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### Structural Design and Thermal Properties of Polymers

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# Structural Design and Thermal Properties of Polymers

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## SUMMARY

Aerospace technology has established the demand for thermally stable polymers which retain useful properties at high temperatures. The reliability of a re-entry shield is directly dependent on the performance of the polymers used as ablaters. Polymeric ablation materials are sacrificial and are classified as subliming and charring ablaters. Subliming polymeric ablaters function by (a) depolymerization-vaporization, (b) pyrolysis-evaporation, and (c) melting-vaporization. Polymers which depolymerize quantitatively and reversibly are ideal subliming ablaters. Under hyperthermal conditions, charring polymeric ablaters must generate a large amount of char residue which will act as a binder at high temperatures for the reinforcements embedded in the char layer. Generally, the higher the thermal stability of the polymer, the higher the yield of char. The maximum thermal stability in polymers is usually obtained when: (a) thermally unreactive ring structures constitute a major portion of the polymer, (b) maximum use is made of resonance stabilization, (c) high bond energies exist between the atoms in the polymer, and (d) the cohesive energy density between polymer chains is high. Carbocyclic polymers, including the graphites, have high thermal stabilities but offer difficulties of fabrication. Thermally stable heteroaromatics which pass through tractable prepolymer stages are more readily prepared and fabricated; their char-forming properties in relation to structure are discussed. The values of "true" and "practical" thermal stabilities as applied to ablaters are also considered. The need for

a multidiscipline "oecumenical" approach to solving difficult problems is stressed. Some recent developments in the methods of syntheses of thermally stable polymers, including isotropic pyrolytic graphitic structures, are surveyed.

## INTRODUCTION

The unprecedented progress in our times in many fields of technology, particularly in the aerospace sciences, has established the demand for thermally stable polymers which retain their useful properties at temperatures above 400°C. This distinguishes them from the so-called "heat-resistant" polymers, such as the phenol-formaldehyde, melamine-formaldehyde, silicone, oxirane, and other polymers, which are limited, under continuous exposure, to a temperature of about 250°C, and, under intermittent use, to a temperature of about 325°C if the period of exposure to thermal stress is limited to short periods of time.

## THE CONCEPT OF THERMAL STABILITY

The thermal stability of a material is usually expressed in terms of the material's ability to withstand specified conditions and still retain the physical properties required of the material in the given application. Accordingly, the thermal stability of polymers is usually described in terms of a time-temperature relationship. One classification [1] defines as thermally stable those polymers which can resist degradation at 200°C for long periods of time, at 500°C for intermediate periods, or at temperatures in excess of 500°C and up to 1000°C for periods of several seconds. Another detailed classification has also been described [2]. It considers as thermally stable those polymers which show no appreciable change in mechanical properties when exposed in an inert atmosphere for 30,000 hr at 175°C, 1000 hr at 250°C, 1 hr at 500°C, or 5 min at 700°C.

Such arbitrary standards can, and frequently do, lead to confusion since they are descriptive only and not explanatory. In the absolute sense, thermal stability refers to values derived from data obtained during the thermal treatment of a polymer in the absence of other degradative agents; this has been interpreted to mean the absence of a reactive atmosphere. Accordingly, values obtained from evaluations performed in such inert

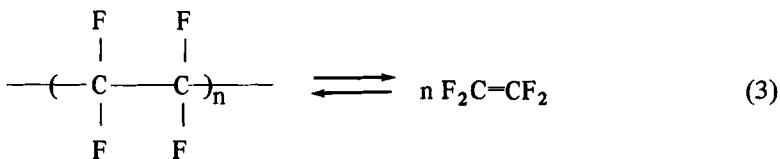
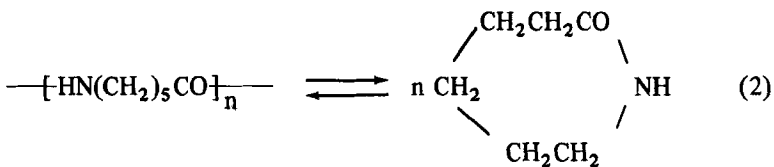
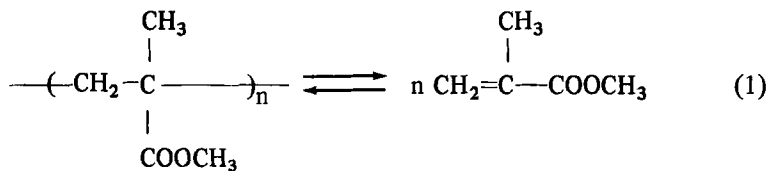
atmospheres as nitrogen, argon, and helium, or in highly evacuated systems ( $10^{-4}$  to  $10^{-6}$  torr), have been considered as yielding "true" thermal stability values. While the knowledge of the "true" thermal stability value is important because it characterizes the overall strength of all the bonds between the atoms in the polymer, the knowledge of the "practical" thermal stability value is equally important in understanding the degradative processes and is an essential element in the successful application of the polymer as an end product. "Practical" thermal stability refers, obviously, to the thermal behavior of the polymer in the environment in which it is to be used. Since most applications involve our earthly atmosphere, values obtained from evaluations in dry air, moist air, and oxygen are offered as "practical thermal stability" values.

### POLYMERIC ABLATORS

The re-entry shield is a most critical component in an aerospace vehicle, and its reliability is directly dependent on the performance of the polymer used as the ablator. Polymeric ablation materials are sacrificial and are classified as subliming and charring ablators, both of which are used as composites in conjunction with high-performance reinforcements in order to effectively resist erosion [3-11]. Subliming polymeric ablators are used as a component of internally ablating composites [12, 13]. In this system, the ablating material is removed from within the composite rather than at the surface. Basically, the system consists of a porous, refractory, continuous-phase matrix filled with a material which gasifies at high temperature. The function of the ablative gas-producing impregnant is to delay the surface temperature rise of the matrix for a sufficient period of time so that it will not melt during the period required for the specific service or mission. The principal types of porous refractory matrices investigated [14] have been alumina, zirconia, and silicon carbide having open cell porosity of 80-90%.

Porous ceramics are, per se, ablative-insulative materials, but their ablative characteristics are greatly improved by polymer impregnation [15-17]. Specifically, the polymer component increases the composite strength and the thermal shock resistance; it decreases the thermal conductivity and permits the toleration of higher environmental temperatures without exceeding the decomposition or melting temperature of the ceramic. Obviously, the polymeric infiltrant must be one that will respond to the hypothermal environment; that is, it must be thermally unstable so that it can ablate from

the porous ceramic substrate. The polymer's response may occur in a variety of ways, such as by (a) depolymerization-vaporization, (b) pyrolysis-evaporation, or (c) melting-vaporization. Suitable polymeric impregnants include polyethylene, polystyrene, poly(methylmethacrylate), polytetrafluoroethylene, some phenolics, certain nylons, and a number of polyurethanes. Of the numerous combinations available, the phenolic resin-impregnated silica composites have found the greatest use. In general, most phenolic polymers ablate in inert atmosphere by pyrolysis-evaporation at high temperatures, leaving a char residue varying from 30 to 55% of the initial weight, the amount depending on the particular type of phenolic polymer used. This char remains in the substrate pores, decreasing one important parameter, namely, the porosity of the refractory matrix. If the matrix is intended for reuse, the elimination of the polymer impregnant must be substantially complete. Polymers that depolymerize quantitatively and reversibly, such as poly(methylmethacrylate), polycaprolactam (Nylon 6), and polytetrafluoroethylene, are particularly suited for this purpose:



Also suitable are those polymers that pyrolyze substantially to volatile products which include products other than the original monomers, as represented by polyethylene, polystyrene, and a host of other polymers. Table 1 compares the residues at various temperatures of a number of polymers when heated in a nitrogen atmosphere at the rate of 150°C/hr.

Table 1. Fraction of Original Weight of Some Ablating Polymers When Heated in Nitrogen

Polymer type	% Initial weight remaining at indicated temperature (°C)										Reference
	200	300	400	500	600	700	800	900	1000	1100	
Phenol-formaldehyde	100.0	98.5	70.0	51.0	46.0	42.5	41.0	40.0			[18]
Poly(methylmethacrylate)	98.0	93.0	2.0	0.0	—	—	—	—	—	—	[19]
Polystyrene	100.0	96.5	50.0	2.0	0.0	—	—	—	—	—	[19]
Polyethylene	100.0	100.0	96.0	0.0	—	—	—	—	—	—	[19]
Polytetrafluoroethylene	100.0	100.0	100.0	97.0	0.0	—	—	—	—	—	[19]
Polycaprolactam	98.0	97.0	80.0	3.0	1.0	0.0	—	—	—	—	[19]
Polyurethane	97.0	62.0	20.0	5.0	0.0	—	—	—	—	—	[19]

A recent development utilizes carbonized reinforced polymers as the refractory matrix [20, 21]. Reinforcement is achieved by use of graphite fabric or other carbonized fibrous polymers such as black orlon or carbonized cellulose [22, 23]. The fabric is impregnated with a phenolic resin binder, conventionally molded, either by the vacuum-bag technique or in a press, and then pyrolyzed in an inert atmosphere at a gradually increasing temperature up to a maximum of about 800°C. The available porosity after pyrolysis ranges from 35 to 55%. The carbonaceous residues from the phenolic resin hold the reinforcing fibers together, forming a continuous phase; thus, the physical and mechanical properties can be controlled, and structural deficiencies such as cracks, delaminations, and spalling can be eliminated.

