PRF#: 57597-ND7

Probing the Role of Chain Stiffness in the Sonochemistry of Polymers

PI: Dr. Robson F. Storey, Department of Polymer Science and Engineering, The University of Southern Mississippi
Co PI: Dr. Yoan C. Simon, Department of Polymer Science and Engineering, The University of Southern Mississippi

The work described herein has expanded upon our initial findings regarding the relationship of homopolymer bottlebrush-scission characteristics when exposed to ultrasonication. Initial work focused on the systematic understanding of sterically crowded homopolymer bottlebrush systems synthesized via ring-opening metathesis polymerization (ROMP) of norbornene end-capped polyisobutylene macromonomers (NBPIB). PNBPIB bottlebrushes were ultrasonicated to determine the role of backbone and sidechain length on scission rates. We expounded upon this idea to include a secondary small molecule monomer, which was used to reduce the density of oligomeric NBPIB side chains (M_n = 3 kg/mol) along the entire backbone or a portion of the backbone. Thus, copolymerization of dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (NBDME) and NBPIB via *grafting-through* ROMP was used to create either statistical (PNBDME-*co*-PNBPIB, M_n = 342.5 kg/mol, $DP_{n,\ PNBDME}$ = 56, $DP_{n,\ PNBPIB}$ = 100) or diblock (PNBDME-*b*-PNBPIB, M_n = 305.4 kg/mol, $DP_{n,\ PNBDME}$ = 93, $DP_{n,\ PNBPIB}$ = 93) brush copolymers with comparable molecular weights (ca. M_n = 300 kg/mol) (**Fig. 1**). The various bottlebrush compositions were exposed to ultrasonication resulting in backbone scission of the copolymers, which was further characterized via size exclusion chromatography (SEC). (**Fig. 2**). After a 24-hour period of ultrasonication, the dispersity of PNBDME-*co*-PNBPIB increased and the molecular weight decreased slightly. Conversely, molecular weight readily decreased upon ultrasonication of PNBDME-*b*-PNBPIB or PNBPIB homobottlebrushes with a comparable increase in dispersity. These preliminary results indicate that the steric congestion of the side chain highly influences the rate of sonication. The introduction of a small molecule "diluent" into the bottlebrush backbone effectively reduces the grafting density of side chains, and correspondingly reduces the extent of scission and scission rate of the bottlebrush.

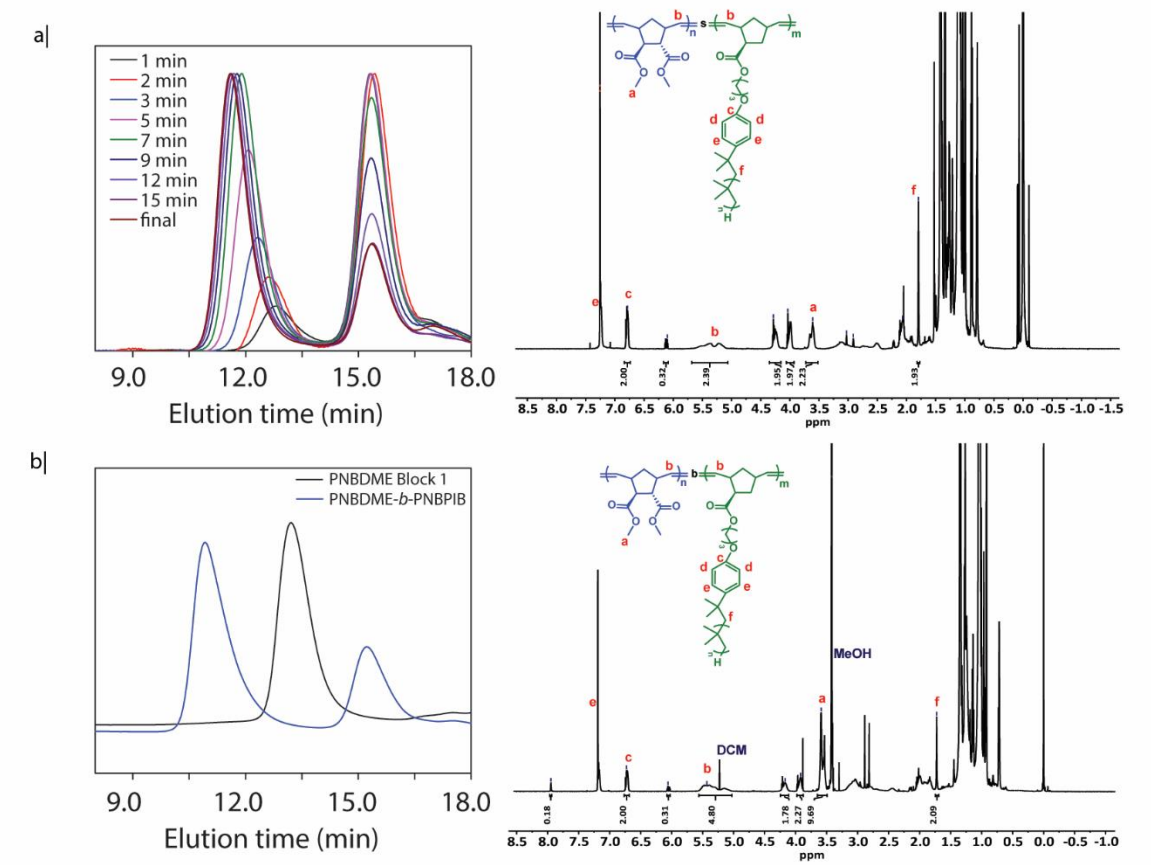

Fig. 1. Representative SEC and ^{1}H NMR data for (a) statistical and (b) block copolymerizations of NBDME and NBPIB.

