

# MOLECULAR WEIGHT CHARACTERIZATION OF ISOTROPIC AND MESOPHASE PITCHES BY MATRIX ASSISTED LASER DESORPTION IONIZATION MASS SPECTROMETRY

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## Introduction

The molecular weight (MW) characterization of heavy petroleum fractions and residues, isotropic pitches, and mesophase pitches is difficult for several reasons. Most of these materials do not dissolve completely in organic solvents. Aggressive solvents, such as pyridine (Py), quinoline (Q), and trichlorobenzene (Cl<sub>3</sub>Ph), dissolve >95% of many of these substances; but typically 1-5% of the residues and isotropic pitches remain insoluble. Mesophase pitches are 10-20X less soluble. Because classical techniques, such as gel permeation chromatography (GPC) and vapor phase osmometry (VPO), used for MW determinations require dissolution of the analyte, Greinke<sup>1</sup> developed ingenious chemical reduction methods to solubilize these materials. These methods provide valuable molecular weight information but are laborious and time consuming. Development of a rapid, easy method, Matrix Assisted Laser Desorption Ionization Mass Spectrometry (MALDI), to obtain accurate average MWs and MW distribution of pitches has recently been reported.<sup>2</sup> We would also like to report on the effectiveness of this technique. In the present study we show that for typical pitch materials the mass spectrometer's laser desorption power and the spectrometer's analyzer polarity affect the mass spectra or MW distribution. Choices of laser power and analyzer polarity are reviewed for these samples. Under the optimum conditions the MW profiles of several different isotropic and mesophase pitches are presented. For each type of pitch, isotropic or mesophase, distinct MW distributions and calculated average MWs,  $M_n$  and  $M_w$ , and polydispersity,  $P_d$ , were obtained from the MW profiles. Differences in the profiles can be used to distinguish pitch type and can be attributed to variations in processing. For certain materials discrete oligomers were resolved by the mass spectrometric technique.

## Experimental

A Perceptive Biosystems Voyager RPDE Time-of-Flight (TOF) mass spectrometer was used to record mass spectra. A 337-nm N<sub>2</sub> laser was used to desorb molecules from the samples. The power of the laser was attenuated from its full power of 10<sup>7</sup> J/cm<sup>2</sup>. Laser power intensities in arbitrary units of 2000, 2190, 2300, 2500, 2600, and 2700 were employed. Mass spectra were recorded with the polarity of the analyzer both in positive- and negative-ion modes. GRAMS/386 software was used to convert the raw data into profiles of the MW distribution and to calculate number- and weight-average MWs,  $M_n$  and  $M_w$ , and polydispersities,  $P_d$ . Two types of isotropic pitch and three types of mesophase pitch were examined on the mass spectrometer. The two isotropic pitches and two of the mesophase pitches were synthesized at Conoco. The other mesophase pitch was a commercial product, Mitsubishi Gas Chemical (MGC) ARA 240 mesophase. With no sample was an ancillary matrix used to

assist in the ionization.

## Results and Discussion

Carbonaceous pitches can be classified as either isotropic or anisotropic. Isotropic pitches are mixtures of relatively high molecular weight (MW) hydrocarbon molecules. In the liquid state the orientation of the molecules in isotropic pitches is random, though the pitches may contain mesogens. Pitch mesogens are the precursors to liquid crystalline or anisotropic pitch, also known as mesophase pitch. Mesophase pitches, like isotropic pitches, are mixtures of high molecular weight hydrocarbons; but the molecules in the liquid state are oriented. The ability to determine the MW and the MW distribution of isotropic and anisotropic pitches is useful for characterizing these materials: the MW and MW distribution can be used to describe differences in pitch materials and the effects of processing. Matrix assisted laser desorption ionization mass spectrometry (MALDI MS) has been shown to be an easy and effective way to determine the MW of carbonaceous pitches once conditions to operate the spectrometer have been optimized.

MW distributions of a commercial mesophase pitch, Mitsubishi Gas Chemical (MGC) ARA 240, recorded after desorption at various laser powers will be presented. This mesophase is produced by catalytically polymerizing naphthalene. Curves will be shown with the analyzer polarity in the positive- and negative-ion modes. As the laser power increases, the MW distribution changes and  $M_n$  and  $M_w$  increase. Similar results were found for mesophase pitches made by thermally polymerizing coker feedstocks.  $M_n$ 's of three thermally processed mesophases will be compared as determined by vapor phase osmometry (VPO) and MALDI. The most consistent representation of the MW distribution of mesophase was judged to be when the laser power was set at 2190 and the analyzer polarity set in the positive-ion mode. A laser power of 2190 is optimal, moreover, based on the amount of baseline signal measured and the increase in intensity measured at higher powers. The increased signal observed at laser powers above 2190 is due to fragmentation and recombination products. Spectra recorded in the negative-ion mode, however, may be more accurate representations of the MW distributions: aromatic carbanions are more stable than aromatic carbonium ions in these systems.

MW distributions for two types of isotropic pitches made using Conoco's proprietary pitch technology will be illustrated. A regular series of peaks can be attributed to distinct oligomers that form upon polymerization of the feedstocks. These isotropic pitches can then, in part, be converted into Conoco's patented solvated mesophase pitches. MW distributions,  $M_n$ ,  $M_w$ , and  $P_d$  for three solvated mesophases will be presented. Peaks in the distributions

correspond to the peaks observed in the isotropic pitches, but the relative heights of the peaks are shifted to higher mass units. Consistent with the shift to higher mass units are greater average MWs for the mesophase pitches. As with MGC mesophase and thermally processed mesophase, mass spectra for solvated mesophases recorded in the negative-ion mode have more intensity at higher mass units than do solvated mesophases recorded in the positive-ion mode. From the profiles of MW distribution and other analytical data the molecular structure of the predominant monomers can be deduced. Some structures of the monomers will be discussed.

Compared to conventional mesophase pitches, MGC ARA 240 and thermally polymerized products, Conoco solvated mesophases are characteristically different. The difference between conventional mesophase pitches and Conoco's solvated mesophases are the following. Conventional mesophases display broad, nondescript, MW distributions.

Conoco solvated mesophases exhibit broad distributions with well resolved peaks. This kind of distribution is more typical of the kind observed for classical polymers such as polystyrene. Furthermore the  $M_n$ 's and  $M_w$ 's for Conoco's solvated mesophases are several hundred daltons greater than the MWs for conventional mesophases. These are unique features of Conoco solvated mesophases which were not easily measurable by prior analytical techniques.

In summary MALDI mass spectrometry has been shown to be a valuable aid in the characterization of isotropic and mesophase pitches. First it is a straightforward technique that requires little sample preparation. Second it allows high molecular weight, intractable carbonaceous materials to be perceived in a new and enlightening manner. And third it can be used to illustrate how products from various processes differ and what is characteristic about the products from these processes.