

Polyaromatics

By C. S. Marvel

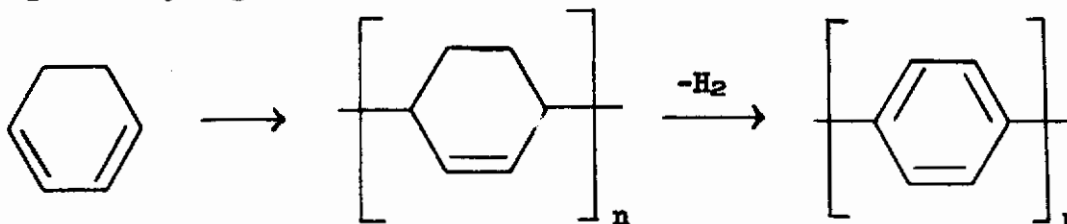
University of Arizona

[Experimental work by M. Hasegawa, D. A. Frey, H. Vogel, J. J. Bloomfield and J. E. Mulvaney]

Research on polymers with recurring aromatic units has been in progress in our group for the past three years at the University of Illinois and University of Arizona. It is not intended that this report is a complete coverage of all work performed, but it will include a discussion of the research on poly-p-phenyls, polybenzimidazoles, polybenzborimidazolines and lattice-type aromatic polymers.

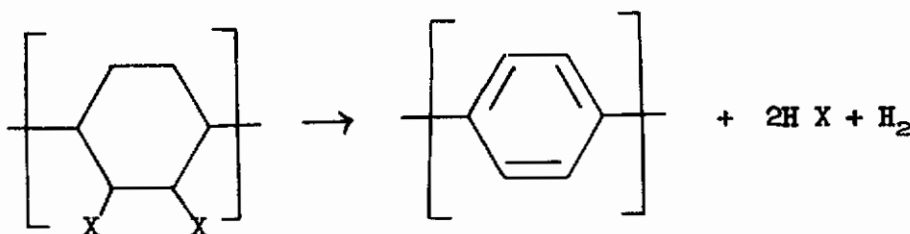
Poly-p-phenyls

These polymers are being prepared via the polymerization of 1,3-cyclohexadiene and subsequent dehydrogenation.



The polymerization has been achieved by means of Ziegler-type catalysts and by cationic initiation with boron fluoride in methylene chloride. It has been impossible to obtain high molecular weight polymer. However, it is consistently possible to produce a soluble polymer with an inherent viscosity of 0.10 to 0.15.

Dehydrogenation has been accomplished by preparing either the bromine or chlorine adduct of the polymer and then heating the halogenated polymer to 350-400°C. to eliminate hydrogen halide and hydrogen.



When the bromine derivative is used this treatment leads to a dark brown powdery product which is soluble in 1-methylnaphthalene and slightly soluble in concentrated sulfuric acid. The very dilute solution in sulfuric acid shows a λ_{max} at 325 m μ . The inherent viscosity of this material (0.25 g./100 g. 1-methylnaphthalene) was 0.09. It still contained about 0.01 mole per cent of bromine. If one assumes one bromine atom per polymer chain this would suggest a

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degree of polymerization of at least 100.

This polymer when heated with sulfuric acid is sulfonated to yield a polymer which has one sulfur atom for about each 12 carbon atoms. This sulfonated material is slightly water soluble. This polyphenyl is probably not completely aromatized but it is quite stable to heating in air and is very slowly oxidized at 420°C.

