Pyrolysis of Phenolic Resins. IV.

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Synopsis

Thermoset resins were made from benzene, naphthalene, phenanthrene, anthracene, or pyrene by condensation with *p*-xylylene dichloride in presence of stannic chloride. The extent of reaction, consequently the crosslink density, was controlled by measurement of the HCl evolved. The absence of oxidation was confirmed by infrared spectroscopy. On pyrolysis at 500, 1000, and 1200°C. *in vacuo* (after Madorsky) it was found that the yield of char was directly related to the number fraction of carbon atoms in the aromatic nucleus used. Benzene was anomalous, and all resins gave lower char yields than standard phenol formaldehyde resins.

INTRODUCTION

We have previously[1] reviewed published work on the pyrolysis of phenol formaldehyde resins and described[2] some studies of the application of thermal analysis techniques in this field.

It has been shown repeatedly that the pyrolysis of such resins in non-oxidative conditions results in the formation of three main types of product: (a) gases, mainly CO, CO_2, CH_4, and H_2, (b) tars of variable composition, mainly aromatic, (c) carbon residue, whose structure and residual content of hydrogen and nitrogen depend on the resin used and the temperature of pyrolysis.

The ratio of solid residue to volatile matter is important in two areas: in flammability, where the volatile matter will burn, if oxygen is present, by a fast gas-phase reaction, and in resistance to very high temperatures, where thermal insulation is provided by a surface layer of carbon.

This paper is concerned with the effect of condensed ring aromatic structures on the carbon yield in pyrolysis *in vacuo* at 500–1200°C.

Resins based on naphthalene and formaldehyde were reported many years ago,[3,4] and also resins based on naphthols and formaldehydes.[5,6] These have not found great use industrially, though occasional patents and other reports on them have been made. Resins made from a variety of phenols have been used[7] as model compounds in studies of coal pyrolysis. Others have been reported by Vanscheidt.[8]

A very flexible method of formation of aromatic resins has been described by Phillips[9] and Vanscheidt.[8] This involves the use of a Friedel-Crafts reaction between *p*-xylylene dichloride and any aromatic compound with a reactive nuclear hydrogen.

In the work projected we were interested only in the effect of the condensed ring nuclei; hence, we did not use phenolic compounds. This was because of the activating effect of the phenolic hydroxyl on methylene bridges in the *ortho* position and the possibility that degradation was oxidative.[10] Additionally, the phenols with condensed rings have rather restricted activity in reactions with formaldehyde.

RESIN FORMATION FROM CONDENSED RING HYDROCARBONS

Reaction of Hydrocarbon with Formaldehyde

The reactivity of aromatic hydrocarbons with formaldehyde is very poor compared with compounds in which activation by electrophilic substitution is obtained, e.g., by hydroxyl groups. This topic has been reviewed by Wegler[11] and Greenhow.[12] The formation of methylene-bridged polymers is favored by a high ratio of aromatic hydrocarbon to formaldehyde, high acid catalyst concentration, high reaction temperature and long reaction periods, and the presence of mutual solvents for the acid and hydrocarbon. Typical conditions[7] are anhydrous zinc chloride catalyst with glacial acetic acid or nitrobenzene solvent. Another system[8] has 17% concentrated H_2SO_4 in glacial acetic acid.

Friedel-Crafts Reaction

The reaction of chloromethyl aromatic compounds in a Friedel-Crafts reaction is controlled by the proportion of reactants, the catalyst used, and the temperature. For fusible or soluble products either a less active catalyst, such as $SnCl_4$, or a low temperature with an active catalyst, such as $AlCl_3$, should be used.

Ratio of Carbon to Hydrogen

What we wished to do was to change the overall ratio of carbon to hydrogen in the cured resin while keeping constant the number of cross-links (i.e., number of bridges per aromatic unit) and the nature of the bridges (i.e., methylenic). Reactive substituents in the aromatic nuclei were avoided.

Hence we used the Friedel-Crafts reaction of *p*-xylylene dichloride (I) with benzene, naphthalene, anthracene, phenanthrene, or pyrene, with stannic chloride catalyst. The ratio of aromatic hydrocarbon to (I) was 1:1.5. The hydrogen chloride evolved was a measure of the degree of reaction, and infrared spectra were used for checking freedom from oxidation.

