Synthesis and characterization of a nematic fully aromatic polyester utilizing biphenyl 3,4'-dicarboxylic acid

Supporting Information

Katherine V. Heifferon, Glenn A. Spiering, Samantha J. Talley, Maruti Hegde, Robert B. Moore, S. Richard Turner, and Timothy E. Long*

Macromolecules Innovation Institute, Department of Chemistry, Virginia Tech, Blacksburg, VA 24061

*To whom correspondence should be addressed. Email: telong@vt.edu. TEL: (540)231-2480 FAX: (540)231-8517

Scheme S1. Hydrolysis of dimethyl 3,4'- bibenzoate (3,4'BB) to synthesize diacid monomer, biphenyl 3,4'-dicarboxylic acid (3,4'BB-COOH), for acidolysis polymerization.

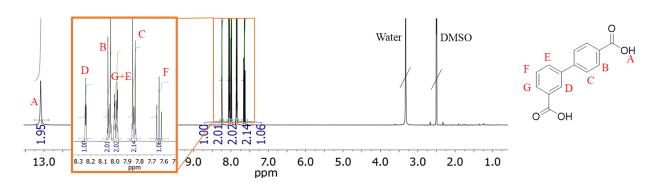


Figure S1. Successful hydrolysis of biphenyl 3,4'-dicarboxylic acid confirmed by ¹H NMR spectroscopy (DMSO-d₆, 400 MHz).

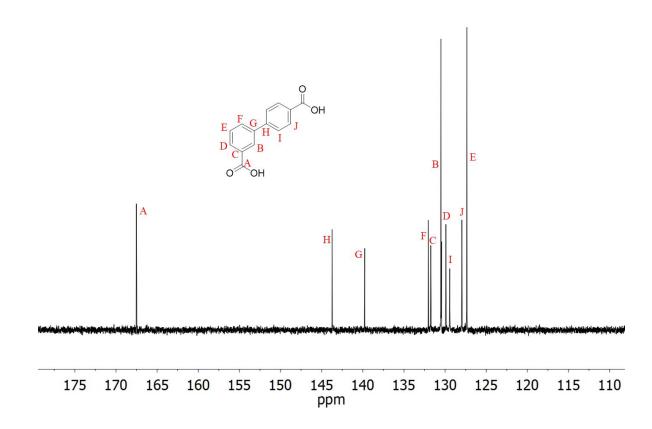


Figure S2. Successful hydrolysis of biphenyl 3,4'-dicarboxylic acid confirmed by ¹³C NMR spectroscopy (DMSO-d₆, 400 MHz).

Scheme S2. Pivilation of hydroquinone with pivalic anhydride yields hydroquinone dipivilate for acidolysis polymerization.

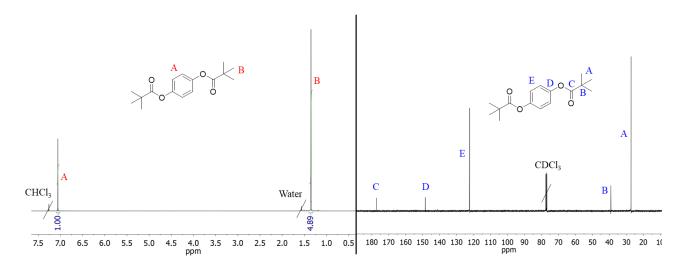


Figure S3. Successful pivalation of hydroquinone confirmed through ¹H and ¹³C NMR spectroscopy. Left: Peak assignment and ¹H NMR (CDCl₃, 400 MHz). Right: Peak assignment and ¹³C NMR (CDCl₃, 400 MHz).

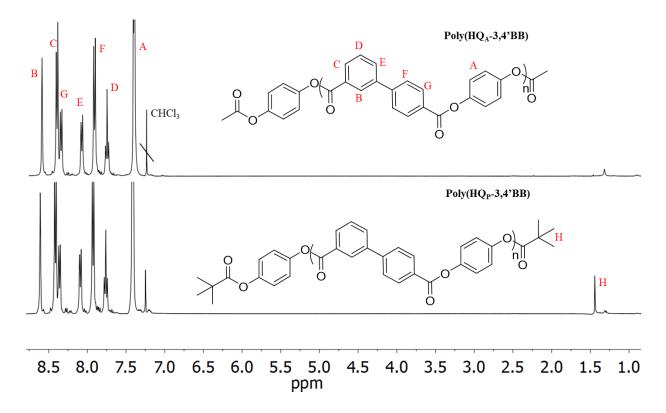


Figure S4. ¹H NMR (CDCl₃:TFA-*d*, 400 MHz) spectroscopy of poly(HQ_a-3,4'BB) (top) and poly(HQ_p-3,4'BB) (bottom).

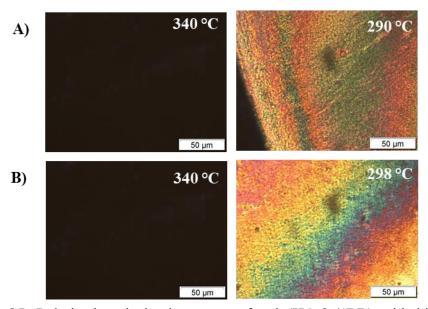


Figure S5. Polarized optical microscopy of poly(HQ-3,4'BB) with higher molecular weight due to receiving 30 m of vacuum during the polymerization reveals possible mosaic nematic texture birefringence. Both sets of images were taken during a slow cool at 10 °C/min from the isotropic phase. A) poly(HQ_p-3,4'BB) B) poly(HQ_a-3,4'BB).

7

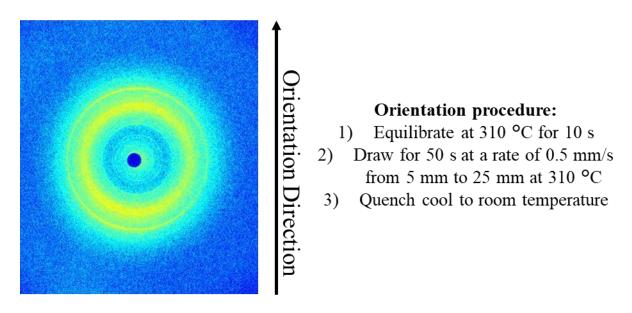


Figure S6. 2D WAXS profile of poly(HQ_p -3,4'BB) after attempts to orient the polymer below the T_i resulting in crystallization.