

POLYSTYRENE AND POLY(VINYL NAPHTHALENE) OLIGOMERS
FOR MOLECULAR WEIGHT ANALYSIS OF COAL LIQUIDS

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INTRODUCTION

Knowledge of the structure of coal derived asphaltenes and preasphaltenes is of significant value because of the current interest in conversion of coals to liquid fuels and/or chemical feedstocks. Considerable effort has been devoted to analyses of the chemical composition and to the postulation of possible structures of these complex aromatic materials (1-3). Physical properties of coal derived liquids (CDL) such as viscosity, solubility, and melting points are to a large extent determined by chemical composition. Molecular size and the distribution of sizes of CDL are also of critical importance to the aforementioned properties. Snape and Bartle (4) have published a paper describing an empirical solubility parameter which relates the average molecular weight, the wt % acidic OH (a measure of polarity) and ratio of junction aromatic carbons to total carbon (a measure of π - π and dispersive interactions) to solubilities of CDL in pentane, benzene and pyridine.

The techniques most commonly used to measure average molecular weights are vapor pressure osmometry (VPO) and gel permeation chromatography (GPC). VPO yields only a number average molecular weight value (M_n) while GPC techniques can give both M_n and a weighted average molecular weight (M_w). Measurement of M_n and M_w by GPC techniques requires knowledge of the detector response on a per weight basis over the range of masses studied. A constant absorbance per gram of material would be most desirable if, for example, a UV detector is used. A second requirement, which is the focus of this report, is that suitable standards be available for the calibration of the GPC column. Mulligan et al. (5) showed that narrow polystyrene fractions ($M_w/M_n < 1.10$) and a series of polynuclear standards without highly condensed structures can be used to calibrate an analytical GPC column for use with the analysis of super-critical gas extracts of coal. It was concluded that the above standards gave reliable molecular weight values for coal derived mixtures containing cata condensed aromatics with alkyl or aryl-aryl linkages between aromatic systems.

Our study was initiated to determine what types of standards would be suitable for the GPC analysis of highly condensed peri aromatics that would result during coal liquefaction under SRL or donor solvent conditions. Analysis of highly condensed aromatic oligomers synthesized in this study indicates that these molecules are subject to retardation and considerable scatter on GPC columns relative to polystyrene standards. The retardation does not appear to be a function of absorption, but rather a length reduction of the oligomer due to aromatic condensation. The GPC response can be made linear by multiplication of the molecular weight by H_{ar}/C_{ar} (a measure of aromatic condensation). These size corrected molecular weights are linear with retention volume, but are not colinear with the retention volume of polystyrene or poly(vinyl naphthalene) (PVN) oligomers of narrow molecular ranges ($M_w/M_n < 1.1$). Coal derived liquids from SRC-I or SRC-II type processes have H_{ar}/C_{ar} values more like the highly condensed aromatics synthesized in our study. Narrow molecular weight fractions of these SRC materials are retarded relative to polystyrene and poly(vinyl naphthalene) standard responses. The response of SRC materials are colinear with the response of highly condensed aromatic standards when the "corrected molecular weight" is plotted versus retention volume.

EXPERIMENTAL

Materials

Polystyrene standard oligomers were obtained from Polysciences, Inc. Other standard compounds and poly(vinylnaphthalene) oligomers were synthesized from various starting materials. The details of these syntheses are described in previous reports (6). Poly(vinyl naphthalene) and polystyrene oligomers were synthesized by anionic polymerizations in diethyl ether initiated by *n*-butyllithium at a proper ratio of initiator to substrate to establish the polymer size. Solvent refined lignite (SRL) asphaltene and preasphaltene samples were obtained from the University of North Dakota Energy Research Center. The samples were produced using synthesis gas or hydrogen at 27.6 MPa and 460°C with or without recycle of the vacuum bottoms of the product. The lignite used was a North Dakota seam, Beulah three.