After the carbonized porous matrix has been suitably prepared, it is impregnated with a polymeric ablator. Though the phenolic resins have been used primarily as the source of the carbonaceous binder in fiber-reinforced matrices, other polymers which meet the characteristics demanded of a polymeric charring ablator can be considered as suitable candidates for binders in this application. The primary requisite of a charring polymeric ablator is that on pyrolysis it must generate and leave a reasonable amount of char residue which will act as a binder at high temperatures for high-performance reinforcements embedded in the thermally degraded char layer. This requires that the polymer used as a binder must have some strength and adhesion after it has undergone pyrolysis. The phenolic polymers thermally degrade to form condensed-ring nuclear residues as chars with the loss of 45-70% of their initial weights. In general, the higher the weight per cent conversion of the polymer to a solid char, the better the retention of the reinforcement and the higher the strength of the remaining char layer. As a corollary, it may be stated that, generally, the higher the thermal stability of the polymer, the higher the yield of char.

### CHEMICAL STRUCTURE AND THERMAL STABILITY

In 1959, it was recognized [24] that the magnitude of polymer stability is proportional to the resistance of its chemical structure to degradation while involving environment and available energy. It is these changes in chemical structure which determine the material's physical properties. The involvement of environment with the energy available in the system implies that the destructive process is not the result solely of the amount of energy

transferred to the polymer but is related implicitly also to the kind of energy, as well as to the amounts and kinds of energies in the subsequent system following from the efficient or inefficient transfer of energy to the polymer.

Achhammer et al. [24] appear to have been among the first to undertake the task of specifying the nature of the chemical structures which would impart thermal stability to polymers. Though the judgment was made primarily on the then available heat-resistant polymers, it represented considerable understanding of the problem and laid the foundations on which others were to build shortly thereafter.

Eirich and Mark [25] described the requirements for achieving "practical" thermal stability in polymers as (a) a high melting or softening temperature, (b) a high resistance to spontaneous pyrolysis, and (c) a high resistance to degradation by chemical action. They related these factors to (1) phase changes as evidenced by both first- and second-order transitions, (2) the tendency of the polymer molecule to depolymerize, and (3) the ease with which the polymer reacts with chemical species in the environment. These requirements do not correlate stability to structure.

The relationship of a polymer's thermal stability to its chemical structure has been discussed and reviewed in several papers [24, 26-28], and some structural criteria which contribute to maximum thermal stability have been formulated. Five factors have been listed [5, 6] which must be present in a polymer to achieve thermal stability: (a) high bond energy between the atoms in the chain, (b) a structure which sterically hinders the elimination of small fragments or allows no easy pathway for rearrangements, (c) resonance-stabilized structures, (d) the absence of structures which can furnish free radicals which initiate chain reactions, and (e) the frequent use of the poly-binding principle. The poly-binding principle requires that each skeletal atom be linked in the chain by more than one route.

It is true that many polymers possessing structures which generate radicals or which are sterically free to rearrange or to eliminate small molecules suffer serious degradation, but, if such structures can be converted to more thermally stable structures by this type of intermolecular or intramolecular chemistry, these structures should be used even if high temperatures are required to achieve the synthesis, because we add thereby another mechanistic tool to the syntheses now available. In due course, such syntheses are illustrated. Accordingly, it may be stated that the maximum thermal stability in polymers is usually obtained when (a) thermally unreactive ring structures constitute a major portion of the polymer composition, (b) maximum use is made of resonance stabilization, and (c) high bond energy exists between the atoms in the polymer.



High resonance energy structures can be incorporated in polymers by use of appropriate aromatic or heterocyclic groups; their thermal unreactivity can be estimated from the thermal reactivity data of Lewis and Edstron [29].

These criteria apply to all polymers without regard to the geometry of the polymer structure, that is, whether they are linear or branched, cross-linked or space structures. However, polymer geometry can and does change the degree of thermal stability.

Generally, in the design of a new polymer, an attempt is made to apply as many of these principles as possible. In most cases, though, these general principles serve only as useful guides—experience has shown that many of them cannot readily be realized simultaneously in a single polymer. Also, in order to achieve a balance of desirable polymer properties, a compromise is usually made so that no single principle is applied to its extreme. It should be stressed that most of the published bond energy values have been determined from studies of small molecules in the gaseous or liquid state. Intermolecular forces, such as dipole, induction, dispersion, and hydrogen bonding forces, influence the properties of polymer molecules as they do in simple molecules [30-45]. Since interactions in polymers can have a considerable effect on the stability of a given bond under a specific set of conditions, the bonds in polymers behave as if they are stronger than in simple monomeric molecules [24].

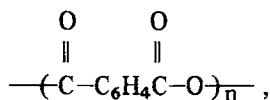
The energy necessary to remove a molecule from a molecular aggregate to a position devoid of interaction with another molecule has been termed molar cohesion; the cohesive energy per unit volume is called specific cohesive energy or cohesive energy density [38]. Whereas heats of combustion are used to determine the dissociation energies of primary valence bonds, the values of molar cohesion are determined by heats of vaporization and sublimation or from Van der Waals' attraction constants [39].

The translation energy in a molecule is a function of its temperature, and this energy determines the molecule's tendency to escape as a gas from its liquid. However, vaporization can occur only when the molecule's translation energy is equal to its cohesive energy which, in turn, is a function of its molecular weight. Accordingly, the boiling point in a homologous series is a function of its molecular weight. Thus, even if the cohesive energy per atom is small, the total cohesive energy per molecule, as the molecular weight increases in a homologous series, is greater than the primary valence bond energy, and the molecules will decompose before they volatilize. Even in the case of the saturated normal paraffins,  $\text{H}(\text{CH}_2)_n\text{H}$ , this point occurs at molecular weights far below the point

where polymer properties appear. The boiling points of the saturated, branched hydrocarbons are lower than those of the normal saturated hydrocarbons of the same number of carbon atoms because, due to branching, dense packing is difficult because of the bulky groups and because the specific cohesion energy is reduced. When the molecules contain polar groups, the cohesive energy between molecules is increased, raising the boiling points. This may be readily demonstrated with a homologous series of paraffin hydrocarbons starting with methane,  $\text{H}-\text{CH}_2-\text{H}$ , which is a gas. By increasing the number of  $-\text{CH}_2-$  units to  $\text{H}-(\text{CH}_2)_8-\text{H}$ , liquid octane, a component of gasoline, is obtained. By further increasing the number of  $-\text{CH}_2-$  groups to  $\text{H}-(\text{CH}_2)_{30}-\text{H}$ , a solid paraffin wax is obtained. By a further increase to  $\text{H}-(\text{CH}_2)_{1000}-\text{H}$ , a giant paraffin molecule results. All the bonds in these homologous paraffins are covalent. Even after an atom forms a covalent bond, it still has residual forces by which it can attract other atoms or molecules, thereby making them neighbors. If this cohesive energy is larger than their energy of motion, the molecules will adhere to each other and form liquids or solids. The cohesive energies are obtained from measurements of boiling points. In the homologous paraffin series,  $\text{H}-(\text{CH}_2)_n-\text{H}$ , the boiling points increase in the value of  $n$ , indicating a progressive increase in cohesive energies.

The value of the cohesive energy is dependent not only on the size of the molecule but also on a polarity factor. Organic molecules which contain nitrogen, chlorine, oxygen, and a few other atoms suitably situated in their molecular structure, are polar molecules with higher cohesive energies than their nonpolar counterparts. For example, methyl chloride boils at about  $0^\circ\text{C}$  compared with the boiling point of methane of about  $-160^\circ\text{C}$ . In a similar fashion, polymers may be polar or nonpolar, with the polar polymers having much higher cohesive energies than nonpolar polymers of the same size. This is an important point to remember, when later we compare the carbocyclic polymers with the heterocyclics, particularly those containing nitrogen. At any rate, because polymers are very large molecules, all polymer molecules, whether polar or not, have reasonably high cohesive energies. The cohesive energies have a very important effect on many polymer properties, particularly the melting point. Accordingly, as chain length increases, the physical properties of a polymer become more dependent on the interaction of cohesive forces between chain segments of adjacent chains than on the interplay between different molecules. For example, the giant paraffin molecules,  $\text{H}-(\text{CH}_2)_{100}-\text{H}$ ,  $\text{H}-(\text{CH}_2)_{200}-\text{H}$ , and  $\text{H}-(\text{CH}_2)_{300}-\text{H}$ , seldom behave as independent molecules because their size is so great that the motion of one end of the chain has little or no effect on the other end of the chain.

An even more extraordinary case of the influence of intermolecular forces on the properties of polymers is found in poly(terephthalic anhydride),

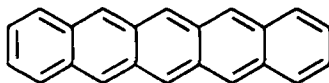


which not only is hydrolytically resistant but is unaffected by hydrochloric acid, nitric acid, and even aqua regia [46].

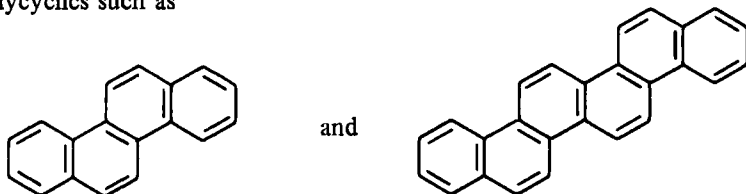
Application of the principles which yield thermally stable polymers produces in many cases insoluble, infusible, intractable, brick-dust polymers, which are difficult or impossible to fabricate as useful products. This is particularly true of the carbocyclic polymers, which contain only carbon and hydrogen as elements in their constitution. The melting points of the polyphenylenes, polyacenes, and polyphenes, as a function of the number of carbocyclic rings, are shown in Fig. 1 [47].

The melting points of the paraphenylenes increase rather regularly; the melting point [56] of the *p*-sexiphenyl is about 470°C. This led to the speculation [48, 49] that poly(*p*-phenylene) would be infusible as well as stable to temperatures in the region of 800-900°C. It was predicted also that, since it was infusible, it would be unsuitable for the fabrication of shaped objects [50], and such was found to be the case [51, 52].

