermochemical reactions at the decomposition temperatures is suggested. Once a desirable trend has been observed with the available looped functionalities, other groups with projected improved properties could be synthesized.

Furthermore, it has been shown that the heat resistance of this class of materials was dependent upon the conditions of synthesis affecting the formation of various supermolecular structures as a result of coiled or uncoiled chain conformations.

The supermolecular structure has also a very large influence upon the impact strength of the polyarylates. For example, the polyester of phenolphthalein and isophthalic acid, of essentially the same molecular weight, when prepared in a "poor" solvent had an impact strength of 2-3 kg cm/cm², and in a "good" solvent 14 kg cm/cm².¹⁴

Finally, correlations of a number of looped functionalities as to their inherent contributions to the heat resistance in polyarylates have been made.¹⁵ The functional groups in question were arranged in the following decreasing order of contribution:



The above correlation was further found to follow a regular decrease in the "reduced" volume of the group to its molecular weight as follows:

$$1.58 > 1.56 > 1.55 > 1.43 > 1.40,$$

respectively.¹⁶ However, the flame resistance or charring tendency of these materials does not appear to have been studied before.

III. STRUCTURE - PYROLYTIC REACTION CORRELATIONS

Once we leave the field of looped functionality polymers, the search for improved flame-resistant polymers is more tenuous, or at least becomes a more long-range problem. Thus, our reflections on this problem have led us to the suggestion of the next three approaches with the structure--pyrolytic reaction correlations having considerable immediacy.

1. The Basis For Structure - Pyrolytic Reaction Correlations

Although the chemistry during pyrolysis of organic compounds is extremely complex, an attempt at summarizing pyrolytic reactions of organic compounds below 1000°C has been made.¹⁷ One of the objectives of those concerned with the production of pyrolytic carbon is to obtain the highest possible carbon yield from a material. It is well known that the carbon yield can be influenced by the choice of the compound to be pyrolyzed, by its thermal and chemical pretreatment, and by the pyrolysis conditions. To decrease the tendency towards volatile species generation, the formation of high molecular weight compounds (aromatization, polycondensation, and cross-linking) in the liquid phase is desired. In the case of non-melting polymers (e.g., cellulose), the control of pyrolysis chemistry can suppress the formation of the highly volatile species: levoglucosan.

In the pyrolysis of hydrocarbons the following three principal types of reactions take place:

1. First reaction set: degradation and dehydrogenation reactions of all nonaromatic hydrocarbons;
2. Second reaction set: cyclization of all hydrocarbon chains to form aromatics--the first and second reaction sets apply in the same way to aromatics with aliphatic side chains;
3. Third reaction set: condensation of aromatics to form polycyclic aromatic systems.

In general, the low molecular weight hydrocarbons are the most stable up to about 500°C. Above 800°C the aromatics become the most stable, and the thermodynamic stability of the olefins lies between that of the paraffins and aromatics in the temperature range considered.

According to the patent literature and the experience of the industry in general, the addition of "cross-linking" agents to pitches (polycyclic aromatics), for example, promotes dehydrogenation and condensation reactions leading to improved carbon yields during pyrolysis.¹⁸⁻²³ Such materials as chloro-substituted organic compounds, Friedel-Crafts catalysts, sulfur, organic nitro compounds, and organic chloronitro compounds have been used.

To understand the chemistry of carbonization in detail, it is necessary to study the pyrolysis of pure organic compounds and to identify the molecular species formed during the decomposition. The current knowledge in the field is summarized below.

a. Polyphenyls

Polyphenyls are extremely stable at high temperatures, as exemplified by their application as heat-exchange liquids at temperatures up to 500°C.

According to Kalka,²⁴ polyphenyl at atmospheric pressure in nitrogen starts decomposing at 530°C by dehydrogenation (fig. 1). The residue exhibits the IR band of isolated hydrogen atoms, their occurrence attaining a maximum at 600°C, and their release at high temperatures leading to planar multiple ring structures of large area. The total weight loss for polyphenyl is only 12 percent during the entire pyrolysis, corresponding to a carbon yield of 93 percent.

b. Coronene

Pyrolysis of coronene using a sealed tube method and heating up to 700°C led to 100 percent carbon residue.

c. Alkyl Aromatics and Methylene-Bridged Aromatics

In the pyrolysis of alkyl aromatics, longer side chains are split off and condensation may take place by way of the alkyl group. Pyrolysis of methylene-bridged aromatics leads preferentially to a separation of a hydrogen atom from the bridges, as well as to a rupture of both the C-C bond within the bridges and the bond connecting the aryl-aryl portions. As an illustration, the dissociation energy of the C-H bond of methane is lowered from 102 to 77.5 kcal by substituting a phenyl group for a hydrogen atom. In the case of bibenzyl, the carbon-carbon bond connecting the two benzyl groups acquires the very low dissociation energy of 48 kcals.²⁵ Large quantities of gases are usually evolved from compounds of this type.

