

Synthesis and Structural Characteristics of Polycyclic Aromatic Hydrocarbon-Containing Phenol Formaldehyde Resites

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ABSTRACT: To probe the formation of polycyclic aromatic hydrocarbons (PAHs) during the carbonization, gasification, and liquefaction of coals and other solid fuels, nonsoftening phenol–formaldehyde (PF) co-resites are ideal since they facilitate the incorporation of individual PAHs into a highly crosslinked matrix. A series of PAH and diphenylalkane-containing phenolic co-resites have been prepared using phenol with, as the second component, 2-naphthol, 4-hydroxy diphenylmethane, 4,4'-dihydroxydiphenylethane, 1-(4-hydroxybenzyl)naphthalene, 9-(4-hydroxybenzyl)anthracene, and 9-(4-hydroxybenzyl)phenanthrene. A mole ratio of 3 : 1 (phenol : second phenolic constituent) was adopted to ensure that a reasonably high degree of crosslinking was achieved. The virtually complete elimination of ether and methylol functions from the resoles by curing at 200°C was monitored by solid-state ¹³C-NMR. The resites were also characterized by Fourier transform infrared spectroscopy. The volatile-matter contents of the PAH-containing resites were all higher than that of the normal resite. The carbonization of the 9-(4-hydroxybenzyl)anthracene-containing resite in a fluidized-bed reactor is used to illustrate the potential applications of the PAH-containing resites in fuel science. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 663–671, 1997

Key words: phenolic resins; polycyclic aromatic hydrocarbons; carbonization

INTRODUCTION

Coals and oil shales have highly complex, macromolecular organic structures^{1–3} and, in order to obtain insights into the multitude of reactions which occur during their thermal breakdown, detailed compositional information on the aromatic, aliphatic, and heteroatomic groups present and

an understanding of how these different functionalities behave under processing conditions are required. To achieve the latter goal, model compound studies performed in both vapor and liquid phases have been used extensively.⁴ However, a major drawback with such studies is that radical species generated by bond homolysis are mobile and free to diffuse independently prior to further reaction. In contrast, for highly crosslinked macromolecular solids such as coals and oil shales, many of the reactive intermediates remain covalently attached to the solid matrix of the solid and thus their reactivity is subject to diffusional constraints. Further, for thermal studies in open systems, the use of nonsoftening substrates that neither melt nor vaporize and hence remain in the reactor is essential.

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In order to probe the effects of restricted mobility in free radical reaction pathways during coal liquefaction, Buchanan and coworkers have studied extensively the thermal decomposition of model compounds immobilized on silica.^{5,6} It was recognized that these substrates also have considerable potential for modeling many other aspects of solid fuel behavior, including the release of sulfur and nitrogen species during conversion processes. The SiO—C bond linking the substrate to the surface is reasonably stable and does not cleave below 500°C.⁷ Immobilized sulfur moieties typical of some of the thiophenic and sulfidic forms considered to be present in solid fuels (namely, dibenzothiophene, diphenyl sulfide, phenyl benzyl sulfide, and thioanisole) were prepared and used as calibrants in temperature-programmed reduction (TPR),⁸ a thermal technique used to specify the different organic sulfur forms from their characteristic reduction temperatures.^{9,10}

Cured phenol-formaldehyde (PF) resoles (resites) were identified as another flexible class of materials that could be used for investigating thermochemical phenomena in the solid state, since a wide range of hydrocarbon and heteroatomic moieties can readily be introduced into their macromolecular framework. A series of sulfur and nitrogen-containing co-resoles and co-resites have recently been prepared from phenol with, as the second component, hydroxy substituted thiophene, dibenzothiophene, diphenylsulfide, benzyl phenyl sulfide, thioanisole, quinoline, and carbazole.¹¹ A mole ratio of 3 : 1 (phenol : heteroatom-containing component) was adopted to ensure that a reasonably high degree of crosslinking was achieved. Resoles containing diphenyldisulfide were also prepared¹¹ but, due to the comparable bond strengths of the S—S and C—O linkages, a curing temperature of only 130°C was used to avoid cleavage of the disulfide bond. The sulfur-containing resites have been used to study the release of sulfur dioxide during coal combustion¹² and as an alternative calibrant to the silica-immobilized substrates for TPR.^{13,14} The nitrogen-containing resites are being used to help study nitric oxide release during coal combustion.

