

# Kinetics of Petroleum Pitch Polymerization by Gel Permeation Chromatography

by

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## Introduction

The thermal transformation of pitches to mesophase and coke involves polymerization reactions.<sup>1</sup> Although the mesophase has received considerable attention, due to its fundamental importance in carbon processes, kinetic studies of pitch polymerization, however, are limited.<sup>1</sup> A few kinetic studies have been accomplished by measuring changes in pitch solubility,<sup>2,3</sup> carbon-hydrogen ratios,<sup>4</sup> and free radical concentrations.<sup>4</sup> Additionally, although pitches contain a broad distribution of molecules with different molecular sizes, the relation of reaction rate to molecular size is not completely understood.<sup>5,6</sup>

The polymerization kinetics of many polymer systems have been followed using gel permeation chromatography (GPC). The GPC technique, developed in this laboratory, which utilizes quinoline eluent and chemical reduction procedures for pitch solubilization, is capable of determining accurate molecular weight distributions (MWD) of mesophase pitches and semi-coke, which have quinoline insoluble (QI) contents as high as 100%.<sup>7</sup> Therefore, the determination of the fundamental kinetic parameters of pitch polymerization to semi-coke, i.e., rate constants, reaction order, and activation energy, as a function of both molecular weight (MW) and reaction time, can be achieved.

## Experimental Procedures

### Heat Treatment of Petroleum Pitches

The kinetic studies were performed utilizing commercial petroleum pitches which produced large domain size mesophase. The petroleum pitches and extracted pitches were heated in tube furnaces under flowing argon atmosphere using a variety of temperature (380°C to 470°C) and time (one hour to 600 hours) conditions to produce polymerized pitches with QI contents varying between 10% and 99%. The tube furnace temperatures were controlled to within 0.3°C.

### GPC

Details of the GPC procedures and pitch solubilization techniques have been described.<sup>7</sup> In order to minimize instrumental

errors in the GPC data, such as those which result from column aging, samples in a kinetic series were chromatographed in as short a time period as possible. The chemically reduced samples evaluated were 100% soluble in the GPC eluent, quinoline.

## Calculation of Fundamental Kinetic Parameters

In order to separate the processes of chemical polymerization and physical distillation, the kinetic parameters were determined only on those samples in which the low MW distillable volatiles had been removed. The kinetic parameters were measured from the GPC curves by monitoring the disappearance of pitch molecules in a specific MW range. For example, for calculating the first order rate constants, the weight percent of a specific MW range was measured from area normalized GPC curves. The cutout areas of the specific MW range were weighed and converted to a weight percent, which was the concentration value used in the first order kinetic equation.

## Experimental Results

### Pitch Polymerization Kinetics During Mesophase Formation

The polymerization of petroleum pitch molecules in the 450 to 750 MW range obeyed first order kinetics. The rate constant values did not change over this MW range (approximately  $0.70 \times 10^{-5} \text{ sec}^{-1}$ ) when measured between four and 16 hours at 400°C. The most striking observation of the GPC curves of this kinetic series is that significant amounts of polymerized pitch with MW greater than 1000 are present in the early stages of reaction, but that molecules with MW of approximately 2000 are not present even after 16 hours. This fact indicates that the reactions of the 1000 MW and larger molecules are negligible, and suggests a rapidly decreasing polymerization rate constant above MW 700. To accurately locate the gradient in rate constants, the highest MW molecules (upper 25% fraction) in the petroleum pitch were separated by fractionation using a toluene-hexane (85-15% volume ratio) mixture. By using this procedure, one could study the reactivity of the 700-1100 MW range molecules separately from the reaction of the 400-800 MW range molecules. The polymerization reactions of the 700 to 1000 MW

molecules obeyed first order kinetics and the rate constants (Figure 1a) decrease significantly with increasing MW. The stability of the larger pitch molecules during mesophase formation (Figure 1a), results in relatively narrow MWD. The activation energy of these molecules measured between 380°C and 420°C were 47 to 51 Kcal/mole, values similar to those obtained by solubility techniques.<sup>2,3</sup>