d. Hydrocarbons Containing Other Elements

Among the raw materials used for the production of carbon, a multitude of hydrocarbons containing a number of other atoms, e.g., oxygen, sulfur or nitrogen, exists. During pyrolysis these heteroatoms can either form

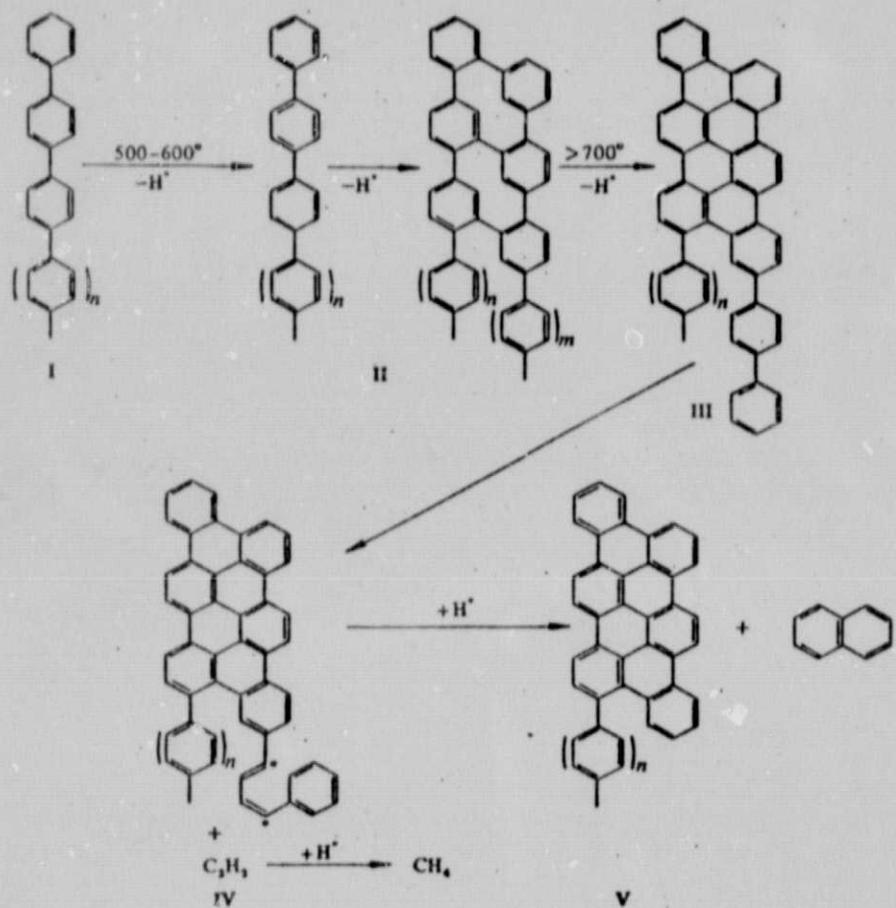


Fig. 1. Dehydrogenation of Polyphenylene (E. Fitzer and J. Kalka, High Temp. - High Press, 3, 53 (1971)).

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stable, volatile byproducts and thus reduce the carbon yield, or they can function as the crosslinking sites in the compounds. This effect will increase the carbon yield. They can also increase the carbon yield by removing hydrogen that may otherwise have to be removed by carbon. This effect is especially pronounced when the other elements are used as additives.

(1) Aromatics containing oxygen

Organic acids decarboxylate rather easily, releasing CO_2 . The decarboxylation is facilitated by an increase in the basicity of the aromatics. Thus, in the case of carboxylated phenylene oxide polymers, decarboxylation starts above 200°C ²⁶ while benzoic acid decarboxylates at 317°C . A second carboxyl group lowers the basicity of the ring and thus renders decarboxylation more difficult. The pyrolysis of esters does not proceed according to general principles and usually is catalyst-sensitive. Hydroxyl groups are relatively stable in both aliphatic and aromatic compounds. In the case of primary alcohols of aliphatic compounds, decomposition of the basic hydrocarbon takes place before the hydroxyl group is split off. In the case of phenols, release of water leads to simultaneous formation of higher aromatics. Alkylated phenols exhibit preferential rupture of the alkyl chain around 750°C , leading to phenols.²⁷ During the thermal decomposition of poly-2,6-dimethylphenylene, oxide hydroxyl groups are formed due to the fracture of the ether bonds, which become unstable around 400°C .²⁴

The hydroxyl group as a site for crosslinking reactions can be best illustrated with the phenol-formaldehyde polymers (fig. 2). Condensation of a CH_2OH group with an activated hydrogen (by phenolic hydroxyl group) takes place very easily with the formation of a methylene bridge. The

