

## KEROGEN MACROMOLECULAR STRUCTURE

John W. Larsen and Harsh M. Parikh<sup>1</sup>, Raymond Michels and Noele Raoult<sup>2</sup>  
and Bernard Pradier<sup>3</sup>,

<sup>1</sup>Department of Chemistry, Lehigh University, Bethlehem, PA 18015

<sup>2</sup>UMR, 7566 G2R Universite Henri Poincare, BP 23, 54501 Vandoeuvre Les Nancy, France

<sup>3</sup>ELF-EP, CSTJF, Avenue Larribau 64018 Pau, France

Keywords: Kerogen, coal, macromolecular

### ABSTRACT

The macromolecular structures of a Bituminous Coal (Illinois No. 6), a Type I kerogen (Green River) and a Type II kerogen (Torcian Shale, Paris Basin) are compared by using solvent swelling measurements. The swelling of Types I and II kerogen roughly follow Regular Solution Theory and show no specific solvent effects. The coal follows Regular Solution Theory for non-polar solvents but shows highly specific interactions with basic molecules. Immature Type I kerogen is much less cross linked than is immature Type II kerogen. Both Type I and Type II kerogen becomes more cross linked during maturation while coals appear to depolymerize during maturation. Only coals are strained. Alkanes dissolve in Types I and II kerogens but not in untreated coals.

### RESULTS AND DISCUSSION

Quantitative studies of coal macromolecular structure began with the paper from Sanada and Honda in which they studied the swelling of coals by organic liquids and used the Flory-Rehner equation to calculate the cross-link densities of those coals.<sup>1</sup> The utility of this approach went unappreciated for many years, but it has since become a standard tool of coal science. Coals are Type III kerogens. Types I and II kerogens have long been known to be three dimensionally cross-linked macromolecular solids,<sup>2</sup> but only recently has systematic study of their macromolecular structure and properties been initiated. It is now possible to compare and contrast some of the macromolecular properties of all three kerogens.

The place to begin is with cross-link densities. All three materials have been studied by solvent swelling and the results are easy to compare. Ironically, the material that was studied first, coal, shows the most complex behavior. Type I kerogen has been selected as the standard to which the others will be compared. Numerous theoretical issues are involved in calculating cross-link densities from swelling measurements.<sup>3</sup> Rather than enter the theoretical underbrush, the maximum solvent swelling observed will be taken as a qualitative measure of cross-link density. The solubility parameters of all three kerogens are surprisingly close permitting use of this simplification. The solvent swelling of Green River kerogen is typical of the Type I kerogens so far studied and is shown in Fig. 1. Swelling is reversible and all solvents (non-polar, polar, and hydrogen bonding) fall on the same curve. That curve roughly follows Regular Solution Theory.<sup>4</sup> The Type II kerogen from Paris Basin Torcian Shale swells much less than does the Type I kerogen and all solvents behave similarly (see Fig. 2). Both kerogens show no specific interactions with the solvents used. The Type II kerogen is much more highly cross linked than Type I. Coals are different (see Fig. 3). First, they swell much more in hydrogen bonding solvents than in non-polar solvents. Two different explanations have been offered for this.<sup>6,7</sup> For non-polar solvents, the swelling and therefore the cross-link density of pyridine extracted Illinois No. 6 coal is similar to that of the Type I and Type II kerogen used here. The similarity is not general. Green River kerogen swelling varies greatly with its maturation.<sup>13</sup> But there are also some puzzling aspects to coal swelling that have not yet been considered adequately. For example, if one swells untreated Illinois No. 6 coal with aromatic solvents, the swellings are quite small on the order of 10% to 20%. Part of this is because some of the coal is extracted into the solvent lowering the solvent activity and thus decreasing swelling, but this is probably not the major effect. The same coal after exhaustive extraction with pyridine in these same solvents now swells by 40% to 50%. The changes that cause this difference have not yet been adequately explained. The first swelling of coals is irreversible demonstrating that coals are strained.<sup>8</sup> This behavior seems to be general and has not been observed with either Type I or II kerogen.

Types I and II kerogen are well behaved showing reversible swelling, no specific solvents effects, and roughly following Regular Solution Theory. Type II is highly cross-linked while Type I is not. Coals are very different. Initial swelling are irreversible and basic solvents interact specifically.

