i.d.) packed with OV-17 (10%) on Chromosorb W (HP 80/100) was used to collect major products. The carrier gas was helium, normally flowing at 20 mL min^{-1}, and the column temperature was usually programmed from 40 °C to a maximum of 300 °C.

α-Hydroperoxy Diazenes 1 and ^{2}H Analogues. The α-hydroperoxy diazenes used in this work have been described.[1] A ^{2}H analogue was prepared by stirring a benzene solution containing between 60 and 100 mg of hydroperoxy diazene with excess D_2O (3 mL) for 20 h at about 5 °C. The benzene layer, together with ca. 0.5 mL of the aqueous phase, was used directly for reactions in which benzene was the solvent. For reactions carried out in neat alkene, the benzene was removed from the hydroperoxy diazene by one of the procedures described earlier.[1]

Thermolysis of Hydroperoxy Diazenes 1 in Norbornene and in 10. The procedure for the preparation of samples and for the workup was essentially that described earlier.[1] The experiment with **1b** and norbornene, to test for redox couples, involved washing the glassware with aqueous EDTA solution, drying, and addition of solid EDTA (5 mg) to the reactants before sealing the tube. EDTA was only slightly soluble in the solution of **1b** and norbornene in benzene, and a solid EDTA phase was present throughout the thermolysis.

Kinetics of Thermolysis of 1b in Benzene Containing Norbornene. Stock solutions of hydroperoxy diazene (0.05M) in benzene containing norbornene (0.3 or 3.0 M) and tetramethylpiperidine-*N*-oxyl (TMPO, 0.03 M) were prepared, and aliquots (1.0 mL) were degassed and sealed into glass tubes, which were then heated at 50 °C in an oil bath. For analysis a tube was chilled and cut, the sample was transferred to a cold, glass-stoppered Erlenmeyer flask (125 mL), cold methanol (4 mL) and dry ice (ca. 0.1 g) were added, and the flask was swirled to displace O_2 with CO_2. Freshly prepared, saturated, aqueous KI solution (1 mL) and glacial acetic acid (15 mL) containing $FeCl_3$ (0.002%) were added, and when no more dry ice remained the flask was stoppered and kept in the dark for 10 min. Water (50 mL) was added, and the resulting solution was titrated to the starch end point with 0.01 N sodium thiosulfate solution. The volume of titrant required for a sample that had reacted to completion (six or more half-lives) was subtracted from the other titration volumes for a given kinetic run.

Products. The products of hydroalkylation and hydroxyalkylation of norbornene with 1 have been reported.[1] Additional products reported here include minor and trace components for which tentative structures were assigned on the basis of low resolution mass spectrometry alone. The mass spectra are reported in order of decreasing values of m/z; peaks smaller than 50% of the base peak (100) being omitted except for molecular ions and for peaks of high diagnostic significance, where the relative intensity is given.

***exo*-Norbornene epoxide**: ^{1}H NMR δ 0.63 (d, J = 9.5 Hz, 1 H); 1.18–1.47 (m, 5 H), 2.39 (s, 2 H), 2.88 (s, 2 H);[26] ^{13}C NMR δ 25.01, 26.11, 36.57, 51.26; MS, m/z 110 (M^+), 67 ($C_5H_7,^+$ 100), 66 ($C_5H_6^+$).

2-(2,2,2-Trifluoroethyl)-3-(2-norbornyl)norbornane: MS, m/z 272 (M^+), 95 ($C_7H_{11}^+$, 100), 67 ($C_5H_7^+$).

2-(2-Methoxyethyl)-3-(2-norbornyl)norbornane: MS, m/z 216 ($M^+ - CH_3OH$), 188 ($M^+ - C_3H_8O$), 95 ($C_7H_{11}^+$, 100), 93 ($C_7H_9^+$), 80 ($C_6H_8^+$), 79 (not assigned), 67 ($C_5H_7^+$), 45 ($C_2H_5O^+$).

2-Hydroxy-3-(2-norbornyl)norbornane: MS, m/z 206 (M^3), 188 ($M^+ - H_2O$, 18), 95 ($C_7H_{11}^+$, 100), 80 ($C_6H_8^+$), 67 ($C_5H_7^+$).

2,3-Dihydro-4,5-benzofuran: MS, m/z 120 (M^+, 100), 94 ($C_6H_6O^+$), 91 ($C_7H_7^+$).

***tert*-Butylethylene oxide**: MS, m/z 100 (M^+), 57 ($C_4H_9^+$, 100), 41 ($C_3H_5^+$). The material that gave this mass spectrum had the same retention time on the analytical GC column as authentic *tert*-butylethylene oxide.

2,2-Dimethyl-5-phenoxypentane: MS, m/z 192 (M^+), 94, ($C_6H_6O^+$, 100), 57 ($C_4H_9^+$).

Phenoxyacetaldehyde: IR 1735 cm^{-1}; MS, m/z 136 (M^+), 94 ($C_6H_6O^+$, 100).

2,2-Dimethyl-6-phenoxyhexan-3-ol: MS, m/z 222 (M^+), 165 ($M^+ - C_4H_9$, 6), 94 ($C_6H_6O^+$), 71 ($C_5H_{11}^+$, 100).

