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Thermally Stable Polymers with Aromatic Recurring Units

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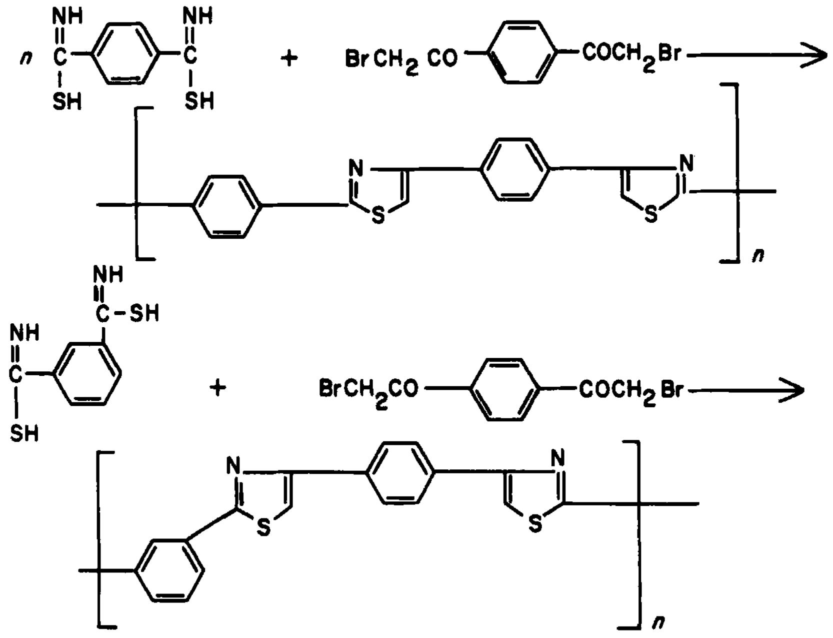
For the past ten years my research group has been interested in preparing polymeric materials that would retain useful properties as films, fibers, rubbers, or plastics at temperatures of 500°C or more. The program has been sponsored by the Materials Laboratory of the Wright Air Development Division, Wright-Patterson Air Force Base. Our early search for heat-stable polymers was in the field of metal chelates, because some of the monomeric materials of this type seemed to show unusual stability at elevated temperatures. We were never able, however, to obtain truly high-molecular-weight polymers that had as good tensile property, modulus, and elongation as were needed for useful structural materials. Moreover, the stability of the low polymers that we did obtain was never quite as good as we had hoped for.

We then turned to a study of aromatic systems. It is well known that such aromatic compounds as benzene, naphthalene, anthracene, pyridine, and quinoline are produced in the destructive distillation of such products as coal, bones, and other animal and vegetable materials. If formed at high temperatures, they can be expected to have some stability under these conditions. The best of our industrial polymeric materials are those which are long-chain molecules held together by covalent links, such as carbon-carbon bonds, carbon-oxygen bonds, and carbon-nitrogen bonds. It therefore seemed logical to try to synthesize polymers with recurring aromatic units joined together with covalent bonds.

Work on the synthesis of polyaromatic heterocyclic polymers in polycondensation reactions is underway in a number of laboratories. This field has been a very active one since 1961. In my laboratories we have been concerned with polythiazoles, polyoxadiazoles, polytriazoles, polybenzimidazoles, polyboroimidazolines, polytetraazopyrenes and, more recently, ladder-type polymers from aromatic tetraamines and aromatic dianhydrides.



Our polythiazoles were made by means of Erlenmeyer's synthesis (*1*) from bisthioamides and bisbromoacetylbenzene (*2*) in dimethylacetamide solution. We later learned that this work had been done earlier (*3*) in Japan with results very similar to those we obtained. In both instances polymers with molecular weights in the 5300 to 5400 range were obtained. The polymers were yellow to yellow-orange in color and soluble only in sulfuric acid or trifluoroacetic acid. When an aliphatic bisthioamide was used to give a mixed aliphatic-aromatic polymer chain, a slightly higher-molecular-weight polymer was obtained. It was soluble in formic acid and could be cast into a weak film. Thermogravimetric analyses (Fig. 1) showed that the polymer with aliphatic units degraded rapidly at 350 to 400°C in nitrogen but that the wholly aromatic

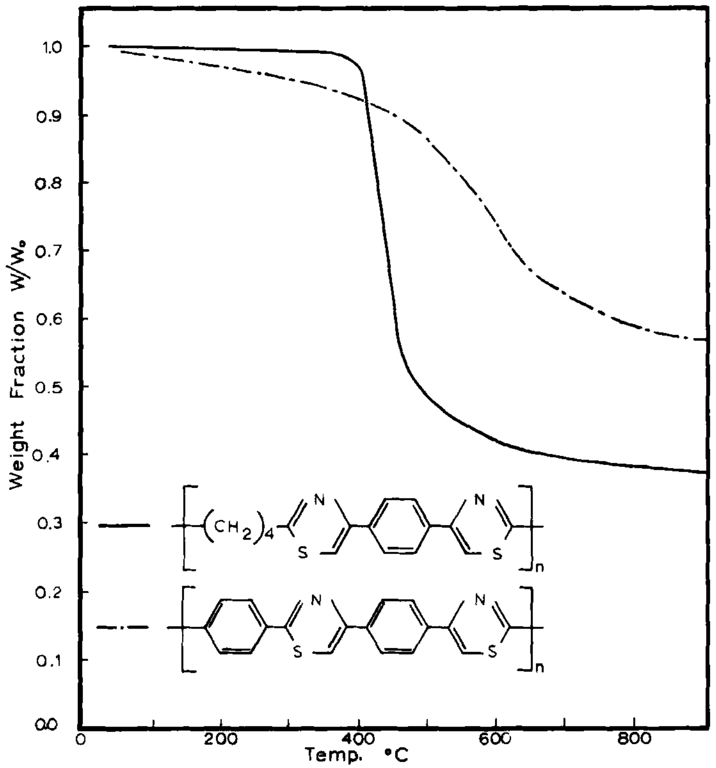
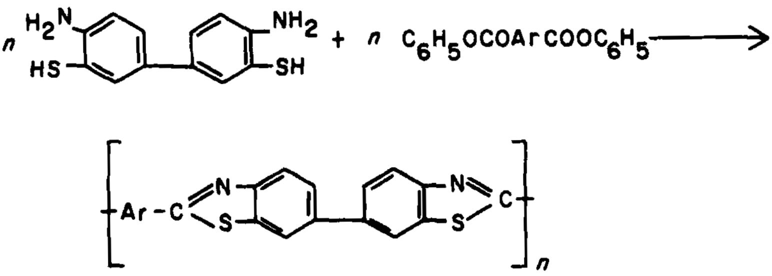


FIG. 1. Thermogravimetric curves of polythiazoles.

