Supporting Information to

Combined Effects of Carbonate and Soft-Segment Molecular Structures on the Nanophase Separation and Properties of Segmented Polyhydroxyurethane

Goliath Beniah[1,#], Xi Chen[1,#], Brice E. Uno[2], Kun Liu[2], Emily K. Leitsch[1], Junho Jeon[3], William H. Heath[3], Karl A. Scheidt[2], and John M. Torkelson[1,4]*

[1]*Dept. of Chemical and Biological Engineering, Northwestern University, Evanston IL, 60208 USA*

[2]*Dept. of Chemistry, Northwestern University, Evanston, IL 60208 USA*

[3]*The Dow Chemical Company, Freeport, TX 77541 USA*

[4]*Dept. of Materials Science and Engineering, Northwestern University, Evanston, IL 60208 USA*

[#]co-first authors

*Correspondence to: Prof. John M. Torkelson (Email: *j-torkelson@northwestern.edu*)

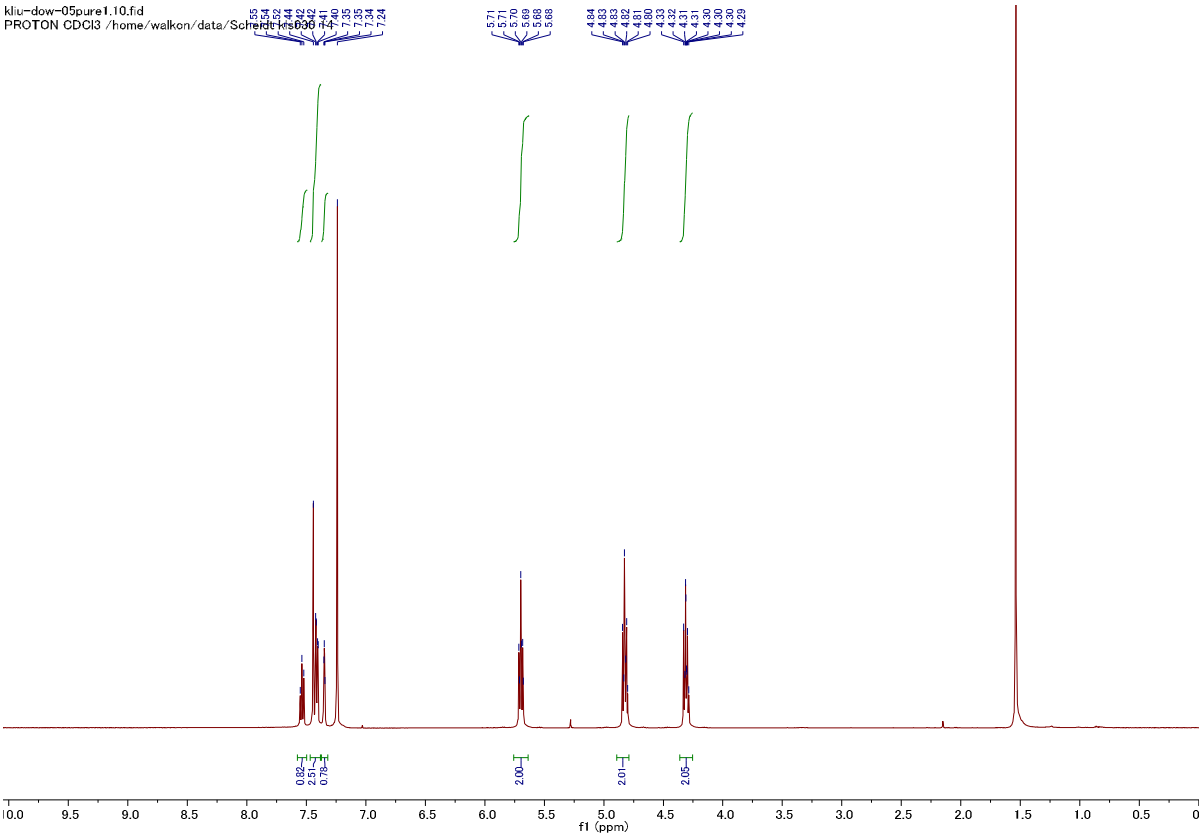

Figure S1. ^{1}H NMR spectrum of DVBDCC.

Divinyl Benzene Dicyclocarbonate (DVBDCC): ^{1}H NMR (500 MHz, CDCl3) δ 7.55 – 7.34 (m, 4H), 5.70 (td, J = 8.0, 2.0 Hz, 2H, CH), 4.82 (td, J = 8.4, 5.0 Hz, 2H, CH2), 4.31 (ddd, J = 8.6, 7.7, 4.9 Hz, 2H, CH2).

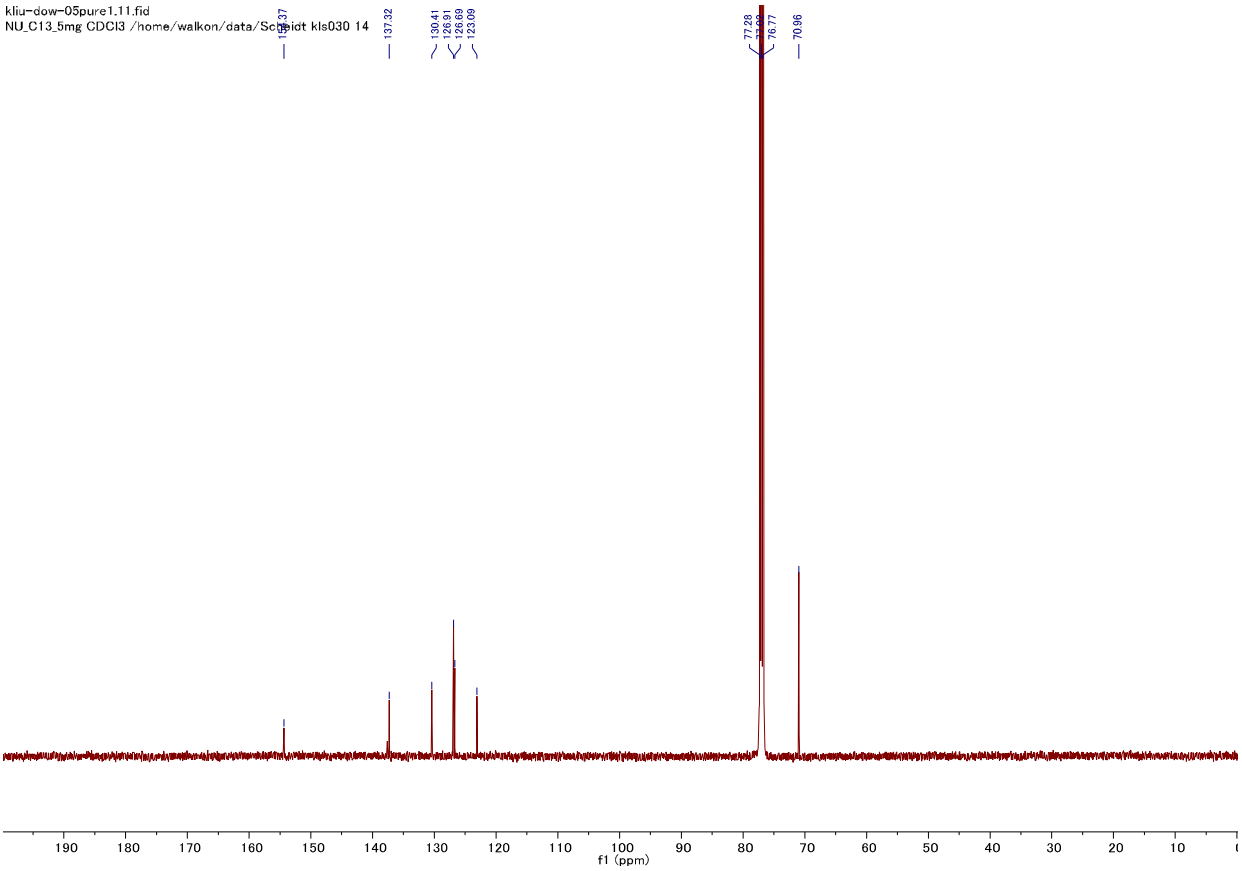

Figure S2. ^{13}C NMR spectrum of DVBDCC.

