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THE PRESENCE OF OLIGOMERIC AROMATIC STRUCTURES IN POLYAROMATICS AND POLAR MATERIALS FROM COAL-DERIVED HEXANE SOLUBLES

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Polyaromatics and polar materials of coal-derived hexane soluble were separated according to molecular size. UV spectra combined with their mass spectra revealed that the high-molecular-weight fractions consist of oligomer structures such as small aromatic units joining by methylene bridges and/or biaryl bonds.

As far as pentane- or hexane-soluble portion of coal-derived liquid is concerned, its detailed structural study has been reported by many workers such as Stompel et al.,[1)] Jones et al.,[2)] and so on.[3,4)] In their studies many kinds of polycondensed aromatic compounds substituted by alkyl chains and mono-, di-, tri-, tetra-, and penta-cyclic alkanes were identified by gc-ms and field desorption mass spectrometry. However, there are few reports confirming the presence of unit aromatic structures linked by alkyl chains except the average molecular structural analysis[5)] suggesting a conceptual polymer structure based on the combination of NMR and IR spectra, elemental analysis and molecular weight measurements.[6)]

Erbatur et al.[7)] assumed the presence of polynuclear aromatic linked to others by direct C-C bonds in the chloroform-soluble material from the pyridine extract of the coking coal, basing on their ^{1}H and ^{13}C NMR spectra. Kuhlmann et al.[8)] assigned the chemical shift from δ 3.58 to 5.40 ppm to protons of methylene bridges and that of CH_2O between aromatic nuclei, based on changes of whose amounts, hydroliquefaction of coal was concluded to proceed by the cleavage of such a methylene group joining aromatic units. Regardless of these assumptions, there has not been any clear-cut evidence concerning about the presence of such oligomer structures above mentioned.

During the course of a structural study on polyaromatic and polar material fractions of coal-derived liquid, we have obtained very interesting results that high-molecular-weight fractions separated from gel permeation chromatography show only two max absorbances at around 215 and 265 nm in their UV spectra. This strongly suggests the existence of low degree of condensation of prevailing aromatic skeletons which, combined with their mass spectra, leads to the presence of oligomer-like structures.

Coal-derived hexane soluble was obtained by Soxhlet-extracting, with hexane, the resulting liquid and solid products from Hunter valley coal which was hydroliquefied at 400°C for 3 hrs in the presence of 5 wt% of $ZnCl_2$. The analyses of original coal and hexane solubles are as follows; original coal: moisture, 4.3%; volatile matter, 33.7%; ash, 7.5%; fixed carbon, 54.5%; C%, 80.1; H%, 5.5; N%, 2.2; O%, 12.2(d.a.f. base); hexane soluble(46.2% yield based on d.a.f. coal): C%, 88.4; H%, 8.9; N%, 1.1; O%, 1.6.

The hexane-soluble portion was separated into saturates, monoaromatics, diaromatics, polyaromatics, and polar materials according to the procedure of Sawatzky et al.,[9)] the analytical results of the last two portions being cited in Table 1. These two fractions were submitted to the separation by gel-permeation chromatography equipped with a series of two columns(Shodex AC-801 and AC-802).

Table 1 Analyses of fractions

	Ultimate analyses				Average M. W.
Fractions	C%	H%	N%	O%	
Polyaromatics	91.6	7.4	-	1.0	300
Polar materials	85.6	7.6	2.2	4.6	300

