

## Supporting Information (SI)

### **Lignin-derivable, thermoplastic, non-isocyanate polyurethanes with increased hydrogen-bonding content and toughness vs. petroleum-derived analogues**

Jignesh S. Mahajan,<sup>a,b</sup> Zachary R. Hinton,<sup>c</sup> Eduardo Nombera Bueno,<sup>a,d</sup>  
Thomas H. Epps, III,<sup>a,b,c,d\*</sup> and LaShanda T. J. Korley<sup>a,b,c,d\*</sup>

<sup>a</sup> *Department of Materials Science & Engineering, University of Delaware, Newark, Delaware 19716, USA.*

<sup>b</sup> *Center for Research in Soft matter and Polymers, University of Delaware, Newark, Delaware 19716, USA.*

<sup>c</sup> *Center for Plastics Innovation, University of Delaware, Newark, Delaware 19716, USA.*

<sup>d</sup> *Department of Chemical & Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, USA.*

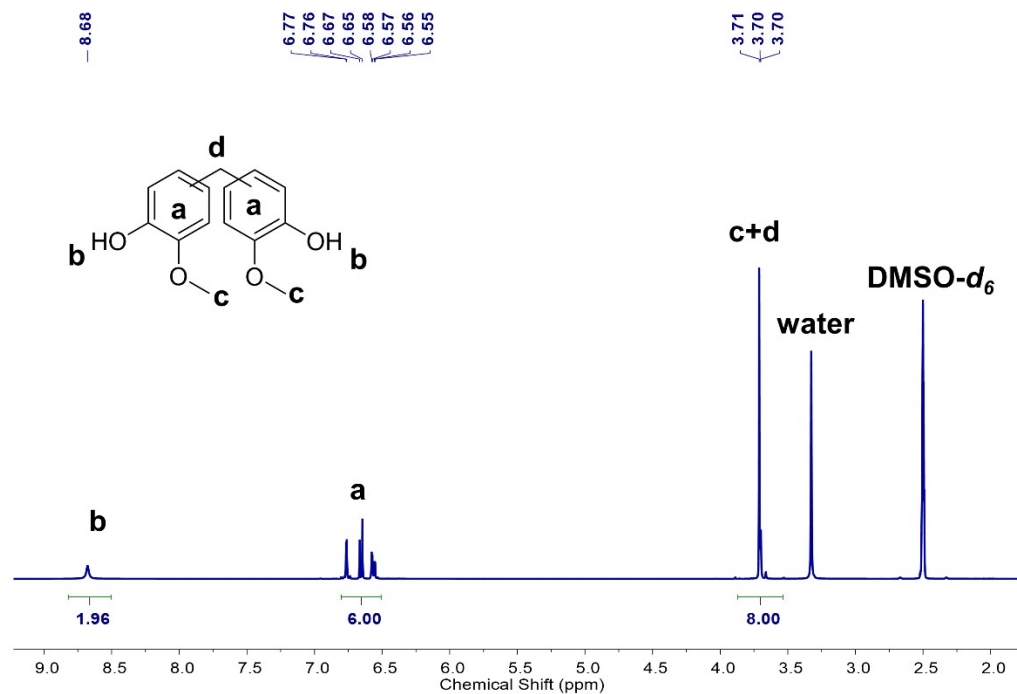
\*Corresponding authors:

thepps@udel.edu

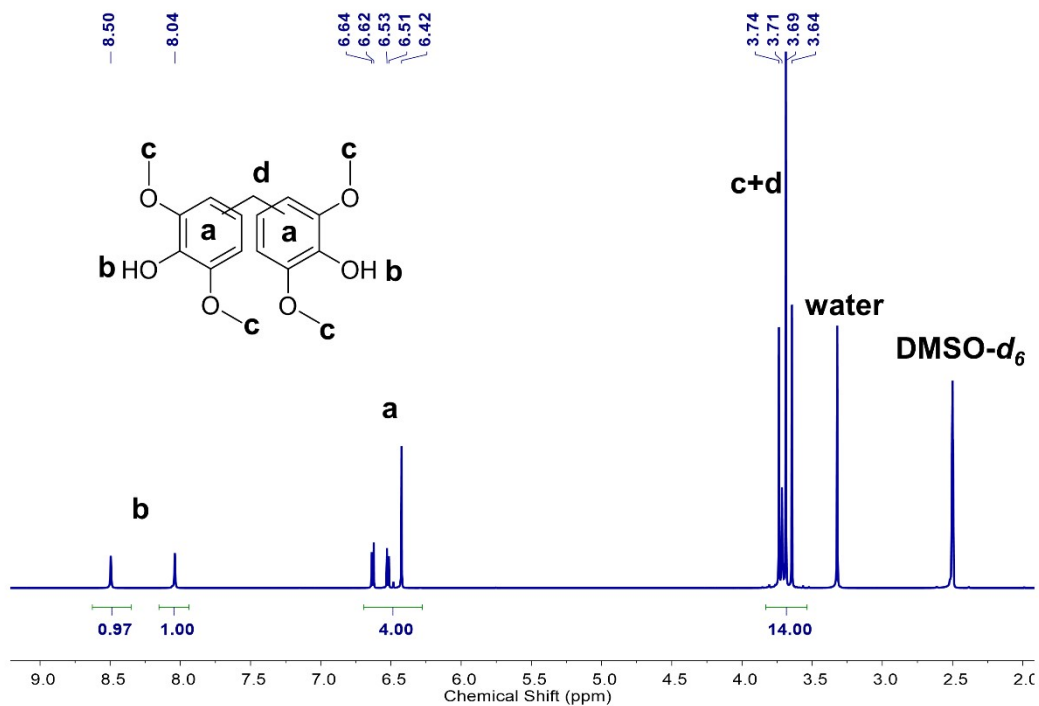
lkorley@udel.edu

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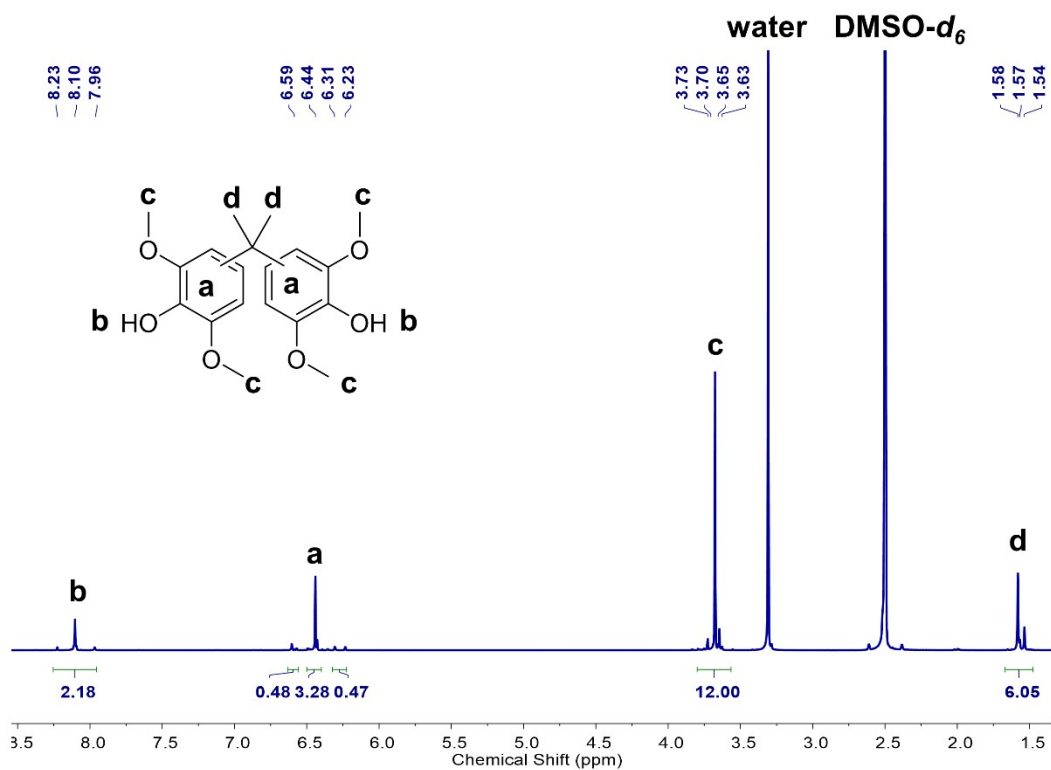
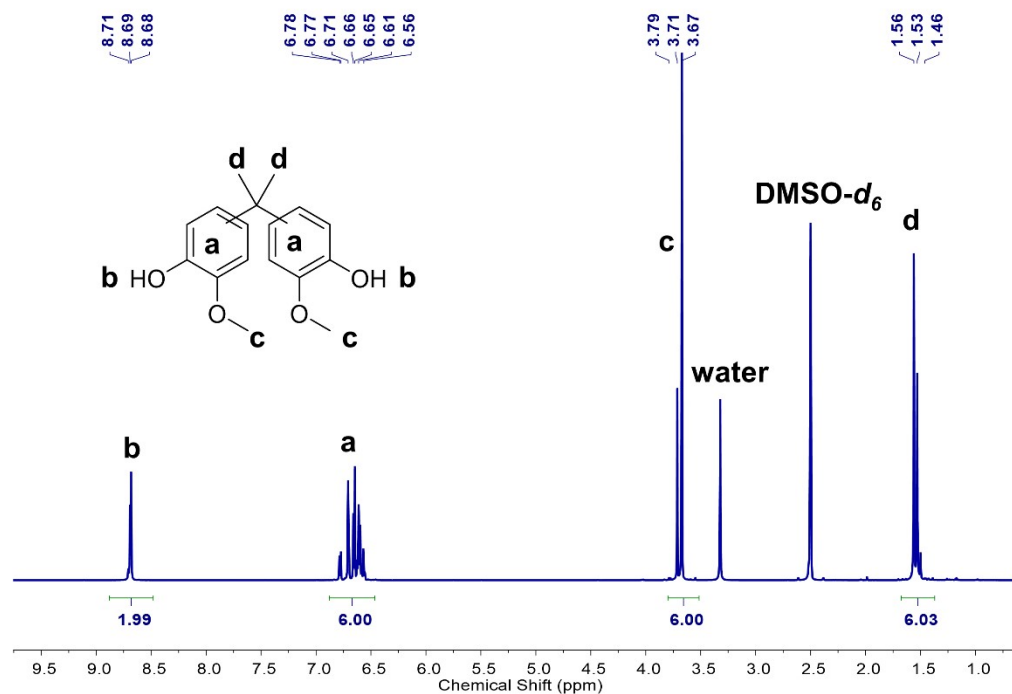
**Proton ( $^1\text{H}$ ) Nuclear magnetic resonance (NMR) spectra for bisguaiacols/bissyringols in deuterated dimethyl sulfoxide ( $\text{DMSO-}d_6$ )**

