

PHENOLIC RESINS AS MODELS FOR THE STRUCTURE OF COAL

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INTRODUCTION

For many years the "standard model" for coal structure has essentially considered most coals to consist of covalently cross-linked networks with a cross-link density and sol fraction that varies systematically with rank (this model excludes arthracites and other high rank coals that are more graphitic in their structure). It has also been proposed that certain types of secondary forces, such as hydrogen bonds or charge-transfer complexes, can act as cross-links, although with respect to hydrogen bonds we disagree with this viewpoint (1). There is also an alternative model, proposed a few years ago, that places even more weight on the role of non-covalent interactions, proposing that most coals are associated structures held together by these secondary interactions acting in some undefined co-operative manner (2-6). These different views of coal structure remain to be resolved.

One of the problems with characterizing coal, particularly the nature of its network structure, is that crucial parameters such as the cross-link density can only be measured indirectly by techniques such as swelling and by recourse to a theoretical model. The most widely used model has been that originally proposed by Flory and Rehner, modified in various ways by different workers over the years to account for the specific character of coal (a high cross-link density, hence "short" chains between cross-linked points, and the presence of strong specific interactions such as hydrogen bonds, see reference 7 and citations therein). What is clearly needed is a model, highly cross-linked system where the cross-link density is known or can be measured directly, thus allowing an experimental test of the validity of various approaches. Here we will propose the use of phenolic resins and present preliminary results that demonstrates the close resemblance of the properties of these materials to coal.

RESULTS

The nature of phenolic resins

Ordinary phenol/formaldehyde resins were the first true synthetic polymers produced commercially (as opposed to chemically modified natural polymers) and were called Bakelite. Depending upon reaction conditions either novolak or resol resins can be produced, the former essentially consists of branched oligomers of phenol units, linked by methylene bridges at their ortho and meta (to the hydroxyl group) positions, as illustrated in figure 1. These materials are not cross-linked, in the sense of forming a densely interconnected network of units through covalent linkages. Resols, on the other hand, form methylol (CH_2OH) groups and their synthesis does lead to a densely cross-linked network, as illustrated in figure 2.

At least superficially one recognizes an immediate correspondence to the "standard model" structure of coal; aromatic clusters linked by methylene and some ether units. Coal, of course is far more heterogeneous, containing larger aromatic units, many of which are heterocyclic, and these are presumably linked

by a broader range of "bridge types" (e.g. ethylene). This is reflected in the infrared spectrum, as can be seen in figure 3, where the spectrum of a simple phenol formaldehyde resol is compared to that of a randomly chosen coal. The bands present in the coal spectrum are generally broader, the aromatic "ring-breathing" mode in the resol near 1600 cm^{-1} is much weaker, as is the aliphatic stretching modes near 2900 cm^{-1} . Methylene bridges between aromatic units clearly absorb very weakly (but it is well known that the absorption coefficient for CH_2 stretching increases as CH_2 units are linked to form longer aliphatic chains). However, the situation becomes much more interesting if we increase the level of complexity of the system just slightly.

Figure 4 compares the spectrum of a phenol/dihydroxynaphthalene/formaldehyde copolymer (50:50, meaning 50% phenol and 50% dihydroxynaphthalene) to that of a coal. Because of the multiplicity of linkage sites on the naphthalene ring, we produce an apparently densely cross-linked network even under conditions used to synthesize novolaks based on phenol alone. The infrared spectrum of this resin is now strikingly similar to that of the coal, the principal differences being in the aliphatic CH stretching region (the bands in the synthetic resin are much weaker) and the C-O stretching region ($1200\text{-}1300\text{ cm}^{-1}$) where the resin absorbs more strongly than coal because of its higher OH content. The spectra can be made even more similar by chemical "tinkering". For example, if we copolymerize with p-cresol instead of phenol, bands in the CH stretching region become more prominent, and so on. However, space does not permit us to explore this here. Next we will briefly describe our synthetic procedure, which we used to produce a range of copolymers, then briefly summarize the results of solvent swelling and extraction experiments, which again bear a striking resemblance to those obtained from coal.

