Molecular modeling of Poly(methyl methacrylate-block-acrylonitrile) as Precursors of Porous Carbon Fibers

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Introduction

- Porous carbon fibers (PCFs) made with block copolymers show controlled, hierarchical distribution of pore sizes (see Figure below) as well as high surface areas, high gravimetric capacitances, and exceptional electrochemical properties.
- However, the rational design of block copolymers as precursors for PCFs remains a challenge in advancing this type of fibrous materials for applications such as energy storage because of the copolymers' large parameter space.
- Our goal is to develop a computational model of PAN-PMMA block copolymers to quickly analyze the interfacial areas between the PAN and PMMA domains and to accelerate the materials discovery process.
- We construct all-atom models of PAN-PMMA block copolymers and perform molecular dynamics simulations using LAMMPS with the PCFF force field.
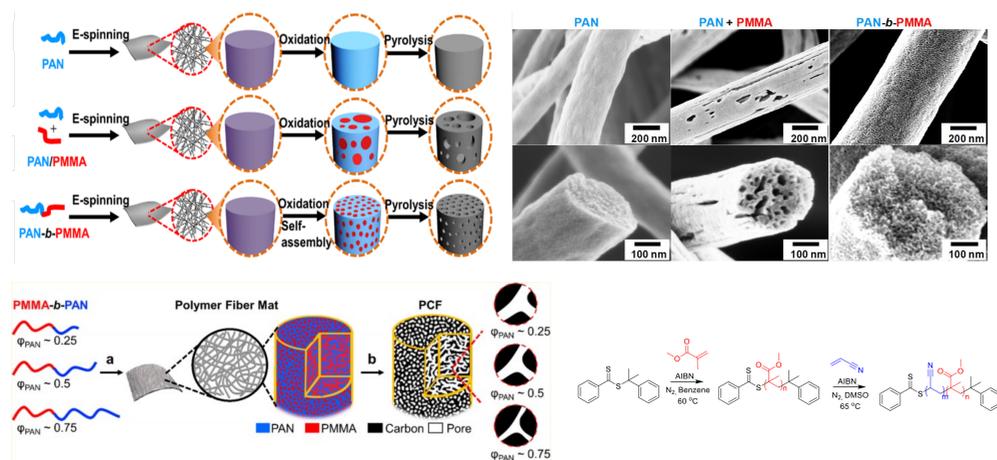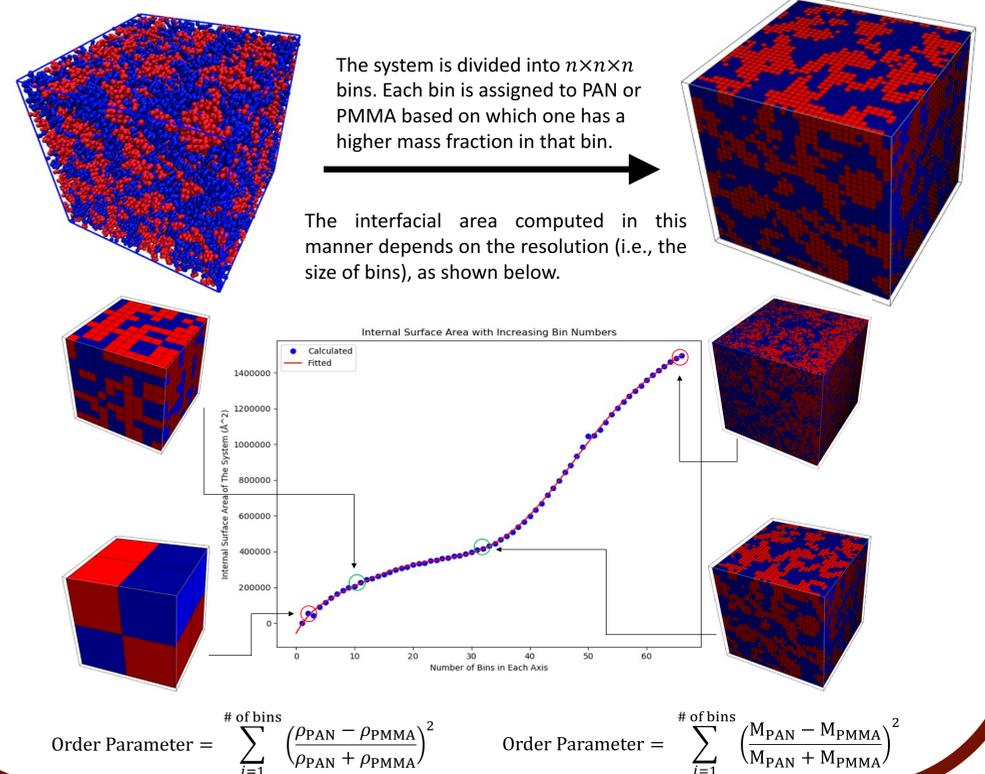

Figure: Experimental results from Liu's group showing the conversion of block copolymer precursors into PCFs [1, 2, 3]. The pore sizes of the PCFs are controlled by varying the composition of each block in the block copolymers. Specifically, longer PAN blocks and shorter PMMA blocks yield smaller pore sizes.

