Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Fluoride-Catalyzed Carbonylation Polymerization: A facile step-growth technique to polycarbonates

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Experimental

Materials and Methods: Vacuum flame-dried flasks, vials and stir-bars were used for all synthetic procedures and all transformations were conducted under Argon atmosphere. Dimethylolpropionic Acid (Bis-MPA) was acquired from Perstorp chemicals and used as received. 1,1'-Carbonyldiimidazole (CDI) was purchased from Carbosynth and used as received. Acetonide-protected Dimethylolpropionic Acid (Bis-MPA-ac) was synthesized according to literature procedure.[1] Isosorbide (98%) was purchased from Aldrich and purified by re-crystallization from acetone prior to use in polymerizations. HPLC grade solvents were used for all synthetic transformations, and dried over vacuum/heat-activated molcular sieves (3Å) prior to use. The Cesium Fluoride (CsF) catalyst was pre-dried by a heat/vacuum, followed by back-filling with Argon atmosphere prior to use in polymerizations. Silica gel, ultrapure, 40-60 μm, 60Å from Acros organics was used for silica gel column chromatography. $CDCl_3$ used for NMR was stored under activated molcular sieves (3Å) prior to use. All other chemicals were purchased from Aldrich and used without further purification.

Size Exclusion Chromatography (SEC): A TOSOH EcoSECHLC-8320GPC system equipped with an EcoSES RI detector and three columns from PSS GmbH was used (PSS PFG 5 μm; Microguard, 100 Å and 300 Å). The mobile phase was DMF with 0.01M LiBr (0.2mL min^{-1}) at 50 °C using a conventional calibration method with narrow linear polymethylmethacrylate (PMMA) standards.

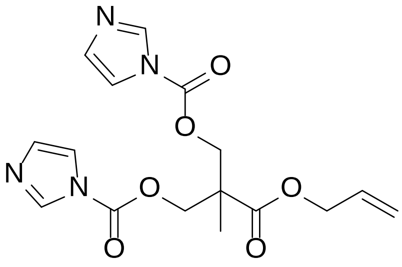
^{1}H NMR and ^{13}C NMR: NMR experiments were performed on a Bruker Avance 400 MHz NMR instrument. Proton NMR spectra were acquired with a spectral window of 20 ppm, an acquisition time of 4 seconds, a relaxation delay of 1 second. ^{13}C NMR spectra were acquired with a spectral window of 240 ppm, an acquisition time of 0.7 seconds, a relaxation delay of 2 seconds. For all NMR experiments, the $CDCl_3$ solvent peak reference was set to 7.26 ppm for ^{1}H-NMR and 77.0 ppm (middle peak) for ^{13}C-NMR.

DSC: Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC820. A heating and cooling rate of 10 °C min^{-1} was used. Unless otherwise noted, the data was collected by starting from 20 °C (first cooling to -50 °C), then the sample was heated to 150 °C, and thereafter cooled to -50 °C, and then heated to 150 °C. Analyses regarding midpoint T_g were performed on the second heating scan. In contrast, polymers **4h** and **4i** were first heated from 20 °C to 180 and 200 °C respectively. Second heating was up to 200 °C for **4h** and 250 °C for **4i**.

Synthetic Procedures

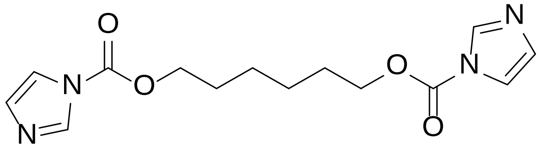
Monomers Synthesis

Synthesis of Dimethylolallylpropanoate Bis-carbonylimidazolide (2a). Bis-MPA (50 g, 0.37 mol) was dispersed in EtOAc (1.3 L), by stirring at room temperature for 10 min. The flask was put under constant Ar-flow, using a long needle, and equipped with a powder funnel on top of the needle. Then, CDI (180.0 g, 1.11 mol) was added in portions by spatula, under a constant Ar-flow, over a period of 15 min with high stirring (900 rpm). Shortly after complete addition, a white cloudy solution began to form, and stirring was maintained for an additional 1 h at room temperature, where after a heavy precipitate was formed and stirring was no longer possible. Then, the temperature was brought up to 60°C and let standing for another hour, until bubbling had stopped. Then, allyl alcohol (22.5 g, 0.38 mol) was added by pipette and the resulting reaction mixture was maintained at 60°C and kept stirring for 1 h (a transparent solution was formed). After cooling to room temperature, the mixture was left standing over night and then transferred to an extraction funnel and washed with $NaHSO_4$ (10%, 5 x 200 ml), organic phase was collected and dried over $MgSO_4$, filtered and evaporated to dryness. The resulting white solid was transferred to a filtration funnel and washed several times with cold Et_2O, then transferred to a rb-flask and dried *in-vacuo*. The product **2a** was obtained as a white solid (92.0 g, 69%). ^{1}H NMR ($CDCl_3$) δ ppm: 1.42 (s, 3H, -C**H**$_3$), 4.62 (m, 6H), 5.23 (d, J=10.2 Hz, 1H, -CH=C**H**$_2$), 5.30 (d, J=17.2 Hz, 1H, -CH=C**H**$_2$), 5.85 (m, 1H, -C**H**=CH$_2$), 7.05 (s, 2H, -C-CON-imidazole-**H**), 7.34 (s, 2H, -CH$_2$-OCON-imidazole-**H**), 8.07 (s, 2H, -C-CON-imidazole-**H**). ^{13}C NMR ($CDCl_3$) δ ppm: 17.7, 46.6, 66.4, 68.2, 116.9, 119.8, 130.9, 131.0, 136.9, 148.0, 170.9.



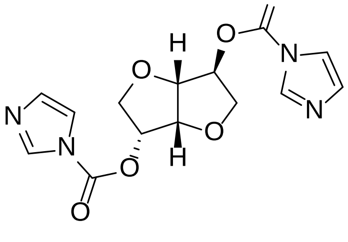
(2a)

Synthesis of 1,6-Hexanediol Bis-carbonylimidazolide (2b). 1,6-hexanediol (50 g, 0.42 mol) was dissolved in EtOAc (1 L) by stirring at room temperature for 5 min (Ar-atm). The flask was put under constant Ar-flow, using a long needle, and equipped with a powder funnel on top of the needle. Then, CDI (171.5 g, 1.06 mol) was added in portions by spatula, under a constant N_2-flow, over a period of 10 min at 20 °C, with high stirring (900 rpm). Each addition was done after the solution had turned homogenous following the previous addition. Then, shortly after complete addition, a white cloudy solution began to form, and stirring was maintained for an additional 1 h at room temperature. Then, stirring was interrupted and the mixture was allowed to stand for 1 h at room temperature. Then, the white precipitate was collected by filtration, washed with EtOAc (2x300 ml), transferred to a 1L rb-flask and dried *in-vacuo*. The product **2b** was obtained as a white solid (124.8 g, 97%). ^{1}H NMR ($CDCl_3$) δ ppm: 1.42 (m, 4H), 1.74 (m, 4H), 4.33 (t, J=6.6 Hz, 4H, -C**H$_2$**-OCO-), 6.96 (s, 2H, imidazole-**H**), 7.32 (s, 2H, imidazole-**H**), 8.03 (s, 2H, imidazole-**H**). ^{13}C NMR ($CDCl_3$) δ ppm: 25.0, 28.1, 67.8, 116.8, 130.4, 136.8, 148.4.



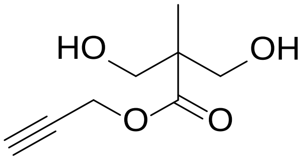
(2b)

Synthesis of Isosorbide Bis-carbonylimidazolide (2c) Isosorbide (20.0 g, 0.17 mol) was dissolved in acetone (400 ml), by stirring at room temperature for 10 min. The flask was put under constant Ar-flow, using a long needle, and equipped with a powder funnel on top of the needle. Then, CDI (55.13 g, 0.34 mol) was added in portions by spatula, under a constant Ar-flow, over a period of 10 min. Shortly after complete addition, a white cloudy solution began to form, and stirring was maintained for an additional 20 h at room temperature, where after a heavy precipitate was formed (still possible to stir). The resulting white solid was collected by filtration and washed several times with Et_2O, then transferred to a rb-flask and dried *in-vacuo*. The product **2c** was obtained as a white solid (40.3 g, 71%). ^{1}H NMR ($CDCl_3$) δ ppm: 4.03 (dd, J=11.1 Hz, J=4.4 Hz, 2H), 4.12 (dd, J=10.8 Hz, J=3.6 Hz, 1H), 4.18 (d, J=11.3 Hz,1H), 4.69 (d, J=4.85 Hz, 1H), 5.08 (t, J=5.3 Hz, 1H), 5.42 (m, 1H), 5.47 (d, J=3.1 Hz, 1H), 7.08 (s, 1H), 7.10 (s, 2H), 7.39 (s, 1H), 7.44 (s, 1H), 8.10 (s, 1H), 8.16 (s, 1H). ^{13}C NMR ($CDCl_3$) δ ppm: 70.8, 72.8, 77.0, 80.9, 81.0, 85.7, 117.0, 117.1, 131.0, 131.1, 137.0, 137.1, 147.6, 148.0.



(2c)

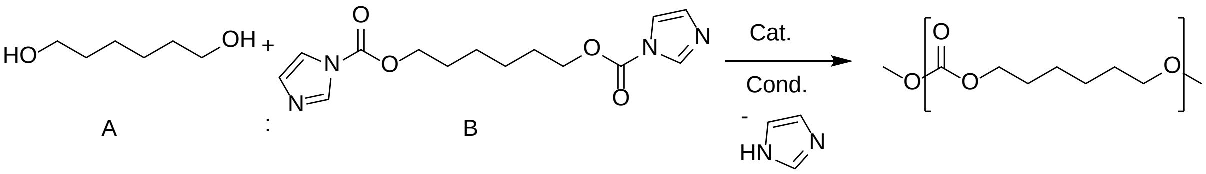
Synthesis of Dimethylolpropargylpropanoate (3c) A 500 ml rb-flask (heat/vacuum-dried), with a stir bar, was filled with Bis-MPA-ac[1] (20.0 g, 0.115 mol) and dissolved in EtOAc (250 ml). Then, CDI (20.5 g, 0.127 mol) was added in portions by spatula, under a constant Ar-flow. Shortly after complete addition, stirring was maintained for an additional 1 h at room temperature, until there was no sign of CO_2 evolution. Then, progargyl alcohol (7.09 g, 0.123 mol) was slowly added, whereafter the temperature was brought up to 60°C, and kept stirring for 2 h. After cooling to room temperature, the solution was washed with $NaHSO_4$ (10%) (4 x 200 ml), then dried over $MgSO_4$ and dried *in-vacuo*. The acetonide protected product was obtained as colorless oil. Acetal deprotection was induced by dissolving the oil in methanol (500 ml) and adding DOWEX (PTSA) (1.0 g) and stirred at room temperature for 5 h. Subsequently, the mixture was filtered and concentrated *in-vacuo*. The final product was purified by column chromatography (EtOAc: Hept 5:2), yielding the product **3c** as a white solid (10.2 g, 52%). ^1H NMR ($CDCl_3$) δ ppm: 1.10 (s, 3H, -C**H**$_3$), 2.50 (t, 1H, J=2.5 Hz, C**H**≡C-), 2.80 (t, 1H, J=6.2 Hz, **H**O-), 3.73 (dd, 2H J=11.3 Hz, J=6.2 Hz), 3.93 (dd, 2H, J=11.3 Hz, J=6.2 Hz), 4.76 (d, 2H, J=2.5 Hz, CH≡C-C**H**$_2$-O-). ^{13}C NMR ($CDCl_3$) δ ppm: 16.9, 49.3, 52.4, 66.9, 75.2, 77.3, 174.9.



(3c)

Step-growth polymerizations

- **Initial screening of polymerization conditions**

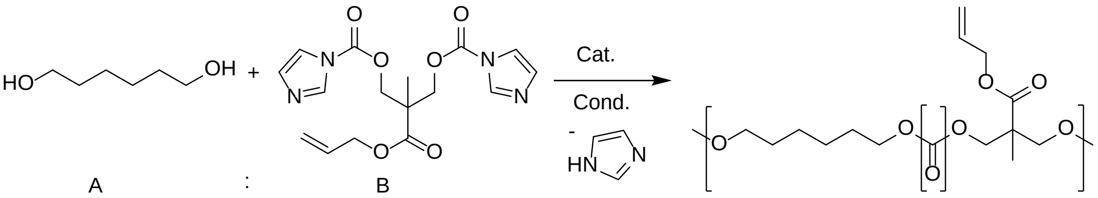


Scheme S1. Optimization of step-growth polymerization of 1,6-hexandiol (**3a**) and **2b**.[a]

Table S1. Optimization of polymerization conditions for **3a** and **2b**.[a]

Entry	*A/B*	*CsF (%)*	*Cond. (°C/h)*	*Solv.*[b] *(4 M)*	*M_n*[c] *(kDa)*	*Đ*[c]
1	1.00/1.10	1	90/5	melt	11.5	1.66
2	1.00/1.05	1	90/5	melt	24.7	1.54
3	1.00/1.05	5	60/16	EtOAc	10.6	1.76
4	1.00/1.00	5	60/16	EtOAc	12.2	1.74

[a] All polymerizations were performed in sealed vials under Argon atmosphere.[b] Concentration of 1,6-hexanediol.[c] Measured by SEC.