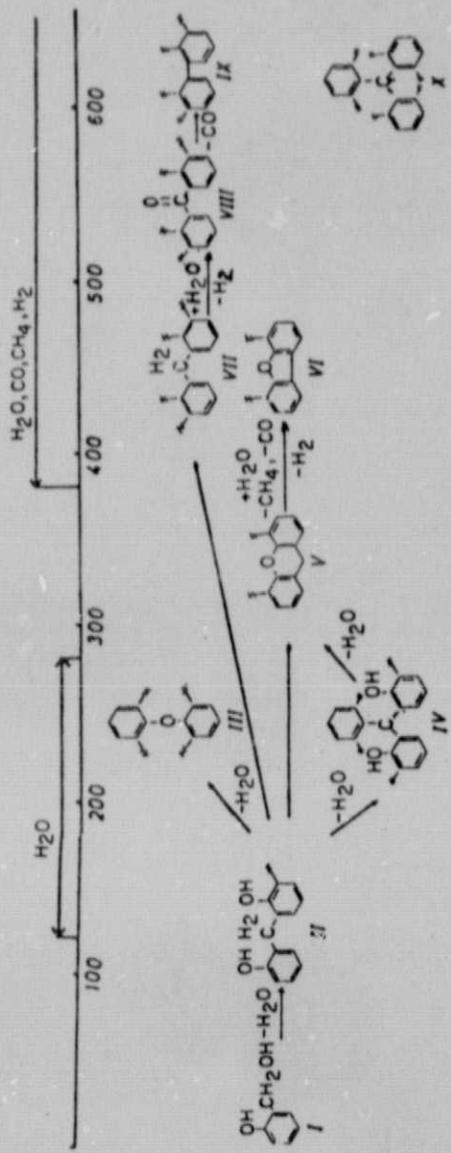


Fig. 2. Schematic of the pyrolysis of phenol-formaldehyde polymers
(E. Fitzer, K. Mueller, and W. Schaefer, "The Chemistry of the Pyrolytic Conversion of Organic Compounds to Carbon," in Chemistry and Physics of Carbon, Vol. 7, Marcel Dekker, Inc., N.Y., 1971).

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starting temperature for the condensation is affected by substituents in the same manner as decarboxylation was.

Aliphatic ethers are the most stable up to 530°C; sterically hindered ethers decompose at lower temperatures. According to Kalka,^{24,28} the fracture of the ether bond in unsubstituted polyphenylene oxide occurs at 460°C. The thermal stability is decreased by substitution, as when in poly-2,6-dimethylphenylene oxide the fracture takes place at 370°C. Halogen substitution also lowers the thermal stability of phenyl ethers, the chlorinated ethers being more stable than the brominated ones.

Limited data are available regarding the thermal stability of keto groups. At 450°C, two molecules of anthraquinone undergo a condensation reaction accompanied by release of carbon monoxide.²⁹ The fact that anthraquinone yields 2 moles of carbon monoxide at 450°C indicates that possibly the phenylene diradical may be formed by scission at the 9,10 positions. In the pyrolysis of phenolic resins, new keto groups are formed from the methylene bridges under the influence of the release of pyrolysis water above 450°C.³⁰ Decomposition of the keto groups in phenolics takes place above 460°C and leads to the evolution of carbon monoxide.

A similar type of pyrolysis is found for aldehyde groups formed by a thermal decomposition of aliphatic ethers as intermediate products.

(2) Aromatics containing sulfur

Contrary to the case of compounds containing oxygen, there are few published reports on the thermal stability of aromatics containing sulfur. The thermal decomposition of p-polyphenylene sulfide occurs above 400°C.³¹ Sulfur-containing polymers of the polythiadiazole type are said to be thermally stable up to 650°C.³² Blayden and Patrick³³ describe the formation of

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sulfur-carbon complexes by reaction of pyrolytic carbon with sulfur vapor at 500°C and find them stable up to 900°C. There is little understanding about the nature of the sulfur-carbon bond.

(3) Aromatics containing nitrogen

Quinoline, isoquinoline, indole, and carbazole do not decompose below 500°C. The most detailed study on a nitrogen-containing polymer has been on polyacrylonitrile.³⁴ The aromatization of the cyclized polyacrylonitrile is enhanced by an oxidizing atmosphere. After heat treatment to 600°C, 80 percent of the original nitrogen is still found in the residue; heating up to 1000°C still leaves 40 percent of the original nitrogen in the residue. This is an illustration of the high thermal stability of nitrogen-containing heterocycles.

(4) Halogen substituted polymers

Due to their high affinity for hydrogen, fluorine and chlorine act as dehydrogenating agents, thus promoting the formation of carbon residues. The carbon yield reaches a maximum for a stoichiometric hydrogen/halogen ratio. For example, polyvinylidene chloride and fluoride yield nearly theoretical amounts of carbon as compared to only 10 percent for polyvinyl chloride.

e. The Use of Crosslinking Additives

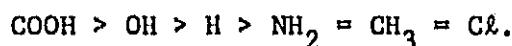
Pyrolytic reactions leading to condensation can be influenced by a variety of additives.