Polycyclic aromatic hydrocarbons (PAH) are a series of ubiquitous environmental pollutants containing two or more fused benzene rings that are widely produced by the incomplete combustion of fossil fuels and other organic materials.^{15–17} Due to the lack of mechanistic information concerning their formation during solid fuel conversion processes, there is a need for suitable model

substrates. In this investigation, a suite of PAH-containing resites has been prepared with, as the second component, diphenylmethane, benzylnaphthalene, benzylanthracene, benzylphenanthrene, and 2-naphthol. The elimination of ether and methylol functions from the resoles by curing at 200°C has been monitored by solid-state ¹³C-nuclear magnetic resonance (NMR). To illustrate the potential application of the resites to study the formation of PAH in the utilization of solid fuels, the carbonization of the 9-(4-hydroxybenzyl)anthracene-containing resite has been investigated in a fluidized-bed reactor.

EXPERIMENTAL

Synthesis of Precursors

The mono- or dihydroxydiphenylalkanes and monohydroxy-phenyl PAHs used to prepare the resins were 4-hydroxy-diphenylmethane, 4,4'-dihydroxydiphenylethane, 2-naphthol, 4-naphthobenzylphenol, 9-(4-hydroxybenzyl)anthracene, and 9-(4-hydroxybenzyl)phenanthrene. Of these, only 4-hydroxydiphenylmethane and 2-naphthol were commercially available. However, as now described, established routes were employed in the synthesis of the other precursors.

To prepare 4,4'-dihydroxydiphenylethane,¹⁸ 40 g (0.33 mol) of powdered tin, 52 g (0.19 mol) of anisoin, 52 mL of concentrated HCl, and 60–70 mL 95% ethanol were refluxed for 24 h. After this time, the boiling mixture was decanted from the undissolved tin and cooled to 0°C, and the white crystals produced were filtered by suction. The filtrate was then heated to boiling and used to wash the tin. The combined washings were then cooled to 0°C and the crystals were again collected by suction filtration. Recrystallization of the combined solids from 450 mL boiling 95% ethanol gave, on cooling to 0°C, colorless crystals of 4'-methoxy-2-(*p*-methoxyphenyl)acetophenone (deoxyanisoin). Next, the deoxyanisoin was then subjected to a Wolff–Kishner reduction by refluxing 0.02 mol of the product with 9 g KOH and 10 mL of 95% hydrazine hydrate and diethylene glycol for 2 h. Once distillation of excess hydrazine hydrate and water was complete, the reaction mixture was refluxed for a further 2 h at 200°C. The mixture was then cooled and poured onto about 100 g of ice and acidified with 3*N* HCl. The products were extracted with CHCl₃ and dried

with MgSO_4 , filtered, and then solvent was removed to yield 4,4'-dimethoxydiphenylethane. This compound was then subjected to demethylation by refluxing for 20 min in 20 g of redistilled pyridine hydrochloride. This yielded the crude product which was recrystallized from hexane-ethylacetate to yield white, shiny, prismatic crystallites [melting point (mp) 198–199°C].

The preparation of 1-(4-hydroxybenzyl)naphthalene was carried out following the method reported by Bukova and colleagues.¹⁹ First, 64 g of resublimed naphthalene was dissolved in dry CCl_4 and acylated with 94 g (0.5 mol) of *p*-anisoylchloride to yield 1-(4-methoxybenzoyl)naphthalene. A Wolff–Kishner reduction was then conducted on the compound as described above to yield 1-(4-methoxybenzyl)naphthalene. This compound was then demethylated by adding 0.1 mol of the methylated compound to 0.2 mol pyridine hydrochloride and stirring for 4 h at 200°C. After cooling, 100 mL of water was added to the mixture, which was then acidified to pH 1 with 10% HCl, extracted in 300 mL of diethylether, and purified by vacuum distillation (180–182°C, 3–4 mmHg). The product was recrystallized from benzene–acetone (3 : 1 v/v) to yield yellow, shiny, needle crystallites (mp 166–167°C).