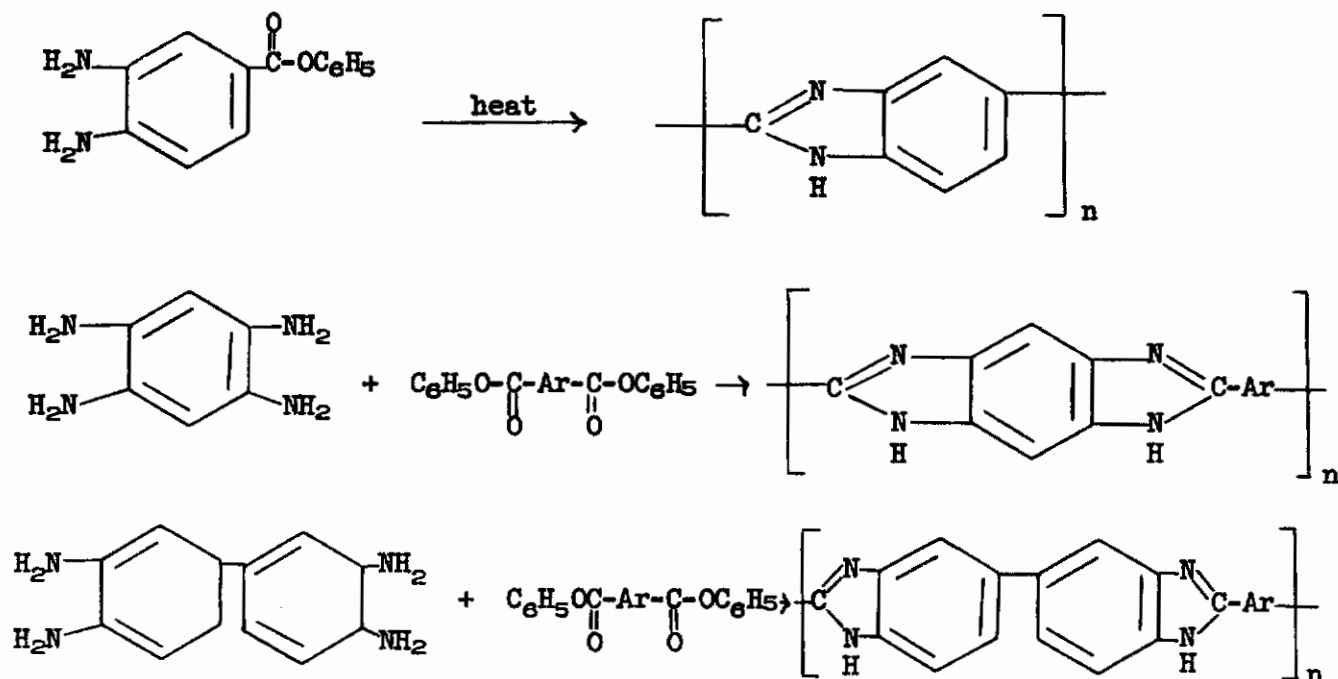
When the chlorine derivative is heated to 350°C. in nitrogen for 8 hours and then at 400°C. under diminished pressure for about 8 hours, a black shiny polymer is obtained which still contains some chlorine and is essentially insoluble in all solvents. The material is so stable to oxidation that we are still having trouble with analyses on samples. This black polymer also seems to be capable of sulfonation. When this polyphenyl (0.005 g.) is heated in an open crucible over a Meker burner at full heat for 5-10 minutes it is gradually burned completely.

Future work is planned to seek higher molecular weight polymers and some other dehydrogenation processes.

Polybenzimidazoles

The reaction of tetraamino aromatic compounds and diphenyl esters of aromatic dibasic acids to yield polybenzimidazoles has been successfully carried out to give a wide variety of new, high molecular weight, heat stable, polymers with good tensile properties. A polymer of this type has also been obtained from the phenyl ester of 3,4-diaminobenzoic acid.

The general classes of polymer which have been obtained are illustrated by the following:

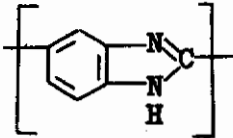
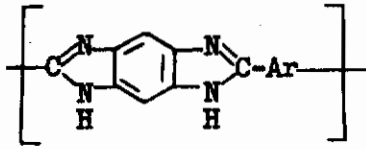
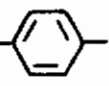
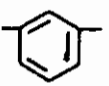
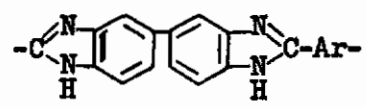
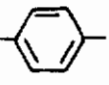
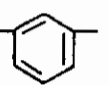


The general procedure for the preparation involves heating the monomer or mixture of monomers in an oxygen-free atmosphere at temperatures of 250-270°C. until the evolution of phenol and water slows down. The solid cake of polymer


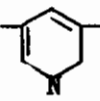

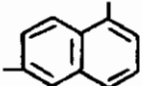
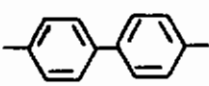
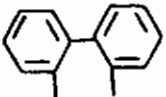
thus produced is then broken up and heated under about 0.1 mm. pressure for several hours with the temperature gradually increasing to 400°C. It is significant that the polymer increases in molecular weight during this heating of the solid pre-polymer. The polymer mass never melts during this phase of the polymerization. All of the polymers are soluble in formic acid and sulfuric acid. A few are soluble in other solvents.

The following table lists polymers which have been prepared and some of their important properties.