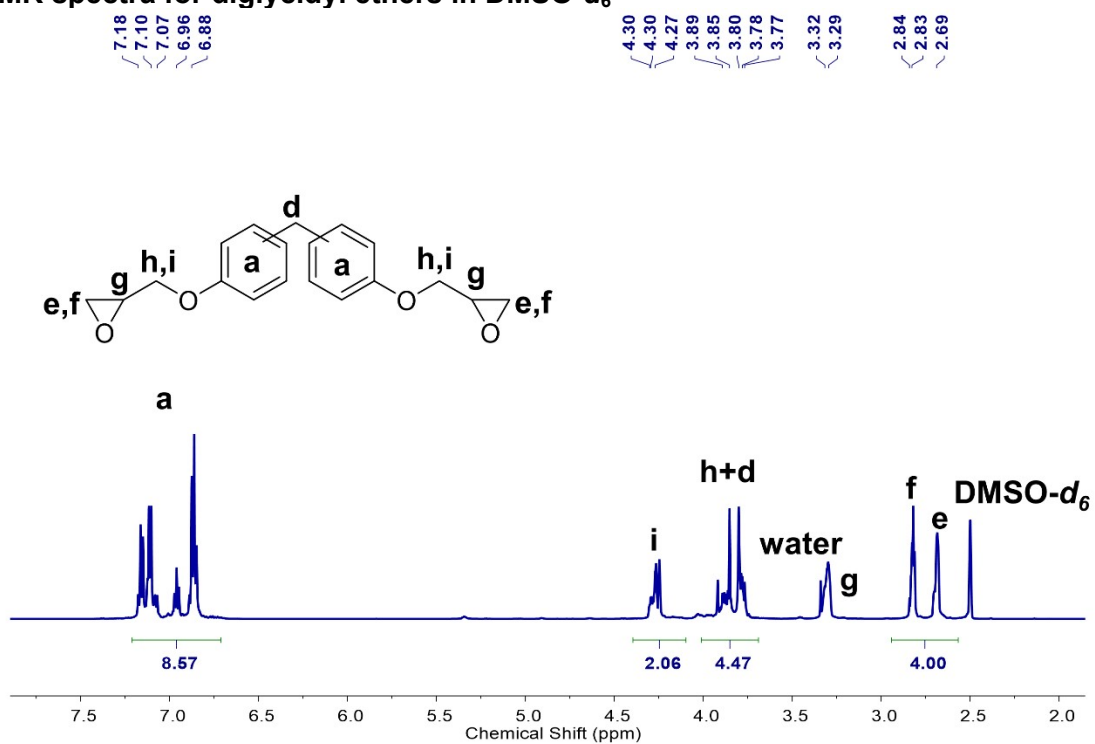
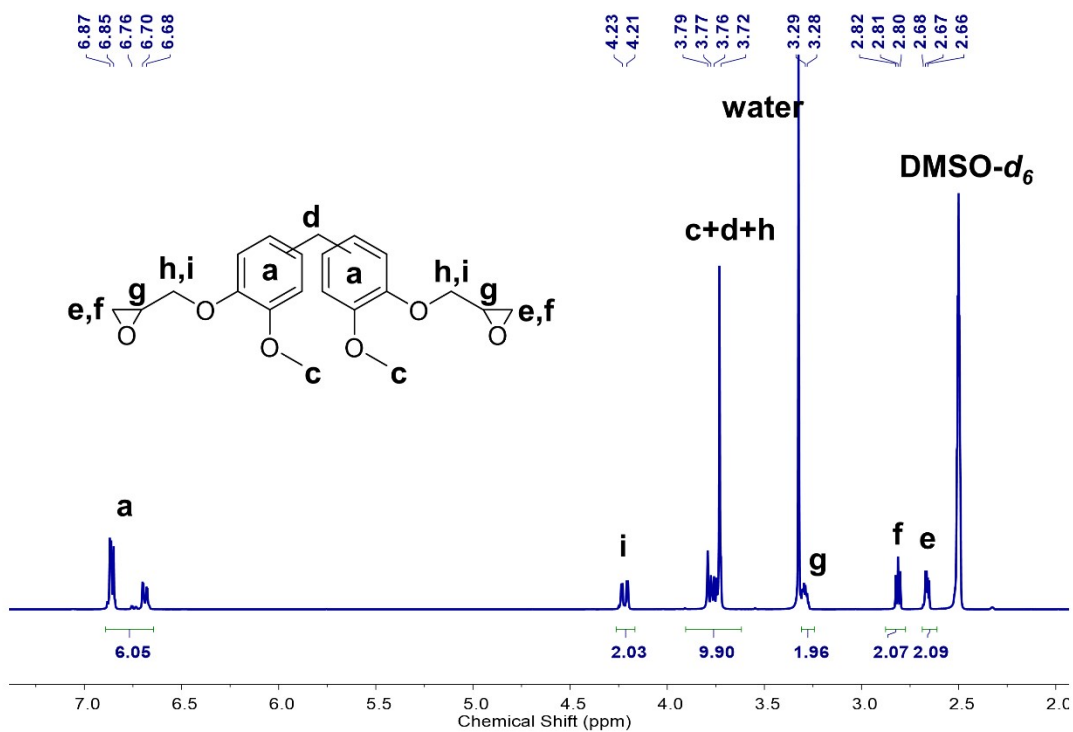


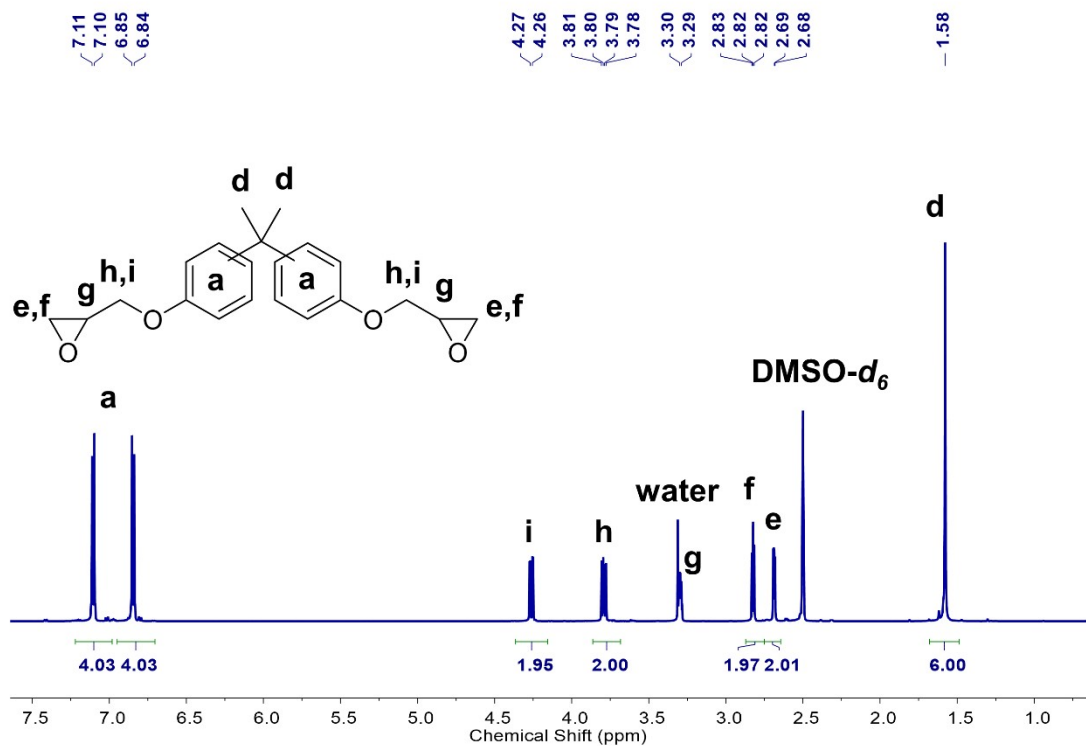
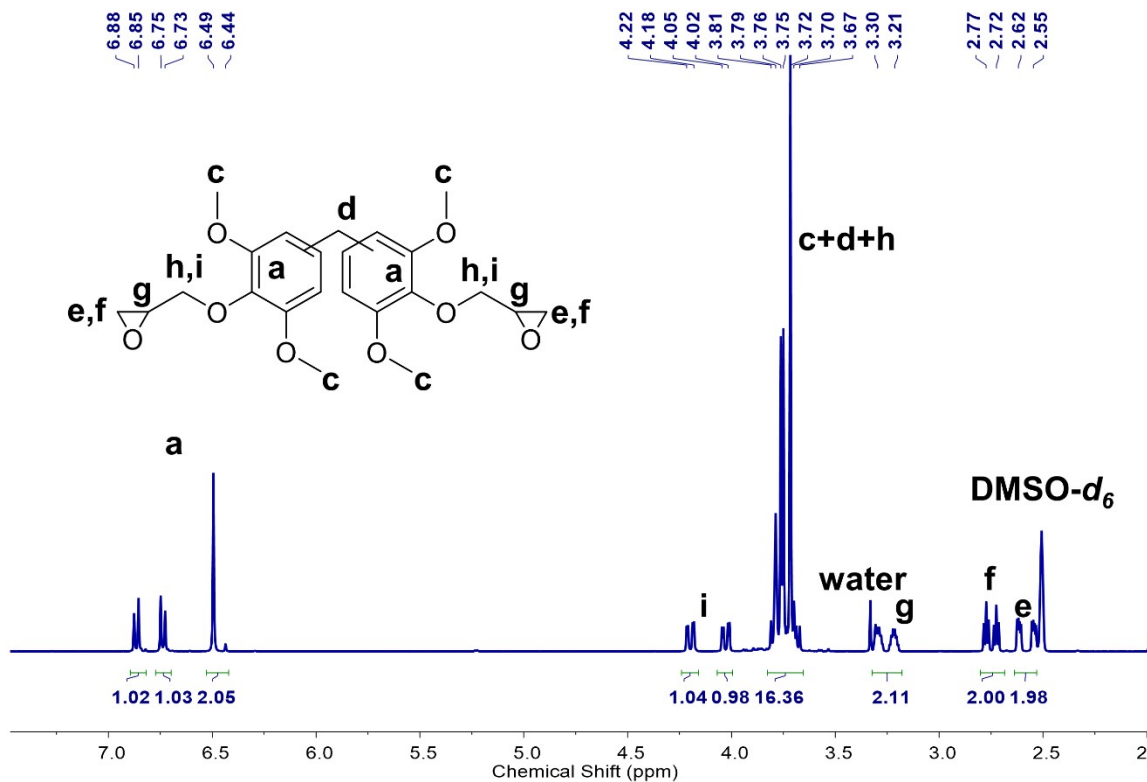
**Figure S1:**  $^1\text{H}$  NMR spectrum of bisguaiacol F (BGF)