The method reported by the same authors¹⁹ was used in the preparation of 9-(4-hydroxybenzyl)anthracene. The initial stage in the preparation involved refluxing 49 g (0.22 mol) 9-anthracenecarboxylic acid with 33 g (0.26 mol) oxalylchloride for 3 h to yield 9-anthracene carbonyl chloride. This compound was then acylated as described previously with anisole to produce 9-(4-methoxybenzoyl)anthracene, which was subjected to a Wolff–Kishner reduction. The resultant 9-(4-methoxybenzyl)anthracene was then demethylated as described above and the crude product was recrystallized from toluene to yield yellow, shiny, needle crystallites (mp 187–188°C).

To prepare 9-(4-hydroxybenzyl)phenanthrene, the methods reported by Gore and associates²⁰ and Bachmann²¹ were followed. Phenanthrene was first acylated, as described above, with *p*-anisoylchloride to yield 9-(4-methoxybenzoyl)phenanthrene. A Wolff–Kishner reduction was conducted on this compound to yield 9-(4-methoxybenzyl)phenanthrene, which was then demethylated as described earlier. The crude product was purified by vacuum distillation (200–201°C, 3–4 mmHg) and recrystallization from hexane, which yielded yellow, shiny, needle crystallites (mp 85–86°C). The

structures of the resin precursors were confirmed by ¹H-NMR analysis, which indicated that purities were in excess of 95%. This is satisfactory, considering the application reported here of using the compounds as resin precursors.

Synthesis of the Resins

The co-resoles were prepared using a total phenol-to-formaldehyde mole ratio of 1 : 2.5, following established procedures.^{22,23} The mole ratio of phenol to the monohydroxydiphenylalkanes and monohydroxybenzyl PAHs was 3 : 1 to ensure that a reasonably high degree of crosslinking was achieved in the initial resoles. Sodium hydroxide was used as catalyst in the condensation reaction at a mole ratio of 0.1 with respect to phenol. Phenol, the monohydroxydiphenylalkane or monohydroxybenzyl PAHs, and formalin (37% v/v formaldehyde) were mixed in a 250 cm³ three-neck round-bottom flask and stirred until all the phenol was in solution. The mixture was then cooled in an ice-bath for about 10 min before sodium hydroxide (0.006 mol, 20M) was added dropwise to the reaction mixture. This was then refluxed at 70°C for 30 minutes and acidified with 85% lactic acid to a pH of 4–5 (indicated by universal indicator paper) before excess water was removed by vacuum distillation. The thick, resinous material was poured into a capped container for curing in an oven purged with nitrogen that was initially set at 70°C for 4 days. The oven temperature was then raised to 130 and 200°C for additional 24-h periods. For purposes of comparison, a normal PF resite and resole were prepared by the same procedure.

Characterization of the Resins

C and H contents of the PF resoles and resites were determined using a Perkin–Elmer 2400 Analyser. Chloroform, toluene, and methanol solubilities of a number of the resoles and resites were determined by heating relatively small sample amounts of sample (about 200 mg) under reflux.

Solid-state ¹³C-NMR spectra of the resoles and cured resites were obtained using a Bruker MSL 100 instrument operating at a frequency of 25 MHz for carbon. The standard cross polarization–magic angle spinning technique was used, the contact time being 1 ms with a recycle delay of 1.5 s between successive contacts. Samples (250 mg, < 250 μ) were packed inside a 7 mm diameter zirconia rotor for analysis. Typically, 1,000 scans

were accumulated and spectra were processed using a line broadening factor of 30 Hz.

Pyrolysis

Volatile matter is defined empirically as the weight loss, excluding moisture, when coals and other solid fuels are heated in the absence of air to the specified temperature of 900°C, according to the British Standard 1016, Part 3. Approximately 1.0 g samples of the co-resoles and co-resites were weighed into silica crucibles which were placed (with lids on) in a furnace at 900°C for 7 min. After heating, the crucibles were transferred to a dessicator and allowed to cool before reweighing.