Scheme S2. Optimization of step-growth polymerization of 1,6-hexandiol (**3a**) and **2a**.[a]

Table S2. Optimization of polymerization conditions for **3a** and **2a**.[a]

Entry	*A/B*	*CsF (%)*	*Cond. (°C/h)*	*Solv.*[b] *(4 M)*	*M_n*[c] *(kDa)*	*Đ*[c]	*Seq.*[d]
1	1.00/1.10	1	100/2	melt	9.53	2.13	
2	1.00/1.10	1	60/40	EtOAc	7.51	2.55	
3	1.00/1.10	5	60/16	EtOAc	6.12	1.74	
4	1.00/1.05	5	60/16	EtOAc	9.03	2.64	
5	1.00/1.00	5	60/16	EtOAc	6.66	1.98	
6	1.00/1.05	5	40/16	DCM	6.69	2.45	

[a] All polymerizations were performed in sealed vials under Argon atmosphere.[b] Concentration of 1,6-hexanediol.[c] Measured by SEC.

- **General procedure for step-growth polymerization**

A vacuum flame-dried vial (3ml) with a stir bar, was charged with CsF (13 mg, 0.084 mmol) and was then put under vacuum at 20°C and heated with a heat gun. After cooling to room temperature, it was back-filled with Argon. Then, diol **3a-d** (8.46 mmol) and bis-carbonylimidazolide **2a-c** (8.88 mmol) monomers were added and the vial was sealed and subjected to three vacuum/Argon cycles and then left under Argon atmosphere. Then, EtOAc (4.5 ml) was added by syringe (Ar-atm). The resulting reaction mixture was heated to 60°C and kept stirring for 16 h. Thereafter, the reaction was allowed to cool to room temperature. A crude aliquot was taken out and analyzed to measure monomer conversion by ^{1}H-NMR($CDCl_3$), and SEC(DMF) to measure molecular number weight (M_n) and PDI. The crude polymer was purified by directly precipitating the reaction mixture solution into a stirring methanol solution (500 ml). The precipitated polymer was collected by decantation of the methanol solution, followed by washing two times with additional methanol (2x5ml), and then dried *in-vacuo*. The resulting polycarbonates **4a-i** were structurally characterized through ^{1}H- and ^{13}C-NMR (Fig. S6-S14). Monomer sequence was determined as either predominantly alternating (*alt*) or random (*ran*) from ^{13}C-NMR analysis of the carbonate peak signal (Figure S15). SEC(DMF) curves (Figure S16) for molecular weight analysis and DSC traces (Figure S17) for thermal behavior.

- **Kinetic experiments: Reaction Monitoring of Step-growth Polymerization**

The experiments were carried out according to the general polymerization procedure, with 1,6-hexanediol **3a** and **2b** using four different molar ratios given in Figure S1. The reactions were monitored by sampling aliquots from the crude reaction mixture, which were diluted with $CDCl_3$. The monomer conversion was obtained from their ^{1}H-NMR($CDCl_3$) spectra and molecular weights were extracted from SEC(DMF) traces.

Kinetic experiments were undertaken to evaluate the relative influence of catalyst (CsF) and bis-carbonylimidazolide monomer **2b** on the polymerization process with diol **3a** (Fig. S1a-b for more detailed information). Kinetic plots of ln([OH]0/[OH]) vs time showed a good fit to a first order reaction in [OH] when using an excess of diol **3a** in the feed (Fig. S1b), and a progressive deviation towards second order behavior when increasing the bis-carbonylimidazolide **2b** loading up to 5% molar excess.

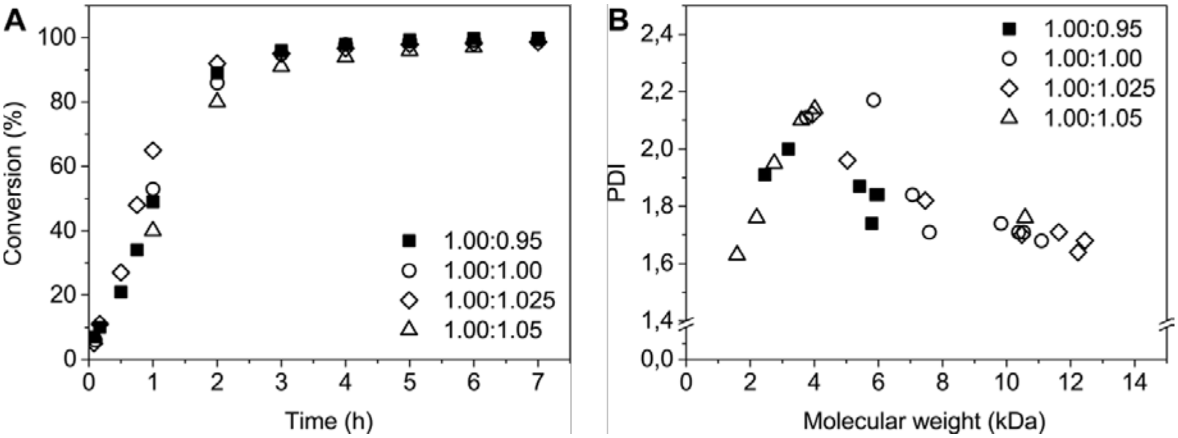


Figure S1a. (A) Conversion vs time, and (B) PDI vs M_n, for step-growth polymerization of 1,6-hexanediol **3a** and **2b** in four different ratios using CsF (5 mol-%) in EtOAc.

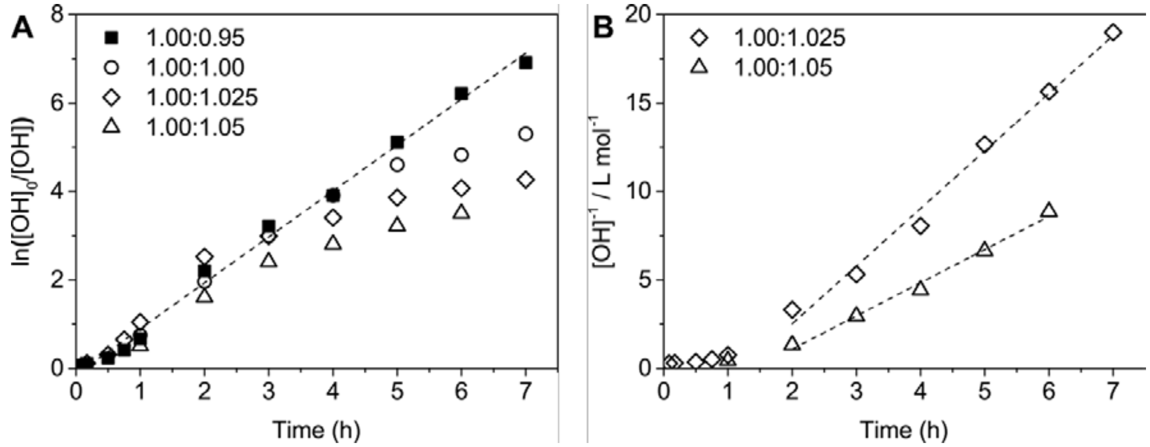
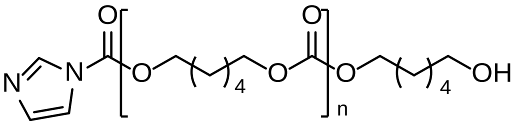


Figure S1b. (A) Kinetic plot of ln($[OH]_0$/[OH]) vs time, for step-growth polymerization of 1,6-hexanediol **3a** and **2b** in four different ratios using CsF (5 mol-%) in EtOAc, as obtained from ^{1}H-NMR. (B) Kinetic plot of $[OH]^{-1}$ vs time, for step-growth polymerization of 1,6-hexanediol **3a** and **2b** for excess bis-carbonylimidazolide in feed, using CsF (5 mol-%) in EtOAc, as obtained from ^{1}H-NMR.

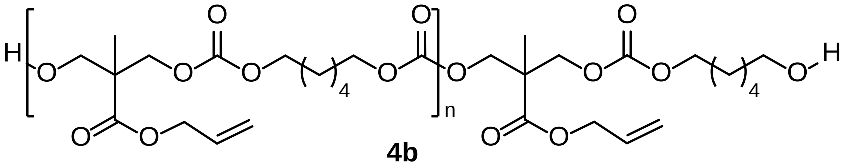
- **Polymers Synthesis**

Synthesis of poly(1,6-hexanediolcarbonate) (4a, Table 1, Entry 1). The polymerization was carried out according to the general procedure from diol **3a** and bis-carbonylimidazolide **2b**. The polymer product **4a** was collected as a transparent solid (2.35 g, 78% yield), which turned white upon standing. ^{1}H NMR ($CDCl_3$) δ ppm: 1.38 (br-m, 4H), 1.65 (br-m, 4H), 4.09 (br-t, 4H, CO-O-C**H**$_2$-), end-groups: 3.61 (br-t, 2H, -CH_2-OH-), 7.04 (br-s, 1H, -C-CON-imidazole-**H**), 7.39 (br-s, 1H, -C-CON-imidazole-**H**), 8.11 (br-s, 1H, -C-CON-imidazole-**H**). ^{13}C NMR ($CDCl_3$) δ ppm: 25.3, 28.5, 67.7, 155.3. M_n SEC(DMF) = 11 kDa, PDI = 1.8. DSC: T_g= -45 °C, T_m= +52 °C.



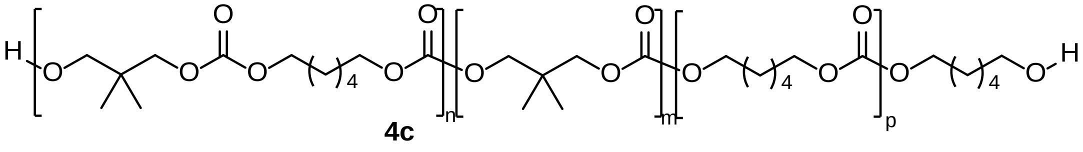
4a

Synthesis of poly(bisMPA-allyl-*alt*-1,6-hexanediol-carbonate) (4b, Table 1, Entry 2). The polymerization was carried out according to the general procedure from diol **3a** and bis-carbonylimidazolide **2a**. The polymer product **4b** was collected as a transparent sticky solid (2.48 g, 86% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 1.28 (br, 3H, -C**H**$_3$), 1.39 (br, 4H), 1.66 (br, 4H), 4.11 (br-t, 4H, J=6.7 Hz), 4.31 (br-m, 4H), 4.62 (br-d, 2H, J=5.6 Hz, -C**H**$_2$CH$_3$), 5.23 (br-d, 1H, J=10.6Hz), 5.31 (br-d, 1H, J=17.4 Hz), 5.88 (br-m, 1H), end-groups: 3.63 (br-t, 2H, -CH$_2$-CH$_2$-OH), 3.72 (br-s, 2H, -C-CH$_2$-OH). ^{13}C NMR ($CDCl_3$) δ ppm: 17.6, 25.3, 28.5, 46.5, 65.8, 68.1, 68.2, 118.4, 131.6, 154.8, 171.9. .M_n SEC(DMF) = 9 kDa, PDI = 2.64. DSC: T_g= -29 °C.



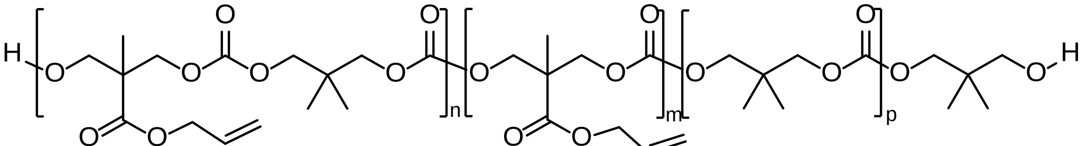
4b

Synthesis of poly(neopentyl-*ran*-1,6-hexanediol carbonate) (4c, Table 1, Entry 3). The polymerization was carried out according to the general procedure from diol **3b** and bis-carbonylimidazolide **2b**. The polymer product **4c** was collected as a transparent sticky solid (1.97 g, 86% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.99 (br, 6H, -C**H**$_3$), 1.40 (br, 4H), 1.67 (br, 4H), 3.95 (br-s, 4H), 4.11 (br-t, 4H, J=6.7 Hz), end-groups: 3.63 (br-t, 2H, -CH$_2$-CH$_2$-OH), 3.72 (br-s, 2H, -C-CH$_2$-OH). ^{13}C NMR ($CDCl_3$) δ ppm: 21.4, 25.3, 28.5, 35.0, 67.9, 72.3, 155.3. M_n SEC(DMF) = 8 kDa, PDI = 1.71. DSC: T_g= -30 °C.