Pyrolysis

Pyrolysis was carried out in the simple equipment described by Madorsky.[13]

TABLE I

Theoretical Details of Polymers, Assuming Complete Reaction and No Weight Loss[a]

Ar[b] (Fig. 4) derived from:	Empir. form.	C/H ratio	No. C	No. arom. C	C, wt.-%	H, wt.-%	Ar mol. wt.	Theor. yld. fr. Ar units, wt.-%
Benzene	$C_{18}H_{15}$	1:0.834	0.544	0.833	93.49	6.51	80	32.7
Naphthalene	$C_{22}H_{17}$	1:0.773	0.564	0.864	93.95	6.05	128	44.3
Phenanthrene	$C_{26}H_{19}$	1:0.731	0.578	0.885	94.25	5.75	178	53.1
Anthracene	$C_{26}H_{19}$	1:0.731	0.578	0.885	94.25	5.75	178	53.1
Pyrene	$C_{28}H_{19}$	1:0.678	0.596	0.893	94.65	5.35	192	56.2

[a] Average number of methylene bridges per aromatic group, 1.2 in all cases.
[b] Ar = aromatic condensed ring unit in the resin.

TABLE II
Results of Pyrolysis

Av derived from:	Run no.	Sample weight, mg.		Residue, wt.-%	Avg. residue, wt.-%	Pyrolysis time, min.
		Init.	Final			
Pyrolysis temperature, 500°C.						
Benzene	1	46.5	18.7	40.2		
	2	47.4	18.9	39.9	39.4	60
	3	50.0	19.1	38.2		
	4	54.05	20.95	38.8	38.8	180
Naphthalene	5	47.3	14.0	29.6	29.5	60
	6	47.3	13.9	29.4		
Phenanthrene	7	46.7	15.8	34.0		
	8	46.7	15.8	34.0	34.05	60
	9	46.2	15.8	34.2		
Anthracene	10	40.5	16.4	40.4	39.3	60
	11	52.8	20.8	38.2		
Pyrene	12	49.6	22.1	44.6		
	13	41.8	18.7	44.6	44.6	60
Pyrolysis temperature, 1200°C.						
Benzene	32	44.5	13.9	31.2		
	33	42.8	13.7	32.0	31.6	10
Naphthalene	34	37.5	9.0	24.0	24.0	10
Phenanthrene	35	39.5	11.6	29.6	29.6	10
Pyrene	36	41.9	13.9	33.3	33.3	10
Anthracene:	no run; all tubes broken.					
Pyrolysis temperature, 1000°C.						
Benzene	14	60.2	15.0	25.0		
	15	48.7	11.8	24.2	24.5	10
	16	44.0	10.7	24.4		
	17	47.2	11.8	25.0		
	18	50.4	12.5	24.8	24.9	20
Naphthalene	19	45.8	10.3	22.7		
	20	42.0	10.3	24.7	23.9	10
	21	35.5	8.3	23.4		
Phenanthrene	22	41.4	12.9	32.1		
	23	50.4	15.0	29.9		
	24	52.4	16.0	30.6	30.4	10
	25	50.2	15.4	30.7		
Anthracene	26	50.8	16.1	31.6		
	27	28.4	12.3	32.0	31.8	10
	28	39.5	12.6	31.9		
Pyrene	29	42.1	14.2	33.6		
	30	48.2	16.7	34.4	34.3	10
	31	37.1	13.0	35.6		
Pyrene[a]	37	39.9	16.6	41.5		
	38	43.2	17.8	41.3	41.3	—

[a] 500°C. for 1 hr., then gradual heating to 1000°C. (35 min.).

EXPERIMENTAL

Resin Preparation

The apparatus used consisted simply of a 50-ml. distillation flask whose sidearm was connected via a Dreschel bottle, containing concentrated H_2SO_4, to a flask containing 1 liter of stirred distilled water. The reactants were charged to the reaction vessel (1 mole of aromatic hydrocarbon to 1.5 moles of p-xylylene dichloride, about 10 g. in total). The apparatus was purged with dry nitrogen for 10 min. and the flask heated by a silicone bath, until a homogeneous melt was obtained. This temperature was held for 10 min., and 0.15 ml. (3 drops) of a 10% solution of $SnCl_4$ in ethylene dichloride was added. Hydrogen chloride evolution started, and the temperature of the bath was increased, until gelation occurred and HCl evolution ceased. The cured polymer was ground coarsely, worked six times with water, and dried at 80°C. for 5 hr. in an air oven. Before pyrolysis the polymers were ground to 150 mesh and postcured in vacuo (0.01 mm. Hg) at 200°C. for 2 hr. Infrared spectrum analyses were made before and after postcuring.

