Supporting Information

Crosslinkable Liquid Crystalline Copolymers with Variable Isotropization Temperature

Kelly A. Burke[1,2a] and Patrick T. Mather[2,3*]

[1]Department of Macromolecular Science and Engineering, Case Western Reserve University, 2100 Adelbert Road, Cleveland, OH 44106, USA

[2]Syracuse Biomaterials Institute, [3]Department of Biomedical and Chemical Engineering, Syracuse University, 121 Link Hall, Syracuse, NY 13244, USA

[*]Corresponding author. Email address: ptmather@syr.edu

[a]Present address: Department of Biomedical Engineering, Tufts University, Medford, MA USA

^{1}H NMR spectra. Shown in Fig. S1-S3 are the ^{1}H NMR spectra for the ***5tB*** homopolymer, **P5tB(100)**, (**Fig. S1**); ***5Te*** homopolymer, (**P5tB(0)** (**Fig. S2**); and a ***5tB-5Te*** copolymer, **P5tB(81.1)** (**Fig. S3**). As shown in Fig. S3, peaks labeled with (**e**) and (**o**) were used to calculate composition of the copolymers.

Free radical crosslinking of P5tB(97.3) with 10 wt-% Lauroyl Peroxide. Shown in Fig. S4 are the plots of ln(1-p) versus cure time t (Fig. S4) for each of the cure temperatures studied. From the linear regression fits to the data in Fig. S4, the temperature-dependent rate constants, $k(T)$, for the cure were determined. These rate constants are plotted versus $1/T$, where T is the absolute temperature of cure, in Fig. S5 to determine the activation energy of the cure.

Free radical crosslinking of P5tB(97.3) with 5.16 wt-% Lauroyl Peroxide Shown in Fig. S6 is the plot of ln(1-p) versus cure time t for the cure at 60 °C. Linear regression was applied to this data to determine the rate constant, k, for this cure.

Burke and Mather Figure S1.