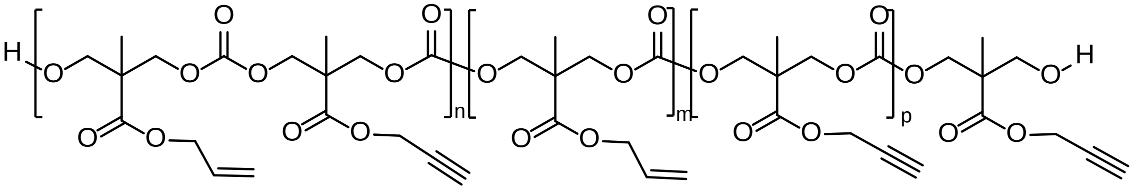
4c

Synthesis of poly(bisMPA-allyl-*ran*-neopentylglycol carbonate) (4d, Table 1, Entry 4). The polymerization was carried out according to the general procedure from diol **3b** and bis-carbonylimidazolide **2a**. The polymer product **4d** was collected as a transparent sticky solid (0.82 g, 29% yield). ^{1}H NMR (CDCl$_3$) δ ppm: 0.97 (br, 6H, (neopentyl-C**H**$_3$), 1.27 (br, 3H, (bisMPA-C**H**$_3$), 3.94 (br, 4H, neopentyl-C-O-C**H**$_2$-C), 4.30 (br, 4H, bisMPA-C-O-C**H**$_2$-C), 4.62 (br, 2H, CH$_2$=CH-C**H**$_2$O-), 5.22 (d, 1H, J=10.6 Hz, cis-C**H**$_2$=CH-CH$_2$O-), 5.30 (d, 1H, J=17.2 Hz, trans-C**H**$_2$=CH-CH$_2$O-), 5.87 (m, 1H, CH$_2$=C**H**-CH$_2$O-), end-groups: 3.33 (br, 2H, neopentyl:-C-CH$_2$-OH), 3.71 (br, 2H, bisMPA:-C-CH$_2$-OH). ^{13}C NMR (CDCl$_3$) δ ppm: 17.5 (m), 21.3 (m), 35.1 (m), 46.5 (m), 65.8 (m), 68.5 (m), 72.5 (m), 118.4 (m), 131.5 (m), 154.8 (m), 171.8 (m). M$_n$ SEC(DMF) = 12 kDa, PDI = 1.34. DSC: T_g= -5 °C.



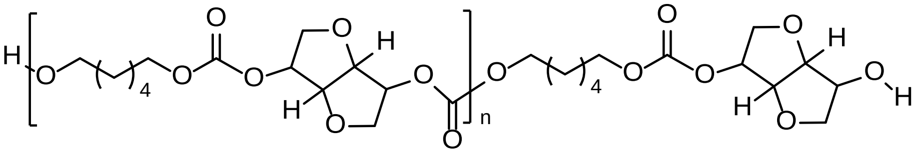
4d

Synthesis of poly(bisMPA-allyl-*ran*-propargyl-carbonate) (4e, Table 1, Entry 5). The polymerization was carried out according to the general procedure from diol **3c** and bis-carbonylimidazolide **2a**. The polymer product **4e** was collected as a transparent sticky solid (2.02 g, 60% yield). ^{1}H NMR (CDCl$_3$) δ ppm: 1.26 (br, 6H, (bisMPA-C**H**$_3$), 2.52 (br, 1H, -C≡C**H**), 4.29 (br, 8H, bisMPA-C-O-C**H**$_2$-C), 4.61 (br, 2H, CH$_2$=CH-C**H**$_2$O-), 4.71 (br, 2H, CH≡CH-C**H**$_2$O-), 5.23 (d, 1H, J=10.6 Hz, cis-C**H**$_2$=CH-CH$_2$O-), 5.30 (d, 1H, J=17.3 Hz, trans-C**H**$_2$=CH-CH$_2$O-), 5.87 (m, 1H, CH$_2$=C**H**-CH$_2$O-), end-groups: 3.71 (br, 2H, bisMPA:-C-CH$_2$-OH). ^{13}C NMR (CDCl$_3$) δ ppm 17.5 (m), 21.3 (m), 35.1 (m), 46.5 (m), 65.8 (m), 68.5 (m), 72.5 (m), 118.4 (m), 131.5 (m), 154.8 (m), 171.8 (m). M$_n$ SEC(DMF) = 6.9 kDa, PDI = 2.90. DSC: T_g= +6 °C.



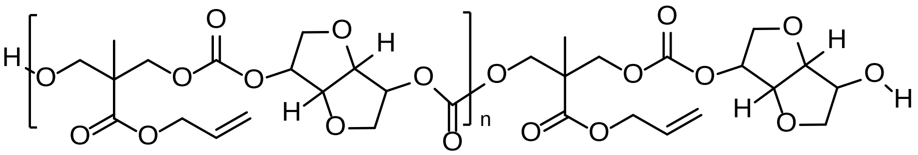
4e

Synthesis of poly(1,6-hexanediol-*alt*-isosorbide carbonate) (4f, Table 1, Entry 6). The polymerization was carried out according to the general procedure from diol **3d** and bis-carbonylimidazolide **2b**. The polymer product **4f** was collected as a transparent sticky solid (1.95 g, 73% yield).^{1}H NMR ($CDCl_3$) δ ppm: ^{1}H NMR ($CDCl_3$) δ ppm: 1.38 (br, 4H, -C**H**$_2$-CH$_2$-CH$_2$O-), 1.66 (br, 4H, -CH$_2$-C**H**$_2$-CH$_2$O-), 3.88 (m, 2H, isosorbide-H), 4.02 (m, 2H, isosorbide-H), 4.13 (m, 4H, -CH$_2$-CH$_2$-C**H**$_2$O-), 4.52 (br-d, 2H, 4.8 Hz, isosorbide-H), 4.86 (br-t, 1H, 4.8Hz, isosorbide-H), 5.05 (m, 2H, isosorbide-H), end-groups: 3.46 (m, 1H, isosorbide: C**H**-OH), 3.62 (br-t, 2H, -CH$_2$-C**H**$_2$-OH). ^{13}C NMR ($CDCl_3$) δ ppm 25.2, 28.4, 68.3, 70.3, 73.2, 76.6, 80.8, 81.0, 85.8, 154.2, 154.5. M_n SEC(DMF) = 8.5 kDa, PDI = 1.91. DSC: T_g= +31 °C.



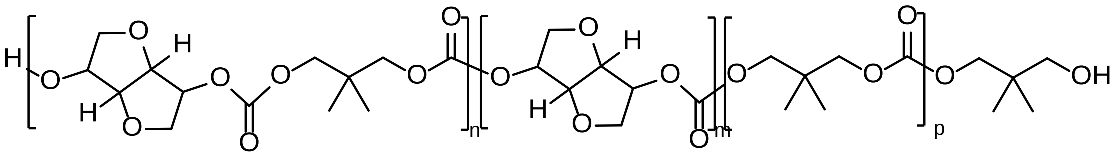
4f

Synthesis of poly(bisMPA-allyl-*alt*-isosorbide carbonate) (4g, Table 1, Entry 7). The polymerization was carried out according to the general procedure from diol **3d** and bis-carbonylimidazolide **2a**, except that acetone (9 ml) was used as solvent. The polymer product **4g** was collected as a transparent sticky solid (2.44 g, 77% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 1.23 (br, 3H, (bisMPA-C**H**$_3$), 3.91 (br, 4H, isosorbide-H), 4.29 (br, 4H, bisMPA-C-O-C**H**$_2$-C), 4.47 (br, 1H, isosorbide-H), 4.58 (br-d, 2H, 5.5 Hz, CH≡CH-C**H**$_2$O-), 4.82 (br, 1H, isosorbide-H), 5.02 (br, 2H, isosorbide-H), 5.20 (d, 1H, J=10.4 Hz, cis-C**H**$_2$=CH-CH$_2$O-), 5.27 (d, 1H, J=17.3 Hz, trans-C**H**$_2$=CH-CH$_2$O-), 5.84 (m, 1H, CH$_2$=C**H**-CH$_2$O-), end-groups: 3.52 (m, 1H, isosorbide: C**H**-OH), 3.73 (br, 2H, bisMPA:-C-C**H**$_2$-OH)). ^{13}C NMR ($CDCl_3$) δ ppm 17.4(m), 46.4(m), 65.7(m), 68.4(m), 70.3(m), 72.9(m), 76.9(m), 80.8(m), 81.2(m), 85.6(m), 118.4(m), 131.4(m), 153.6(m). M_n SEC(DMF) = 4.7 kDa, PDI = 2.90. DSC: T_g= +37 °C.



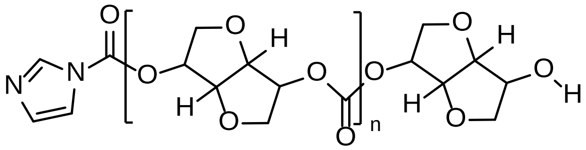
4g

Synthesis of poly(neopentyldiol-*ran*-isosorbide carbonate) (4h, Table 1, Entry 8). The polymerization was carried out according to the general procedure from diol **3b** and bis-carbonylimidazolide **2c**, except that acetone (9 ml) was used as solvent. The polymer product **4h** was collected as a white solid (1.49 g, 58% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.99 (br, 6H, neopentyl-2xC**H**$_3$), 3.90 (br, 2H, isosorbide-H), 3.97 (br-m, 5H, isosorbide-H, neopentyl -C**H**$_2$O-CO-), 4.06 (br, 1H, isosorbide-H), 4.53 (br, 1H, isosorbide-H), 4.88 (br, 1H, isosorbide-H), 5.08 (br, 2H, isosorbide-H, endgroups: 3.57 (m, 1H, isosorbide: C**H**-OH), 3.71 (br, 2H, neopentyl:-C-C**H**$_2$-OH), 7.07 (br, 1H, imidazolyl), 7.42 (br, 1H, imidazolyl), 8.13 (br, 1H, imidazolyl). ^{13}C NMR ($CDCl_3$) δ ppm 21.1(m), 35.0(m), 70.4(m), 72.5, 72.6, 72.8, 72.9, 73.1(m), 76.9(m), 80.8(m), 81.0(m), 81.3(m), 85.5, 85.6, 85.7(m). M_n SEC(DMF) = 5.7 kDa, PDI = 1.90. DSC: T_g= +113 °C.



4h

Synthesis of poly(isosorbide carbonate) (4i, Table 1, Entry 9). The polymerization was carried out according to the general procedure from diol **3d** and bis-carbonylimidazolide **2c**, except that a 1.00:1.00 (diol:bis-carbonylimidazolide) stoichiometric ratio was used and acetone (9 ml) was used as solvent. The polymer product **4i** was collected as a white hard solid (2.42 g, 83% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 3.90 (br, 2H, isosorbide-H), 3.99 (br, 1H, isosorbide-H), 4.07 (br, 1H, isosorbide-H), 4.53 (br-d, 2H, 15.7 Hz, isosorbide-H), 4.88 (br, 1H, isosorbide-H, endgroups: 3.58 (m, 1H, isosorbide: C**H**-OH), 7.09 (br, 1H, imidazolyl), 7.43 (br, 1H, imidazolyl), 8.15 (br, 1H, imidazolyl). ^{13}C NMR ($CDCl_3$) δ ppm 70.5 (m), 72.9 (m), 77.1(m), 80.9(m), 81.4(m), 85.6(m), 153.2, 153.5, 153.9. M_n SEC(DMF) = 20.4 kDa, PDI = 2.2. DSC: T_g= +169 °C.