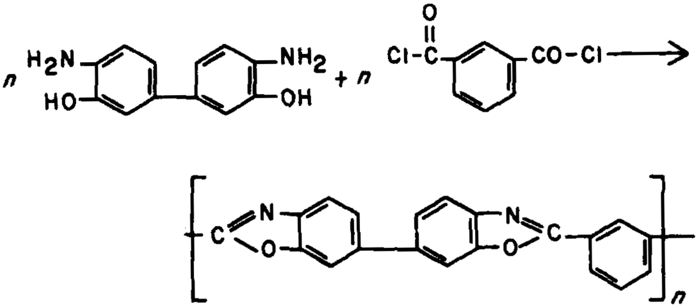
polymers held up well to 500 to 600°C and lost only 40% of their weight up to 900°C. This seems to be the case in most of the series we have studied. Aliphatic chains rarely withstand more than 400°C, whereas the aromatics are usually good up to 550°C or better.

As reported in a recent paper, Sheehan, Cole and Picklesimer (*4*) studied this polymerization reaction further and developed it to the state where by means of aliphatic bisthioamides they obtained high polymers with inherent viscosities as high as 5.83. From some of them fibers were drawn and films were cast. Some of the fibers had strengths of 2 to 3 g/den and the films had tensile strengths of up to 6800 psi.

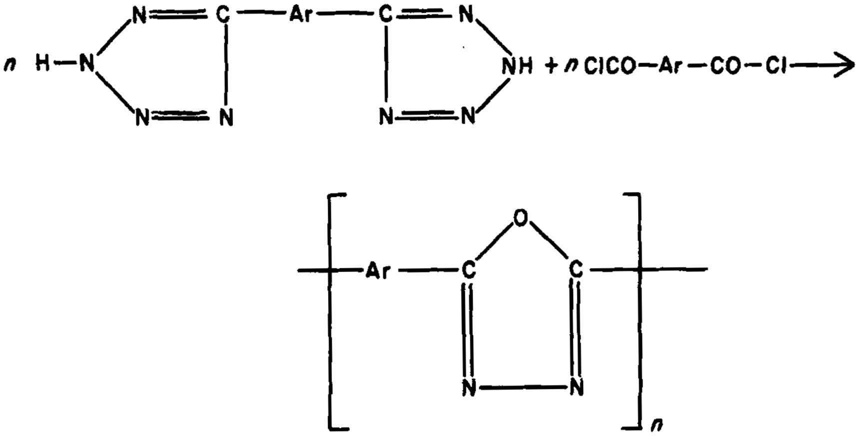
Hergenrother et al. (*5*) prepared a series of polybenzthiazoles by condensing diphenyl esters of aromatic acids with bisorthoaminothiophenols and obtained polymers with remarkable thermal



stability both in air and nitrogen (weight loss of 6% up to 600°C in static air). The polymers are soluble only in sulfuric acid and have not yet been converted to useful films or fibers.



Using 3,3′-dihydroxybenzidine and isophthalyl chloride, Kubota and Nakanishi (6) have made polybenzoxazoles that are soluble in sulfuric acid and have inherent viscosities in the range of 1 to 1.2.



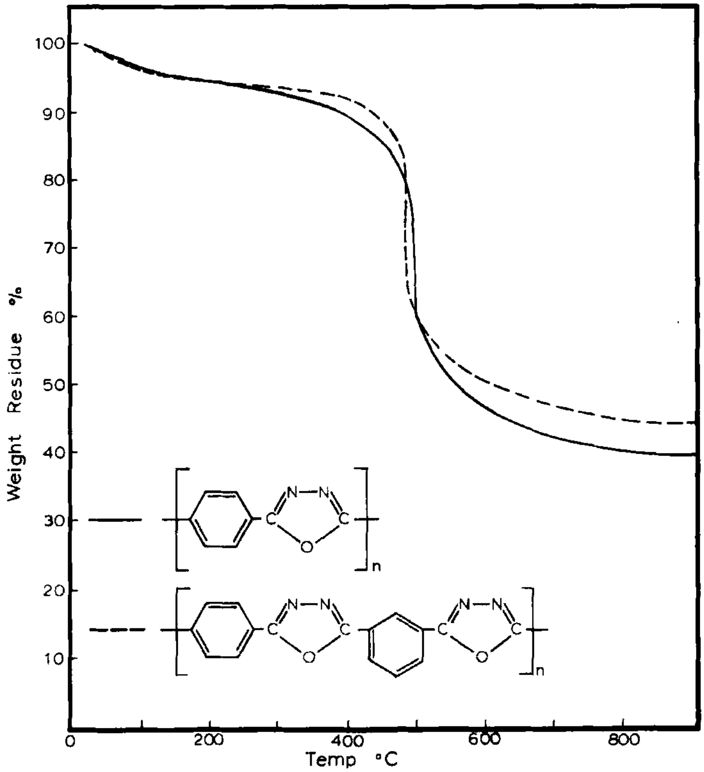
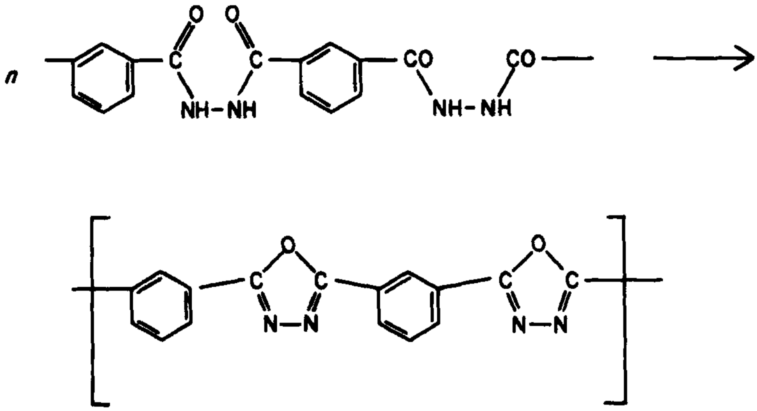


FIG. 2. Thermogravimetric analysis of two typical oxadiazole polymers. [From C. J. Abshire and C. S. Marvel, *Makromol. Chem.*, **44–46**, 394 (1961); by permission of Huethig & Wepf Verlag, Basel, Switzerland.]

They show good thermal stability up to 500°C. Moyer, Cole and Anyos (7) made similar polymers by the diphenyl ester technique. These, too, are intractable but quite thermally stable products.

By using Huisgen's (8) oxadiazole synthesis, Abshire (9) and I were able to synthesize polyoxadiazoles that had molecular weights in the 6000's. The polymers were soluble in sulfuric acid but not in conventional organic solvents. They are quite stable up to 500°C in nitrogen (Fig. 2) but, prepared by our method, are not of sufficiently high molecular weight to be useful or practical.