Divinyl Benzene Dicyclocarbonate (DVBDCC): ^{13}C NMR (CDCl3, 126 MHz) δ 154.3, 137.3, 130.4, 126.9, 126.6, 123.1, 70.9. LRMS (EI): Mass calcd for [M]+ C12H10O6: 250.0; found 250.1.

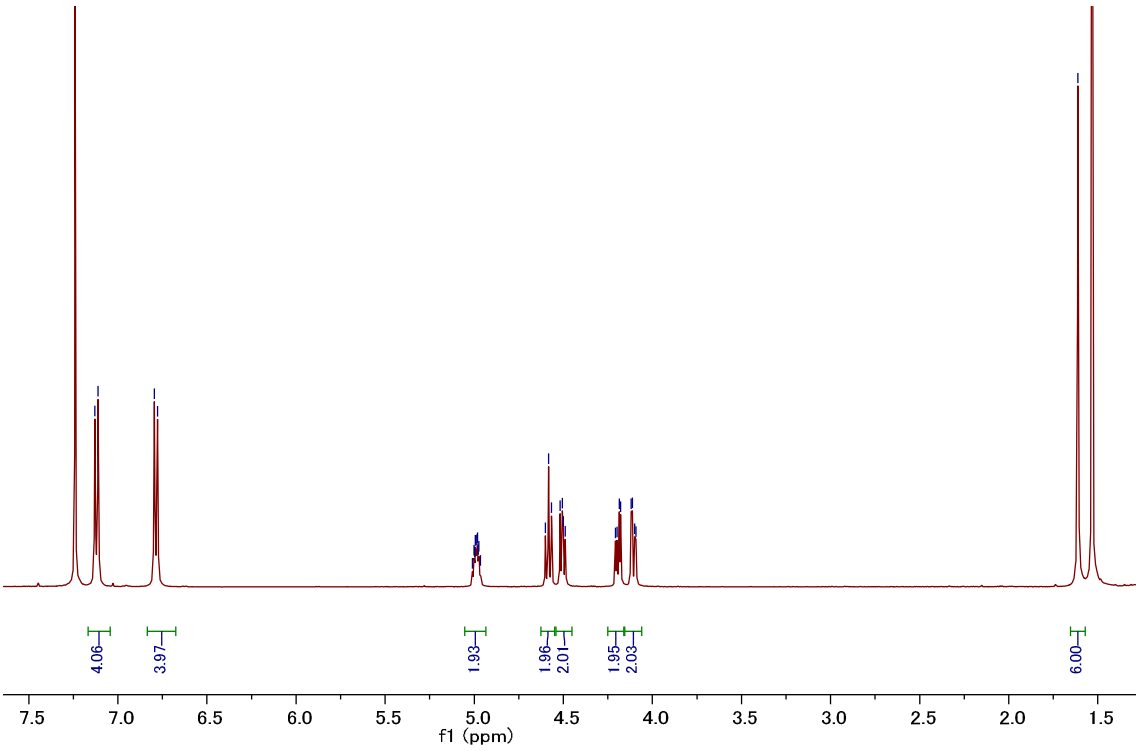

Figure S3. ^{1}H NMR spectrum of BPADC.

Bisphenol A Dicarbonate (BPADC): 1H NMR (500 MHz, CDCl3) δ, 7.12 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 5.01 – 4.97 (m, 2H, CH in cyclic carbonate moiety) 4.58 (t, J = 8.4 Hz, 2H, CH2 in cyclic carbonate moiety), 4.50 (dd, J = 8.5, 5.9 Hz, 2H, CH2 in cyclic carbonate moiety), 4.19 (dd, J = 10.6, 4.4 Hz, 2H, CHCH2OAr), 4.11 (dd, J = 10.5, 3.5 Hz, 2H, CHCH2OAr), 1.61 (s, 6H, CH3);

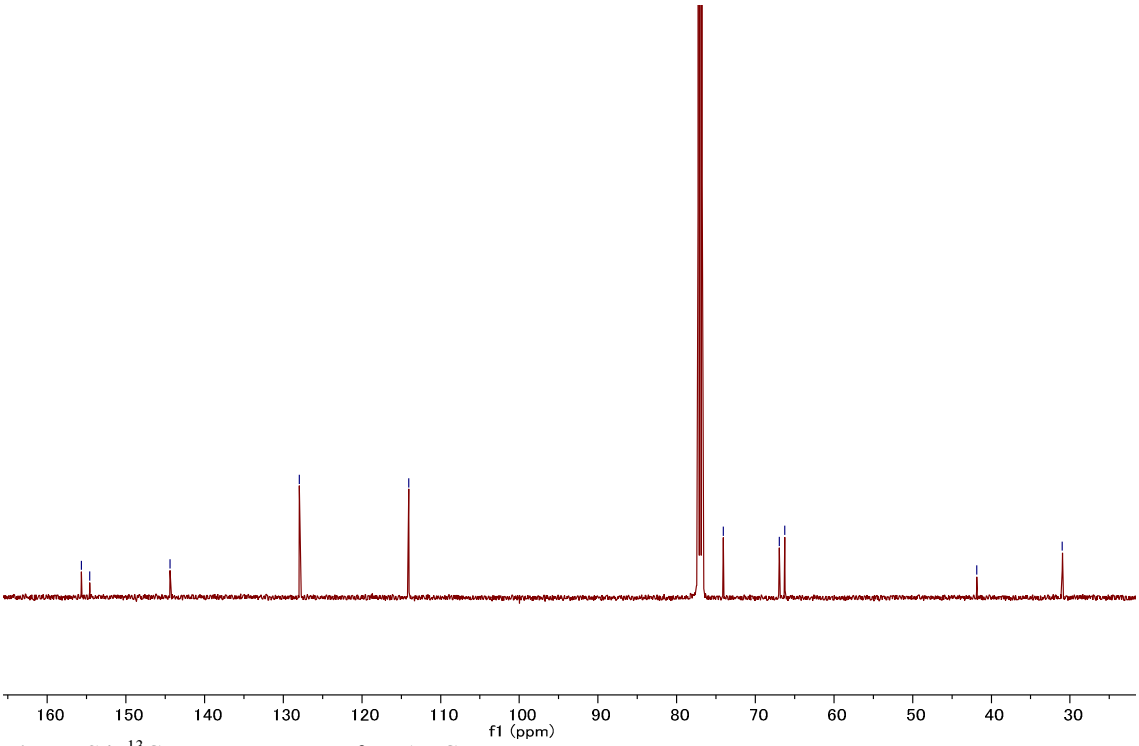

Figure S4. ^{13}C NMR spectrum of BPADC.

Bisphenol A Dicarbonate (BPADC): ^{13}C NMR (CDCl3, 126 MHz) δ 155.6, 154.6, 144.3, 127.9, 114.0, 74.0, 66.9, 66.2, 41.8, 30.9; LRMS (EI): Mass calculated for [M]+ C23H24O8: 428.0; found 428.0