The melting points of the linearly fused ring polycyclic aromatics also increase with the number of rings from 80°C for naphthalene to about 600°C for the five-ring structure,



Though one ring less, this is about 130°C higher than that of the six-ring numbered polyphenylene. The melting points of the angularly fused ring polycyclics such as



increase in a similar fashion with the number of rings, but their melting

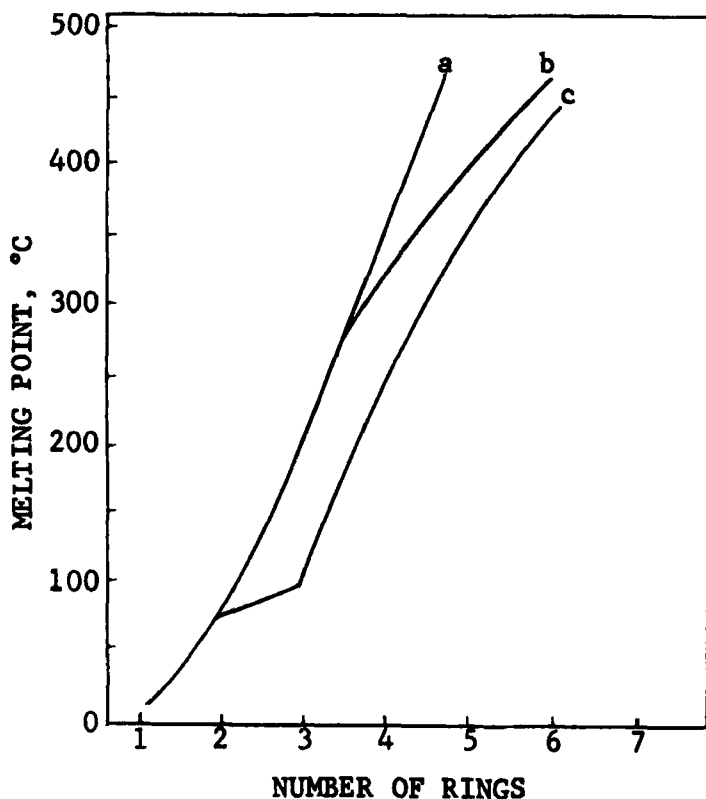
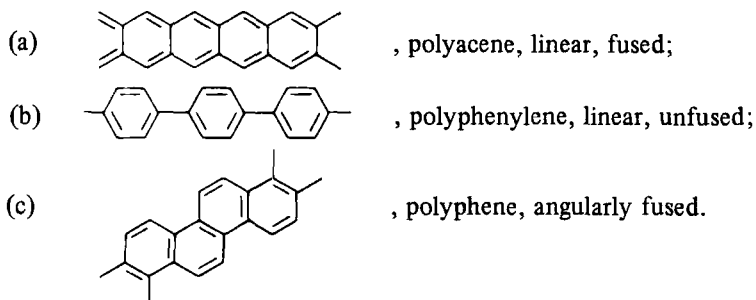


Fig. 1. Melting points of polycyclic aromatics:



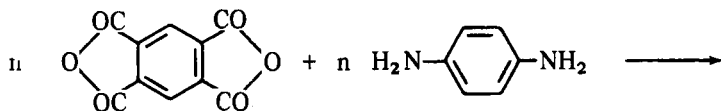
points are slightly lower, of the order of about  $50^{\circ}\text{C}$ , than the linear unfused polycyclics and about  $100^{\circ}\text{C}$  lower than the linearly fused polycyclics. An increase in the number of fused rings in the linearly fused polycyclics yields a polyacene; a comparable increase in the angularly fused polycyclic leads to a polyphene. The successful syntheses of polyacene and polyphene has not been reported, though a number of attempts have been recorded [53-56].

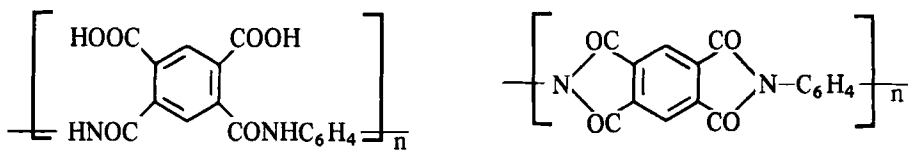
Natural graphite and synthetic graphite are true carbocyclic polymers. Synthetic graphite is now a product of industry [57, 58]. One step in the synthesis of synthetic graphite comprises the deep pyrolysis of hydrocarbons. Industry has, therefore, labeled it "pyrolytic graphite." It is an extraordinary polymer in many respects; when properly synthesized its thermal stability is similar to that of natural graphite, though in a number of other respects, natural and pyrolytic graphites are dissimilar.

The thermal stability of the graphites is very high and can serve as a reference for most organic polymers. This fact, and the observation that the melting points of linearly and angularly fused polycyclic aromatics increase very steeply with an increase in the number of rings, indicate that the yet unknown polyacene and polyphene should be as intractable and infusible as graphite and comparable to graphite in thermal stability.

Polymers which possess desirable physical properties at high temperature, but which pass through a tractable or soluble stage which permits them to be fabricated easily into an ultimate product, have been a long-standing, challenging goal of the polymer scientist. In recent years, a number of polymers have been synthesized which pass through a fabricable stage and which, in the final stage, show remarkable thermal stability.

This objective has been achieved in most cases by interrupting the polymerization at a stage which has been described variously as the "prepolymer," "hemi-polymer," or "semi-polymer" stage—the stage in which they are soluble or tractable. This achievement was possible only because of the substitution of some of the carbon atoms in the carbocyclic polymers by heteroatoms, such as oxygen, nitrogen, and sulfur, in monomer reactants which would allow reasonable control of the chemistry in distinct stages so that noncyclic, fusible or soluble, tractable polymers could be isolated and fabricated before the final reaction to the final, insoluble, infusible, intractable structure. This prepolymer concept is illustrated by the intermolecular reaction of pyromellitic anhydride with *p*-phenylenediamine to form the hemi-polymer, which then by an intramolecular condensation, forms the polyimide; a reaction of the anhydride with a tetraamine yields a pyrroline:

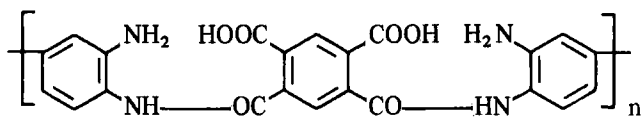
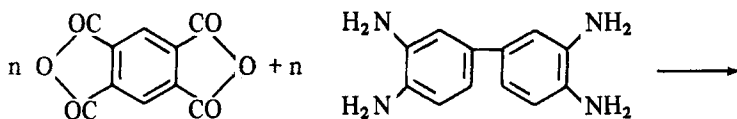




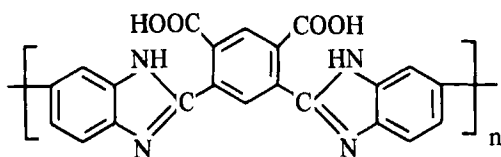
a poly(hemipyromellitimide)  
(a polyamic acid)

a poly(pyromellitimide)

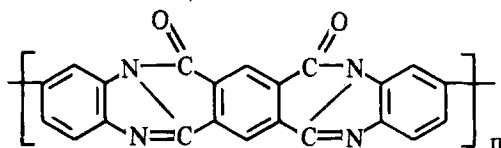
(4)



a polyamic acid



a polyimidazolamic acid



a polypyrrone

(5)

This "hemi-polymer" technique is applicable only to those polymers which, in their course of synthesis, pass through an isolable, fusible stage. A large number of thermally stable polymers do not pass through such an isolable stage. In such cases other expediciencies are used. For example, the polyphenyls and pyrolytic graphite are intractable; shaped structures are obtained from them only by special fabrication techniques.

Extensive and expensive effort has led to the syntheses of several classes of thermally stable polymers. All of them contain aromatic structures as recurring units and at least one heteroatom appropriately located in their structures; most of them belong to the aromatic carbocyclic-heterocyclic class of polymers.

Most likely, the first aromatic-heterocyclic chain polymer prepared [59] was a polyphthalimide, prepared by heating aminophthalic acid. Undoubtedly it contained some imide segments, though most of the polymer thus prepared was found to consist of a three-dimensional polyamide structure [60]. Some of the more recent aromatic chain polymers, all synthesized since 1955, are the polyimides [61-63], the polybenzimidazoles [64], the polyoxadiazoles [65, 66], the polybenzothiazoles [67, 68], the polytriazoles [69], the polypyrazoles [70], the polybenzoxazoles [71, 72], the polyquinoxalines [73, 74], the polypyrrones [75], the BBB polymers [76], the  $N,N'$ -diphenyl-polybenzimidazoles [77], and the poly-Schiff bases [78-84].

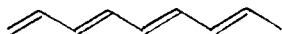
All of these polymers have, or are presumed to have, uninterrupted, conjugated or pseudoconjugated, aromatic or aromatic-heterocyclic backbone structures; they can be related to one or more of the model structures shown in Fig. 2.

By a relatively simple comparison of the typical polymer structures, one can appreciate that the polyimides and the poly-Schiff bases are the heteroaromatic analogues of polyphenylene, that the polybenzimidazoles are the heteroaromatic analogues of the polynaphthalenes, and the pyrrones and the BBB polymers of the polyacenes. Since the properties of the simple carbocyclic aromatic compounds and their heteroaromatic analogues are very similar, the thermal properties of polyphenylene, polynaphthalene, and polyacene, as shown in Fig. 1, can give some indication of the thermal properties that can be expected for the heteroaromatic analogues.

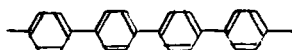
In contrast to the difficulties encountered in the syntheses of tractable polyphenyls, polyacenes, and polyphenes, the syntheses of their heteroanalogues have been particularly fruitful in terms of effort, time, and expense. This is so because the aromatic-heterocyclics lend themselves to the hemipolymer technique. In these stable polymers, the location of the aromatic-type rings relative to the main chain is important.