4i

Structural Characterization

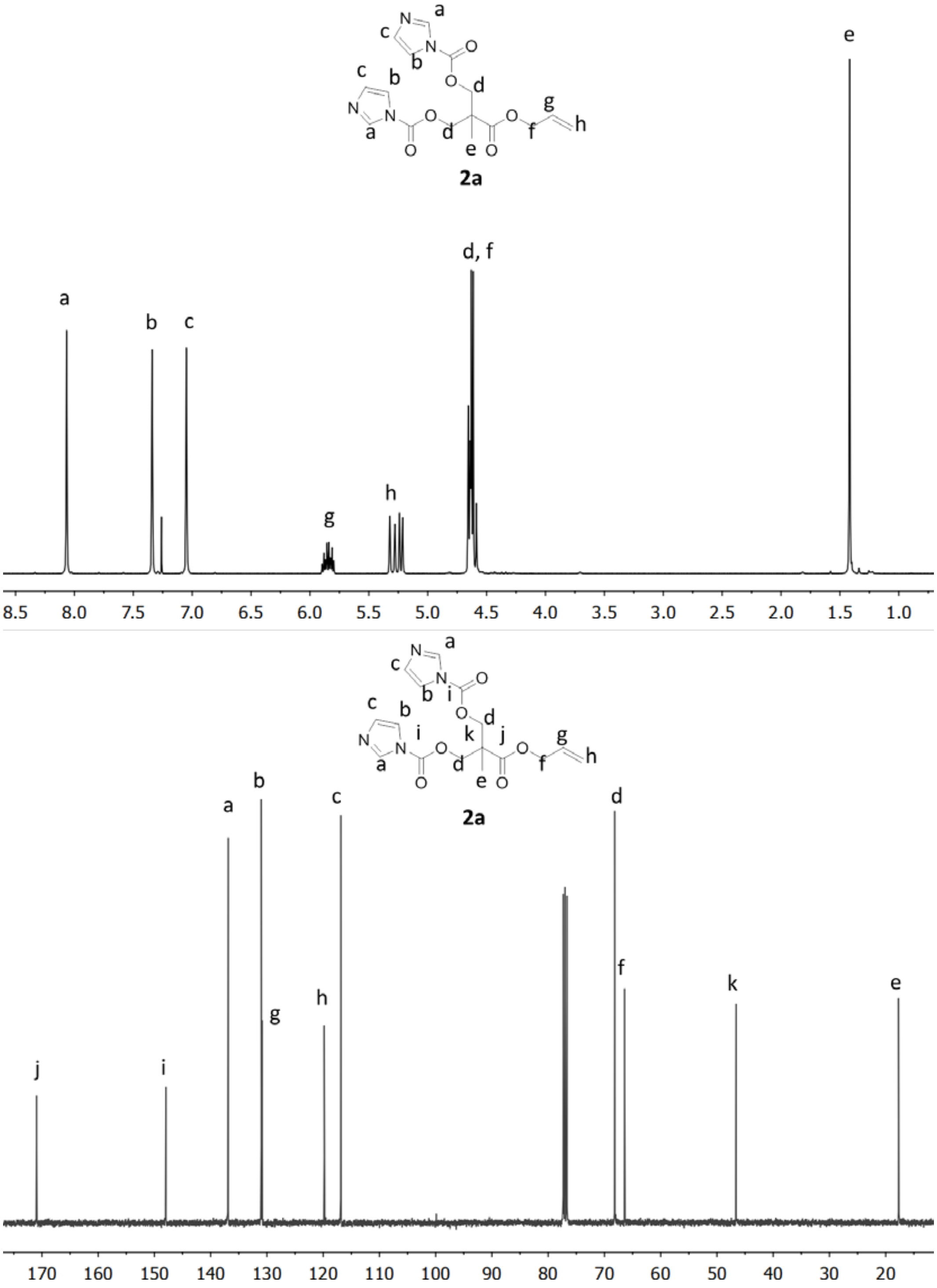


Figure S2. ^{1}H and ^{13}C{^{1}H} NMR spectra of monomer **2a**.

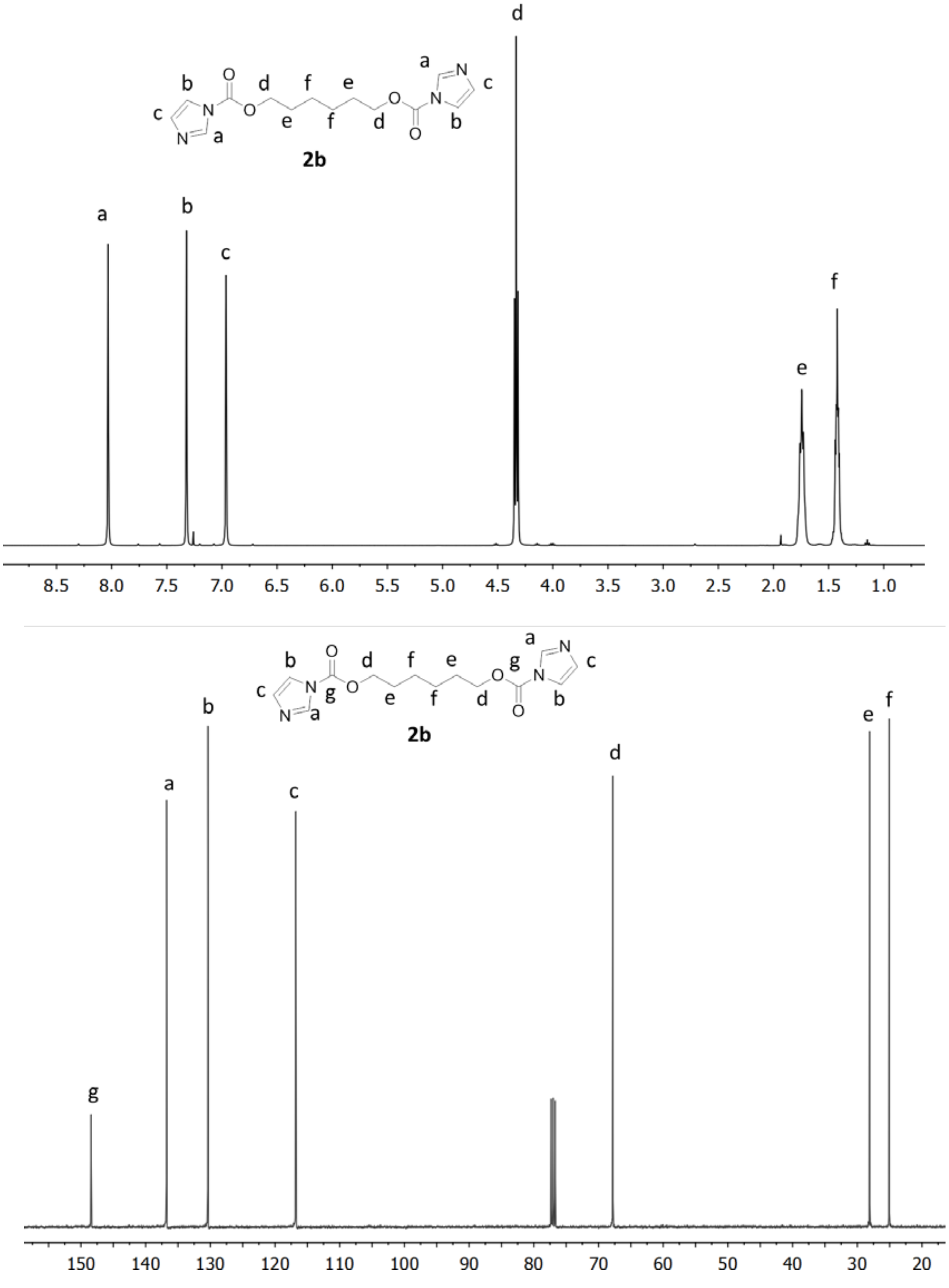


Figure S3. ^{1}H and ^{13}C{^{1}H} NMR spectra of monomer **2b**.

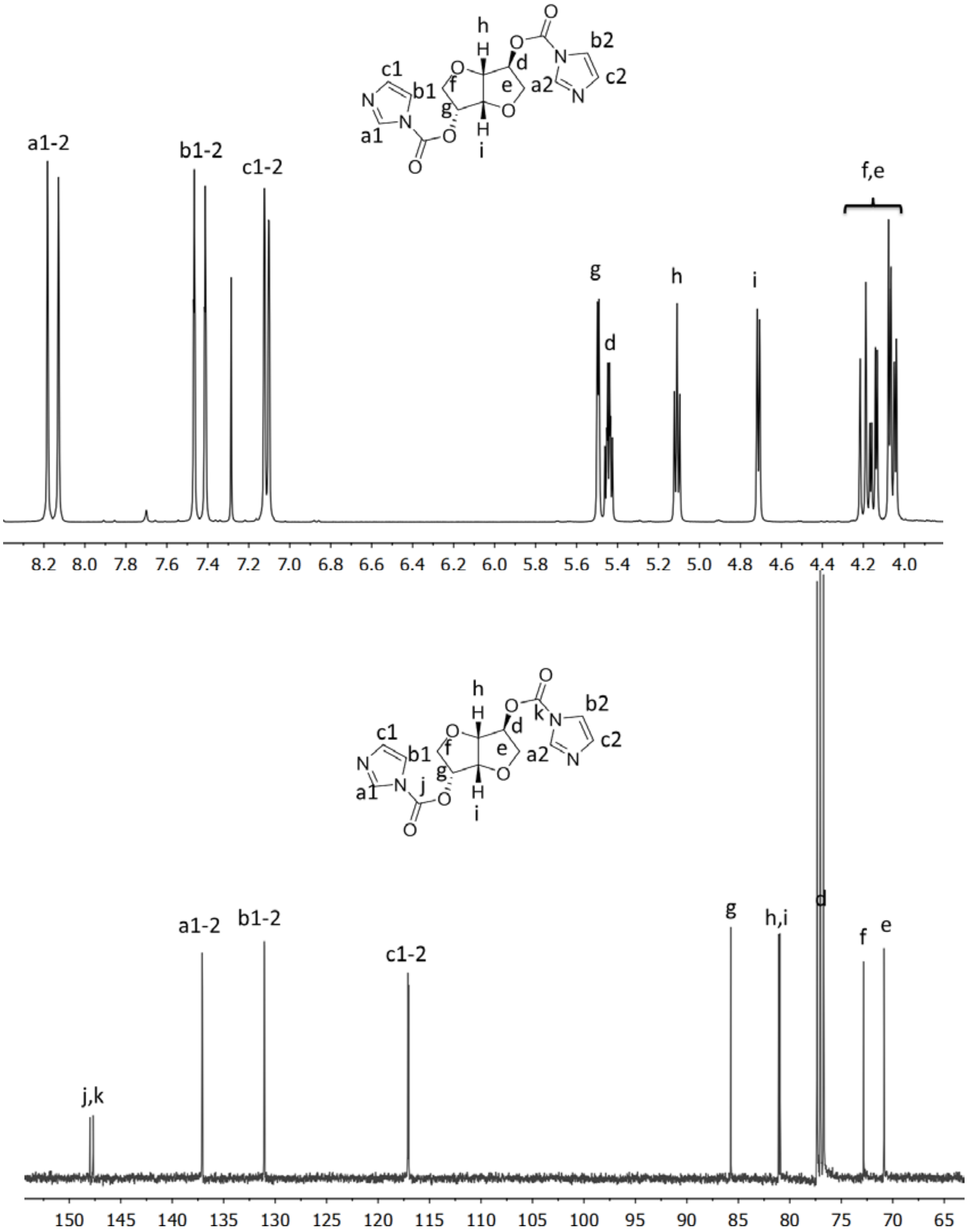


Figure S4. ^{1}H and ^{13}C{^{1}H} NMR spectra of monomer **2c**.

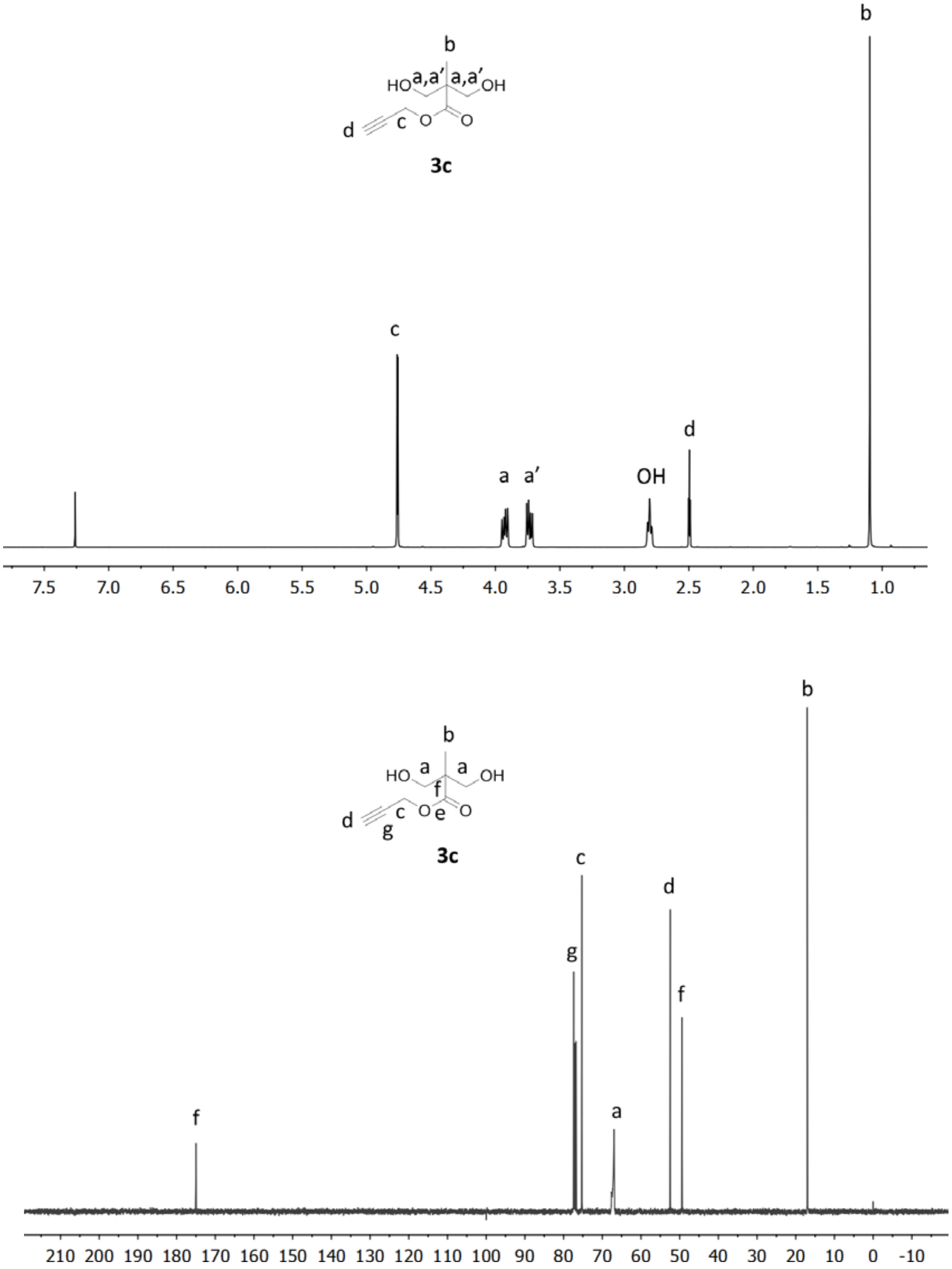


Figure S5. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of monomer **3c**.

