

Supporting Information

Controlling healing and toughness in polyurethanes by branch-mediated tube dilation

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1. Synthesis of malonate molecules

1.1. Diethyl 2,2-diheptylmalonate (C7DE)

The synthesis was performed using the same procedure described in Section 2.1. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 23.20 g (0.15 mol) of diethyl malonate, 79.80 g (0.45 mol) of 1-bromoheptane and 18.20 g of sodium hydride (0.46 mol, 60 wt% in mineral oil) . The crude product (72.40 g) was used without further purification.

1.2. Diethyl 2,2-dioctylmalonate (C8DE)

The synthesis was performed using the same procedure described in Section 2.1. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 16.04 g (0.10 mol) of diethyl malonate, 57.93 g (0.30 mol) of 1-bromooctane and 12.0 g of sodium hydride (0.30 mol, 60 wt% in mineral oil). The crude product (53.42 g) was used without further purification.

1.3. Diethyl 2,2-dinonylmalonate (C9DE)

The synthesis was performed using the same procedure described in Section 2.1. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 16.88 g (0.11 mol) of diethyl malonate, 61.79 g (0.30 mol) of 1-bromononane and 12.0 g of sodium hydride (0.30 mol, 60 wt% in mineral oil). The crude product (45.04 g) was used without further purification.

1.4. Diethyl 2,2-didodecylmalonate (C12DE)

The synthesis was performed using the same procedure described in Section 2.1. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 12.87 g (0.08 mol) of diethyl malonate, 62.28 g (0.25 mol) of 1-bromododecane and 9.86 g of

sodium hydride (0.25 mol, 60 wt% in mineral oil). The crude product (50.4 g) was used without further purification.

1.5. Diethyl 2,2-dioctadecylmalonate (C18DE)

The synthesis was performed using the same procedure described in Section 2.1. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 9.62 g (0.06 mol) of diethyl malonate, 62.46 g (0.19 mol) of 1-bromononane and 7.42 g of sodium hydride (0.19 mol, 60 wt% in mineral oil). The crude product (45.04 g) was used without further purification.

2. Syntheses of diol monomers

2.1. 2,2-Dioctylpropane-1,3-diol (C7DA)

The synthesis was performed following the same procedure described in Section 2.2. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 49.50 g of crude C8DE and 16.30 g (0.26 mol) lithium aluminium hydride. Preliminary purification was carried out by column chromatography using 450 g of silica and pure hexane. The product final product was eluted by increasing the polarity of the eluent by mixing hexane and ethyl acetate (hexane:ethyl acetate, 7:3(v/v)). Yield = 74%.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 3.50 (s, 4H); 3.20-3.13 (m, 2H); 1.31-1.15 (m, 24H), 0.89-0.82 (t, 6H). $^{13}\text{C-NMR}$ (CDCl_3 , 400 MHz) δ : 69.06; 40.89; 31.87; 30.67; 30.53; 29.25; 22.80; 14.05.

2.2. 2,2-Dioctylpropane-1,3-diol (C8DA)

The synthesis was performed following the same procedure described in Section 2.2. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 53.13 g of crude C8DE and 9.93 g (0.26 mol) lithium aluminium hydride. Preliminary purification was carried out by column chromatography using 450 g of silica and pure hexane.

The product final product was eluted by increasing the polarity of the eluent by mixing hexane and ethyl acetate (hexane:ethyl acetate, 7:3(v/v)). Yield = 84%.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 3.55 (s, 4H); 2.28 (s, 2H); 1.25 (m, 28H), 0.86 (t, 6H). $^{13}\text{C-NMR}$ (CDCl_3 , 400 MHz) δ : 69.41; 40.95; 31.86; 30.74; 30.65; 29.53; 22.82; 14.07.

2.3. 2,2-Dinonylpropane-1,3-diol (C9DA)

The synthesis was performed following the same procedure described in Section 2.2. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 39.10 g of crude C9DE and 11.96 g (0.32 mol) lithium aluminium hydride. Preliminary purification was carried out by column chromatography using 450 g of silica and pure hexane. The product final product was eluted by increasing the polarity of the eluent by mixing hexane and ethyl acetate (hexane:ethyl acetate, 9:1(v/v)). Yield = 75%.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 3.55 (s, 4H); 2.25 (s, 2H); 1.25 (m, 32H), 0.87 (t, 6H). $^{13}\text{C-NMR}$ (CDCl_3 , 400 MHz) δ : 69.48; 40.98; 31.87; 29.60; 29.30; 22.83; 14.07.

2.4. 2,2-Didodecylpropane-1,3-diol (C12DA)

The synthesis was performed following the same procedure described in Section 2.2. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 43.67 g of crude C12DE and 11.84 g (0.32 mol) lithium aluminium hydride. Preliminary purification was carried out by column chromatography using 450 g of silica and pure hexane. The product final product was eluted by increasing the polarity of the eluent by mixing hexane and ethyl acetate (hexane:ethyl acetate, 9:1(v/v)). Yield = 77%.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 3.53 (s, 4H); 2.70 (s, 2H); 1.24 (m, 44H), 0.86 (t, 6H). $^{13}\text{C-NMR}$ (CDCl_3 , 400 MHz) δ : 69.33; 40.93; 31.90; 29.68; 29.67; 22.82; 14.08.

2.5. 2,2-Dioctadecylpropane-1,3-diol (C18DA)

The synthesis was performed following the same procedure described in Section 2.2. of the main manuscript. The following materials and quantities were used: 400 mL of anhydrous THF, 47.77 g of crude C18DE and 11.62 g (0.31 mol) lithium aluminium hydride. Preliminary purification was carried out by column chromatography using 450 g of silica and pure hexane. The product final product was eluted by increasing the polarity of the eluent by mixing hexane and ethyl acetate (hexane:ethyl acetate, 9:1(v/v)). Yield = 91%.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 3.56 (s, 4H); 2.08 (s, 2H); 1.24 (m, 68H), 0.87 (t, 6H).

3. Syntheses of brush polyurethanes

3.1. HDI_C7DA

The compound was synthesized following the procedure described in Section 2.3. The following materials and quantities were used in the synthesis: C7DA (6.0 g, 22.0 mmol) hexamethylene diisocyanate (3.70 g, 22.0 mmol), dibutyltin dilaurate (0.10 mL) and N,N-Dimethylformamide (36 mL). The compound appears as a transparent glassy polymer (yield = 9.7 g, 62%).

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 4.83 (s, 2H); 3.86 (m, 4H); 3.11 (m, 4H); 1.47 (m, 8H); 1.23 (m, 24H); 0.86 (t, 6H).

3.2. HDI_C8DA

The compound was synthesized following the procedure described in Section 2.3. The following materials and quantities were used in the synthesis: C8DA (12.0 g, 40 mmol) hexamethylene diisocyanate (6.72 g, 40 mmol), dibutyltin dilaurate (0.15 mL) and N,N-Dimethylformamide (67 mL). The compound appears as a transparent glassy polymer (yield = 12.47 g, 65%).

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 5.99-4.80 (s, 2H); 3.92-3.81 (m, 4H); 3.16-3.03 (m, 4H); 1.52-1.40 (m, 4H); 1.34-1.14 (m, 32H); 0.89-0.81 (t, 6H).

3.3. HDI_C12DA

The compound was synthesized following the procedure described in Section 2.3. The following materials and quantities were used in the synthesis: C12DA (3.71 g, 9.02 mmol) hexamethylene diisocyanate (1.51 g, 9.02 mmol), dibutyltin dilaurate (0.15 mL) and N,N-Dimethylformamide (10.5 mL). The compound appears as a transparent glassy polymer (yield = 3.32 g, 63%).

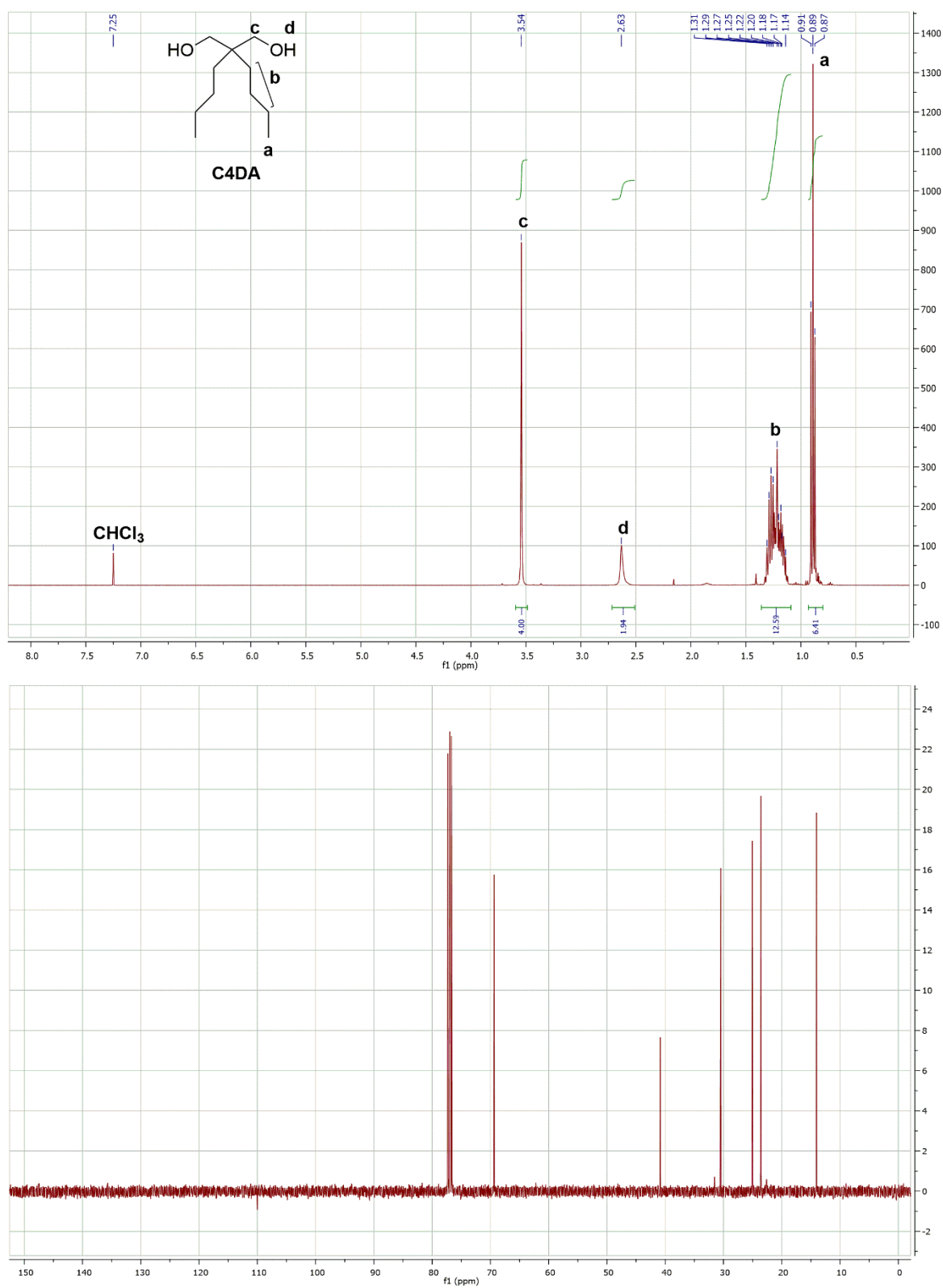
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 4.78 (s, 2H); 3.85 (m, 4H); 3.10 (m, 4H); 1.46 (m, 4H); 1.23 (m, 32H); 0.85 (t, 6H).

