

*****SUPPORTING INFORMATION*****

**Effect of Systematic Hydrogenation on the Phase Behavior and
Nanostructural Dimensions of Block Copolymers**

**Arman R. Ashraf,[§] Justin J. Ryan,[†] Michael M. Satkowski,[§] Steven D. Smith^{§*}
and Richard J. Spontak^{†‡*}**

[§]Corporate Research & Development, The Procter & Gamble Company, Cincinnati, OH 45224, USA

[†]Department of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695, USA

[‡]Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, USA

* To whom correspondence should be addressed (E-mail: smith.sd@pg.com and rich_spontak@ncsu.edu)

In this Supporting Information, we provide experimental methods and results that are not included in the main narrative. Samples of non-hydrogenated copolymers were isolated by precipitation of copolymer solutions in cyclohexane with methanol, and the resultant materials were stabilized with 0.25 wt% Irganox-1010 (to avoid high-temperature degradation during analysis) and vacuum-dried. Copolymer samples earmarked for hydrogenation were terminated by adding the minimum amount of methanol required for anion termination and subsequently stored in cyclohexane. The hydrogenation catalyst was prepared by dissolving 0.345 g nickel(II) bis(2-ethylhexanoate) in 40 ml cyclohexane, followed by deoxygenation with a nitrogen gas purge and then addition of 2.6 ml triethyl aluminum solution. This homogeneous (unsupported) catalyst solution was syringed into the copolymer solution at 60°C and stirred rapidly under hydrogen at 2.76 bar. Hydrogenated samples were vigorously agitated with 0.05 M HCl(aq) until the organic layer appeared colorless. The aqueous HCl layer was discarded and the organic layer was first extracted with 0.05 N NaHCO₃ and then twice with water. Target DOH levels were predicted from consumption of hydrogen in a pressure reservoir, and samples were removed at predetermined values. Actual DOH levels were confirmed by proton nuclear magnetic resonance (¹H NMR) analysis (performed on a GE QE-300 spectrometer) of the remaining unsaturated isoprene units. Irganox-1010 was added to stabilize the copolymers isolated by vacuum drying. In all cases, molecular weight and molecular weight distributions were measured by size exclusion chromatography (SEC), and compositions were discerned by ¹H NMR spectroscopy.

In **Figure S1**, illustrative data acquired from size-exclusion chromatography (SEC) are provided to confirm that the change in the molecular weight distribution (in terms of maximum, breadth and shape) of BRC1 from 0% to 80% hydrogenation is negligible and within the experimental accuracy of the characterization technique.

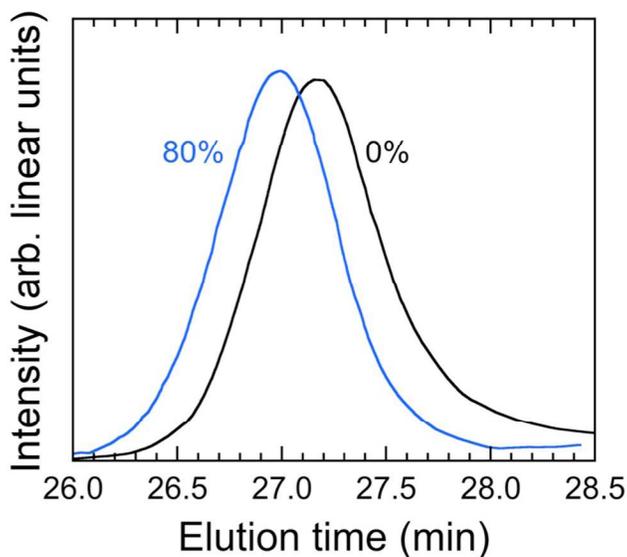


Figure S1. SEC profiles acquired from the BRC1 copolymer before and after hydrogenation to 80% (labeled).

Similarly, representative ^1H NMR spectra measured from several BRC1 copolymers at different hydrogenation levels are provided in **Figure S2**. The spectral peaks corresponding to the unsaturation in polyisoprene and used to quantify the degree of hydrogenation (DOH) are highlighted and display a progressive reduction in peak area as the DOH is systematically increased.

While the temperature-dependent rheological signatures for the BRC1 copolymer series are portrayed in **Figure 1a** of the main narrative, **Figure S3** displays the corresponding behavior for the BRC2 copolymer series. Moreover, several example temperature-dependent SAXS profiles collected from the BRC1 copolymer series are included in **Figure S4** at different DOH levels.