Synthesis

Appropriate quantities of phenol, 1,5-dihydroxynaphthalene and oxalic acid were first dissolved in water. The mixture was then stirred and preheated at 65°C for 30 minutes. Formaldehyde was then added and the mixture was refluxed at 100°C for 2-3 hours. As the polymerization proceeded the solution or suspension gradually changed color. Finally, water was then removed by heating under vacuum at a temperature of 200°C . The resulting resin is a black solid copolymer, only partially soluble in solvents such as pyridine, THF and NMP.

The samples were characterized by ^{13}C nmr, FTIR and pyrolysis GC/MS. The latter results were particularly interesting because we have always been concerned that reactions leading to larger aromatic clusters could occur when this technique is applied to coal. We had no evidence for this in our studies of the synthetic resins. The details of this characterization work will be presented in a separate publication.

Extraction and Swelling Experiments

Extraction and swelling experiments were performed on the resins using the usual techniques applied to coal. In these initial experiments the solvent used was pyridine. Swelling experiments (measured on ground particles placed in a graduated cylinder) were performed on the extracted material. The results are presented in Table I.

It can be seen that an ordinary resol has 32% pyridine soluble material and swells to approximately twice its original dimensions in pyridine, very similar to results obtained with coals like Illinois #6. Copolymers synthesized with dihydroxynaphthalene units behave similarly at low concentrations of this co-

Substituting p-cresol, which can only polymerize in a linear, non-branched fashion, for phenol, restores much of the extractability.

CONCLUSIONS AND RAMIFICATIONS

We have synthesized resins that mimic the spectroscopic, swelling and solubility characteristics of coal. The crucial point is that we start with a knowledge of the structure of these materials and whether or not they are covalently cross-linked. We are comparing the behavior of these materials in various solvents as a means to determine the role that association through secondary forces plays in swelling and solubility. Although the cross-link density of these resols is not known (but could possibly be estimated by the pattern of linkages revealed by the aromatic CH out-of-plane bending modes in the IR spectrum), it is a relatively easy task to chemically cross-link initially oligomeric novolaks with labeled compound and measure this parameter directly. We believe this approach will prove valuable in sorting out various models of coal structure and the role of secondary interactions such as hydrogen bonds.

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REFERENCES

1. Painter, P.C. *Energy and Fuels*, 1996, **10**, 1273.
2. Nishioka, M., Gebhard, L.A. and Silbernagel, B.G. *Fuel*, 1991, **70**, 341.
3. Nishioka, M. *Fuel*, 1991, **70**, 1413.
4. Nishioka, M. *Fuel*, 1992, **71**, 941.
5. Nishioka, M. *Energy and Fuels*, 1991, **5**, 487.
6. Takanohashi, T., Iino, M. and Nishioka, M. *Energy and Fuels*, 1995, **9**, 788.
7. Veytsman, B. and Painter, P.C. *Energy and Fuels*, 1997, **11**, 1250.

Table 1

Sample	Extraction Yield in Pyridine %	Swelling Ratio
Resol (phenol formaldehyde)	32%	2.06
PDHNF20	42%	2.01
PDHNF30	12%	
PDHNF40	6%	
PDHNF50	6%	1.74
PCDHNF50	35%	
PDHNFx	= Phenol-co-dihydroxynaphthalene/formaldehyde copolymer with x wt% of dihydroxynaphthalene.	
PCDHNFx	= p-cresol-co-dihydroxynaphthalene/formaldehyde copolymer	

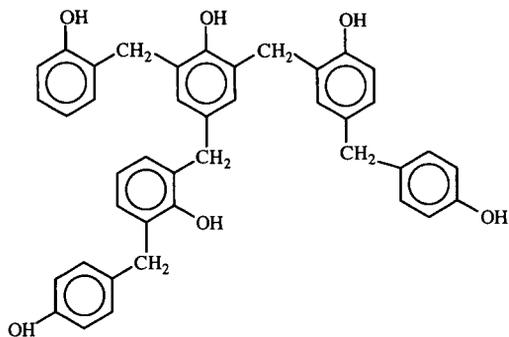


Figure 1. Typical oligomeric structure found in a novolac resin.