**Figure S2:**  $^1\text{H}$  NMR spectrum of bissyringol F (BSF)



**<sup>1</sup>H NMR spectra for diglycidyl ethers in DMSO-*d*<sub>6</sub>****Figure S5:** <sup>1</sup>H NMR spectrum of bisphenol F (BPF) diglycidyl ether**Figure S6:** <sup>1</sup>H NMR spectrum of BGF diglycidyl ether



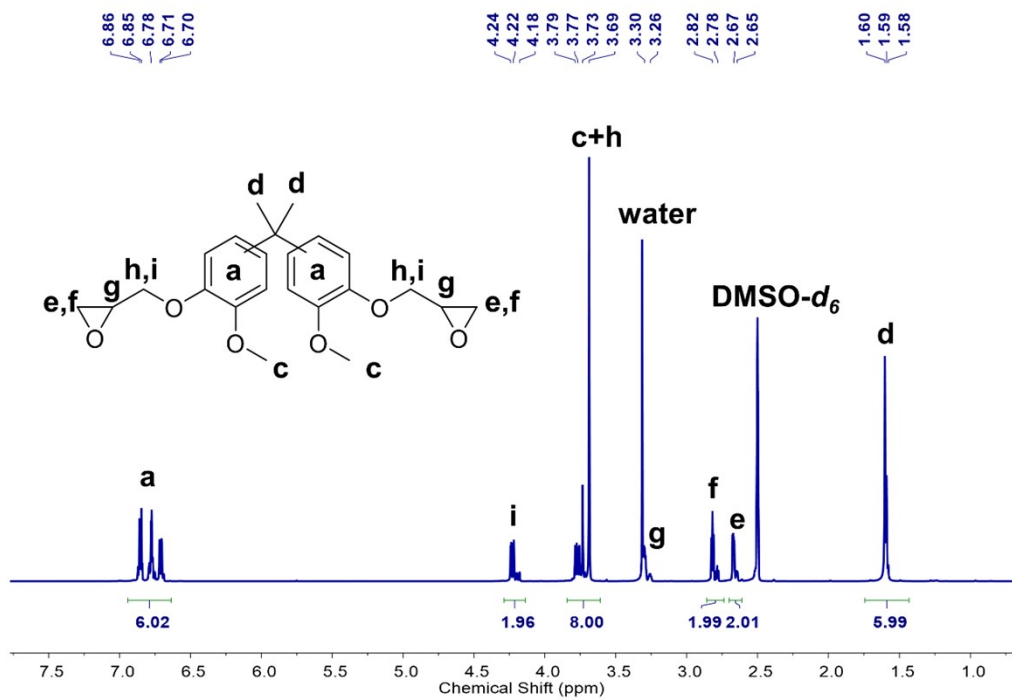