The three kerogens differ in the way the macromolecular structure changes during maturation. The single Type I kerogen studied in detail shows a sharp increase in cross-link density early and late in the maturation process, but in the middle a broad region of constant cross-link density (see Fig. 4). The macromolecular structure changes occurring during the maturation of only one Type I kerogen has been studied, and only three samples of that kerogen. The swelling changes are shown in Fig. 2. They show little beyond increasing cross-linking during maturation. The differences in cross-link density between the Type I and II kerogen will translate into greater capacity of immature Type I kerogen for hydrocarbons and more rapid diffusion from the Type I, other things being equal.

A survey of coal swelling reveals confusing dependence of swelling on rank.<sup>9</sup> An analysis of the amount and molecular weight distribution of coal extracts led to the conclusion that coalification was a net depolymerization.<sup>10,11</sup> This is opposite to the behavior of the Types I and II kerogen so far studied. Whether the chemical processes are the same or different, they have opposite effects on the cross-link density of the material.

The capacity of the kerogen to dissolve hydrocarbons has a great effect in the expulsion of petroleum from source rocks. A full discussion of this issue is deferred, but some interesting observations are noted here. The capacity of native coals for alkanes is approximately 0. They do not swell in alkanes. Regular Solution Theory predicts that the enthalpy of coal-alkane interactions will be endothermic compared to coal-coal and alkane-alkane interactions. Native coals will not dissolve saturated hydrocarbons. Such hydrocarbons may be diffusionally trapped in coals. Saturated hydrocarbons swell Type I kerogen by as much as 10-15% in spite of unfavorable thermodynamics. We offer a speculative explanation. If the kerogen structure is inhomogenous and contains regions rich in aliphatic materials, aliphatic liquids might dissolve in these regions. Type II has a very low, but measurable, capacity for alkanes. Perhaps this situation is similar to that of Type I kerogens. These results and conclusions should not be translated to source rocks in petroleum kitchens because pressure effects on polymer structure (e.g. Tg) and mobilities may be significant.

#### ACKNOWLEDGMENTS

Studies of coals have been supported by the U. S. Dept. of Energy and the Exxon Education Foundation to whom we are grateful. Acknowledgment is made to the Petroleum Research Fund administered by the American Chemical Society for the partial support of this research. We are grateful to Elf for financial support and for the provision of samples.

#### REFERENCES

1. Sanada, Y.; Honda, H. *Fuel* 1966, 45, 295.
2. Tissot, B. P.; Welte, D. H. *Petroleum formation and occurrence: a new approach to oil and gas exploration* Springer-Verlag, New York: 1978.
3. Faulon, J.-L. *Energy Fuels* 1994, 8, 1020-3 and references therein.
4. Larsen, J. W.; Li, S. *Energy Fuels* 1994, 8, 932-936.
5. Hildebrand, J. H.; Prausnitz, J. M.; Scott, D.L. *Regular and Related Solutions* Van Nostrand Reinhold Co., New York: 1970.
6. Larsen, J. W.; Gurevich, I.; Glass, A.S.; Stevenson, D.S. *Energy Fuels* 1996, 10, 1269-1272.
7. Painter, P. C. *Energy Fuels* 1996, 10, 1273-1275.
8. Larsen, J. W.; Flowers, R. A. II; Hall, P.; Carlson, G. *Energy Fuels* 1997, 11, 998.
9. Quinga, E. M. Y.; Larsen, J. W. in *New Trends in Coal Science*, NATO ASI Series, Y. Yurum Ed., 1991
10. Larsen, J. W.; Mohammadi, M.; Yiginsu, I.; Kovac, J. *Geochim et Cosmochim Acta*. 1984, 48, 135.
11. Larsen, J. W.; Wei, Y. C. *Energy Fuels* 1988, 4, 344.
12. Larsen, J. W.; Green, T. K.; Kovac J. *J. Org. Chem.* 1985, 50, 4729.
13. Larsen, J. W.; Li, S. *Energy Fuels* 1997, 11, 998.
14. Larsen, J. W.; Li, S. *Organic Geochemistry*, 1997, 5/6, 305-309.