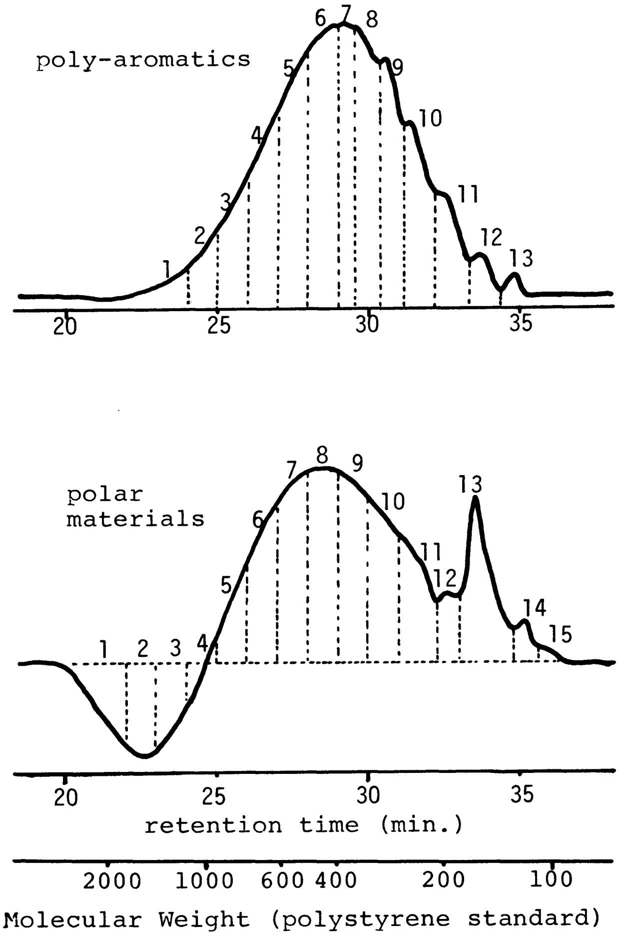

Figure 1 Gel-permeation chromatogram of poly-aromatics and polar materials

The instrument(Yanagimoto model L-2000) was operated at ambient temperature with $CHCl_3$ as the mobile phase. The flow rate was 1 ml/min. The sample in chloroform was injected into the g.p.c. through a millpore (0.5 μm) filter assembly. As for two fractions, the chromatograms are shown in Figure 1. The abscissa in Figure 1 is elution volume in ml. The molecular weight shown there is obtained using appropriate standards. The mass range of parent peaks confirmed that each fraction is clearly separated according to molecular size. A Hitachi RMU 6MG spectrometer was used for mass measurement at 20 eV.

As Shriner et al. stated in their publication,[10)] the ultra violet spectra are of great use as a diagnostic tool of degree of aromatic condensation. The UV spectrum of fraction(Figure 2 (a)) of polyaromatic fraction shows absorption at 200, 243, 275, 291, 337, 367, and 388 nm, in which the absorption at 243, 275, and 337 nm are characteristic for pyrene skeleton and the absorption at 367 and 388 nm for benz[a]pyrene skeleton. Z numbers obtained from the mass spectrum of this fraction are believed to be 22, 24, 28, and 30, being assigned to peri-condensed four rings, cata-annellated four rings,