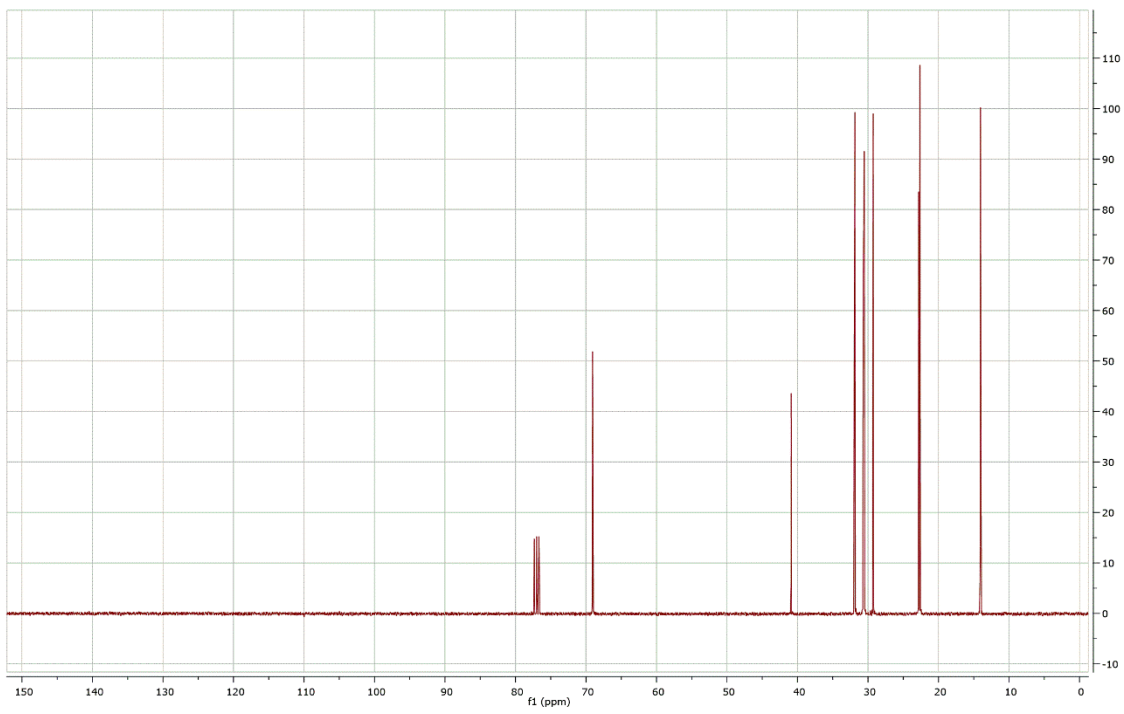
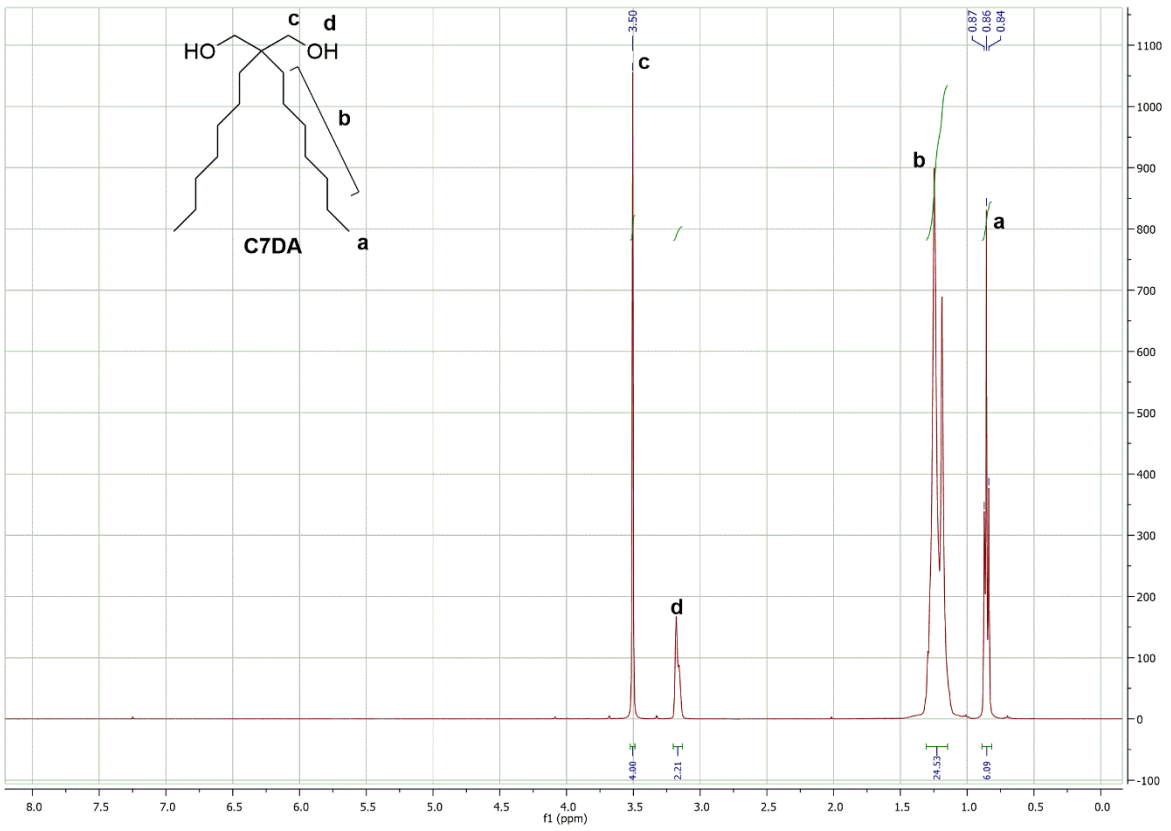
3.4. HDI_C18DA

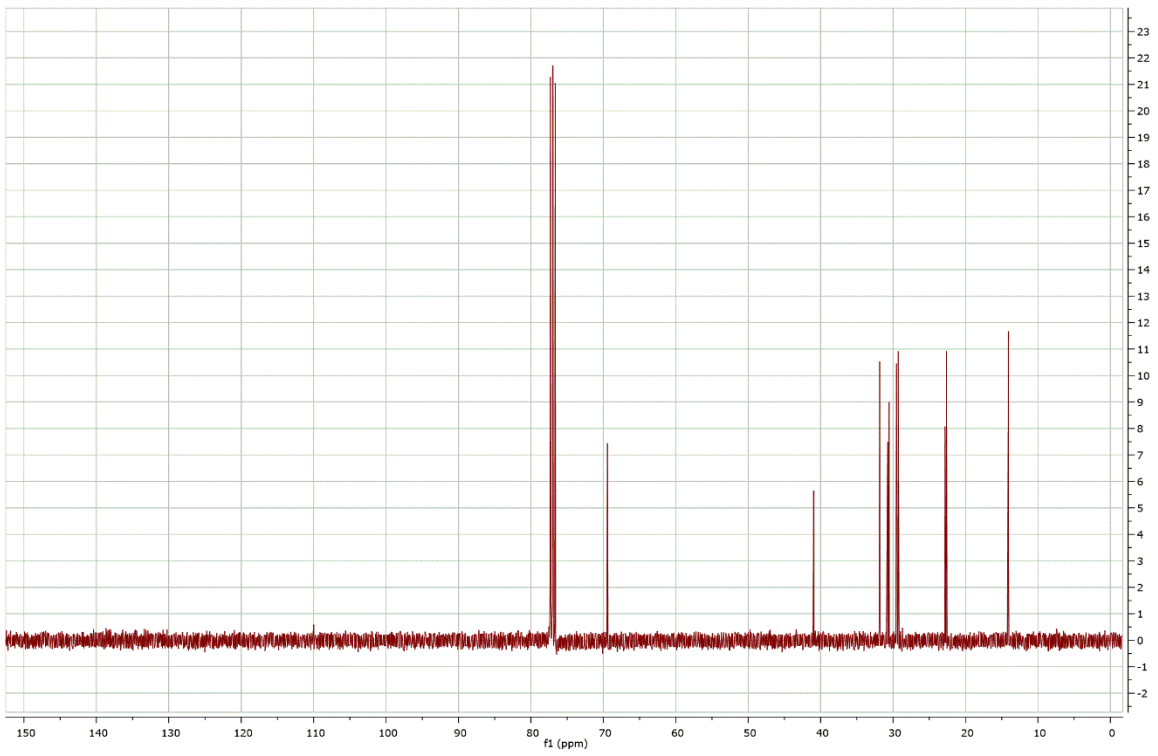
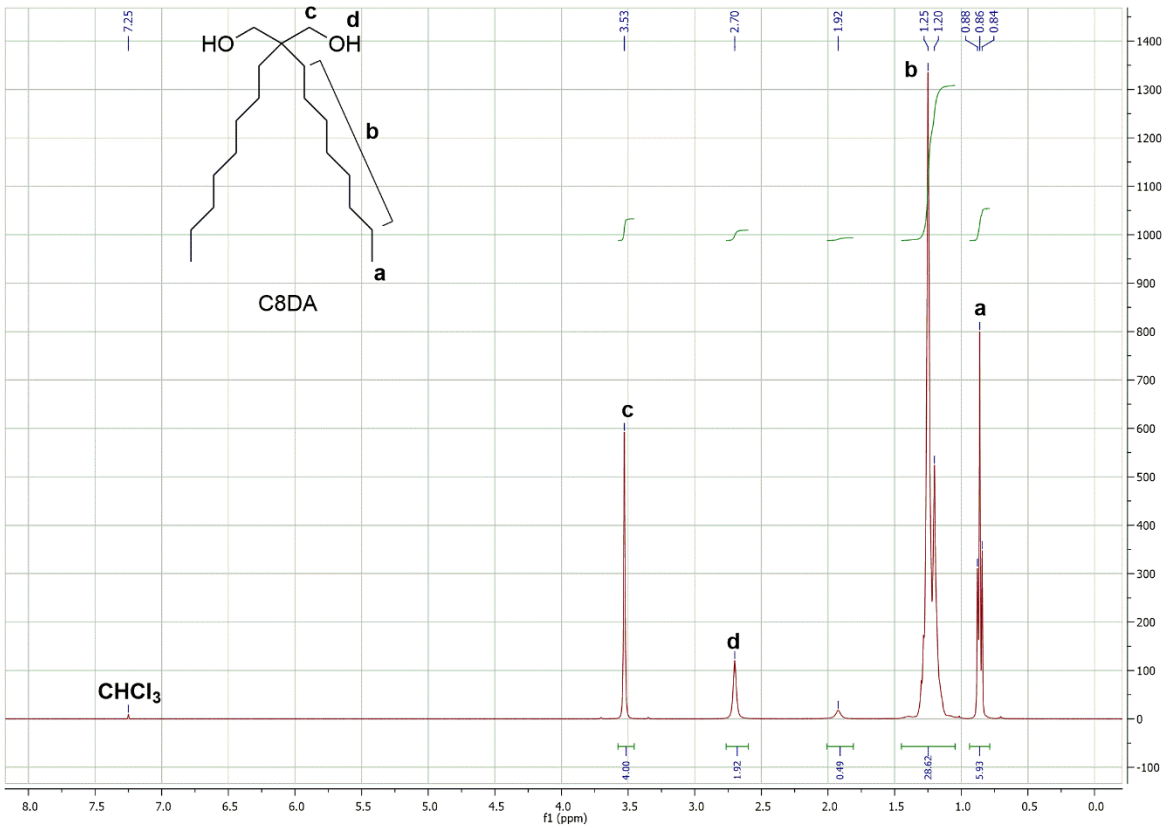
The compound was synthesized following the procedure described in Section 2.3. The following materials and quantities were used in the synthesis: C18DA (3.0 g, 5.17 mmol) hexamethylene diisocyanate (0.87 g, 5.17 mmol), dibutyltin dilaurate (0.12 mL) and N,N-Dimethylformamide (10.0 mL). The compound appears as a fine white powder (yield = 3.23 g, 83%).