**Table 1. The identity of the swelling solvents in the Figures.\***

No.	Solvent	$\delta(\text{cal/cm}^3)^{1/2}$		
1.	n-pentane	7.0	16.	acetonitrile 11.9
2.	n-heptane	7.4	17.	nitromethane 12.7
3.	methylcyclohexane	7.8	18.	pyridine 10.7
4.	cyclohexane	8.2	19.	tetrahydrofuran 9.1
5.	o-xylene	8.8	20.	2-propanol 11.5
6.	toluene	8.9	21.	ethanol 12.7
7.	benzene	9.2	22.	acetone 9.9
8.	tetralin	9.5	23.	dimethyl sulfoxide 12.0
9.	chlorobenzene	9.5	24.	o-dichlorobenzene 10.0
10.	1-methylnaphthalene	9.9	25.	chloroacetonitrile 12.6
11.	carbon disulfide	10.0	26.	carbon tetrachloride 8.1
12.	nitrobenzene	10.0	27.	1,2-trichloroethane 9.6
13.	biphenyl	10.6	28.	1,2-dibromoethane 10.4
14.	propionitrile	10.8	29.	methylene chloride 9.9
15.	nitroethane	11.1	30.	1-butanol 11.4
			31.	1-propanol 11.9

\*Brandrup, J. and Immergut, E. H., *Polymer Handbook, 3rd ed.* John Wiley & Sons., 1989.

Figure 1. Swelling ratio of Green River kerogen as a function of swelling solvent solubility parameter. ( $\square$ ) nonpolar solvents, ( $\blacksquare$ ) polar solvents, ( $\diamond$ ) H-bonding solvents. The solid line was calculated using the Flory-Rehner equation: assuming  $\delta_p=9.75$ ,  $M=242$ , and  $V_e=95 \text{ cm}^3/\text{mol}$ . This figure is from Ref. 14. See Table 1 for solvent identification.

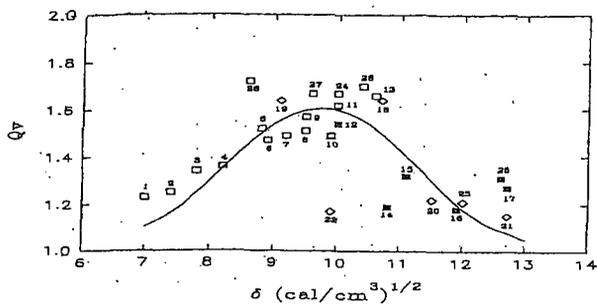


Figure 2. Swelling Ratios of Immature ( $\square$ ) fully mature ( $\circ$ ) Paris Basin Type II kerogen. See Table 1 for solvent identification.

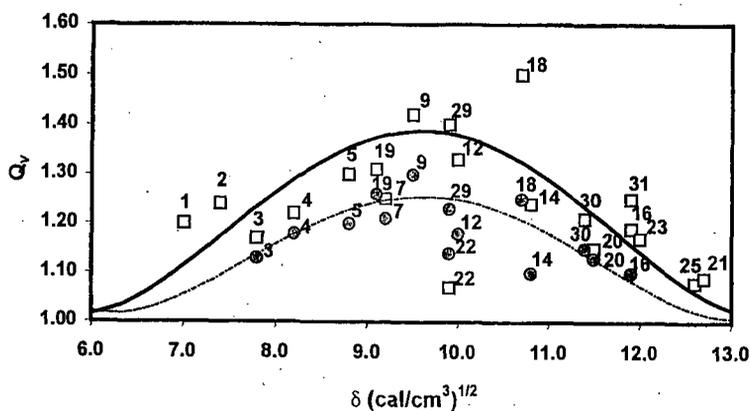


Figure 3. Swelling ratio of Illinois No. 6 coal as a function of swelling solvent solubility parameter ( $\square$ ) nonpolar solvents, ( $\blacksquare$ ) polar solvents, ( $\diamond$ ) H-bonding solvents. See Table 1 for solvent identification. Non-polar solvents are plotted using their non-polar solubility parameters. This figure is from Ref. 12.

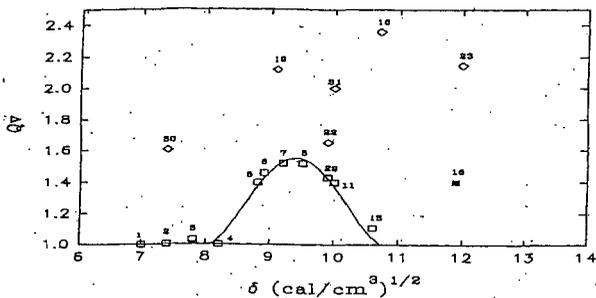


Figure 4. Change in Number Average Molecular Weight Between Cross Links ( $M_c$ ) as a factor of Maturation for Green River (Type I) kerogen figure from Ref. 13.