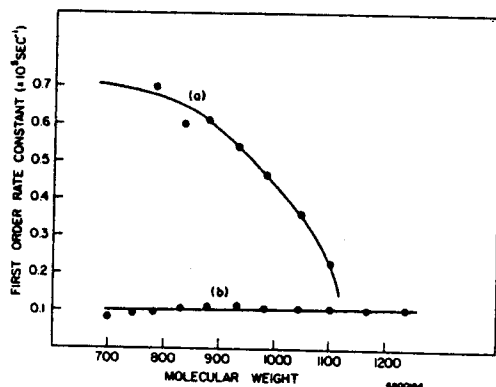


Figure 1. Rate Constants of Molecules in Extracted Pitch at 400°C. (a) 5-25 Hours, 19-55% QI; (b) 25-161 Hours, 55-99% QI.

#### Pitch Polymerization Kinetics During Semi-Coke Formation

Polymerization kinetics were obtained on both pitch and the extracted pitch samples which were heated between 390°C and 470°C to form 55% to 99% QI materials. The differences observed from the GPC curves of a kinetic series in this high QI regime compared to the low QI regime are: (1) that the reactivity of pitch molecules between MW 800 and 1500 are now similar, (2) that the rate constants are much lower, and (3) that the MWD is broadening. A first order kinetic plot of the 800 to 1500 MW molecules is not linear indicating that the reactions are no longer first order. However, second order plots are linear. In order to compare the reactivity of pitch molecules that occur at short (mesophase formation) and long (semi-coke) reaction times, the best first order rate constants were calculated as a function of MW at the longer times at 400°C and are plotted in Figure 1b. The rate constants at the longer times are smaller by a factor of seven and are all equal.

#### Other Kinetic Experiments

The abrupt change in the rate constants of pitch molecules after mesophase had formed was found to correlate with the loss of the methyl protons in the pitch. A recently developed <sup>1</sup>H-NMR technique,<sup>8</sup> coupled with elemental hydrogen analysis was used to monitor the disappearance of the methyl side chain protons during polymerization of the pitch to the semi-coke. The results indicated: (1) that the methyl group cracking rate constants also abruptly change after mesophase formation, and (2) that the values of these rate constants are essentially identical to the GPC polymerization

rate constants of Figure 1 measured during the two regimes.

In another kinetic experiment, the quinoline soluble (QS) fraction was removed from a semi-coke containing 60% QI and was subjected to thermal polymerization. The QS molecules, which reacted very slowly in the semi-coke, reacted more than a factor of ten faster after isolation.

#### Discussion

The kinetic study shows that the rate constants of pitch molecules varies both as a function of size and time. Fortunately, the pitch polymerization process during mesophase formation does not proceed like the chain reaction typical for conventional polymers. The stability of the larger molecules, which correlates with the formation of highly stable free radicals,<sup>9</sup> ensures that the mesophase remains highly fluid during a wide range of reaction conditions. The abrupt decrease in the rate constants, which occurs after the completion of mesophase formation, appears related to a physical phenomenon in which solid state, rather than liquid state reactions, are occurring in the polymerized pitch. The effect is identical to reactions in other thermosetting systems, whose reactions also proceed slowly after vitrification.<sup>10</sup> The equal reactivity of molecules after mesophase vitrification results in a broadening of the MWD, a condition which is now similar to chain reactions of many polymer systems. The similarity of the measured rate constants for the loss of methyl protons to the pitch polymerization rate constants as measured by GPC, suggests that the methyl group is involved in the polymerization process through the semi-coke stage. The significant increase in the reactivity of the low molecular weight QS fraction which was removed from the semi-coke confirms that a physical phenomenon (solid state versus liquid state reactions) is responsible for the significant change in the rate constants.

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