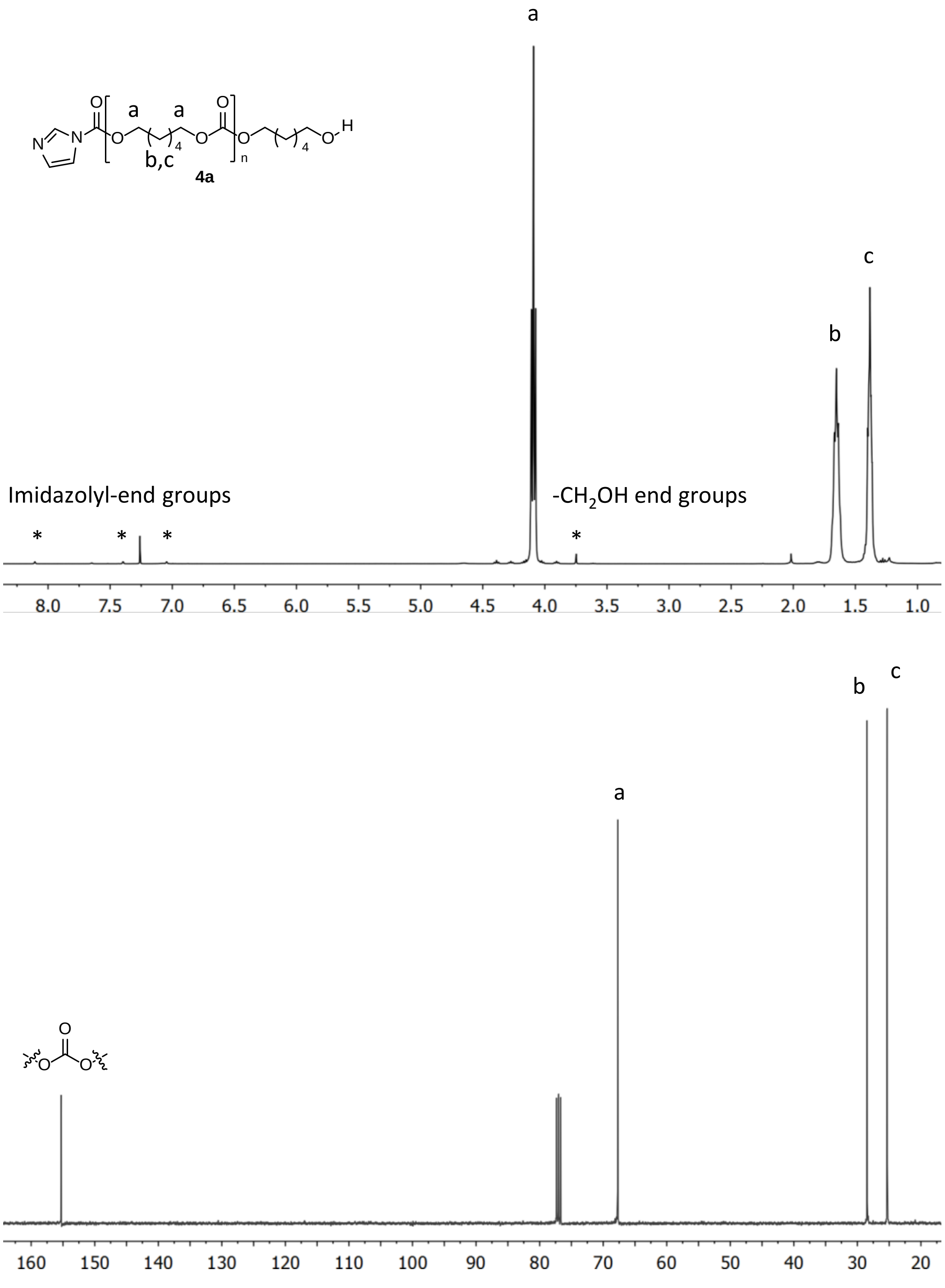


Figure S6. ^{1}H and ^{13}C{^{1}H} NMR spectra of polymer **4a**.

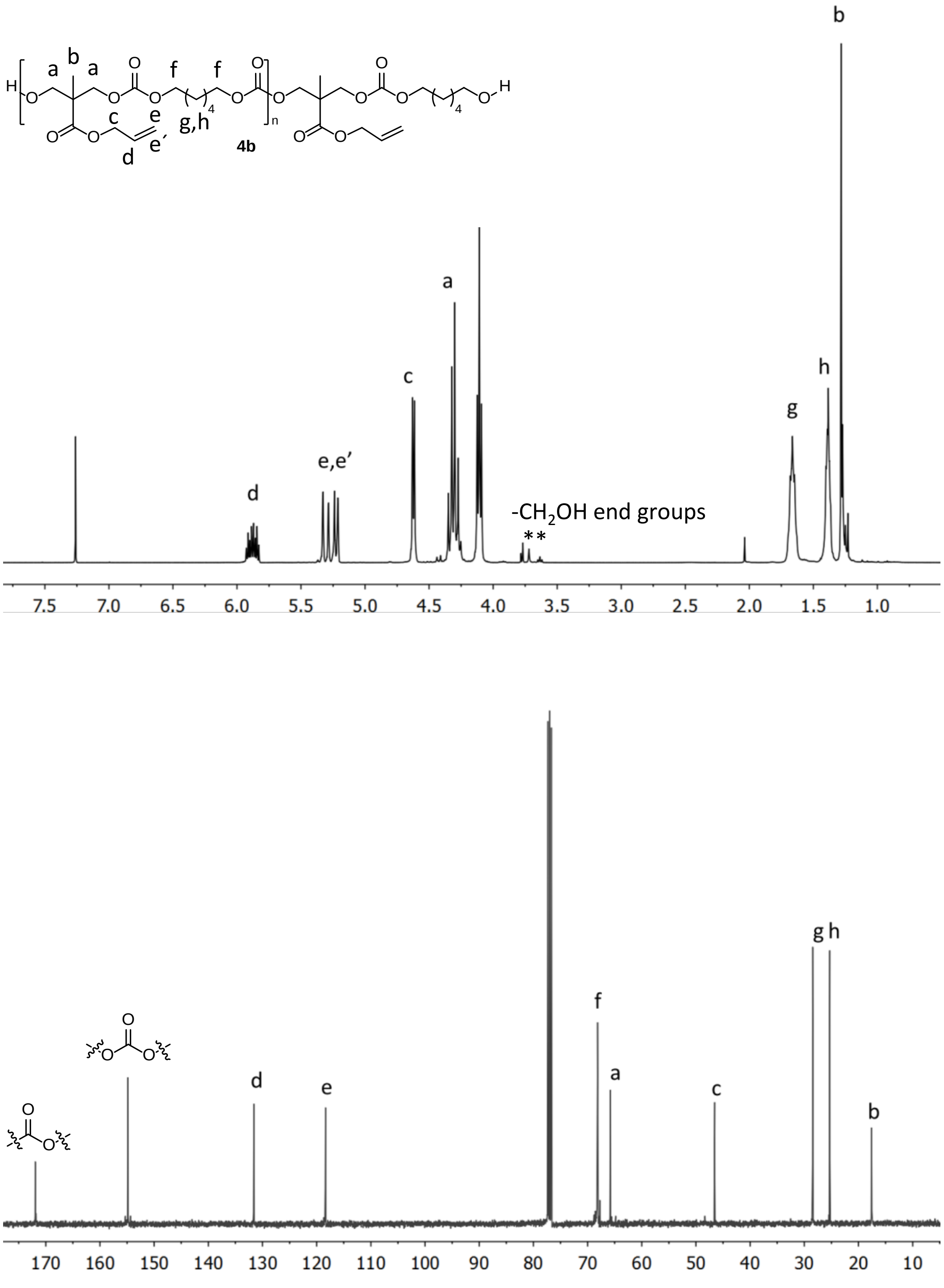


Figure S7. ^{1}H and ^{13}C{^{1}H} NMR spectra of polymer **4b**.

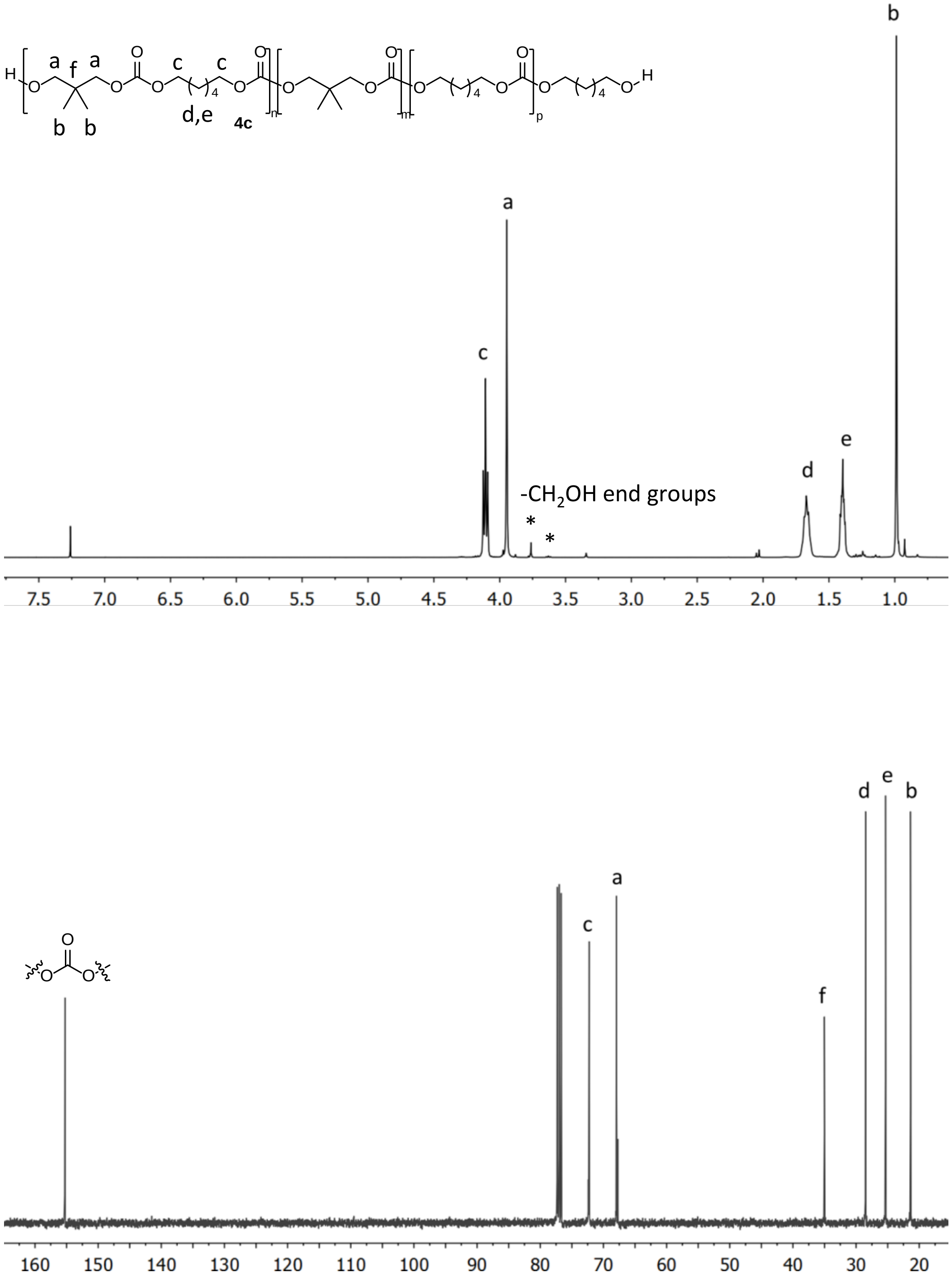


Figure S8. ^{1}H and ^{13}C{^{1}H} NMR spectra of polymer **4c**.