Preparative Scale GPC

Prior to GPC separation all the SRL samples were acetylated in order to convert the hydroxyl sites to their acetate forms. The SRL asphaltenes and preasphaltenes were further separated into narrow molecular weight fractions using a 50 mm id x 120 cm glass column packed with Bio-Beads S-X3 (200-400 mesh) styrene-divinyl benzene. Freshly distilled toluene or pyridine was used as the solvent. The polydispersive indices for the SRL fractions, M_w/M_n , were measured to be in the range 1.05 to 1.15 using the analytical chromatographic analyses described below. Polystyrene and poly(vinyl naphthalene) oligomers were also isolated into narrow molecular weight ranges using benzene as the solvent with S-X8 or S-X3 columns. Elemental analyses of the fractions were performed by Spang Microanalytical Laboratory and number average molecular weights were determined in our laboratory using a Wescan Model 117 Vapor Pressure Osmometer. In normal runs, 2-3 concentrations over the range 1 to 50 g/kg of pyridine were employed for extrapolation to infinite dilution.

Analytical Scale GPC

Analytical scale GPC analyses (HPLC) were carried out using three 10 nm and one 50 nm μ -styrigel columns in series, with THF (UV grade, Burdick and Jackson) as the mobile phase. A Laboratory Data Control Model 1205 UV Monitor was used as the detector (254 nm) and a Waters Model UK6 injector was used to inject samples of about 10 μ l at 10 mg/ml. Samples were filtered across a 0.5 μ m millipore filter prior to injection. The flow rate was usually maintained at 1.0 mL/min to prevent pressures in excess of 1000 psig.

RESULTS AND DISCUSSION

The influence of aromatic ring condensation is illustrated in Figure 1a for plots of logarithm MW versus length of model compounds and polystyrene. The model compounds consist of aromatics from benzene to pyrene with methylene, ether or aryl-aryl linkages. The length was estimated using Dreiding stereomodels assuming the oligomers are fully extended in the THF solvent used in the GPC experiments. The corrective nature of the $H_{\text{aru}}/C_{\text{ar}}$ (fraction of edge aromatic carbons) is shown in Figure 1b. The slope changes from 0.024 ± 0.003 in Figure 1a to 0.026 ± 0.0015 in Figure 1b. Polystyrene, which is a different shaped polymer with benzene pendant groups follows its own linear plot (slope = 0.015 ± 0.0035). Figure 2a illustrates the log MW versus retention volume for both polystyrene and the model compounds. Note the highly condensed model compounds lie above the polystyrene line, which is consistent with a reduced volume or length per molecule. The inclusion of the $H_{\text{aru}}/C_{\text{ar}}$ term with MW greatly reduces the scatter of the models. The slope changes from -0.049 ± 0.008 in Figure 2a to -0.058 ± 0.004 in Figure 2b. The uncertainties reported are at the 90% confidence levels. The uncertainty of the models are reduced by 50% by use of the factor $H_{\text{aru}}/C_{\text{ar}}$.

That SRL narrow molecular weight fractions tend to elute at longer times relative to polystyrene is illustrated in Figure 3a. This retardation would be consistent with these SRL samples being so condensed that the length of the molecules has been shortened relative to the polystyrene standards. The application of H_{aru}/C_{ar} to the MW term drops the SRL compounds below the polystyrene line as shown in Figure 3. However, the scatter is improved with SRL slopes of -0.067 ± 0.005 in Figure 3a to -0.061 ± 0.003 in Figure 3b. The uncertainty is reduced because the highest and lowest MW fractions are the most condensed for these SRL samples. Mulligan et al. (5) reported that polystyrene and not highly condensed aromatic model compounds could be used to calibrate GPC columns for super-critical gas (SCG) extracts of coal. The aromatic portions of SCG extracts would not be nearly as condensed as the recycle SRL samples used in our work.

Two additional types of oligomers are being synthesized and studied. First, poly(vinyl naphthalene) and poly(vinyl phenanthrene) oligomers from 300 to 3000 g/mole are being prepared to test the significance of the length factor. The length of these oligomers is predominantly determined by the alkyl chain, as with polystyrene. A second set of oligomers of polynuclear aromatic moieties connected by aryl-aryl, methylene and ether linkages in the range 600 to 3000 g/mole are being synthesized to extend the range of the highly condensed oligomers.