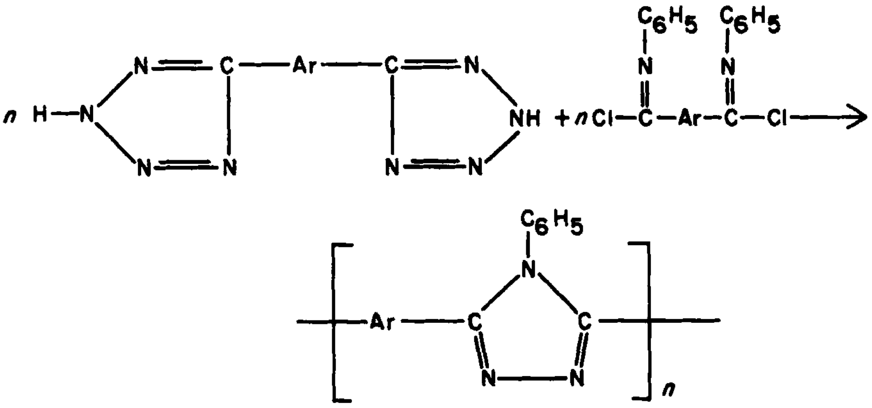
Frazer and Wallenberger (*10*) obtained this type of polymer by dehydrating polyhydrazides. In this manner polymers that have sufficient tensile strength and elongation to yield good fibers have

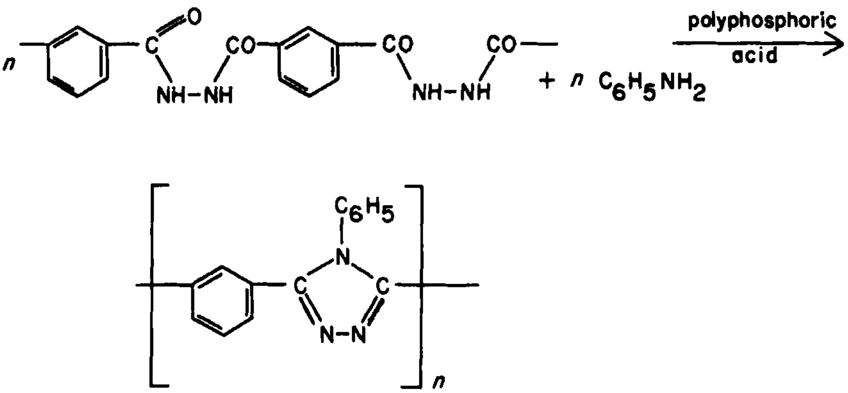


been obtained. Although the final polyoxadiazole is insoluble, fabrication at the polyhydrazide stage works well. These polymers have better oxidation resistance than many other polyheterocyclic aromatic types. They do not degrade at 450°C and will retain 60% of their room-temperature tensile properties at 300°C.

Closely related to the polyoxadiazoles are the polytriazoles that Abshire (9) prepared by means of Huisgen's reaction (*11*). They were slightly more soluble than analogous oxadiazoles, slightly higher in molecular weight, as evidenced by their inherent viscosities, but somewhat less thermally stable.

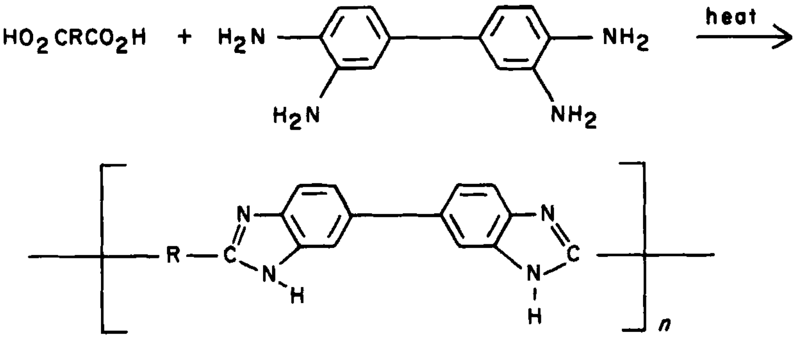
Lilyquist and Holsten (*12*) have reported on the formation of triazoles in the reaction of polyphosphoric acid on a mixture of polyhydrazide and aniline. In this way they succeeded in obtain-



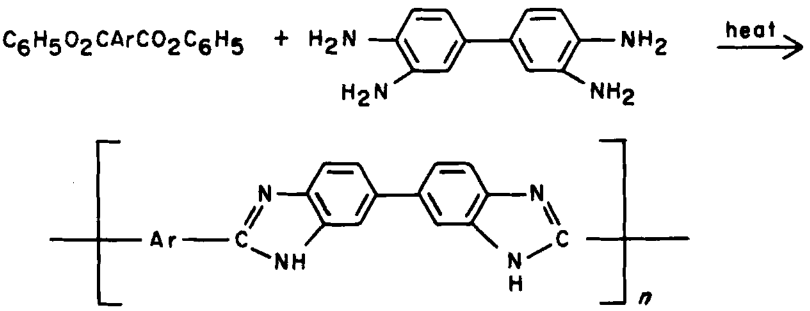


ing high-molecular-weight polytriazoles that gave good films and fibers with good thermal stability up to 450°C in air.

Our most successful work on thermally stable polyaromatics has



been in the polybenzimidazole field. Brinker and Robinson (*13*) prepared some polybenzimidazoles from aliphatic dibasic acids and aromatic tetraamines but did not follow up the reaction to obtain



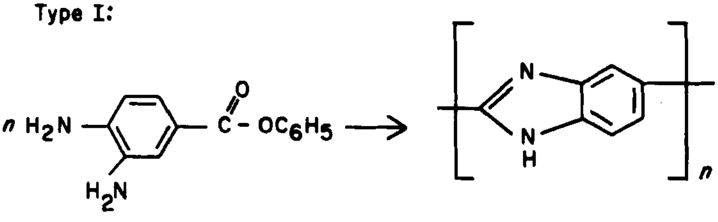
polyaromatics of high molecular weight. We have found that aromatic benzimidazole polymers are readily prepared with the use of diphenyl esters of aromatic diacids with aromatic tetraamines (*14*).

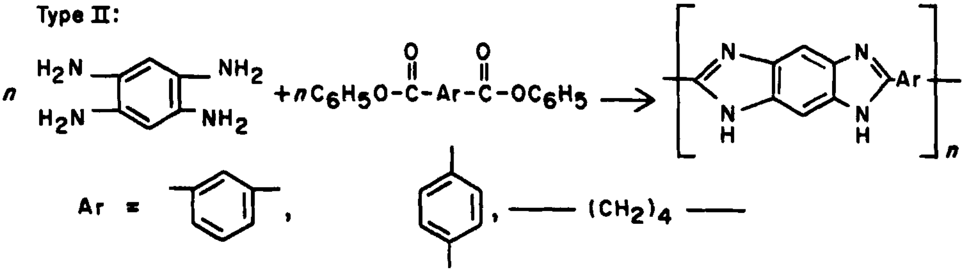
We have tried to make polybenzimidazoles by heating the free acid with the tetraamine, but some decarboxylation occurred to destroy the balance of terminal groups, and high-molecular-weight polymers could not be obtained. With acid chlorides the reaction is too fast, and all amines get substituted, so ring closure for the imidazole nucleus is unsatisfactory. With methyl esters of the acids some polymer is formed, but some methylation of the amine groups also occurs and upsets the balance of end groups. With phenyl esters, however, a clean reaction takes place, and high polymers with molecular weights of 50,000 to 100,000 are obtainable.