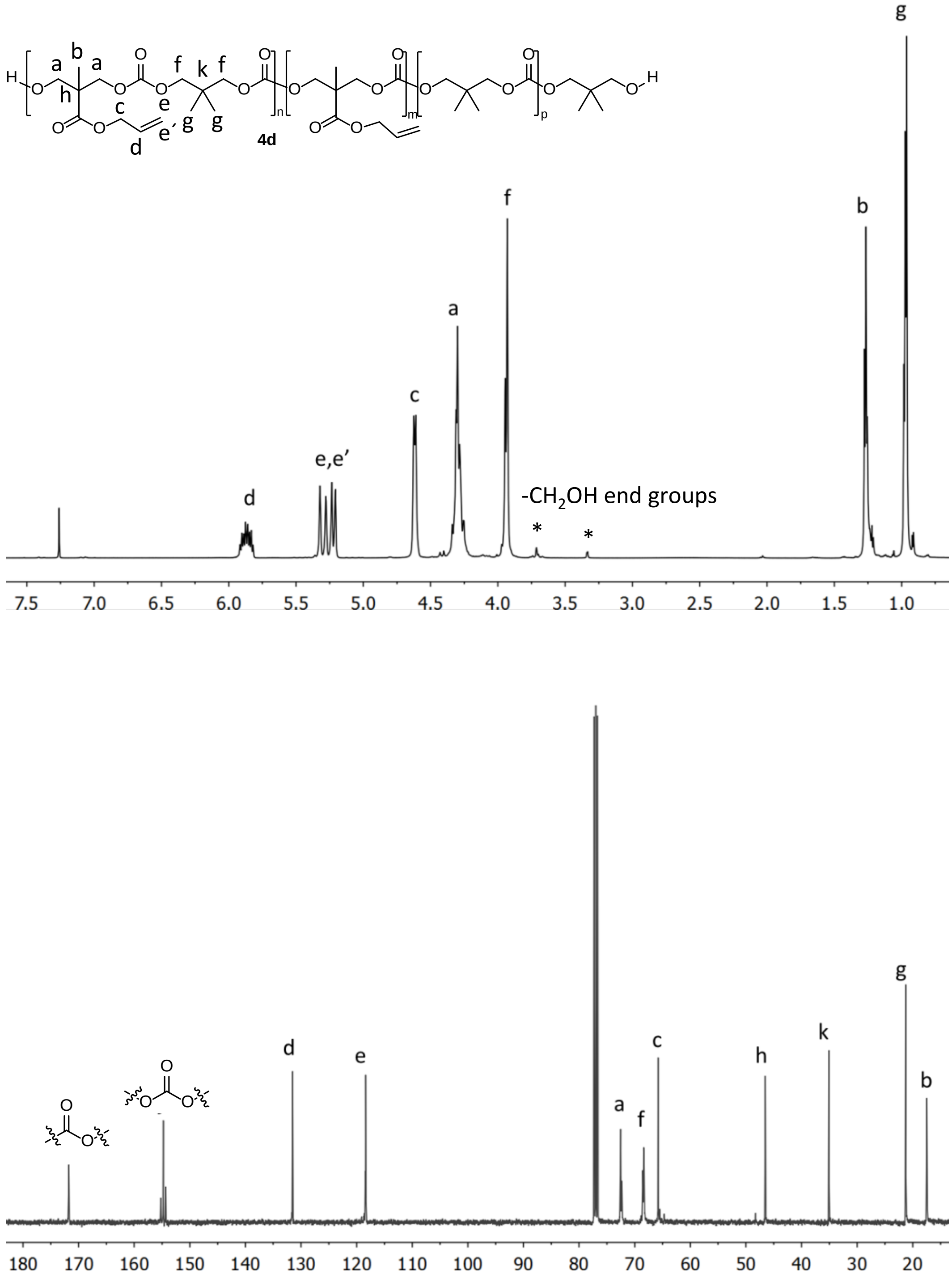


Figure S9. ^{1}H and ^{13}C{^{1}H} NMR spectra of polymer **4d**.

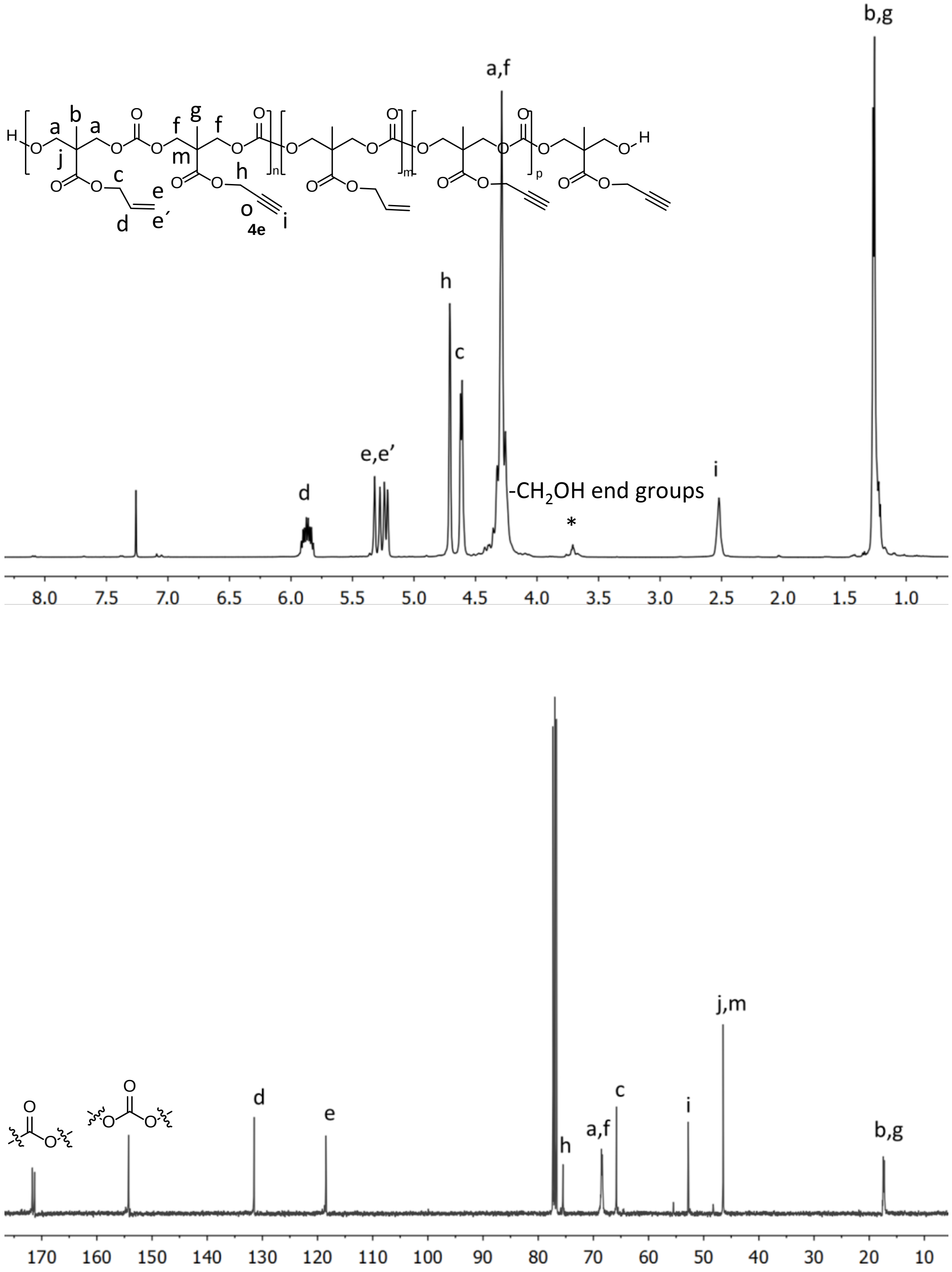


Figure S10. ^{1}H and ^{13}C{^{1}H} NMR spectra of polymer **4e**.

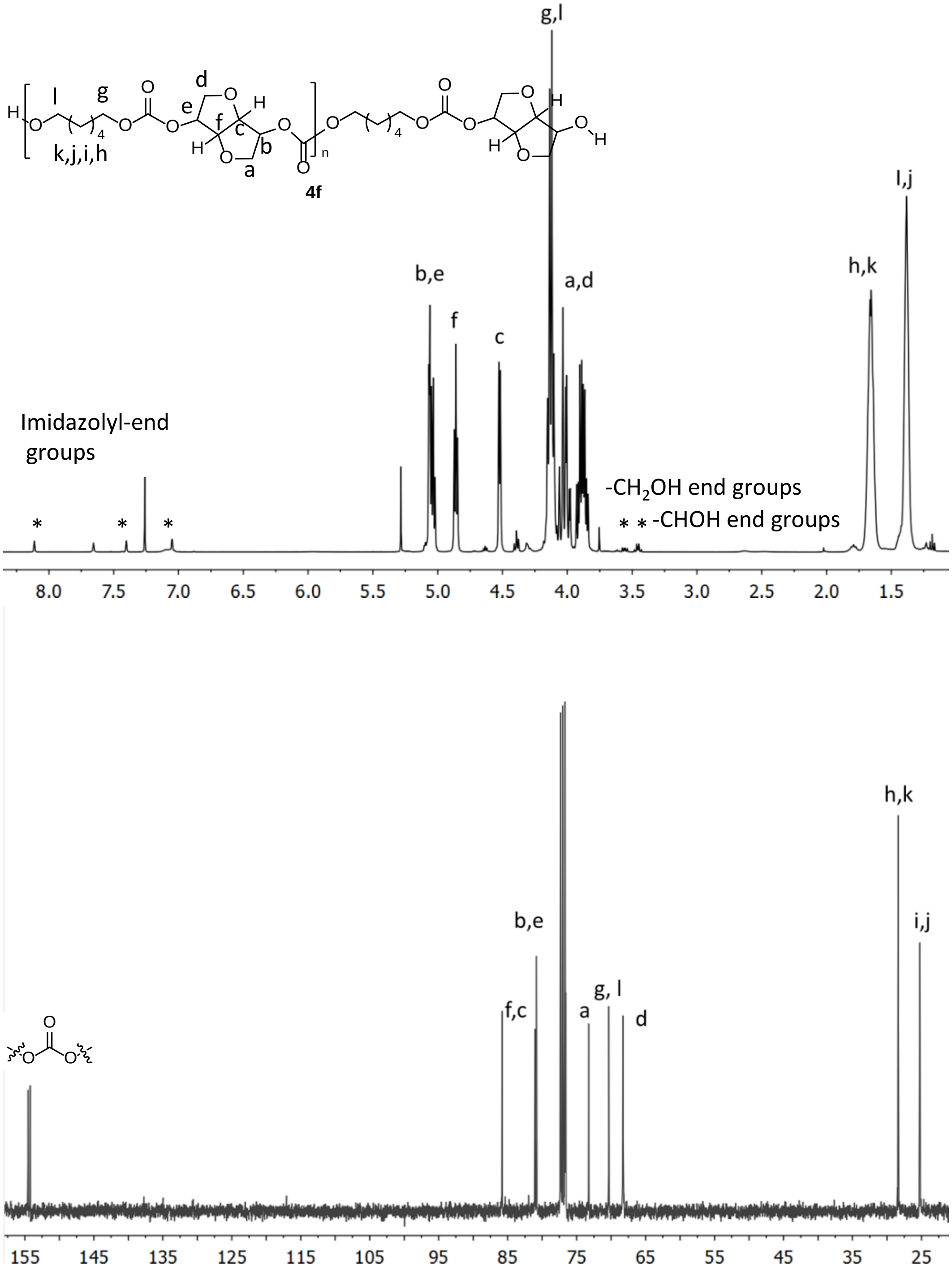


Figure S11. ^{1}H and ^{13}C{^{1}H} NMR spectra of polymer **4f**.

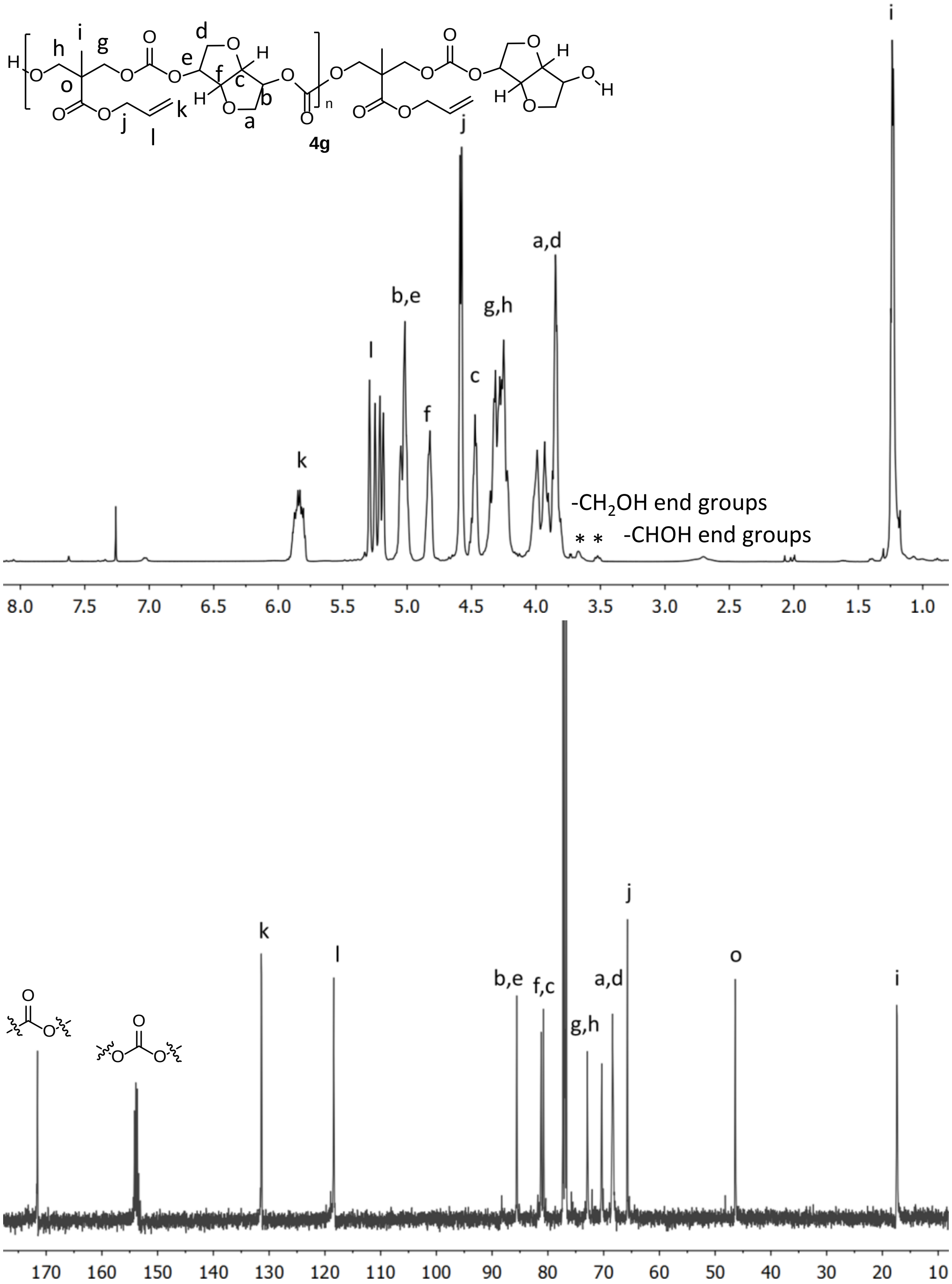


Figure S12. ^1H and $^{13}C\{^1H\}$ NMR spectra of polymer **4g**.