Table I

Polybenzimidazoles					
	m.p. °C.	Inherent viscosity (0.2% in HCO ₂ H)	Wt. loss at 600°C. in N ₂ - 5 hrs.	Crystallinity	Solvents
	>600°	1.27	7.3%	?	--
					
-Ar- = 	>600°	0.80	10.2	+	--
Ar = 	>600°	1.10	5.2	+	--
					
-Ar = 	>600°	1.00	4.7	+	--
-Ar- = 	>600°	3.34	4.5	-	$\left\{ \begin{array}{l} \text{DMF, DMAC} \\ \text{DMS, NMP,} \\ \text{HMP} \end{array} \right\}^a$

Contrails

Ar = 	>600°	4.13	8.2		
-Ar- = 	>600°	1.48	5.6	+	DMS ^a
-Ar- = 	480°	0.74	10.0	+	DMS, DMF ^a
-Ar- = 	>600°	2.70	6.5	-	DMS ^a
-Ar- = 	>600°	0.86 (in H ₂ SO ₄)	3.5	+	--
-Ar = 	430°	2.99	17.5	-	DMS, DMF ^a

a - DMF = dimethylformamide
 DMA = dimethylacetamide
 DMS = dimethyl sulfoxide
 NMP = N-methyl pyrrolidone
 HMP = hexamethyl phosphoramide

All polymers are colored and the color varied from light yellow to deep yellowish brown.

The polymers which are listed as melting above 600°C. are cross-linked since after heating at about 450-500°C. none is soluble in any solvent which has been tried. It seems probable that this cross-linking is due to loss of hydrogen and formation of diphenyl links since benzene is known to give diphenyl at about 500°C.

The polymer from 3,3'-diaminobenzidine and diphenyl isophthalate can be cast from dimethyl sulfoxide solution to yield films with fair tensile strength (0.7 g. per denier) and the tensile at 200°C. is essentially the same as the tensile at 25°C. This is an outstanding property of this polymer.

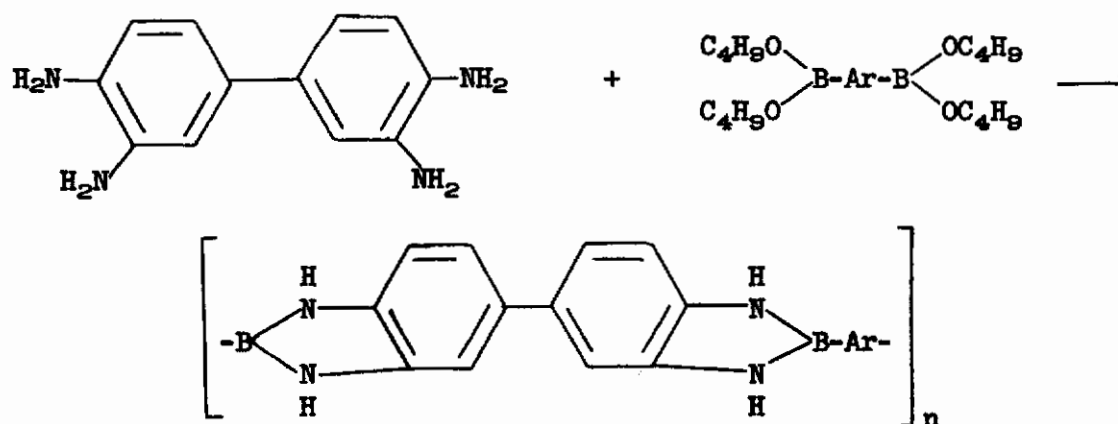
Thermal gravimetric analysis curves on this polymer show only slight weight loss in nitrogen up to 600°C. and then approximately 30% weight loss up to 900°C.

In air the weight loss becomes rapid at 450°C. Although in air there is little weight loss up to 450°C. there is obvious degradation of the polymer above 350°C. since thin films quickly lose their strength at this temperature. The polybenzimidazoles are extremely stable to hydrolysis. Samples of the m-phenylene polymer were refluxed with 70% sulfuric acid and with 25% potassium hydroxide solution for 10 hours each and recovered with no change in inherent viscosity.

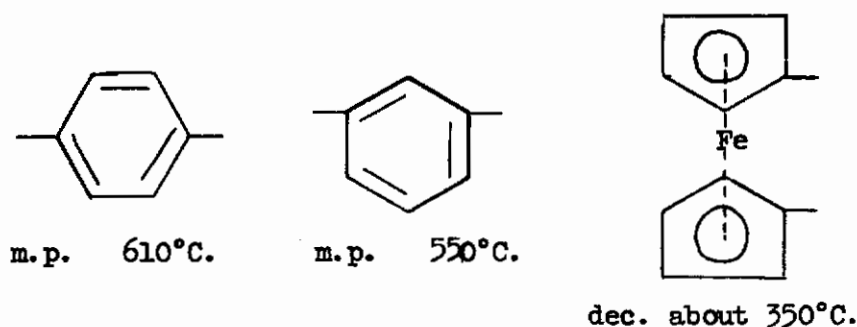
Work is currently under way to try to further modify this type of polymer so that a thermo plastic can be obtained. Also, attempts are in progress to make derivatives which it is hoped may be metal adhesives.