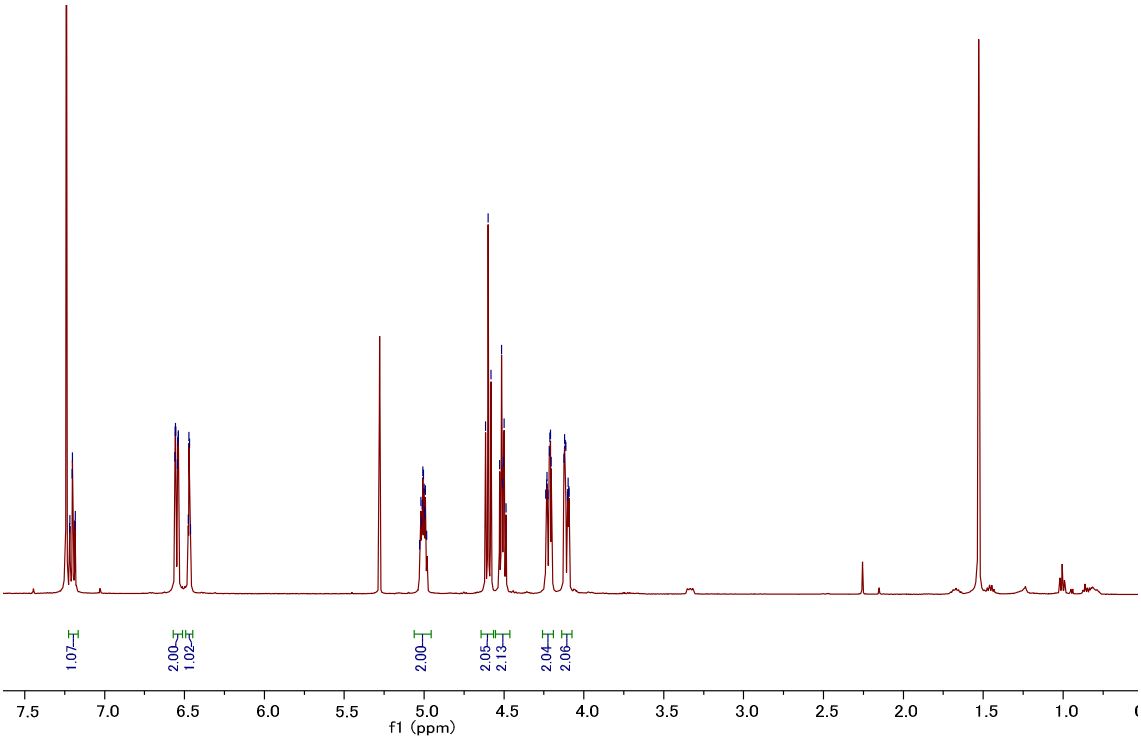

Figure S5. ^{1}H NMR spectrum of RBC.

Recorsinol Bis-carbonate (RBC): ^{1}H NMR (500 MHz, CDCl3) δ, 7.20 (td, J = 8.2, 0.9 Hz, 1H), 6.56 – 6.54 (m, 2H), 6.48 – 6.40 (m, 1H), 5.03 – 4.98 (m, 2H, CH in cyclic carbonate moiety) 4.60 (t, J = 8.5 Hz, 2H, CH2 in cyclic carbonate moiety), 4.51 (dt, J = 8.6, 5.8 Hz, 2H, CH2 in cyclic carbonate moiety), 4.22 (dd, J = 10.7, 3.9, 2.7 Hz, 2H, CHCH2OAr), 4.11 (ddd, J = 10.7, 3.5, 1.1 Hz, 2H, CHCH2OAr).

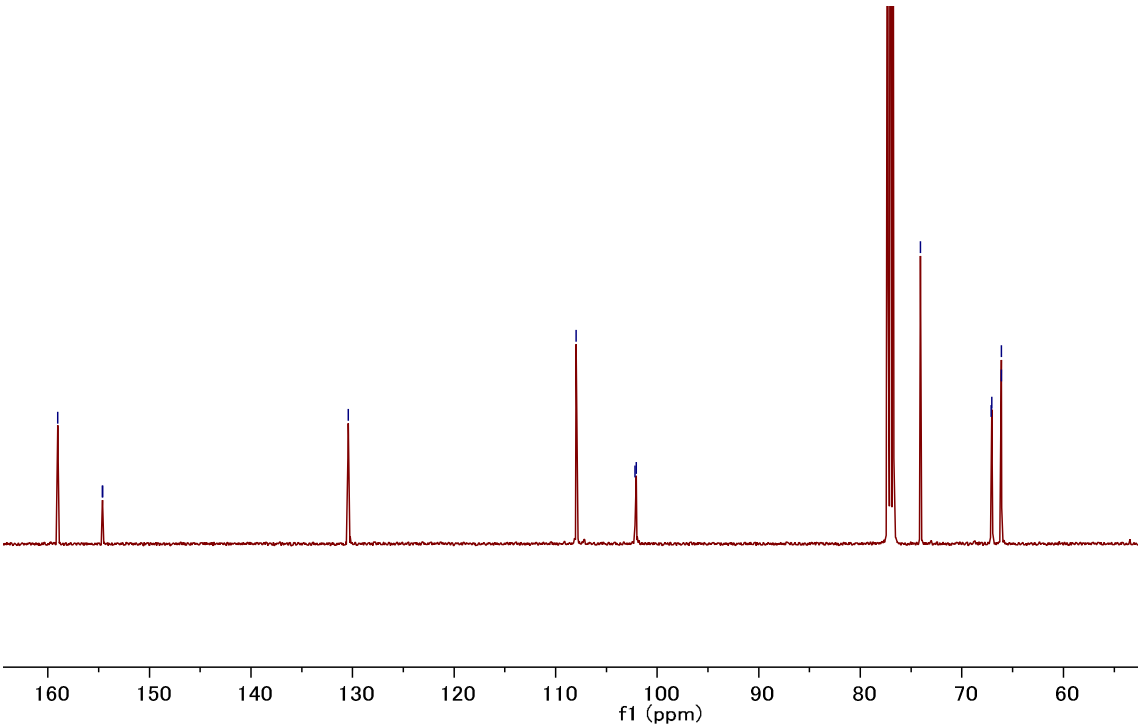

Figure S6. ^{13}C NMR spectrum of RBC.

Recorsinol Bis-carbonate (RBC): ^{13}C NMR ($CDCl_3$, 126 MHz) δ 159.0, 154.6, 154.6, 130.4, 107.9, 102.1, 102.0, 74.0, 67.1, 67.0, 66.1, 66.0; LRMS (EI): Mass calculated for $[M]^+$ $C_{14}H_{14}O_8$: 310.1; found 310.1.

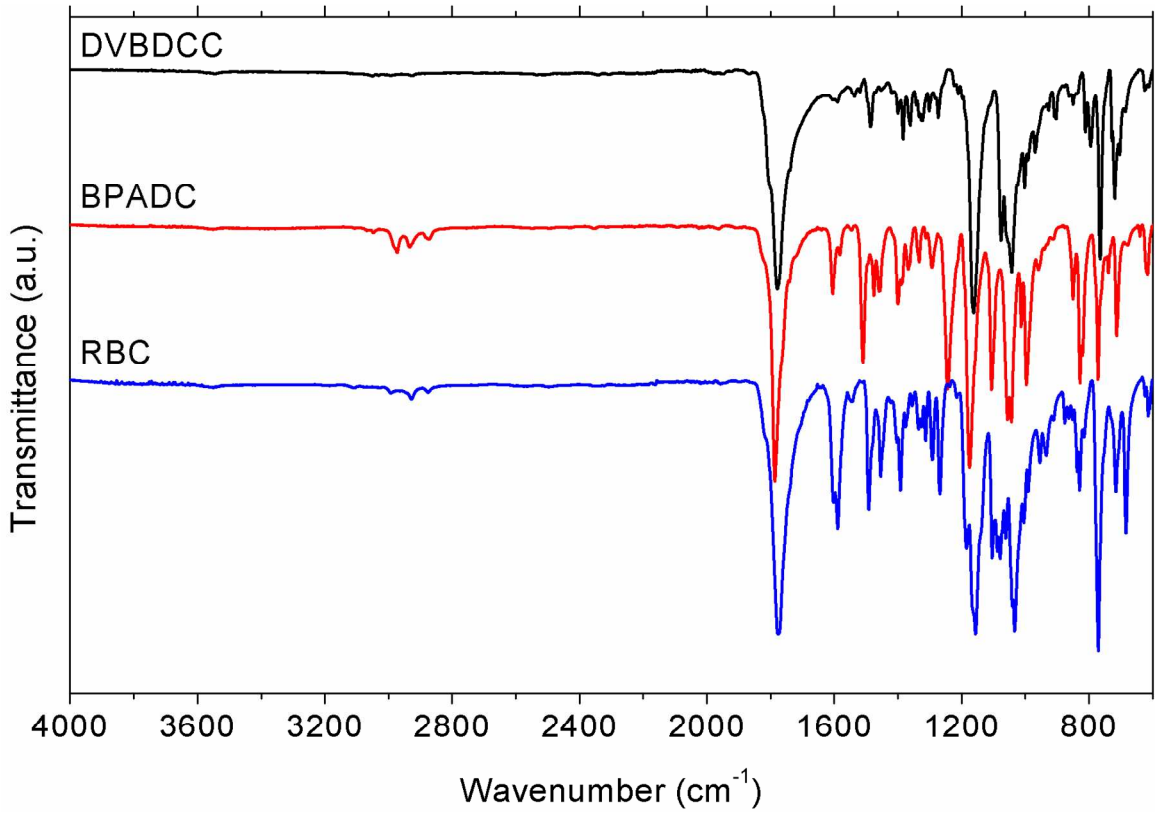

Figure S7. FTIR spectra of DVBDCC, BPADC, and RBC.