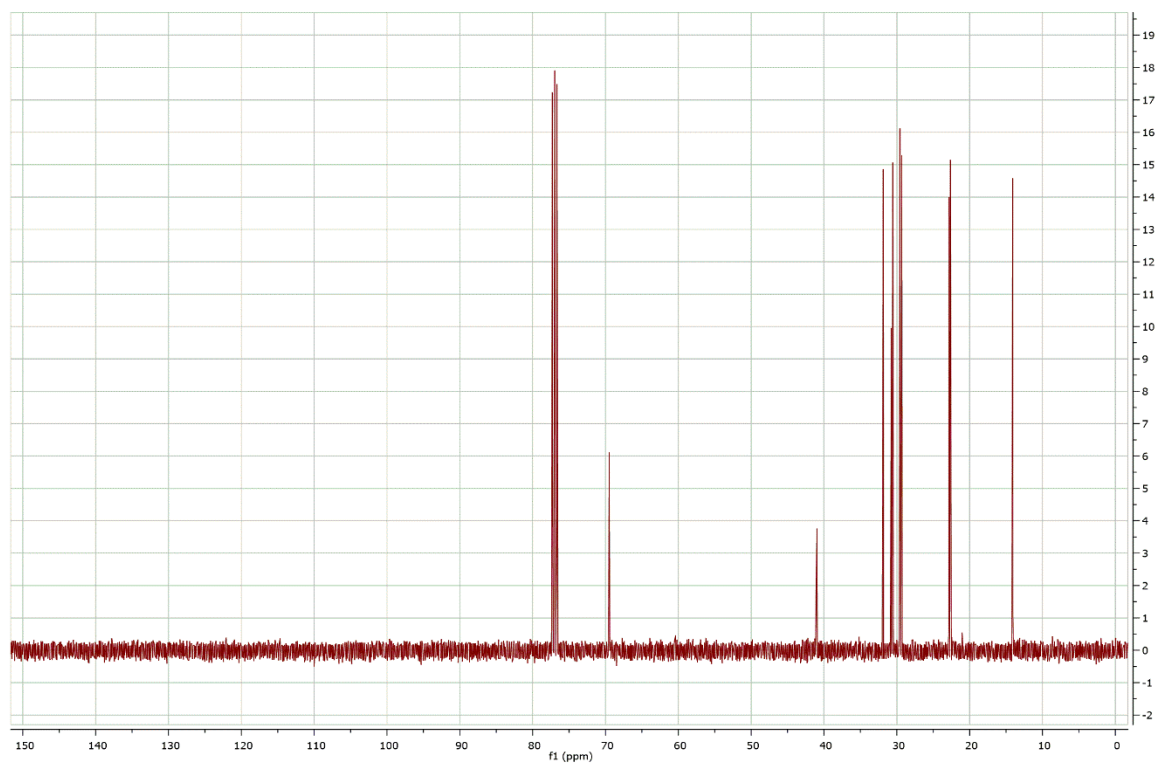
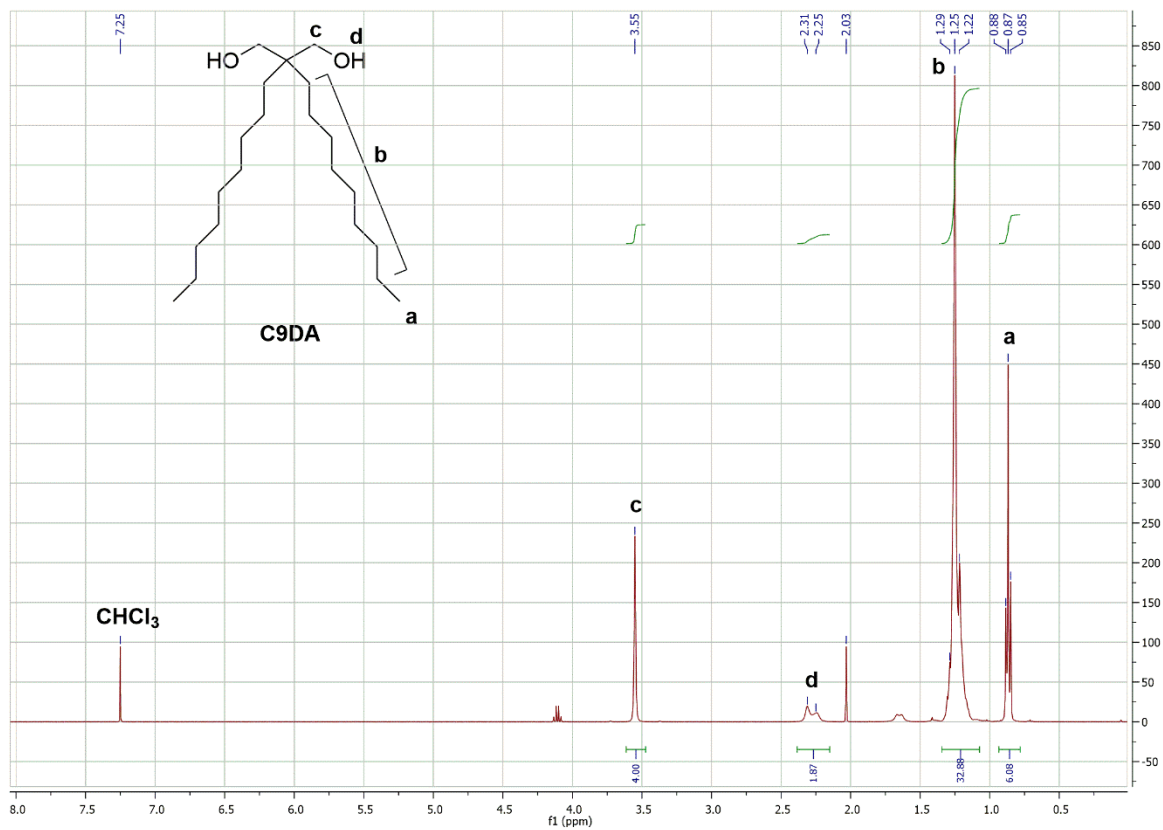
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 4.76 (s, 2H); 3.86 (m, 4H); 3.12 (m, 4H); 1.72 (m, 4H); 1.24 (t, 72H); 0.86 (t, 6H).

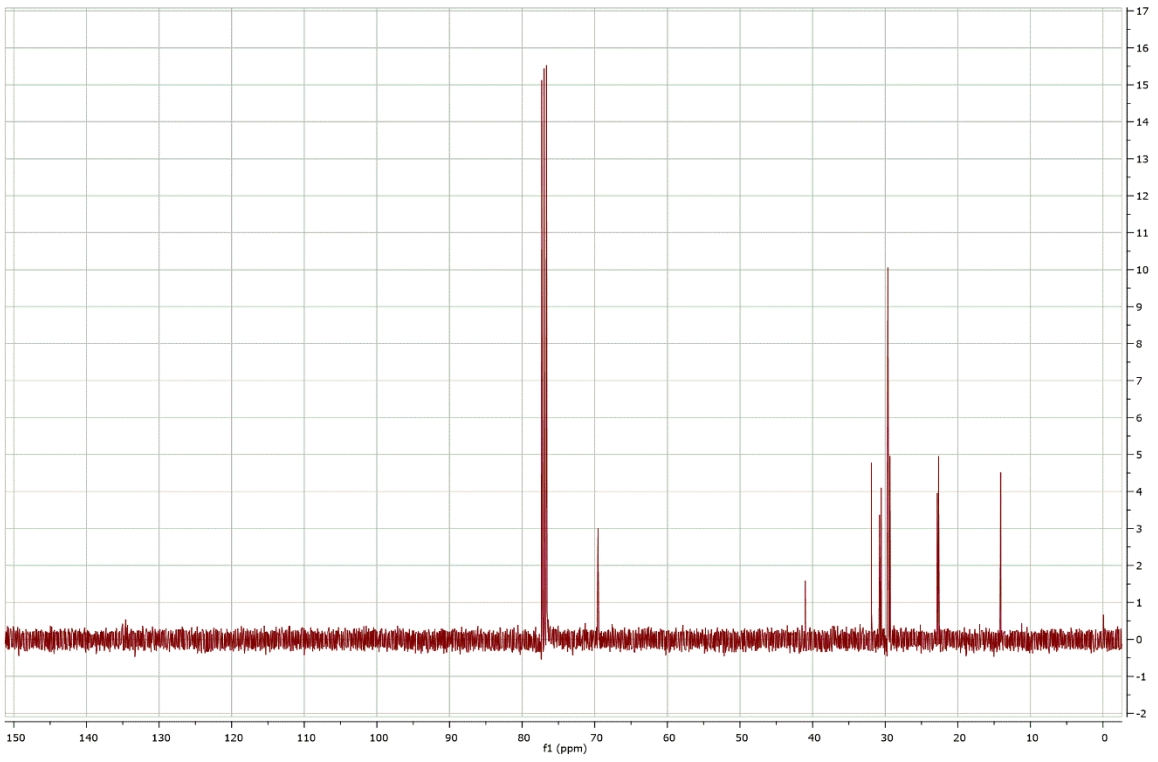
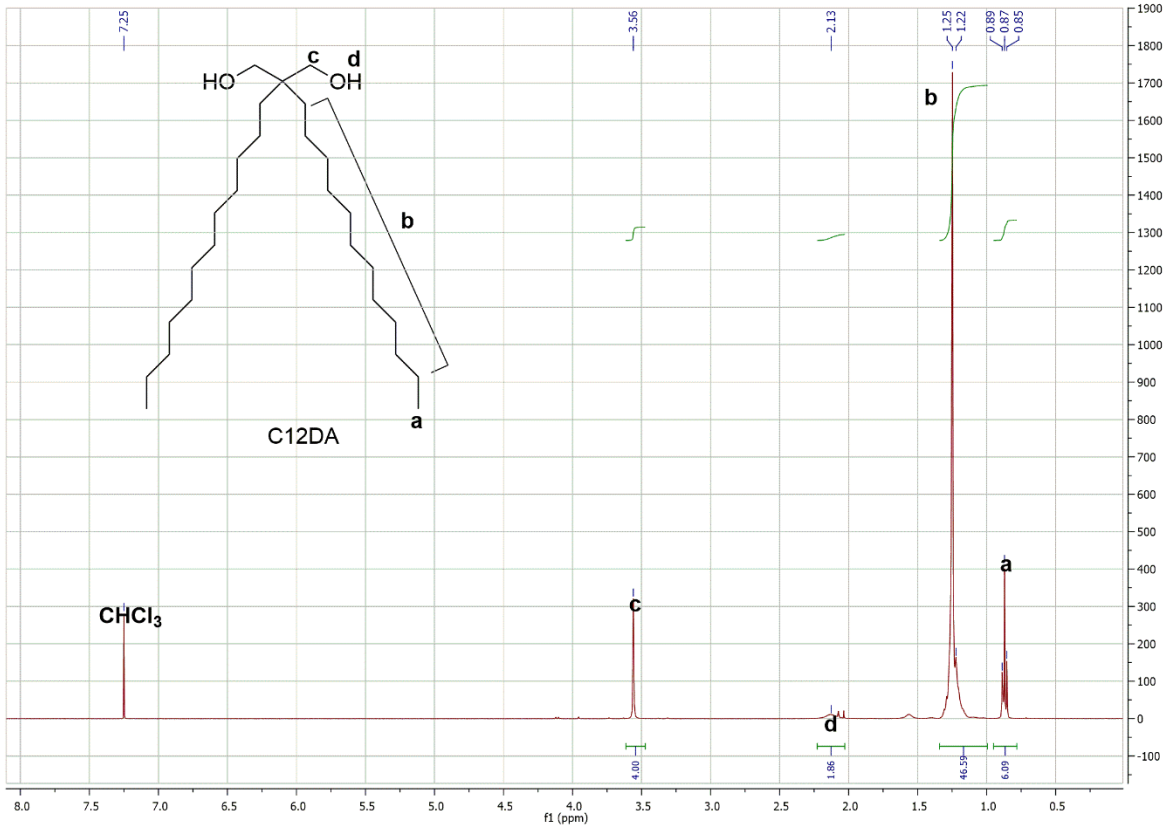
Figure S1. ^1H -NMR and ^{12}C -NMR spectra of synthesized diols