The general procedure developed for making polymers consists of heating the reactants in the complete absence of oxygen first at temperatures of about 220 to 280°C. Usually this is done under reduced pressure. In the early experiments this produced a solid, which was later broken up and further heated for several hours at temperatures gradually increasing to 400°C under a pressure of about 0.1 mm. The mass does not melt at this temperature, and this is essentially a solid-phase polymerization.

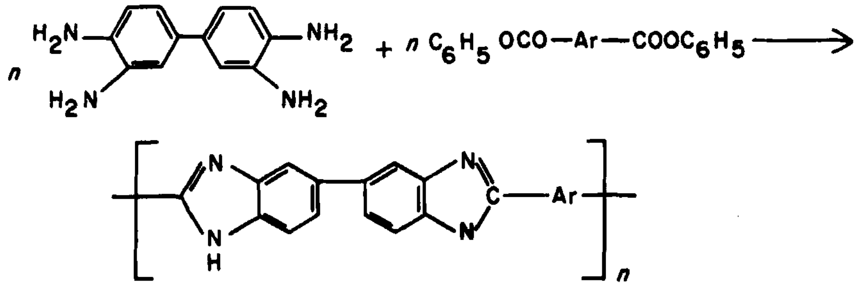
Polybenzimidazoles of three principal types have been prepared, as shown.

Type I:





Type III:



All of these polymers are colored. Most are yellow-orange; some are black. All are soluble in formic and sulfuric acid. Some show a high degree of crystallinity under x-ray examination. Those which

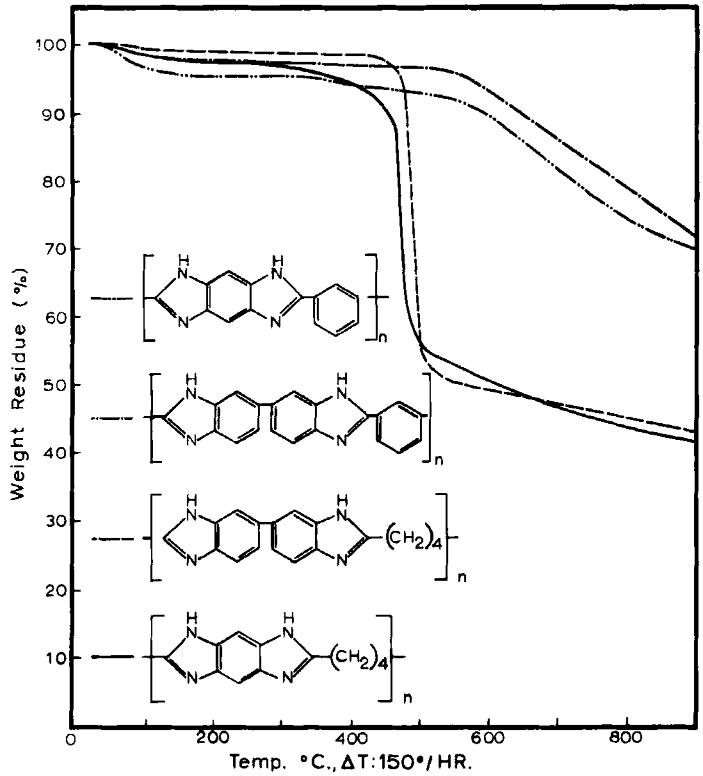


FIG. 3. Thermographic analyses of four polybenzimidazoles. [From H. Vogel and C. S. Marvel, *J. Polymer Sci.*, **50**, 523 (1961); by permission of John Wiley & Sons, Inc., New York.]

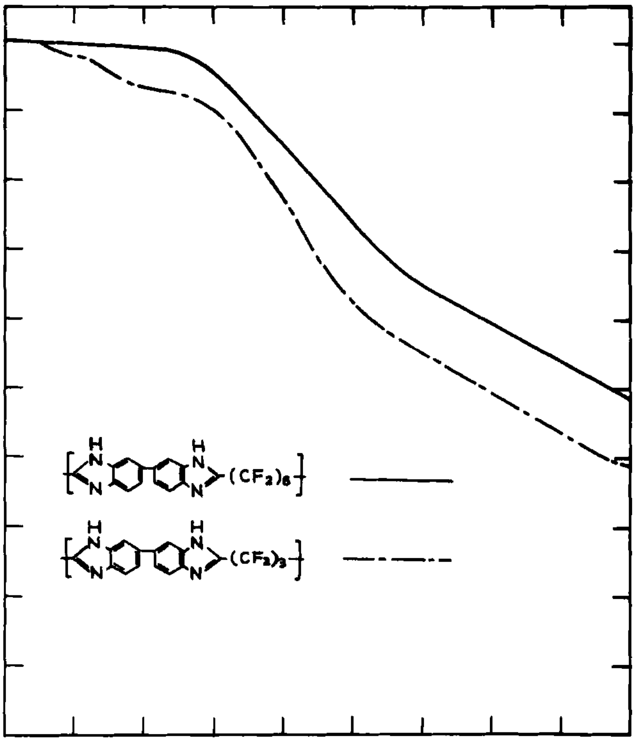


FIG. 4. Thermogravimetric-analysis curves for fluorine-containing polybenzimidazoles. [From L. Plummer and C. S. Marvel, *J. Polymer Sci.*, **A2**, 2563 (1964); by permission of John Wiley & Sons, Inc., New York.]

are noncrystalline, such as the polymers made from diaminobenzidine and diphenyl isophthalate, are soluble in such solvents as dimethyl sulfoxide, dimethyl formamide, dimethylacetamide, N-methylpyrollidone, and hexamethylphosphoramide. Very few of the polymers show a melting point. When heated for a short time above 400°C, they become insoluble in all solvents, indicating that a cross-linking reaction has occurred, and this apparently takes place before the polymer melts. We believe this is a reaction similar to the conversion of benzene to diphenyl, which runs at about 500°C.

Recently Korshak, Frunze, et al. (*15*) reported on some experiments dealing with the synthesis of polybenzimidazoles according to our general procedure. They obtained primarily insoluble materials. This leads me to suspect they did not exclude air as completely as is necessary to do to obtain high-molecular-weight soluble polymers. They also could not prepare polymers from diaminobenzidine and diphenyl perfluoroadipate because of loss of hydrogen fluoride.

Thermogravimetric analyses of many of the polymers have been made. It may be noted that the polymers containing aliphatic saturated sections degrade rapidly above 350°C in nitrogen, whereas the aromatic derivatives are rather stable up to 500°C in nitrogen (Fig. 3). It will be noted that an aliphatic perfluoro chain is no better than a hydrocarbon chain (Fig. 4).