2,2-Dimethyl-6-phenoxyhexan-3-one: IR 1712 cm^{-1}; MS, m/z 220 (M^+), 163 ($M^+ - C_4H_9$, 5), 127 ($C_8H_{15}O^+$, 100), 57 ($C_4H_9^+$).

1,3-Diphenoxypropane: MS, m/z 228 (M^+), 135 ($C_9H_{11}O^+$), 107 ($C_7H_7O^+$, 100), 77 ($C_6H_5^+$).

1,4-Diphenoxybutane: MS, m/z 242 (M^+), 149 ($C_{10}H_{13}O^+$), 107 ($C_7H_7O^+$, 100), 77 ($C_6H_5^+$).

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The Nature of the Macromolecular Network Structure of Bituminous Coals

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Received May 21, 1985

The macromolecular network structure of bituminous coals has been studied by using the classical solvent-swelling techniques of polymer chemistry. Solutions of nonpolar solvents in coals follow regular solution theory. Solvents which are hydrogen bond acceptors show strongly enhanced solubility (coal swelling) which correlates with the strength of the hydrogen bond between the solvent and *p*-fluorophenol. A family of network active hydrogen bonds exists in bituminous coals. In native coals, their strength appears to range from 5 to 8 kcal/mol. The use of solvent-swelling data to calculate the number average molecular weight between cross-links ($\bar{M}_c$) has been explored. It is not yet possible to calculate correct absolute values for $\bar{M}_c$, but changes in $\bar{M}_c$ can be followed. The treatment of coals as macromolecular networks is possible and provides significant new insight into their structure.

The principal component of bituminous coals, vitrinite, consists of a porous, cross-linked macromolecular network in which is dissolved a complex mixture of soluble molecules. This structure plays a dominate role in determining many of the physical properties of coals such as the various mechanical properties and mass transfer rates. Similarly, much of a coal's chemistry is determined by its macromolecular structure. The macromolecular network structure of this complex material must be fully characterized if we are to have any real hope of understanding its chemistry.

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0022-3263/85/1950-4729$01.50/0

There are several statements in the early literature that coal must be "polymeric" and that this is important structurally. The first person to use this idea to design experiments and to incorporate it into a structural model for coal was van Krevelen,[1-3] although the coal structure proposed by Vahrman[4] clearly recognized its macromolecular character without using the terminology. Within the past 5 years, the three-dimensional macromolecular network character of coals has become broadly, but not universally,[5] accepted in the coal research community. With its acceptance have come investigations of the network structure using established techniques of polymer chemistry such as solvent swelling and mechanical properties.[6,7] The experiments described here utilize solvent swelling.

The most elementary molecular property of a polymer network is the number average molecular weight between cross-links or junction points ($\bar{M}_c$). This quantity is a measure of the "mesh size" of the network and, to a first approximation, it determines the physical properties of the network. It is possible to determine ($\bar{M}_c$) by swelling the network in solvents.[8,9] At equilibrium, the elastic restoring force of the network is exactly balanced by the driving force for penetration of the network by the solvent. $\bar{M}_c$ is calculated from an equation which is derived by equating theoretical expressions for the elastic chemical potential of the network and the network–solvent chemical potential. The elastic contribution is ordinarily represented by the simple Gaussian theory of rubber elasticity.[9] This contribution contains the quantity $\bar{M}_c$. The network–solvent thermodynamics is treated by using the Flory–Huggins theory of polymer solutions which is an extension of regular solution theory.[8] The basic assumption of the regular solution approach is that the mixing is completely random.[10] The entropy of the solution is then the Flory–Huggins ideal entropy and the enthalpy is contained in the Flory interaction parameter, χ, which must be obtained experimentally. This approach is valid only in the case where strong specific interactions such as hydrogen bonding are absent. Since coals contain significant concentrations of hydroxyl groups and interact strongly with hydrogen-bond acceptors,[11,12] swelling measurements using hydrogen-bonding solvents cannot be interpreted by using this theory. This introduces a constraint which has had a large effect on our experimental approach. To calculate $\bar{M}_c$, the swelling of the coal in a given solvent must be known and the Flory χ parameter must be known for the coal–solvent pair at that concentration. The first quantity is easy to obtain, while the χ parameter presents difficulties. These difficulties and their resolution will be discussed below.

The first to apply solvent swelling to coals were Sanada and Honda who measured the pyridine swelling of a series of coals and obtained χ values from the concentration dependence of the osmotic pressure of pyridine solutions of coal extracts.[13] This involves the good assumption that the pyridine extracts are similar enough to the insoluble network so that meaningful χ values will be obtained. They studied extracted coals using a gravimetric technique. Since pyridine will extract up to 25% of the coals used, it is necessary to remove the soluble portion to prevent it from dissolving in the pyridine present in the pores, lowering its vapor pressure, and causing more pyridine to condense than is necessary to swell the network. $\bar{M}_c$ was calculated by using the Flory–Rehner equation.[8] Three criticisms can be made of this pioneering study. First, the solvent which filled the coal pores was included in their calculations. Since coals have pore volumes as high as 20% of their total volume,[14] coal swellings were overestimated by this amount. Second, pyridine interacts specifically and strongly with coals, violating the assumptions of the model used to calculate $\bar{M}_c$. Finally, the Flory–Rehner equation is not expected to hold for systems as tightly cross-linked as coals.[8,15] Nevertheless, this important work demonstrated the potential of this approach, one which we now are following. Their $\bar{M}_c$ values ranged from 700 to 15 000 for the coals studied.[16]

The next application of this technique was by Kirov and co-workers who swelled 3 coals in 17 solvents and used a regular solution approach to calculate χ.[19] Many amine solvents were used together with the Flory–Rehner equation, so this work is subject to some of the same criticisms as Sanada and Honda's. Similar values of $\bar{M}_c$ were obtained.

