THERMOLYSIS OF A POLYMER MODEL OF AROMATIC CARBOXYLIC ACIDS IN LOW-RANK COAL*

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ABSTRACT

To compliment our current investigation into the role that decarboxylation of aromatic carboxylic acids plays in the low-temperature cross-linking of low-rank coals, we are investigating the thermolysis of a polymeric coal model compound to determine if the polymeric network structure of coal can alter the decarboxylation pathways. In this investigation, a bibenzylic polymer, poly-(m-xylylene-co-5-carboxy-m-xylylene), **1**, was synthesized containing 2.3 carboxylic acids per 100 carbons, which is similar to that found in Zapp lignite. The pyrolysis of **1** was compared to poly-m-xylylene, **2**, and the methyl ester of **1**, **3**, to determine if the carboxy group enhances cross-linking reactions. The major product from the pyrolysis of **1** at 375 °C or 400 °C for 1 h was a THF insoluble residue (60-75 wt%), while pyrolysis of **2** or the methyl ester of **1** produced only a THF soluble product. The mechanistic pathways leading to cross-linking will be discussed.

INTRODUCTION

In recent years, it has been proposed that oxygen functional groups (i.e. carboxylic acids, phenols, and ethers), prevalent in low rank coals, are major contributors to retrograde reactions that inhibit the efficient conversion of low-rank coals to liquid fuels and chemicals. In the pyrolysis and liquefaction of low rank coals, low-temperature (T ≤ 400 °C) cross-linking reactions (measured by the solvent swelling technique) have been correlated with the loss of carboxyl groups in the char and the evolution of CO_2 and H_2O [1,2]. The pyrolytic loss of solvent swelling in coal has also been modeled by including one cross-link for every CO_2 evolved [1]. Cross-linking can be reduced by methylation, demineralization, or a hydrogen donor solvent and increased by oxidation or ion-exchanging Na^+, K^+, or Ca^{2+} into a demineralized coal [1]. These results suggest that the reaction pathways that lead to decarboxylation may play an important role in cross-linking. However, the reaction pathways for decarboxylation and cross-linking in low-rank coals are not known. Therefore, to gain a better understanding of the reaction pathways that lead to decarboxylation at temperatures relevant to coal processing, we have studied the pyrolysis of 1,2-(3,3'-dicarboxyphenyl)ethane ($HO_2CC_6H_4CH_2CH_2C_6H_4CO_2H$) neat and diluted in naphthalene or tetralin at 400 °C as a model of free carboxylic acids in low rank coal [3]. In these studies, decarboxylation did not produce any significant amount of coupling or other high molecular weight products that might be indicative of cross-linking reactions. However, recent pyrolysis studies of a monoacid, 1-(3-carboxyphenyl)-2-(4-biphenyl)ethane, diluted in naphthalene have shown the formation of small amounts (<3 mol %) of coupled products. It was proposed that decarboxylation occurred predominantly by an acid promoted ionic pathway. However, it is realized that simple model compounds may not be able to completely portray the complex chemistry and physical environment found in coal. Moreover, a small amount of cross-linking chemistry (1-5%) could go undetected in a simple model compound study (showing up as mass balances slightly less than 100% or a series of small unidentified peaks in a GC or GC-MS trace), but a small amount of cross-linking could have a profound impact on the solvent swelling properties of a complex macromolecule. For example, polystyrene (an organic polymer highly soluble in organic solvents) can be made insoluble by cross-linking with only 1-2 mol % divinylbenzene. Therefore, to determine if a polymeric network can alter the reaction pathways, we have incorporated aromatic carboxylic acids into a polymeric network and studied the pyrolysis of the polymer under a variety of conditions.

In this investigation, we have synthesized poly(m-xylylene-co-5-carboxy-1,3-xylylene), **1**, as a polymeric model for aromatic carboxylic acids in low-rank coal. The density of carboxylic acid in the polymer, 2.3 carboxylic acids per 100 carbons, is similar to that reported for Beulah-Zap coal, 2.2 acids per 100 carbons [4]. To determine if the carboxy functional group enhances cross-linking reactions, the pyrolysis of **1** will be compared to the unsubstituted homopolymer,

2. Our previous studies on the pyrolysis of carboxy-substituted bibenzyls will also provide useful insights into interpreting the pyrolysis results for **1** [3].

$$\left[CH_2-\bigcirc-CH_2\right]\left[CH_2-\bigcirc_{CO_2R}-CH_2\right]_2 \qquad \left[CH_2-\bigcirc-CH_2\right]$$

