STRUCTURAL CHARACTERIZATION OF THE MAJOR COMPONENTS OF PETROLEUM PITCH

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Introduction

Petroleum pitches are generally obtained from the thermal polymerization of fluid catalytic cracking (FCC) decant oil, a byproduct of the catalytic cracking of the heavy gas oil fraction of crude oil. As shown in Fig. 1, this highly aromatic material is oligomeric in nature, with a molecular weight (mol wt) that extends from about 200 to above 1000 Da [1,2]. Dimer species are assumed to be formed by the reaction of two monomeric species, with analogous reactions creating the trimer and tetramer peaks that are shown. Petroleum pitches can serve as raw materials for a wide variety of carbon products, such as high thermal conductivity carbon fibers [3]. The mol wt and structure of pitches are known to play a role in their processability and their suitability for a given application [1,3,4]. For example, the rate of stabilization of fibers produced from pitch precursors has been tied to the presence of naphthenic groups and short alkyl chains in these materials[5]. However, this understanding is being limited by our inability to properly characterize the constituents of pitch.

Narrow, oligomeric cuts of a representative petroleum pitch, M-50, were prepared by subjecting the pitch to a dense-gas extraction (DGE) process. These pitch cuts, along with a model anthracene pitch, were then subjected to preparative-scale gel permeation chromatography (prep-scale GPC) [6,7]. Matrix-assisted laser desorption and ionization, time-of-flight mass spectrometry (MALDI) and MALDI-post source decay (PSD) analyses of the monomer-rich DGE pitch cuts and GPC fractions were performed to determine the mol wts of the most prevalent monomer species, as well as the nature of the substituent groups present. High-performance liquid chromatography with photodiode array detection (HPLC/PDA) was used to determine the identities of the PAH backbone structures present in the monomer. The oligomeric fractions were subjected to MALDI, PSD, and UV-Vis absorption analyses in order to determine the molecular weight, extent of alkylation, and the nature of bonding between the monomeric units for the most prevalent species in the dimer, trimer, and tetramer cuts of M-50 pitch.

Experimental

Details concerning the preparation of the DGE pitch cuts (as well as a more detailed description of the procedures described in this section) are given elsewhere [6,7,8]. A Waters Alliance GPCV2000 high-temperature GPC model was adapted to perform prep-scale GPC fractionations on the DGE pitch cuts and the anthracene pitch at 140° C, with 1,2,4-trichlorobenzene as the mobile phase. We have previously put forth a detailed procedure describing the manner in which the GPC fractionation experiments took place, as well as the procedure used to identify, by HPLC/PDA, the molecular structures most prevalent in selected monomer fractions [6,7].

MALDI and PSD analyses were performed using a Bruker Daltonics Autoflex MALDI mass spectrometer equipped with a 337 nm nitrogen laser. The sample preparation procedure [2] and the operating parameters [8] for both techniques are described in detail elsewhere.

Results and Discussion

Molecular structures for four of the most prevalent monomer constituents are shown in Fig. 2. M-50 monomer is primarily composed of benzenoid PAHs – that is, those PAHs containing only 6-membered aromatic rings. MALDI analyses of M-50 dimer, trimer, and tetramer give the mol wts of the most prevalent M-50 oligomers; mol wt data for selected oligomers are given in Table 1. Results indicate that the molecular structures given in Fig. 1 can be used to "build" the most common oligomers by assuming that 4 hydrogen atoms are lost for each monomer-monomer linkage (that is, 4 H atoms are lost in the formation of the dimer, 8 for the trimer, and 12 for the tetramer). Therefore, there are two bonds between each monomer-monomer pair. UV-Vis analysis of narrow mol wt, GPC fractions of the oligomers indicate that these bonds are arranged such that a 5-membered ring is formed. The strongest peak in the MALDI spectrum for a narrow, dimer-rich fraction of M-50 pitch, occurring at m/z = 468 (see Fig. 3a), corresponds to a dimethylpyrene molecule (mol wt 230) linked to a methylchrysene molecule (mol wt 242). Because the UV-Vis absorption spectrum of this fraction (Fig. 3b, thick gray line) bears a much greater similarity to that of the non-alternant PAH 2.3-benzonaphtho-(2".3":11.12)-fluoranthene (BNF: Fig. 3b, thick black line) than it does to that of the fully alternant, benzenoid PAH 1.2,7.8-dibenzoperylene (DBP: Fig. 3b, thin black line), we conclude that M-50 dimer is composed primarily of monomer units joined such that a 5-membered ring forms in the linkage.