Pyrolysis

The equipment was as described by Madorksy,[13] except that a thick nickel–chromium steel tube (heat sink) was inserted between the furnace wall and the silica pyrolysis tube. A 50 mg. amount of polymer was weighed in a platinum boat, plugged with quartz wool to prevent loss. This boat was inserted in the pyrolysis tube, which was flushed three times with white spot nitrogen. The furnace, heated to 20°C. above the required temperature, was moved into position, and pyrolysis was carried out for 1 hr. at 500°C. or 10 min. at 1000 or 1200°C. The boat was recovered and reweighed. (At 1200°C. the silica tubes devitrified.)

DISCUSSION

(1) The infrared spectra of all the polymers showed no absorption at 1670–1660 cm.$^{-1}$, which corresponds to the C=O band in diaryl ketones.[14] We assumed, therefore, that no oxidation had taken place at the methylene bridges.

(2) On the basis of a mass balance and the amount of HCl evolved the average number of methylene bridges was approximately 1.2 for all polymers except that from benzene, which may have had a higher crosslink density than indicated (Table I).

(3) The results are presented as plots of weight per cent of char versus C/H ratio, i.e. number fraction of carbon atoms (Fig. 2), versus ratio of aromatic C to aliphatic C, i.e., number fraction of aromatic carbon atoms (Fig. 3), and versus molecular weight of the polyring aromatic compound used (Fig. 4). In Figure 4 the results of van Krevelen et al.[7] have been plotted on the same basis.
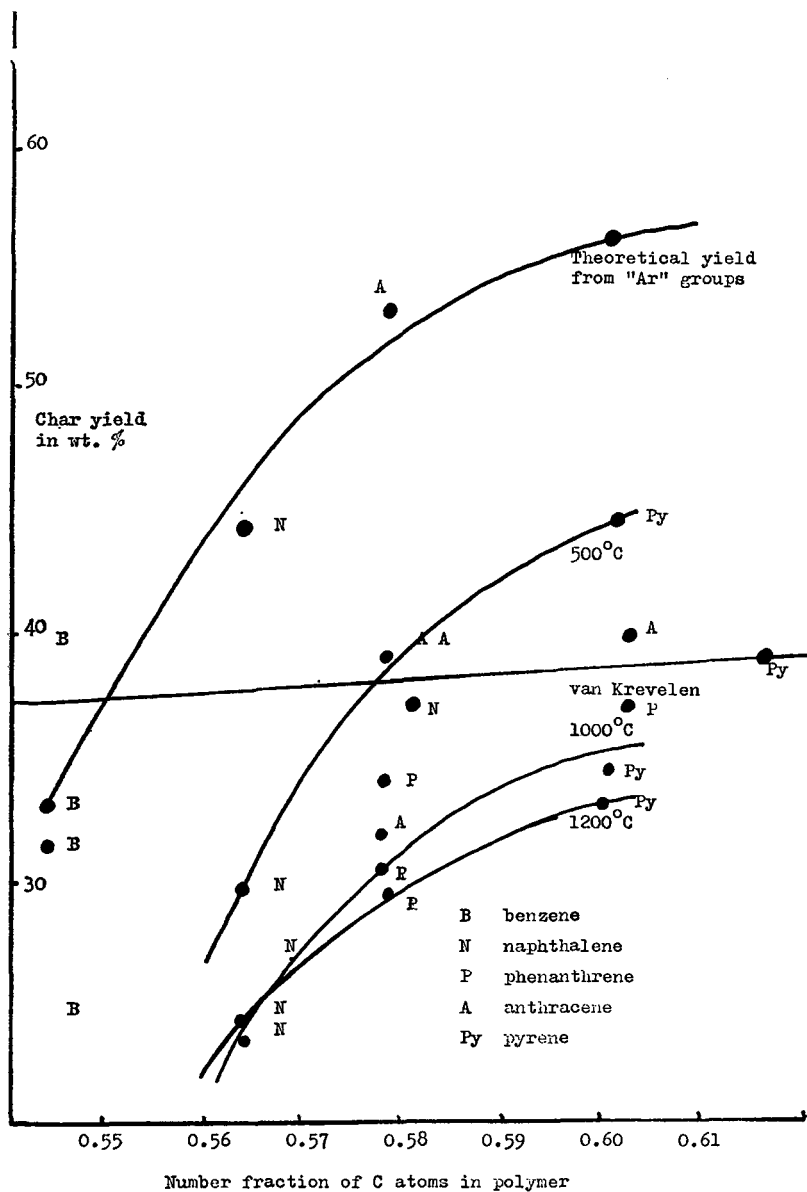
Fig. 1. Weight per cent char yield versus number fraction of carbon atoms.