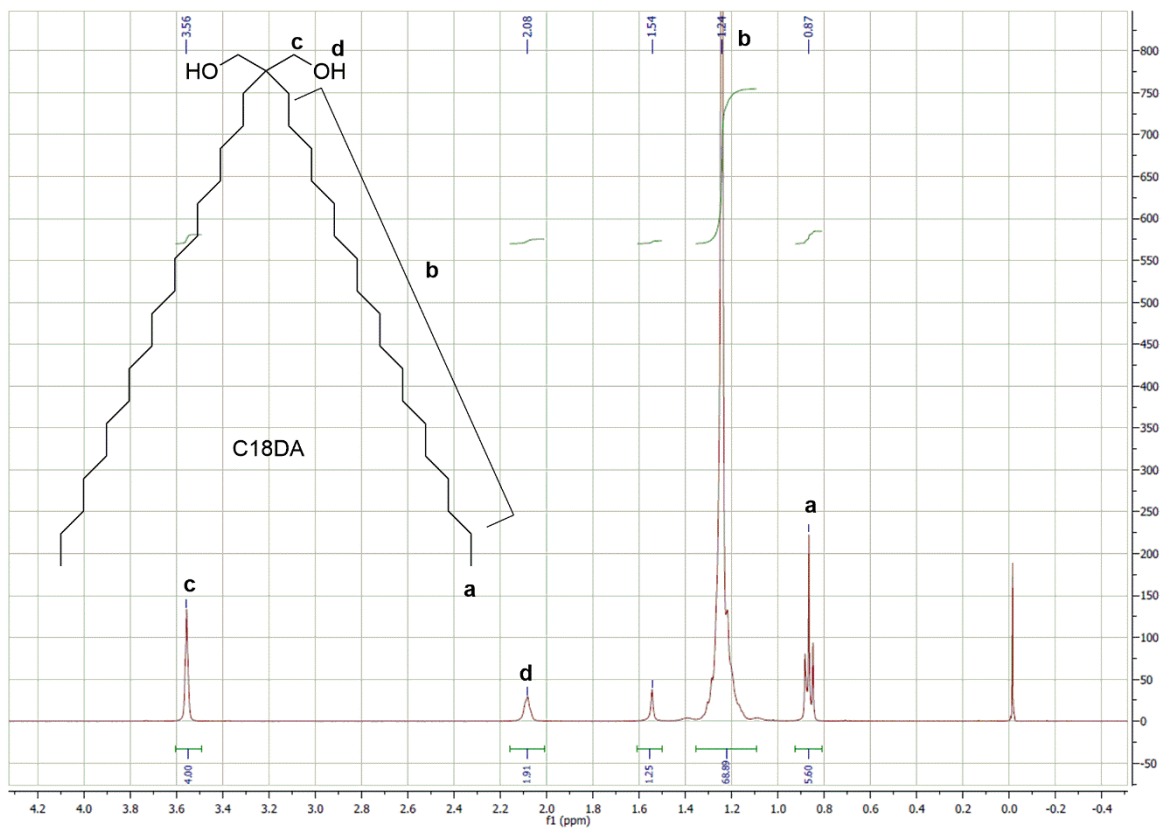
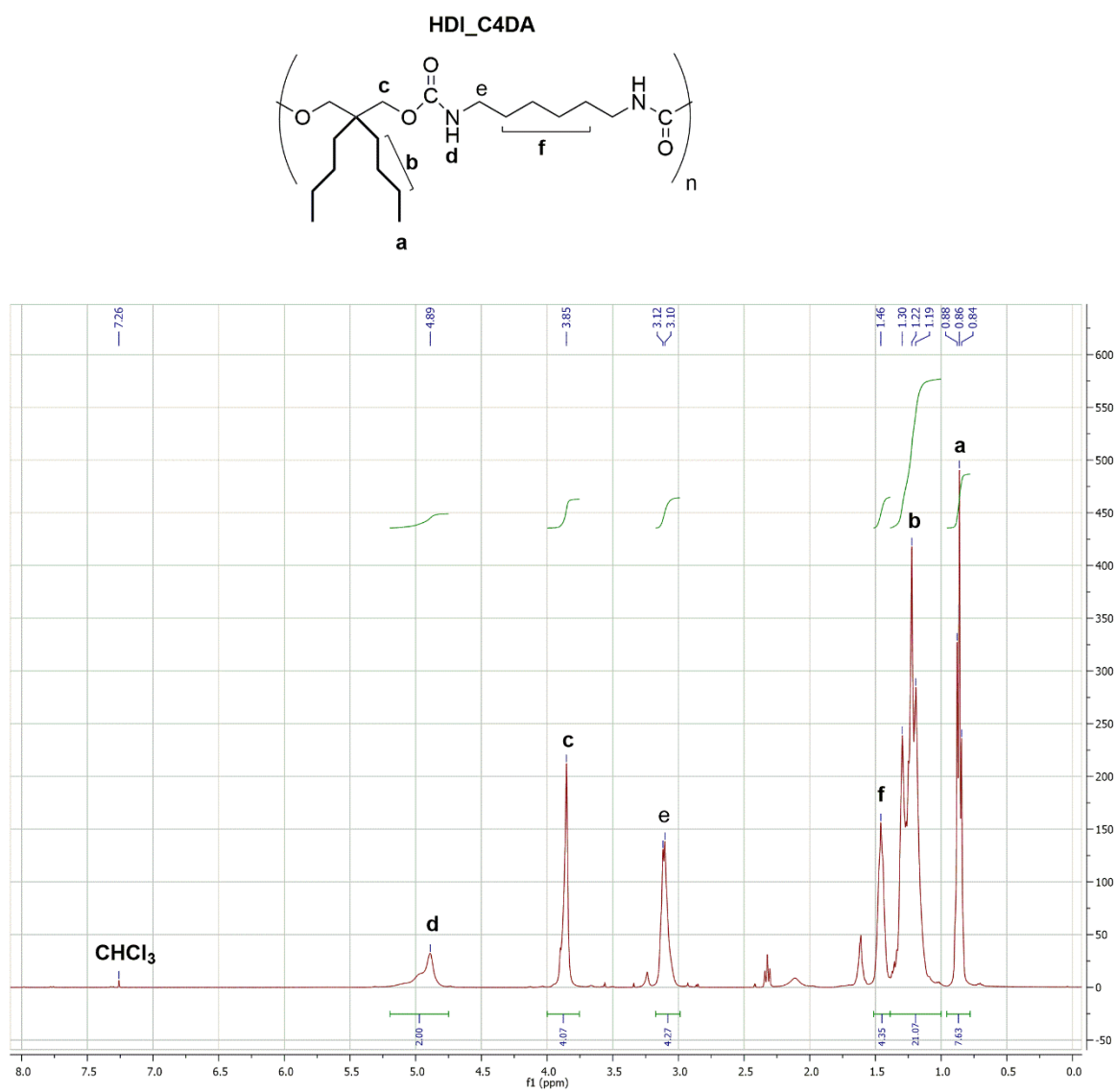
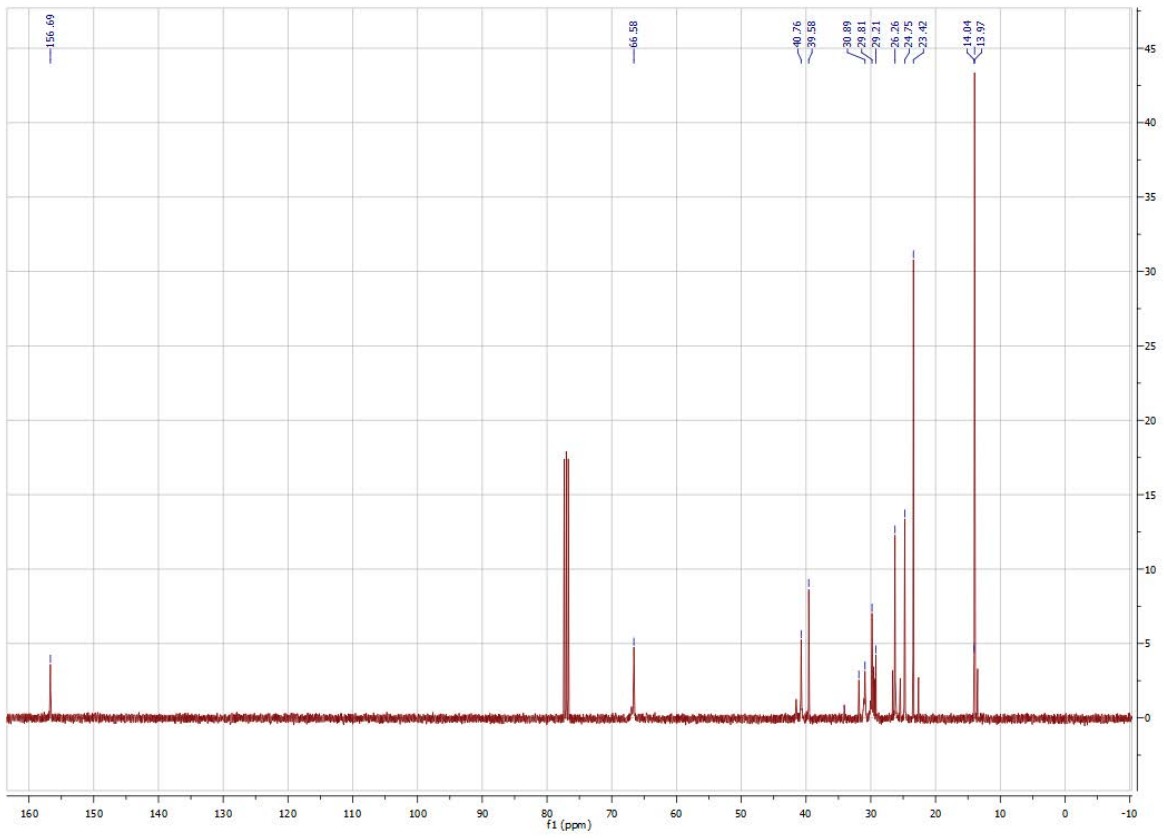
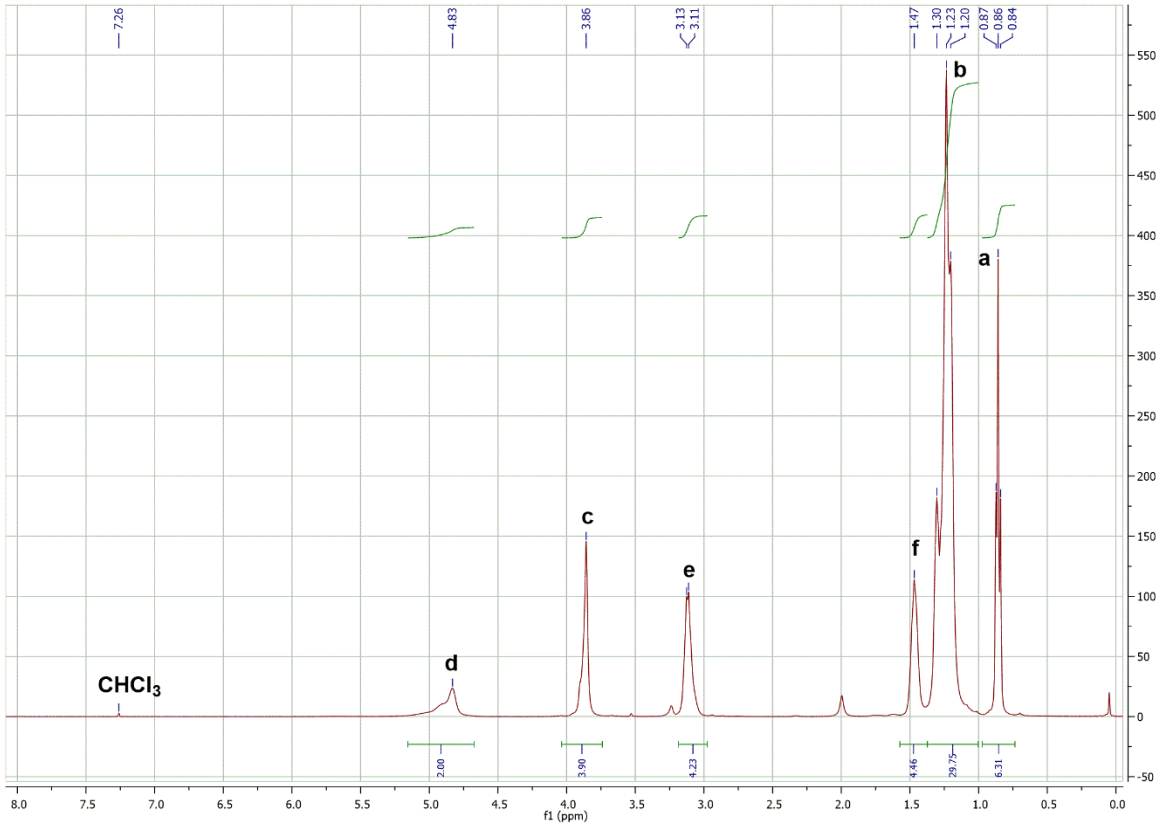
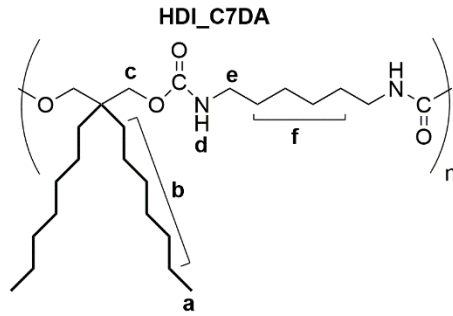
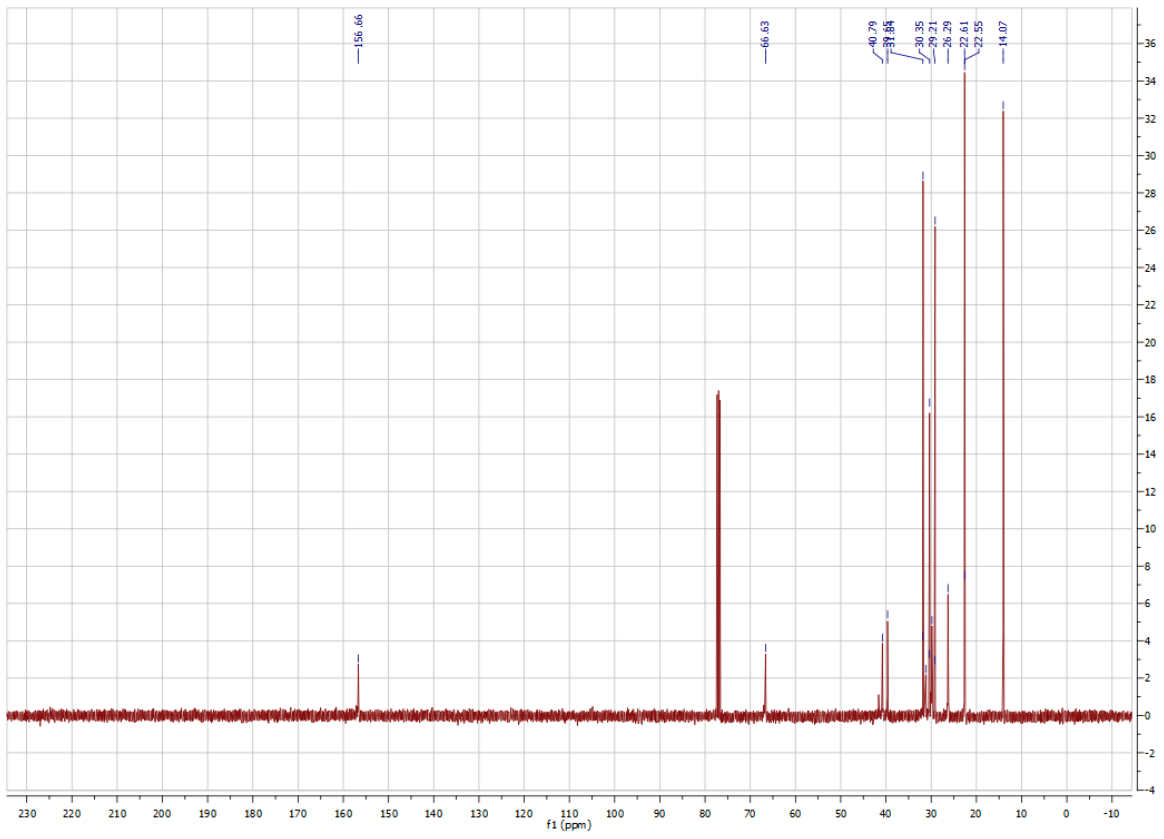