Polybenzborimidazolines

These polymers which are boron analogs of the polybenzimidazoles have been prepared by heating 3,3'-diaminobenzidine with tetraalkyl aryldiboronates under the same general conditions used to make the polybenzimidazoles.



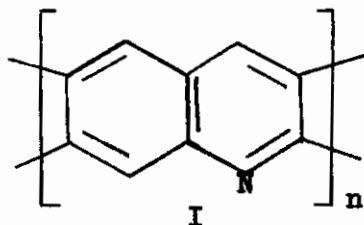
The aryl groups used were the following:



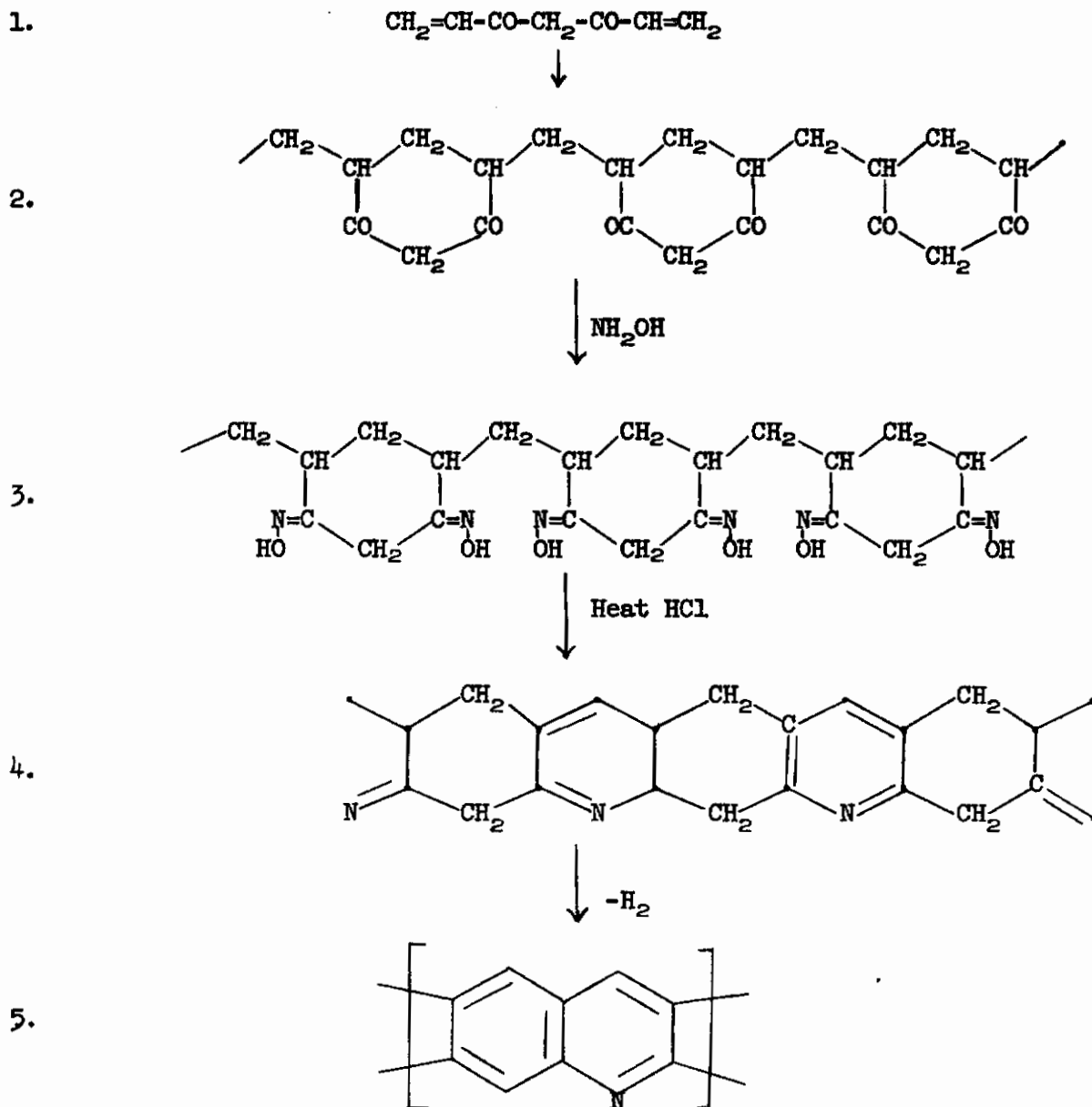
Some polymers were prepared in dimethylacetamide solution and this in general gave lower molecular weight materials. Film forming polymers were obtained but the films were brittle. The polymers first prepared were white but gradually darkened on standing. The polybenzborimidazolines were obtained with inherent viscosities of 0.13 to 0.35. Heat stabilities were about the same as those of the polybenzimidazoles except that the ferrocene derivative is decomposed at about 350°C. The boron derivatives were however much less stable to acids. In general this class of materials seemed less interesting than the polybenzimidazoles and work has been suspended.