Nelson measured the swelling of a set of coals in benzene and tetralin and observed a maximum in the degree of swelling at 75% carbon.[18] He suggested a minimum in the cross-link density occurred with coals of this composition. Others have suggested that such a minimum exists at ca. 86% C.[20] Additionally, he used swelling in methanol to attempt to calculate $\bar{M}_c$ for the coals.[15] He corrected his gravimetric swellings for solvent condensation in the pores and did not correct for possible additional solvent condensation due to extraction of some material from the coals by the solvents used. He concluded that the Flory–Rehner equation and variants of it[21] were inadequate for treating coals because coals are too highly cross-linked. Subsequently, it was learned that methanol binds to coals at specific sites making it particularly unsuitable for use with these equations.[22]

The solvent-swelling data presented in this paper are analyzed by using a non-Gaussian model of cross-linked networks.[31] The chains in the coal network are too short and the branch points are too close together to be treated adequately by Gaussian models such as Flory's. Peppas has also applied non-Gaussian models to coals and has

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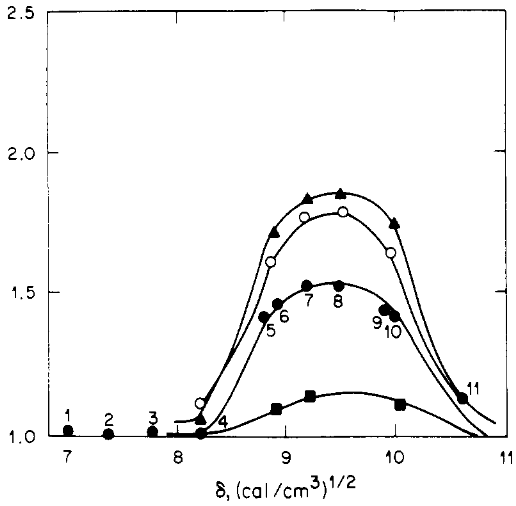

Figure 1. Swelling ratio ($Q_{v,dry}$) for Native Illinois No. 6 coal (■), the pyridine-extracted coal (●), the oxygen-methylated unextracted coal (○), and the pyridine-extracted oxygen-acetylated coal (▲) as a function of the Hildebrand solubility parameter (δ) of the swelling solvent. The swelling solvents are (1) *n*-pentane, (2) *n*-heptane, (3) methylcyclohexane, (4) cyclohexane, (5) *o*-xylene, (6) toluene, (7) benzene, (8) tetralin, (9) naphthalene, (10) carbon disulfide, (11) biphenyl.

presented an insightful analysis of the dependence of $\bar{M}_c$ on χ.[39] This work utilized the data of Sanada[13] and Kirov[19] and so is also subject to uncertainties due to the use of specifically interacting solvents.

This paper describes the use of solvent swelling to probe the macromolecular structure of two typical bituminous coals and their derivatives. Evidence is accumulating that hydrogen bonding plays a large role in the macromolecular structure of coals and that solvents capable of donating or accepting hydrogen bonds interact specifically with coals. For this reason coals were studied with a set of non-hydrogen-bonding solvents. Coals derivatized to prevent hydrogen bonding were also studied. We sought first to establish thermodynamic models capable of rationalizing coal swelling in nonpolar solvents. This done, the impact of internal hydrogen bonds could be evaluated. Finally, attempts were made to estimate $\bar{M}_c$.

Results and Discussion

Regular Solution Treatment of Swelling in Nonpolar Solvents. Figure 1 shows the swelling in a set of non-hydrogen-bonding solvents of native Illinois No. 6 coal, the same coal extracted with pyridine, the methyl ether of the coal, and the acetylated coal. The swelling ratio is plotted as a function of the Hildebrand solubility parameter of the solvent (δ_s). The swelling ratio ($Q_{v,dry}$) is the ratio of the volume of the swollen coal to that of the unswollen sample.[23] The methylation and acetylation reactions were carried out by using standard procedures, and careful FTIR spectroscopy showed the derivatization of all hydroxyl groups.[24,25] Similar curves for Bruceton coal are shown in Figure 2. The behavior observed is exactly that expected from regular solution theory.[10] A maximum in swelling occurs when the macromolecular network and a swelling solvent have the same value, and swelling decreases as the δ values diverge as the solvent–network interactions become less favorable. The experimental results exhibited in Figures 1 and 2 allow us to identify the swelling maximum with the Hildebrand solubility parameter of the coal.