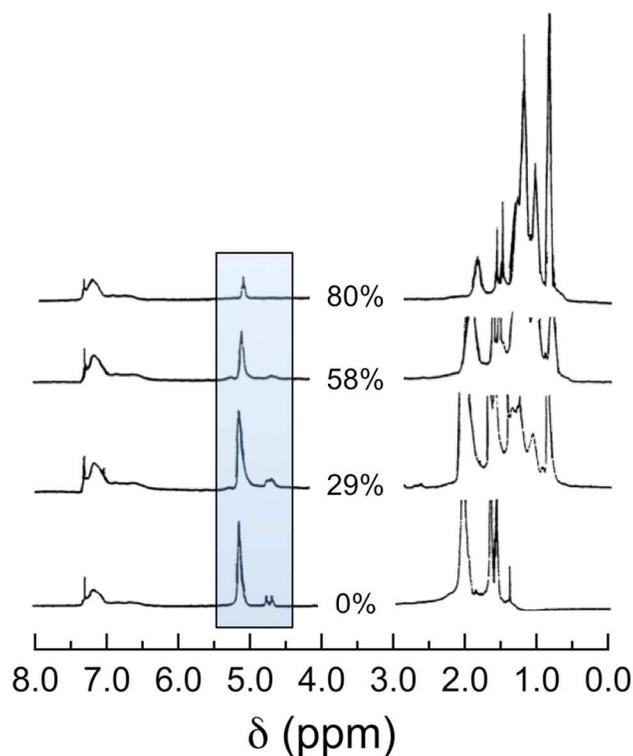


Figure S2. ^1H NMR spectra obtained from BRC1 copolymers at different DOH levels (labeled). Peaks identifying the unsaturated bonds in polyisoprene are highlighted and used to calculate the DOH.

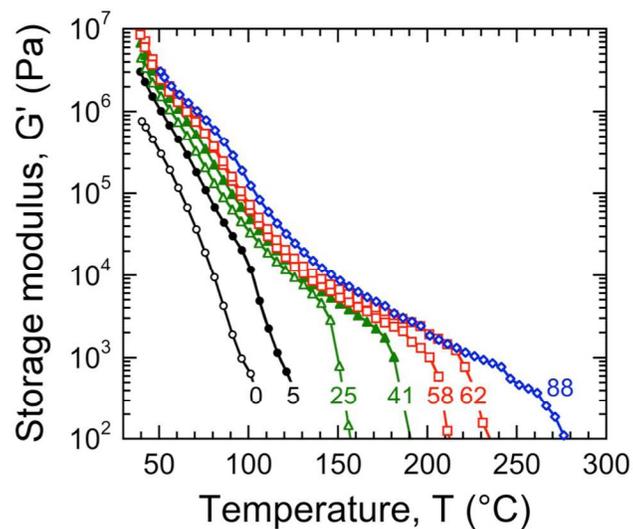


Figure S3. Dependence of G' on temperature for the BRC2 copolymer series at different DOH levels (labeled and color-coded) and measured under the same experimental conditions used in **Figure 1a**.