Interfacial Area Determination

The rectangular simulation box is divided into a lattice of bins. Each bin is assigned to either PAN or PMMA, based on their mass fractions in that bin. The interfacial areas between the PAN and PMMA bins are then computed, and the sum is taken as the interfacial area between the PAN and PMMA domains.


The system is divided into $n \times n \times n$ bins. Each bin is assigned to PAN or PMMA based on which one has a higher mass fraction in that bin.

The interfacial area computed in this manner depends on the resolution (i.e., the size of bins), as shown below.

$$\text{Order Parameter} = \sum_{i=1}^{\text{\# of bins}} \left(\frac{\rho_{PAN} - \rho_{PMMA}}{\rho_{PAN} + \rho_{PMMA}} \right)^2 \qquad \text{Order Parameter} = \sum_{i=1}^{\text{\# of bins}} \left(\frac{M_{PAN} - M_{PMMA}}{M_{PAN} + M_{PMMA}} \right)^2$$

System Setup and Simulation Details

- We perform molecular dynamics simulations for a series of PMMA-*b*-PAN block copolymers with various block molecular weights and develop a model to characterize the morphology and compute the interfacial area between the PAN and PMMA domains.
- Block molecular weights in simulations are 1/20 of the corresponding block molecular weights in experiments.

| Designation	PMMA M_n kDa (# monomers)	PAN M_n kDa (# monomers)	φ_{PAN}	PMMA (# monomers)	PAN (# monomers)
BCP 39-13	39 (390)	13 (245)	0.25	20	13
BPC 39-36	39 (390)	36 (679)	0.47	20	34
BPC 39-149	39 (390)	149 (2808)	0.79	20	141
BPC 62-20	62 (620)	20 (377)	0.24	31	19
BPC 62-56	62 (620)	56 (1056)	0.47	31	53
BPC 62-200	62 (620)	200 (3770)	0.76	31	189
BPC 85-40	85 (849)	40 (754)	0.31	43	38
BPC 85-60	85 (849)	60 (1131)	0.41	43	57
BPC 85-215	85 (849)	215 (4052)	0.71	43	203
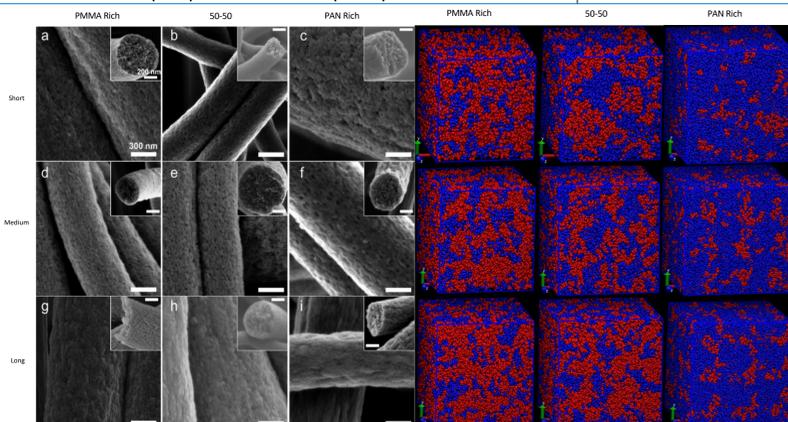
Crosslinking

Enhanced nonbonded interaction between N and C atoms is used to mimic the crosslinking between PAN segments.

Order Parameter Analysis

We studied the order parameter of systems, both melted and crosslinked, starting from different initial states.

Simulation vs. Experiment
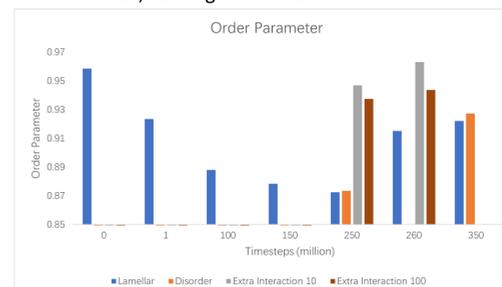
Summary

- We developed an approach to determine the interfacial area between the PAN and PMMA domains in PAN-*b*-PMMA block copolymers, which is indicative of the surface area of PCFs made from such copolymers.
- Crosslinking between PAN segments can be modeled by introducing extra nonbonded interactions.
- Simulation results are consistent with experimental results. Both show that the interfacial area is maximized when the volume (or mass) fraction of either block is close to 50%.

Reference

1. Serrano, J. M.; Liu, T.; Khan, A. U.; Botset, B.; Stovall, B. J.; Xu, Z.; Guo, D.; Cao, K.; Hao, X.; Cheng, S.; Liu, G., Composition Design of Block Copolymers for Porous Carbon Fibers. *Chemistry of Materials* **31**(21), 8898-8907 (2019).
2. Liu, T., Zhou, Z., Guo, Y. *et al.* Block copolymer derived uniform mesopores enable ultrafast electron and ion transport at high mass loadings. *Nature Communications* **10**, 675 (2019).
3. Z. Zhou, T. Liu, A. U. Khan, and G. Liu, Block copolymer–based porous carbon fibers. *Science Advances* **5**, eaau6852 (2019).

Acknowledgement