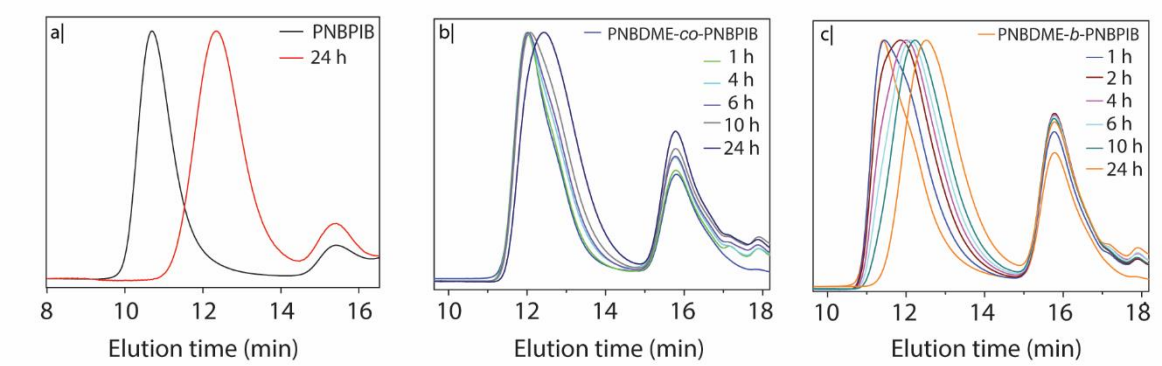

Fig. 1. SEC traces (dRI detector), before and after ultrasonication, for (a) PNBPIB homobottlebrush (DP_n = 100), (b) $PNBDME_{50}$-*co*-$PNBPIB_{50}$ statistical bottlebrush copolymer and (c) PNBDME-*b*-PNBPIB diblock bottlebrush copolymer (sonication conditions: 1 second ON, 1 second OFF, 15 kHz, 1.5 mg mL^{-1} THF, 5 °C)

A different polymer side chain was also investigated to determine whether polymeric side chain stiffness influences backbone scission. Norbornene-end-functionalized polystyrene macromonomers (NBPS, M_n = 3.48 kg/mol) were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization and chosen for their stiff backbone as compared to polyisobutylene-based macromonomers. NBDME was again employed as the comonomer for copolymerizations via ROMP. Initial investigations included homobottlebrushes of NBPS (PNBPS, M_n = 67.8 kg/mol) and diblock bottlebrushes of NBDME and NBPS (PNBDME-*b*-PNBPS, M_n = 92.23 kg/mol). Upon ultrasonication, some scission was observed to occur for both PNBS and PNBDME-*b*-PNBPS via SEC (**Fig. 3**). After exposure to 24 h of ultrasonication, SEC traces of the PNBPS homobottlebrush undergo a slight shift to a greater elution volume, indicative of minimal backbone scission(**Fig. 3b)**. Interestingly, PNBDME-*b*-PNBPS marginally decreased in molecular weight after 24 hours of sonication (**Fig. 3c**); however a larger library of higher molecular weight copolymers is necessary to fully evaluate the implications of side chain stiffness on scission rate.

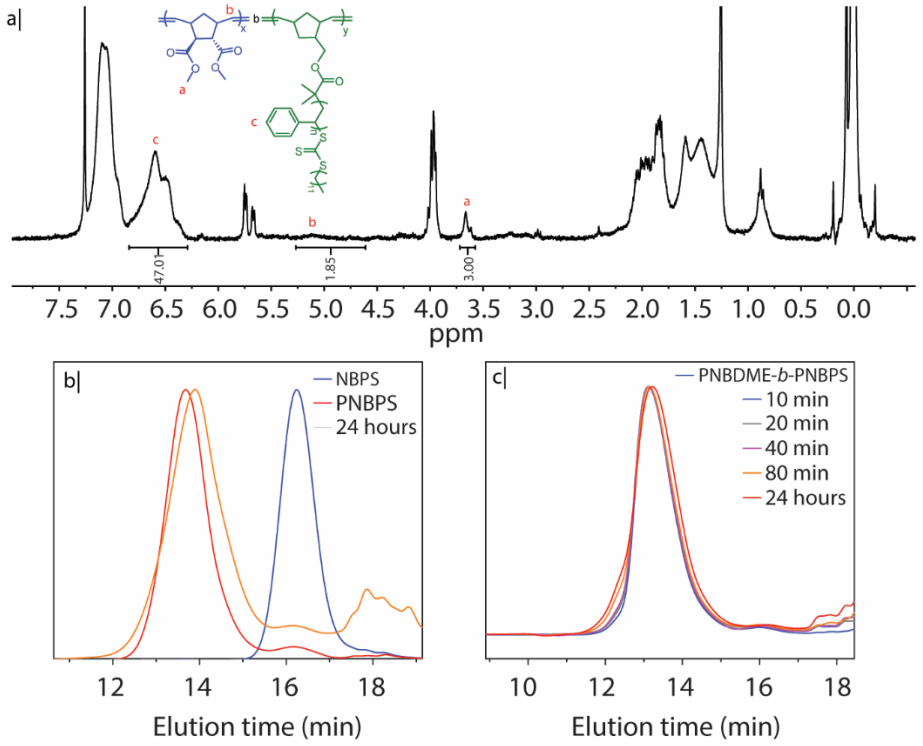

Figure 2. Representative (a) ^{1}H NMR of PNBDME-*b*-PNBPS, and SEC traces before and after ultrasonication for (b) PNBPS and (c) PNBDME-*b*-PNBPS (sonication conditions: 1 second ON, 1 second OFF, 15 kHz, 1.5 mg mL^{-1} THF, 5 °C).