Figure S9: <sup>1</sup>H NMR spectrum of BGA diglycidyl ether

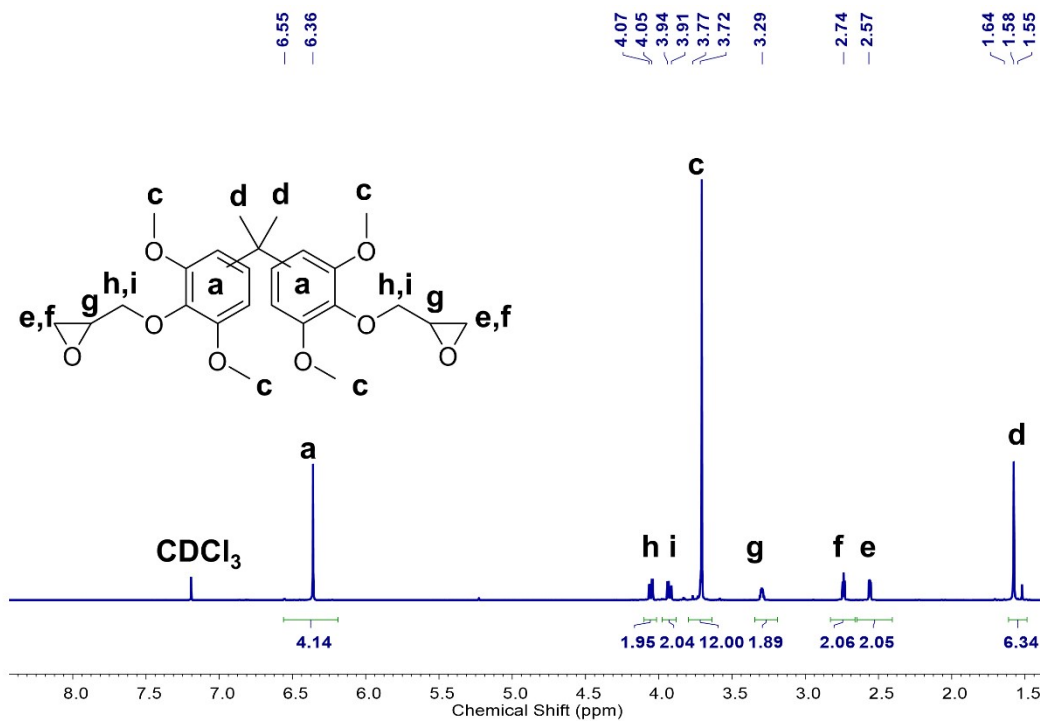
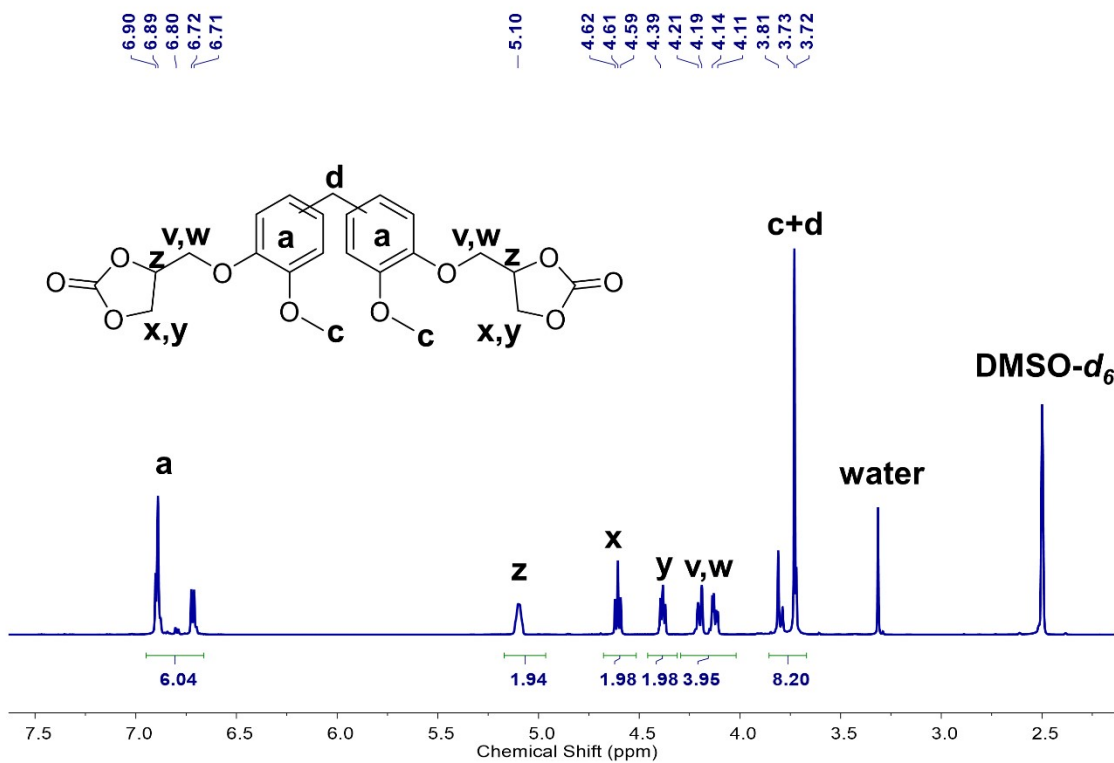
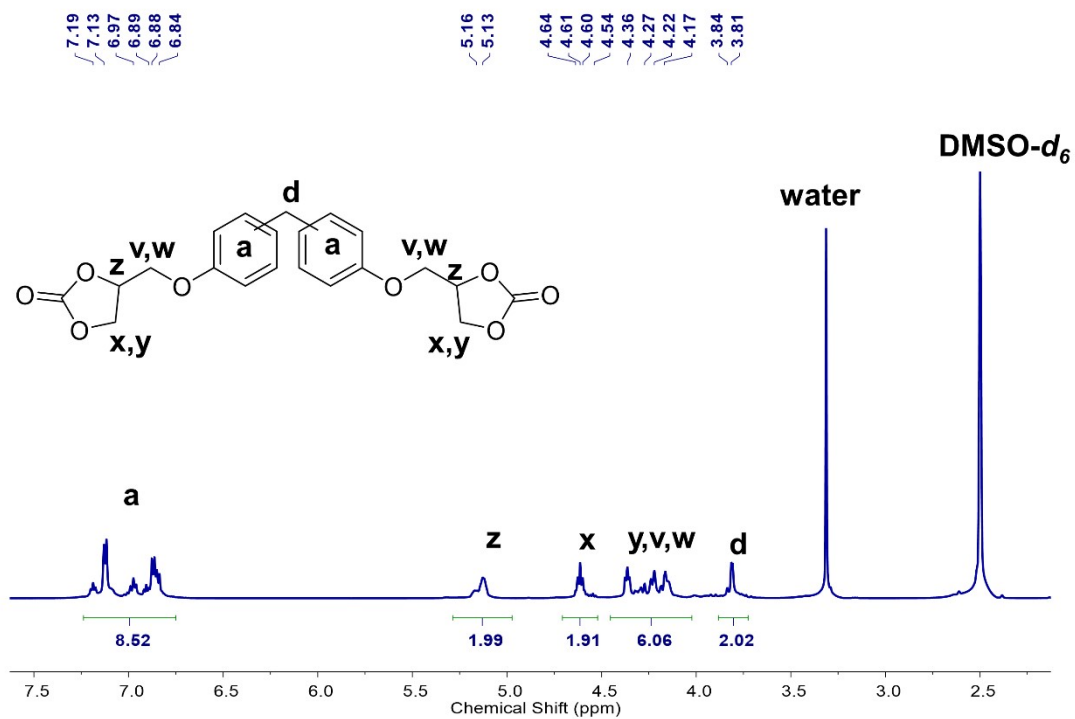
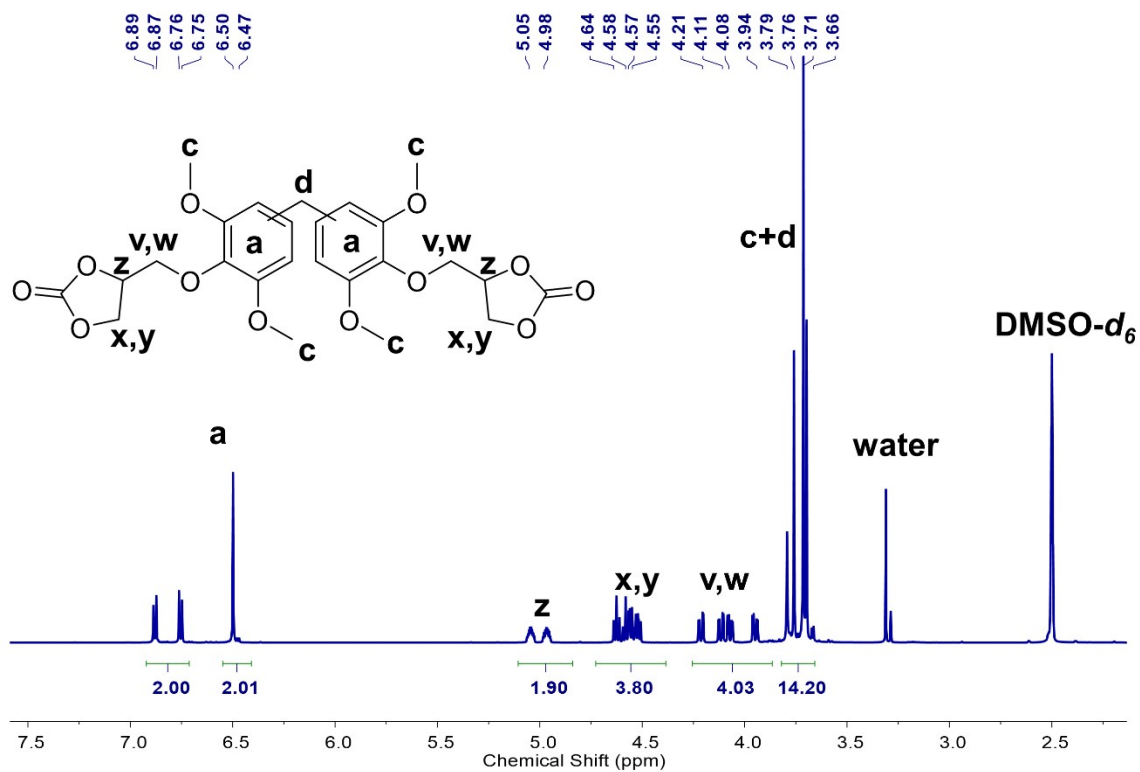
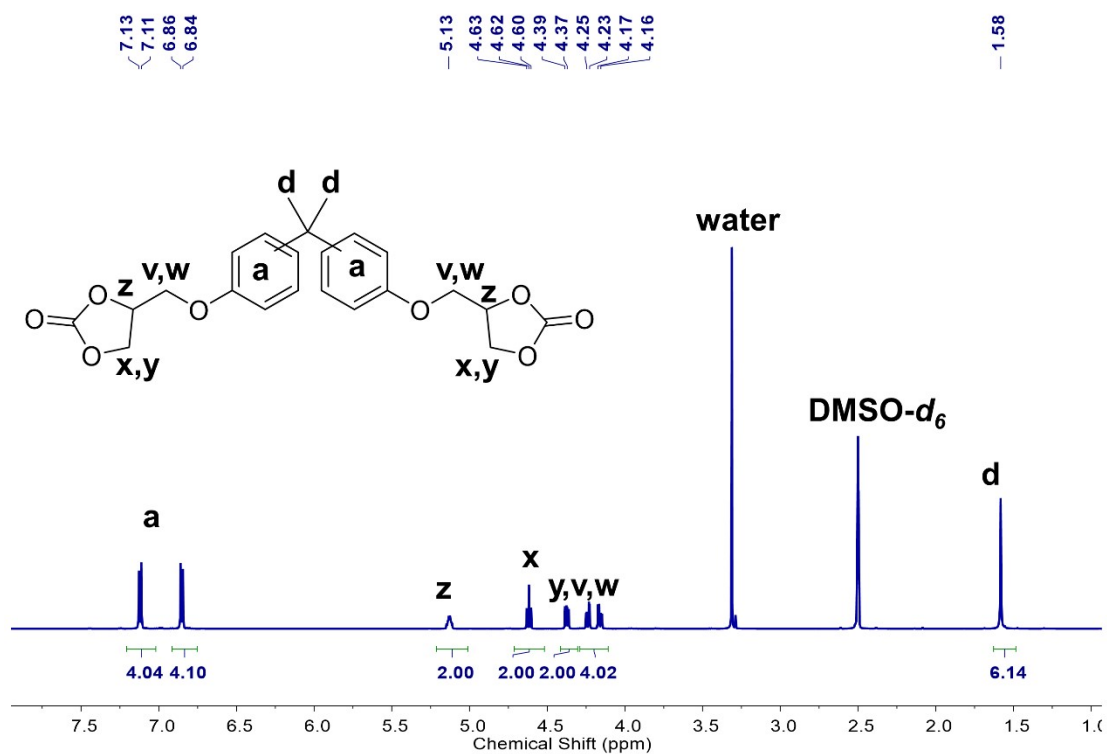
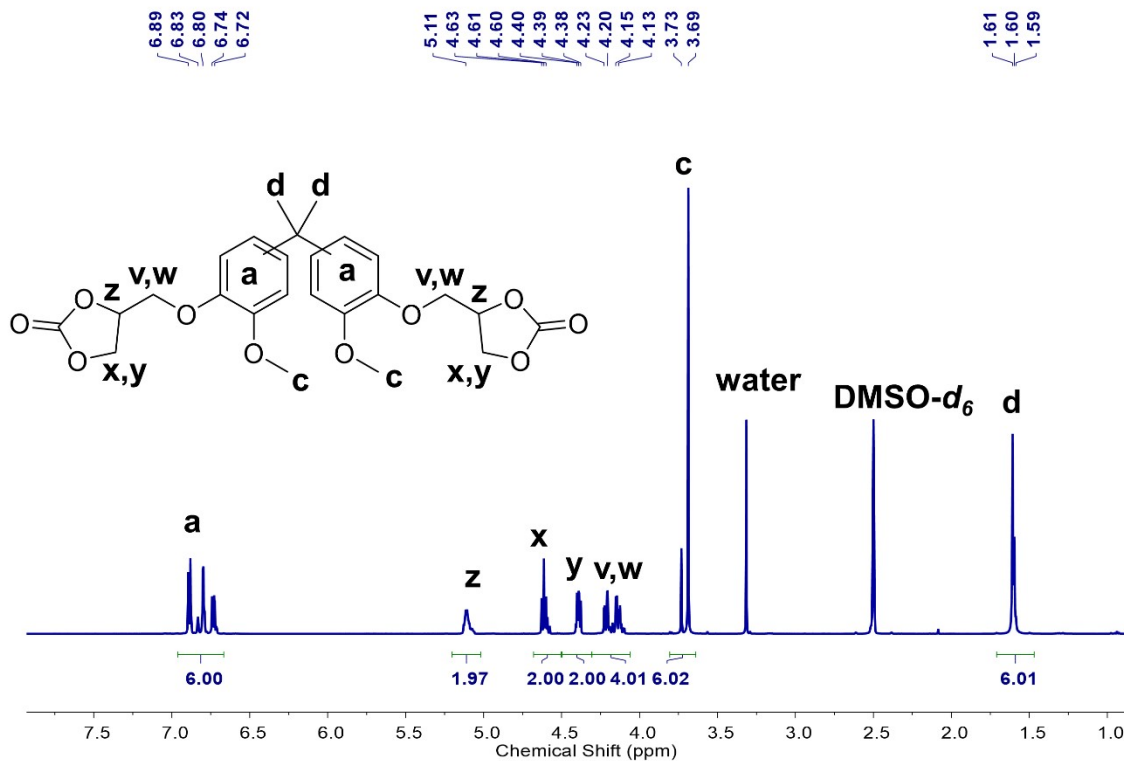
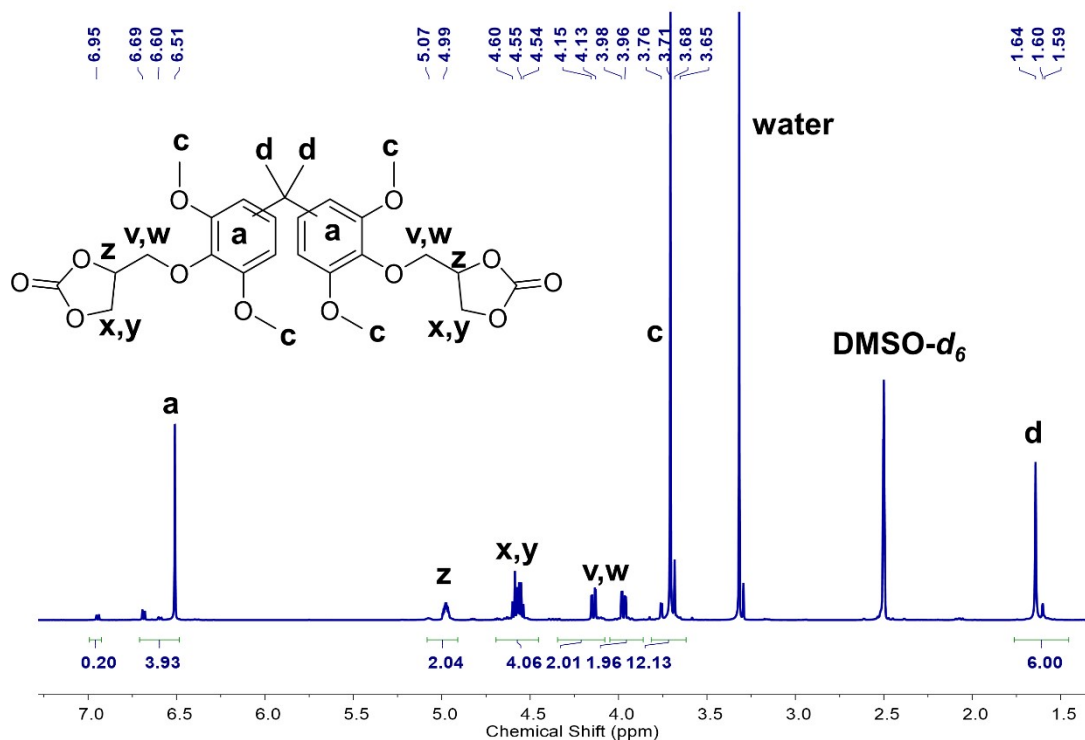