MODEL STRUCTURES

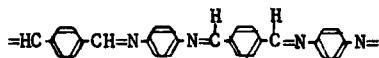
TYPICAL POLYMER STRUCTURES



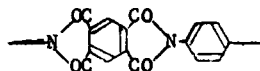
A Conjugated linear polymer



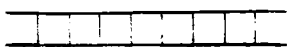
A1 Polyphenylene



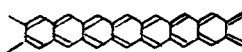
A2 Poly-Schiff Base



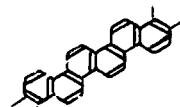
A3 Polyimide



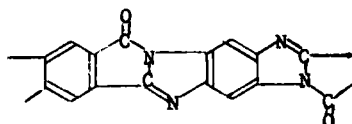
B Conjugated ladder polymer of multiple fused rings. Illustrative of the poly-binding principle.



B1 Polyacene



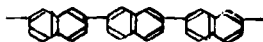
B2 Polyphene



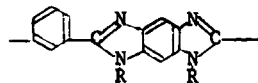
B3 ladder pyrrone; (or ladder BBB polymer)



C Stepladder polymer. A hybrid of conjugated ladder and conjugated linear structures.



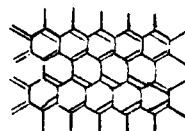
C1 Polynaphthalene



C2 Polybenzimidazole



D Conjugated Sheet Polymer (A Chicken Wire Polymer)



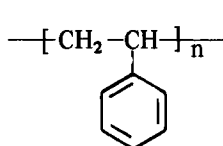
D1 Natural Graphite

D2 Pyrolytic Graphite

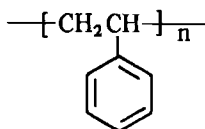
Fig. 2. Relationship of model structures to typical polymer structures.



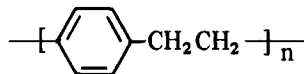
The significance of the location of the aromatic rings relative to the main chain is best demonstrated by reference to the melting point of linear, amorphous, and isotactic polystyrene,  $(C_8H_8)_n$ , and comparing it to the melting point of the isomeric poly-*p*-xylylene [85, 86].



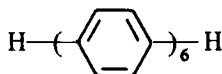
amorphous polystyrene  
m.p. 108°C



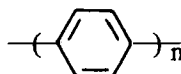
isotactic polystyrene  
m.p. 240°C



poly-*p*-xylylene  
m.p. 400°C



polysexiphenyl  
m.p. 470°C

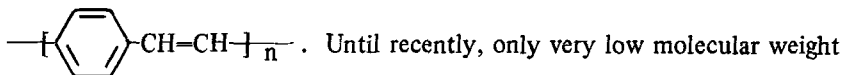


poly-*p*-phenylene  
m.p. infusible

Both have the same ratio of one aromatic ring to two methylene groups. In polystyrene the aromatic ring is pendant and in the polyxylylene the ring is in the backbone of the chain. Isotactic polystyrene and poly-*p*-xylylene are polymers with a high degree of crystallinity, and their high melting points relative to amorphous polystyrene reflect the energy necessary to separate the polymer chains from their crystalline lattices. The melting point of isotactic polystyrene is 240°C and that of poly-*p*-xylylene is 400°C; though their molecular weights are much higher than polysexiphenyl, their melting points are lower than the 470°C of the crystalline sexiphenyl and much lower than that of the infusible polyphenyls. In part, this is explained in terms of conjugation. There is no conjugation in polystyrene, and at best, there is some pseudoconjugation [87] in the polyxylylene as a result of pi-orbital overlap from the aromatic carbon atoms adjacent to the  $\text{CH}_2$  groups.

Even though the poly-*p*-xylylene is not a conjugated polymer, its thermal stability is remarkably high as a consequence of a high cohesive density resulting from the interaction of the aromatic phenylene rings in a crystalline structure. The same high cohesive density explains the remarkable properties of poly(ethyleneterephthalate). In both of these polymers, the cohesive density is seriously reduced by increasing the length of the

aliphatic chain between the phenylene rings. If we retain the cohesive density of the phenylene rings of polyxylylene and synthesize its conjugated analogue by stripping two hydrogens from  $-\text{CH}_2\text{CH}_2-$  group, we derive the structure of a poly(p-phenylene ethylene), a polystilbene,

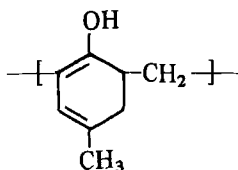


Until recently, only very low molecular weight polystilbenes, of approximately decamer chain length, were known, and even in these oligomers the effect of uninterrupted conjugation is spectacular. These low molecular polystilbenes do not melt. Heteroatoms, which possess unshared electrons such as nitrogen, oxygen, and sulfur can contribute to the cohesive density. In particular, nitrogen does so readily by hydrogen bonding with atoms of neighboring polymer chains.

### Linear and Cross-Linked Polymers

An indication of the thermal stability of a polymer and its ability to form a char can be obtained by thermogravimetric analyses in an inert atmosphere such as helium or nitrogen. A number of the more recently synthesized polymers have considerably higher weight residues than the heat-resistant type of phenolic, as shown in Table 2.

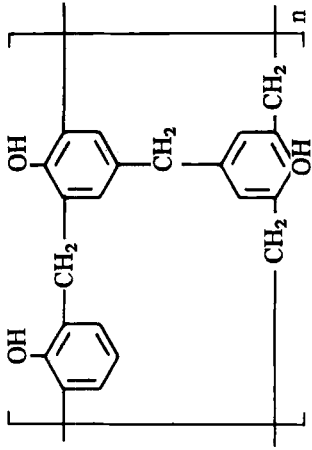
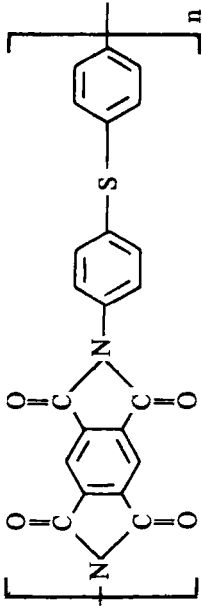
In carbon backbone polymers, high weight per cent residues are normally associated with a highly cross-linked structure. The phenolic resin shown in Table 2 is highly cross-linked, leaving a 40% weight residue; this compares to a linear, non-cross-linked para-cresol-formaldehyde resin of the structure



which leaves a weight residue of less than 10% at 500°C and about 5% at 900°C. That cross-linking is beneficial to char formation is evident in the comparison of the thermogravimetric data of polystyrene, a styrene-divinylbenzene copolymer and polydivinylbenzene, as shown in Table 3.

By slow and careful temperature control, large weight per cent residues have been obtained by the pyrolysis of polydivinylbenzene in the synthesis of abstracted semiconducting polymers [89]. The polymers shown in Table 2, with the exception of the polysiloxane, are not cross-linked and

Table 2. Thermogravimetric Analysis of Some High-Temperature Polymers

Type of polymer	Structure	% Residue at indicated temperature (°C)								Reference
		300	400	500	600	700	800	900		
Phenolic		98	70	51	46	42	41	40	[19]	
Polyimide		100	99	98	68	62	60	58	[19]	

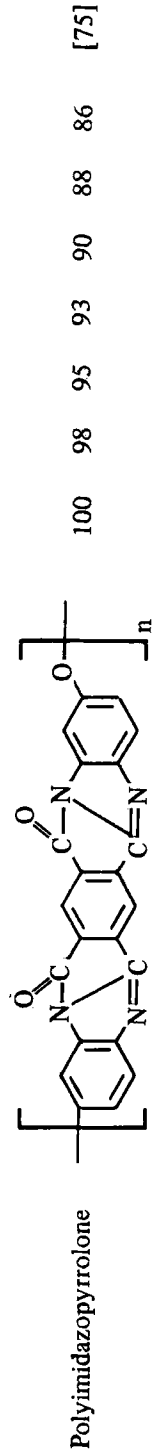
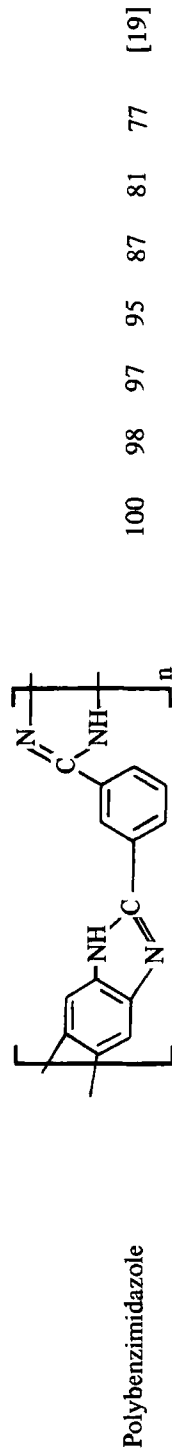
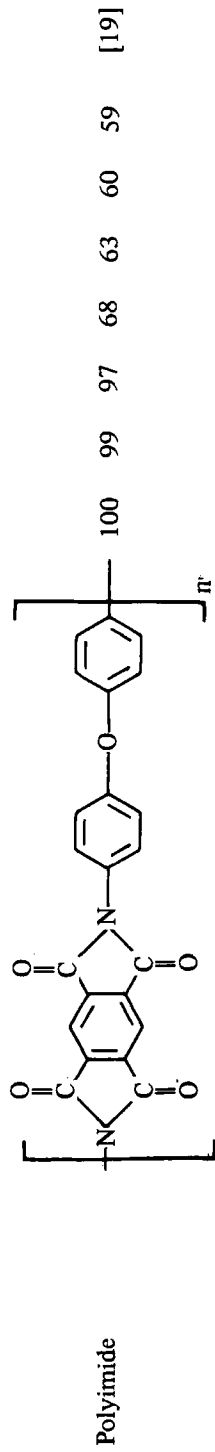

