CARBON 79 (2014) 265–273

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

Liquid crystallinity in trimer oligomers isolated from petroleum and pyrene pitches

David F. Esguerra [a], *Wesley P. Hoffman* [b], *Mark C. Thies* [a,*]

[a] *Department of Chemical and Biomolecular Engineering, Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634-0909, USA*

[b] *Air Force Research Laboratory, AFRL/RQRC, 10 E. Saturn Blvd. Edwards, CA 93524-7680, USA*

ARTICLE INFO

Article history:
Received 5 February 2014
Accepted 24 July 2014
Available online 1 August 2014

ABSTRACT

The first unsubstituted, monodisperse polycyclic aromatic hydrocarbon (PAH) to form a liquid crystalline phase (100% mesophase) has been isolated. With a molecular weight of 598 Da and consisting of only 14 aromatic rings, this pyrene trimer is also the lowest molecular weight (mol wt) PAH species for which the existence of liquid crystallinity has been reported. Multiple isomers of the pyrene trimer exist, providing the melting-point depression (mpt = 290 °C) necessary for the existence of a liquid phase and the possibility of mesophase formation. The trimer cut of M-50 pitch (mol wt = 645–890 Da; mpt = 330 °C) has also been isolated and was found to consist of ~40% mesophase. This trimer is the lowest average mol wt carbonaceous pitch for which significant mesophase formation has been reported. Both trimers were isolated from their starting pitches via packed-column supercritical extraction, using toluene and N-methylpyrrolidone (NMP) mixtures as the extractive solvent. Mass spectrometry and UV–vis and fluorescence spectroscopy were used for molecular characterization. The results of this study indicate that for PAHs, the molecular weight for which liquid crystallinity occurs can be significantly reduced by creating PAH oligomers with lower polydispersity and increased monomer-unit homogeneity.

1. Introduction

Since the discovery of carbonaceous mesophase by Brooks and Taylor in the early 1960s [1,2], researchers in the carbon community have sought to understand what mesophase pitch is in terms of its molecular structure and composition. Although this issue has been addressed with quality work over a number of years [3–14], both the polydispersity of the pitch and the poor solubility of the polycyclic aromatic hydrocarbon (PAH) oligomers comprising mesophase pitch have limited the ability of researchers to accurately isolate, characterize, and quantify the constituent oligomers comprising mesophase. The formation of liquid crystalline phases in carbonaceous pitch is known to be thermodynamically favored at certain combinations of molecular weight (mol wt), molecular structure, and mixture composition [10]. However, the quantitative effect of these and other factors, such as polydispersity and oligomeric composition, is still not well understood.

To the best of our knowledge, there are only a few examples of work directly addressing the effects of molecular composition and structure on the development of mesophase.

---

[*] *Corresponding author*: Fax: +1 864 656 0784.
E-mail address: mcths@clemson.edu (M.C. Thies).

http://dx.doi.org/10.1016/j.carbon.2014.07.067

Lewis and Kovac [3] evaluated a wide range of pure PAHs containing up to 10 aromatic rings (i.e., up to molecular weights of ~450 Da) and reported that none formed a liquid crystalline phase upon melting. However, when they heat-treated terrylene (8 aromatic rings with mol wt = 376) at 350 °C, the reaction produced a liquid crystalline phase. The authors concluded that the dimer of terrylene (15 rings with a mol wt of 748 Da) must have formed, indicating that PAHs containing at least 15 aromatic rings should readily form mesophase. However, no attempt was made by the authors to determine the actual composition of the claimed "dimer" product. Greinke and Lewis [7] suggested oligomer sizes of pentamer to heptamer as the average composition for their naphthalene- and methylnaphthalene-pitch mesophases, with number average mol wts of the two mesophases (as obtained by gel permeation chromatography (GPC)) being 880 and 900, respectively. Similarly, Greinke and Singer [6] reported number average mol wts of 900–930 for thermally produced, petroleum-derived mesophase pitches produced at 3 different heat-treatment conditions.

In more recent work, Hurt and Hu [10] analyzed the relationship between melting point and molecular weight for both pure PAHs and carbonaceous pitches. They pointed out that mesophase is typically observed in pitches at 350–500 °C, with these pitches having a broad mol wt distribution, typically somewhere within the 470–2000 Da range. For pure PAHs, however, the situation is markedly different. Even PAHs in the 500–600 Da region (e.g., hexabenzocoronene, mol wt 522 Da) decompose before melting, bypassing mesophase formation. As discussed above [3], lower mol wt PAHs do melt, but they form only an isotropic liquid phase. Hurt and Hu [10] emphasize this point by reminding the reader that "*no* unsubstituted, single-component PAH" has ever been observed to form mesophase. We note in passing that Müllen and coworkers [15] synthesize pure giant PAHs, e.g., hexa-*peri*-hexabenzocoronenes that self-assemble into columnar liquid crystalline phases. But it is only the presence of their long alkyl substituent chains (which makes them liquids at near-ambient temperatures) that makes this phenomenon possible.