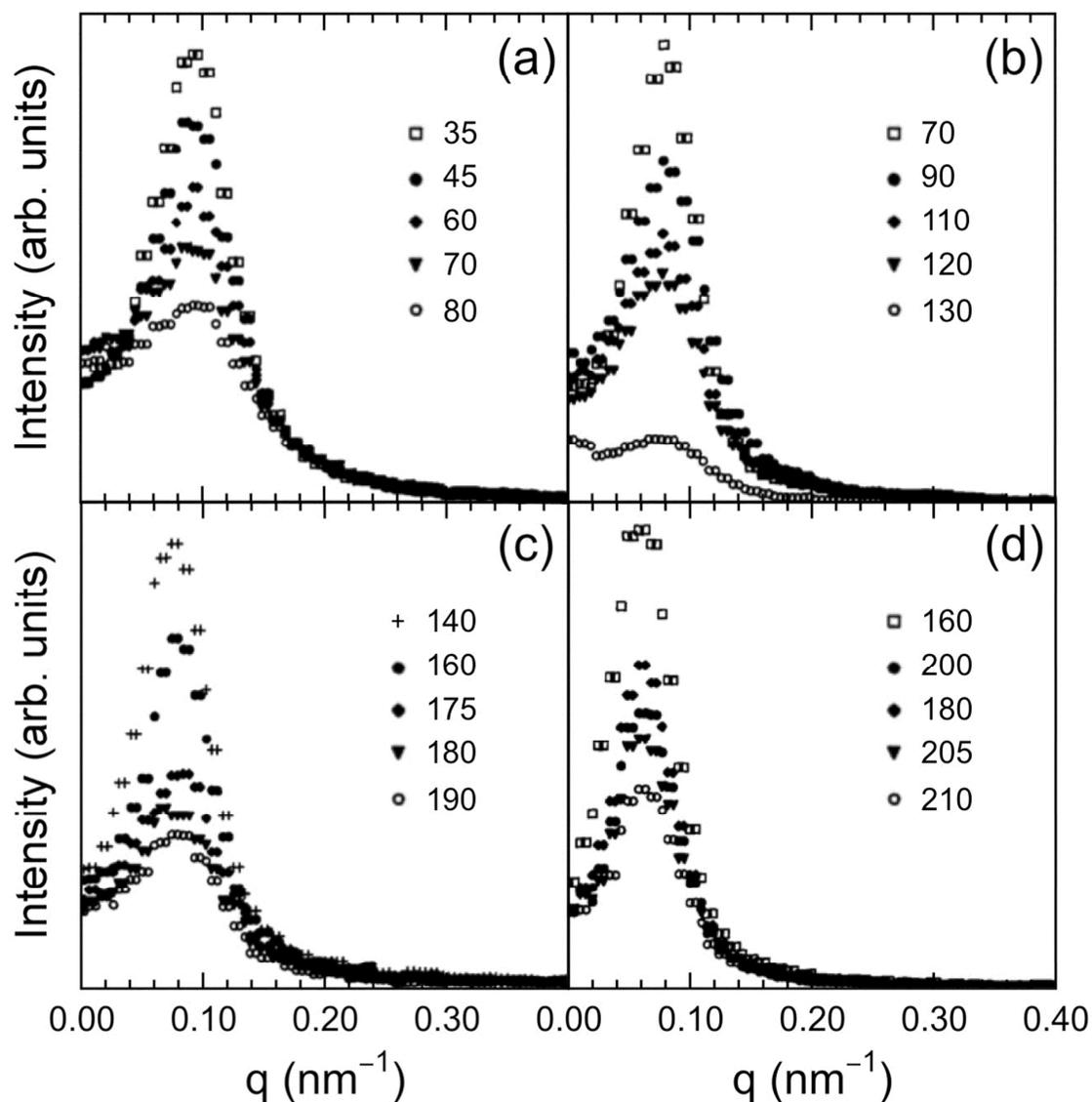


Figure S4. SAXS intensity profiles for four specimens in the BRC1 copolymer series at different DOH levels (in mol%): (a) 0, (b) 29, (c) 58, and (d) 80. The temperatures at which the profiles were acquired (in °C) are listed in each panel legend.

To reduce the likelihood that the polyisoprene-containing BRC copolymers undergo thermal degradation upon analysis at elevated temperatures, a radical scavenger is added to all the materials prior to characterization (see the Experimental section of the main text for details). To discern if such degradation occurs, select specimens have been subjected to first and second heat cycles. The results for BRC1 after 80% hydrogenation (requiring analysis beyond 200°C) are

presented for comparison in **Figure S5** and confirm that the data are reproducible with no sign of degradation (scission or crosslinking).

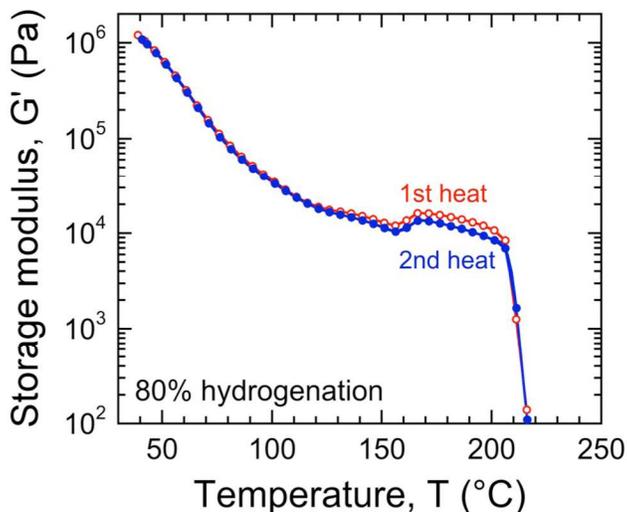
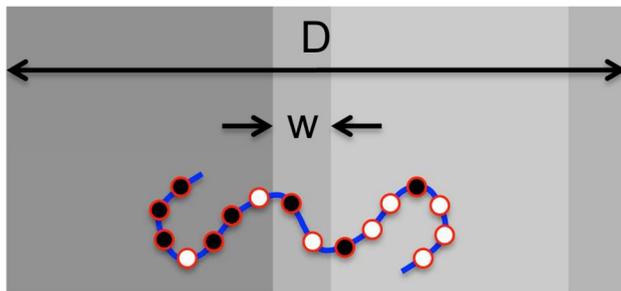


Figure S5. G' as a function of temperature for BRC1 after 80% hydrogenation with $T_{\text{ODT}} > 200^{\circ}\text{C}$. The 1st and 2nd heats are labeled and color-coded to indicate that heating does not adversely affect G' or T_{ODT} .

Specific characteristics of the block copolymer lamellar morphology alluded to in the narrative focus on the microdomain periodicity (D) and interphase thickness (w). These are schematically depicted in **Scheme S1**.



Scheme S1. Illustration of the lamellar morphology formed upon microphase separation in a BRC composed of two random-copolymer blocks.