An all-silica fluidized-bed reactor system (5-cm diameter), based on the design used by Nelson and coworkers,²⁴ was used to pyrolyze a normal PF resite and the 9-(4-hydroxybenzyl)anthracene-containing resite at a temperature of 900°C in a bed comprising about 100 g of acid-washed sand (200–300 μm). This was fluidized using a flow of 2–3 $\text{dm}^3 \text{min}^{-1}$ of nitrogen. Approximately 4 g resite (75–112 μm) was fed at a constant rate from a hopper, which was also fluidized with a flow of nitrogen (1 $\text{dm}^3 \text{min}^{-1}$), over a 20–30-min period into the fluidized bed at 900°C. Two 500- cm^3 Dreschel bottles in series, cooled with dry ice, were used to trap the tars with virtually no carryover into the gas.

After the tests, the tars were recovered in toluene for analysis. The char and tar yield were calculated from the weight gains of the bed and the traps during each run, with the weight gains of the traps being corrected for any water present determined via the Dean–Stark method. After the water had been removed from the toluene solutions of the tars, these were concentrated to facilitate fractionation of the tars by preparative-scale open-column alumina chromatography to provide aromatic fractions for high pressure liquid chromatographic (HPLC) and gas chromatographic (GC) analysis. The alkanes, aromatics, and polars were eluted successively from the column containing activated alumina (500°C for 16 h) with *n*-hexane, toluene, and methanol.

For HPLC separation of the aromatic fractions by ring size, an electron deficient, nitroaromatic-bonded silica column manufactured by Shandon (Hypersil CTA, 25 cm by 4.6 mm, 5 μm particles) was used in conjunction with an Applied Chromatography Systems Model 352 gradient elution pump, a Waters 486 UV detector at 254 nm, and

a PC-based software package for peak integration. The volumetric flowrate was set at 0.6 $\text{cm}^3 \text{min}^{-1}$ and a standard mixture of 16 PACs (supplied by Supelco) was used to optimize the separation achieved with *n*-hexane and dichloromethane (DCM) mixtures, the most satisfactory gradient elution scheme being 10% v/v DCM in hexane for 20 min, then 10 to 100% v/v DCM for 60 min, and finally, 100% v/v DCM.

GC analyses of the aromatic fractions were carried out on a Carlo Erba 4130 GC equipped with an FID detector. Separation was achieved on a 25-m fused silica capillary column coated with BP1 (0.25 μm thickness). Helium was employed as the carrier gas and a temperature program of 50°C (2 min) to 300°C (15 min) at 8°C min^{-1} was used. The injection and detection limits were both set at 300°C.