To help us understand the effects of factors such as molecular weight, molecular structure, and polydispersity on mesophase formation in pitches, our group has developed a strategy for the isolation and analytical characterization of the individual constituents of carbonaceous pitches [16–20]. First, oligomeric fractions (e.g., dimers and trimers) are isolated from the starting pitch via packed-column supercritical extraction (SCE). These oligomers are then further separated into their individual species via chromatographic methods, such as GPC and Reverse-Phase (RP) HPLC, so that the species can be characterized. By using such an approach, Tekinalp et al. [21] isolated a 99% dimer fraction from a petroleum pitch (M-50) produced by the heat soaking of aromatic decant oil. However, that fraction formed a 100% isotropic phase upon melting. Thus, the goals of this work were to evaluate higher mol wt oligomers for mesogenic behavior – in particular, to isolate, structurally characterize, and analyze for mesophase pure *trimer* fractions from two representative pitches: M-50 petroleum pitch and a synthetic pitch produced by the catalytic polymerization of pure pyrene monomer with $AlCl_3$.

2. Experimental

2.1. Materials

A petroleum-derived isotropic pitch (M-50) was obtained from Marathon Petroleum Company LLC and was used as received. A Matrix-Assisted Laser Desorption/Ionization Time-of Flight (MALDI-TOF or MALDI) mass spectrum of this pitch is presented as Fig. 1a. The oligomeric fractions in this pitch are classified by molecular weight as follows: monomer (i.e., species in the 210–388 Da range); dimer (388–645 Da); trimer (645–890 Da); and tetramer (890–1120 Da).

Pyrene pitch was prepared by the catalytic polymerization of pyrene monomer (95% purity, CAS 129-00-0, from Sigma Aldrich) in a pressurized reactor (reactor volume: 500 mL) for 1 h at temperatures of 350–400 °C using aluminum trichloride ($AlCl_3$; 98% purity, CAS 7446-70-0, from Sigma Aldrich) as the catalyst. No attempts were made to remove the catalyst at the end of the polymerization. A MALDI mass spectrum of this pitch is given as Fig. 1b. Monomer (202 Da), dimer (400 Da), trimer (598 Da), and tetramer (796 Da) species are observed as well as methylated monomer and oligomers (e.g., methyl and dimethyl pyrene at 216 and 230 Da; methyl and dimethyl pyrene dimers at 414 and 428 Da respectively),

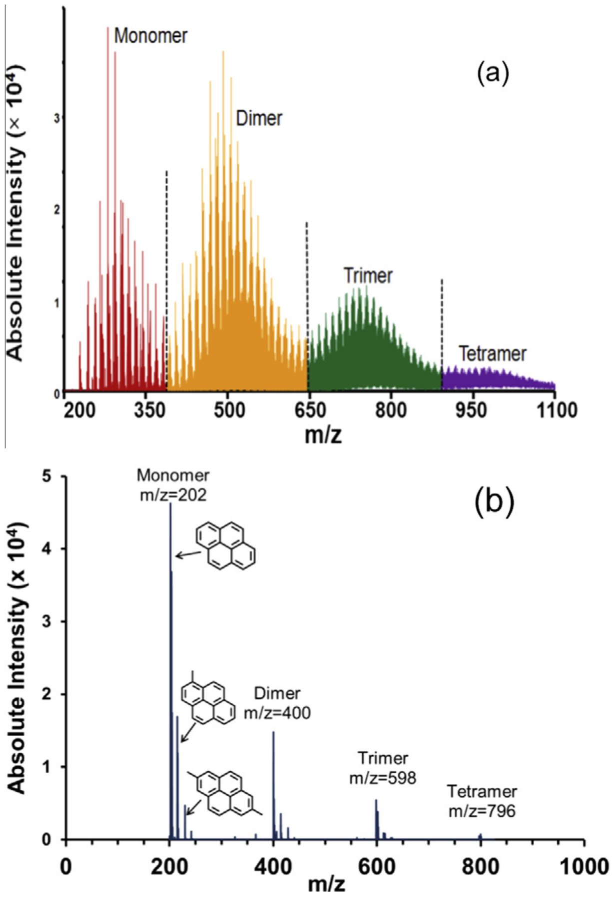

Fig. 1 – (a) MALDI mass spectrum of M-50 Pitch [18]. (b) MALDI mass spectrum of a pyrene pitch produced catalytically using $AlCl_3$ [19]. (A color version of this figure can be viewed online.)