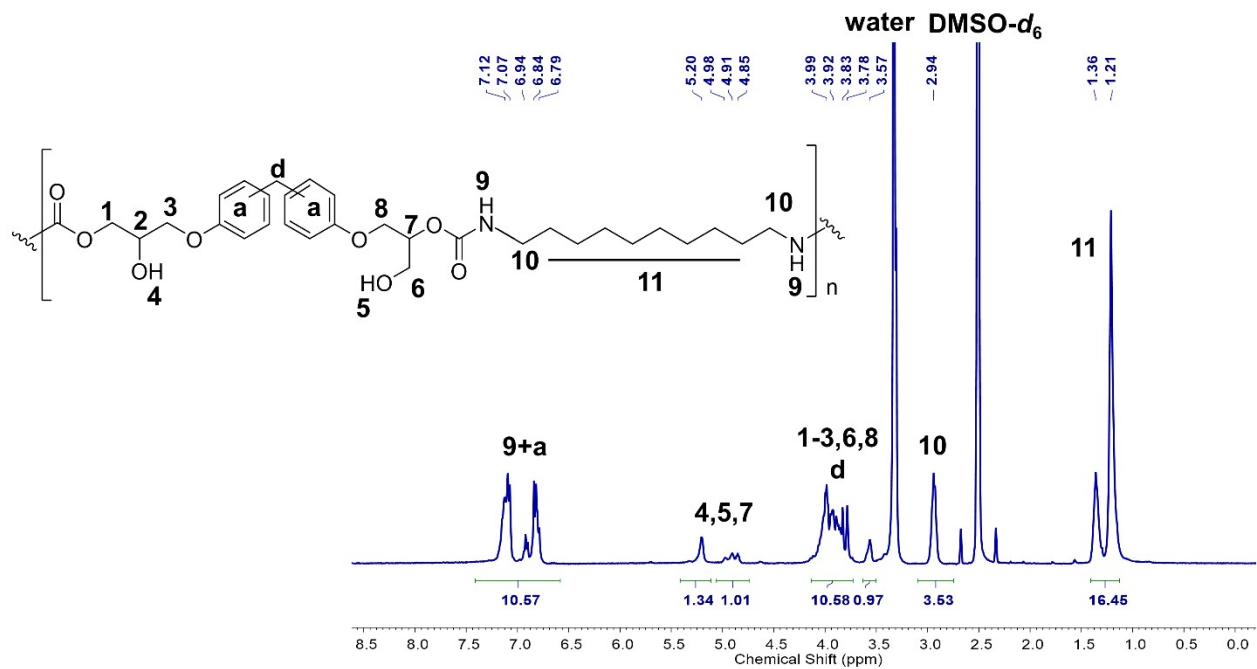
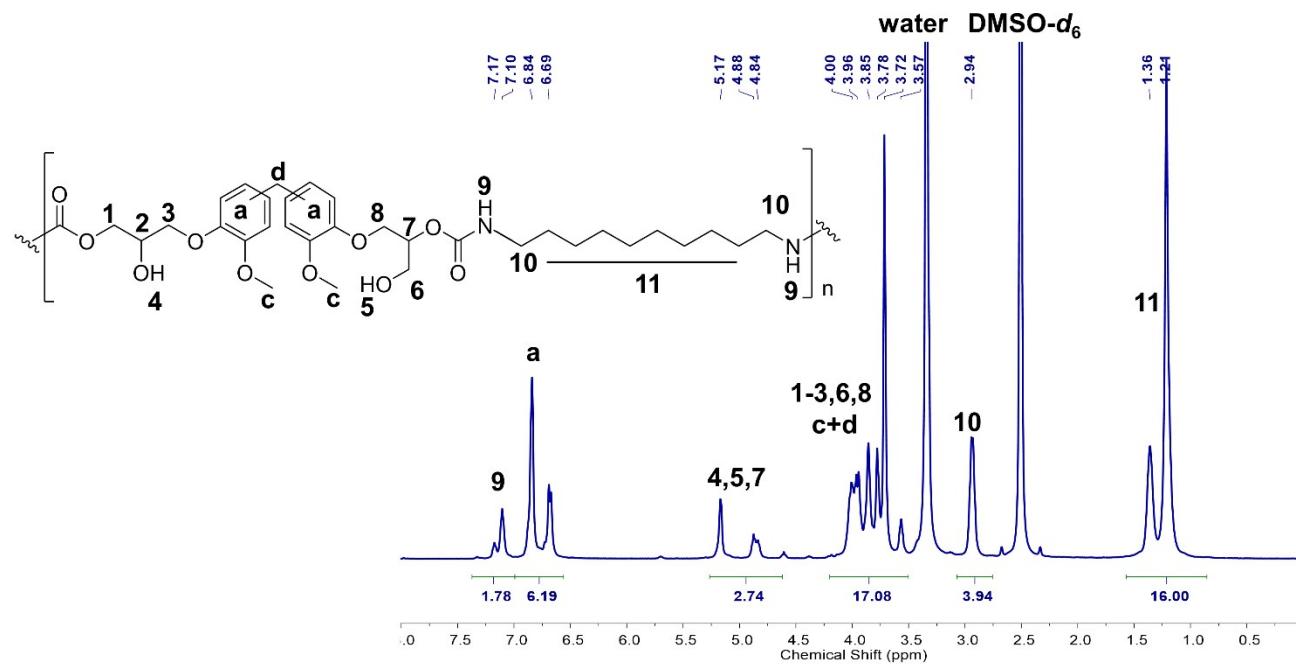
Figure S10: <sup>1</sup>H NMR spectrum of BSA diglycidyl ether in deuterated chloroform (CDCl<sub>3</sub>)  
(Note: BSA diglycidyl ether was not completely soluble in DMSO-d<sub>6</sub>)

**<sup>1</sup>H NMR spectra for cyclic carbonates in DMSO-*d*<sub>6</sub>**

Figure S13: <sup>1</sup>H NMR spectrum of BSF cyclic carbonate (BSFCC)Figure S14: <sup>1</sup>H NMR spectrum of BPA cyclic carbonate (BPACC)



Figure S15: <sup>1</sup>H NMR spectrum of BGA cyclic carbonate (BGACC)Figure S16: <sup>1</sup>H NMR spectrum of BSA cyclic carbonate (BSACC)

**<sup>1</sup>H NMR spectra for non-isocyanate polyurethanes (NIPUs) in DMSO-d<sub>6</sub>****Figure 17:** <sup>1</sup>H NMR spectrum of BPF-NIPU**Figure 18:** <sup>1</sup>H NMR spectrum of BGF-NIPU