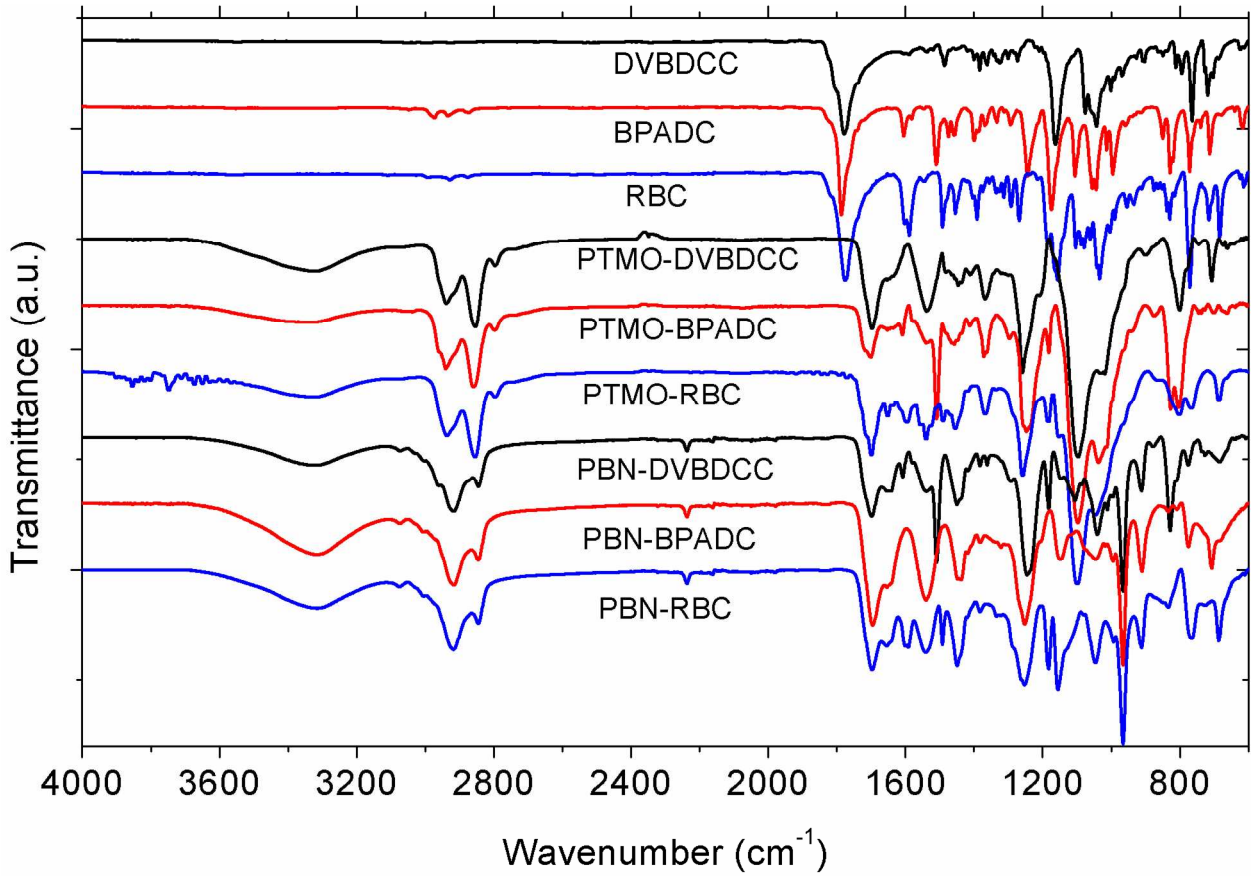

Figure S8. FTIR Spectra of all PHUs with their corresponding carbonate molecules.

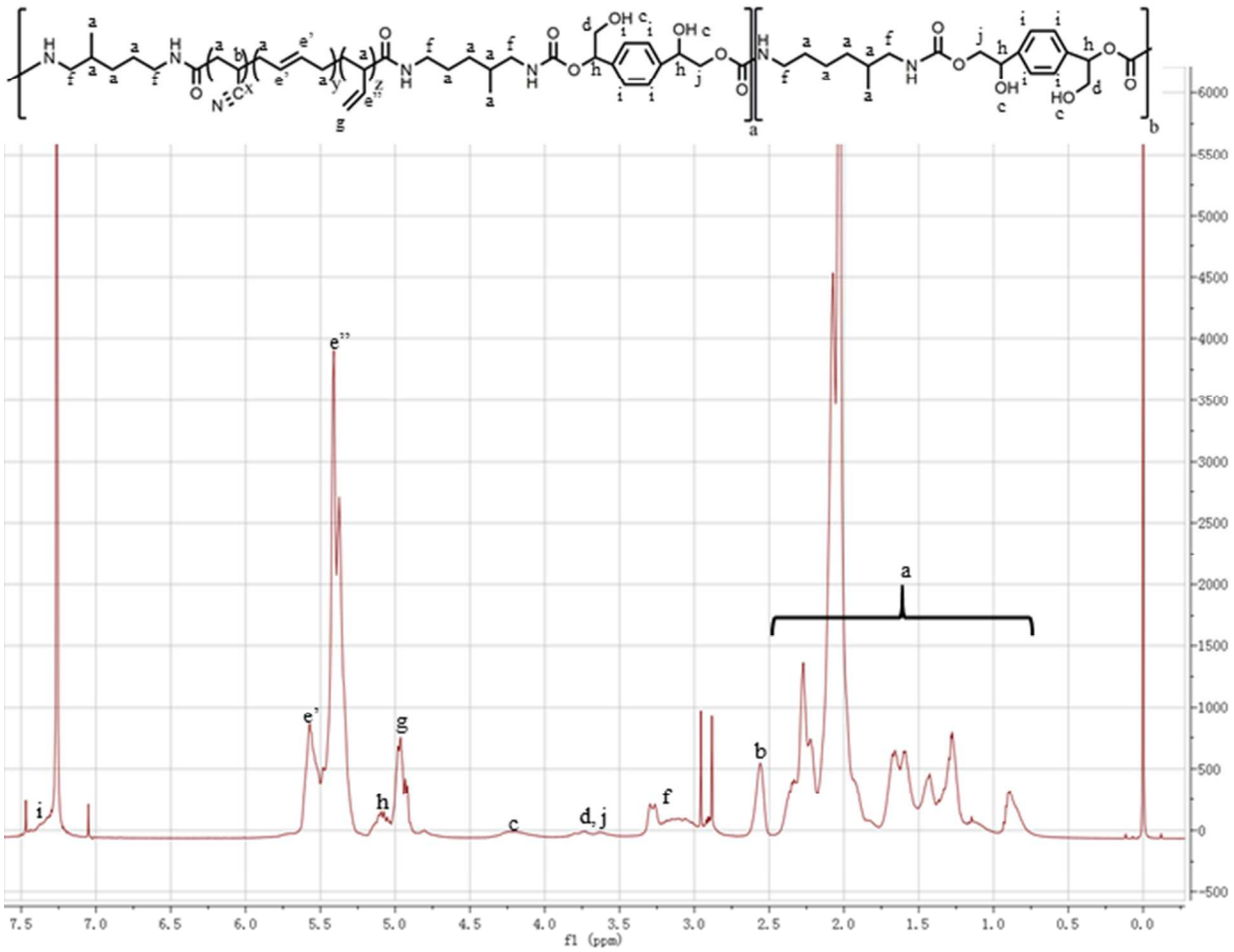

Figure S9. ^{1}H NMR spectrum of PBN-DVBDCC.