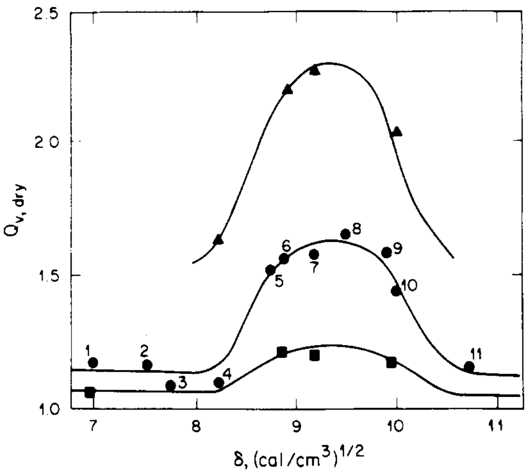

Figure 2. Swelling ratio ($Q_{v,dry}$) for Bruceton coal (■), pyridine-extracted bruceton coal (●), and oxygen-acetylated, pyridine-extracted Bruceton coal (▲) as a function of the Hildebrand solubility parameter of the swelling solvent. See Figure 1 legend for solvent identification.

There is a straightforward rationalization of the behavior shown in these figures, and we will build up evidence for the correctness of this explanation as we go along. The unextracted, native coals show the lowest swelling in these nonpolar solvents. A threefold increase in the maximum swelling is observed after these coals have been extracted with pyridine and 19% and 21% (wt) removed from Illinois No. 6 and Bruceton coal, respectively. There are two possible explanations for this great increase in swelling. It is well-known that it is impossible to remove all the pyridine from extracted coals[26] and these coals each contain 3.1% pyridine as measured by the weight increase after extraction and vacuum drying. This corresponds to 12% of the hydroxyl groups in Illinois No. 6 coal and 22% of the hydroxyl groups in Bruceton coal. The presence of this amount of pyridine in extracted Illinois No. 6 coal increases its swelling in chlorobenzene by 10%,[22] a much smaller increase than the 130% increase observed here. The enhanced swelling is not due to the presence of a small amount of residual pyridine in the sample. We therefore believe the large increase in swelling is due to the destruction of coal–coal hydrogen bonds which occurs during the pyridine extraction. During this extraction, the coal swells by some 2.5 times, then collapses as the pyridine is removed. During the collapse, not all of the hydrogen bonds reform, so many hydrogen-bond cross-links are lost. Additionally, pyridine is trapped in the macromolecular gel during its collapse and cannot diffuse out. The trapped pyridine is not necessarily hydrogen bonded.

When all of the hydrogen bonds are removed by derivatizing the hydroxyl groups, maximum swelling is obtained. This supports the hypothesis that the differences between the curves in Figures 1 and 2 are due to the presence or absence of hydrogen-bond cross-links. In the absence of other factors, the curves for the methylated coal and the acetylated coal should be coincident. They are not. The simplest explanation is that the two derivatives interact somewhat differently with this set of solvents, not an unreasonable supposition given the difference in the concentration of carbonyl groups in the two samples. It is also

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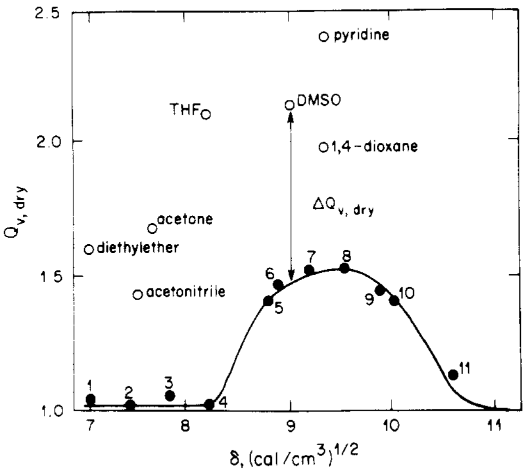

Figure 3. Swelling ratio ($Q_{v,dry}$) for pyridine-extracted Illinois No. 6 coal as a function of the Hildebrand solubility parameter of nonpolar solvents (●) and the nonpolar solubility parameter of polar solvents (⊙).

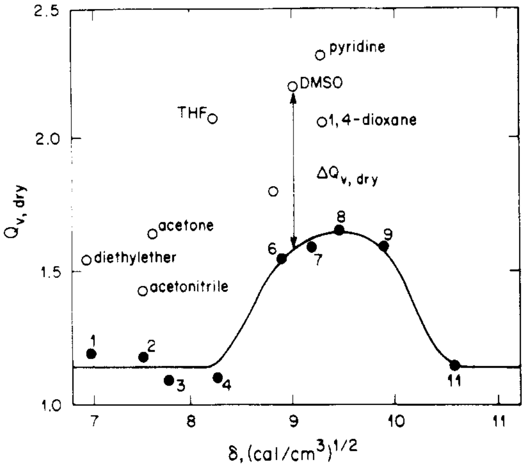

Figure 4. Swelling ratio ($Q_{v,dry}$) for pyridine-extracted Bruceton coal as a function of the Hildebrand solubility parameter of non-polar solvents (●) and the nonpolar solubility parameter of polar solvents (⊙).

possible that the derivatization reactions altered the network in some way by breaking or making a few labile bonds or that different amounts of extractable material were removed during the reactions. The differences are small and the overall behavior is consistent with the existence of many network-active hydrogen bonds in coals. That the hydroxyls in coals are hydrogen bonded has long been known as it is obvious from their IR spectra.[27]

Interactions with Hydrogen-Bonding Solvents. Figures 3 and 4 show the solvent swelling of Illinois No. 6 and Bruceton coals in solvents which are hydrogen-bond acceptors together with the curves generated by swelling with nonpolar solvents. The polar solvents are plotted by using their nonpolar solubility parameters calculated by using Prausnitz' method.[28] While thermodynamically illegitimate, the splitting of a solubility parameter into various contributions is frequently done because it often is a useful first-order approximation.[11] Our use of it here is straightforward; we need to separate the contribution of the polar interactions of the heteroatom to coal swelling from those of the rest of the molecule. Prausnitz' technique is based on the use of isomorphs and should provide an estimate of the contributions of the polar functionality to the overall intermolecular interactions of these molecules.

