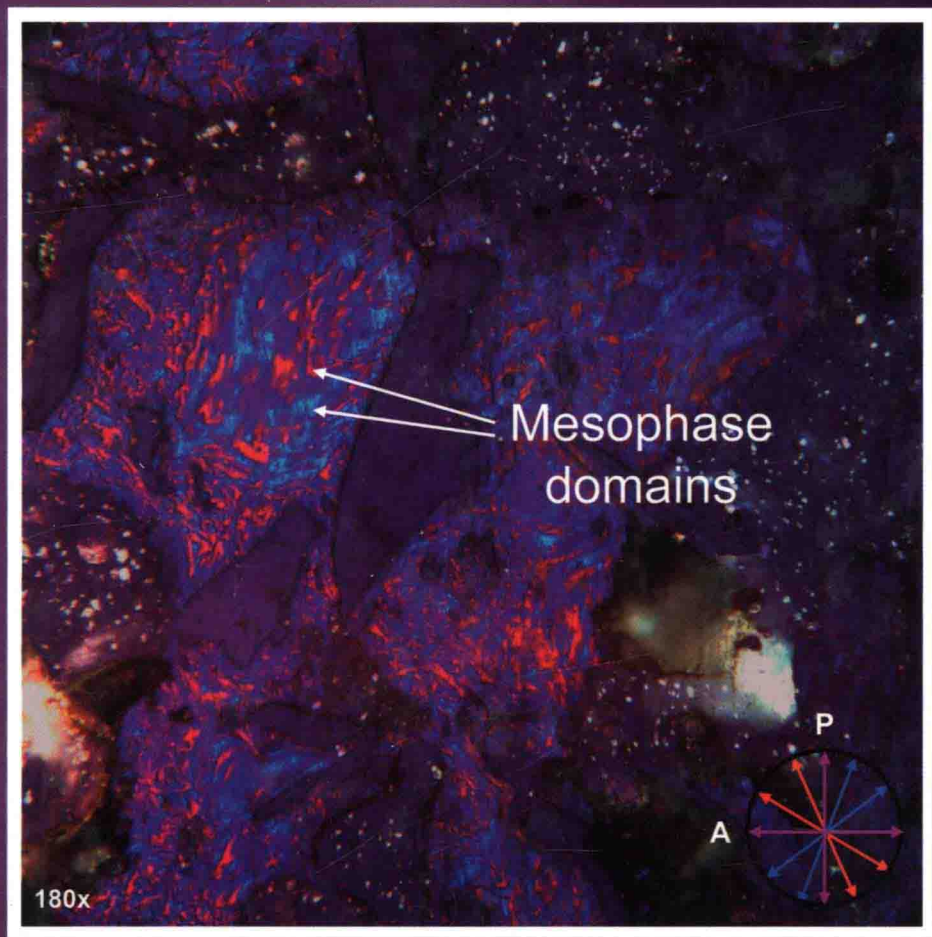


ACS SYMPOSIUM SERIES 1173

# Polymer Precursor-Derived Carbon



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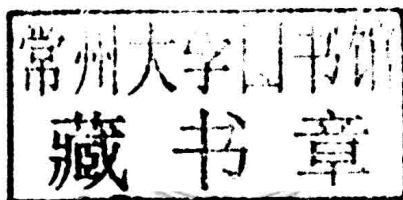
**Amit K. Naskar and Wesley P. Hoffman**

ACS SYMPOSIUM SERIES **1173**

# Polymer Precursor-Derived Carbon

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Sponsored by the  
ACS Division of Polymer Chemistry, Inc.



American Chemical Society, Washington, DC

Distributed in print by Oxford University Press



## Library of Congress Cataloging-in-Publication Data

Polymer precursor-derived carbon / Amit K. Naskar, editor, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Wesley P. Hoffman, editor, Air Force Research Laboratory, Edwards AFB, California ; sponsored by the ACS Division of Polymer Chemistry, Inc.

pages cm. -- (ACS symposium series ; 1173)

Includes bibliographical references and index.

ISBN 978-0-8412-2966-2 (alk. paper)

I. Carbon composites. 2. Carbon. 3. Polymers. I. Naskar, Amit K., editor. II. Hoffman, Wesley P., editor. III. American Chemical Society. Division of Polymer Chemistry.

