

PRF# 56380-DNI7

Project Title: Controlling Polarization in Polystyrene

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## Research Progress

This PRF-funded program focuses on controlling the polarity and bulk structure of organic polymers by replacing one or more CC bonds with the isosteric, isoelectronic, and polar BN bond. In the course of the proposed work, we carried out fundamental research into both organic reactive intermediate chemistry and the properties of novel petroleum-derived polymers.

Polystyrene (PS) is produced industrially on massive scale each year from benzene and ethylene, assuring its status as an essential commodity petrochemical. PS derivatives arising from chemical modification of the benzene ring are important materials in their own right, such as polystyrene sulfonate, the ion exchange resin Dowex. Boron incorporation into organic materials for functional purposes is a growing area of investigation and these organoborane materials have found applications in sensing, optoelectronics, and other areas. In work reported during a prior funding period, we described a scalable and short synthesis of BN 2-vinylnaphthalene (BN2VN), a novel boron-containing vinyl monomer that mimics styrene in structure.<sup>1</sup>

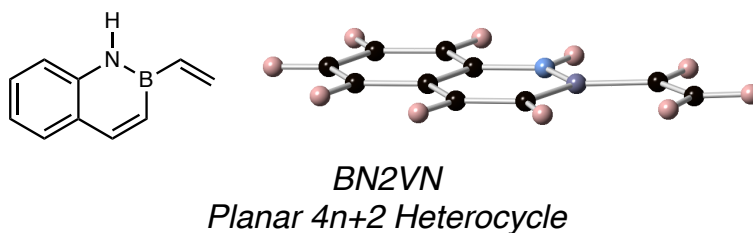


Figure 1. Chemical structure of BN 2-vinylnaphthalene (BN2VN) and side-on view of calculated BN2VN structure, highlighting planarity. Black = carbon; pink = hydrogen; blue = nitrogen; lavender = boron.

In 2018, we characterized the styrene-like radical reactivity of BN2VN by carrying out copolymerization studies with styrene (Figure 2).<sup>2</sup> Statistical copolymers of BN2VN and styrene were obtained by free radical polymerization initiated by azoisobutyronitrile (AIBN, 1 mol%), in toluene or in neat styrene (Figure 2). Copolymerizations were conducted with feed ratios of 60 wt %, 33 wt %, or 14 wt % BN2VN. Good agreement between feed ratio BN2VN content and copolymer BN2VN content was observed, as measured by an optical assay previously reported by us.<sup>1</sup>

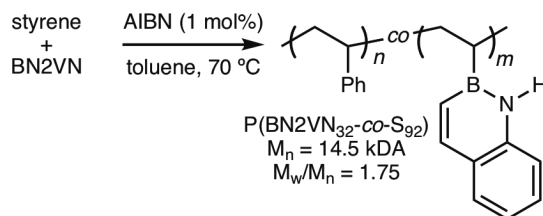


Figure 2. Synthesis of statistical PS-co-PBN2VN by free radical copolymerization initiated by azoisobutyronitrile (AIBN). BN2VN content varies from 10-50 weight percent.

Polymer number average molecular weight (M<sub>n</sub>) ranged between 12-40 kDa, with moderate dispersities ( $\mathcal{D}$  = 1.5-2.00) in toluene. Neat reaction conditions provided high molecular weight polymers with high molecular weight distributions (32.6–39.6 kDa,  $\mathcal{D}$  = 4.23–5.40). GPC curves show a shoulder at high molecular weight that contributes to the high dispersity (Figure 3, shoulder indicated with black arrow). Homopolymerization of each monomer is unlikely as the shoulder is also observed in a PS control reaction. Instead, we suggest that the shoulder is a consequence of the gel effect in which at high molecular weight, the slow diffusion of the viscous polymer results in accelerated chain growth.