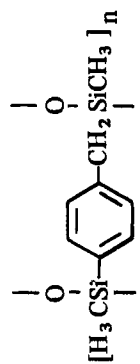
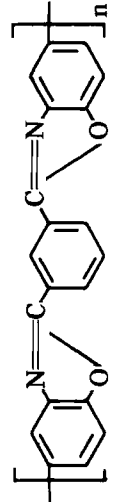
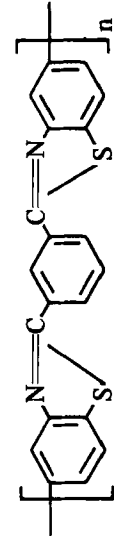
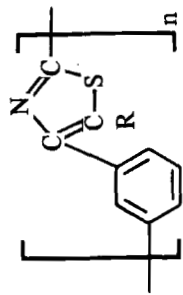


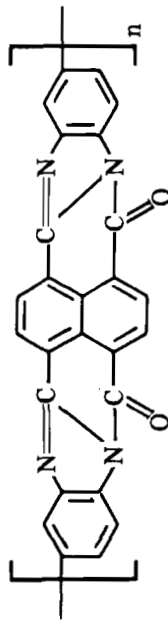
Table 2. (continued)

Poly-Schiff base		100	100	99	96	92	88	86	[87]
Polysiloxane		99	98	97	95	92	89	89	[19]
Polybenzoxazole		100	100	100	95	78	76	74	[88]
Polybenzothiazole		100	100	100	98	96	93	90	[67, 68]



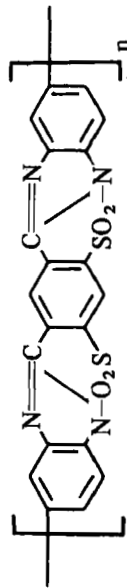
**Polythiazole**

96 94 91 78 64 61 60 [19]



**BBB**

100 100 100 100 100 90 84 83 [76]



**Polythiazone**

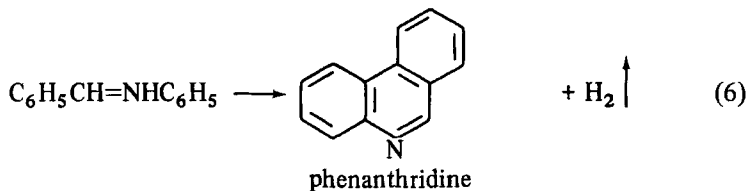
100 100 100 100 100 100 100 91 [92]

Table 3. Effect of Cross-linking of Char Formation in Styrene-Type Polymers [19]

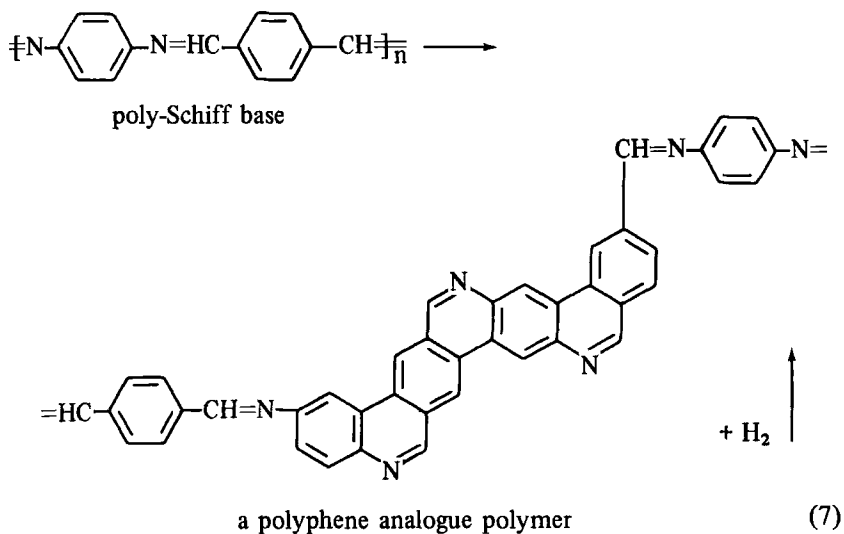
Polymer	% Weight residue at indicated temperature (°C)						
	300	400	500	600	700	800	900
Polystyrene	96.0	50.0	2.0	0.0	0.0	0.0	0.0
Styrene-divinyl- benzene copolymer 40-60	96.0	70.0	22.0	18.0	17.0	15.0	14.0
Polydivinyl- benzene	100.0	90.0	28.0	23.0	22.0	22.0	20.0

appear to be an exception to this generalization. When normally synthesized, these polymers have the classical linear molecular structure and can be dissolved in a variety of solvents, and all of them can be dissolved in concentrated sulfuric acid. Their structures allow the polymers to be heated to high temperatures without apparent fragmentation of the backbone chain. However, after heating, they are no longer soluble even in concentrated sulfuric acid. Marvel has attributed [90] this insolubility to the formation of cross-links most probably by a dehydrogenation reaction between aromatic rings. The same phenomena have been observed in other polymers.

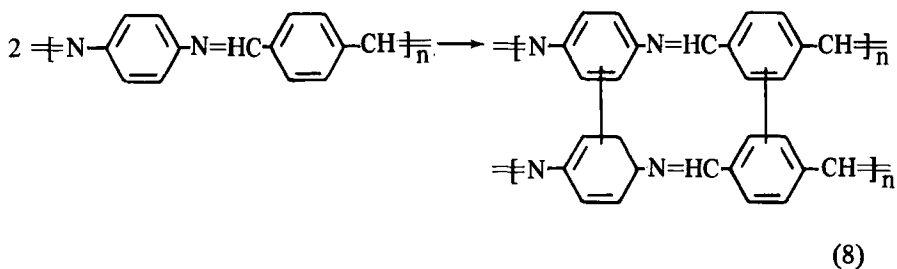
The poly-Schiff bases show good stability in an inert atmosphere [83, 87]. Above 500°C the polycondensation still continues to approximately 600°C, at which point another process, which eliminates hydrogen, begins to occur and continues to about 1100°C without catastrophic damage to the polymer. When re-evaluated thermogravimetrically, the derived abstracted polymer is stable in nitrogen to 1176°C, the limit of the apparatus, and to 600°C in oxygen. Infrared spectral studies did confirm, indeed, that the structure of the polymer had changed as the result of intramolecular and intermolecular reactions which were accompanied by the elimination of hydrogen, similar to that observed in the monomeric Schiff base [91].



Thus, by rearrangement, hydrogen elimination, and cross-linking, then, poly-(para-xylylidene-p-phenylenediamine) of good thermal stability was converted to one which contains phenanthroline segments and is of higher thermal stability, thus:



and





Similarly, the isomeric para-meta, meta-para, and meta-meta Schiff base polymers yield isomeric angularly fused ring structures [78-84]. If chemistry of this kind requires high temperatures, there is no choice but to use high temperatures.

In the cases studied, the cross-links were the incidental or accidental result of the thermal treatment of the polymers. Such was not the case for the polysiloxane shown in Table 2. The chemistry was so selected that the cross-links would form in the course of the polymerization, and all, if not most, of the cross-links were established before the thermogravimetric test. The beneficial influence of these cross-links is evident in the fact that approximately 90% of the polymer remained as a char at 900°C. This raises the question as to whether or not the deliberate, rather than accidental, introduction of a controlled number of cross-links in the other linear polymers given in Table 2 would cause an increase in the weight per cent of char residue. Published literature on this aspect is nonexistent. Deliberately introduced cross-links appear [92] to increase char yields in some polymers but not in others. It seems that if the linear non-cross-linked polymer is stable in nitrogen to about 450-500°C, sufficient cross-links form at these temperatures so that the resulting abstracted polymer yields high char residues.

### Unstable Polymers

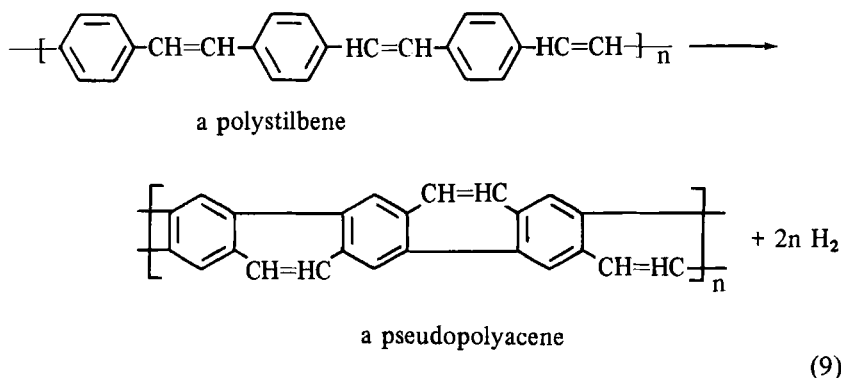
The question arises as to whether polymers which contain structures which rearrange, or which yield ionic or radical fragments when heated to high temperatures, should be synthesized and considered as candidates for high-temperature application or as charring ablators. If the rearranged polymers, as in the case of the poly-Schiff bases, are more stable than their progenies, and if there is no alternate synthesis for the derived rearranged polymer, then the answer is obvious. If chemistry of this kind requires high temperatures, there is no choice but to use the high temperature as a mechanistic tool of synthesis. The answer to the question concerning systems involving reactive fragments, such as radicals and ions, is best considered by a case history.

The polyazines,  $\text{=}\left[\text{N=N-CH-C}_6\text{H}_4\text{-CH}\right]_n$ , are analogues of the poly-

Schiff bases, and were synthesized [82] with the expectation that they would be unstable; their thermal behavior would, therefore, contrast with that of the Schiff bases. The parent unsubstituted polyazine decomposes at

about 300°C; then, as the temperature is raised, decomposition continues at slower rates up to and beyond 600°C. This decomposition was investigated in some detail; the main gaseous product of decomposition was found to be nitrogen and the residual polymer was polystilbene. The nitrogen was completely eliminated in the temperature range of 700°C, and the chain length of the polystilbene corresponds, at least, to the chain length of the original polyazine. End-group coupling undoubtedly also extended the chain length.