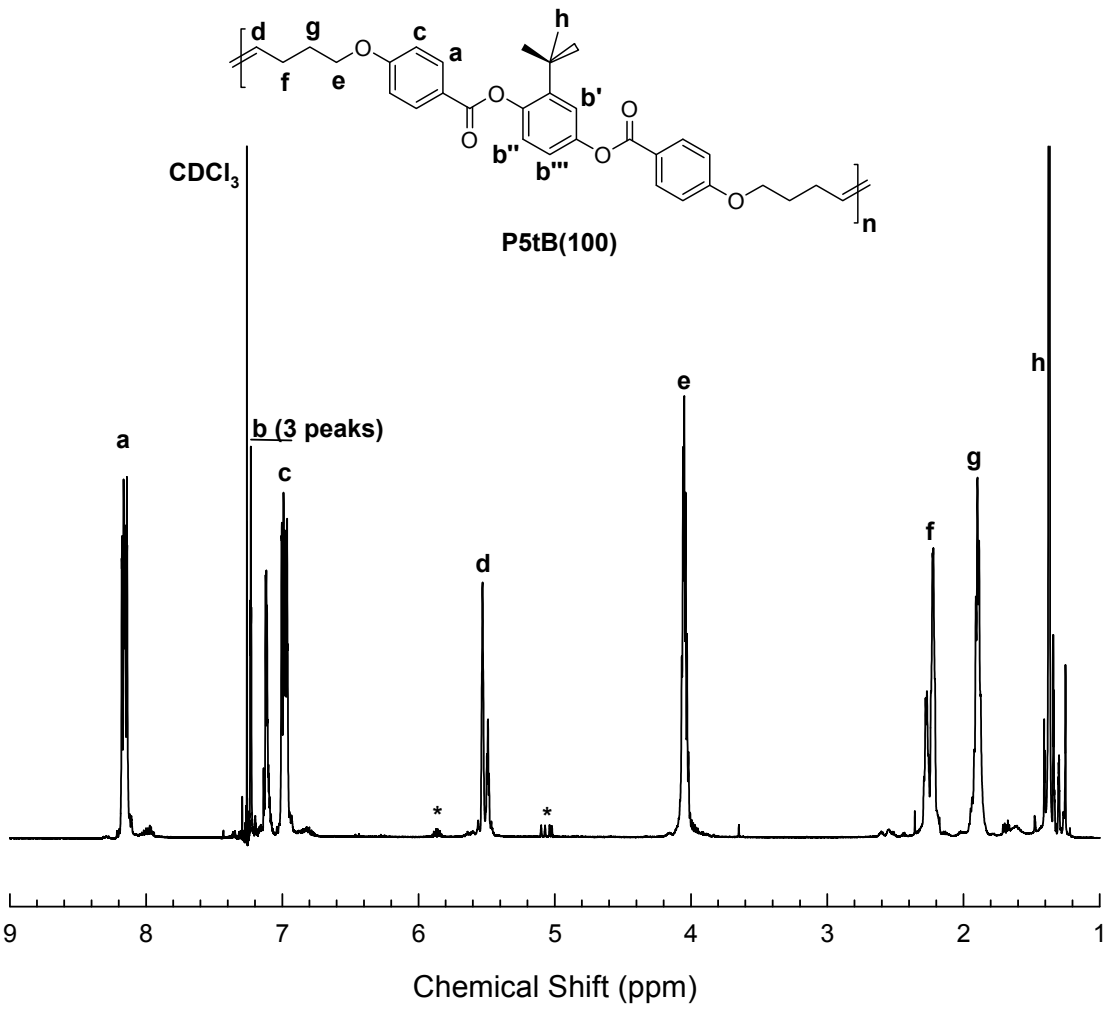

Figure S1. ^{1}H NMR spectrum of the ***5tB*** homopolymer (**P5tB(100)**, M_n=17.1 kDa) run in $CDCl_3$. The peaks in the spectrum are labeled according to the structure shown. The peaks labeled with the asterisk are due to residual monomer in the polymer product.

Burke and Mather Figure S2.