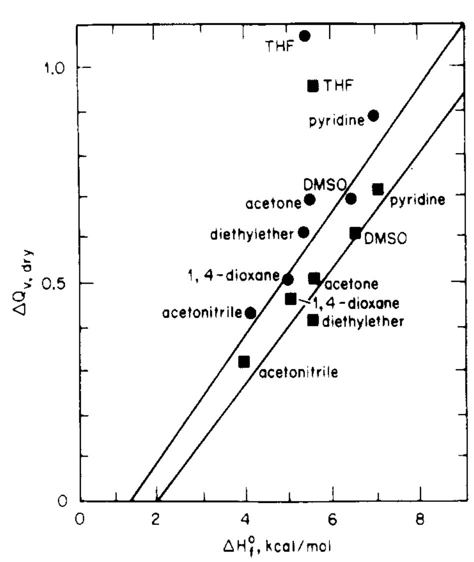

Figure 5. Excess swelling ratio ($\Delta Q_{v,dry}$) for pyridine-extracted Illinois No. 6 (●) and Bruceton (■) coals as a function of the heat of hydrogen-bond formation between the swelling solvent and *p*-fluorophenol.

If the nonpolar solubility parameter correctly assesses the nonpolar contribution to coal–solvent interactions, the points for the polar solvents would lie on the curve were it not for the presence of specific interactions. The excess swelling must be due to specific interactions and we have argued that these are coal–solvent hydrogen bonds. Coal–coal hydrogen bonds should cover a range of strengths. A solvent which forms strong hydrogen bonds should replace many of the coal–coal hydrogen bonds with coal–solvent hydrogen bonds. If the coal–coal hydrogen bonds are active cross-links, this will reduce the cross-link density of the coal and the swelling will increase. A solvent which forms weaker hydrogen bonds will increase the swelling less, since more hydrogen-bond cross-links will remain intact. There should be a quantitative relationship between the hydrogen-bonding ability of these solvents and their ability to swell coals. This is shown in Figure 5. Here the heats of hydrogen bonding between each solvent and *p*-fluorophenol, measured by Arnett,[29] are plotted against the excess swelling, the difference between the observed swelling and the curve generated by the nonpolar solvents. Since almost all of the hydroxyl groups in these coals are phenolic,[30] *p*-fluorophenol should be a good model system. Good straight lines are observed which come close to the origin. That they do not pass through the origin may be due to the presence of some non-hydrogen-bonding interactions or a partial failure of the use of nonpolar solubility parameters. We will present evidence that THF may be interacting specifically, although we see no reasonable route for such interactions. Finally, any interactions in these systems whose enthalpies are linear in hydrogen-bonding enthalpies will be nicely incorporated in the straight lines and cannot be separated by using this analysis. These data are for pyridine-extracted coals and reveal a broad distribution of hydrogen-bond strengths. Even a weakly hydrogen-bonding solvent will show some increase in swelling due to the disruption of hydrogen-bond cross-links in the coal.

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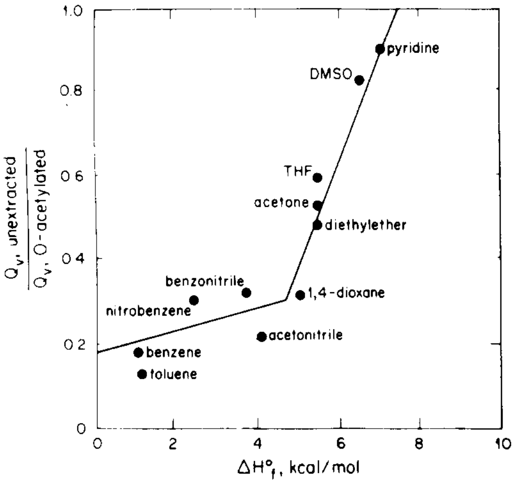

Figure 6. Ratio of the swelling of Illinois No. 6 coal to acetylated Illinois No. 6 coal vs. the heat of hydrogen-bond formation between the swelling solvent and *p*-fluorophenol.