PBN-DVBDCC. ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm): 0.6-2.4 (15H, -NHCH$_2$C***H***$_2$C***H***$_2$C***H***(C***H***$_3$)CH$_2$NH-, -C***H***$_2$C***H***(CH$_2$=CH$_2$)C***H***$_2$-, -C***H***$_2$CH(CN)-), 2.5-2.6 (1H, -CH$_2$C***H***(CN)-), 3.0-3.3 (2H, -C***H***$_2$NHC(=O)OCH$_2$-), 3.6-3.8 (4H, -C***H***$_2$OH, -C***H***$_2$OC(=O)NH)-), 4.1-4.3 (2H, -CH$_2$O***H*****,** PhCH(O***H***)CH$_2$-), 4.8-5.0 (2H, -CH(CH=C***H***$_2$)), 5.0-5.2 (1H, PhC***H***(OH)CH$_2$O-), 5.3-5.5 (1H, -CH(C***H***=CH$_2$)), 5.5-5.6 (2H, -CH$_2$C***H***=C***H***CH$_2$-), 7.0-7.5 (4H, Ph).

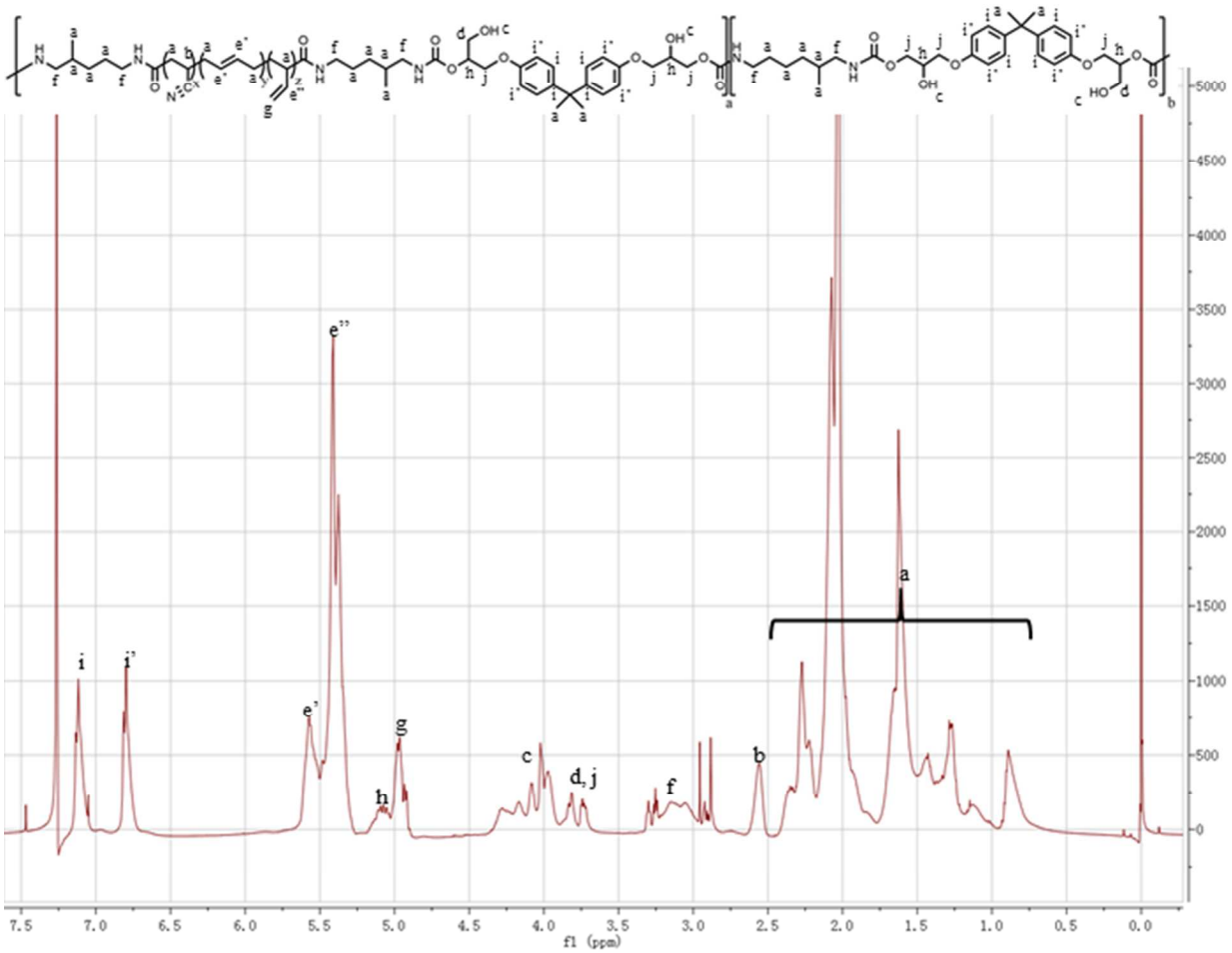

Figure S10. ^{1}H NMR spectrum of PBN-BPADC.

PBN-BPADC. ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm):

0.6-2.4 (21H, -NHCH$_2$C***H***$_2$C***H***$_2$C***H***(C***H***$_3$)CH$_2$NH-, -C***H***$_2$C***H***(CH$_2$=CH$_2$)C***H***$_2$-, -C***H***$_2$CH(CN)-, PhC(C***H*****$_3$**)(C***H*****$_3$**)Ph), 2.5-2.6 (1H, -CH$_2$C***H***(CN)-), 3.0-3.3 (2H, -C***H***$_2$NHC(=O)OCH$_2$-), 3.6-3.8 (6H, -C***H***$_2$OH, -C***H***$_2$OC(=O)NH)-, -CH(CH$_2$OH)C***H*****$_2$**O-), 3.9-4.3 (2H, -CH$_2$O***H*****,** PhCH(O***H***)CH$_2$-), 4.8-5.0 (2H, -CH(CH=C***H***$_2$)), 5.0-5.2 (1H, PhC***H***(OH)CH$_2$O-), 5.3-5.5 (1H, -CH(C***H***=CH$_2$)), 5.5-5.6 (2H, -CH$_2$C***H***=C***H***CH$_2$-), 6.7-7.2 (8H, Ph).

