

MOLECULAR WEIGHTS OF LIGNITE MACROMOLECULES

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Introduction

A knowledge of how to determine molecular weights and molecular weight distributions of coal macromolecules has been a long-standing goal of coal scientists (1). A fundamental understanding of the chemical and physical units in coals requires a knowledge of the population of various sizes of molecular entities in the coal. Information on the molecular weight distribution of coal macromolecules can aid in understanding the behavior of the macromolecules in various chemical and physical processes. In the high temperature processes such as liquefaction and pyrolysis, many bonds in the coal are broken and relatively small molecular weight material is obtained. These products have been extensively studied and are not the concern of this paper.

The goal of our research is to apply reliable and accurate polymer characterization methods to the high molecular weight macromolecules of the lignite. We have utilized low-angle laser light scattering (LALLS) photometry in a static mode and also coupled with size exclusion chromatography (SEC) for the determination of weight average molecular weights and molecular weight distributions. Polymers can be separated on the basis of size by SEC, thus providing information about molecular weight distributions; however, molecular weight values depend on calibration data which are subject to large errors (2). These errors result from the lack of similarity between the shapes and polarities of the calibration standards and the materials whose molecular weights are to be determined. Since light scattering techniques give absolute molecular weight values, a LALLS photometer was used as an on-line detector in an SEC system and no error prone calibrations of the size exclusion column were necessary. A refractive index (RI) detector was used in series with the LALLS flow cell to provide concentrations of the eluting solute.

Measurement of the molecular weights of the coal macromolecules of course requires that they be solubilized. Our initial studies (3) were carried out with humic acids from a North Dakota lignite (Beulah-Zap seam), mainly because the humic acids are conveniently obtained by extraction with base at ambient temperatures. Thermal cleavage reactions which could have extensively degraded or depolymerized the coal macromolecules would not have occurred under these conditions, although base initiated depolymerizations may have occurred.

In order to observe the scattering and interpret the results without complications, it is important that the optical absorbance of the macromolecules at the laser wavelength of 633 nm be negligible. Obviously coal-derived macromolecules must be decolorized and considerable effort was expended in finding the best way to reduce the molar absorptivity of the humic acids. The most successful method was found to be reduction of the exhaustively methylated humic acid with zinc dust in acetic anhydride (3). The resulting light powder was soluble in THF and exhibited satisfactory chromatographic profiles in the SEC, indicating that significant adsorption of the material to the SEC column was not a problem.

Results and Discussion

Having reduced the molar absorptivity of the methyl humates, we were able to determine Rayleigh factors for solutions in THF using the static LALLS cell. A linear dependence of Kc/R_{90} with c was obtained ($r^2 = 0.99$) (Figure 1). Thus the weight average molecular weight could be obtained from the intercept (1.3×10^6) (Table 1). These data contrast significantly with those of Hombach (4) where a nonlinear scattering plot was obtained. In that case, it was necessary to introduce a modification to the virial equation so that the non-linear curve could be resolved into a linear and an exponential component. A theoretical justification for the modification was not presented. Our data required no such manipulation, which would have made calculations of molecular weight distributions from the flow cell interfaced with the SEC system more complex. Furthermore the reduction eliminates the fluorescence which would cause an additional complication in determining the molecular weight from scattering plots (5).

Table 1. Molecular weights for humic acid and oxidized lignite derivatives

	Reduced methyl humate	Reduced oxidation product
<u>Static LALLS:</u>		
M_w	1.3×10^6	1.3×10^6
dn/dc	0.22	0.18
A_2	-4.2×10^{-5}	-3.6×10^{-5}
<u>SEC-LALLS:</u>		
M_n	9.7×10^5	6.6×10^5
M_w	1.4×10^6	7.8×10^5
M_z	1.8×10^6	9.1×10^5
$M_z:M_w:M_n$	1.9:1.3:1	1.4:1.1:1

A solution of the reductively acetylated methyl humate in THF was characterized in the SEC-LALLS-RI system. The LALLS chromatogram exhibited a single symmetrical curve whereas the corresponding RI chromatogram was nearly symmetrical (Figure 2). Values for the number average, weight average, and z average molecular weights were calculated from the LALLS and RI data ($M_n = 9.7 \times 10^5$, $M_w = 1.4 \times 10^6$, $M_z = 1.8 \times 10^6$) with polydispersity ratios of $M_z : M_w : M_n = 1.9 : 1.3 : 1$.