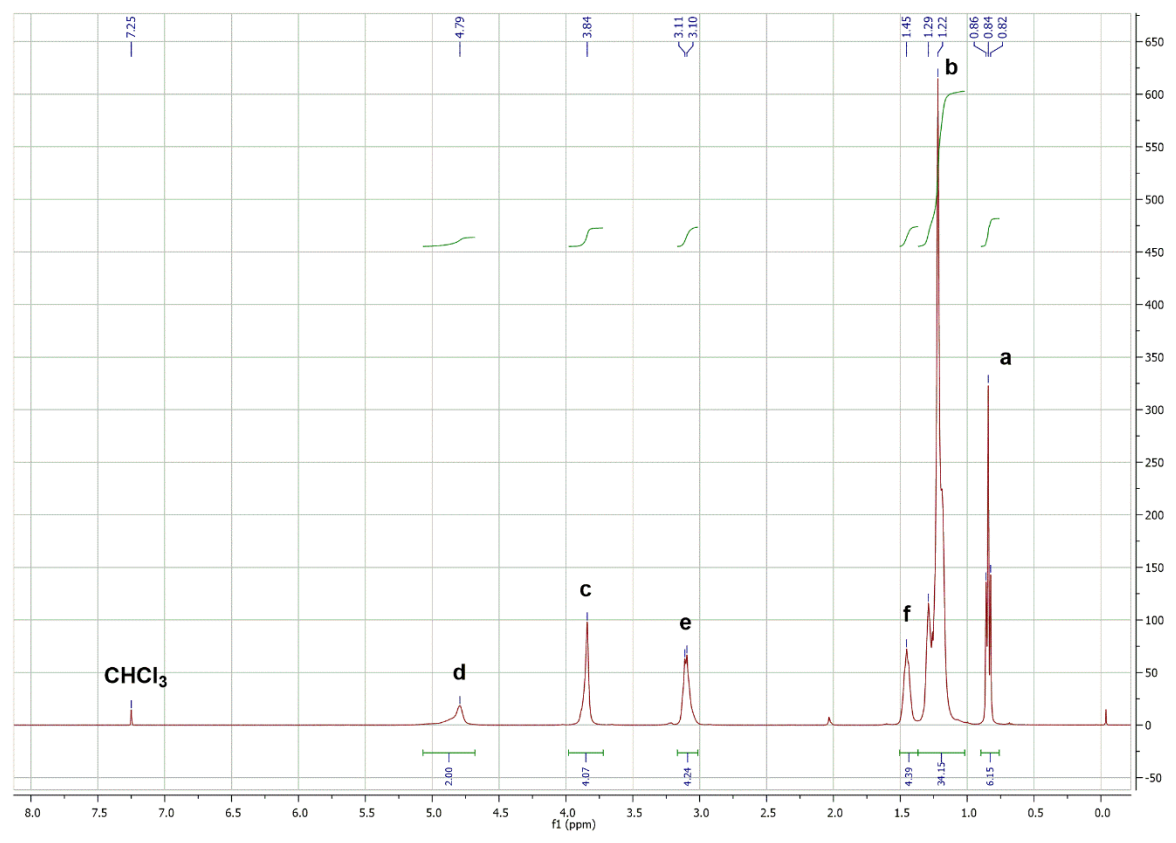
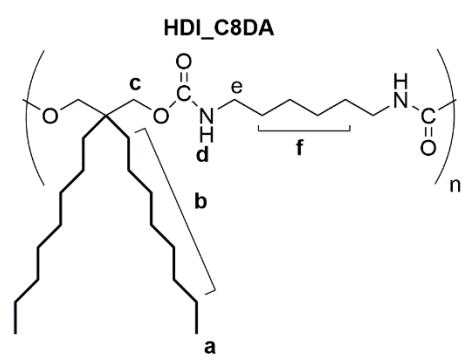
Figure S2. ^1H -NMR and ^{13}C -NMR of synthesized brush polyurethanes