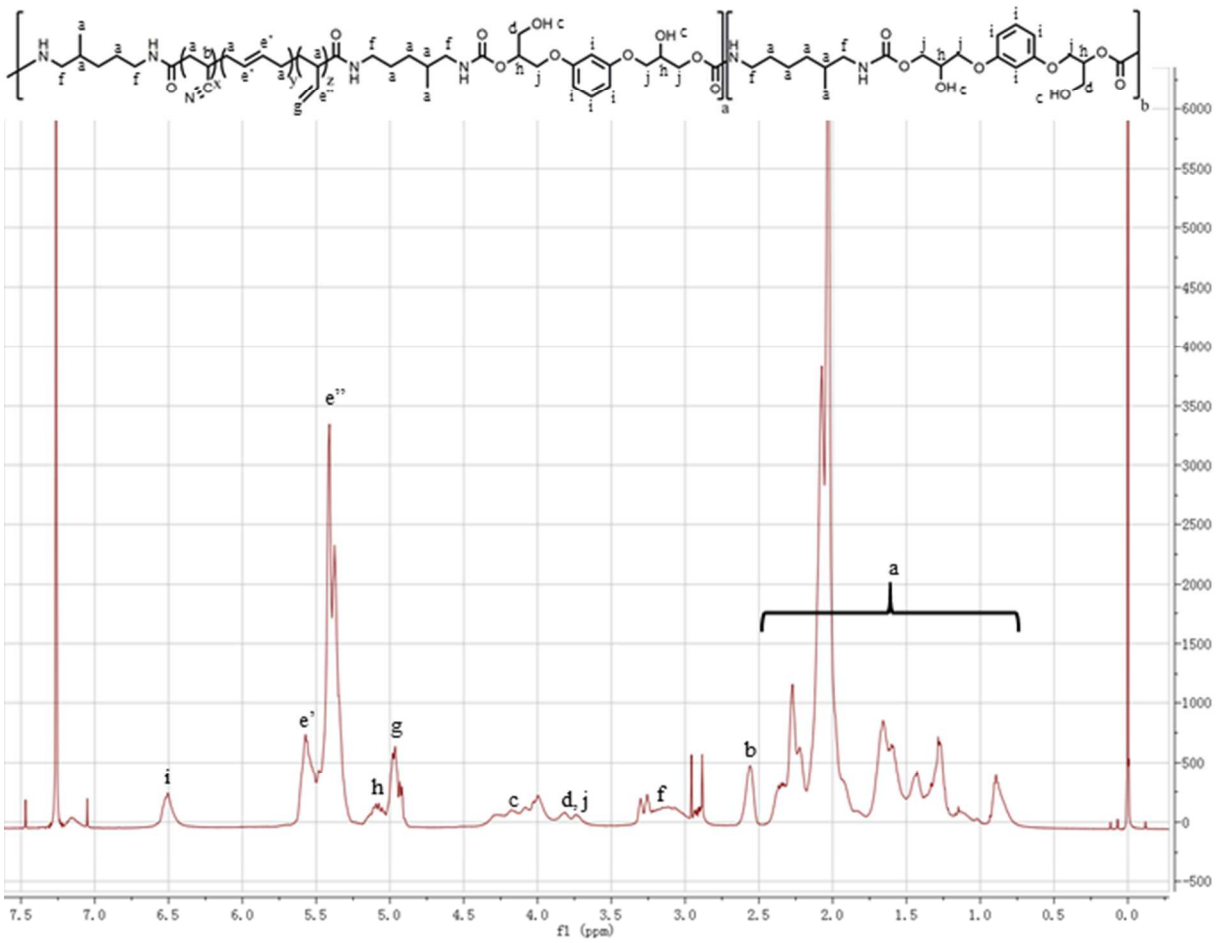

Figure S11. ^{1}H NMR spectrum of PBN-RBC.

PBN-RBC. ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm): 0.6-2.4 (15H, -NHCH$_2$C***H***$_2$C***H***$_2$C***H***(C***H***$_3$)CH$_2$NH-, -C***H***$_2$C***H***(CH$_2$=CH$_2$)C***H***$_2$-, -C***H***$_2$CH(CN)-), 2.5-2.6 (1H, -CH$_2$C***H***(CN)-), 3.0-3.3 (2H, -C***H***$_2$NHC(=O)OCH$_2$-), 3.6-3.8 (6H, -C***H***$_2$OH, -C***H***$_2$OC(=O)NH)-, -CH(CH$_2$OH)C***H***$_2$O-), 3.9-4.4 (2H, -CH$_2$O***H*****,** PhCH(O***H***)CH$_2$-), 4.8-5.0 (2H, -CH(CH=C***H***$_2$)), 5.0-5.2 (1H, PhC***H***(OH)CH$_2$O-), 5.3-5.5 (1H, -CH(C***H***=CH$_2$)), 5.5-5.6 (2H, -CH$_2$C***H***=C***H***CH$_2$-), 6.4-6.6 (4H, Ph).

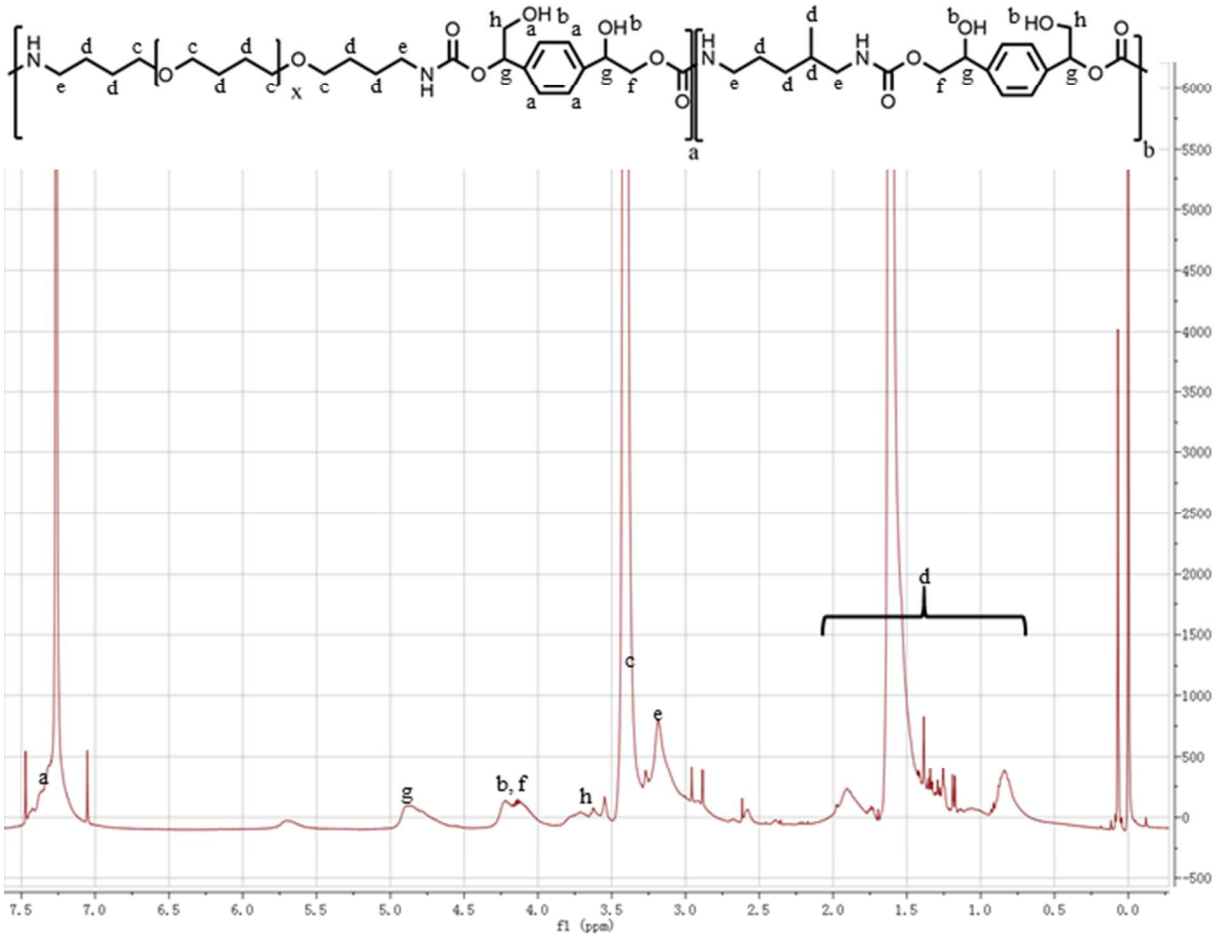

Figure S12. ^{1}H NMR spectrum of PTMO-DVBDCC.

PTMO-DVBDCC. ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm): 0.5-2.0 (16H, -$OCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2CH_2O$-, -$NHCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2CH_2O$-, -$NHCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2C\boldsymbol{H}(C\boldsymbol{H}_3)$CH2NH-), 2.8-3.2 (4H, -$NHC\boldsymbol{H}_2CH_2CH_2CH_2O$-, -$NHC\boldsymbol{H}_2$-), 3.3-3.5 (6H, -$C\boldsymbol{H}_2OC\boldsymbol{H}_2$-, -$NHC(=O)OC\boldsymbol{H}_2$-), 3.6-3.8 (1H, -$C\boldsymbol{H}_2OH$), 4.0-4.2 (2H, -$C\boldsymbol{H}_2OC(=O)NH$-), 4.2-4.3 (2H, -$CH_2O\boldsymbol{H}$, $PhCH(O\boldsymbol{H})CH_2$-), 4.8-5.0 (1H, $PhC\boldsymbol{H}(OH)CH_2$-), 7.0-7.5 (4H, Ph).