A different approach can be used to probe the range of hydrogen-bond enthalpies in an unextracted coal. The ratio of the swelling of the coal to the swelling of the acetylated coal is used. The acetylated coal contains no hydrogen bonds. A solvent which breaks all of the hydrogen bonds in a coal will swell the coal and the acetylated coal to the same extent; the ratio will be one. As solvent hydrogen-bonding ability decreases, the ratio will drop, as shown in Figure 6. Solvents having a hydrogen-bond strength with *p*-fluorophenol below about 5 kcal/mol cause little excess swelling. Pyridine breaks nearly all of the hydrogen bonds in these coals and a solvent which formed 8.5 kcal/mol hydrogen bonds to phenol would break all of the coal–coal hydrogen bonds. In this unextracted coal, the range of hydrogen-bond strengths is about 5 kcal/mol to 8.5 kcal/mol. The solvents used to swell the unextracted coal will themselves extract varying amounts of material from the coal and the solvent activity will be changed due to the presence of this dissolved material. This is an unavoidable consequence of working with an unextracted coal and contributes to the uncertainty of this first estimate of hydrogen-bond strengths in a coal. Note that in Figure 6 THF falls on the correlation line. When a coal and a derivatized coal are compared, THF appears to be a normal solvent. When *p*-fluorophenol is used as the standard, THF is exceptional. This suggests the existence of specific interactions in addition to hydrogen bonding between THF and the phenol or, more reasonably, with the coal.

The distribution of hydrogen-bond strengths in native coal and in pyridine-extracted coal are different. The pyridine-extracted coal has a continuous distribution of hydrogen-bond strengths while the natve coal seems to have few hydrogen bonds of strengths less than 5 kcal/mol. Extracting the coal with pyridine will break almost all of the coal–coal hydrogen bonds as the coal network expands. As the pyridine is removed and the coal contracts, some hydrogen bonds are formed, and the new hydrogen bonds have a continuous distribution of strengths, weak as well as strong. The apparent absence of weak hydrogen bonds in the native coals is striking. We can speculate about the reasons for this. One possibility is that the coal network is mobile enough so that with the passage of very long time, the most favorable hydrogen bonds gradually build up. Another, more reasonable, possibility is the selective loss of weakly interacting hydroxyl groups during the coalification process. Loss of hydroxyl groups during coalification is well established.[3] If the transition state for this process is not stabilized by hydrogen bonding, the higher energy, non-hydrogen-bonded hydroxys would be lost faster in a very slow, very selective process. This is speculation, and before proceeding further in this vein, the phenomenon must be better characterized.

Calculation of the Number Average Molecular Weight between Branch Points ($\bar{M}_c$). Two equations will be used. We have little confidence in the absolute accuracy of the $\bar{M}_c$ values we shall calculate using either equation. The theory is too far removed from the reality of coal structure. However, changes in $\bar{M}_c$ over a series of coals or changes in a single coal due to reactions should be accessible by using the techniques outlined here. Better theories are being developed. The Flory–Rehner equation (eq 1) was derived for use with normal rubbers and is not

$$\bar{M}_c = \frac{\rho_c V_s V^{1/3}}{-[\ln (1 - V) + V + \chi V^2]} \qquad (1)$$

expected to be applicable to coals. The assumptions include affine distortion, phantom chains, a Gaussian distribution of chain lengths, and regular solution behavior as described by the Flory–Huggins theory. Coals are probably too highly cross-linked and their chains too stiff for this equation to be applicable. Nevertheless, it is familar, its derivation[8] is easy to follow, it has been applied to coals before,[13,15,18,19] and we are curious about how well it might work. For these reasons, it has been used. A simple non-Gaussian theory has been developed by Kovac.[31] This theory should describe coal swelling better, since it incorporates chain stiffness and the finite extensibility of the network in an approximate way. The expression for $\bar{M}_c$ derived by Kovac is given in eq 2. In the

$$\bar{M}_c = \frac{\rho_c V_s V^{1/3} + \rho_c V_s / N V^{1/3}}{-[\ln (1 - V) + V + \chi V^2]} \qquad (2)$$

limit of very low cross-link densities, the Kovac equation reduces to the Flory–Rehner equation except that it does not include the somewhat controversial logarithmic term in the free energy. Since the observed swellings are not large, its omission is justified.

Both of these equations require the same experimental data: the volume fraction polymer at equilibrium swelling (V) and the Flory χ parameter for the coal–solvent pairs. The first of these is readily obtained from the volumetric swelling ratios. If the swelling ratio is 2, the volume fraction polymer is 0.5. Obtaining reliable χ values is more difficult. A good review of methods for measuring χ exists,[32] and we tried a number of approaches which failed, including inverse gas chromatography and calorimetry. We eventually settled on an approach which takes advantage of the good regular solution behavior of these coals with nonpolar solvents. We assumed the coal densities (ρ_c) are 1.3 g/mL and the solvent molar volumes (V_s) are readily available.

The necessary χ values can be calculated by using eq 3 if the solubility parameters of the macromolecular net-

$$\chi = \frac{V_s}{RT}(\delta_s - \delta_c)^2 + \chi_s \qquad (3)$$

work and the solvent are known. Since the maximum in the swelling curves occurs when the solubility parameter of the network is equal to the solubility parameter of the swelling solvent, it can be obtained for the two coals from Figures 1 and 2. The value of 9.5 cal$^{1/2}$ cm$^{-3/2}$, the same for both coals, was used to calculate the values shown in

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(32) Orwoll, R. A. *Rubber Chem. Technol.* **1973**, *50*, 451.