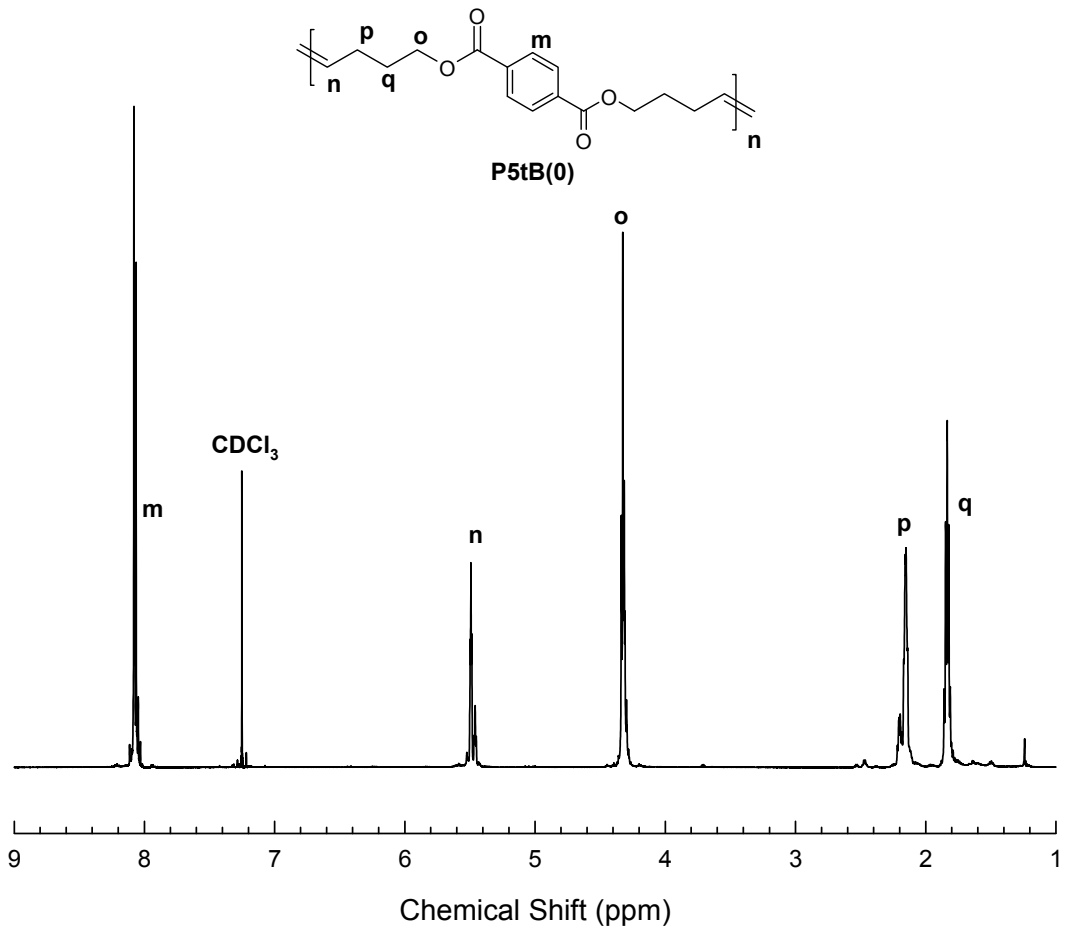

Figure S2. ^{1}H NMR spectrum of the ***5Te*** homopolymer (**P5tB(0)**, M_n=21.0 kDa) run in $CDCl_3$. The peaks in the spectrum are labeled according to the structure shown.

Burke and Mather Figure S3.