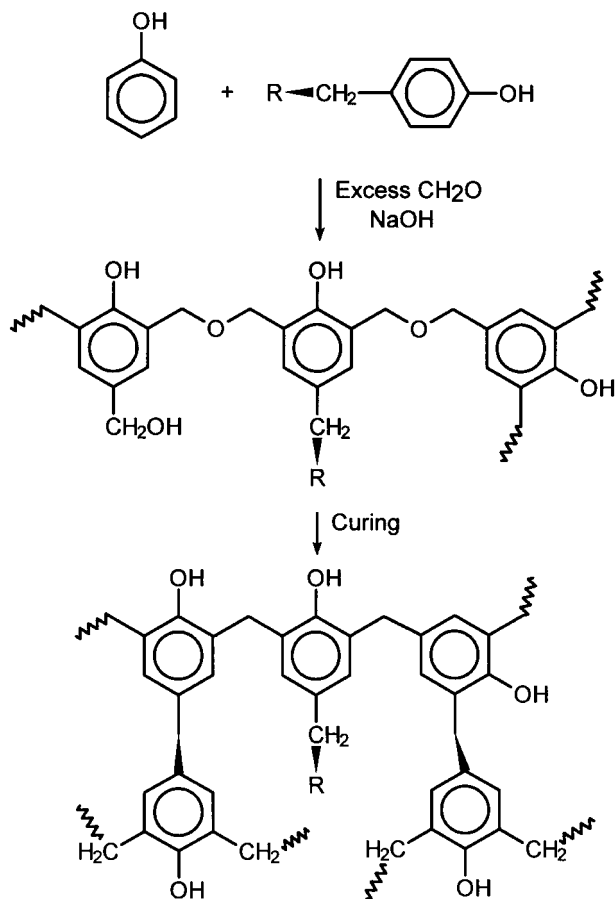
RESULTS AND DISCUSSION

General Considerations

The incorporation of PAH-substituted phenolic compounds into a cured PF co-resole and the resultant co-resite is depicted in Figure 1. As for the sulfur and nitrogen-compound-containing resins synthesized recently,¹¹ a mole ratio of 3 : 1 for phenol to the PAH-containing component was adopted here to ensure that a reasonably high degree of crosslinking was achieved and to ensure that the PAHs were reasonably dilute in the macromolecular structure. As anticipated, the cured PF resins were all found to have low methanol solubilities (<1%) and were essentially insoluble in nonpolar solvents such as chloroform and toluene.

The C and H contents of the co-resites are listed in Table I, which indicates that the fully cured co-resites have C contents in the range 70–75% (dry basis). Allowing for about 5% H present, this makes the O contents to be about 20–25% by difference which is higher than the predicted 15% for the fully cured resins (assuming that the only O present is phenolic). The apparently low C contents may arise from strongly physisorbed water, given that the concentrations of ether and methylol groups in the resites are fairly low (see ¹³C-NMR results), although diarylether linkages are also present.

As anticipated, the volatile matter contents of the resites are all significantly lower than those of the corresponding resoles (Table II) due to the



R= Naphthyl, anthracyl, phenanthryl, phenyl.

Figure 1 Incorporation of PAH-substituted phenols into the structure of the co-resole and resultant resite.

elimination of the thermally labile ether bridges and methylol groups (see following). However, the volatile-matter contents of all the PAH-containing resoles and resites are significantly higher than those of the corresponding normal PF resins (Table II). The achieved increases of 10–20%

clearly arise from the PAHs being anchored into the resins by a single diarylmethane linkage, compared with the phenolic moieties which have either two or three methylenes attached (*o* and *p* positions). The mole ratio of 3 : 1 (phenol : PAH) used to prepare the resins corresponds approximately to the PAH moieties, accounting for between 20 and 30% w/w of the resites. In relation to coals, the volatile matter contents are superficially close to those of lignites.¹ However, probably due to the highly crosslinked state of the initial structure (both diarylmethane bridges and hydrogen-bond crosslinks), the chars obtained from PF resins have been found to have a higher degree of closed porosity than both bituminous and low-rank coals.²⁵

Solid-state ¹³C-NMR

As for their sulfur and nitrogen-containing counterparts synthesized recently,¹¹ solid-state ¹³C-NMR was used to establish the most appropriate curing regime for the PAH-containing resins. Figure 2 shows the solid-state ¹³C-NMR spectra of the 9-(4-hydroxybenzyl)anthracene co-resin after various curing periods. There is no apparent difference in the spectra of the resin cured for 6 and 12 h at 200°C. However, after the resin has been cured for 24 h, the intensity of the peak at 70 ppm (ether bridges, Table III) was vastly reduced with an increase in that at 35 ppm indicating that ethers have largely been converted into methylene bridges. As for the sulfur and nitrogen-containing resites,¹¹ there appears to be a shoulder at 160 ppm which was assigned by Maciel and associates²⁶ to aromatic carbon in aryl ethers which are likely to arise from condensation reactions involving two phenolic moieties. A peak at 18 ppm is evident, which has been attributed to ortho to phenolic hydroxy (Table III).

Table I C and H Contents of the Co-resites

Co-resite	C (%, dry basis)	H (%, dry basis)
2-Naphthol	71.8	4.5
4-Hydroxydiphenylmethane	70.6	5.0
4,4'-Dihydroxydiphenylethane	74.4	6.3
1-(4-Hydroxybenzyl)naphthalene	73.4	5.0
9-(4-Hydroxybenzyl)anthracene	72.5	5.4
9-(4-Hydroxybenzyl)phenanthrene	72.2	5.1
Normal PF	74.7	4.7

