HYDROGEN BONDING AND COAL STRUCTURE

P. C. Painter, J. Nowak, M. Sobkowiak and J. Youtcheff

Polymer Science Program
Penn State University
University Park, PA 16802

Introduction

There is now a wealth of literature that discusses coal structure in terms of the concepts of polymer science (1-7). Coal is considered to be a macromolecular network with a degree of cross-linking and a sol/gel ratio (soluble extract/insoluble network) that varies with rank. Although we consider the central premise of this approach intuitively pleasing, we believe there are a number of major problems with the applications of specific theories, notably those that involve the assumption of Gaussian chains and the use of the Flory-Huggins equation to calculate molecular weights from mechanical and swelling measurements. In addition, during the last ten years there has been a revolution in polymer theory based predominantly on the work of the French schools and summarized in de Gennes book (8). In many areas this supplements rather than replaces the classic approach of Flory (9), but recent work on swollen polymer gels by Candau and co-workers (10,11) clearly demonstrates that measurements on the swelling of coal have to be considered in a totally different fashion.

In this communication we will attempt to critically assess these factors. In particular, we will point out the key role played by hydrogen bonding in coal structure and how the presence of such strong, directional interactions does not permit the use of Flory-Huggins solution theory. We will then discuss aspects of various new theoretical approaches that hold promise for describing the structure of coal.

Hydrogen bonding and the macromolecular structure of coal

At the last ACS meeting we discussed various aspects of hydrogen bonding in coal and presented FTIR results that demonstrated that the predominant species present involved various chains and/or cyclic complexes of phenolic OH groups, typical examples of which are illustrated in figures 1 and 2. There are certainly some hydroxyl/ether and hydroxyl/pyridine-type base hydrogen bonds as well, but in most coals these do not seem to be the principle species present. We will not reproduce the experimental evidence, as this will be presented in a special issue of Fuel (12). As far as the arguments we wish to make here are concerned, the precise nature of the hydrogen bonded complexes are not important. Just the fact that hydrogen bonds are present in significant concentrations has a profound influence on the behavior of a polymer material and what theoretical tools can be successfully applied to a description of structure.

The molecular weight or chain length between cross-link points (M_c) is a key parameter in describing polymer networks. Theoretical descriptions of

these materials are of necessity based on a number of simplifying assumptions. The most critical of these are that the chain statistics are Gaussian, all the chain ends are joined to the network, entanglements can be neglected and deformations are affine (the displacements of the cross link points are linear in strain). In testing the predictions of theory it has proved necessary to put together (with some very clever polymer chemistry) networks with precisely defined structures. Monodisperse chains are synthesized and linked through their ends in solution. This minimizes entanglements and provides a prior knowledge of the quantity of interest, M_c. Even so, the effect of "dangling ends", those chains with only one end joined to the network, can be important (10,11). Clearly, in coal the situation is far worse. The chain segments between cross link points are probably too short and too stiff to be anywhere near Gaussian and it would be extraordinary if dangling ends were not present. If this were not bad enough, some measurements have been made on solvent swollen samples. Here, even if the chains were long and flexible enough to be considered Gaussian, the distance between cross links no longer scales as $N^{0.5}$ (where N is the number of "repeat units"). Instead, excluded volume effects become important and M_c scales as $N^{0.6}$ (8,10). Of course, there have been various modifications of rubber elasticity theory to account for some of these factors, but the virtue of simplicity is lost and the equations incorporate additional parameters that have to be fitted to the data.

Although these problems are considerable, and have been clearly recognized by a number of workers that have attempted to apply rubber elasticity theory to coal, if all that we required was a very rough "ballpark" estimate of M_c, it might be possible to live with these limitations. There are two additional factors that have to be considered, however, and they are so crucial that they make estimates of molecular weight presented in the literature essentially meaningless. The second of these will be considered in a separate section. The first is the use of Flory-Huggins theory to describe polymer solvent interactions. This theory provides beautiful insight into the major factors that affect solubility, but in terms of predictive calculations it has two major defects, well-recognized in the polymer literature, but largely ignored when this equation is applied to coal. The first problem involves free volume effects. These have been accounted for, most notably in the equations of state approach (13) and we presume that a modified or approximate treatment could be applied to coal. This is not the principle concern at this stage of our research program, however. We are much more interested in the second "defect" of Flory Huggins theory when applied to coal, the use of the χ interaction parameter.