It is significant that conjugation through a carbon-carbon double bond gives a stable polybenzimidazole (Fig. 5). This polymer is the only one that is very black. The ferrocene derivative has the stability of an aliphatic derivative, whereas the imidazole derivative is

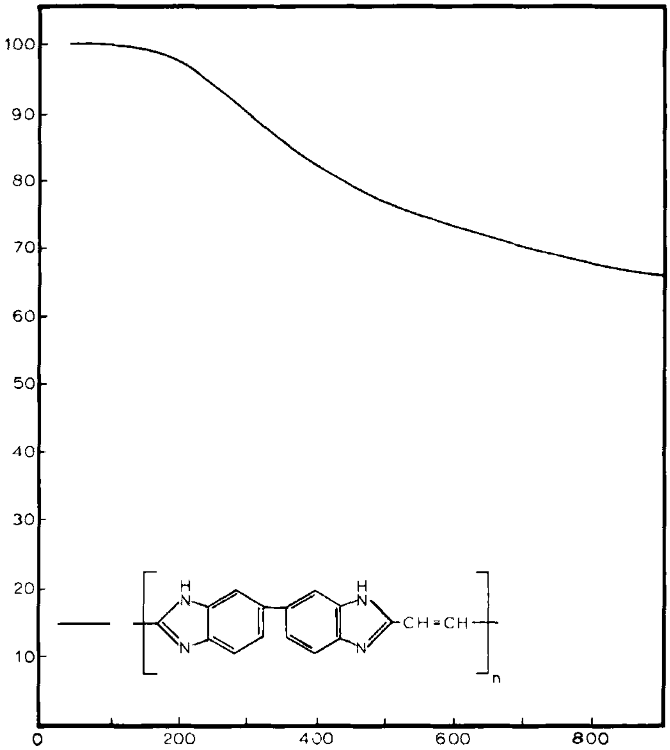


FIG. 5. Thermogravimetric-analysis curve for olefinic polybenzimidazole.

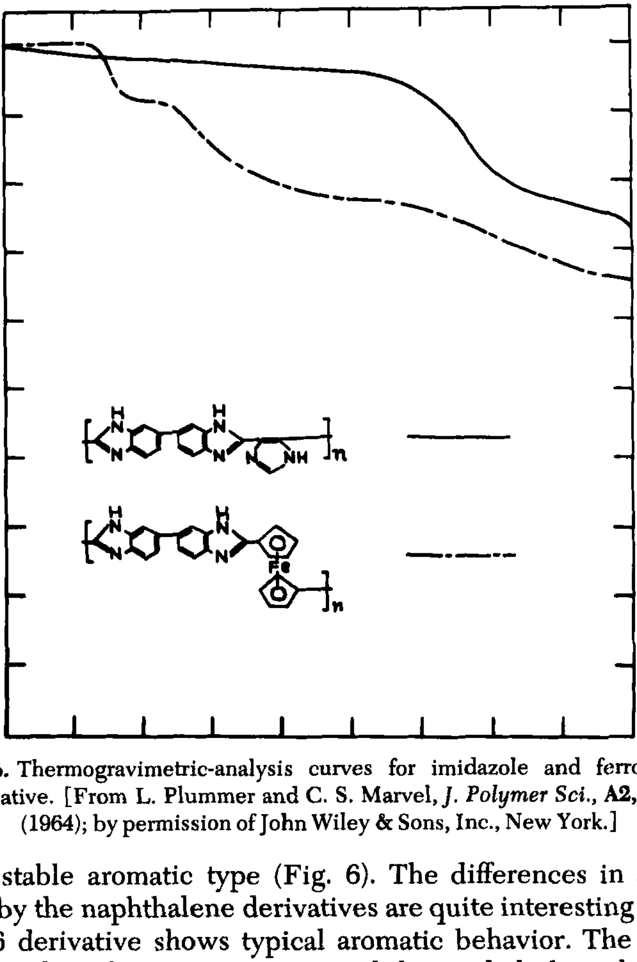
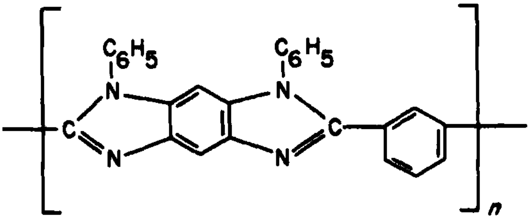


FIG. 6. Thermogravimetric-analysis curves for imidazole and ferrocene derivative. [From L. Plummer and C. S. Marvel, *J. Polymer Sci.*, A2, 2561 (1964); by permission of John Wiley & Sons, Inc., New York.]

a very stable aromatic type (Fig. 6). The differences in stability shown by the naphthalene derivatives are quite interesting (Fig. 7). The 2,6 derivative shows typical aromatic behavior. The 2,3 and 2,7 are midway between aromatic stability and aliphatic behavior.

It was felt that replacing the hydrogen atom of the imidazole group with a phenyl group might increase the stability of the poly-



mer, particularly with respect to oxidation. Such a polymer was synthesized (*16*). Thermographic curves (Fig. 8) of two samples, one with hydrogen and one with phenyl on the imidazole nitrogen, show that there is very little difference in their behavior either in or out of air.