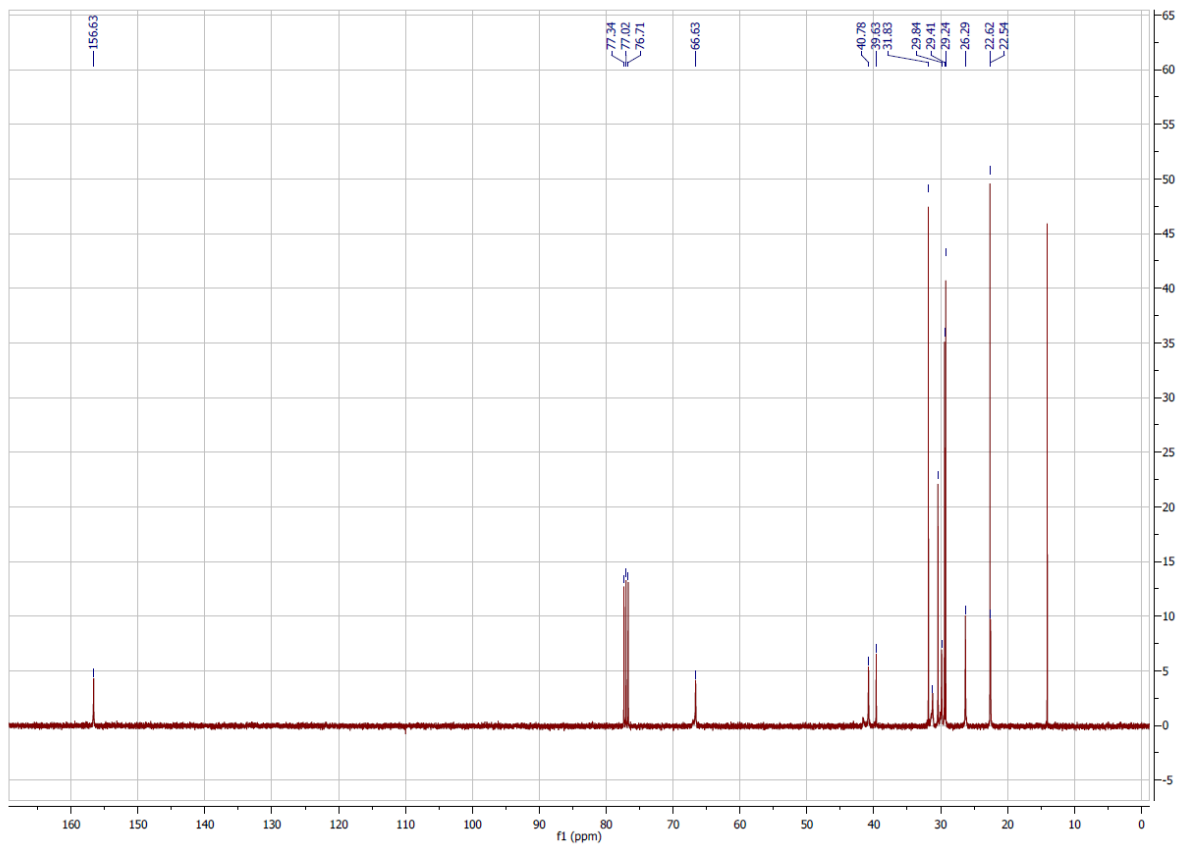


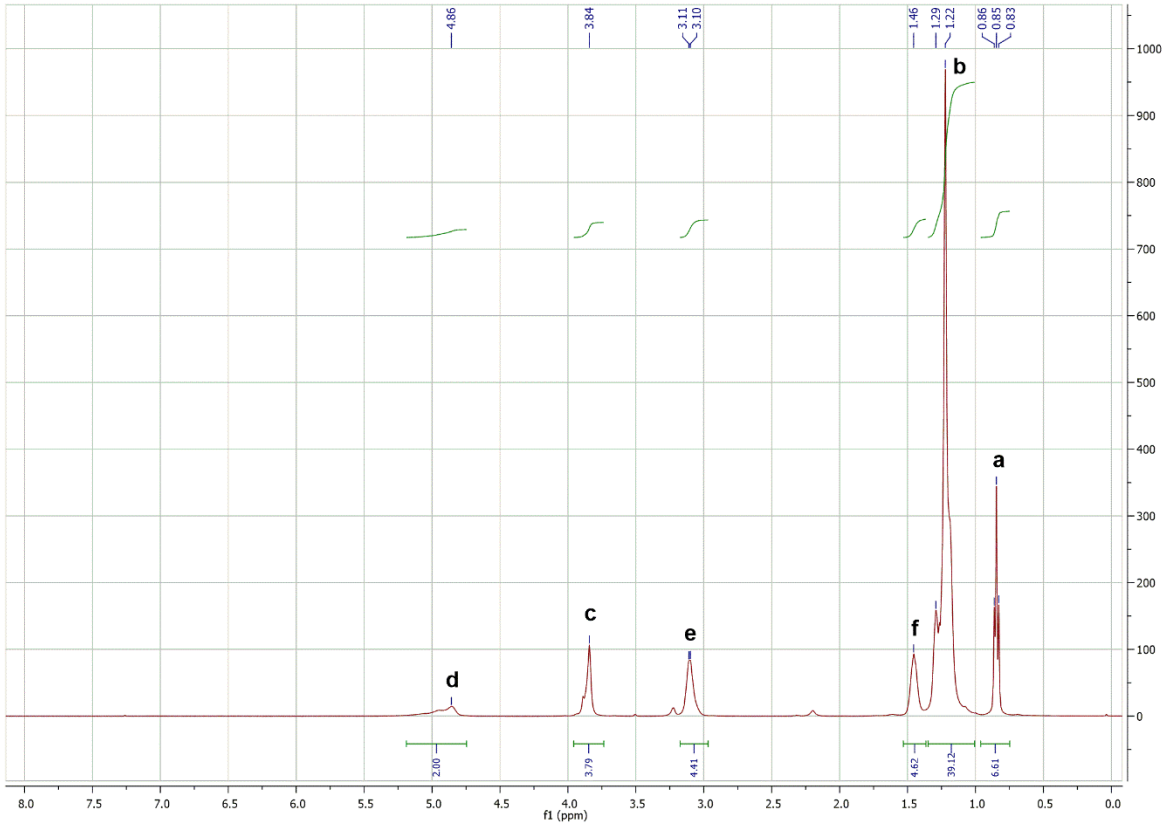
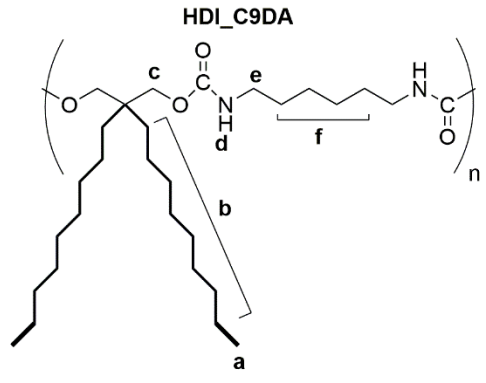