Thus the humic acid extracted from lignite with base is a large macromolecule; the relationship between the molecular weight of this material and that of the macromolecules which comprise the major humin portion of the coal must next be established. Although increased yields of humic acids can be obtained by more severe treatments with base (higher temperatures or ultrasonication), the issue of thermal degradation reactions of the macromolecules cannot be neglected in materials obtained from lignite under these conditions. Instead a mild oxidative reaction was chosen to obtain soluble material from the lignite. This oxidation was carried out with 4-nitroperbenzoic acid, a reagent which was recently reported to be effective for the cleavage of benzyl ethers (6). Benzyl ether linkages occur in the lignin

structure between the coniferyl groups and have been suspected to be present in coals as linkages between aryl groups (perhaps largely between coniferyl-derived groups or conjugates thereof). Treatment of the Beulah lignite with 4-nitroperbenzoic acid in refluxing chloroform gave only a small amount of material soluble in organic solvents; this material was similar in composition to the waxy material normally extracted from lignites with organic solvents. After removal of 4-nitrobenzoic acid and 4-nitroperbenzoic acid with hot methanol, the residue was extracted with base to give large amounts of humic acids in yields up to 90 % (on a maf basis). Thus the reagent was presumed to have converted the major portion of the lignite humin to a base-soluble form by cleavage of sufficient number of cross-linking groups of the benzyl ether or some other oxidatively labile type to give carboxylic acid and phenolic groups. The reaction rates and yields varied considerably depending on the particle size and length of sample storage; these oxidation studies are still under investigation. Oxidations of model compounds indicate that carbon bridges between aryl groups (such as in diphenylmethane) are not cleaved by this reagent. However polynuclear aromatic systems (such as in phenanthrene and anthracene) may be oxidized to quinones or other products.

A sample of the base-extractable product from the 4-nitroperbenzoic acid oxidation of lignite was converted to the methylated derivative with dimethyl sulfate followed by diazomethane in DMF-ether, and was reductively acetylated with zinc dust in acetic anhydride as in the humic acid derivatization above. A light tan THF-soluble material was obtained. The molecular weight was determined in the static LALLS cell in THF solution. A linear relationship was obtained in the Kc/R_{90} versus c plot ($r^2 = 0.95$) (Figure 3). The molecular weight obtained for the derivative of the oxidation product (1.3×10^6) was the same as the value obtained for the humic acid derivative.

The reductively acetylated oxidation product was also examined with the SEC-LALLS-RI system. A symmetrical peak was observed for the LALLS response, and a non-symmetrical peak for the RI response (Figure 4). Somewhat lower values for the number average, weight average and z average molecular weights were calculated from these data ($M_n = 6.5 \times 10^5$, $M_w = 7.8 \times 10^5$, $M_z = 9.1 \times 10^5$).

These data indicate that by oxidatively cleaving the benzyl ether groups with the peracid, a substantial macromolecule is produced which is comparable in size to that obtained by simple base extraction of the lignite. This implies that there is some basic unit of this molecular weight making up the coal structure, and that in base extraction some of these units are released, whereas in peracid oxidation a large number of them are released by scission of cross-linking bonds.

Experimental

Humic acids were isolated from lignite from the Beulah mine in Mercer Co. ND (Beulah-Zap seam, Sentinel Butte formation, Fort Union Region) and methylated with dimethyl sulfate followed by diazomethane as described in reference 3. The methyl humate was reduced with zinc dust in acetic anhydride.

Oxidation of the lignite was carried out by refluxing 11 g of Beulah lignite with 12.4 g of 4-nitroperbenzoic acid in 150 ml of chloroform for 20 hours. The mixture was filtered while hot and the residue was extracted with hot methanol to remove the 4-nitrobenzoic acid. A 3.8 g portion of the residue was extracted with NaOH solution and the resulting solution was treated with dimethyl sulfate as in the preparation of methyl humates. The methylated product was acidified with HCl, centrifuged, and dried to give a 1.75 g yield of methylated oxidation product. This material was treated with diazomethane in DMF-ether followed by zinc dust in acetic anhydride to give 0.70 g of reductively acetylated methylated product.