More recently Mitsuhashi (*17*), working in my laboratory, has

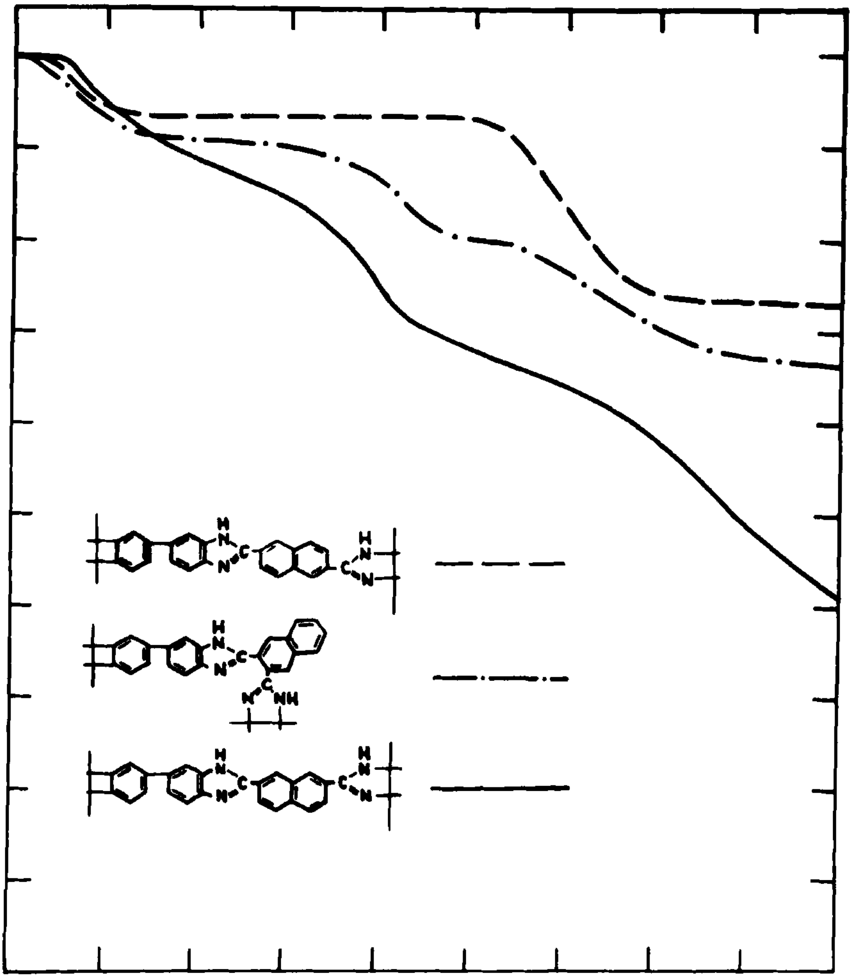


FIG. 7. Thermogravimetric-analysis curves for some naphthalene derivatives. [From L. Plummer and C. S. Marvel, *J. Polymer Sci.*, **A2**, 2560 (1964); by permission of John Wiley & Sons, Inc , New York.]

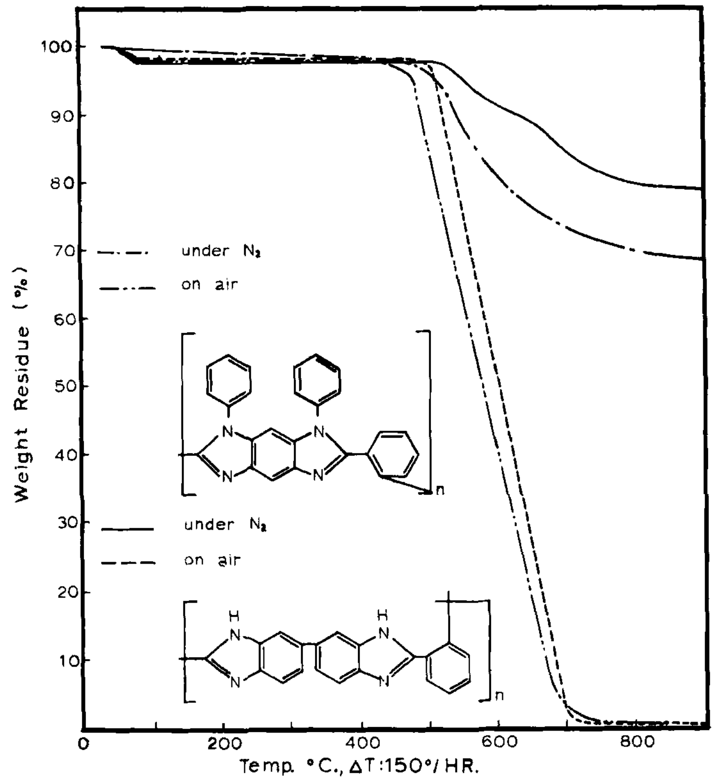


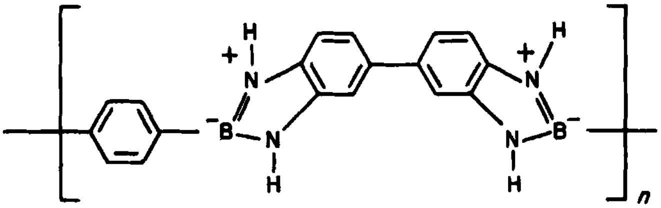
FIG. 8. Thermogravimetric curves of benzimidazole polymers with a substitution. [From H. Vogel and C. S. Marvel, *J. Polymer Sci.*, **A1**, 1532 (1963); by permission of John Wiley & Sons, Inc., New York.]

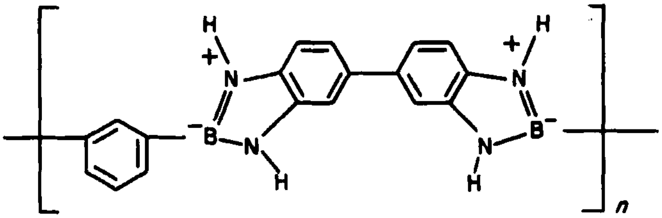
prepared the corresponding N-methyl derivative. This polymer seems to be slightly less sensitive to oxidation than is the phenyl-substituted polymer, but the difference is slight.

Much of our evaluation work has been concentrated on the polymer prepared from 2,3-diaminobenzidine and diphenyl isophthalate. This polymer is quite soluble in dimethyl sulfoxide and also in dimethyl formamide and dimethylacetamide, N-methylpyrollidone, and hexamethylphosphoramide. Light-scattering molecular-weight measurements of a sample having an inherent viscosity of 2.36 in formic acid and 0.6 in dimethyl sulfoxide indicate a value of about 54,000 (we are indebted to Dr. Maurice Morton for making this determination for us). Polymers with viscosities of 0.8 to 1 have been obtained. All of these polymers have shown marked stability to hydrolysis. Boiling in 25% sulfuric acid or even

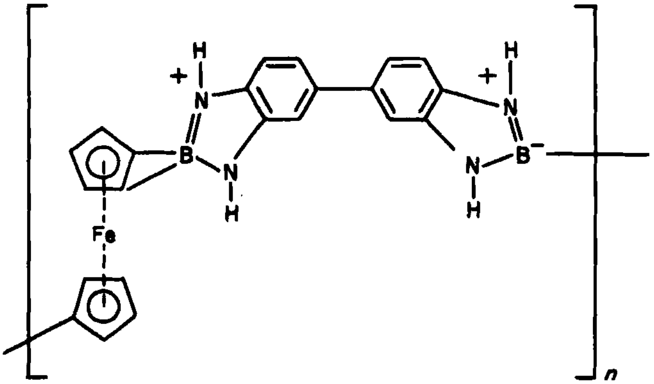
75% sulfuric acid does not change them; neither does treatment with hot 25% aqueous potassium hydroxide.

A piece of film cast from a dimethyl sulfoxide solution and without orientation showed the following properties. At 25°C: tensile strength, 0.7 g/den; elongation, 7%; modulus, 35 g/den. At 200°C: tensile strength 0.5 g/den; elongation, 9%; modulus, 15 g/den. Fibers have been spun from solution and after some orientation show 4.5-g/den tensile strength and retain this up to about 300°C.