QD181.C1P58 2014

546'.681--dc 3

2014037321

The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences—Permanence of Paper for Printed Library Materials, ANSI Z39.48n1984.

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# **Polymer Precursor-Derived Carbon**



# Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

**ACS Books Department**



# **Dedication**

In memory of Professor James E. McGrath,  
who inspired us to organize this endeavor.





# Preface

Carbon is essential to life on Earth, and it forms complex molecules with oxygen, hydrogen, and nitrogen that are ubiquitous in the biosphere. Elemental carbon has been valued for thousands of years for its use in processing metal ores. The variety of carbon allotropes as well as the vast variety of carbon's architectures, and forms is made possible by its ability to form  $sp$ ,  $sp^2$ , and  $sp^3$  electronic orbitals through hybridization. These various architectures and forms can encompass a very broad spectrum of properties, which, in turn enable a myriad of applications. Traditional methods for synthesizing carbon-based materials include catalytic vapor growth, hydrothermal processing of colloids, chemical vapor deposition, as well as pyrolysis of precursors, such as fibers, bulk monoliths, fuels, and fuel derivatives. Some of these methods follow a combinatorial optimization approach, which does not necessarily enable the desired control of carbon architecture. The science of controlling carbon structure with predefined geometries and controlled levels of long-range order from atypical char-forming precursors has yet to be established.

Over the last two decades there have been significant improvements in synthesis routes of carbon materials, analytical tools for characterization, and in the properties of carbon materials. Monolithic or continuous matrix carbon products are commercially produced from polymeric and pitch carbon precursors. Specialty carbon materials are used for energy applications and reduction in carbon emission, membrane separation, energy storage, catalysis, solar utilization, electronics, and sensing. New generation higher-performance structural carbon fibers have the potential to enhance vehicle efficiency and reduce greenhouse gas emission when used as composite lightweight structures.

This book, *Polymer Precursor-Derived Carbon*, is based on an international symposium organized by the editors, along with Professor Dennis W. Smith Jr. of UT-Dallas, and held at the 2013 national ACS meeting in New Orleans, Louisiana. Many exciting new findings were reported in the symposium, which was attended by researchers from academia, industry, and government research laboratories.

The editors would like to thank the authors for their timely contributions to this endeavor, for without their cooperation this undertaking would not have succeeded. The editors would also like to thank POLY Division of the American Chemical Society and Oak Ridge National Laboratory for sponsoring the symposium. A very special thank you goes to Professor Dennis Smith, who has worked in this field for years, conceived the idea for this symposium, spearheaded its organization, and worked tirelessly toward its success.

We are also grateful to the publishing editor and editorial office of the American Chemical Society for their efforts and professionalism in publishing this book.

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## Chapter 1

# Self-Assembly of Polyaromatic Precursors for 1D and 2D Carbon Structures

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Self-assembly of amphiphiles is used as a tool for structuring carbonaceous materials in one and two dimensions. The dynamics of low-molecular weight amphiphiles are combined with the stability of their high-molecular weight analogues in order to control the self-assembly of these molecules. Two concepts for structuring carbon by self-assembly are presented. In the first, hexaphenylbenzene-polyethylene glycol (HPB-PEG) derivatives lead to fiber-like structures in aqueous solution. The water content in the hydrogel fibers of HPB-PEG derivatives can be controlled by the substitution pattern of the amphiphile and by the length of the PEG chains. The fiber formation is verified by light scattering and TEM. In the second concept, homogeneous porous carbon membranes are obtained after electron irradiation and pyrolysis of a thiol-substituted HPB. In both concepts, amphiphilicity, geometry and size of the molecules are decisive parameters for the formation of defined structures.

## Introduction

Synthesis of carbonaceous materials is becoming more and more important in materials science. Most prominent examples of the obtained materials are fullerenes (1), carbon nanotubes (CNTs) (2) and carbon fibers. Fullerenes and CNTs are fabricated by chemical vapor deposition (CVD) (3), laser ablation (4) or arc discharge (5). Carbon fibers can be produced by spinning of poly(acrylonitrile) or other carbon sources and pyrolysis (6). Another well-known allotrope of carbon is graphene. Graphene is a monolayer of graphite. Segments of graphene can be prepared as graphene nanoribbons (GNRs). They are produced by electron beam lithography, opening of CNTs (7) or synthetically starting from small aromatic molecules (8–11). They can be used in field-effect transistors due to their finite band gap (12).