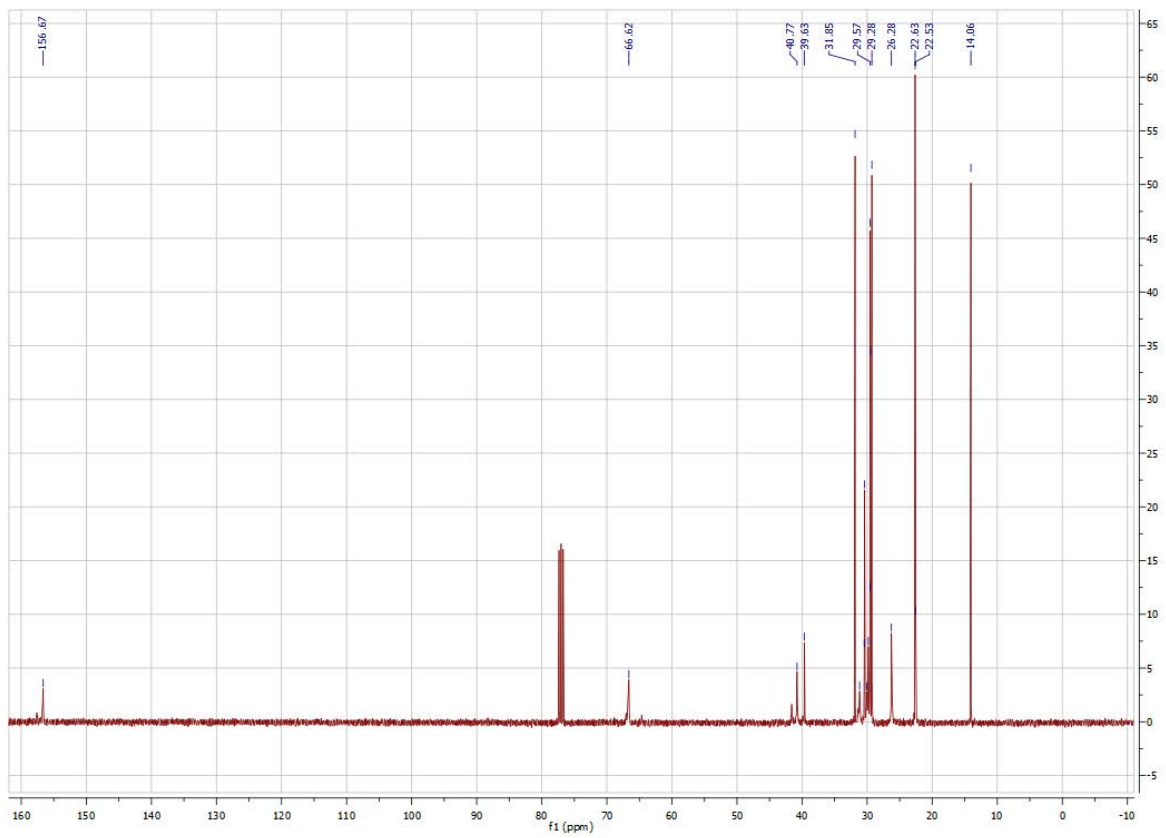


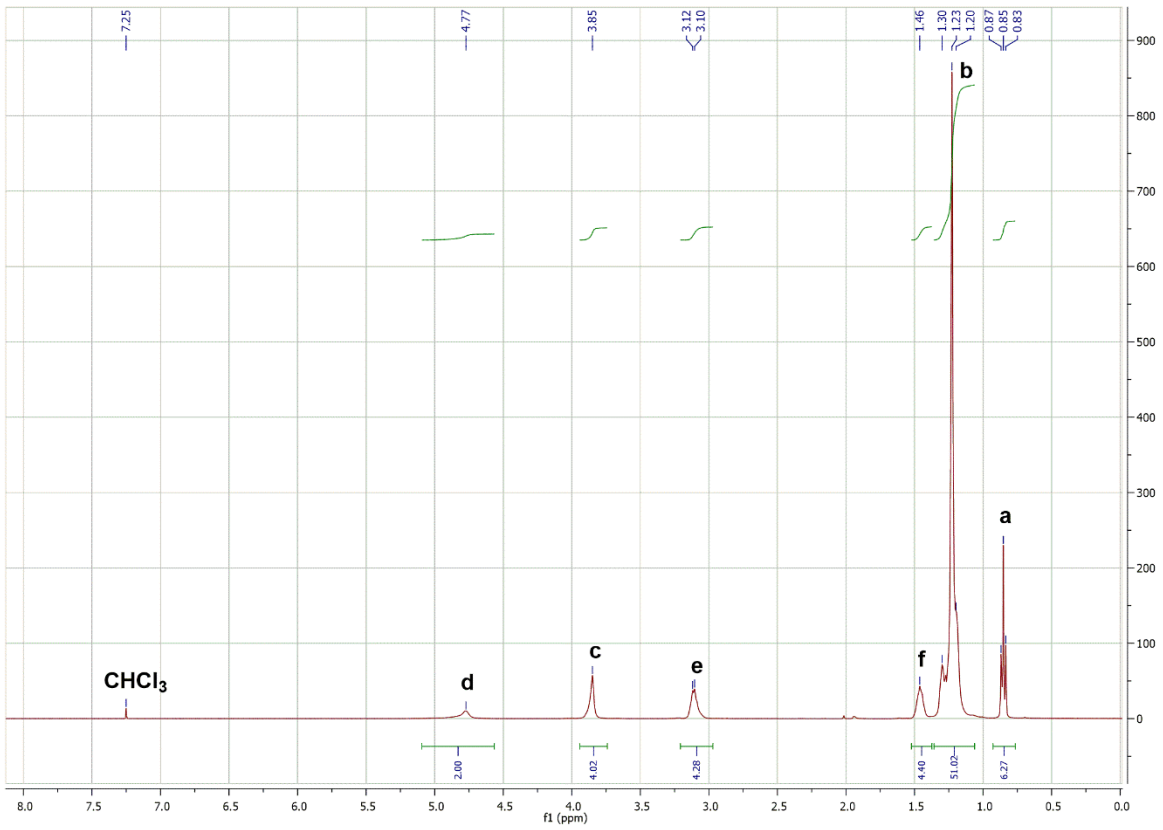
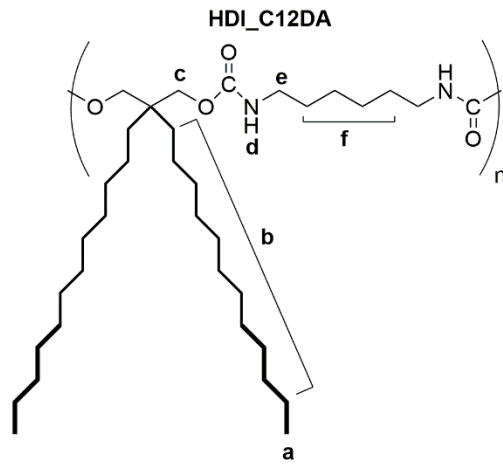




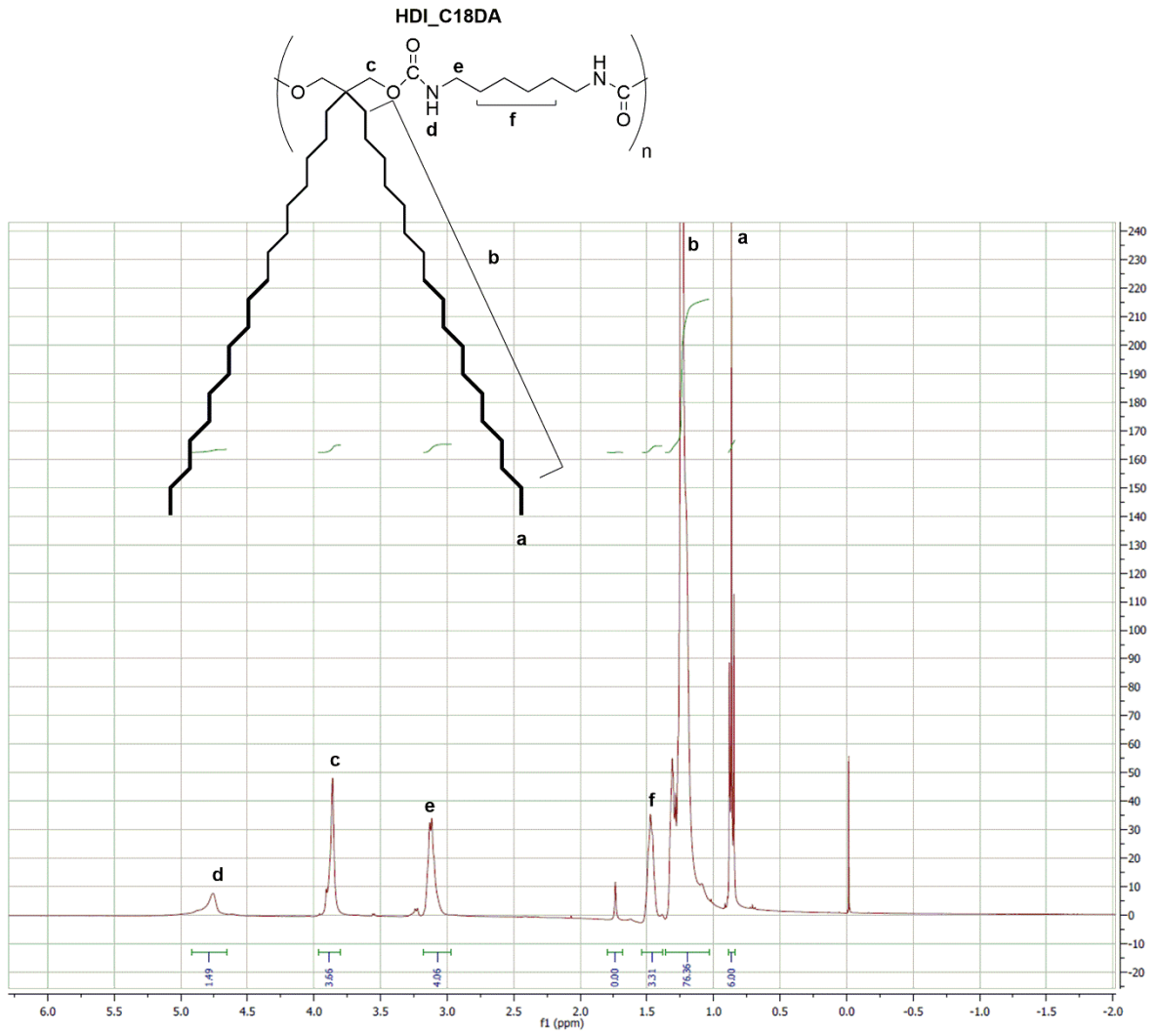








HDI_C18DA



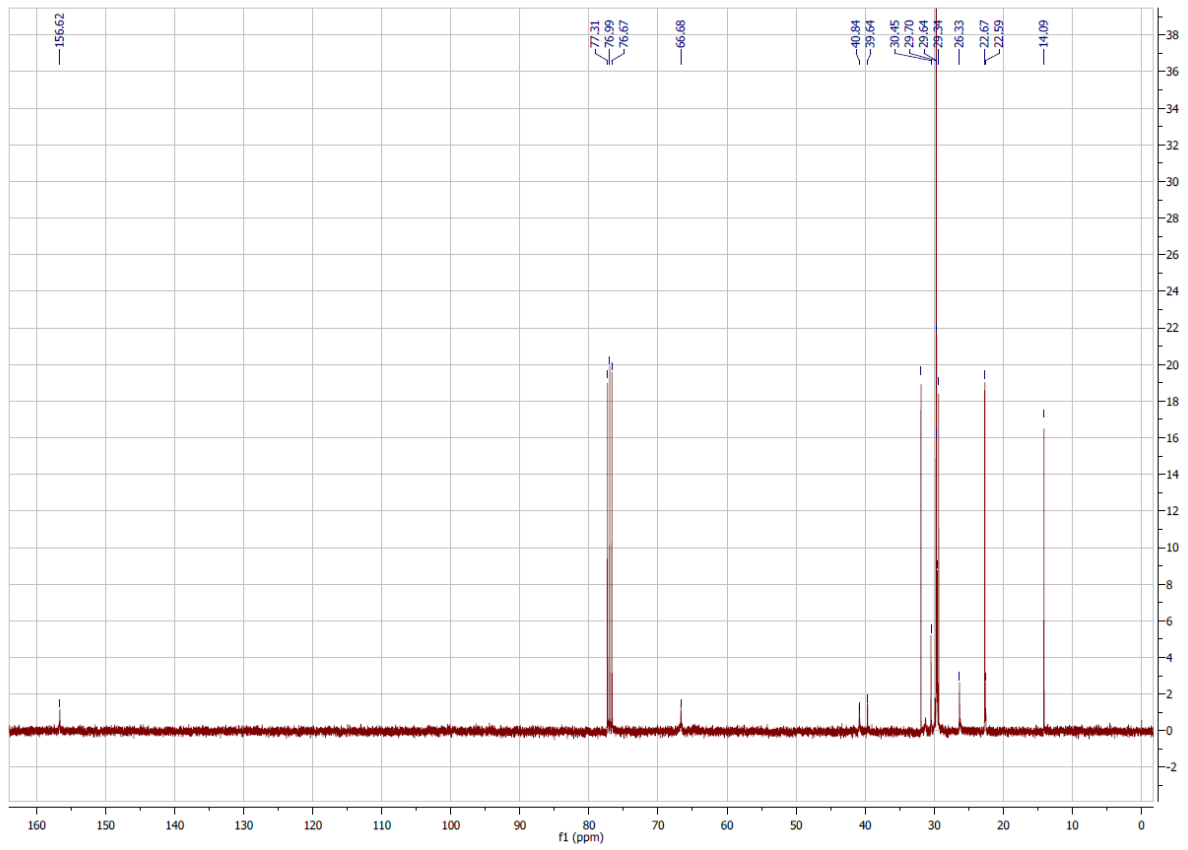


Figure S3. XRD spectra of HDI_BDO and HDI_C18DA

HDI_BDO and HDI_C18DA are semicrystalline polymers when cooling from the melt. XRD spectra support the formation of high crystalline phase.