Table 1. Molecular Weights of Monomer Units Comprising Prevalent M-50 Pitch Oligomers.

Prevalent M-50 oligomers are comprised of monomers joined by 5-membered rings.					
Mol Wt of Monomer (g/mol)				H Atom	Mol Wt of Oligomer
1	2	3	4	Loss	Product (g/mol)
230.3	**242.4**	------	------	**4**	**468.7**
230.3	242.4	266.5	------	8	731.3
230.3	242.4	266.5	270.5	12	997.5
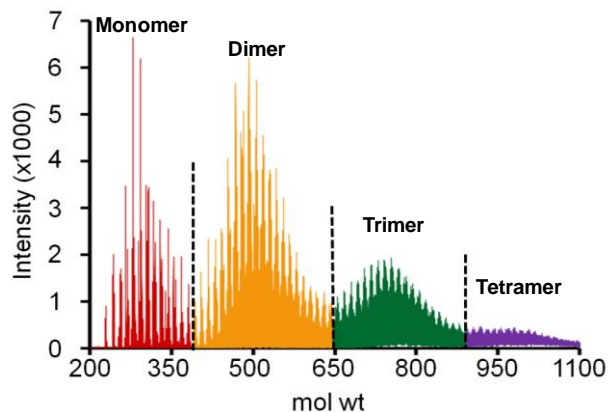
Figure 1. MALDI spectrum for M-50 pitch.

Dimethylpyrene
Mol Wt 230 Da

Methylchrysene
Mol Wt 242 Da

Methylbenzo[a]pyrene
Mol Wt 266 Da
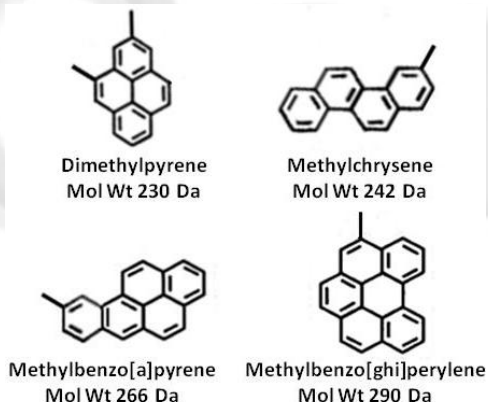
Methylbenzo[ghi]perylene
Mol Wt 290 Da

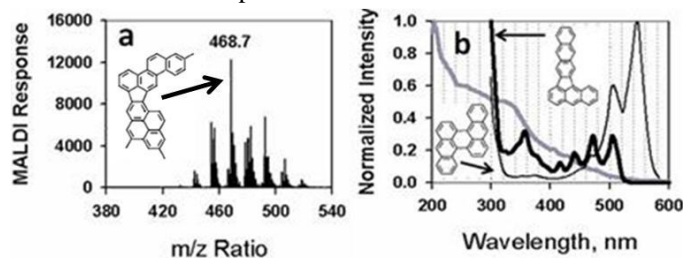**Figure 2.** Molecular structures for four of the most prevalent constituents of M-50 pitch.

Figure 3. MALDI spectrum for a GPC fraction rich in M-50 dimer (panel a). In panel b, the UV-Vis absorption spectrum for this fraction (thick gray line) has a greater similarity to the non-alternant BNF (thick black line) than to the benzenoid DBP (thin black line).

Conclusions

Application of a two-step fractionation method (DGE followed by prep-scale GPC) to carbonaceous pitches results in the production of narrow, oligomeric fractions. Subsequent analytical characterization of these fractions using MALDI, PSD, HPLC/PDA, and UV-Vis determined that M-50 monomer is primarily comprised of benzenoid species possessing varying degrees of alkyl (primarily methyl) substitution. Meanwhile, the monomers comprising the various oligomers are joined such that a 5-membered ring is formed in the linkage.

References
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