Table I. Number Average Molecular Weight per Cross-Link of the Bruceton and Illinois No. 6(2) Coals Using the Flory–Rehner Equation

solvent	χ	unextracted	extracted	*O*-acetylated
		Illinois No. 6(2)		
o-xylene	0.40		430	
toluene	0.36	100	410	700
benzene	0.31	110	360	630
tetralin	0.30		540	990
naphthalene	0.33		380	
CS_2	0.32	60	190	380
average		90	390	680
		Bruceton		
o-xylene			550	
toluene		190	500	1420
benzene		150	410	1120
tetralin			690	
naphthalene			520	
CS_2		110	210	590
average		150	480	1040

Table I. We took a common approach to the entropic contribution to χ and estimated it to be 0.30. There is ample precedent for this in other polymeric systems,[33] and it is worthwhile to explore this approach with coals. Table I reports $\bar{M}_c$ calculated for the two coals by using several nonpolar solvents and the approach outlined. We are limited to nonpolar solvents since only these do not interact specifically with the coals. Also given in Table I are the $\bar{M}_c$ values calculated for pyridine-extracted coals and derivatized coals.

All of the values for $\bar{M}_c$ are unreasonably small, and we shall pass quickly to the use of the Kovac equation, pausing for a few comments relevant to both treatments. There are two problems with the measurements on *unextracted* coals. A minor problem is that most of the solvents have extracted some material from the coal, thus changing their activity. The error introduced by this is probably small. A much greater difficulty is that this coal, even after swelling with a nonpolar solvent, may be in a glassy state, rather than a rubber. The free motion of the chains characteristic of a rubber is required by both Flory's and Kovac's treatment. There is evidence that coals swollen by basic solvents and hydroxyl-derivatized coals containing swelling solvents are rubbers.[6,34] There are also indications that swollen, pyridine-extracted coals are also rubbery, although this has not been unquestionably established. But there are no published data indicating the state of coals swollen with nonpolar solvents. Because of this, and because the systems are so highly cross-linked, our estimates of $\bar{M}_c$ for native coals are much less reliable than the others.

Table II. Number Average Molecular Weight per Cross-Link of the Illinois No. 6(2) Coal Using the Kovac Equation

		$\bar{M}_c$			
unextracted	*N*	0.4	0.5	1.0	2.0
toluene		430	310	200	150
benzene		400	340	220	170
CS_2		240	200	130	100
average		360	280	190	140
$\bar{M}_0$		900	560	190	70
extracted	*N*	1.0	1.25	2.0	3.0
o-xylene		980	870	710	620
toluene		940	830	670	580
benzene		840	740	600	520
tetralin		1250	1100	900	780
naphthalene		860	760	620	540
CS_2		430	390	310	270
average		880	780	640	550
$\bar{M}_0$		880	620	320	180
O-acetylated	*N*	1.5	2.0	3.0	4.0
toluene		1370	1200	1030	950
benzene		1260	1110	950	870
tetralin		1920	1680	1440	1320
CS_2		740	650	560	510
average		1320	1160	1000	910
$\bar{M}_0$		880	580	330	230

Table III. Number Average Molecular Weight per Cross-Link of the Bruceton Coal Using the Kovac Equation

		$\bar{M}_c$			
unextracted	*N*	0.5	0.75	1.0	2.0
toluene		630	490	410	300
benzene		440	330	270	190
CS_2		370	280	240	180
average		480	370	300	220
$\bar{M}_0$		960	490	300	110
extracted	*N*	1.0	1.5	2.0	3.0
o-xylene		1290	1080	920	800
toluene		1180	950	840	730
benzene		970	780	690	600
tetralin		1650	1330	1170	1020
naphthalene		1240	1000	880	760
CS_2		470	380	340	300
average		1130	920	810	700
$\bar{M}_0$		1130	610	400	230
O-acetylated	*N*	2.0	3.0	4.0	5.0
toluene		2630	2230	2030	1910
benzene		2100	1780	1610	1520
CS_2		1070	910	830	780
average		1930	1640	1490	1400
$\bar{M}_0$		970	550	370	280

The Kovac equation introduces an additional parameter, *N*, which can be associated with the number of repeating units (clusters) between branch points. We accept the prevailing structural view that coals consist of various condensed aromatic and hydroaromatic "clusters" linked together by short flexible chains of methylene groups and ethers.[35,36] *N* describes the deviations from Gaussian behavior. In the limit of large *N*, the Kovac equation reduces to the Flory–Rehner equation. *N* can be defined as the ratio of $\bar{M}_c$ to the number average molecular weight of the clusters, $\bar{M}_0$. The Kovac equation was used to calculate $\bar{M}_c$ for several values of *N* and the results are given in Tables II and III. These data were then used to generate the plots of $\bar{M}_0$ vs. *N* shown in Figures 7 and 8.

The cluster size in any coal must be constant in the absence of any chemical reaction. Thus, if a cluster molecular weight is chosen, *N* can be obtained from the figure and $\bar{M}_c$ calculated directly. The scatter in the data used to generate the figures is large, the standard deviations being between 30% and 40%. Many discussions of average cluster size exist, with many authors guessing values around 400 for bituminous coals.[36] By selecting any cluster size, the same qualitative changes in the coals are obtained. The number of branch points (cross-links) decreases upon pyridine extraction and again on derivatization. We have

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(35) Davidson, R. M. *Coal Science* **1982**, *1*, 84.

(36) Benjamin, B. M.; Douglas, E. C.; Canonico, D. M. *Fuel* **1984**, *63*, 888.