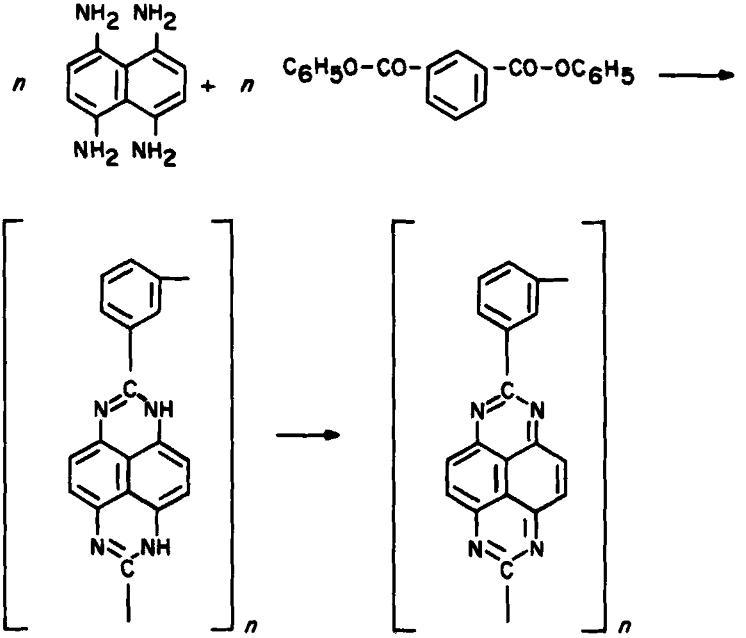


Films and fibers degrade rapidly above 300°C in air. A news report (*18*) has indicated that, when properly used, the polybenzimidazoles may have good adhesive properties. The fact that this polymer retains good properties at temperatures up to 300°C (even in air) indicates its novel behavior.



A few related polymers containing boron have been synthesized from 3,3′-diaminobenzidine and the dibutyl esters of some aromatic diboronic acids (*19*).

The two aromatic derivatives have good high-temperature stability. The ferrocene derivative again shows its aliphatic character by degrading at about 350°C (Fig. 9). None of these polymers had good hydrolytic stability, especially toward acid reagents, and they have not been extensively studied.



Dawans et al. (*20*) in my laboratory have synthesized a new type of polyaromatic polymer by means of the condensation of diphenyl isophthalate and 1,4,5,8-tetraaminonaphthalene.

This polymer does not melt below 350° but is soluble in dimethylsulfoxide and methanesulfonic acid.

The thermographic analyses (Figs. 10 and 11) show it to be quite stable in nitrogen, and even in air the weight loss is very little at temperatures below 400°C.

Stille et al. (*21*) have described new thermally stable polymers with quinoxaline units prepared by means of the following condensation:

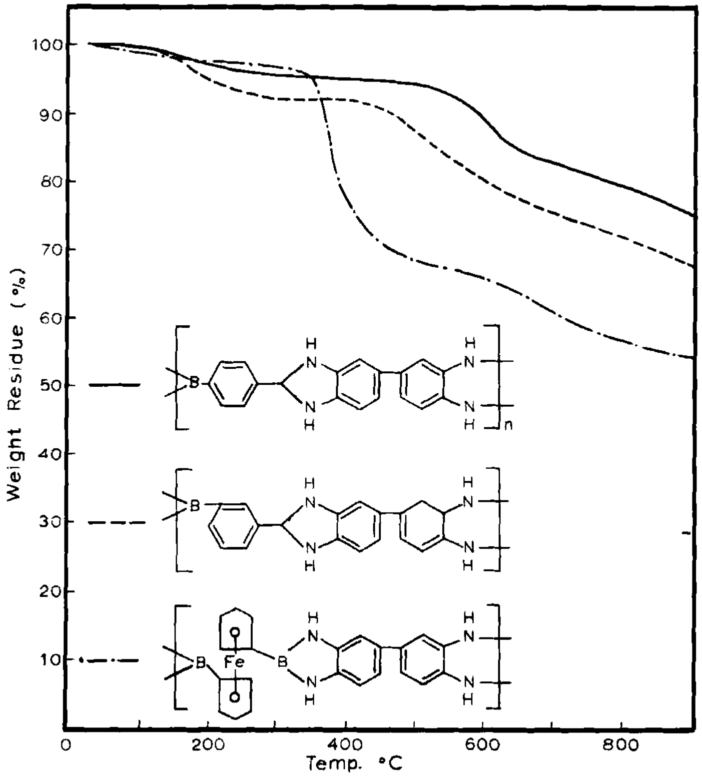
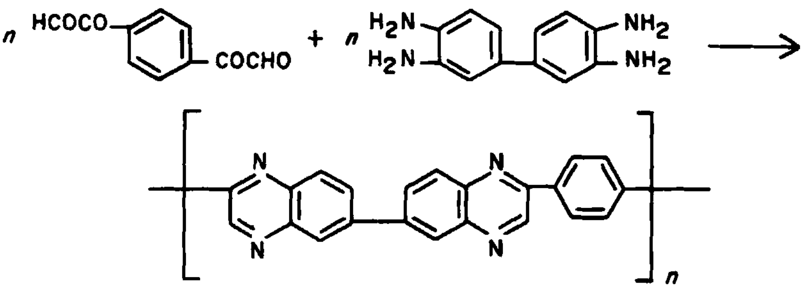


FIG. 9. Thermogravimetric-analysis curves of benzborimidazoline polymers. [From J. E. Mulvaney, J. J. Bloomfield, and C. S. Marvel, *J. Polymer Sci.*, **62**, 64 (1962); by permission of John Wiley & Sons, Inc., New York.]



These polymers are stable to 550°C in nitrogen but have not yet been fabricated.

Schaefer and Bertram (22) have condensed tetraacetylethane

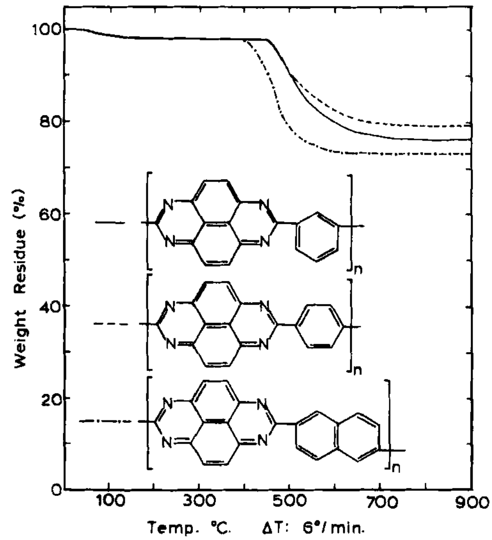
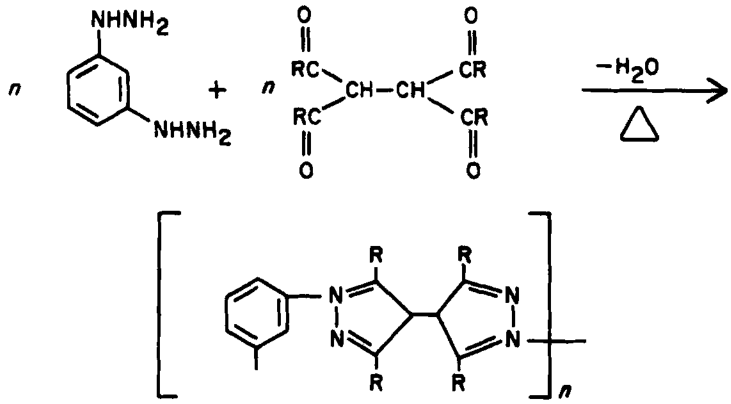


FIG. 10. Thermogravimetric analysis, in nitrogen. [From F. Dawans, B. Richel, and C. S. Marvel, *J. Polymer Sci.*, **A2**, 5010 (1964); by permission of John Wiley & Sons, Inc., New York.]

and *m*-dihydrazinobenzene, obtaining a polymer with inherent viscosities up to 2 in formic acid solution; the polymer shows remarkable thermal stability in nitrogen.