Mechanism studies on various monomeric unsubstituted and substituted azines,  $RC_6H_4CH=N-N=HC_6H_4R$ , and on structurally similar polymers have definitely established [93] the decomposition as a combination of radical and ionic mechanisms. Here, then, is a spectacular example of a polymer structure deliberately selected so that at some definite low temperature it decomposes into radicals, and, in the process of decomposition eliminates an inert gas while simultaneously synthesizing an extremely stable polystilbene. Certainly, mechanisms of this kind cannot be excluded as tools of synthesis in the creation of thermally stable polymers. The thermal treatment of polystilbene at temperatures of the order of 700°C or higher also apparently introduces other structural changes simultaneously with the elimination of hydrogen. This reaction has not been studied in detail, but the preliminary interpretations of limited data indicate that an intramolecular rearrangement with the simultaneous elimination of hydrogen, similar to that observed in the poly-Schiff base conversion, is also in operation in this case. By analogy, then, we propose the following reaction for at least part of the chain:



## CRITERIA FOR CHAR-FORMING POLYMERS

In the course of this discussion reference has been made to a reasonable number of polymers as being thermally stable and char forming. What were the criteria for these judgments? The description of the logic by which these judgments were made is a general one, since the details of minor differences of technique are not truly essential.

A small sample of the polymer, in the form of film, chunks, or as a fine powder, is placed in a thermogravimetric analyzer and heated from ambient temperature to higher temperatures at a preselected heating rate of 15, 10, 5, or 2°C/min either under a reduced pressure of about  $10^{-5}$  torr or in an atmosphere of nitrogen, helium, or air at a gas flow rate of 1 standard liter/min, or at some fraction or multiple thereof, while the changes in polymer weight are traced by an X-Y recorder on a chart called a thermogram. These thermograms are then interpreted and the "true" and "practical" thermal stabilities of the polymers recorded. What do these thermograms really tell us? In reality, they tell us no more than the behavior of the polymers under these specific parameters used in the test. They do not specify the "practical" thermal stability of the polymer unless the environmental parameters experienced outside of the thermogravimetric cell are identical in all respects with the parameters of the tests; this means that between the two there must be a complete identity of particle size, atmosphere, rates of heating and gas flow, etc. Provided the parameters are exactly specified, thermogravimetric data of this kind primarily give reference values which can be used by oneself and other experimenters to verify that a polymer duplicated by the specified synthesis is, or is not, a facsimile of the one used in the first test. These data serve also to eliminate from further consideration polymers which obviously are unstable. But, on the basis of these values, one may make only an educated guess that a specific polymer may or may not be suitable for a very specific application, provided the application is not a critical one. Where the application is so critical that it involves national interest, the application of a particular polymer on the basis of a judgment so derived, has in my estimation, only a limited probability of success. If the application does succeed, it is fortuitous; if it fails, it is truly disastrous.

Let us consider one device intended for use under such prespecified conditions that a thermally stable, char-forming polymer would be required. For the specific mission of the moment, we are requested to select the correct charring polymer from several whose "true" and "practical" thermal stabilities are listed. We choose polymer X, and in doing so, we

assume that the "practical thermal stability values" in air truly characterize the polymer in an environment equivalent to that in a re-entry situation, solely because the atmosphere specified is air. Even a superficial analysis indicates that hot air is the only common denominator in these two systems. The thermal stability of the polymer is dependent not only on the available energy but also on (a) the amount and kind of energy absorbed by the polymer and (b) the subsequent system or systems resulting from these processes. In re-entry, the gaseous molecules impact upon the heat shield at supersonic velocities, thereby increasing the temperature of the shield to the point where radiative and convective processes are evident; but not so evident is the process of thermal conduction, in which an advancing front decomposes the polymer into the gaseous fragments which must diffuse from the region of origin. If the concentration and pressure of the gaseous fragments are sufficiently high, they can prevent impingement of additional air on the now radiating surface, so that the observed burning is not a combustion of the surface of the shield but of a gaseous front removed from it, which in turn pumps radiative and conductive energy back into the shield surface. At charring temperatures, ionic and electronic conduction exists in polymers, and these processes conceivably could play some role in the destruction of the metal substrate to which the shield is attached and thereby grounded. If this reasoning is less than completely correct, one must question the role played by air in charring ablator mechanisms and, even more, the wisdom of relying on thermogravimetric analyses performed in air as standards for the selection of the polymer. For char-forming systems, perhaps, it may have been more judicious to have made the decision on values obtained from tests performed in an inert atmosphere. We truly have no basis for making a selection of polymers for such critical applications until we evaluate, characterize, or isolate the extent to which char-forming pyrolysis is dominated or influenced by radiative, convective, or conductive processes and compare these processes to oxidative processes.

### POLYMER FABRICABILITY

What, then, would be the assurance of success if a polymer intended for use in ablative shields was evaluated correctly environmentally? Polymers are not synthesized in reactors in the form of shields; they are usually produced as powders or granules and require fabrication into the desired product. This is a crucial step even for the conventional polymers with which fabricators have had years of experience. The maximum physical properties

are seldom realized in fabricated polymers and vary greatly with the method of fabrication, the size and shape of the object, the temperature and pressure used in the fabrication, post-treatment of the formed object, the completeness of cure, the presence of strains, etc. This criticality assumes greater dimensions in the fabrication of thermally stable polymers. Many of the heteroaromatic polymers are insoluble and infusible in their ultimate structure, but they can be fabricated by a two-step process in which the soluble, linear, precursor polymer is first formed, then fabricated, and finally converted to the cyclized form by heating. The last step involves the simultaneous elimination of the by-product of the intramolecular reaction.

This process is reasonably effective for the fabrication of thin films or laminate-composites and of low-denier fibers from the hemipolymers of such polymers as the benzimidazoles, the BBB polymers, and others. Massive structures, on the other hand, most often are deeply pitted and highly porous due to the retention of by-products in a medium of solid-state viscosity. The deviations from the expected physical properties become even greater when foamed or reticulated structures are produced from thermally stable polymers. The broad distribution of bubble-size and post-dimensions magnify the inhomogeneity of the sample. Many thermally stable polymers cannot be fabricated by conventional methods or by the hemipolymer techniques. Hydraulic, high-pressure molding of high molecular weight polyphenylene illustrates the type of fabrication research that must be done as polymers of higher and higher stability are synthesized. This hydraulic molding method is unorthodox and is in sharp contrast to the method introduced [94] in England recently for fabricating low molecular weight "polyphenylenes." Meta-benzenedisulfonyl chloride and terephenyl are reacted in the presence of cuprous chloride catalyst to yield a cross-linked "polyphenylene." In reality, because of the ratios of reagents used, the final product is a polysulfone with a few polyphenylene linkages and not a polyphenylene.

That the molecular structure of the polymer has a direct bearing on its fabricability and on the techniques of fabrication is obvious in this comparison between polyphenylene and the hemipolymers. There is a similar interdependence between the molecular structure of a polymer and its environmental behavior. This is indicated to some extent in the comparison of the structure of polyphenylene at one end of the scale with the structures of polyacene and graphite at the other end. One need not reach that far to appreciate the relationship. The hemipolymer of polypyromellitimide is a precursor intermediate, in a soluble, tractable stage, which must be cyclized to yield the ladder polymer. If complete ring closure is not

achieved in the last step, the product is a stepladder polymer and the purpose of the synthesis has been defeated. The same defect is introduced if, in the cyclization step, the hemipolymer is of too low a molecular weight and is heated too rapidly at too high a temperature. This induces decarboxylation with the loss of carbon dioxide and creates a step instead of a rung.

Recent experiences in the synthesis of BBB polymers [76] in the laboratories at Wright-Patterson Air Force Base, where naphthalene tetracarboxylic acid was reacted with tetraamines to make a ladder polymer, taught the lesson that, in critical syntheses, one must first assure oneself of the purity of the reagents. Titer values are usually used to adjust the amounts of carboxylic acid and amine used in the synthesis to equivalent quantities; this adjustment avails nothing in eliminating the stepladder linkages introduced into the structure by contaminating tricarboxylic acid.

### POLYMER CHARACTERIZATION

Multistage reactions provide opportunities for side reaction, and the syntheses of most ladder polymers involve multistage systems. Usually this fact is ignored in sketching out a beautiful, rhythmical, symmetrical structure for the polymer. Most such structures are idealized and, as written, represent what the polymer chemist hopes to make. Polymer scientists, like other humans, have their fads. You're "in" as a polymer chemist, if your insoluble, infusible, thermally stable polymer is a nice, clean ladder and is pictured free of cross-links or steps. In most cases, we really do not know the fine details of the structure and, in fact, are often forced to accept whatever unknown structure the reaction yields. These exotic polymers cannot be characterized by the traditional methods used for the polymers of yesterday. But characterize them we must, if we are ever to understand the relationship of structure to properties for these polymers. The degree of success of a charring ablator made from a polyheterocyclic may well depend on the number of cross-linkages in its structure, even though their structures are usually written as being free of such linkages. Today, we have no way of counting cross-links in these polymers, whether they exist in the polymer as accidents of synthesis or fabrication, or as the result of deliberate molecular design. In the latter case, we like to give the impression that we do know how many links there are in these structures, because in the course of synthesis, we deliberately introduced modifying monomers which would be expected to produce these tie-points. We further assumed that they perform this function with an efficiency of 100% or nearly so.

## THE STATUS OF POLYMERS IN MATERIALS APPLICATION SCIENCE

The rapid and consistent growth in polymer science in the last 10 years, to the point where polymers are competing with metals in many applications, is truly phenomenal. These accomplishments would make it appear that polymer scientists now have a major tool for solving many of the current technological problems requiring exotic aerospace materials. The truth of the matter is that we have arrived at a transition stage in materials application science which is overwhelming polymer scientists, metallurgists, and aerospace engineers. Much remains to be learned before we can solve many of the problems that aerospace has generated, because the technological use of polymers has not been supported by sufficient basic and fundamental knowledge. Many difficult problems have consistently resisted solution by empirical methods but disappeared when attacked with fundamental physical and chemical knowledge. The empirical approach attempts to soothe the intellectual conscience by describing what happens, but descriptions are not explanations.