(1) Friedel-Crafts catalysts

Bruckner and Huber³⁵ have studied the effect of anhydrous $AlCl_3$ on the pyrolysis of different pitches. The amounts of $AlCl_3$ needed for an efficient crosslinking were very small (0.1 to 0.5 percent), and the mechanism of the reaction was the same as that known from classical organic chemistry.

(2) Polar bifunctional compounds

The influence of additives containing nitro groups on the condensation of aromatics is an oxidation reaction. This influence can be enhanced by a second substituent in the following order of effectiveness:³⁶



No systematic investigations of these compounds on pure hydrocarbons have been conducted; only the oxidation of pitches has been studied. It is assumed that these additives are capable of polarizing the aromatic components of the pitch to such an extent that nucleophilic crosslinking results. The degree of crosslinking, as reflected in hardening of the pitch, is a linear function of the number of nitro groups introduced by the additive.

(3) Sulfur

The addition and exchange reactions of sulfur are well known in the vulcanization of rubber. By the addition of sulfur, crosslinking reactions can be initiated in the addition of sulfur.³⁷ Furthermore, by the addition of sulfur, the temperature of thermal dehydrogenation of aromatic hydrocarbons is lowered by 300°C. In addition to the dehydrogenating action of sulfur, heterocycles containing sulfur are also formed.³⁸ Pyrolysis of an acenaphthylene-sulfur mixture having an H:S ratio of 1.7:1 yielded a theoretical amount of carbon, as opposed to only 30 percent for the sulfur-free acenaphthylene.

2. Conclusion

Thus, according to the above survey of the chemistry of pyrolytic reactions of organic substrates, improved carbon yield will be obtained if:

- one starts with an aromatic hydrocarbon substrate with a minimum of alkyl, carboxylic acid, and ester substitution;
- one uses Friedel-Crafts Catalysts, polar bifunctional compounds, or sulfur as crosslinking agents with the aromatic hydrocarbons;
- one uses aromatic hydrocarbons containing such other elements as oxygen (of certain functionality), nitrogen, and sulfur with a minimum of alkyl, carboxylic acid, and ester substitution;
- one uses fluorine- or chlorine-substituted aromatic hydrocarbons with the hydrogen/halogen ratio of 1:1;
- in general, if one uses the "crosslinking" additives with most any substrate according to the following guidelines:
 - Friedel-Crafts Catalysts in amounts probably not exceeding 0.5 percent.
 - nitro compounds, increasing amounts producing increasing crosslinking (however, the stoichiometry has not been worked out);
 - sulfur, increasing amount producing increasing crosslinking.

We suggest that the above guidelines also constitute a good starting point for the objective of achieving improved flame-resistant materials.

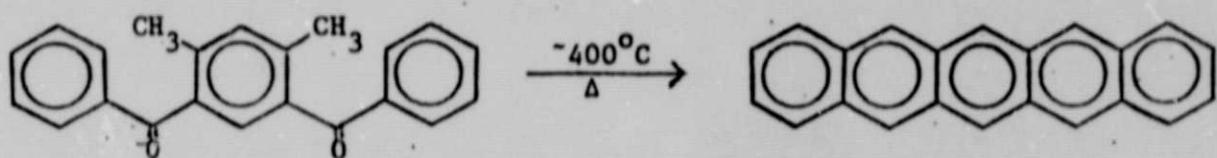
IV. HIGH TEMPERATURE REACTIONS

In general, the systematic use of crosslinking as an aid to increased flame resistance has not been extensively studied. The concept of generating crosslinks by thermochemical reactions at the decomposition temperatures of polymers is also practically unexplored. Furthermore, the thermal environment in an "intense" fire is such that any known organic polymer (excepting possibly graphite and diamond) will be degraded at a "significant" rate. The question then becomes: "What do we know about the chemistry of organic polymeric structures that would help us in designing materials leading to *in situ* heat-resistant product formation?" Perhaps the people concerned with the pyrolytic conversion of organic materials to carbon residues can teach us the most. However, even they admit that the knowledge to date does not permit a detailed understanding of pyrolytic decomposition reaction mechanisms.¹⁷