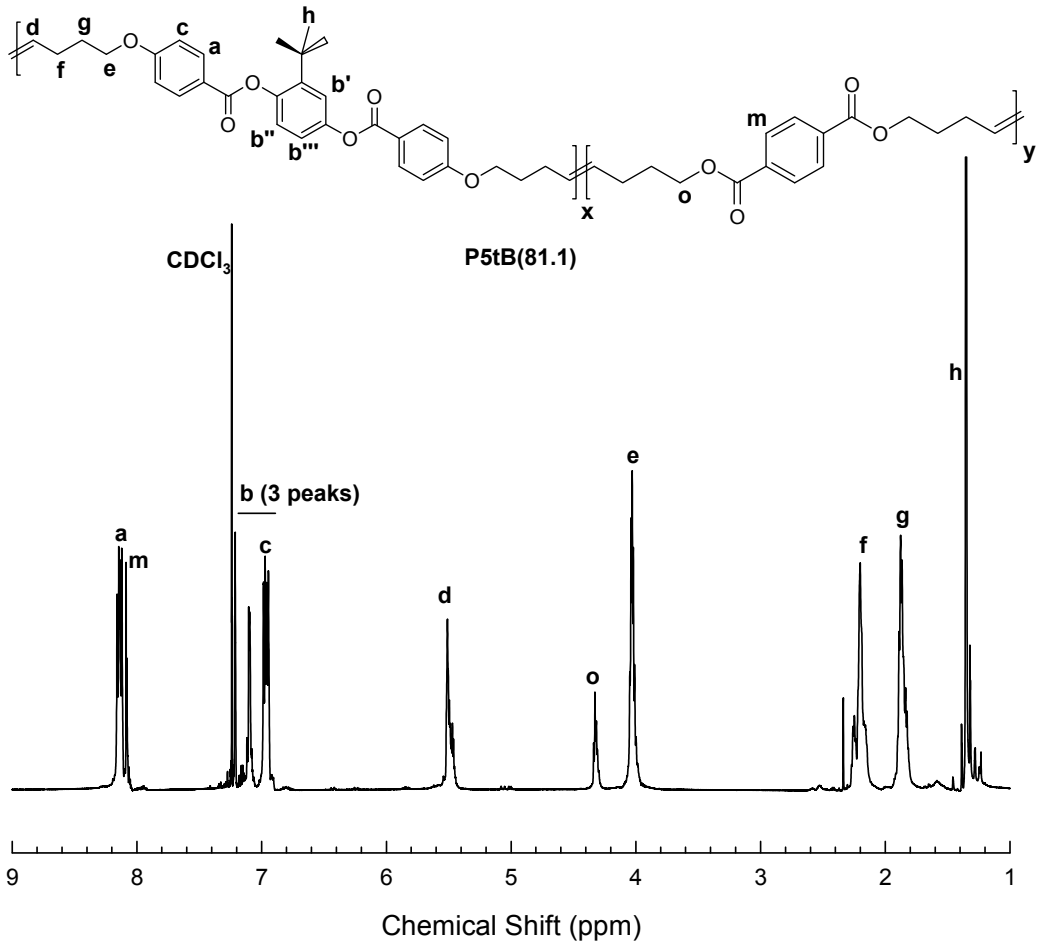

Figure S3. ^{1}H NMR spectrum of **P5tB(81.1)** (M_n=16.2 kDa) run in $CDCl_3$. The peaks **o** and **e** in the spectrum are the peaks from ***5tB*** (**e**) and ***5Te*** (**o**) that were used to calculate molar ratio of the monomers incorporated into the polymer.

Burke and Mather Figure S4.

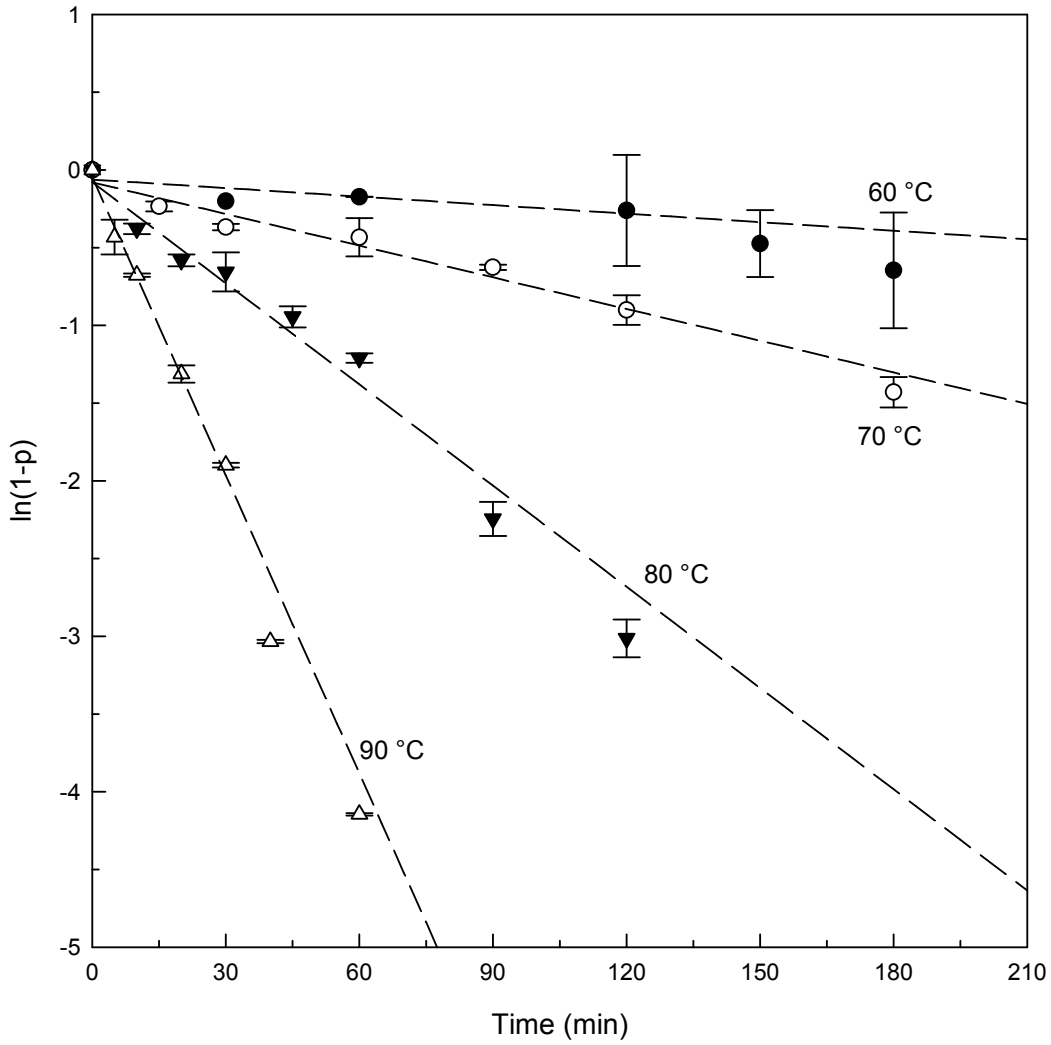

Figure S4. Free-radical crosslinking of **P5tB(97.3)** with 10 wt-% lauroyl peroxide. The natural logarithm of (1-*p*) (where *p* is the fractional extent of cure) is plotted versus isothermal cure time. At shorter cure times, the data is linear with respect to time and can be fitted using linear regression to determine a rate constant for the early stages of the reaction.