### PARAMETERS IN THE TECHNICAL USE OF POLYMERS

It proved to be an interesting experience for me to attempt to write an equation which would relate maximum technological use,  $T_U$ , of polymers to essential parameters. "Molecular structure,"  $M_{ch}$ , of the polymer is obviously the first parameter. Maximum knowledge of structure, which is essential in relating structure to polymer properties and behavior, can be obtained only by a positive, unequivocal characterization,  $ch$ . Our structural knowledge of these new aerospace polymers is very limited. Many techniques which yield structural data on the old-fashioned polymer are not easily applied to these polymers because of their complexity of structure or their insolubility. There is a great need for both improvement in techniques and development of new tools in characterization research. High-resolution nuclear magnetic resonance spectroscopy has been used to obtain structural data, including information concerning the stereoregularity of molecular groups attached to the polymer backbone. This technique follows from the fact that certain atoms undergo an energy transition from one spin state to another, and the resonance frequency corresponding to the transition for a particular nucleus is dependent on its structural environment. NMR spectra are obtained from polymers in solution. Aerospace polymers are insoluble—no solution, no NMR spectra. Infrared spectros-

copy which shows characteristic vibrational bands for different atomic groupings provides much information on the microstructure of many polymers. The broadening of bands and band-overlaps complicate the interpretation of the infrared spectra of most polyaromatic-heterocyclics. Other well-known techniques for characterizing ordinary polymers are well developed; these include ultraviolet spectroscopy, viscosity, osmotic pressure, light scattering, fractionation, birefringence, optical rotary dispersions, and a host of others. In some cases, many of these techniques, and in other cases, most of these techniques, cannot be used to characterize the polymers of the aerospace age. New studies, utilizing computer programming, may provide the required techniques.

The second parameter is also an essential one; it relates to the behavior of the polymer in its true environment, to which we assign the symbol  $E_v$ . This requires an evaluation of the polymer in a system that accurately describes the environment, including the shape and mass of the polymer, convective, conductive, radiative, and diffusive processes, shock extension, and so forth. New studies to develop the new tools and techniques of evaluation are needed here to a degree comparable to that required for polymer characterization.

The last essential parameter is  $F_t$ , it relates to fabrication techniques. The need for research on new techniques of fabrication peculiarly suited to aerospace polymers has been obvious for some time to those engaged in producing the required structures. We won't belabor this point, since we have made prior reference to it, but let us ask one question. How would a foam of maximum physical and thermal properties be produced from NASA's pyrrone polymers? Undoubtedly, we could and would, in a reasonable time, produce some sort of foamed product, but the approved product would be obtained only as the result of fabrication research which would have to investigate not only rates of bubble formation but the fundamentals of bubble nucleation and extent of chemical ring closure.

Maximum technical utilization, then, is some function of molecular structure; it is also a function of behavior in environment, and is dependent, too, on a fabrication factor. The equation which incorporates these parameters can be expressed in the form:

$$T_u(\max) = f(M_{ch}) f'(E_v) f''(F_t) \quad (10)$$

$$T_u(\max) = k(M_{ch})(E_v)(F_t)$$



in which  $k$  is the constant that describes  $f$ ,  $f'$ , and  $f''$ . We can now rejoice! Our emotions tell us that we have arrived. Then, we evaluate the equation. The result is a miserable failure. Why? Because  $k$  does not truly describe the correct inter- or intrarelations of  $f$ ,  $f'$ , and  $f''$ ;  $f$  represents the polymer chemist,  $f'$  the polymer physicist, and  $f''$  the materials engineer. The chemist is absolutely certain that the physicist and the engineer do not know a thing about polymers—if they did, they would make them—and above all, the chemists create them, don't they? The physicist of this trinity is convinced that he alone understands solid-state physics, molecular orbitals, and interactions in molecules and atoms. I am the engineer, just give me the material and I'll make it work—who cares whether it's a ladder, a stepladder, or even a footstool?

### OECUMENICAL APPROACH TO POLYMER UTILIZATION

The maximum value of  $T_u$  cannot, and will not, be achieved by an independent, piecemeal approach of separate disciplines. It will be obtained only through a highly sophisticated, interdisciplinary system which joins the essential specialists in a single effort. This concept is not new; it has been proposed frequently by the National Academy of Sciences and by many of our learned scientific societies. All of us have heard argument after argument as to why an interdisciplinary system would not be effective. To make it effective, it would only be necessary to change the constant, a small  $k$ , to the correct constant, a capital  $K$ , with the appropriate subscript,  $oe$ :

$$T_u = K_{oe} (M_{ch})(E_v)(F_t) \quad (11)$$

This new constant requires conversions in the attitudes and beliefs of each specialist toward the specialists of other disciplines. The subscript,  $oe$ , stands for oecumenism, spelled with an  $o$ ; its etymology is Greek and it is the alternate spelling of the subsequently Latin-derived ecumenism. I use the  $oe$  spelling to distinguish it from the theological implications of the latter form, even though many times a prayer is the only solution to many of the current technical problems. Nonetheless, the essential meanings of both spellings are the same; they mean universal or general.

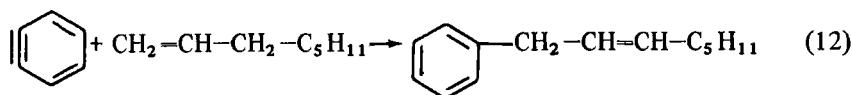
In our situation, the oecumenical spirit in polymer science means not only that maximum communication must exist between the specialists of varied disciplines but that this communication must be dignified by a

maximum appreciation for the wealth of knowledge contained in each other's discipline. Some time ago, the polymer group at Wright-Patterson put such a system into effect on a major effort involving high-temperature fibers. It is known as the VIC Program—the Vertically Integrated Coupling Program. It assembled four groups of specialists—one group for structural syntheses, a second for characterization and evaluation, a third on the fabrication of polymers into fibers, and the fourth to assimilate and use the knowledge of the first three groups in converting the fibers into the specific end product required. The individuals in the VIC Program are indeed fortunate to have been selected as participants in this oecumenical attack on the problem. The system will work, if the team is an assembly of individuals who believe that it can be made to succeed. The participants are all fervent converts because they sense, as I do, that  $T_u$  in this case is headed for the maximum. When it reaches maximum, VIC can stand for intellectual as well as material victory. I plead for more such oecumenism in the attacks on the “impossible” polymer problems. Such oecumenical programs can assure our country that its national interest will never suffer.

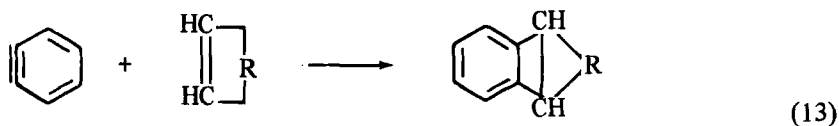
### THE FUTURE OF POLYMERS

The technological future of polymers in general and of thermally stable polymers is bright. The quantity of fundamental research in polymers emanating from university, government, and industrial laboratories in the last decade has increased sharply and its quality has improved greatly. All signs indicate a continued advance. However, in predicting the future of human endeavor, one must be guided by the experiences of the present. This is more true of science than it is of the arts and literature. In literature and art one seeks and treasures old masters and editions which have withstood the test of time. In science one relies on the latest editions which report an ever-changing status.

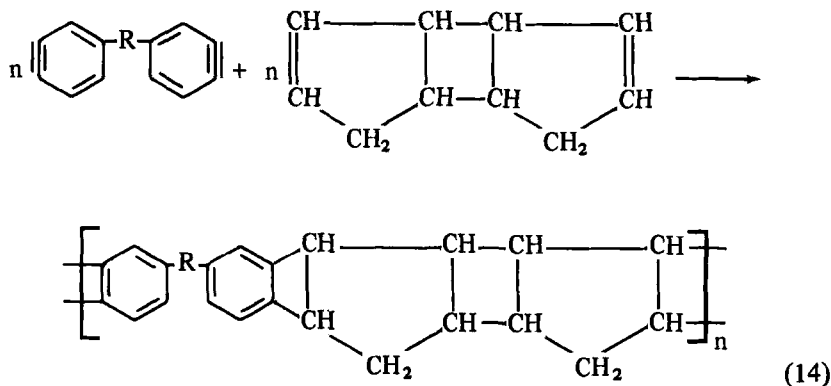
The latest editions report new syntheses of cyclic, heterocyclic, and monomeric compounds by addition reactions. These are interesting because they accomplish the synthesis without the necessity of eliminating a by-product. For example, benzyne reacts [94-97] with olefins containing allylic hydrogens by substantive addition, for example,



and, in the absence of allylic hydrogens, by cycloaddition,

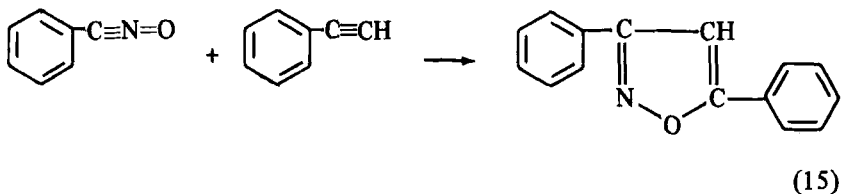


This fundamental knowledge can be applied to the syntheses of polycyclics by the use of polyfunctional molecules, as, for example, by reacting an appropriate *debenzyne* with dicyclopentadiene:

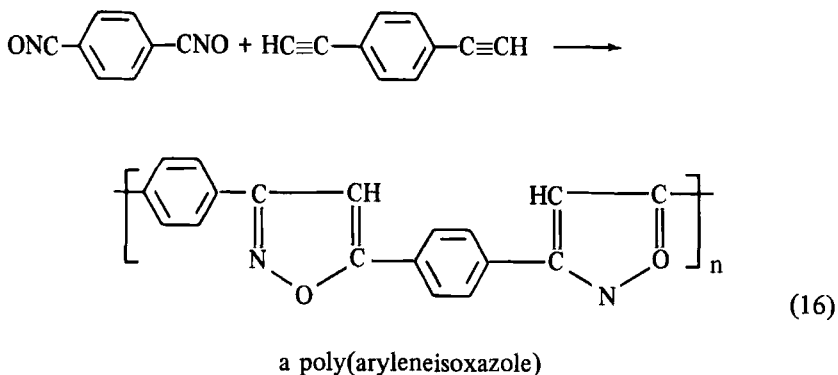


This polymer should be tractable as well as soluble, and post-treatment at high temperature would induce intramolecular rearrangements and hydrogen eliminations with consequent increase in thermal stability. These reactions should be more facile than systems requiring complete cyclization of functional groups.