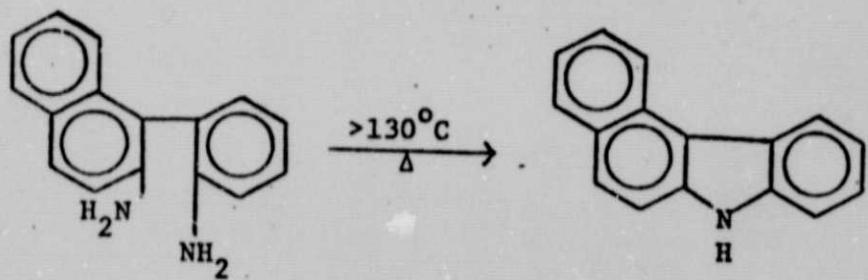
A more answerable question then is: "What are some of the organic thermochemical reactions that take place in a 'controlled' manner at 'high' temperatures?" A survey of the literature will reveal that such standard synthetic organic chemists' guides to chemical reactivity as the Woodward-Hoffman Rule, the frontier electron method, or the theory of charge-transfer force, are of no help. The two synthetic techniques of using protective groups for functional groups to protect them from premature reaction and the latent functional group approach are only a little more helpful. Thus, in this section we shall simply list some typical high-temperature organic reactions. Applicability of any of these reactions to a specific polymer has not been considered in this brief survey.

1. Some Organic Reactions Requiring High Temperatures

a. Elbs Reaction-³⁹

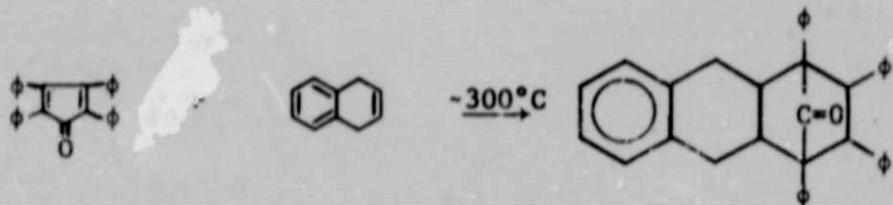


b. Bucherer Reaction (last step)-⁴⁰

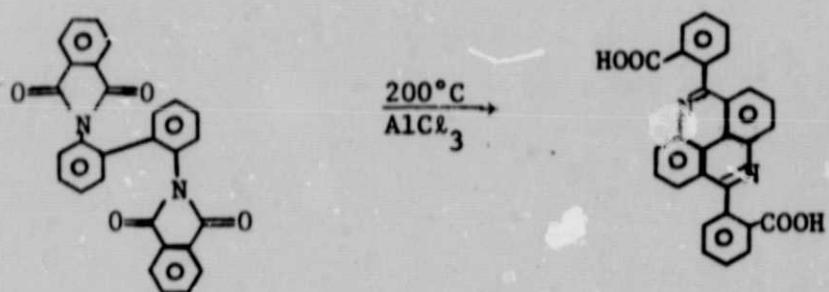


Marvel and coworkers have used the above reaction to synthesize polymers with quinoxaline repeating units.⁴¹

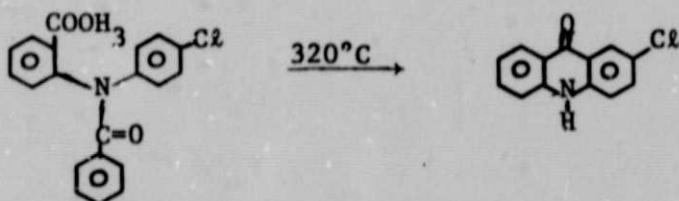
c. Diels-Alder Reaction-⁴²



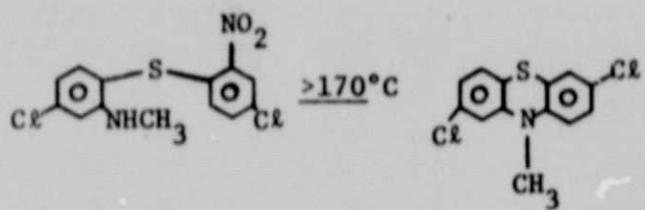
d. Bischler-Napieralski Reaction-⁴³



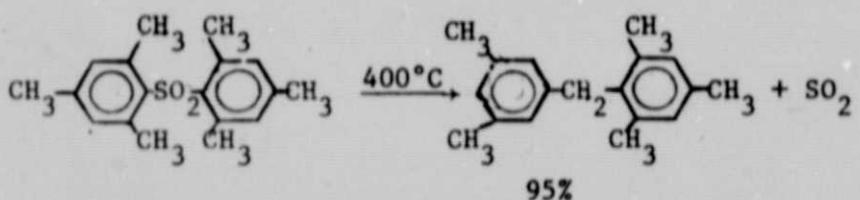
e. Cyclization of Chapman Rearrangement Product-⁴⁴



f. Smiles Rearrangement Variation⁴⁵



g. Truce-Smiles Rearrangement⁴⁶



h. Friedel-Crafts Reaction⁴⁷

Perhaps the F-C reaction is the one that will turn out to be the most appropriate to generate the crosslinks. Certainly, it is one of the best known and most versatile reactions in chemistry. We will not attempt to illustrate its versatility here as this has been done in a four-volume monograph of 5000 pages and 20,000 references in 1963.⁴⁸ We will simply list a series of selected facts, which we offer to buttress our contention that this is the reaction to be exploited in the generation of a high crosslink density.

