

THE DEPOLYMERIZATION OF A MODEL COAL POLYMER

I. Lee, C. M. Sliepcevich and R. G. Mallinson

School of Chemical Engineering and Materials Science
University of Oklahoma
Norman, Oklahoma 73019

INTRODUCTION

While the macromolecular nature of the organic matter of coal has been known for some time (1), the manner in which the organic structure is held together has been a focus for a much shorter time and is still the subject of considerable scrutiny (2,3,4). It has been established that the macromolecular crosslinked structure of coal is the primary reason for its insolubility, but swellability, in organic solvents. The nature of the crosslinks, whether of a covalent or lesser type, is not really in dispute, but, rather, the relative amounts and importance of the probable interactions. The difficulties in establishing a clear concept no doubt lie in the very heterogeneous nature of coal, including the presence of trapped or "guest" molecules, and the diversity of coals of widely varying origins and ages.

The most successful approach in attempting to understand the macromolecular structure of coal has been the application of techniques and models from the field of polymer science in considering coals as crosslinked polymer networks (3,4). The difficulties of adapting a theoretical approach for ideal systems to such a heterogeneous, non-ideal, system as coal, have recently been pointed out (5,6). Nevertheless, for a pure polymer system used as a model for coal, the results should provide helpful insights into the nature of the thermal degradation of crosslinked polymer networks and coals.

In this work, a model coal polymer network has been synthesized under conditions of thermal liquefaction. The degradation of the macromolecular network and production of soluble products are followed as a function of reaction time.

EXPERIMENTAL

A crosslinked polymer network was produced using the difunctional monomers *a,a'*-dichloro-xylene and hydroquinone with trihydroxy benzene as the trifunctional crosslinking agent. The polymer which was desired was a crosslinked aromatic based polymer in which all of the linkages, including the crosslinks, were relatively thermally labile. Thus, the linkages produced in the condensation polymerization of these monomers should all be of the benzyl phenyl ether type, which cleave readily at 350 ° C to produce phenolic hydroxyl and aromatic methyl groups when tetralin is used as a solvent (7). Figure 1 shows the monomer structures and the steps in the production of the polymer. The hydroxyl monomers were converted to their sodium salts and dissolved in water, while the dichloride was dissolved in acetone. These were then mixed and refluxed at atmospheric pressure for four hours to produce an insoluble product. The polymer which was produced was insoluble in all solvents tested, including THF and pyridine. Analysis of the polymer included carbon, hydrogen, oxygen, sodium and chlorine elemental analyses which were carried out by Huffman Laboratories, and swelling analysis. Swelling analyses were carried out in pyridine using the procedure of Larsen et al. (8).

Once the polymer had been synthesized, degradation experiments were carried out in a micro-tubing bomb type reactor. Approximately 0.5 grams of polymer, accurately weighed, was put into the reactor with 2.0 grams of tetralin. The reactor was then sealed and pressurized with nitrogen gas to 1000 psig. The reactor was immersed in a fluidized bed sandbath maintained at 350 ± 5 ° C. The internal reactor temperature reached the steady state temperature within one minute and, at the end of the desired reaction time, was removed from the bath and quenched in water for an essentially

instantaneous cool down.

The reactor contents were then removed and a Soxhlet extraction with THF was carried out to separate soluble and insoluble materials. The THF (and tetralin) was removed from the soluble fraction by rotary evaporator and the THF removed from the insoluble matter in a vacuum oven. Both fractions were weighed and the material balance could be closed to within five percent with a few exceptions which were within ten percent. The insoluble material was then subjected to swelling analysis and hydroxyl group analysis using the acetylation technique following the procedure of Cronauer et al. (9). The soluble material was analyzed by gel permeation chromatography.

RESULTS

As mentioned above, it was initially intended that all linkages in the polymer would be of the benzyl phenyl ether type. However, the degradation results showed that after significant conversion of the initial insoluble polymer to soluble products at short reaction times, an asymptotic limit of about 40 percent was reached after which no increase in conversion was observed, as can be seen in Figure 2. After examining the elemental analysis data and the organic chemistry literature, it appeared that a side reaction involving nucleophilic attack of the aromatic rings by the hydroxyl groups was possible. This reaction altered the structure of the polymer by including diphenyl ether type structures, which are considerably more refractory than the benzyl phenyl ethers (7). This additional structure is illustrated in Figure 3 by the symbol, T. With this knowledge, the polymer structure could be broken down into the groups shown in Figure 3 for purposes of analysis. A sample of the polymer structure is shown in Figure 4 with the different structural groups outlined. The quantities of all of these groups could be determined by their algebraic relationships with the elemental analyses, including the end group analysis provided by the sodium and chlorine analyses. The reduction of the structure into groups allowed the determination of the quantities and types of crosslinks present in the polymer structure. This knowledge about the crosslinks, with the use of a modified Flory-Rehner (10,3,4) theory, provides detailed information about the network. The molecular weight between crosslinks as well as the size of the "loops" in the network may be determined.