1: R = H
3: R = CH₃

2
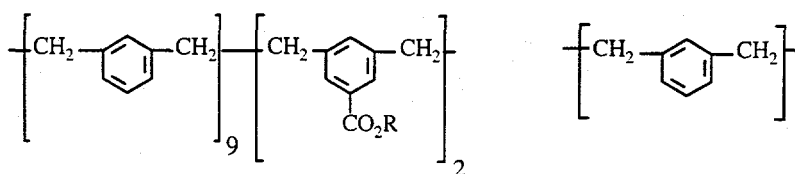
EXPERIMENTAL

The synthesis of **1** and **2** has been previously described [5]. The methyl ester of the carboxy polymer, **3**, was prepared by methylation of **1** with an excess of diazomethane. Molecular weight distributions were determined by gel permeation chromatography (GPC) using a Waters chromatography system consisting of a 600E system controller and pump, 717 autosampler, and 410 differential refractometer interfaced to a computer running Waters Millennium 2010 software for GPC analysis. A bank of three columns (Waters Styragel HR1, HR3 and HR5E) were calibrated using six narrow molecular weight standards (polystyrene, Mw 89,300; 25,400; 12,600; 4,000; 687 and bibenzyl, Mw 182) at 32 °C in THF at a flow rate of 1.00 mL/min. The molecular weight, M_N, and polydispersity (M_w/M_N) of **1** and **2** were 11,300 (2.8) and 9900 (2.5), respectively. A similar molecular weight was obtained for the methyl ester **3**. The polymers were characterized by ^{13}C-NMR, FTIR, and elemental analysis. By CP/MAS ^{13}C-NMR, there is one acid per 5.4 ± 0.5 aromatic rings or 2.3 acids per 100 carbons. Similar results were obtained by elemental analysis.

In a typical pyrolysis experiment, the polymer (ca. 45 mg) and a small plug of glass wool was loaded into a T-shaped tube (8 mm), the tube was pumped down, and sealed under vacuum (<10^{-5} Torr). One end of the tube was place in a liquid nitrogen trap and the polymer was placed in a Carbolite three zone tube furnace (38 mm ID). The pyrolysis temperature was measured by a RTD thermocouple placed beside the sample, and the temperature was held ±1.0 °C over the sample length. After the reaction, the tube was opened, the glass wool plug was rinsed with THF, and THF (2.0 mL) was added to the pyrolysis residue. The tube was capped and heated to 60-70 °C for 18-24 h. The THF layer was removed and the insoluble residue was washed with THF (2x). The combined washings were concentrated, dried under vacuum, weighed, redissolved in THF, filtered, and analyzed by GPC, GC, and GC-MS. The insoluble residue was dried under vacuum and weighed. The volatile products that collected in the cold trap were dissolved in CH_2Cl_2 (1.0 mL) containing an internal standard (pentamethylbenzene), and analyzed by GC and GC-MS.

Infrared spectra were recorded on a Bio-Rad FTS-60 FT-IR in a KBr matrix or as a thin film formed by pressing the polymer melt between Teflon sheets. TGA was performed on a Sinku-Riko differential thermal-galvimetric analyzer TGD 7000 and TGA-MS was performed on a TGD 7000 interfaced to a VG mass spectrometer. The heating rate for the TGA and TGA-MS experiments was 5 °C min^{-1} and the experiments were run under argon. Samples sizes were typically 10-25 mg for these experiments.

RESULTS AND DISCUSSION

Figure 1 show the weight loss curves for **1**, **2**, and **3** at a heating rate of 5 °C min^{-1} under argon. The thermograms for the three polymers are very similar: weight loss starts at ca. 400 °C with the major degradation occurring between 425 - 500 °C. However, the carboxylated polymer forms ca. 2.5 times more char than the unsubstituted polymer. Methylation of the carboxylic acid decreases char formation. A similar trend has been observed in the pyrolysis of lignite coal in which methylation increased tar yield and reduce cross-linking [1]. Figure 2a shows the evolution of volatile materials from the depolymerization of the homopolymer, **2**, by monitoring the benzyl fragment m/e 91 (C₇H₇⁺) from the fragmentation of the pyrolysis products in the mass spectrometer. From the sealed tube pyrolysis of **2** and **1** (see below), the major volatile products identified by GC-MS were monomer (m-xylene), dimer, trimer, and tetramer (which contain m/e 91 in their mass spectral fragmentation patterns). A similar TGA-MS evolution profile was found for **2** by monitoring the xylylene fragment (m/e 105). Figure 2b shows that the evolution of CO_2 (m/e 44) from **1** precedes depolymerization of the polymer backbone (by monitoring the benzyl fragment, m/e 91). For low-rank coals, a similar trend in gas evolution,

measured by TGA-FTIR, has been reported [1] in which CO_2 evolution precedes tar evolution. To our delight, these simple bibenzylic polymers reproduce many of the qualitative trends found in the pyrolysis of low-rank coals, but in a much simpler matrix such that it may be possible to gain mechanistic insight into specific reaction pathways that lead to cross-linking.