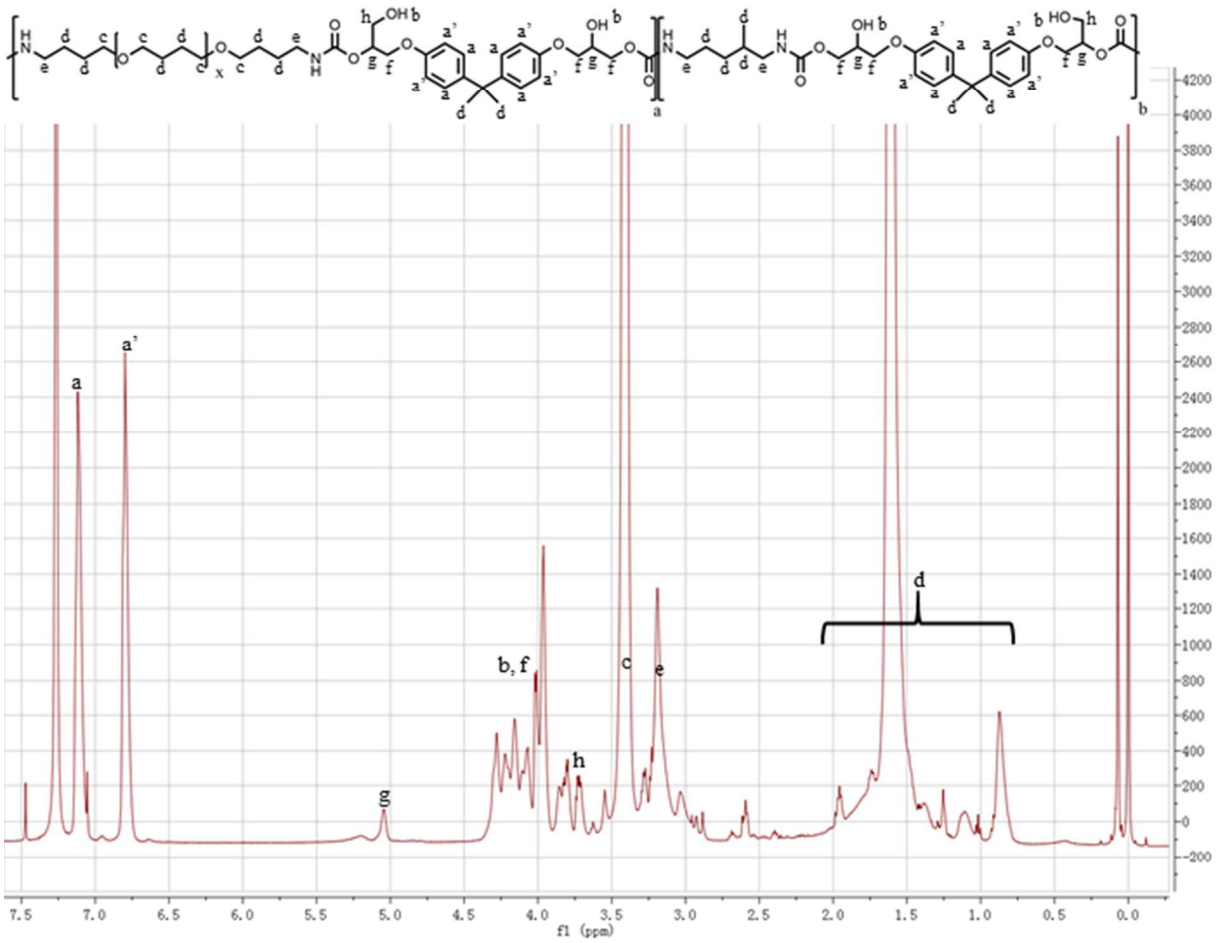

Figure S13. ^{1}H NMR spectrum of PTMO-BPADC.

PTMO-BPADC. ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm): 0.5-2.0 (22H, -$OCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2CH_2O$-, -$NHCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2CH_2O$-, -$NHCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2C\boldsymbol{H}(C\boldsymbol{H}_3)$CH2NH-, PhC($C\boldsymbol{H_3}$)($C\boldsymbol{H_3}$)Ph), 2.8-3.2 (4H, -$NHC\boldsymbol{H}_2CH_2CH_2CH_2O$-, -$NHC\boldsymbol{H}_2$-), 3.3-3.5 (6H, -$C\boldsymbol{H}_2OC\boldsymbol{H}_2$-, -NHC(=O)$OC\boldsymbol{H}_2$-), 3.6-3.8 (1H, -$C\boldsymbol{H}_2$OH), 4.0-4.2 (4H, -$C\boldsymbol{H}_2$OC(=O)NH-, -$CH(CH_2OH)C\boldsymbol{H_2}O$-), 4.2-4.3 (2H, -$CH_2O\boldsymbol{H}$, PhCH($O\boldsymbol{H}$)$CH_2$-), 4.8-5.0 (1H, Ph$C\boldsymbol{H}(OH)CH_2$-), 6.7-7.2 (8H, Ph).

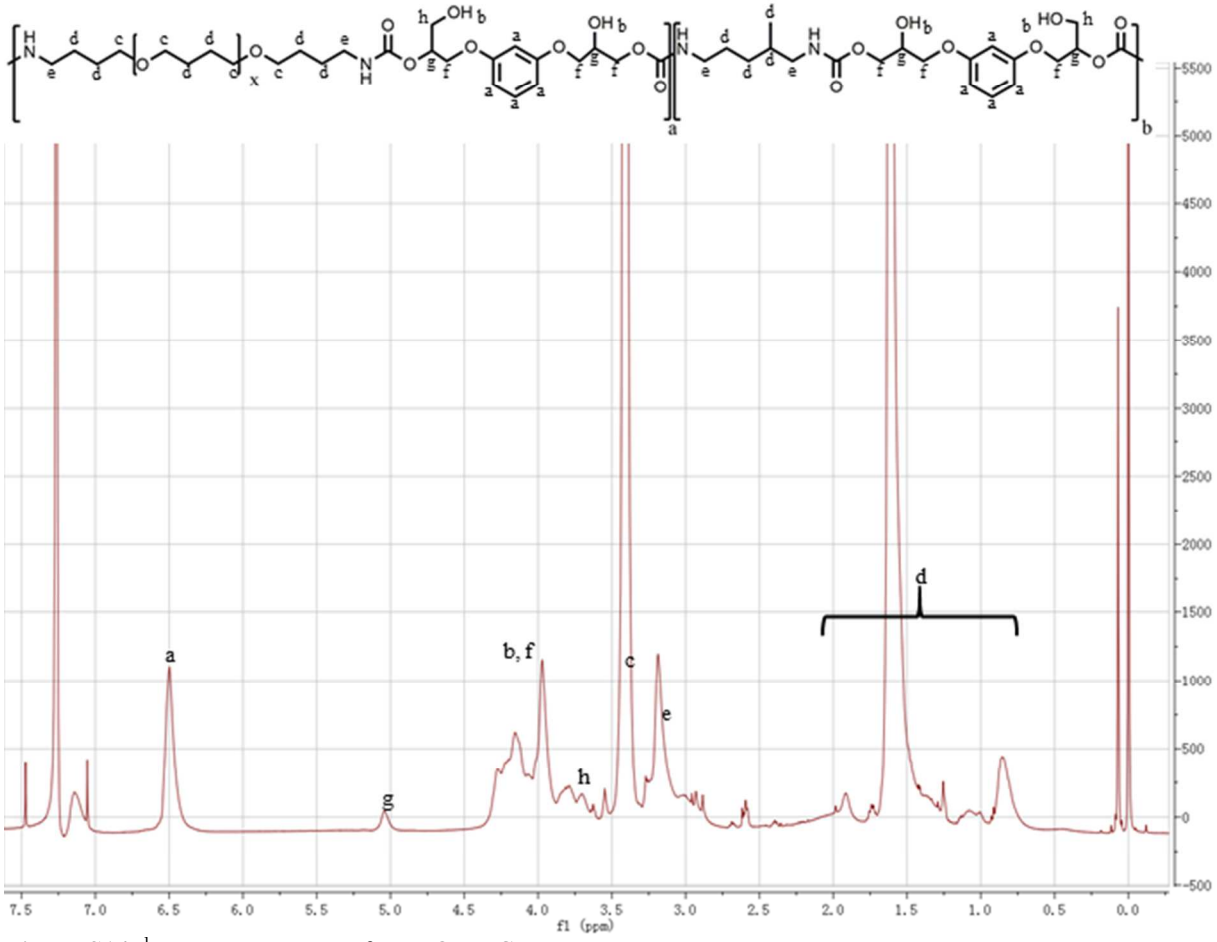

Figure S14. ^{1}H NMR spectrum of PTMO-RBC.