Another edition tells [98] us that an aryl nitrile oxide adds to an aryl-acetylene to produce an aromatic-heterocyclic structure:

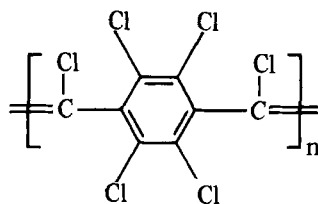


and that difunctional reagents, as expected, would produce polymers, thus:



The thermal stabilities of the poly(aryleneisoxazoles) are similar to those of the polybenzoxazoles. Other polar addition reactions of this type are beginning to appear.

Still another edition [99] reports the syntheses of some interesting macromolecular chlorocarbons of which the parent polymer is perchloropoly-p-xylylidene (PP-xynene),



perchloropoly-p-xylylidene (PP-xynene)

which, in spite of the presence of chlorine atoms, displays a high thermal stability and chemical inertness.

The choice bits of information, of course, are found in the limited editions which have not yet become available to the technical community generally. One such tidbit concerns pyrolytic graphite. Pyrolytic graphite is a form of elemental carbon which possesses rather unique thermal and mechanical properties. For this reason, it is finding increasing application in space and in missile technology where the extremes of erosion and temperature stress demand reliability in materials. Pyrolytic graphite is pure crystalline graphite deposited from a carbon-bearing vapor at temperatures

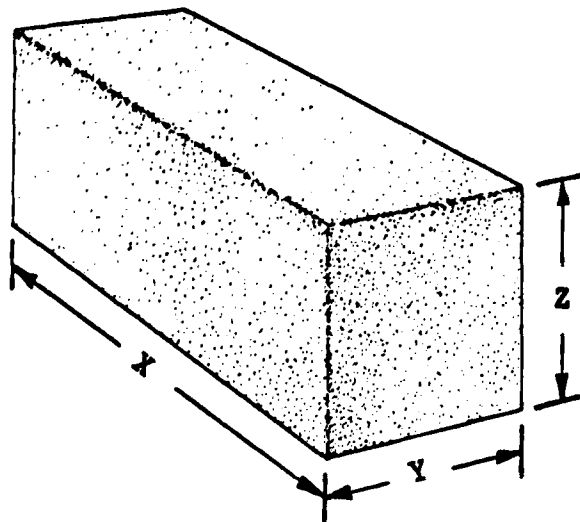


Fig. 3. Anisotropic pyrolytic graphite.

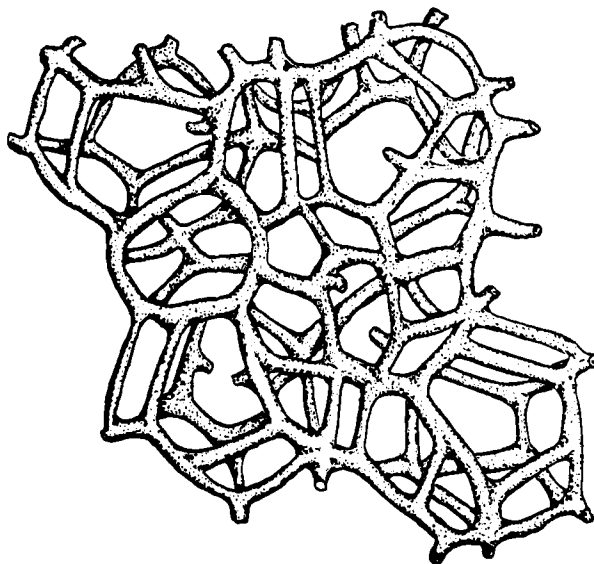


Fig. 4. Reticulated isotropic structure of anisotropic graphite posts.

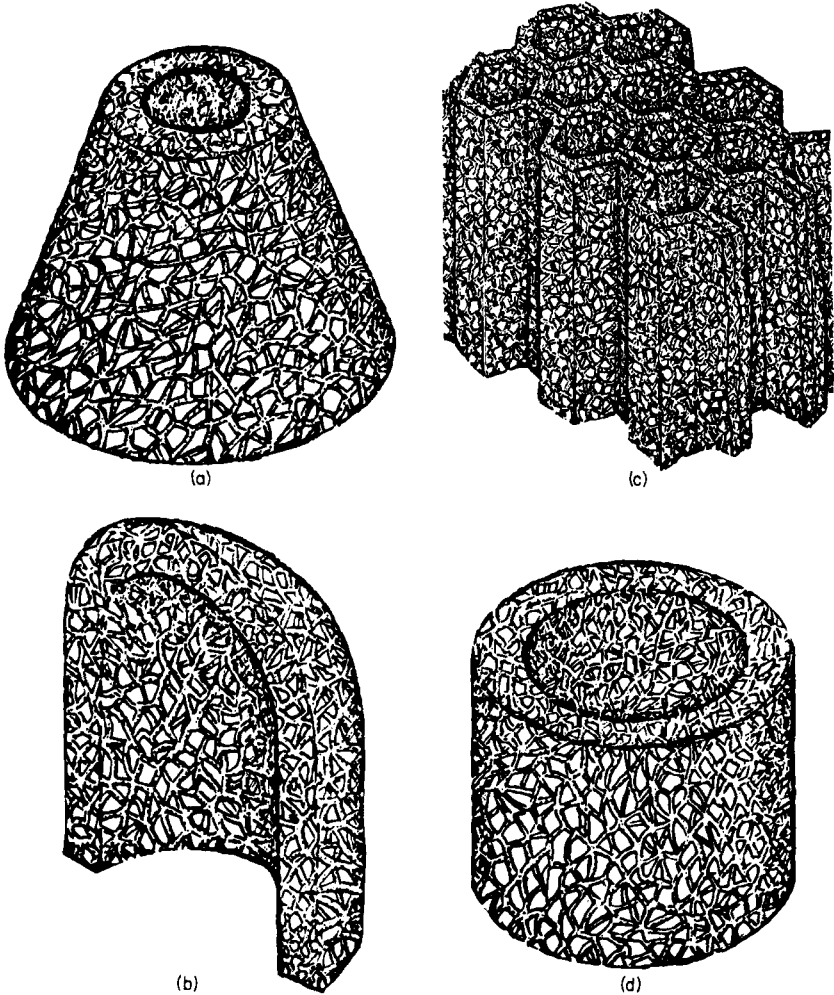


Fig. 5. Isotropic pyrolytic graphite structures from preformed shapes.

in excess of  $2000^{\circ}\text{C}$ . It is metallic in appearance, impervious to gases, and contains no binders such as are found in the regular commercial graphite used as electrodes. X-ray diffraction patterns of pyrolytic graphite show significant deviations from those of normal graphite as evidenced by an unusually high degree of preferred orientation. The crystals have their basal planes aligned parallel to the surface of deposition. This orientation is a function of deposition temperature and density and is responsible for

the marked anisotropic properties of pyrolytic graphite. This means that its physical properties along the X, Y, and Z axes, as shown in Fig. 3, are not identical.

The anisotropic characteristics of pyrolytic graphite are apparent from measurements of the thermal, electrical, and physical properties made along the X, Y, and Z axes. The properties in one plane are usually higher by several orders of magnitude than those of the other planes. In those cases, where the requirement of the structure demands that the properties be independent of its axes, the deficiencies due to the anisotropic properties of pyrolytic graphite complicate both the design and the engineering, and the end product usually compromises both design and engineering.

In cases where directional properties are required, there is as yet no thermally resistant polymer that will compete with it. Nonetheless, the utility of pyrolytic graphite can be extended and its application multiplied if it could be produced as an isotropic structural material.

The anisotropy of pyrolytic graphite is a direct result of the method of synthesis, and the request for an isotropic pyrolytic graphite is thereby self-contradicting. Pyrolytic graphite is always anisotropic. One possible solution to the dilemma is to design isotropic structures from anisotropic pyrolytic graphite. On first impression, this suggestion appears to be an illogical one. The clue to the solution is found in a tinker-toy model of a symmetrical, three-dimensional wire grid. If the wires in the grid represent the surface of deposition, the basal plane of the crystallites will be aligned parallel to the surface of deposition—thus, each rod will be anisotropic but the total structure will be isotropic. Deposition can be continued until a solid mass is obtained, or terminated at the point when the desired ratio of mass to void is reached. Grids of this kind are also known as reticulated structures and are characterized by the number of pores or holes per unit area, and this number can be varied over a wide range. A typical reticulated isotropic graphitic structure comprised of pentagonal units, is shown [100] in Fig. 4. If the composition of the reticulated base structure is such that it can be shaped before graphite deposition, the final structure can be obtained in almost any design [100]. A few illustrative examples are shown in Figs. 5(a)-5(d); these can be in solid or reticulated forms. These reticulated structures can be coated with metals or other nonoxidizing refractory inorganic materials, or their voids can be filled with a variety of materials. As a refractory matrix they can serve as the depository for subliming polymeric ablators.

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