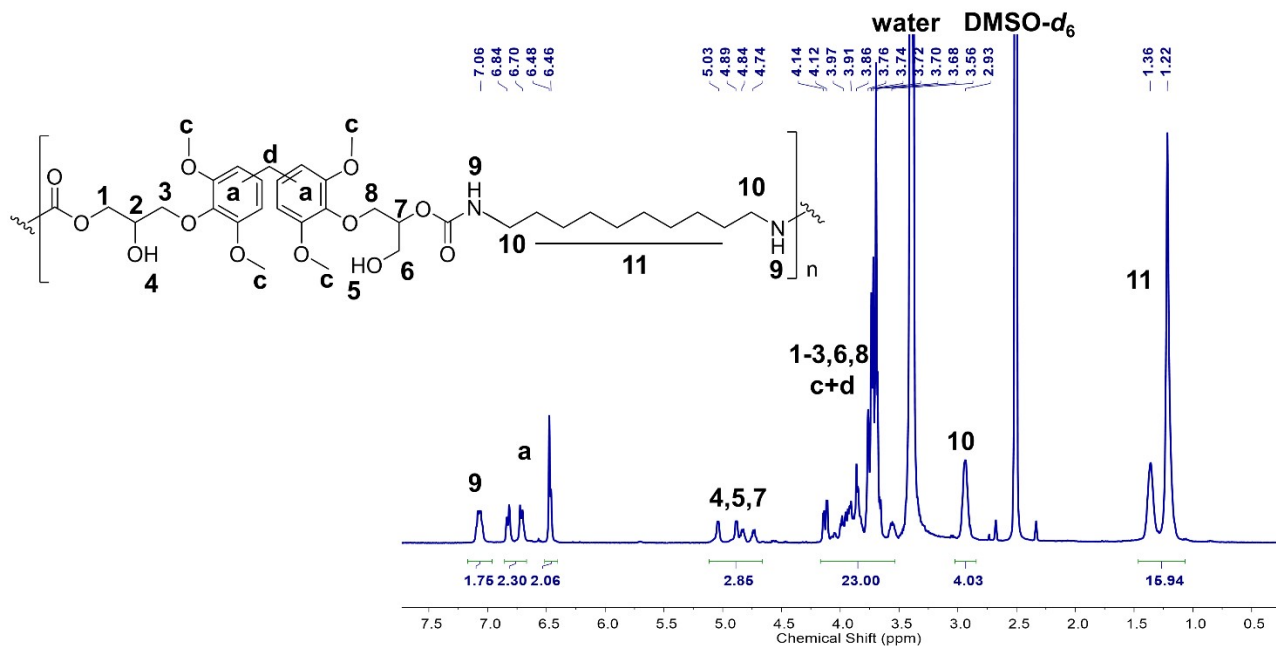


Figure 19:  $^1\text{H}$  NMR spectrum of BSF-NIPU

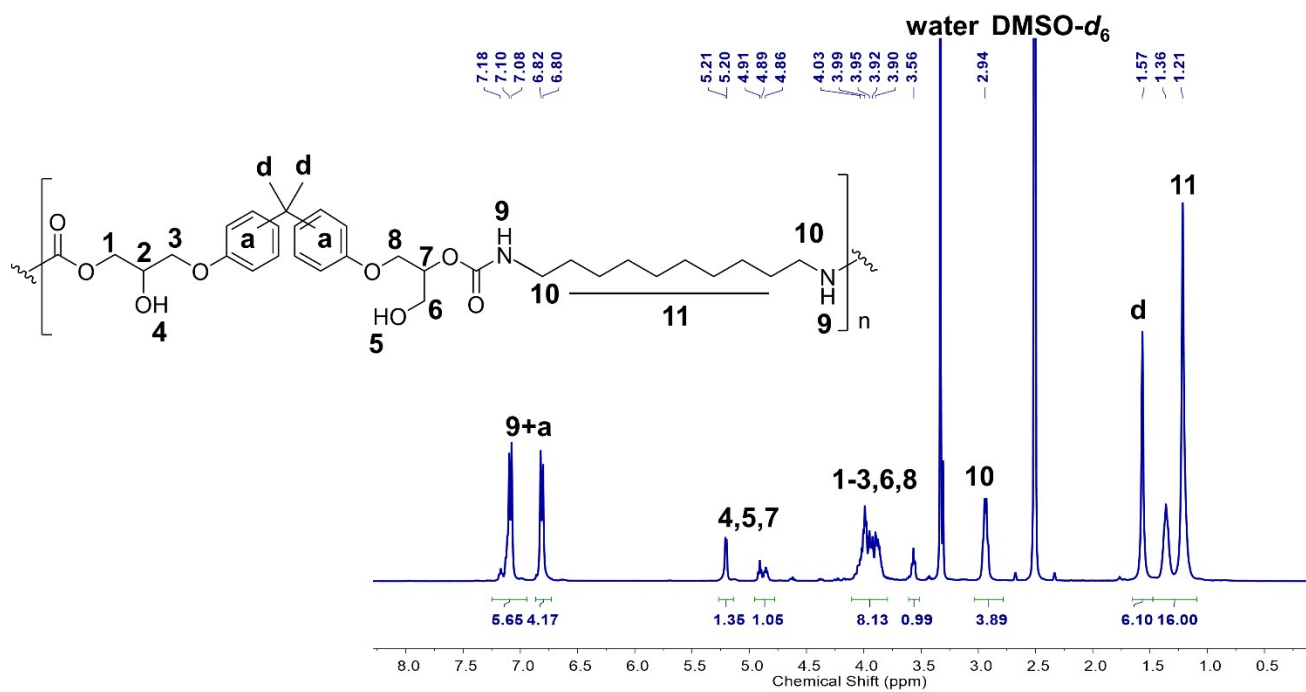


Figure 20:  $^1\text{H}$  NMR spectrum of BPA-NIPU

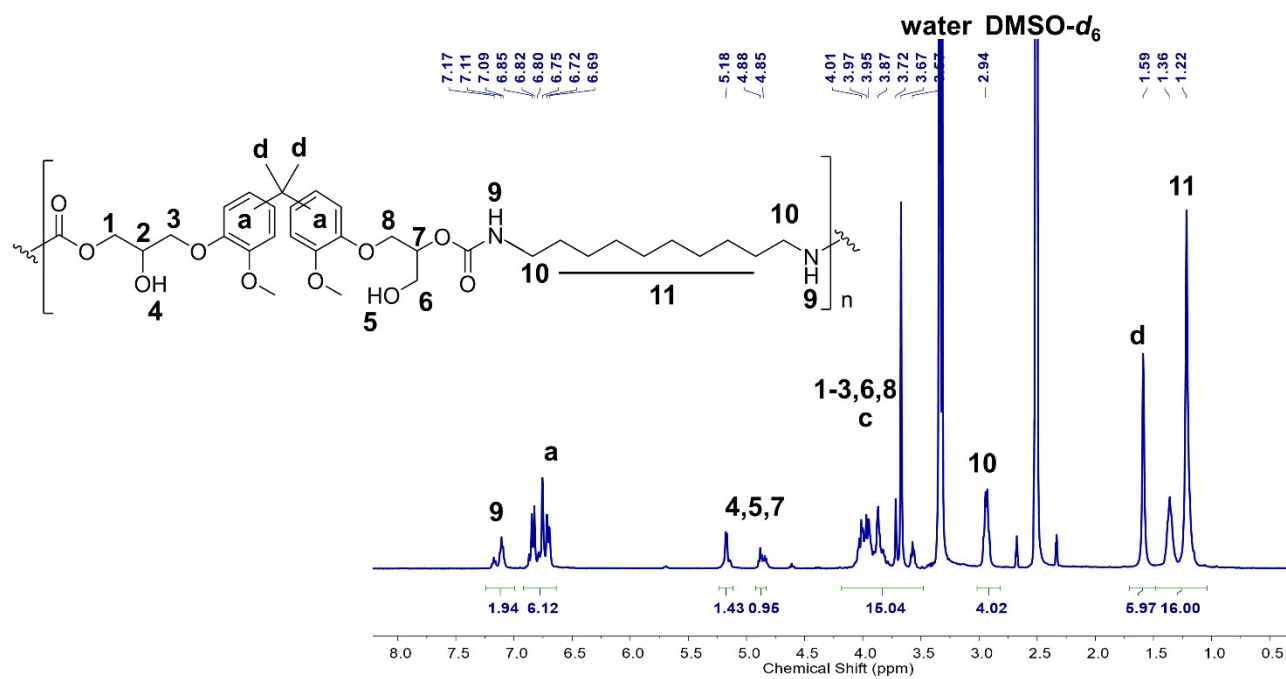


Figure 21: <sup>1</sup>H NMR spectrum of BGA-NIPU

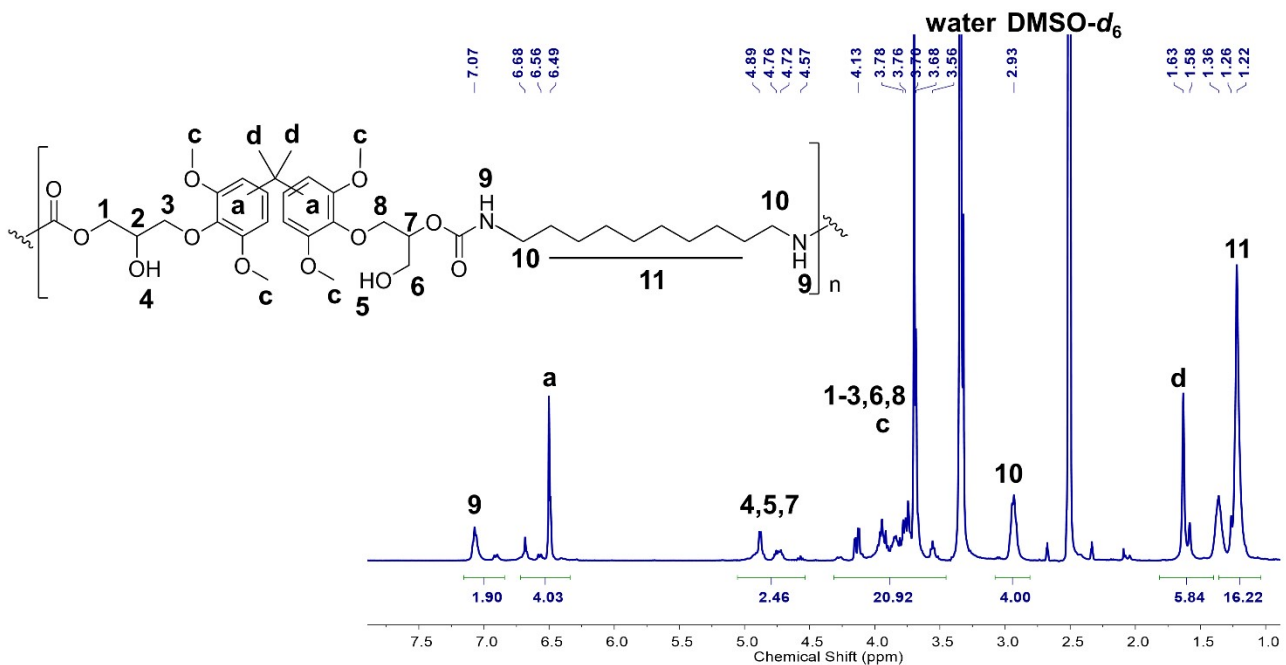
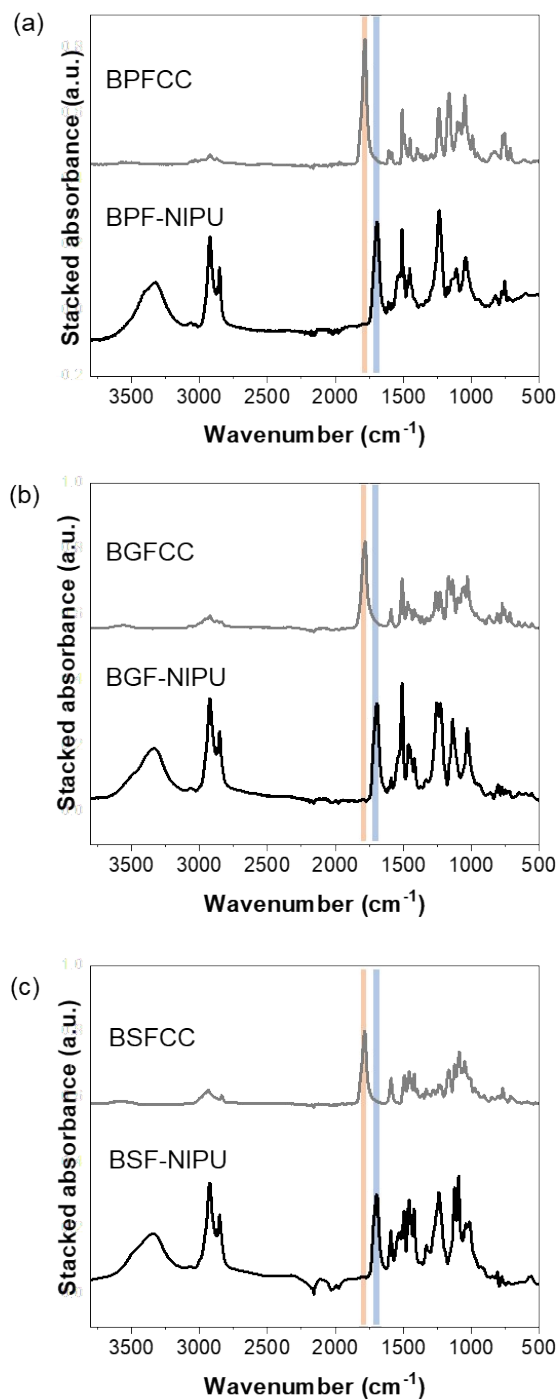
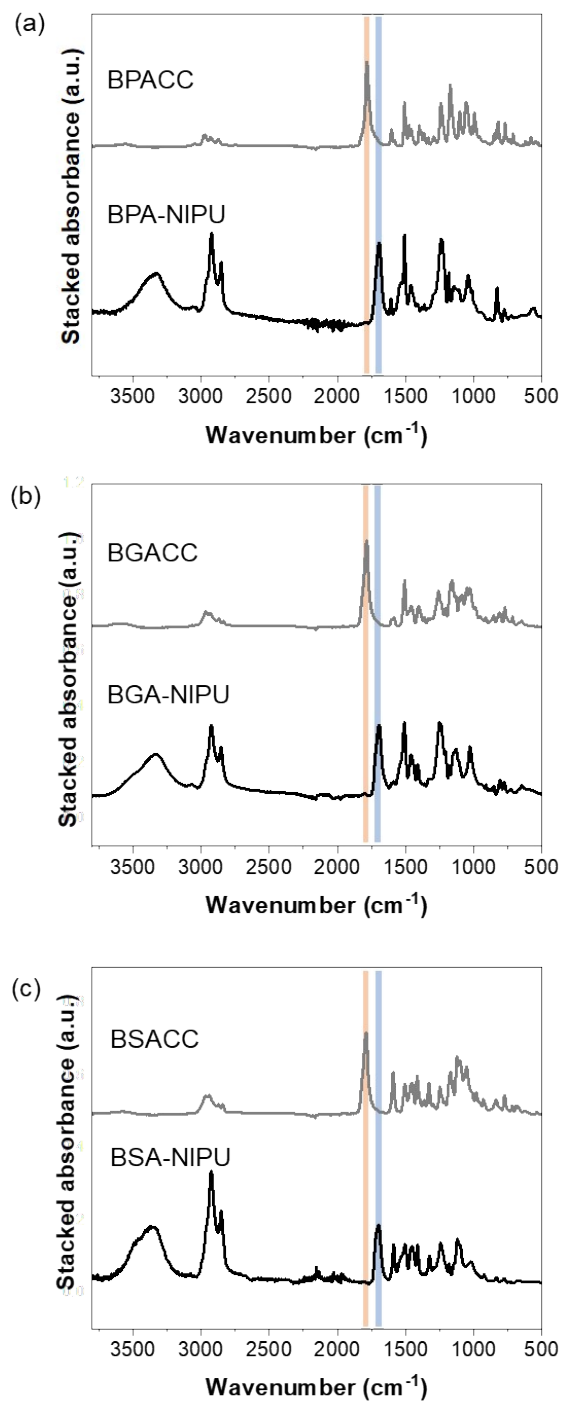


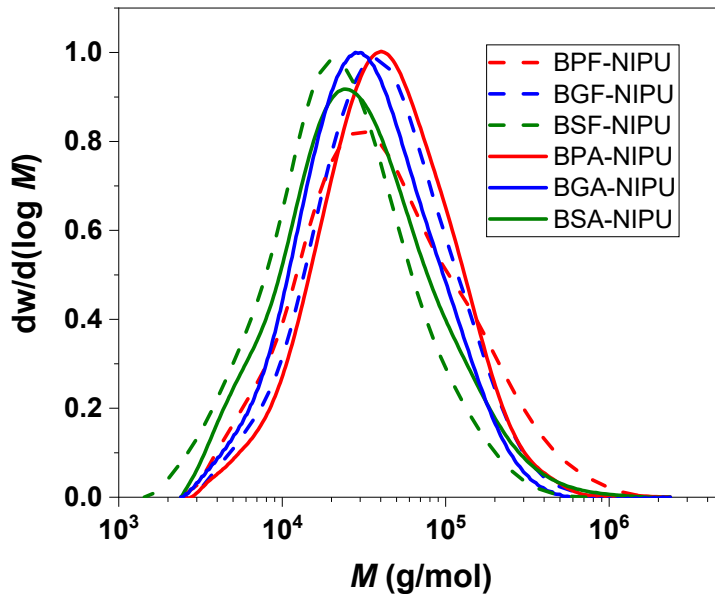
Figure 22: <sup>1</sup>H NMR spectrum of BSA-NIPU

**Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra**

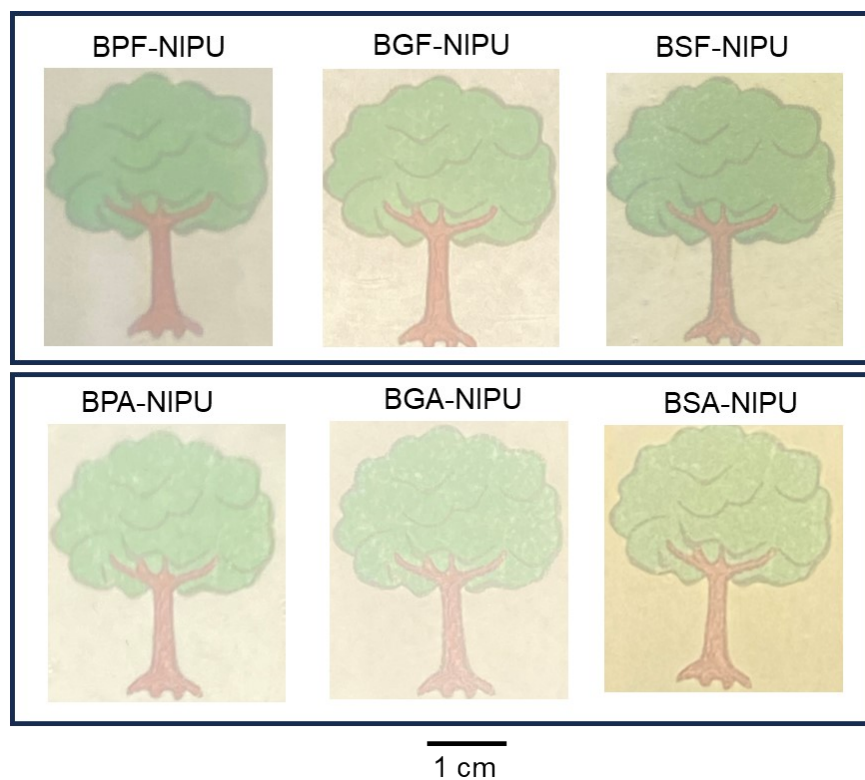
**Figure S23:** Stacked ATR-FTIR spectra of (a) BPFCC and BPF-NIPU, (b) BGFCC and BGF-NIPU, and (c) BSFCC and BSF-NIPU. The NIPU formation was assessed through the disappearance of the carbonyl stretching vibration of the cyclic carbonate at  $\sim 1790\text{ cm}^{-1}$  (highlighted in orange) and the appearance of the urethane carbonyl stretching vibration band  $\sim 1700\text{ cm}^{-1}$  (highlighted in blue). Additionally, the signals at  $\sim 3100\text{--}3700\text{ cm}^{-1}$  for  $\text{--OH/--NH}$  confirmed the characteristic functionalities of NIPUs. Curves are shifted vertically for clarity.