Rayleigh scattering was measured with a KMX-6 LALLS photometer in THF solution. The dn/dc values were determined using a KMX-16 differential laser refractometer at several concentrations in THF solution. The size exclusion chromatography was carried out with a 30 cm by 7.5 mm 105 A PLgel column in THF at a sample concentration of 2 mg/ml. The KMX-6 LALLS photometer with a flow-through

cell and a Model 401 RI detector were used for measurement of the Rayleigh scattering and RI response of the effluent from the SEC column. Data were acquired at 3.5 points/sec for each detector. The LALLS and RI peaks were divided into 100 area slices each for calculation of the molecular weights.

References

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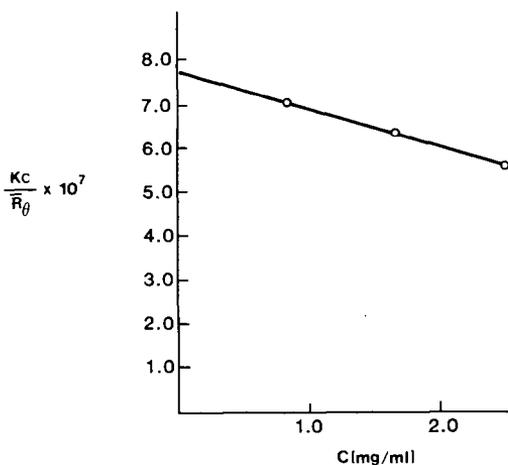


FIG. 1. Kc/\bar{R}_θ versus c plot for reduced methyl humate.

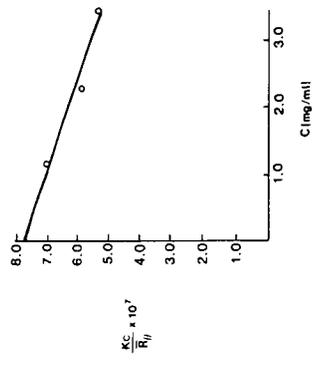


FIG. 3. Kc/\bar{R}_g versus c plot for reduced lignite oxidation product.

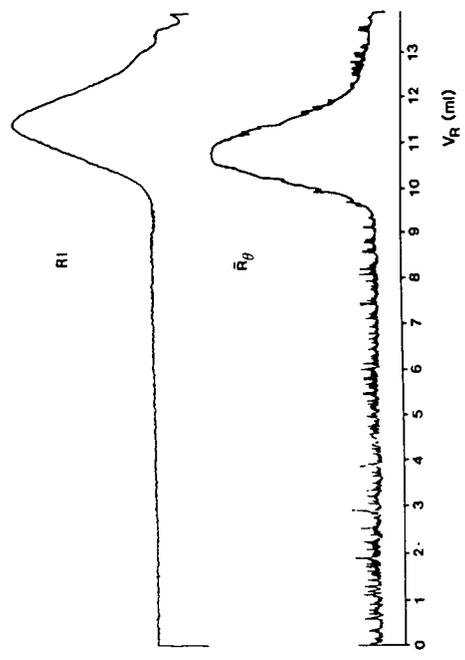


FIG. 2. SEC-LALLS of reduced methyl humate.

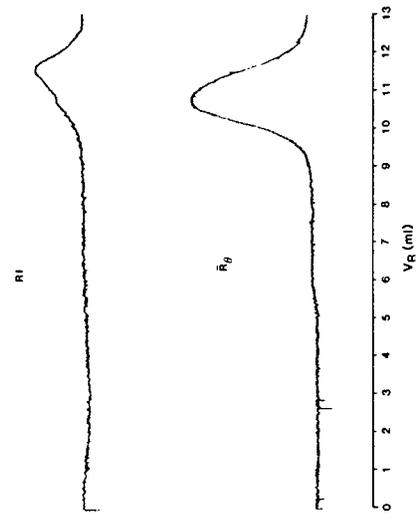


FIG. 4. SEC-LALLS of reduced lignite oxidation product.