(4)   The resins of van Krevelen et al.[7] contained only one aromatic species, and in degradation up to 600°C. in nitrogen probably no oxidative scission took place (since weight loss below 450°C. was insignificant).   Their results suggest that the number of scissions per aromatic group is independent of the group used; hence, there is little variation in char yield with molecular weight of the aromatic unit.
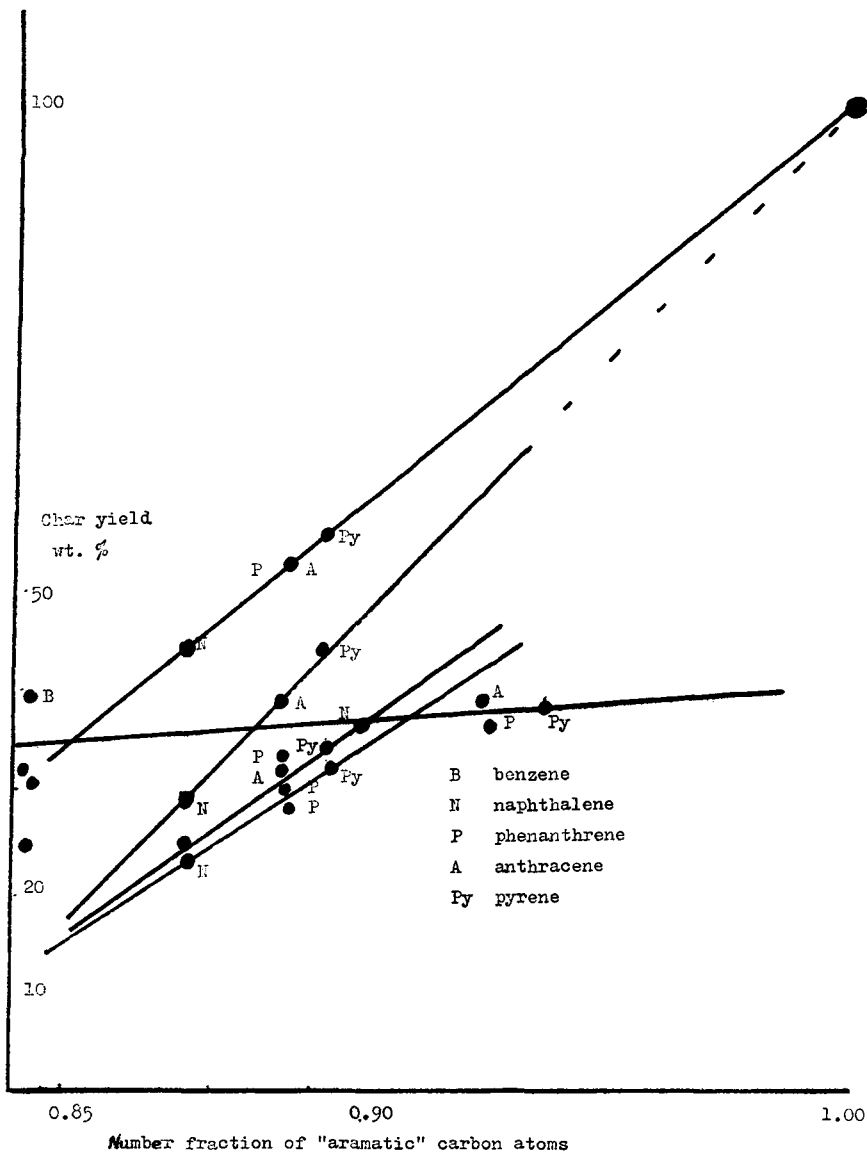
Fig. 2. Weight per cent char yield versus number fraction of "aromatic" carbons.