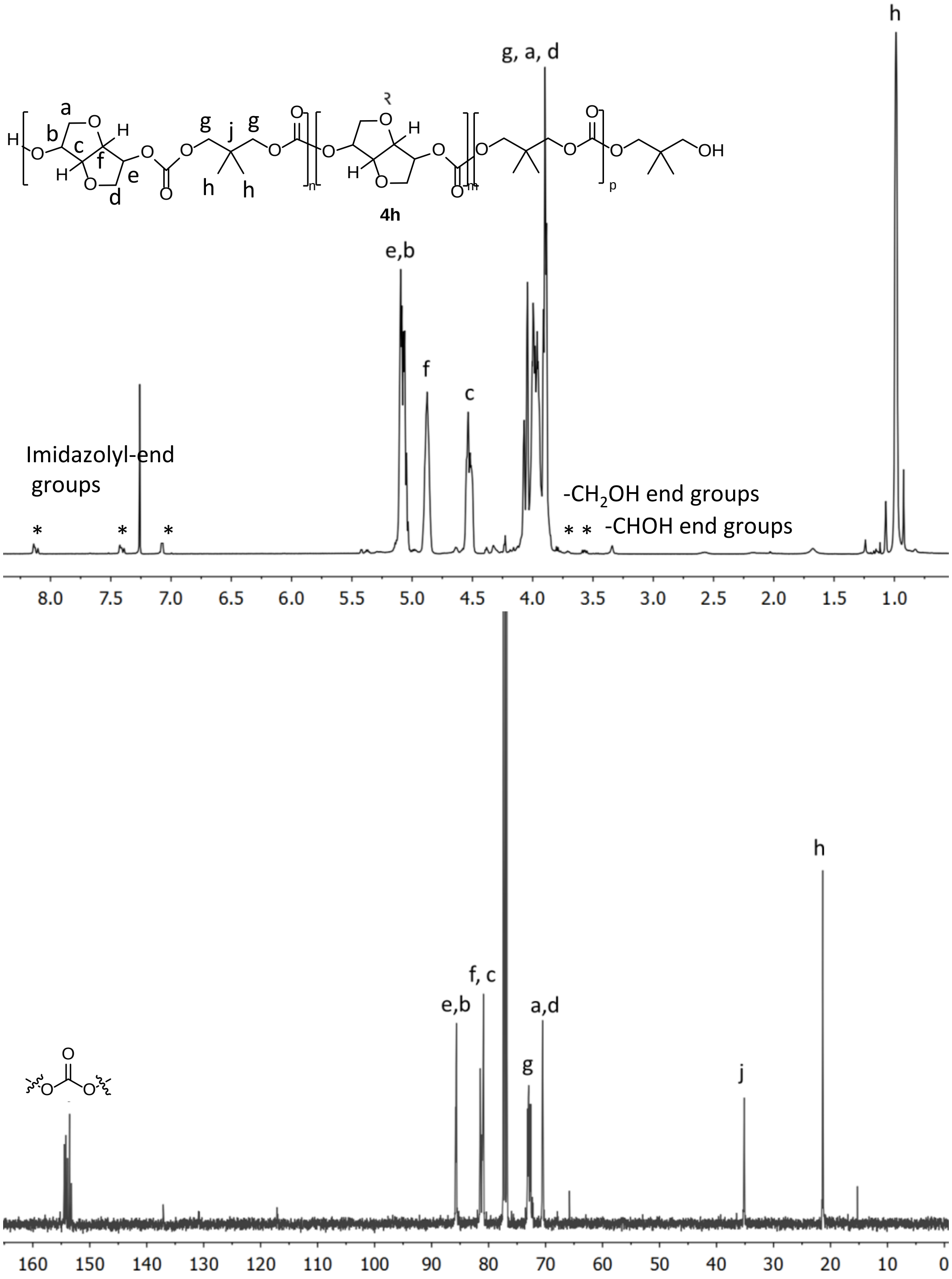


Figure S13. ^{1}H and ^{13}C{^{1}H} NMR spectra of polymer **4h**.

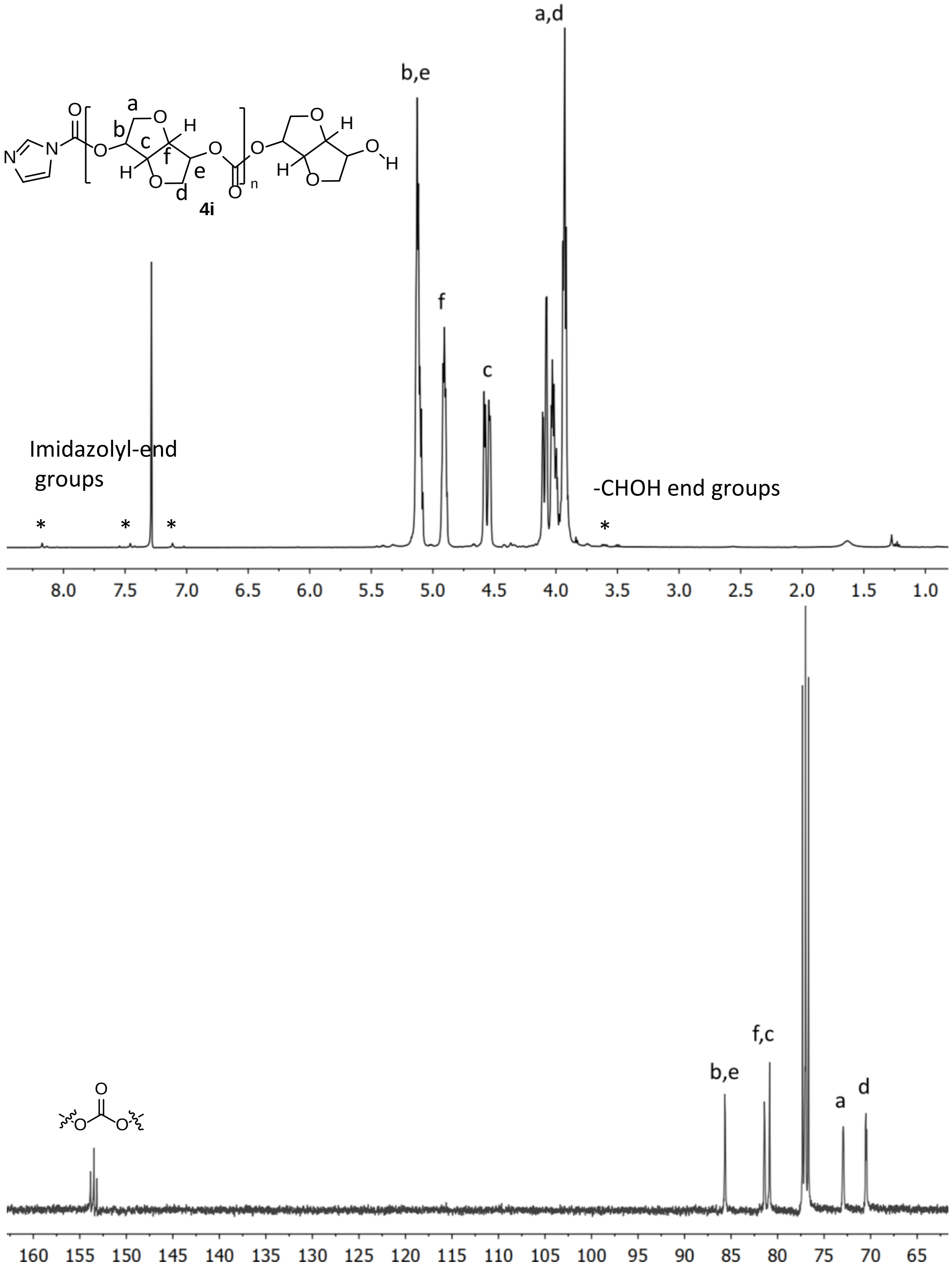


Figure S14. ^{1}H and ^{13}C{^{1}H} NMR spectra of polymer **4i**.

- **^{13}C-NMR for homopolymers 4x and 4y achieved by ROP**

The homopolymers **4x** and **4y** achieved by ROP, previously reported by our group,[2] were used as reference for the assignment of ^{13}C-NMR carbonyl peaks.

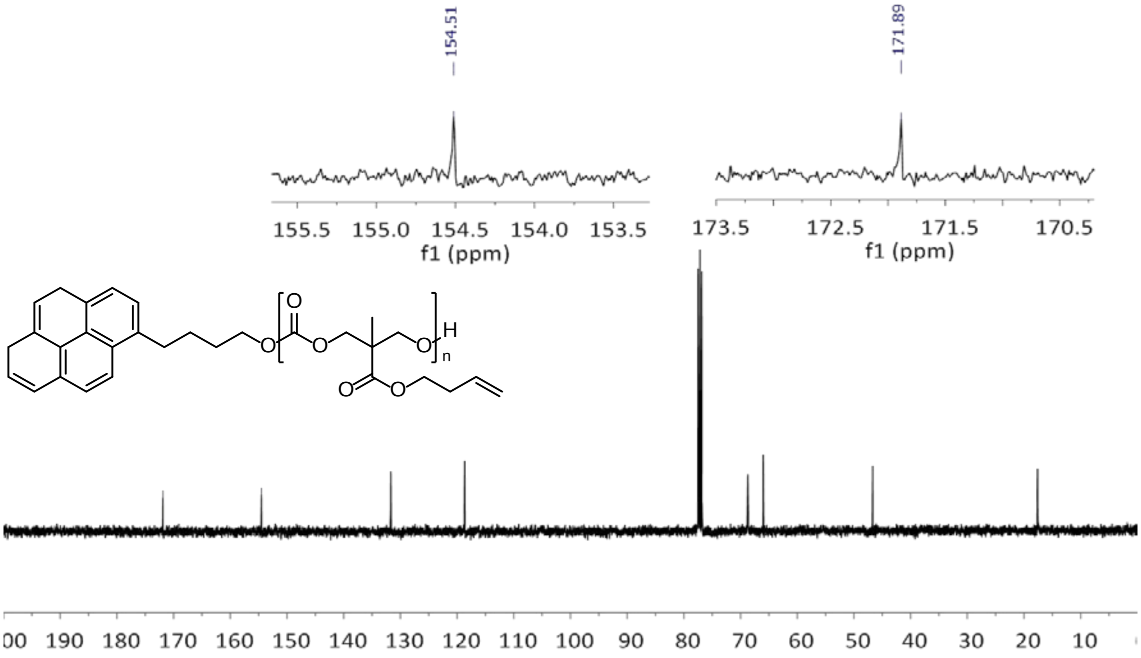


Figure S15. ^{13}C{^{1}H} NMR spectrum of polyBisMPA-Allyl (**4x**).