A. XRD Spectrum of HDI_BDO

B. XRD Spectrum of HDI_C18DA

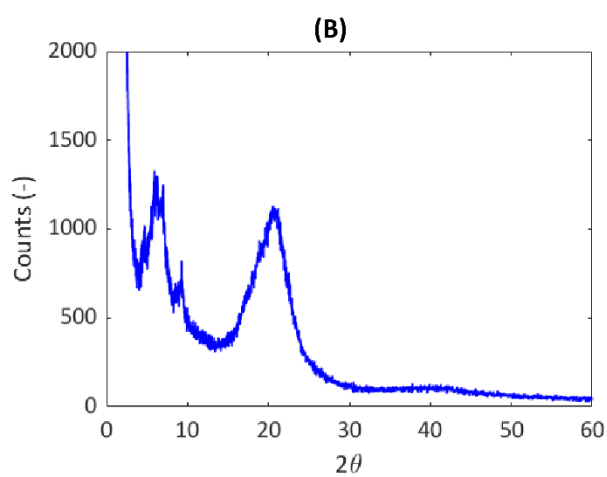
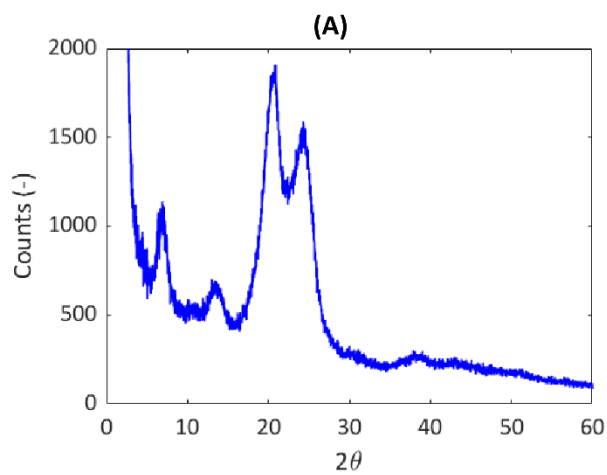


Table S-I. Young's modulus (E), yield stress (σ_y), ultimate tensile strength (σ_{UTS}) and strain at break (ε_{break}) of selected brush polyurethanes

Polymer	E (MPa)	σ_y (MPa)	σ_{UTS} (MPa)	ε_{break} (%)
HDI_C4DA	150	5.3	3.9	260
HDI_C7DA	60	1.5	10.5	660
HDI_C8DA	34	1.3	10.2	764
HDI_C9DA	4	0.2	0.6	862
HDI_C12DA	68	4.7	3.9	200

Figure S4. Frequency master-curves of HDI_C4DA and HDI_C7DA shifted at $T_0 = 20\text{ }^\circ\text{C}$

A. HDI_C4DA mastercurve

B. HDI_C7DA mastercurve

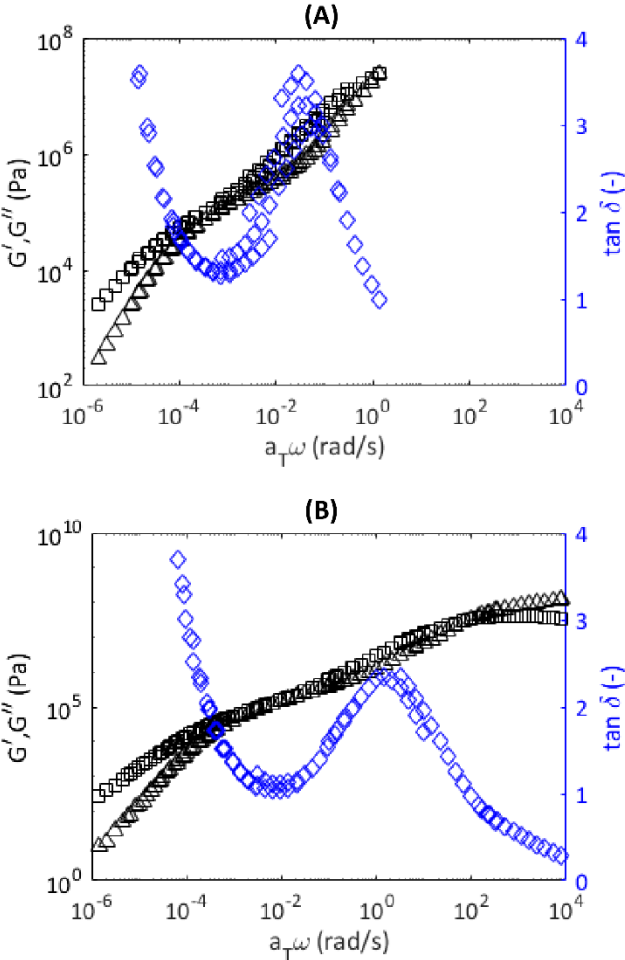


Figure S5. Frequency mastercurve of low molecular weight HDI_C8DA

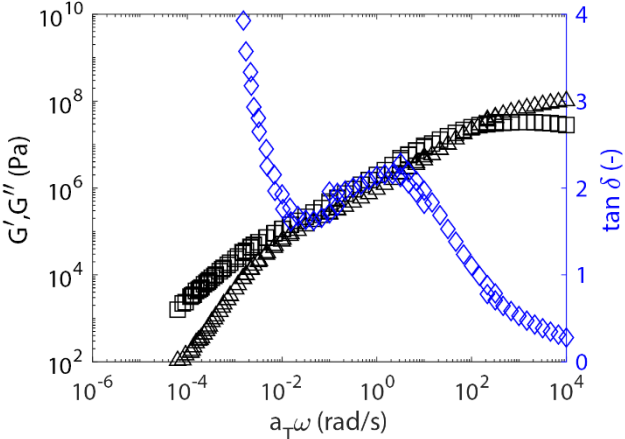


Figure S6. Temperature sweep analyses of amorphous and semicrystalline brush

polyurethanes.

(A) Temperature sweep analyses of HDI_C4DA, HDI_C7DA, HDI_C8DA, HDI_C9DA. **(B)** Effect of brush length on maximum damping temperature ($T_{max\ tan\ \delta}$) and terminal relaxation temperature ($T_{terminal}$). Note that increasing dangling chain length determines a shift to lower temperature of $T_{max\ tan\ \delta}$ and $T_{terminal}$. **(C)** Effect of brush length on maximum absolute value of damping ($\tan\ \delta_{max}$). Note that increasing brush length determines a decrease of mechanical damping. **(D)** Temperature sweep analyses of HDI_C8DA, HDI_C9DA, HDI_12DA. Note that for HDI_C9DA and HDI_C12DA no clear restriction of dynamics was observed. For these polymers the change of slope in $\tan\ \delta$ was attributed to a competitive crystallisation behaviour from side chain stacking.

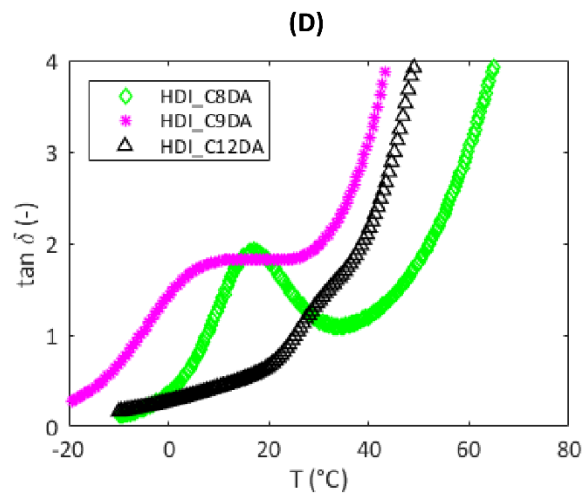
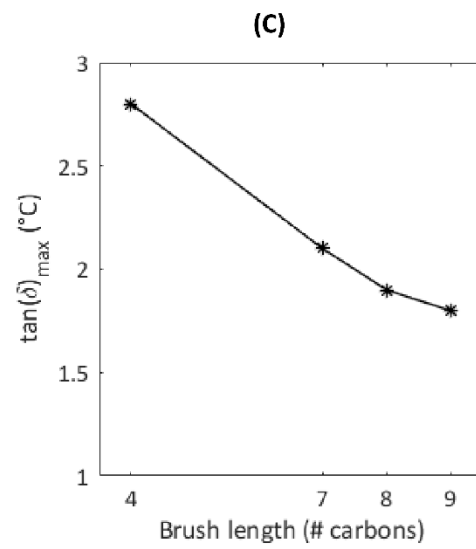
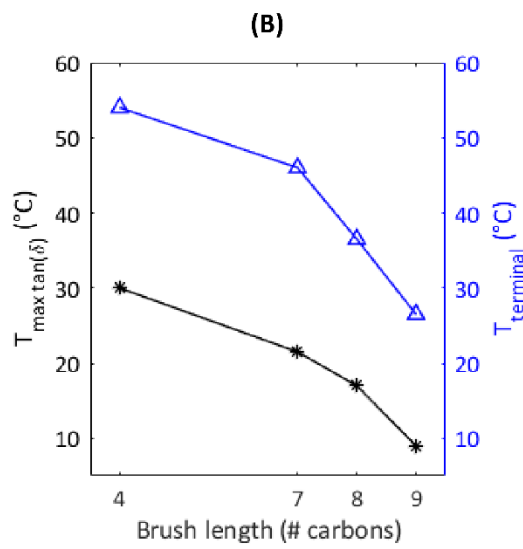
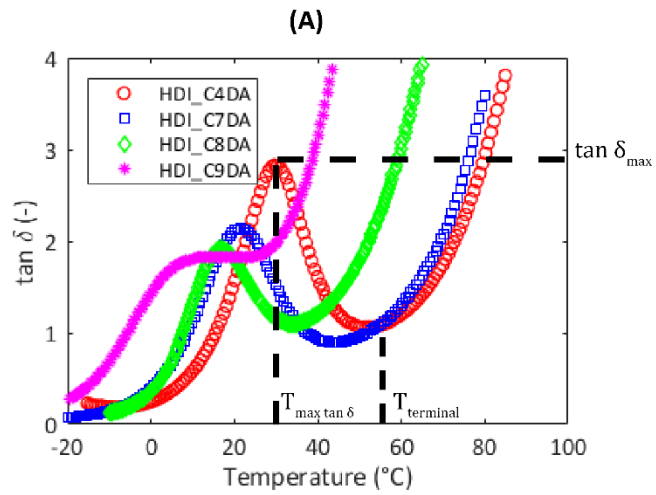


Figure S7. XRD spectra of HDI_C8DA at different annealing times.

The figure shows the evolution of the x-ray diffraction patterns with long-term annealing.

After 7 days at 21 °C, HDI_C8DA shows some degree of long range order.

A. XRD spectrum immediately after high temperature processing

B. XRD spectrum recorded after annealing for 7 days at 21 °C