With the appropriate parameters, the initial molecular weight between crosslinks is calculated to be 600 for the observed swelling ratio of 1.34. The interaction parameter, χ , was determined from the correlation of Lucht (11) based solely on the carbon content of the material, which was developed for coals. This parameter is currently being determined experimentally for this system. Upon degradation, the swelling behavior follows the conversion results in that the ratio increases dramatically within the first four minutes, and then levels off to an asymptotic limit of about 1.8, as may be seen in Figure 5. From the modified Flory-Rehner theory, a molecular weight between crosslinks of 900 is calculated. The behavior of both the conversion and molecular weight between crosslinks is qualitatively quite similar to what one might expect of a coal at this temperature. It follows that the more thermally labile crosslinks have been cleaved and then stabilized by the donor solvent, causing a significant amount of soluble material to be produced. At the same time the network opens up, but there remains a substantial amount of insoluble material due to the stability of the more refractory crosslinks. Figure 6 shows the hydroxyl group concentration of the polymer as a function of reaction time with the results as expected for the cleavage of the benzyl phenyl ether linkages at the conversions observed.

The soluble materials produced show a range of molecular weights from below 300 up to about 1000. Calibration of the GPC was accomplished with model compounds having molecular weights up to 532, so the values above that could have some absolute error from the extrapolation. Figure 7 shows the evolution of the molecular weight distribution with reaction time. The data are normalized per gram of initial polymer used so that the area under the curve is proportional to the mass of soluble material produced and becomes larger with higher conversions at longer reaction times. As may be seen, the general trend is for increased material of all molecular weights to be produced as the reaction

time and conversion increases. However, the lower molecular weight material, below about 300 tends to increase more rapidly than the bulk of the curve, which may be indicative of continued depolymerization within the material which has already become soluble. Also, at the higher molecular weights, above about 700, the increase is also larger than for the bulk of the curve, with a pronounced peak developing for the two longest reaction times shown. It may be that as more crosslinks are broken, larger "pieces" of structures become soluble because of increases in the numbers of hydroxyl and methyl groups per "molecular piece", which aid the solubility of such "pieces".

SUMMARY

In summary, the goal of this work has been to develop a synthetic macromolecular network which may be used as a model for coal networks, and to take advantage of the high degree of characterization available such that the network may be thermally degraded and insights into the degradation of the networks in coal may be gained. Also, with the increased use of thermosetting polymer networks for materials applications, this knowledge is applicable to the understanding of thermal (or random) degradation and stability of these systems. This experimental work is being conducted in parallel with a modeling effort for the degradation of polymer networks.

ACKNOWLEDGEMENTS

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STRUCTURE	FORMULA	SYMBOL
	$C_{14}H_{20}O_2$	M
- Na (OR-H)	Na	Q
	C_8H_8Cl	R
	$C_6H_3O_3$	N
	C_8H_8	P
	$C_{26}H_{19}O_6$	T

Figure 3. Basic Structural Units of the Polymer Network.

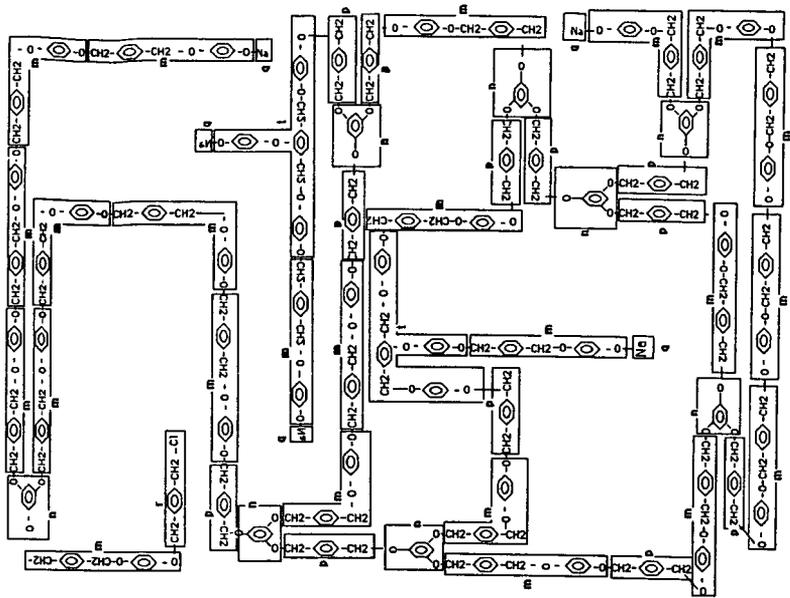


Figure 4. The Polymer Network.