Lattice Polymers

For some time attempts have been under way to produce a lattice polymer with an all aromatic recurring unit. Particularly the polyquinoline (I) has been the



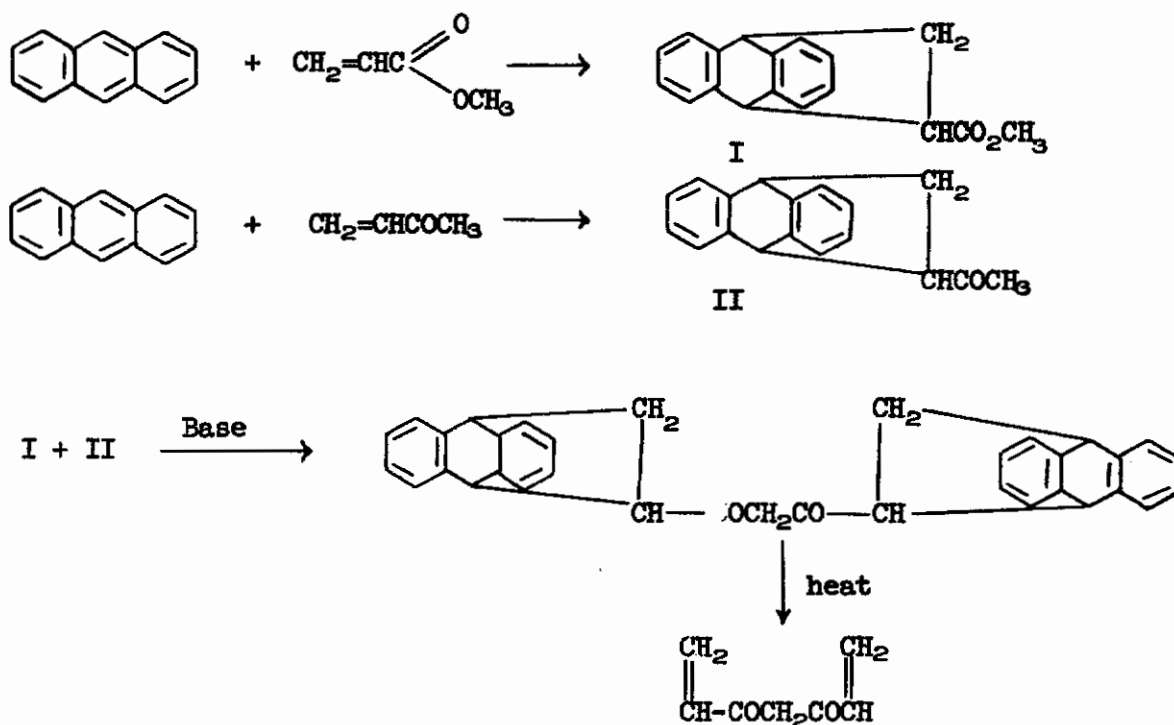
object of our research. A method which looks feasible to use for the synthesis of this polymer is the following:



Contrails

The cyclic polydiketone indicated at step 2 has been claimed in a patent by Jones of Goodrich but his product is obviously not a pure homopolymer but probably contains units of methyl vinyl ketone. His monomer was never isolated as a pure product but was polymerized as made in the presence of methyl vinyl ketone.

A synthesis of this pure monomer has now been realized and the rest of the series of reactions are now being studied.



In conclusion it can be stated that several varieties of polymers with recurring aromatic units have been prepared and all have good thermal stability. Polybenzimidazoles have been obtained which are high molecular weight, have good tensile strength even at 200°C . and possess excellent hydrolytic stability.