In the last three years we have been concentrating our efforts on the synthesis of ladder polymers with heterocyclic condensed aromatic structures.

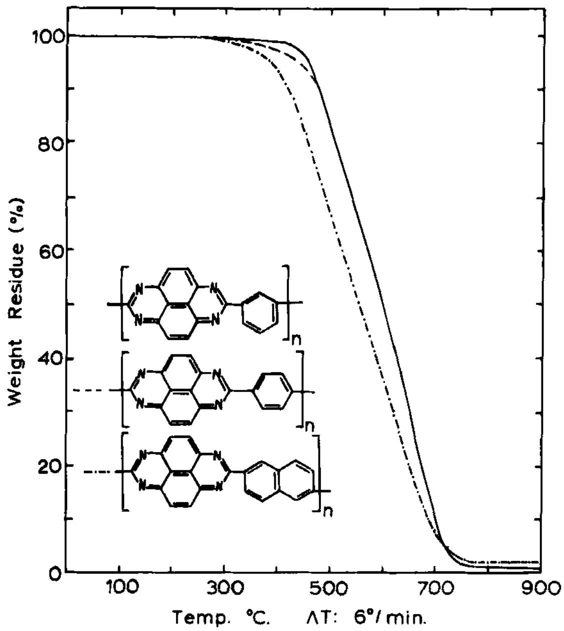


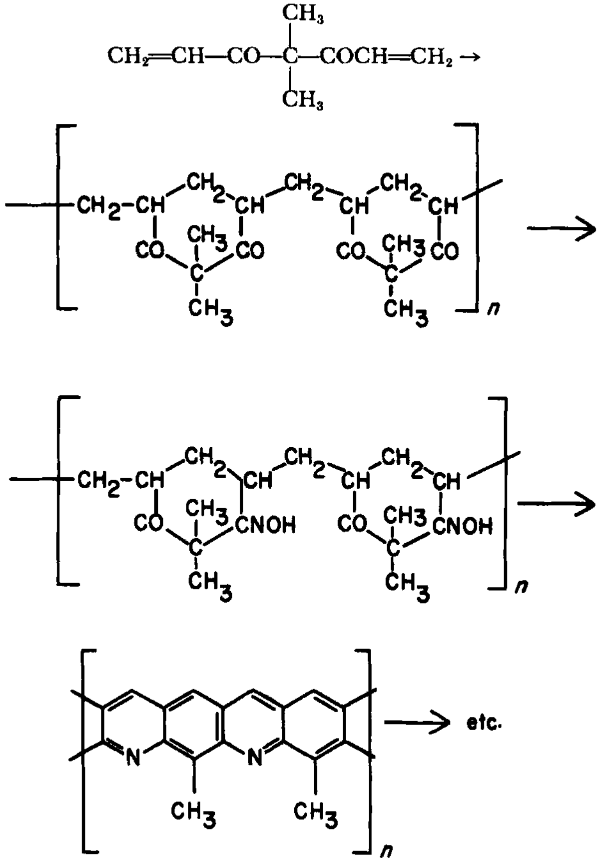
FIG. 11. Thermogravimetric analysis, in air. [From F. Dawans, B. Reichel, and C. S. Marvel, *J. Polymer Sci.*, **A2**, 5011 (1964); by permission of John Wiley & Sons, Inc., New York.]

It has been known for a long time that, when polyacrylonitrile is heated, it cyclizes to a polyquinizarin type of structure:

On hydrolysis it further splits at the open-chain portion and leaves a low-molecular-weight unit, which can be heated to red heats with little further weight loss.

It was felt that, if a system could be derived whereby the cyclizing groups were properly paired, it would be possible to make a complete ladder structure without open-chain units and, thus, a stable high-molecular-weight polymer.

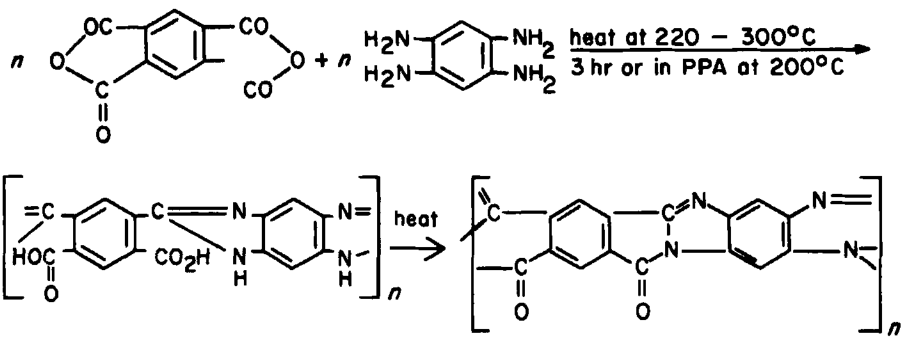
De Winter (*23*) tried to make such a polymer by using the cyclopolymerization technique of Butler on dimethyldiacrylylmethane, followed by the pyridine synthesis from the poly-1,5-diketone.



$$CH_2{=}CH{-}CO{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}COCH{=}CH_2 \rightarrow$$

It was not possible, however, to obtain a pure monooxime of the proper composition and, although a heat-stable material was obtained, its structure could only be partially explained.

Dawans (*24*), working with me, has now been successful in obtaining ladder polymers by condensing pyromellitic anhydride and aromatic tetraamines. The reaction has been carried out with numerous aromatic tetraamines, but ladder structures have been obtained only from 1,2,4,5-tetraaminobenzene and 1,4,5,8-tetraaminonaphthalene.



The polymer is soluble in aprotic solvents when in the amide acid stage but is only soluble in sulfuric acid after the ladder structure is completely formed. Materials with inherent viscosities up to 1.1 in concentrated sulfuric acid have been obtained. The weight loss in nitrogen seems to show stability to between 500 and 600°C. and the weight loss that is occurring there appears to be due to loss of water with more complete formation of the ladder structure.

In a recent news item in *Chemical and Engineering News* (25) the National Aeronautics and Space Administration has announced polyimidazopyrrolones made from dianhydrides and aromatic tetraamines, but few details are described. They are presumably much the same as the polymers we have made. This general lead seems to yield the most thermally stable polymers of good molecular weight that have been made from organic raw materials.

Acknowledgment

I am indebted to the Materials Laboratory of Wright Air Development Division of the United States Air Force and to the Plastics and Textile Fibers Departments of E. I. du Pont de Nemours & Company for financial support of this research. I am also indebted to a large number of co-workers who have done the actual laboratory work on this program.

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