Four poly(vinyl naphthalene) oligomers from 300 to 2000 g/mol when plotted on Figure 2a fall on the same line as polystyrene. Poly(vinyl naphthalene) oligomers are shorter molecules with less molar volume than a polystyrene oligomer of similar molecular weight. Thus, one would predict that poly(vinyl naphthalene) should elute at longer retention times relative to polystyrene, contrary to the observed results. The data suggest that the PVN oligomers are associated with more THF molecules than are the polystyrene oligomers, giving a larger volume (or length) to the PVN materials or that neither oligomer is fully extended in the THF solvent. Further studies will be carried out to test these hypotheses.

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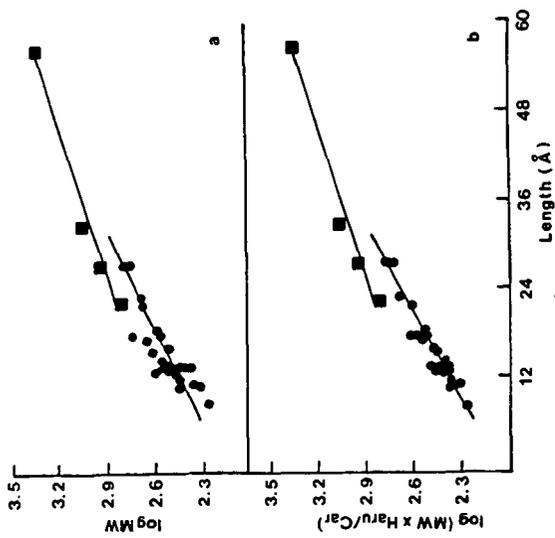


Figure 1. Molecular Weight versus Length.
 Polystyrene (■) Model Compounds (○)

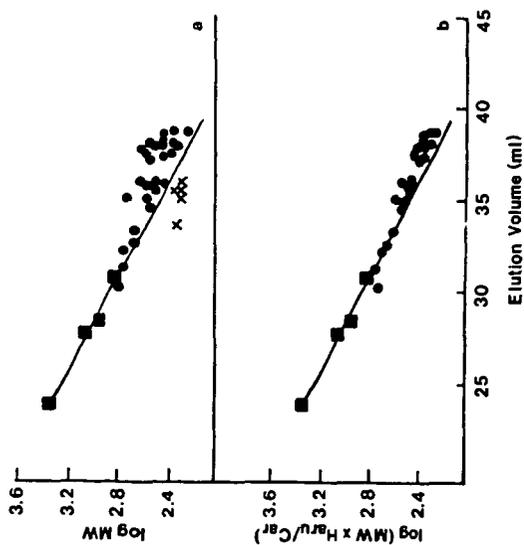


Figure 2. Molecular Weight and Elution Volume Response.
 Polystyrene (■) Model Compounds (○)

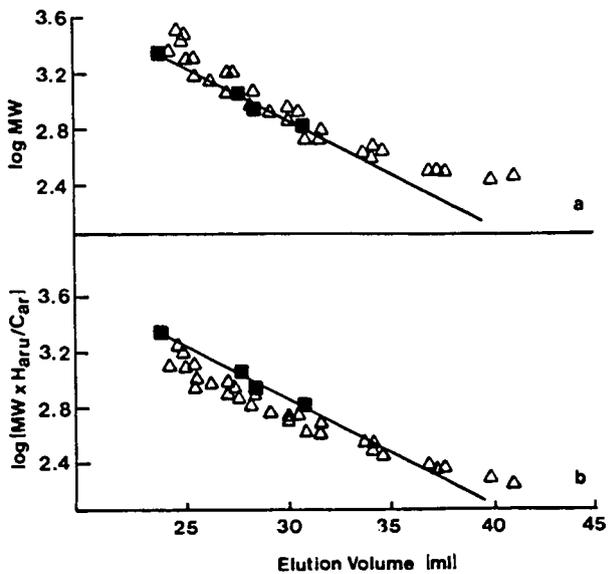


Figure 3. SRL Response.
 Polystyrene (■) SRL (△)