Table II Volatile Matter Contents of the Co-resoles and Co-resites

Second Component	Co-resoles (% w/w)	Co-resites (% w/w)
2-Naphthol	70.1	53.2
4-Hydroxydiphenylmethane	67.8	50.0
4,4'-Dihydroxydiphenylethane	65.9	52.4
1-(4-Hydroxybenzyl)naphthalene	66.7	55.2
9-(4-Hydroxybenzyl)anthracene	69.2	57.6
9-(4-Hydroxybenzyl)phenanthrene	68.5	61.1
Normal PF	50.0	40.0

Fourier transform infrared (FTIR) examination has provided confirmatory evidence that concentrations of ether groups in the resites are low. All of the resins partially cured at 130°C gave rise to peaks at 1050 cm⁻¹ due to the C—O bonds, but these peaks disappeared upon curing at 200°C (Fig. 3). Although a number of side reactions are known to occur above 150°C, there was no evidence from ¹³C-NMR spectra that quinones had been formed in significant concentrations.^{27,28}

Fluidized-bed Pyrolysis

The total yields of tar and aromatics and the yield of anthracene obtained from the fluidized-bed py-

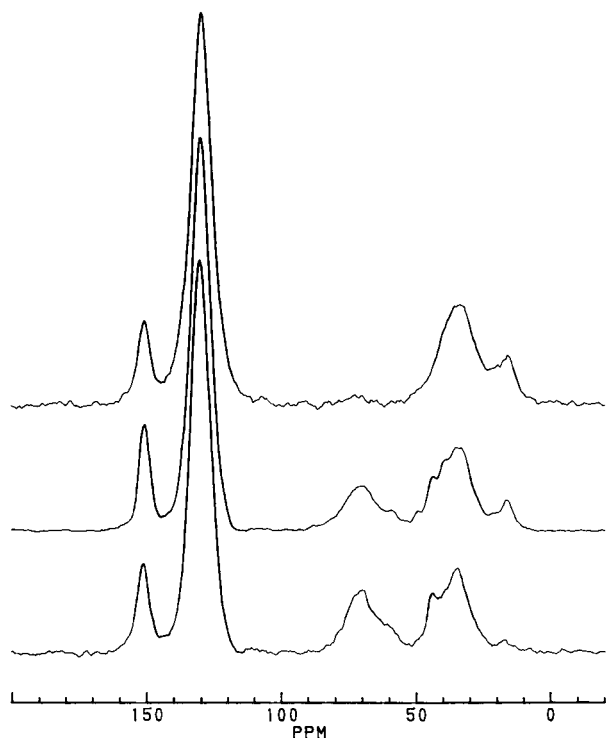


Figure 2 Solid-state ¹³C-NMR spectra of the 9-(4-hydroxybenzyl)anthracene co-resite after curing at 200°C for 6 h (bottom), 12 h (middle), and 24 h (top).

rolysis experiments on the normal PF and the 9-(4-hydroxybenzyl)anthracene-containing resite are listed in Table IV, together with the HPLC-determined distribution of ring size in the aromatics. Figure 4 compares the HPLC traces for the aromatics obtained from the two resites. The high pyrolysis temperature of 900°C ensures that parent PAH dominate over the alkyl-substituted counterparts (most alkyl and parent PAH coelute in the HPLC separation), which has been confirmed by gas chromatography. As expected from the volatile matter contents (Table II), a much higher tar yield was obtained from the 9-(4-hydroxybenzyl)anthracene-containing resite (Table IV). Indeed, the higher tar yield is accounted for completely by the additional aromatic material obtained (about 10% w/w resite).

As anticipated, anthracene dominates the HPLC and GC traces of the aromatics for the 9-(4-hydroxybenzyl)anthracene-containing resite

Table III ¹³C-NMR Peak Assignments for the Resoles and Resites

Chemical Shifts (ppm)	Assignment
18	Arylmethyl, <i>ortho</i> position to phenolic OH
30, 35, and 40	2,2'-, 2,4-, and 4,4'-methylene carbon, respectively
58–65	Methylol carbon, <i>ortho</i> or <i>para</i> position to phenolic OH, ArCH ₂ OH
68–73	Dimethylene ether linkages; Ar—CH ₂ —O—CH ₂ —
95	Hemiacetals, OCH ₂ O
110–135	Phenolic ring carbons other than C—OH
152, 160	Phenolic, C—OH; aryl ether, C—O; respectively