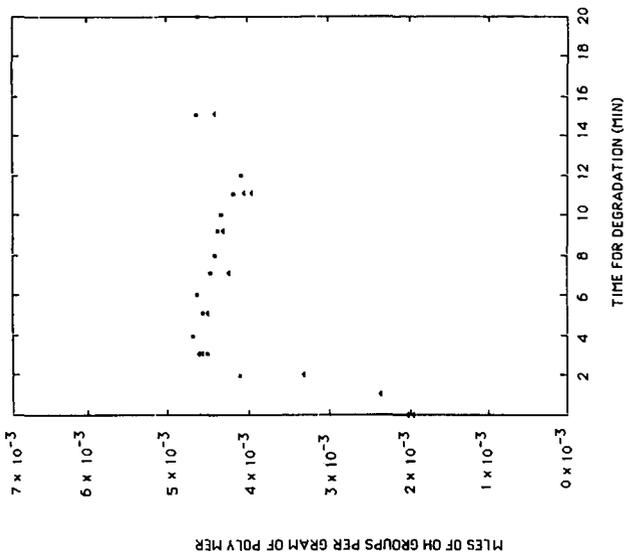


Figure 6. Hydroxyl Group Content of the Degraded Polymer.

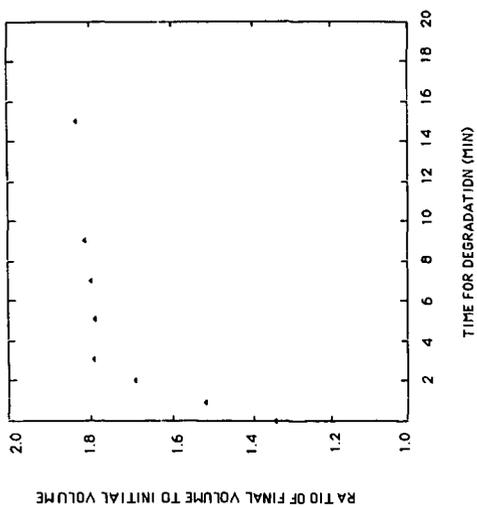


Figure 5. Swelling Ratio of the Network as a Function of Reaction Time.

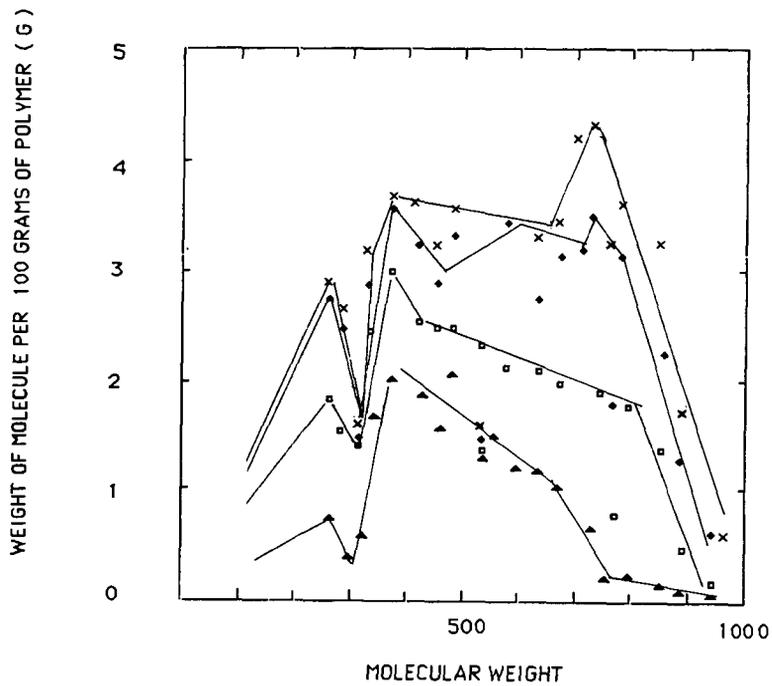


Figure 7. Molecular Weight Distributions of the Soluble Products.