

Probing the Role of Chain Stiffness in the Sonochemistry of Polymers

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The current work probes the interplay between copolymer composition, chain stiffness, and polymer sonochemistry. Systematic understanding of homopolymer, copolymer and sterically crowded bottlebrush systems synthesized via ring opening metathesis polymerization (ROMP) will reveal the underlying mechanism of polymeric chain scission under solvodynamic shear. To achieve this, students have engaged in understanding the importance of selecting reproducible reactions between macromonomers and small molecule analogs. The representative ^1H NMR and GPC of cationic polymerization prepared norbornene end-capped polyisobutylene macromonomer (NBPIB, **2**) is shown in **Figure 1**. NBPIB was synthesized to 3, 5, and 10 kDa for either block or statistical copolymerization with dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (NBDME) via *grafting-through* ROMP. Copolymers were terminated with UV-active (Z)-7,7'-(but-2-ene-1,4-diylbis(oxy))bis(4-methyl-2H-chromen-2-one) (**3**). A representative statistical and block copolymer is shown in **Figure 3**, and the corresponding characterization is shown in **Figure 4**.

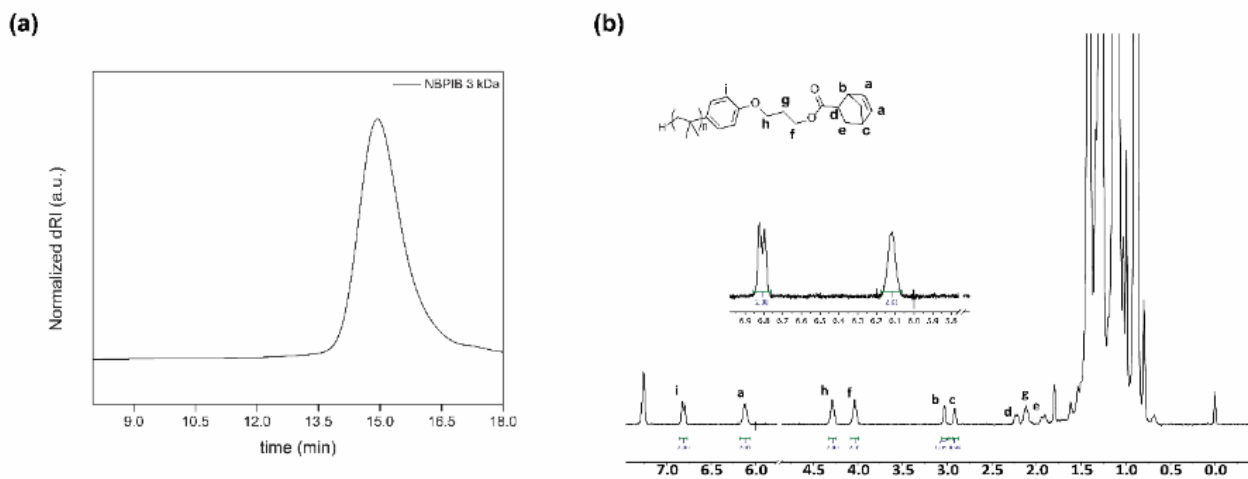


Figure 1. Representative (a) GPC trace and (b) ^1H NMR of NBPIB 3 kDa macromonomer, **2**. Molecular weights calculated based on mass recovery.