Flory-Huggins theory is basically an extension of regular solution theory. Two terms are considered, a combinatorial entropy expression and a van Laar type exchange interaction term that has the form $\phi_1 \phi_2 \chi$, where χ is the exchange energy and ϕ_1 ϕ_2 are the volume fractions of solvent and polymer in the mixture. The product $\phi_1\phi_2$ represents the probability of contact between polymer segments and solvent molecules and implicitly assumes random mixing. The χ term for hydrocarbons is derived by assuming weak London dispersion forces and in the original formulation is always positive (actually $\geqslant 0$). Hydrogen bonding cannot be accounted for in this scheme. Secondary forces that are strong, specific and directional will result in a number of 1:2 contacts that exceeds that due to random mixing by an amount that will depend upon the energy of the interaction. Furthermore, the formation of hydrogen bonds results in a change of entropy as well as enthalpy (that is, an additional

entropy term to that describing combinatorial mixing). As Prigogine (14) has pointed out, there is no satisfactory theory of strong interactions, principally because the rotational partition function is not independent of the translational partition function. It is possible to use an equilibrium scheme to describe these systems, however, and we have recently adapted treatments used to describe the behavior of alcohols in hydrocarbon solvents. This is described in detail elsewhere (15), but the key point as far as this discussion is concerned is that the Flory-Huggins equation is modified by the addition of a term ΔG_H, which describes the change in the free energy due to the change in the pattern of hydrogen bonding when a material that self associated (eg. coal, through OH groups) is mixed with a species that competes with these hydrogen bonds. The equations are obtained in a conceptually simple fashion, but the algebra necessary to describe and explain the result is too lengthy to reproduce in this short preprint. The key point is that we obtain an expression for ΔG_H^M that consists of parameters that are experimentally determinable (most significantly, the fraction of OH groups that are <u>not</u> hydrogen bonded, measured by FTIR). We will discuss the application of this approach more completely in a future publication. The central point we are making is that hydrogen bonds do not permit the use of conventional solution theory and a new approach is required.

Before proceeding to a discussion of the second factor that obviates the use of traditional polymer theory for determining coal molecular weights, it is important to consider one or two additional factors associated with hydrogen bonding in coal. First, in many studies the degree of swelling of coal samples is plotted as a function of solvent solubility parameter values. Two maxima were observed in one recent study (17) and these were separately assigned to the solvation of the macromolecular network by a solvent with a solubility parameter similar to the coal, while the second was assigned to the breaking of hydrogen bonds. This interpretation is just plain wrong. Solubility parameters are related to the Flory χ parameter and are simply a different formulation of a van Laar type interaction term. Plotting data for hydrogen bonding materials as a function of such parameters is meaningless for the reasons given above. A double maximum was observed because THF and pyridine both contain hydrogen bond "acceptor" groups (atoms with a lone pair of electrons) and so will both hydrogen bond to coal phenolic OH groups. However, they have very different "solubility parameters" and so are separated in this dimension by non-hydrogen bonding solvents. The double maxima are simply an artifact of this condition. If, instead, we could plot swelling against the strength of competing hydrogen bond formation (coal/solvent vs coal self-association), then a much more credible plot would be obtained. Szeliga and Marzec (17) produced one such plot using the donor number-acceptor number approach of Gutmann (18). The physical meaning of these numbers is obscure, however. In order to illustrate our point we therefore plot swelling measurements reported in the literature against the strength of the hydrogen bonds formed between the solvents in question and phenolic OH groups, which can conveniently be measured by shifts in OH stretching modes (12). There is a straightforward correlation and no double maxima (see Figure 3).

Finally, the presence of hydrogen bonds has an extremely important but largely ignored effect on the determination of the molecular weight of soluble coal derived liquids. These will hydrogen bond to form multi-molecular complexes. The size of these aggregates will depend upon the hydrogen bonding capacity of the solvent. Because this is an equilibrium process, however, it

is easy to show that there will always be aggregates present (15), even in extremely dilute solutions of hydrogen bonding solvents. Discounting other problems associated with molecular weight measurements, this alone brings into question the reliability of most published values.

Desinterspersion

The final "problem" in using the concepts of polymer science that we wish to discuss is a phenomenon called desinterspersion by Candau et al. (10,11). This concept arose from observations made in neutron scattering studies of model polymer networks. LITTLE or NO CHAIN EXTENSION WAS OBSERVED IN SWOLLEN POLYMER NETWORKS, relative to the unswollen state. Following Flory (13), it was then noted that this effect is not topologically forbidden. A distinction can be made between topological neighbors (crosslink points connected by the same chain in the network) and spatial neighbors, connected by longer network pathlengths, as illustrated schematically in Figure 4. Desinterspersion is then an accordionlike unfolding of to give the type of swollen structure shown in Figure 5. A considerable degree of "untangling" can occur before chains change conformation or end-to-end distance.

It is more than likely that coal, with its relatively short, stiff chains, swells at least in part in such a fashion. Theoretical descriptions of swelling have to change to account for this. One promising approach is the analogy to polymer semidilute solutions suggested by De Gennes (8). Much work remains before this can sensibly be applied to coal, however.

Conclusions

Our conclusions, stated baldly, sound rather harsh. Previous applications of polymer theory to coal are unsound and quantitatively without meaning because hydrogen bonding and desinterspersion have been largely neglected. However, these statements have to be placed in the context that it is only recently that these factors have been considered by polymer theoreticians. It is our view that the scientists who pioneered the study of coal as a macromolecular network made a major conceptual advance. The work presented here is not a criticism of this fundamental premise, but a refinement based on recent advances.