Much of the experimental data on the cross-linking behavior of low-rank coals has been obtain in pyrolysis experiments in which the volatile materials are swept away (sometimes for additional analysis) from the char by an inert gas. To investigate the pyrolysis of 1, 2, and 3 under conditions in which the volatile products are removed, the pyrolysis was performed in sealed T-shaped tubes (see experimental) under vacuum in which one leg of the tube was place in a liquid nitrogen trap to remove the volatile products. After pyrolysis, the tubes were broken. THF was added, and the solutions were heated to 60-70 °C overnight (16 h). The soluble and insoluble fractions were separated (if present) and the molecular weight distribution of the soluble fraction was determined by GPC. The results from the pyrolysis of the polymers are summarized in Table 1. Pyrolysis of 1, 2, and 3 at 375 °C for 1 h produced very small amounts of volatile products (as anticipated from the TG analysis and the low reactivity of bibenzyl at 375 °C). Analysis by GC and GC-MS found monomer, dimer, trimer, and tetramer as the major products. The residue from the pyrolysis of 2 and 3 was soluble in THF, but a large fraction of the residue from the pyrolysis of 1 was still insoluble in THF. As shown in entries 1, 2, 5-8 in Table 1, pyrolysis of 1 for <60 min at 375 or 400 °C typically produced 60-75 wt% of an insoluble polymer. The reactions that lead to a loss of solubility occur quickly at 400 °C because the yield of insoluble polymer is established after 15 min and does not change significantly except for long reaction times. However, the molecular weight of the THF soluble fraction decreases as the longer reaction times increase as a consequence of C-C homolysis. At very longer reaction times (60 h) at 400 °C, the yield of volatile products increased and some of the insoluble residue was converted to lower molecular weight products, but a significant fraction of the polymer still remained insoluble in THF. In contrast, no insoluble residue was found in the pyrolysis of 2 or 3 at 375 °C or 400 °C even at long reaction times (60 h, see entry 9 Table 1).

These results indicate that cross-linking reactions can occur in the bibenzyl polymer as a consequence of the carboxyl group to produce an insoluble polymer. This is in stark contrast to the results previously obtained in the pyrolysis of simple model compound (1,2-(3,3'-dicarboxyphenyl)ethane) in which no cross-linking was observed [3]. This highlights the importance of the polymeric network in influencing reaction chemistry. When the carboxylic acid is removed or methylated, the pyrolysis residue is completely soluble in THF and the yield of char decreases. The reaction pathways leading to the cross-linking reaction are currently under investigation and the results will be discussed in the presentation.

ACKNOWLEDGMENTS

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5. (a) Britt, P. F.; Buchanan, III, A. C.; Hoenigman, R. L. *Coal Science* Pajares, J. A.; Tascon, J. M. D. Eds.; Coal Science and Technology 24; Elsevier; Amsterdam, Netherlands, 1995, 437. (b) Mungall, W. S.; Britt, P. F.; Buchanan, III, A. C. manuscript in preparation.

Table 1. Thermolysis of **1. 2**, and **3** in sealed tubes under vacuum.

Entry	Polymer[a]	Temp °C	Time min	Volatile Products	THF Soluble	M_w x10³ [b]	THF Insoluble	Mass Balance
1	1	375	60	1 %	41 %	10.8	60 %	102 %
2	1	375	60	1 %	31 %	23.2	67 %	99 %
3	3	375	60	1 %	93 %	74.7	–[c]	94 %
4	2	375	60	1 %	95 %	19.0	–[c]	96 %
5	1	400	15	2 %	24 %	7.3	73 %	99 %
6	1	400	30	4 %	18 %	4.4	76 %	98 %
7	1	400	60	7 %	21 %	3.5	73 %	101 %
8	1	400	3600	49 %	7 %	1.3	39 %	95 %
9	2	400	3600	26 %	70 %	7.6	–[c]	97 %