In most cases, pyrolysis of precursors or CVD yield carbonaceous materials with defect structures or multilayers. For more defined materials, we propose self-assembly processes which are known from nature (cf. protein folding, DNA, cell membranes, tobacco mosaic virus) (13) as a useful tool for structuring carbonaceous materials on the nanometer scale. In particular, we suggest the formation of well-defined aggregates of precursor molecules for the formation of carbon rich materials is possible. Self-assembly is defined as the formation of discrete architectures from building blocks that can range in size from atoms and molecules up to macroscopic units (14). Despite the great deal of progress made over the last several years, understanding the parameters and predicting the properties of self-assembly remain fundamental problems. The driving force for self-assembly is microphase separation of hydrophilic and hydrophobic blocks in ordered structures (15). The structures can be controlled by intramolecular and intermolecular interactions such as hydrogen bonds,  $\pi$ - $\pi$  stacking and van der Waals forces.

A prerequisite for the use of self-assembly for carbonaceous materials is the understanding of the process and the parameters for the aggregation. In order to tune the structures by self-assembly, there must be a balance between the stability and the thermodynamic control. Small amphiphiles like sodium dodecyl sulfate or lutensols with high critical micelle concentration (cmc) ( $\text{cmc} > 10^{-2} \text{ mol l}^{-1}$ ) form small aggregates (micelles) in an equilibrium while amphiphilic block copolymers with a high-molecular weight ( $\text{cmc} < 10^{-7} \text{ mol l}^{-1}$ ) lead to kinetically arrested non-equilibrated structures (16–18). By preparing amphiphiles with intermediate molecular weights, the potential advantages of low-molecular weight (dynamics) and high-molecular weight copolymers (stability) can be combined and investigated. The self-assembly of these structures with respect to the different size of the polar groups and the shape of the molecules is explored (Figure 1).

Until now, self-assembly of functionalized aromatics has dealt with linear rigid aromatics (e.g. tetra-*p*-phenylene, oligo(phenylene vinylene)) (19). In contrast to literature, we have chosen amphiphiles with a bulkier headgroup to study the influence of the shape of the hydrophobic and hydrophilic part of the self-assembly. We focus on the propeller-like hexaphenylbenzene (HPB) because the corresponding dehydrogenated disk-like hexa-*peri*-hexabenzocoronene

(HBC) as hydrophobic building block (Figure 2) is already known for forming extended columns in solution due to the strong  $\pi$ - $\pi$  stacking between the extended polyaromatic units. Therefore, a thermodynamic control of the self-assembly process cannot be guaranteed (20).

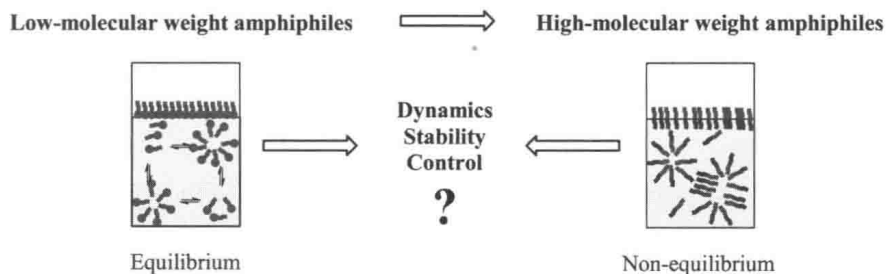


Figure 1. Schematic representation of low-molecular weight amphiphiles (left) and of high-molecular weight analogues (right).

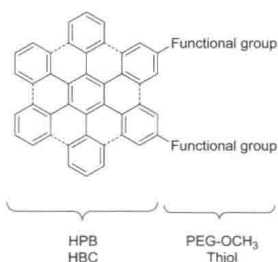


Figure 2. Schematic structural formula of the molecules whose self-assembly is presented in this work.