We also note that the industrial experience of the carbon technologist suggests Friedel-Crafts catalysts as one of the additives to pitch for improved carbon yields during pyrolysis.

Friedel-Crafts reaction is involved in:

- alkylations,
- dealkylations,
- acylations,
- polymerizations,
- substitutions,
- additions, and
- isomerizations.

The catalyst may be of Lewis acid type acidic halides or proton acids.

When proton acids function as the catalyst, higher reaction temperatures are required.

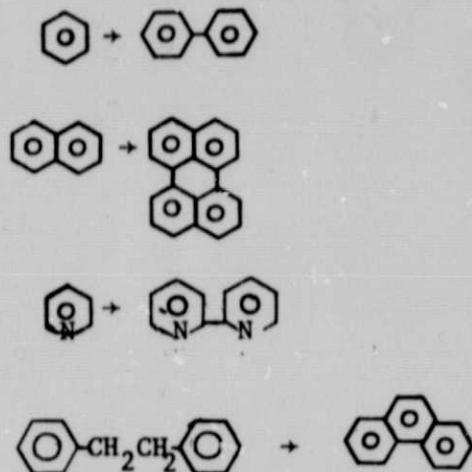
Contrary to the general belief that in F-C reactions only hydrogen is substituted by an alkyl or acyl group, other atoms or groups than hydrogen are also substituted. The following have been used as alkylating agents in aromatic alkylations:

- alkyl halides,
- alkenes,
- alkynes,
- alcohols,
- esters,
- ethers,
- aldehydes and ketones,
- mercaptans,
- sulfides, and
- paraffins.

The most characteristic feature of F-C alkylation is a general tendency to form dialkylated and polyalkylated products.

As a result of "cyclialkylation" reactions, aromatic heterocyclic systems containing O, S, and N can also be generated.

In addition to alkylation of aromatics, arylation is also possible. For example, a dehydrogenating condensation of aromatic nuclei, known as the SCHOLL REACTION, may be illustrated as follows:



Scholl reaction generally requires high temperatures and strong acid catalysts.

F-C catalysts may be also generated in situ as a result of some reaction.

In high temperature F-C reactions, the preferred catalysts are various oxides and sulfides.

2. Protected Functionality.

Diels-Alder reaction product to protect the diene or dienophile that can be thermally regenerated at high temperatures.

Phenol esters to protect the phenolic hydroxyl that can be regenerated at high temperatures via the Fries Rearrangement.

Sulfones and aryl sulfides to protect the sulfinic acid and SH, respectively, and which can be regenerated at high temperatures via the Smiley Rearrangement.

3. Latent Functionality

Amides and ammonium carboxylates to generate nitrile thermally.

Pyrolysis of melamine to generate $\text{H}_2\text{N}-\text{C}\equiv\text{N}$, which in turn polymerizes into
 $-\text{(\text{C}=\text{N})}_n-$
 NH_2

Pyrolysis of aryl anhydrides or halides to generate benzyne.

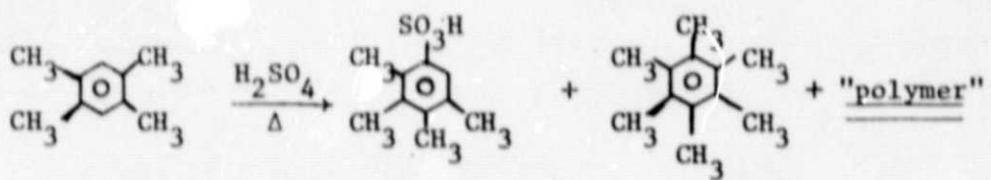
Pyrolysis of acetates to generate highly reactive olefins.

Pyrolysis of allyl sulfides to generate thiocarbonyl compounds; of allyl amines to generate imines; of allyl silanes to generate highly reactive carbon-silicone double-bonded intermediates; and of allyl phosphines to generate highly reactive carbon-phosphorus double-bonded intermediates.