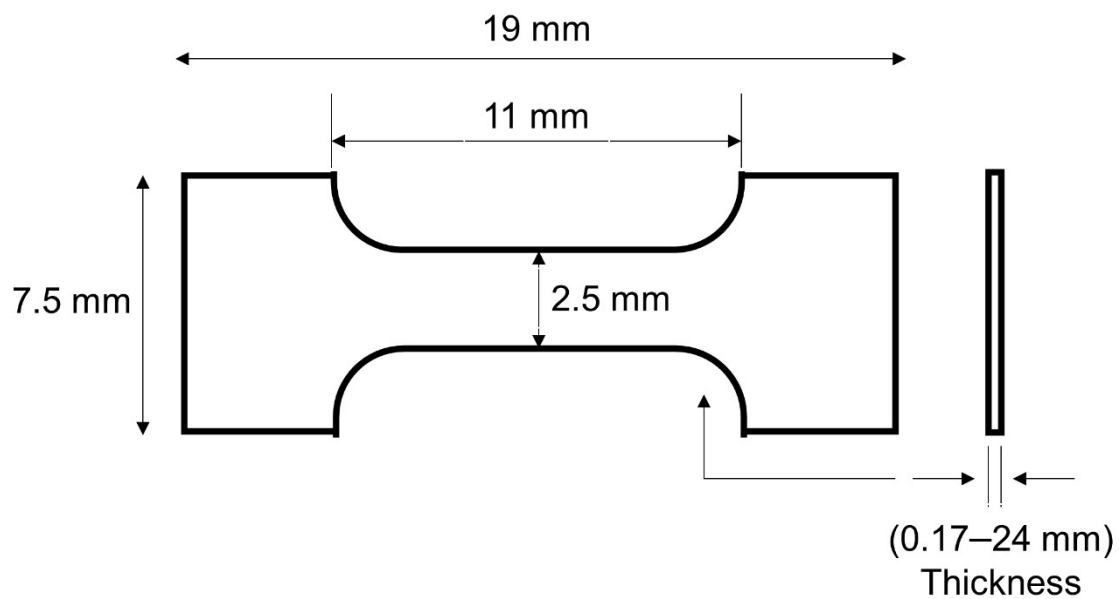
**Figure S24:** Stacked ATR-FTIR spectra of (a) BPACC and BPA-NIPU, (b) BGACC and BGA-NIPU, and (c) BSACC and BSA-NIPU. The NIPU formation was assessed through the disappearance of the carbonyl stretching vibration of the cyclic carbonate at  $\sim 1790 \text{ cm}^{-1}$  (highlighted in orange) and the appearance of the urethane carbonyl stretching vibration band  $\sim 1700 \text{ cm}^{-1}$  (highlighted in blue). Additionally, the signals at  $\sim 3100\text{--}3700 \text{ cm}^{-1}$  for  $\text{--OH/--NH}$  confirmed the characteristic functionalities of NIPUs. Curves are shifted vertically for clarity.



**Figure S25:** Differential weight fraction distributions as a function of molar mass ( $M$ ) measured *via* gel permeation chromatography (GPC) for NIPUs. Molar masses were determined relative to poly(methyl methacrylate) standards using data from GPC with a refractive index detector [GPC solvent: *N,N*-Dimethylacetamide + 0.5 wt% lithium bromide]. See **Section 2.3.4.** in the main text for more details on GPC protocols/sample preparation.

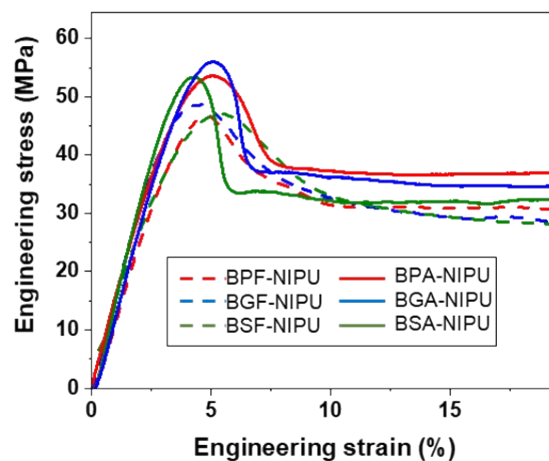


**Figure S26:** Optical images of NIPU films. See **Section 2.3.5** in the main text for film formation protocols.

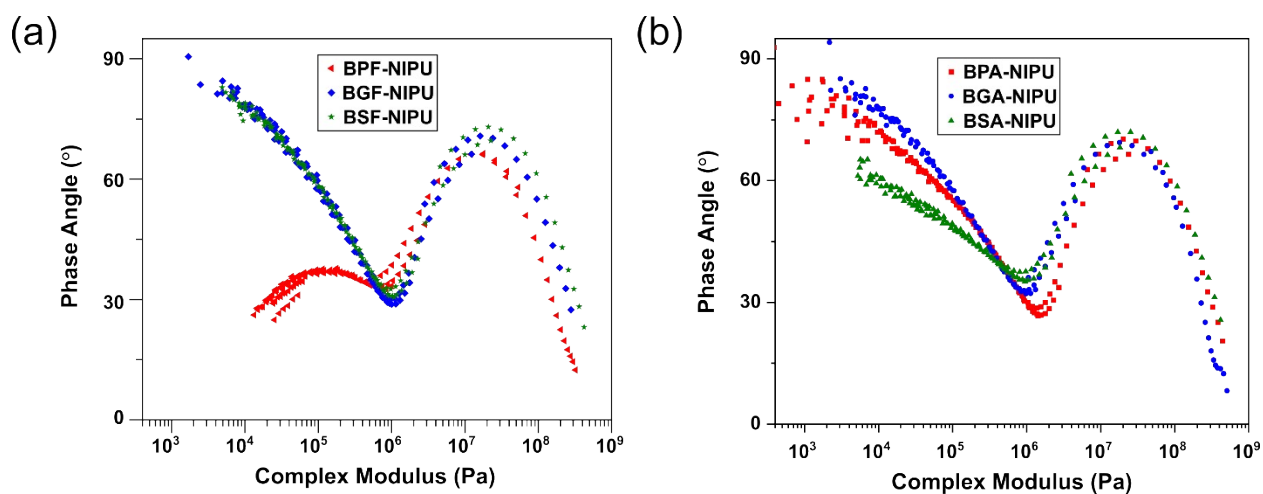


**Figure S27:** Dimensions of the NIPU films used for uniaxial tensile testing.

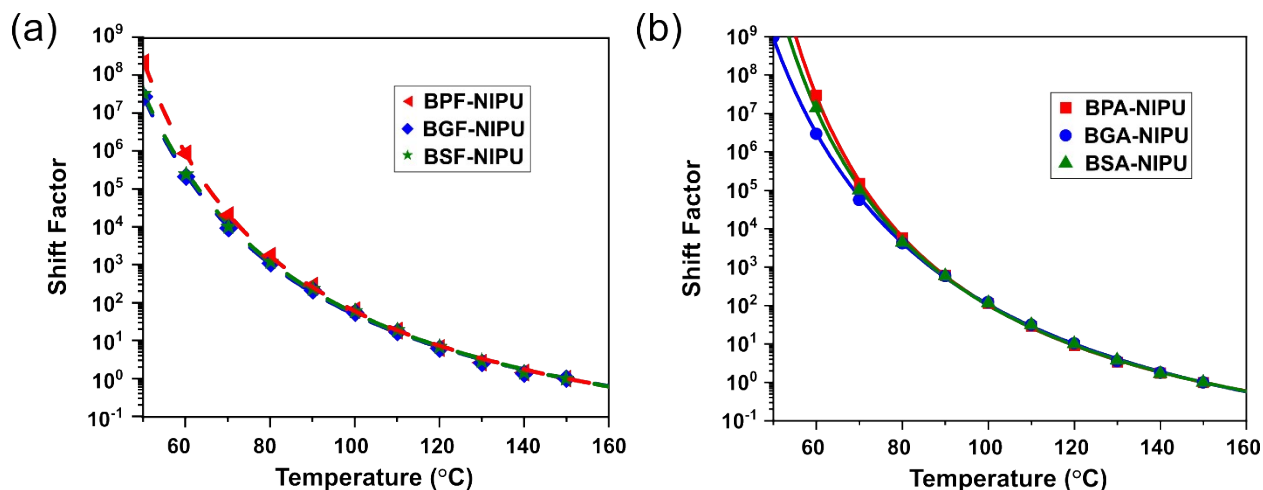




**Figure S28:** Representative engineering tensile stress vs. engineering strain (from 0% to 18%) curves, which shows necking for NIPUs acquired during uniaxial tensile testing using a load cell of 100 N and a strain rate of  $10 \text{ \% min}^{-1}$  at  $\sim 20 \text{ }^\circ\text{C}$ .



**Figure S29:** van Gorp-Palmen representation of the linear viscoelastic spectrum for (a) unsubstituted, bridging-carbon- and (b) dimethyl-substituted, bridging-carbon-based NIPUs.



**Figure S30:** Thermorheological (vertical) shift factors (referenced to 150 °C) for (a) unsubstituted, bridging-carbon- and (b) dimethyl-substituted, bridging-carbon-based NIPUs. Lines represent fits using the Williams-Landel-Ferry equation.

## Abbreviations

|                             |   |
|-----------------------------|---|
| ATR-FTIR                    | Attenuated total reflectance-Fourier transform infrared |
| BGA                         | Bisguaiacol A   |
| BGACC                       | Bisguaiacol A cyclic carbonate                          |
| BGF                         | Bisguaiacol F   |
| BGFCC                       | Bisguaiacol F cyclic carbonate                          |
| BPA                         | Bisphenol A   |
| BPACC                       | Bisphenol A cyclic carbonate                            |
| BPF                         | Bisphenol F   |
| BPFCC                       | Bisphenol F cyclic carbonate                            |
| BSA                         | Bissyringol A   |
| BSACC                       | Bissyringol A cyclic carbonate                          |
| BSF                         | Bissyringol F   |
| BSFCC                       | Bissyringol F cyclic carbonate                          |
| CDCl <sub>3</sub>           | Deuterated chloroform                                   |
| DMAc                        | <i>N,N</i> -Dimethylacetamide                           |
| DMSO- <i>d</i> <sub>6</sub> | Deuterated dimethyl sulfoxide                           |
| GPC                         | Gel permeation chromatography                           |
| <i>M</i>                    | Molar mass  |
| NIPU                        | Non-isocyanate polyurethane                             |
| NMR                         | Nuclear magnetic resonance                              |