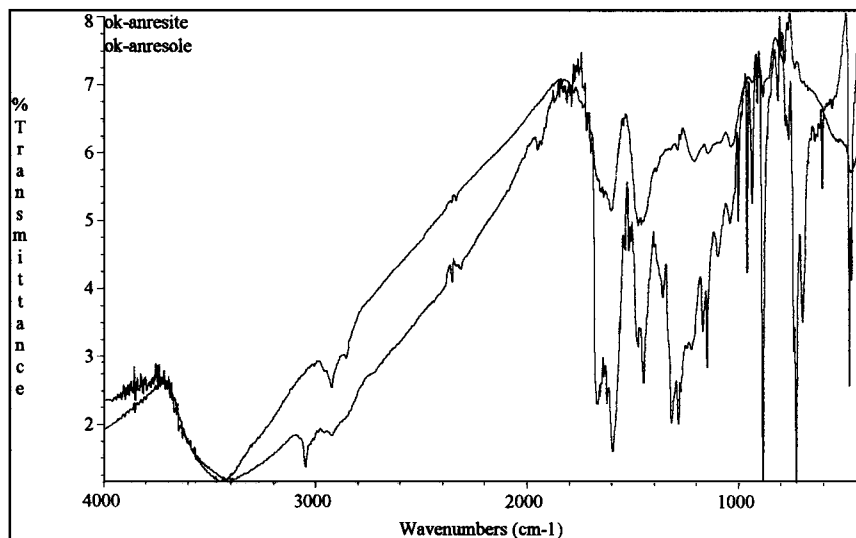


Figure 3 FTIR spectra of the 9-(4-hydroxybenzyl)anthracene co-resole (bottom) and co-resite (top).

(Fig. 4; phenanthrene is the major peak in the trace for the normal resite). However, the increase in anthracene yield of about 5% w/w resite (Table IV) only accounts for about half that in the total tar yield. Furthermore, when this fact is taken with the estimated anthracene content of about 30% in the initial resite, strong evidence emerges for the anthracene becoming involved in many reaction pathways other than simple homolytic cleavage of the anthracylbenzyl methane linkage. Since the total tar yield is only 34% (Table IV), it can be inferred that a substantial portion of the anthracene is incorporated into the char. In addition, the following HPLC results provide evidence that some of the anthracene present rearranges to form other low-molecular-mass

Table IV Yields from the Fluidized-bed Pyrolysis Experiments on the Resites

Product	Normal PF	Anthracene-Containing Resite
Tar (% w/w resin)	25	34
Aromatics (% w/w resin)	10	20
Anthracene (% w/w resin)	1.8	7.0
Anthracene (% aromatics)	18	34
2-ring (% aromatics)	25	9
3-ring (% aromatics)	64	85
4-ring (% aromatics)	9	5
5-ring (% aromatics)	2	1

PAH, particularly phenanthrene and acenaphthene during pyrolysis.

Table V compares the mass ratios of phenanthrene (the major constituent in the aromatics from the normal resite, Fig. 4) to a number of the other PAHs present. GC results confirm that the degree of alkylation has been minimized by pyrolyzing samples at 900°C, with parent PAH predominating over alkylated species. Indeed, extremely close agreement has been observed between HPLC and GC for the PAHs listed. With the exception of acenaphthene the ratios increase

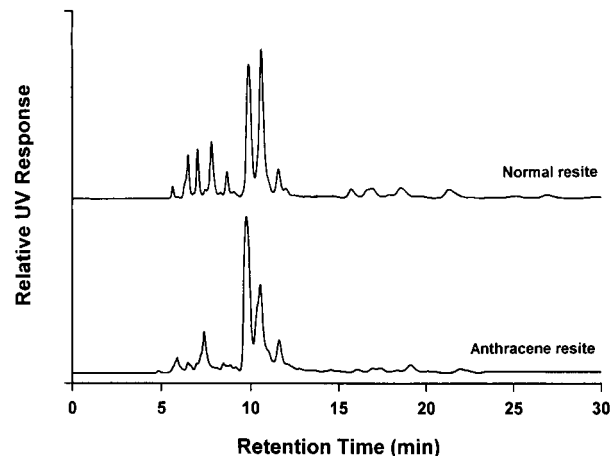


Figure 4 HPLC traces of the aromatic fractions obtained from fluidized-bed pyrolysis of the normal PF resite (top) and the 9-(4-hydroxybenzyl)anthracene-containing resite (bottom).