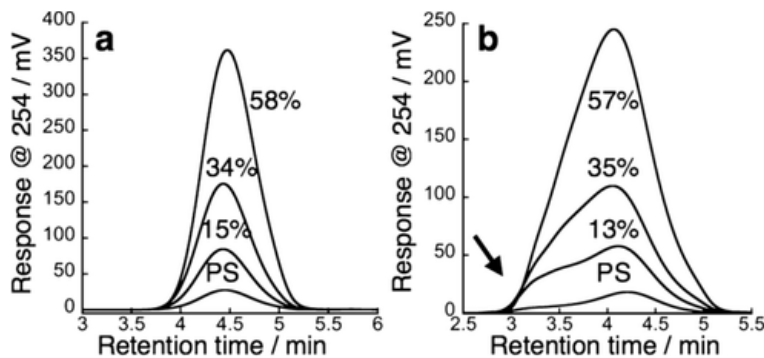


Figure 3. GPC curves of copolymers. a) Polymerization in toluene. Labels refer to the wt % of BN2VN. b) Polymerization in neat styrene. Arrow indicates a high-molecular-weight shoulder.

The long-term impact of this fundamental research is broad. We have established that BN2VN exhibits styrene-like radical reactivity, which points to future opportunities in copolymerization with other activated monomers (e.g. acrylates). The high reactivity and versatility of BN2VN appears to be unique compared to BN styrene, which provides only low molecular weight polymers. Initial funding from the Petroleum Research Fund has established the long-term viability of a research program focusing on both the fundamental chemistry of BN2VN polymers and copolymers, as well as their unique properties.

- (1) van de Wouw, H. L.; Lee, J. Y.; Klausen, R. S. Gram-Scale Free Radical Polymerization of an Azaborine Vinyl Monomer. *Chem. Commun.* **2017**, *53*, 7262–7265.
- (2) van de Wouw, H. L.; Lee, J. Y.; Awuyah, E. C.; Klausen, R. S. A BN Aromatic Ring Strategy for Tunable Hydroxy Content in Polystyrene. *Angew. Chemie Int. Ed.* **2018**, *57* (6), 1673–1677.

### Impact on PI's Career

The work described in this progress report was published in *Angewandte Chemie*, a high impact factor journal. It was also featured on #BoronWednesday by Steve Ritter, a writer for Chemistry & Engineering News. The high visibility of this research has positively benefited the PI's career and resulted in invitations to give seminars at conferences, such as the 4<sup>th</sup> Functional Polymeric Materials Fusion Conference and the American Chemical Society Fall Meeting. The PI was also invited to give six departmental seminars at American universities in the current funding period.

The support of the Petroleum Research Fund Doctoral New Investigator Award allowed the PI to build an independent publication record and obtain preliminary data supporting a federal award. In 2018, the PI was recognized with a five-year, \$675,000 CAREER Award from the National Science Foundation to continue the development of this research into polar polyolefins.

### Impact on Students' Careers

The lead graduate student on this project (Ms. Heidi van de Wouw) attended two conferences in 2018 with the PI: the 4<sup>th</sup> Functional Polymeric Materials Fusion Conference in Nassau, Bahamas and the American Chemical Society Fall Meeting in Boston, MA. Ms. Van de Wouw presented two posters on her research. She has now set a date for her thesis defense and is pursuing a postdoctoral position in polymer research. Ms. Van de Wouw is first author on the *Angewandte Chemie* paper reported in this funding cycle. Ms. Van de Wouw has used her PRF-supported research to enhance her mentorship and leadership abilities, including mentoring three undergraduate researchers (Mr. Jae Young Lee (B.S./M.S. 2018, JHU), Mr. Elorm C. Awuyah, and Ms. Jodie I. Baris).

Mr. Eric Marro, also a graduate student, attended two conferences in 2018 with the PI: the 40<sup>th</sup> US-Japan Symposium on Hybrid Materials in Newark, NJ and the American Chemical Society Fall Meeting in Boston, MA. He presented a poster and gave an oral presentation, respectively, at these meetings.