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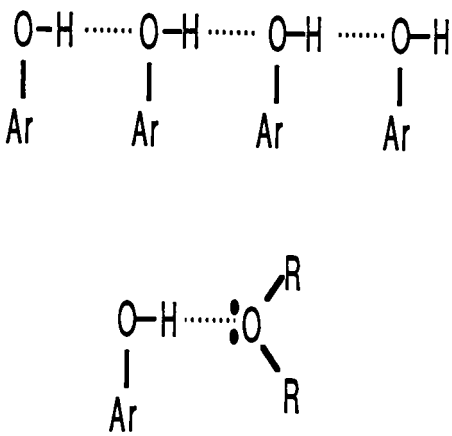

Figure 1 Schematic representation of (top) chains of hydrogen bonds formed between phenolic OH groups and (bottom) phenolic OH-ether hydrogen bonds.

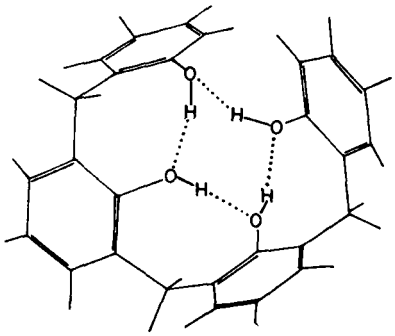

Figure 2 Cyclic tetranuclear complex formed between four phenolic OH groups.

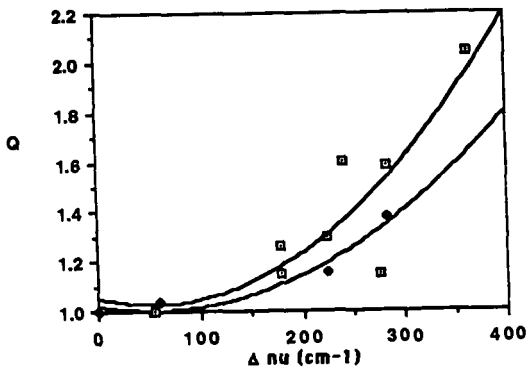

Figure3 Degree of swelling of coal (data from References 16 and 17) plotted against the infrared frequency shifts of the phenolic OH group when dissolved in the same solvents.

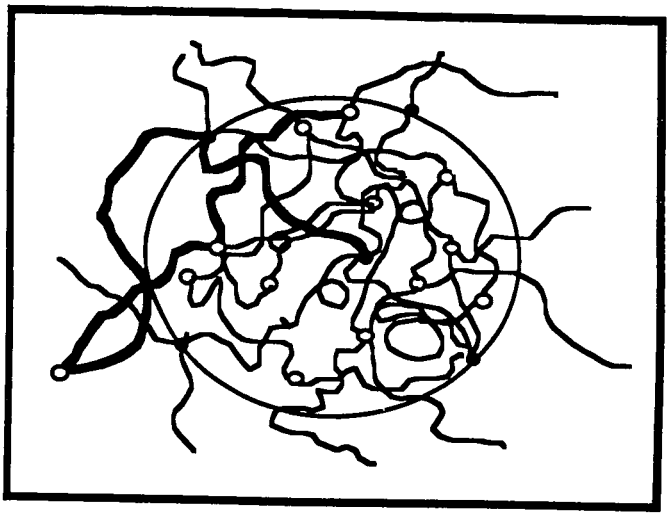

Figure 4 Schematic representation of a polymer network. The heavy lines illustrate the spatial separation between topological neighbors (after Candau et al., References 10,11).

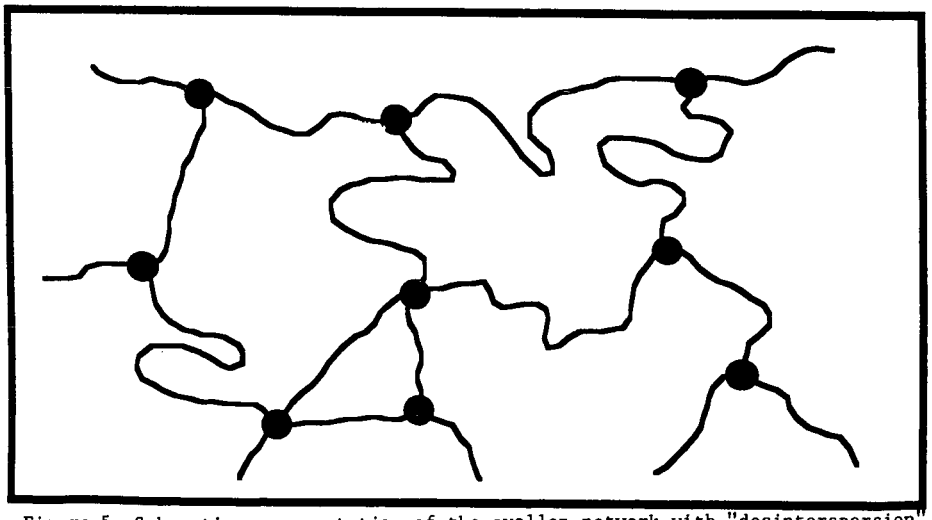

Figure 5 Schematic representation of the swollen network with "desinterspersion" of the cross link points.