PTMO-RBC. ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm): 0.5-2.0 (16H, -$OCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2CH_2O$-, -$NHCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2CH_2O$-,-$NHCH_2C\boldsymbol{H}_2C\boldsymbol{H}_2C\boldsymbol{H}(C\boldsymbol{H}_3)$CH2NH-), 2.8-3.2 (4H, -$NHC\boldsymbol{H}_2CH_2CH_2CH_2O$-, -$NHC\boldsymbol{H}_2$-), 3.3-3.5 (6H, -$C\boldsymbol{H}_2OC\boldsymbol{H}_2$-, -NHC(=O)$OC\boldsymbol{H}_2$-), 3.6-3.8 (1H, -$C\boldsymbol{H}_2OH$), 4.0-4.2 (4H, -$C\boldsymbol{H}_2OC$(=O)NH-, -$CH(CH_2OH)C\boldsymbol{H}_2O$-), 4.2-4.3 (2H, -$CH_2O\boldsymbol{H}$, PhCH(O***H***)$CH_2$-), 4.8-5.0 (1H, PhC***H***(OH)CH_2-), 6.4-6.6 (4H, Ph).

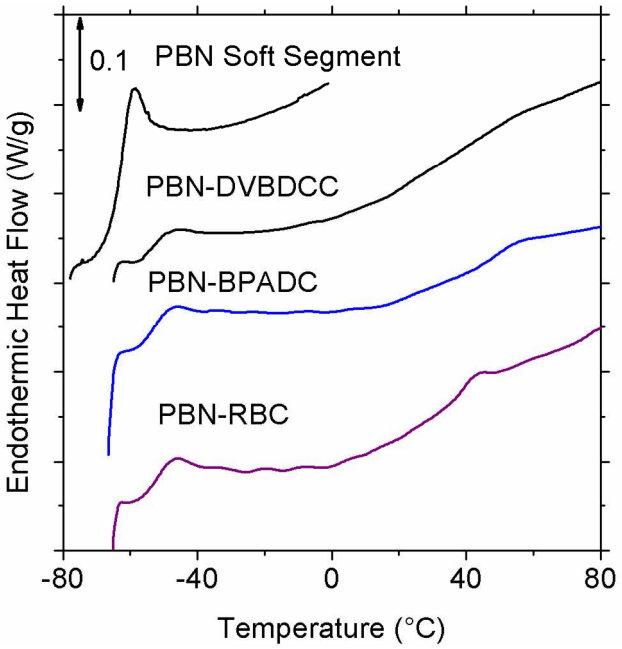

Figure S15. DSC heating scan of PBN-based PHUs.

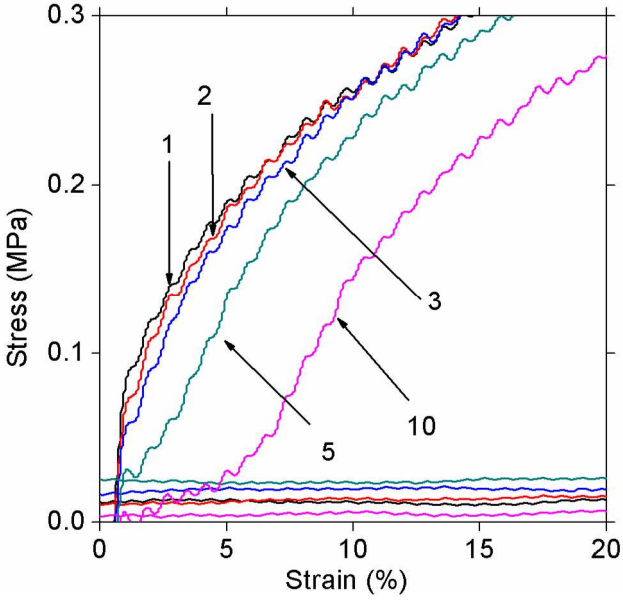

Figure S16. Zoomed version of PBN-RBC hysteresis.

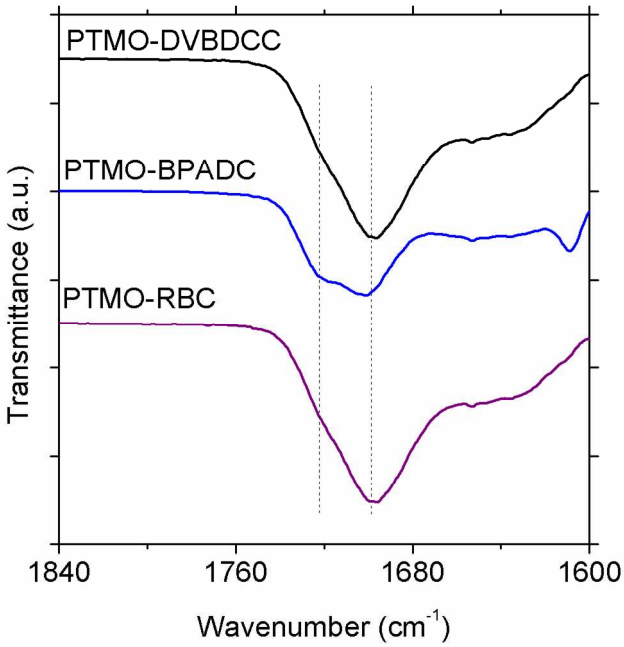

Figure S17. Comparison of FTIR spectra of PTMO-based PHUs in the carbonyl region. Free, non hydrogen-bonded carbonyl appears ~1720 cm^{-1} while hydrogen-bonded carbonyl appears ~1690 cm^{-1}.

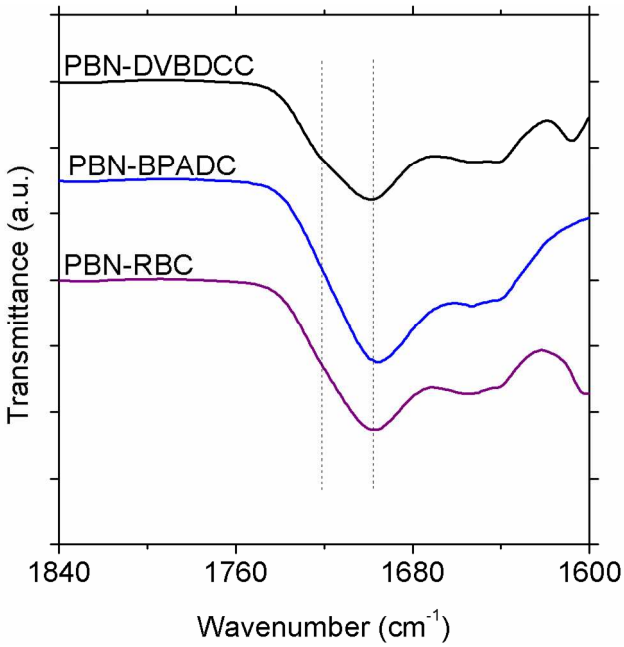

Figure S18. Comparison of FTIR spectra of PBN-based PHUs in the carbonyl region. Free, non hydrogen-bonded carbonyl appears ~1720 cm^{-1} while hydrogen-bonded carbonyl appears ~1690 cm^{-1}.

Table S1. Apparent Weight-Average Molecular Weights of PHUs.*

Sample	M_w (kg/mole)
PTMO-DVBDCC	30.8
PTMO-RBC	37.9
PTMO-BPADC	37.7
PBN-DVBDCC	37.0
PBN-RBC	22.4
PBN-BPADC	25.0

*The overall signal to noise in RI detector was not high enough to reveal the details of molecular weight moments. It is likely due to low dn/dc values of samples in DMF.