(5) Our results indicate a proportional increase in char yield with molecular weight of the aromatic unit. This may be due to preferential loss of benzene-ring-based fragments, since our polymers contained both simple and multiple ring aromatic nuclei. Some confirmation of this is obtained from Figure 3, where actual char yields at 500°C. and theoretical yields assuming only condensed ring aromatics coincide at a theoretical 100% point.
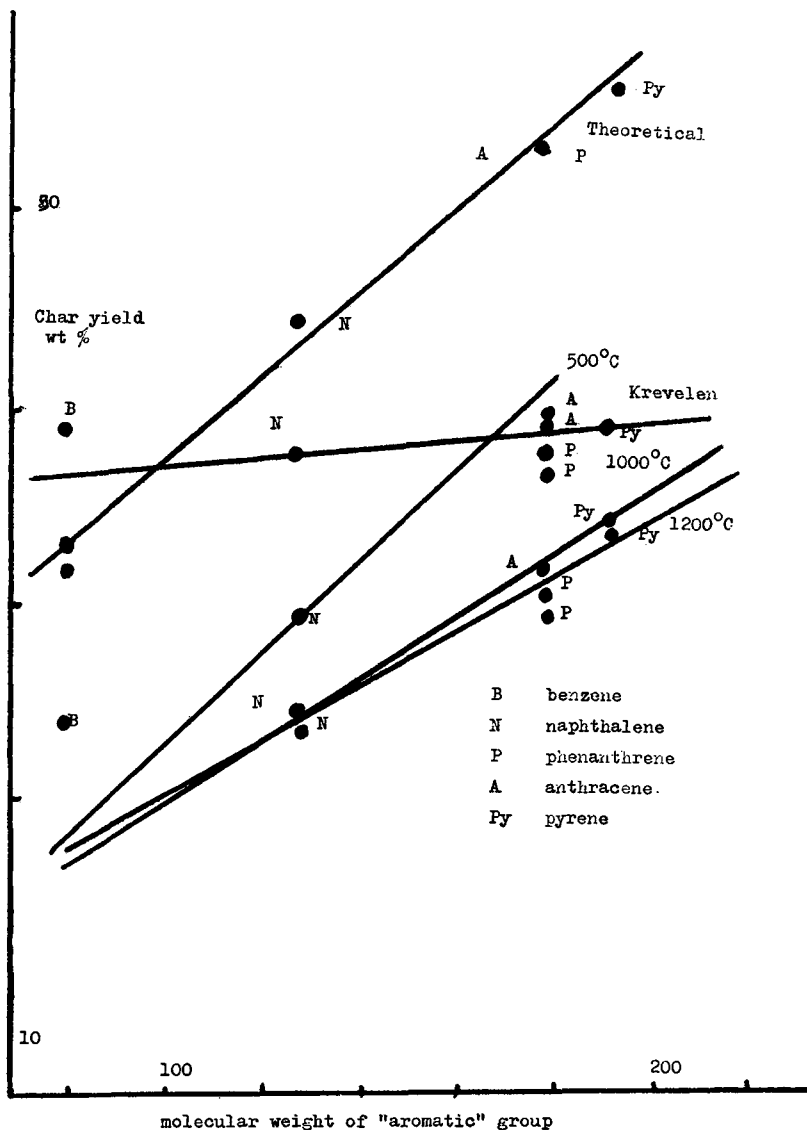
Fig. 3. Weight per cent char yield versus molecular weight of "aromatic" groups (Ar).

(6)   This preferential loss of benzene rings may be due to (a)   larger residue times of fragments of higher molecular weight, (b)   larger proportion of methylene groups on the larger nuclei, or (c)   easier abstraction of hydrogen from the polyring aromatic.

(7)   Our char yields are lower than those of van Krevelen,[7] and this may be due to the heterogeneity of the aromatic groups present, resulting in less stable residues.   In this case the higher yield of the benzene ring material may be due to its higher crosslink density.

Another factor whose effect has not been fully assessed is the "unnatural" 1:4 methylene bridge linkage imposed by the method of synthesis used.

(8)   Comparison with previously reported results for phenolic resins is difficult, since the crosslink density of these is not known.   However, they yield 50–60% char, and previous workers[15,16] indicate that preoxidation both increases char yield and gives harder and more bulky residues than those under true nonoxidative conditions.

Since phenol formaldehyde resins cured in air are known to be "preoxidized," it would be of interest to examine the effect of controlled oxidation on the polyarylene methylenes.

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