Table V Mass Ratios of Phenanthrene to Other PAH in the Fluidized-bed Pyrolysis Tars

PAH Compound	Normal PF		Anthracene- Containing Resite	
	HPLC	GC	HPLC	GC
Naphthalene	6	5	9	8
Acenaphthene	4	4	3	3
Acenaphthylene	10	9	27	29
Fluorene	6	7	16	18
Anthracene	1.2	1.0	0.8	0.7
Fluoranthene	16	15	40	44
Pyrene	12	11	34	32
Benzanthracene	9	10	28	30
Chrysene	8	8	15	13

HPLC, high-pressure liquid chromatography; GC: gas chromatography.

considerably, indicating that the yields of phenanthrene and acenaphthene are both considerably greater for the 9-(4-hydroxybenzyl)anthracene-containing resite, with the implication that they have been formed by rearrangement of the anthracene present. Indeed, it is estimated from the data in Table V that the phenanthrene yield increases from 2.2% (w/w) for the normal resite to 5.5% for the 9-(4-hydroxybenzyl)anthracene-containing resite. This confirms work by Scott and Necula,²⁹ who have shown that PAHs undergo structural rearrangement at elevated temperatures, and reports by Zander and Collin³⁰ and Lewis,³¹ who have investigated intramolecular rearrangements of PAHs during the high-temperature carbonization of coal-tar pitch.

The fact that the yield of aromatic material is significant from the normal PF resites provides direct confirmation that phenolic moieties can transform directly into PAH during devolatilization. The first step in this complex reaction pathway probably involves dehydration to form diphenyl ether and furan moieties, which then undergo subsequent ring growth with further dehydration. Since phenolic moieties are the major building blocks of both low-rank and highly volatile bituminous coals,¹ these are likely to be the prime source of PAH rather than the much smaller concentrations of large aromatic ring systems in these coals.

Further Applications of the PAH-Containing Resites

Although van Krevelen was the first to use PF resins in coal science to account for the plasticity

behavior of different coals,¹ the approach adopted here for PAH and, in the recent article, for sulfur and nitrogen-containing resins,¹¹ represents a new direction in fuel science for investigating, in a macromolecular environment, the behavior of the individual functional groups during conversion processes. The fluidized-bed pyrolysis results described above illustrate how the resins can be used to study the formation and release of PAH during the devolatilization of solid fuels. The experiments are currently being extended to the naphthalene and phenanthrene-containing resites, and the reactor conditions (flow rate, temperature) are also being varied to gain a much better understanding of how both phenolic and individual PAH moieties affect the overall distribution of PAH released during devolatilization of solid fuels. Further, it is also intended to extend the syntheses to include ¹³C-labeled PAH which have the potential to provide a wealth of information on the reaction pathways involved. Normal and diphenylmethane-containing resins have also been used to show the effect of OH substituents through keto-enol tautomerism on the ease of cleavage of diarylmethane linkages during coal liquefaction with hydrogen-donor solvents, such as tetralin, at temperatures close to 400°C.³²

CONCLUSIONS

Nonsoftening PF co-resites are ideal substrates for probing the reaction pathways leading to PAH formation during devolatilization since they facilitate the incorporation of individual PAHs into a

highly crosslinked matrix. The volatile matter contents of the PAH-containing resoles and resites are higher than those of the corresponding normal PF resins due to the lability of the single diarylmethane linkage anchoring the PAHs into the macromolecular structure. The carbonization of the normal PF and the 9-(4-hydroxybenzyl)anthracene-containing resite in a fluidized-bed reactor served to illustrate the complexity of the reaction pathways undergone by the anthracene moiety.

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