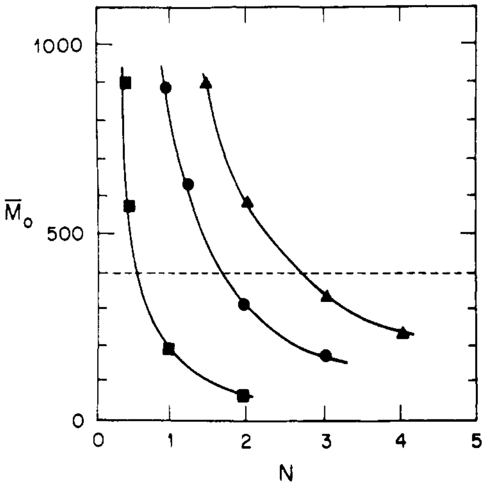

Figure 7. Relationship between the number average molecular weight of a "Cluster" ($\bar{M}_0$) and the number of "clusters" between branch points (*N*) for Illinois No. 6 coal (■), pyridine-extracted Illinois No. 6 coal (●), and oxygen acetylated pyridine-extracted Illinois no. 6 coal (▲) from the Kovac equation (eq 2).

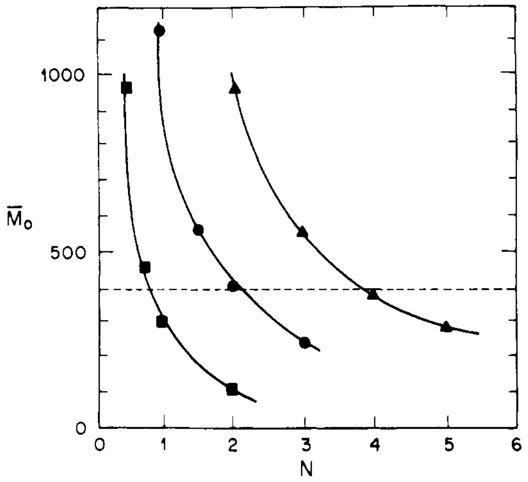

Figure 8. Relationship between the number average molecular weight of a "cluster" ($\bar{M}_0$) and the number of clusters between branch points (*N*) for Bruceton coal (■), pyridine-extracted Bruceton coal (●), and oxygen acetylated pyridine-extracted Bruceton coal (▲) from the Kovac equation (eq 2).

ascribed this decrease to the loss of hydrogen-bond cross-links.

It is useful to consider the source of the scatter in the calculated $\bar{M}_c$ values (Tables II and III) which is too large to be experimental. We are confident of the calculation of χ_H. However, the entropic contribution to χ has been held constant at 0.30. This is the probable source of the scatter. The calculated $\bar{M}_c$ values are good straight-line functions of the molar volumes of the solvents, suggesting that χ_s should be allowed to vary. In fact, a scheme for varying χ_s has been developed[37] which strongly reduces the scatter, an unsurprising result since it introduces an additional variable parameter.

Table IV. Elemental Analyses of Coals Used

coal	% C	% H	% N	% O (diff)	% ash
Bruceton	83.1	5.3	1.6	8.8	5.4
Illinois No. 6	79.8	5.1	1.8	11.2	7.0

We have little confidence in the absolute accuracy of the reported $\bar{M}_c$ values but do think their relative values are significant and reasonable. Changes in $\bar{M}_c$ can be followed and will provide insight into the effects of chemical changes on the cross-link density of the network. A very powerful tool is thereby added to the coal chemists kit. In addition, the treatment of coal as a macromolecular network is just beginning and we have every confidence that this simple treatment will point the way to better ones.

The structural model that emerges from this work differs significantly from the classical models in that it adds to the classical model extensive, internal, network active, strong hydrogen bonds. From the data in Figures 7 and 8, Bruceton coal has about 4.5 times as many hydrogen-bond cross-links as covalent cross-links, virtually independent of the estimated cluster size. For Illinois No. 6 coal, there is a fivefold preponderance of hydrogen-bond cross-links. Coals consist of a covalently bonded network of clusters which are extensively hydrogen bonded to each other. Once the hydrogen bonds are removed, the covalently cross-linked coals are not brittle solids but are somewhat flexible. It is the hydrogen bonding between clusters which provides most of the cross-links and which is responsible for the brittle, rock-like character of bituminous coals. Destruction of the network of internal hydrogen bonds greatly changes the character of bituminous coals. No published structural models have included this internal network of coal–coal hydrogen bonds.[35] Subsequent papers will deal with the role which these hydrogen bonds play in chemical reactivity, pyrolysis, mass transport, and structure of coals.

Experimental Section

The elemental analyses of the coals used are given in Table IV. The Illinois No. 6 coal was obtained from Exxon and the Bruceton coal came from the U.S. Department of Energy's experimental mine at Bruceton, PA. All solvents were purified by using standard methods. The solvent swelling technique used has been described in detail.[23] The coals were acetylated by using Blom's standard procedure which was also used to determine hydroxyl group contents.[24] Our results for Illinois No. 6 coal agreed exactly with those of Liotta,[25] who used a different procedure. Liotta's methylation technique[25] was used without alteration.

Acknowledgment. We thank the U.S. Department of Energy and the Exxon Education Foundation for support of this work.

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