Burke and Mather Figure S5.

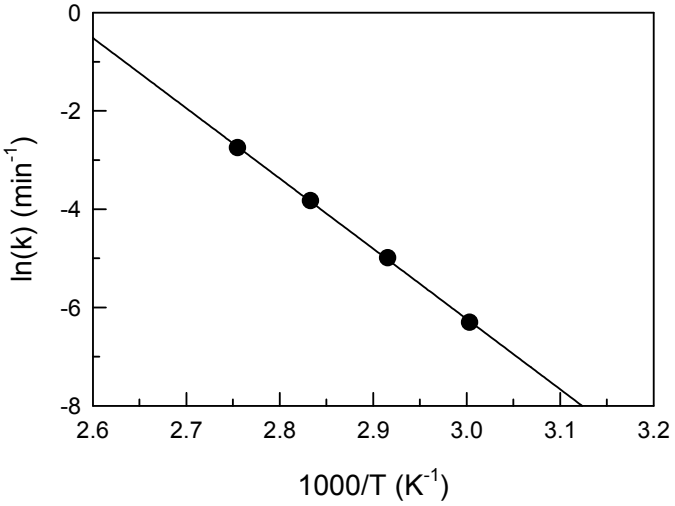

Figure S5. Arrhenius dependence of the first order rate constants from the free-radical crosslinking of **P5tB(97.3)** with 10 wt-% lauroyl peroxide. The line shown was fit to the data using linear regression ($R^2 = 0.999$), and the activation energy for the cure was found to be 118.9 kJ/mol using the slope of this line.

Burke and Mather Figure S6.

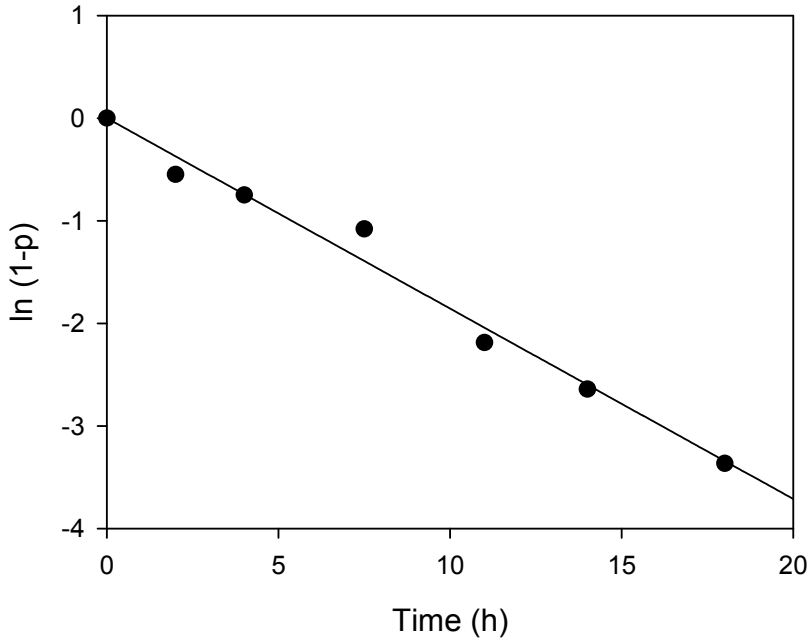

Figure S6. Free-radical crosslinking of **P5tB(97.3)** at 60 °C using 5.16 wt-% lauroyl peroxide. The natural logarithm of (1-*p*) (where *p* is the fractional extent of cure) is plotted versus isothermal cure time. The line shown was fit to the data using linear regression ($R^2 = 0.983$), and the rate constant for cure at this temperature and initiator loading was found to be 0.186 h^{-1}.