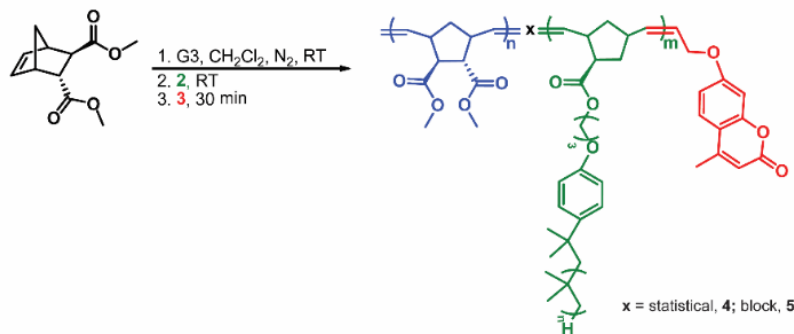


Figure 2. Linear bottlebrush/statistical copolymer bottlebrush synthesis

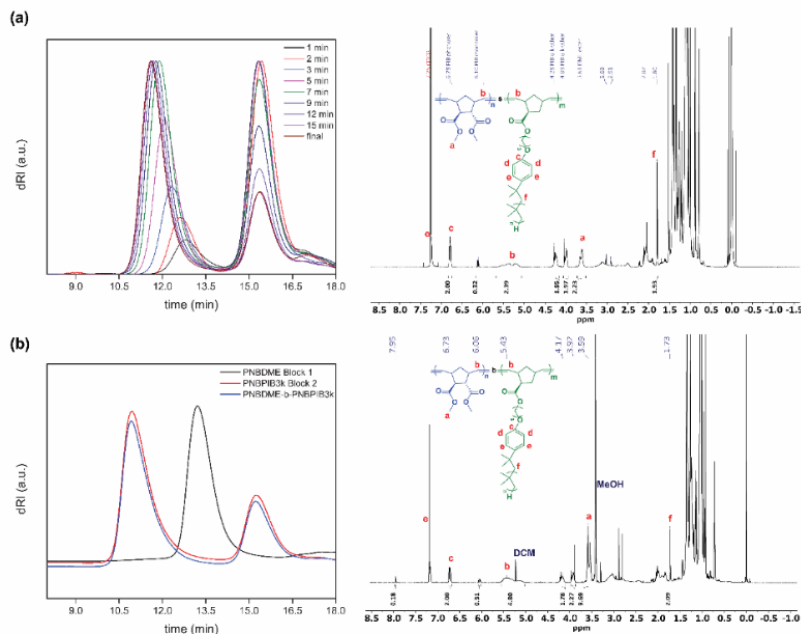


Figure 3. Representative GPC and NMR of (a) statistical, **5**, and (b) block, **4** copolymerization of NBDME and NBPIB3k

Preliminary ultrasonication studies are shown in **Figure 4** have found the limiting molecular weight (M_{lim}) of linear PIB to be 20 kDa and linear PNBDM to be 17 kDa. The ultrasonication of PNBPIB bottlebrushes show few chain scission events below 50 backbone DP_n . The next steps are to sonicate the asymmetric linear-bottlebrush block copolymer and statistical copolymer of PNBDM-*s*-PNBPIB_{3kDa} shown in **Figure 3** to understand how more complex polymeric architecture behaves under ultrasonication conditions compared to their neat cousins. Bottlebrushes with residual macromonomer will be isolated via preparatory HPLC to ensure sonication experiments are representative of only bottlebrush materials. Characterization of the residual macromonomer peak will provide crucial understanding that has yet to be explored in the synthesis of bottlebrush polymers. The authors believe that the groundwork shown in this report will be key to elucidating chain scission events in asymmetric bottlebrush architectures exposed to high shear forces.

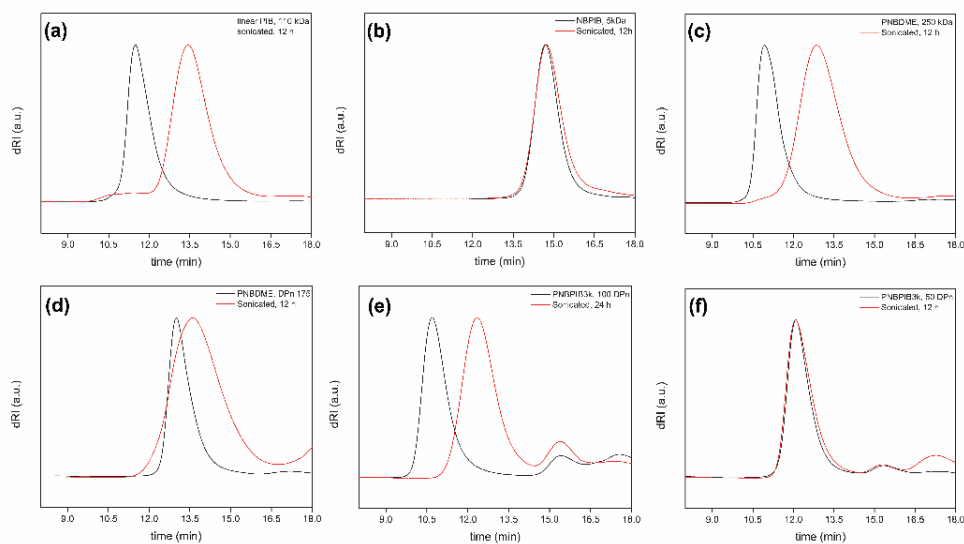


Figure 4. Representative sonication GPC traces of (a) linear PIB, 110 kDa; (b) NBPIB, 3 kDa; (c) PNBDM 250 kDa; (d) PNBDM 50 kDa; (e) PNBPIB 3k bottlebrush 100 DP_n ; (f) PNBPIB 3k bottlebrush 50 DP_n run in a Suslick cell under N_2 at 5 °C with 1 second ON/OFF intervals.