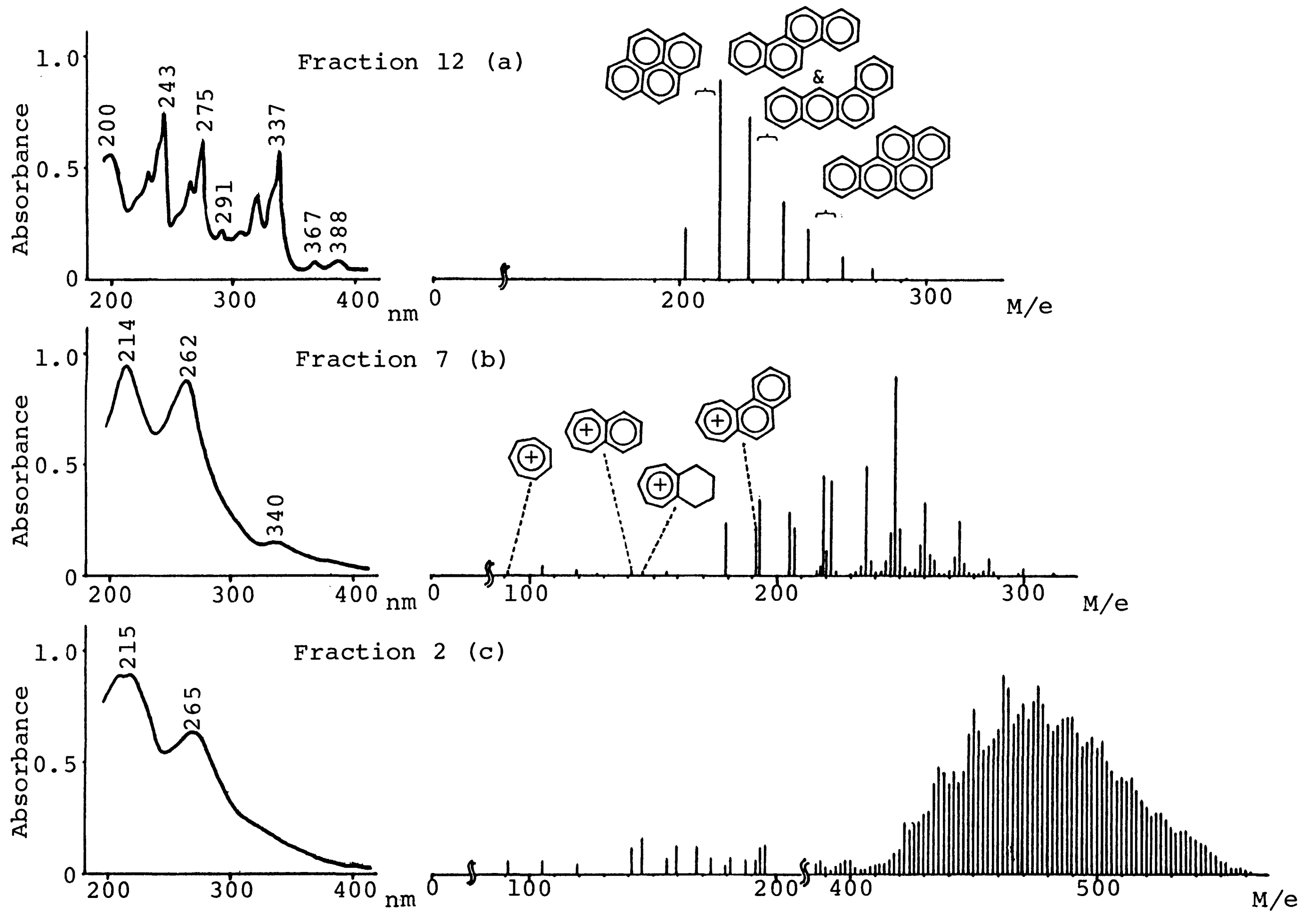

Figure 2 UV and Mass spectra of poly-aromatics separated by GPC

peri-condensed five rings and cata-annellated five rings, respectively. Tetraphene (the β-bands at 291 nm)- and/or chrysene(The β-bands might be superimposable with the β-bands at 265 and 275 nm of pyrene)-skeletons could be possible for cata-annellated four rings. From m/e values of parent peaks, the presence of pyrene, tetraphene and/or chrysene, and benz[a]pyrene and their methyl derivatives was confirmed.

The UV spectrum of fraction 7 shows two max absorbances at 214 and 262 nm with a small shoulder at 340 nm which could be assinged to pyrene skeleton. So the parent peaks of its mass spectrum observed at m/e 244, 258, 272 and 286 are indicative of the presence of C_3-, C_4-, C_5- and C_6- substituted pyrene in this fraction. The fragment peaks at m/e 91, 141, 145 and 191 could be assigned as tropylium ions of C_7H_7, $C_{11}H_9$, $C_{11}H_{13}$ and $C_{14}H_{11}$, this confirming that this fraction contains toluene, methylnaphthalene, methyltetrahydronaphthalene and methylanthracene(or methylphenanthrene). The mass spectra at 20 eV showed parent peaks from m/e 200 to m/e 350, z numbers being 18-28.

The UV spectrum of fraction 2 shows close similarity to that of fraction 7, in spite of its relatively larger molecular weight. Fraction 2 as well as fraction 7 are supposed to consist of a complicated mixture of aromatic hydrocarbons bearing different alkyl groups which tends to make its UV spectrum much simpler losing the fine structure characteristic of unit aromatic rings. The absorption at 215 nm could be attributed to the β-bands of alkyl-substituted naphthalene as well as p-bands of benzene derivatives and the one at 265 nm to absorption of red-sifted β-bands of three condensed aromatic rings overlapped with p-bands of naphthalene derivatives.[11) Parent peaks of its mass spectrum range from m/e 380 to 550, z number being 28 to 42. Hitherto high z numbers has been considered to be assignable to poly condensed aromatic nuclei such as benzpyrene(z number 28), coronene(36) and benzcoronene (42). However, this fraction contains one to three condensed aromatic skeletons judging from its UV spectrum. So these two fractions include oligomeric structure in which benzene, naphthalene and anthracene(phenanthrene) units join each other by methylene bridge and/or biaryl bonds.

As for polar material fractions similar conclusion could be drawn from their spectral results; fraction 13: UV spectrum; 204, 293 and 306 nm(max), and 220, 240, 260 and 280 nm(shoulder): parent ion peaks of mass; m/e 180-300, fragment ion peaks; m/e 107 and 121(very weak, assignable to hydroxy tropylium ion and methyl hydroxy tropylium ion); fraction 8: UV spectrum; 205 nm(max) and 280 nm(shoulder): parent ion peaks of mass; m/e 180-330, fragment ion peaks; m/e 107, 121 and 135(strong, assignable to hydroxy tropylium ion, methyl hydroxy tropylium ion and ethyl or dimethyl hydroxy tropylium ion); fraction 4:UV spectrum; 212 nm(max) and 280 nm (shoulder): parent ion peaks of mass; m/e 350-500, fragment ion peaks; m/e 107, 121 and 135(very strong).

In fraction 4 and 8, relatively intensive peaks were observed at m/e 107, 121 and 135, these being attributed to hydroxy tropylium ion, methyl hydroxy tropylium ion and ethyl or dimethyl hydroxy tropylium ion. Therefore polar materials of these fractions consist of compounds having oligomeric structures such as monoaromatic and diaromatic units substituted by hydroxy group joined each other by methylene bridges and/or biaryl bonds. The significance of ether bonds which act as connecting bonds of aromatic units is scarce because the measurement of hydroxy group shows that about 70% of oxygen exists as phenolic hydroxy group.

Structural studies on similar fraction obtained from Wandoan and Yallourn coal liquefaction are in progress.

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