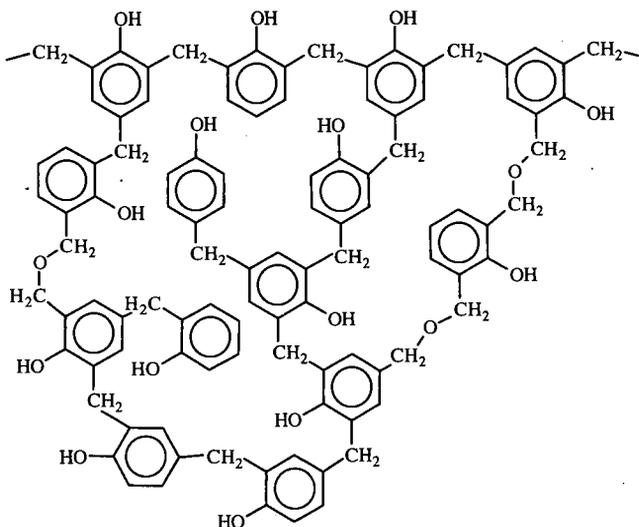


Figure 2. Schematic representation of part of the structure of a cured phenolic resin.

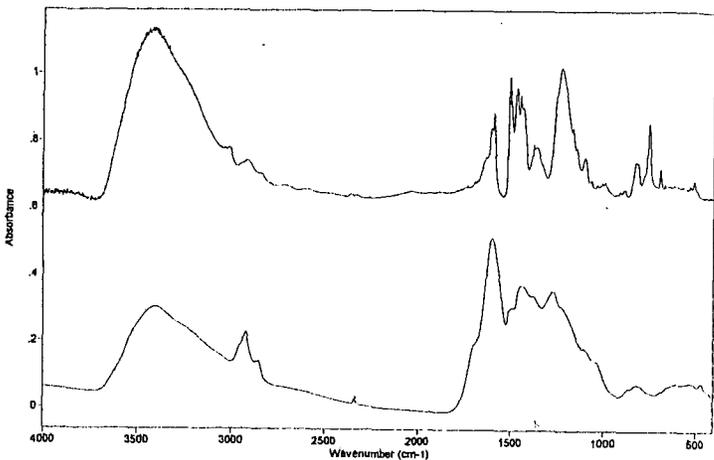


Figure 3. Comparison of the infrared spectrum of a cured resol (phenol-formaldehyde to a coal (PSOC 1423 P, 70% C)

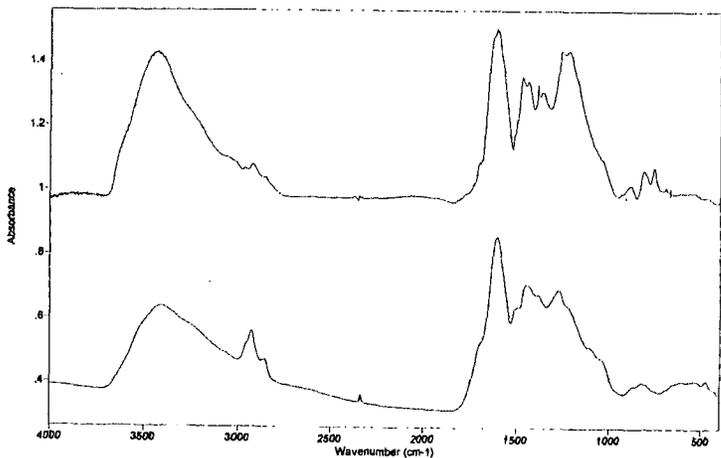


Figure 4. Comparison of the infrared spectrum of a cured phenol-co-dihydroxynaphthalene (50%) formaldehyde copolymer to that of a coal (PSOC 1423 P, 70% C)