[a] M_w of **1, 2**, and **3** is 31,500, 24,700, and 33,100, respectively. [b] Weight averaged molecular weights determined by GPC vs. polystyrene standards. [c] No insoluble material was detected.
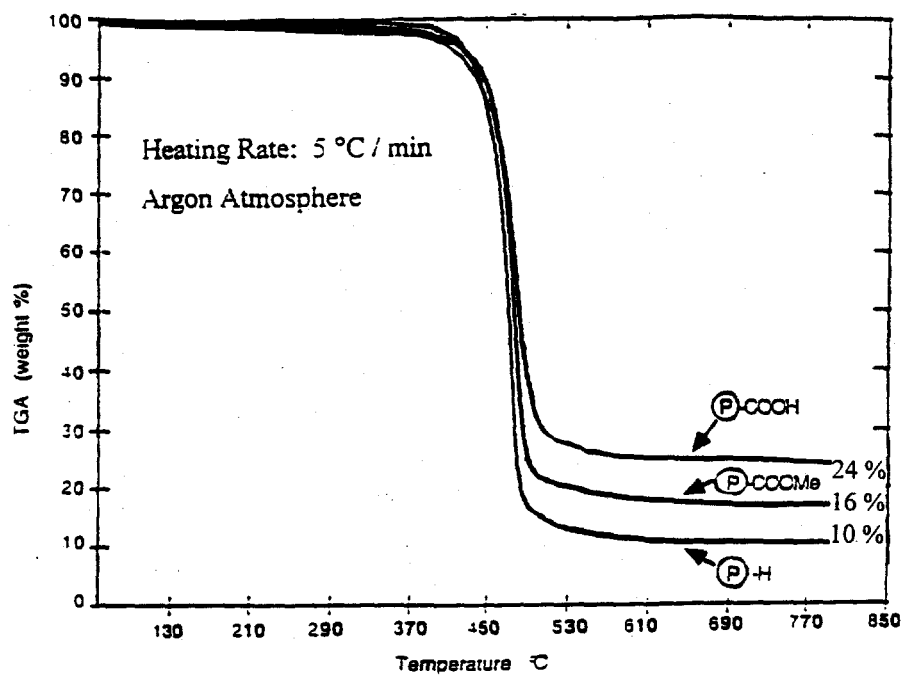

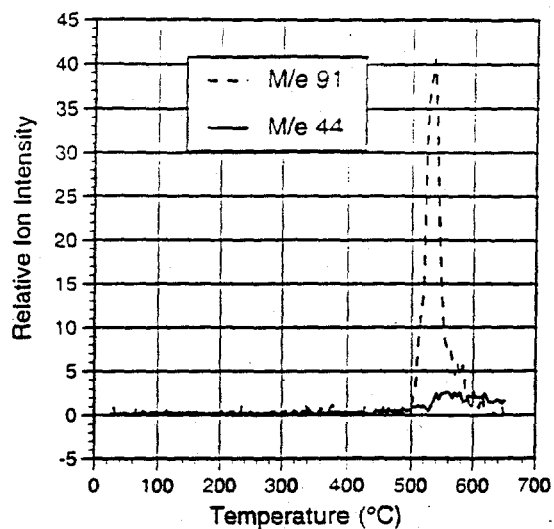Figure 1. TG curves for polymers **1** (P-COOH), **2** (P-H), and **3** (P-COOMe).

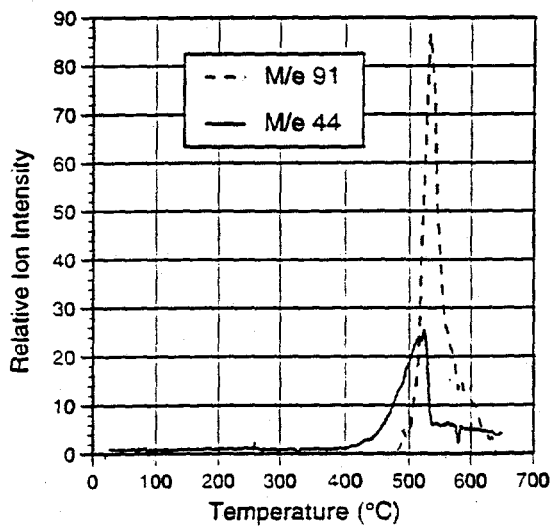Figure 2a. TG-MS of **2** (P-H) monitoring *m/e* 91 (benzyl fragment) and *m/e* 44 (CO_2).

Figure 2b. TG-MS of **1** (P-COOH) monitoring *m/e* 91 (benzyl fragment) and *m/e* 44 (CO_2).