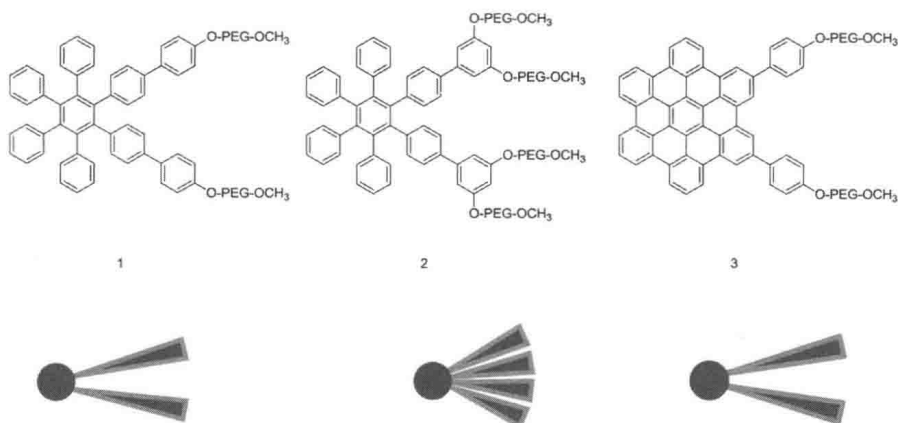


Figure 3. Molecular structure of Molecule 1 - 3 and a schematic representation of the aspect ratio. (see color insert)



The main focus of this work is on the fiber formation in one dimension and on membranes in two dimensions based on these amphiphiles. In the first concept, HPB is decorated with two and four PEG chains (Figure 3). It will be shown that depending on the molecular structure, the self-assembly can be adjusted. We are able to demonstrate that HPB-PEG derivatives form either micelles or lamellar structures. Sheet-like structures are achieved by surface deposition of dithiol functionalised HPB on gold. Subsequent crosslinking by electron beam followed by pyrolysis yields nanomembranes.

## Fibers of HPB/HBC with PEG Chains – 1D

In fiber formation processes, either physical methods such as extrusion (21), microfluidic processes (22), electrospinning (23) or spontaneous self-organization (24) are used. We investigate the self-assembly of aromatics with PEG chains for fiber formation. It is expected that supramolecular structures are formed by the amphiphilicity. Self-assembly of aromatics with PEG chains have been described in many cases in literature (25). However, a dense packing inside the core and the shell is always assumed and the role of water has been ignored. In order to better understand the kinetics of the self-assembly and water's possible role in these processes, we make a comparison of amphiphilic, aromatic propeller-like molecules and planar, rigid molecules. Therefore, the self-assembly of HPB-PEG derivatives is compared with the more rigid HBC-PEG derivative (3) (Figure 4).

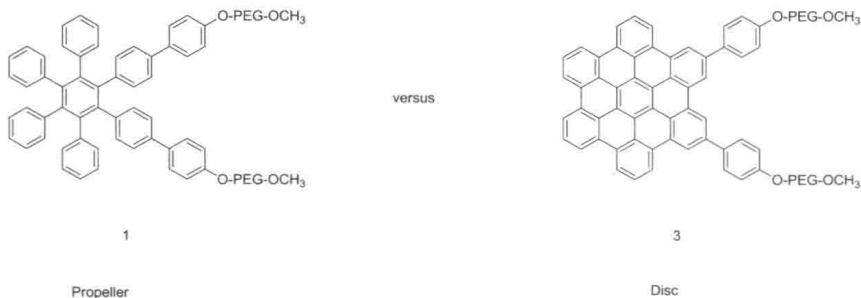


Figure 4. Molecular structure of HPB with two PEG chains (1) and HBC with two PEG chains (3).

### Self-Assembly of HPB-PEG Derivatives

Two HPB derivatives **1** and **2** were designed (Figure 5) in order to study the influence of the amphiphility and the shape on the self-assembly process. Molecule **1** has two long PEG chains ( $M_n = 750 \text{ g mol}^{-1}$ ) whereas molecule **2** has four short PEG chains ( $M_n = 380 \text{ g mol}^{-1}$ ). In both molecules the weight percentage of PEG is the same but the number of attached chains and the length of the PEG chain is different, which results in an alteration of the overall shape of the molecule (Figure 5).