V. NEW POLYMER-FORMING REACTIONS

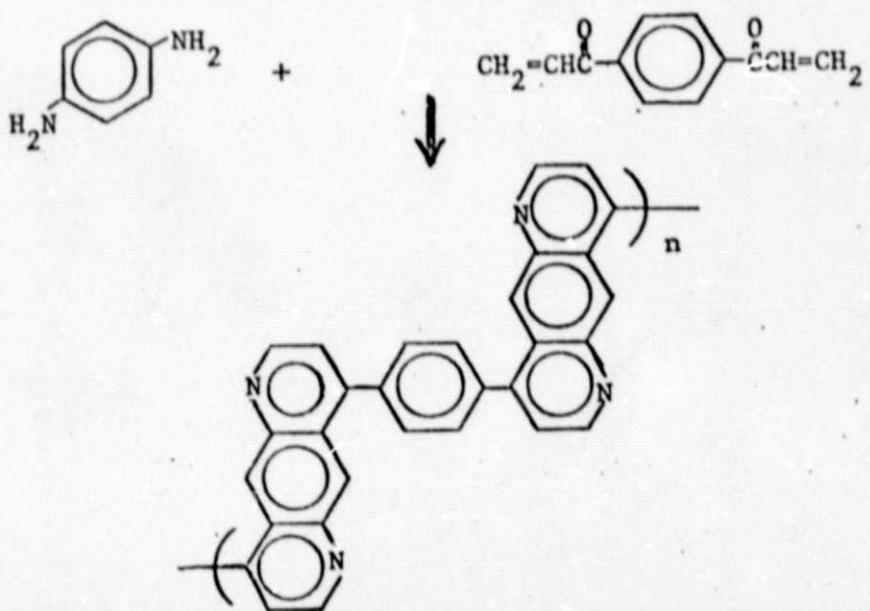
Finally, as a result of the literature survey we can not resist mentioning at least a few classical organic reactions that may be of interest in the synthesis of polymers never made before.

1. The Jacobsen Reaction 49



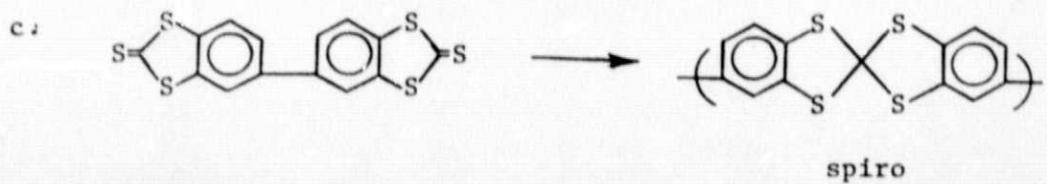
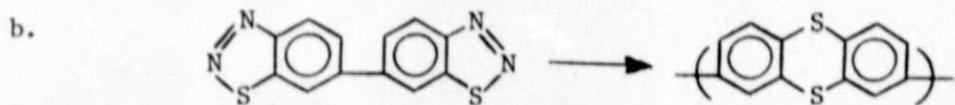
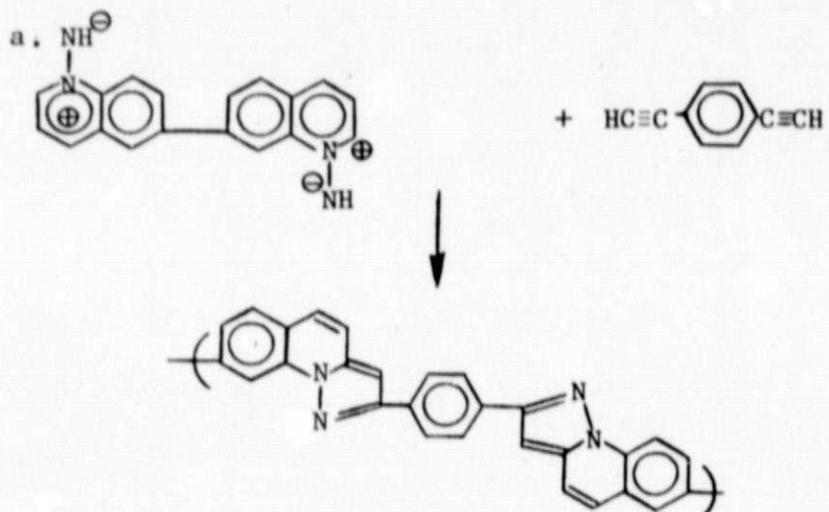
2. Skraup Synthesis of Quinolines

The polymer-forming reaction may be formulated as follows:



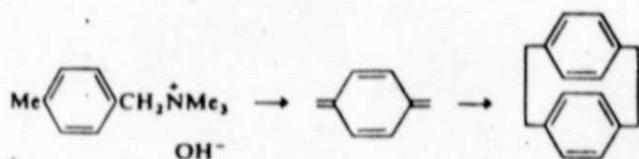
3. 1,3-Dipolar Addition Reactions 51

The polymer-forming reactions may be formulated as follows:

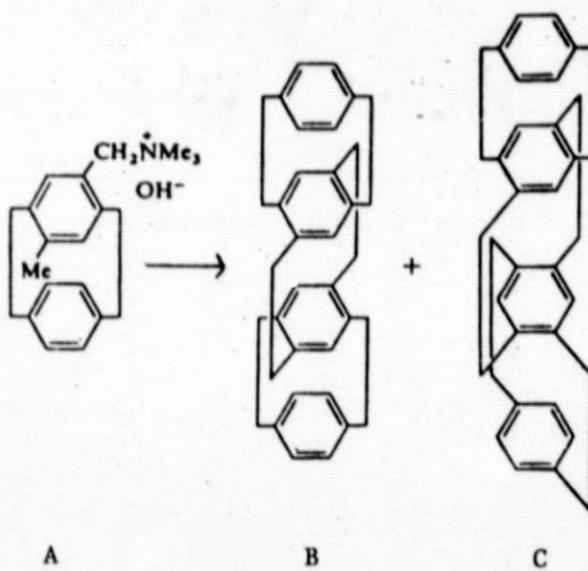


4. The Cyclophane-forming Reaction

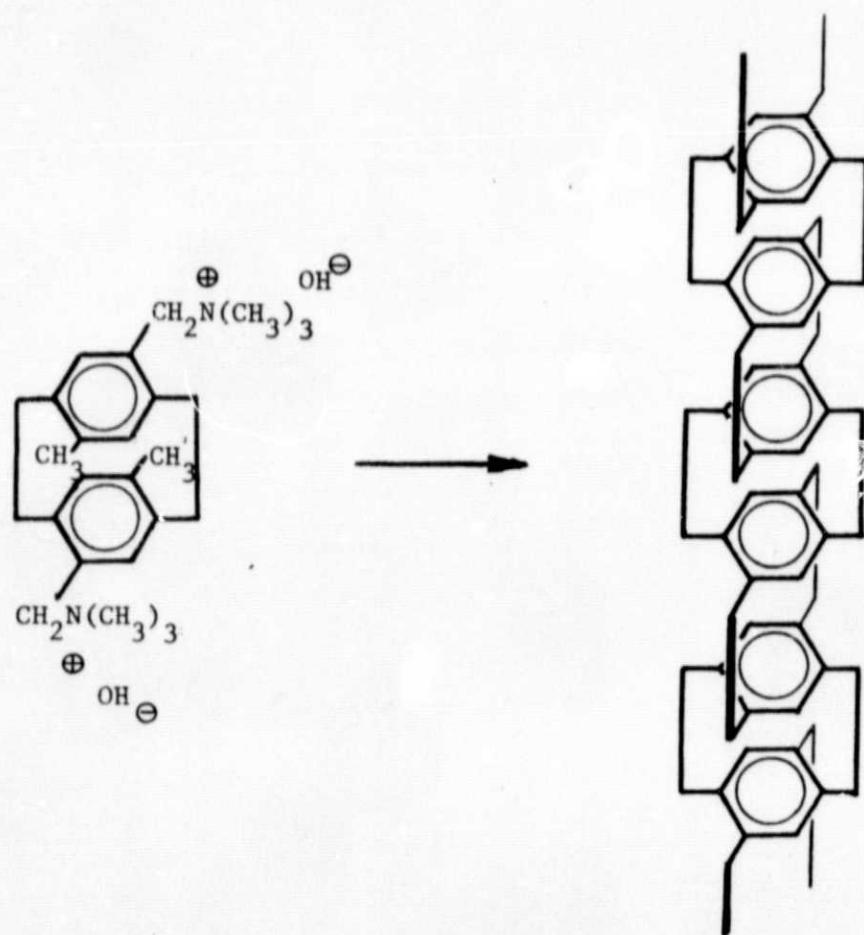
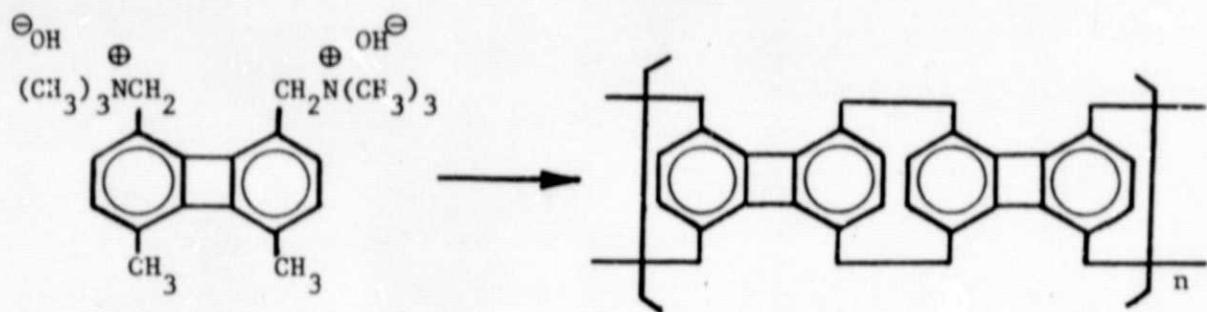
The proposal here is based on the dimerization of transient p-xylylene to give [2,2]-paracyclophane:⁵²



Pyrolysis of the quarternary hydroxide, A, in boiling xylene gives a mixture of the isomeric quadruple-layered cyclophane, B and C.⁵³



Thus, it may be of interest to look into structures of the following type:



various isomers