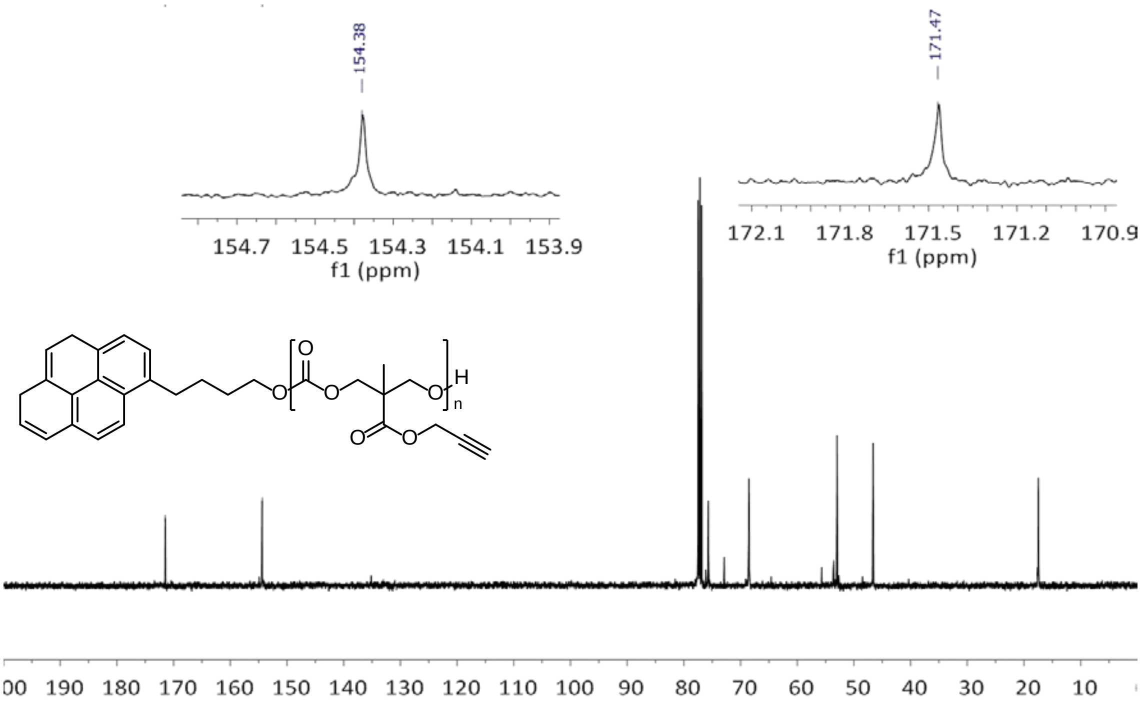


Figure S16. ^{13}C{^{1}H} NMR spectrum of polyBisMPA-Propargyl (**4y**).

- **^{13}C-NMR carbonyl assignment for polymers 4a to 4i**

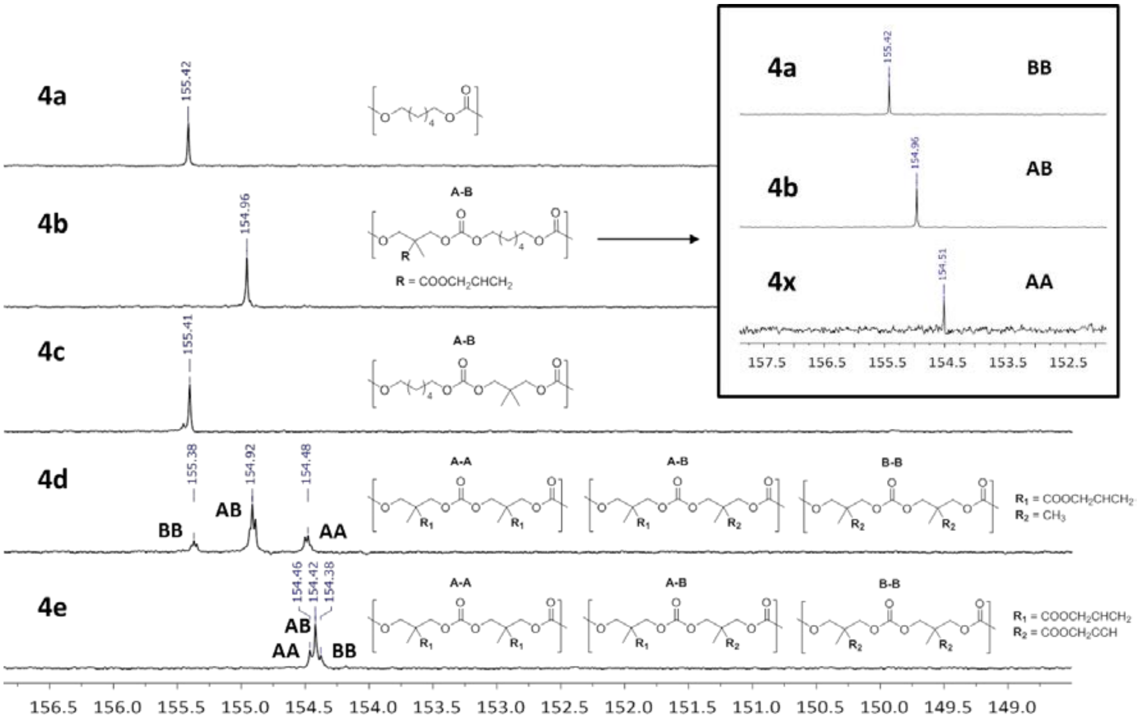


Figure S17. ^{13}C-NMR ($CDCl_3$) carbonyl shifts for polymer **4a** to **4e**. Insert show carbonyl shifts for 1,6-hexanediol homopolymer **4a**, alternating homopolymer **4b** and homopolymer **4x** from ring opening polymerization (ROP) of cyclic carbonate analog of BisMPA-Allyl. Polymer **4c** show a slight shoulder above the assigned shift indicating slight scrambling. Polymer **4d** indicate a scrambling mechanism, whereby, the BB dyad corresponding to the carbonyl of two neopentyl glycol units, similar to **4a** and **4c**. The AB dyad of **4d** is comparable with **4b**, while the AA dyad has a similar shift to the BisMPA-Ally homopolymer **4x**. Polymer **4e** show a similar scrambling mechanism with shift values assigned by comparing with homopolymers attained from ROP of cyclic carbonate analogs **4x** (AA) and **4y** (BB).[2]

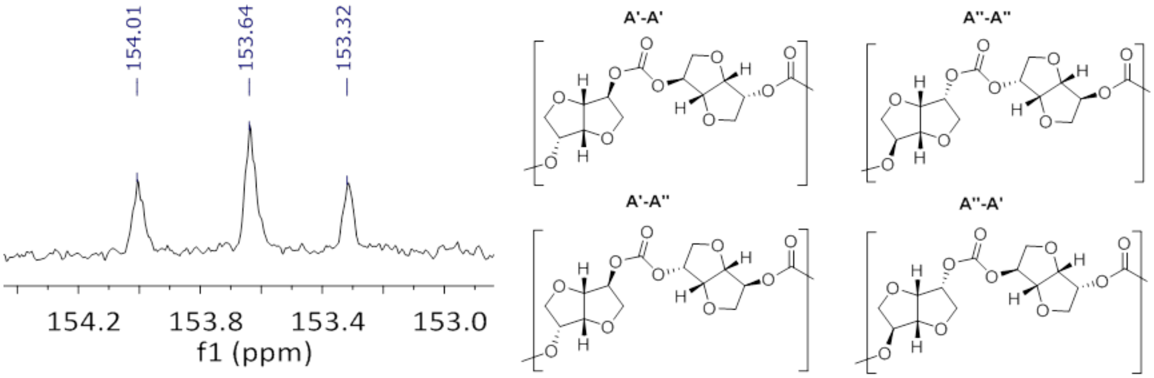


Figure S18. ^{13}C-NMR ($CDCl_3$) carbonyl shifts for poly-isosorbide **4i.** Isosorbide contain two different hydroxyl groups exo and endo, giving rise to three carbonyl shifts in ^{13}C-NMR, here assigned as A' and A''. The three peaks correspond to exo-exo, exo-endo, endo-exo and endo-endo, affording an intensity ratio of 1:2:1.[3]

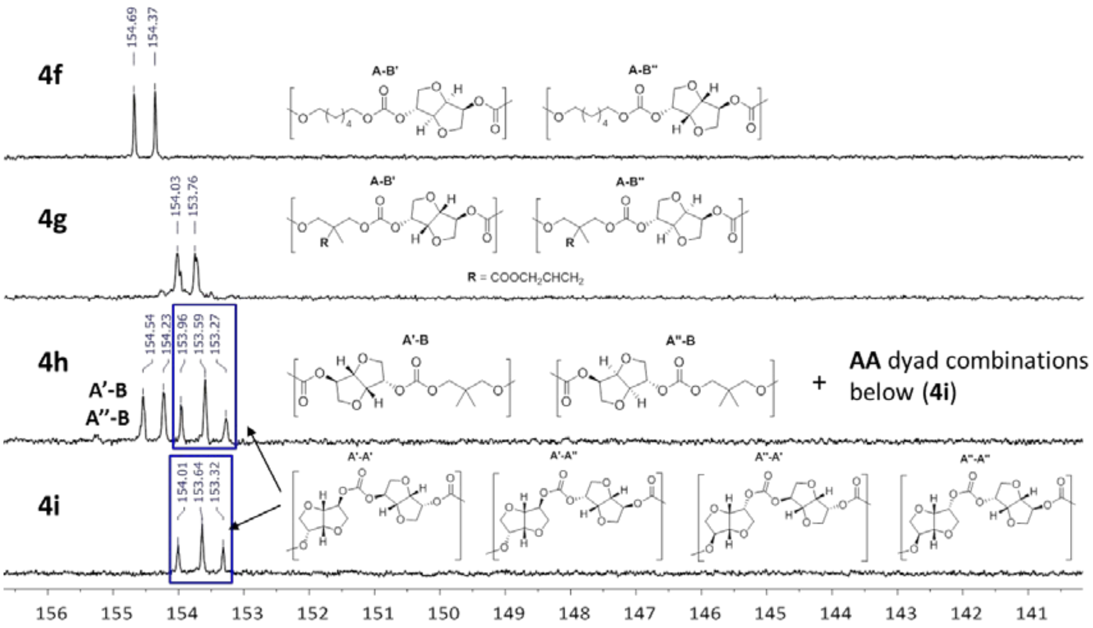


Figure S19. ^{13}C-NMR ($CDCl_3$) carbonyl shifts for polymer **4f** to **4i**. Polymer **4f** and **4g** show two distinct peaks corresponding to carbonyl carbons substituted on the endo and exo hydroxyl of isosorbide, indicating a purely alternating configuration on the polymer backbone. Polymer **4h** show the same two distinct peaks from the AB dyad of the endo and exo hydroxyls of isosorbide as the 1,6-hexanediol case **4f**, combined with the AA dyad (1:2:1) observed for the pure isosorbide homopolymer case **4i**.

- **Evidence of ring-closing of 1,3-diol: Poly(neopentyldiol-ran-isosorbide carbonate) (4h, Table 1, Entry 8)**

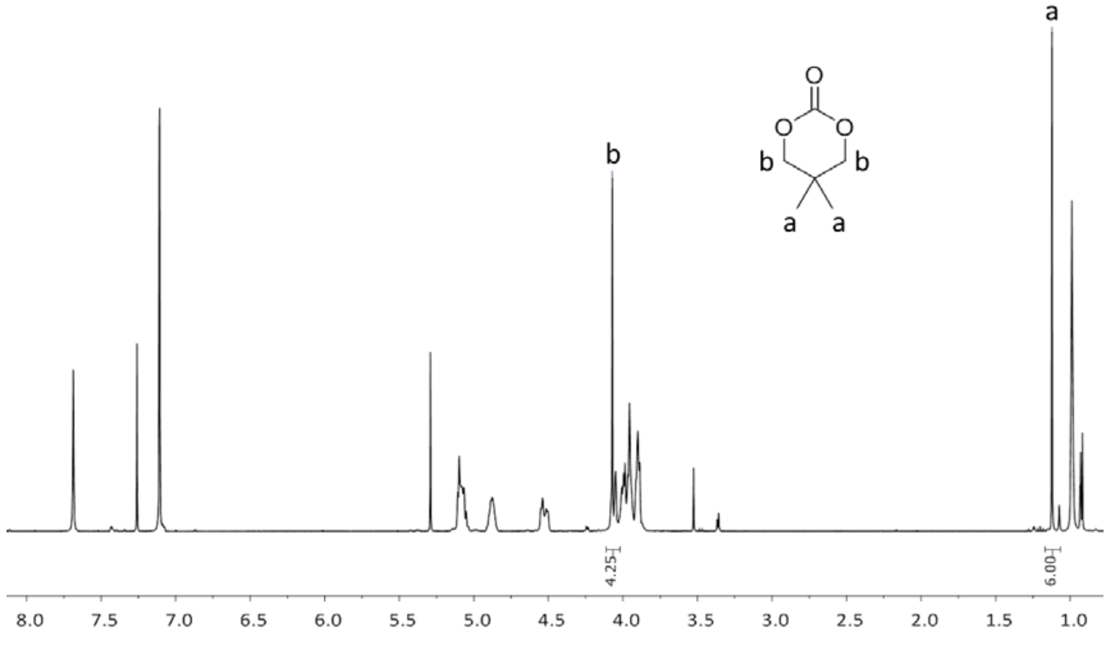


Figure S20. Crude ^{1}H-NMR (CDCl$_3$) from polymerization of **4h**, showing the characteristic shifts corresponding to the cyclic carbonate of analog of neopentyl glycol, 5,5-Dimethyl-1,3-dioxane-2-one (NPC). ^{1}H NMR (CDCl3) δ ppm: 1.12 (s, 6H, –C**H**$_3$), 4.07 (s, 4H, –C**H**$_2$O).[4]

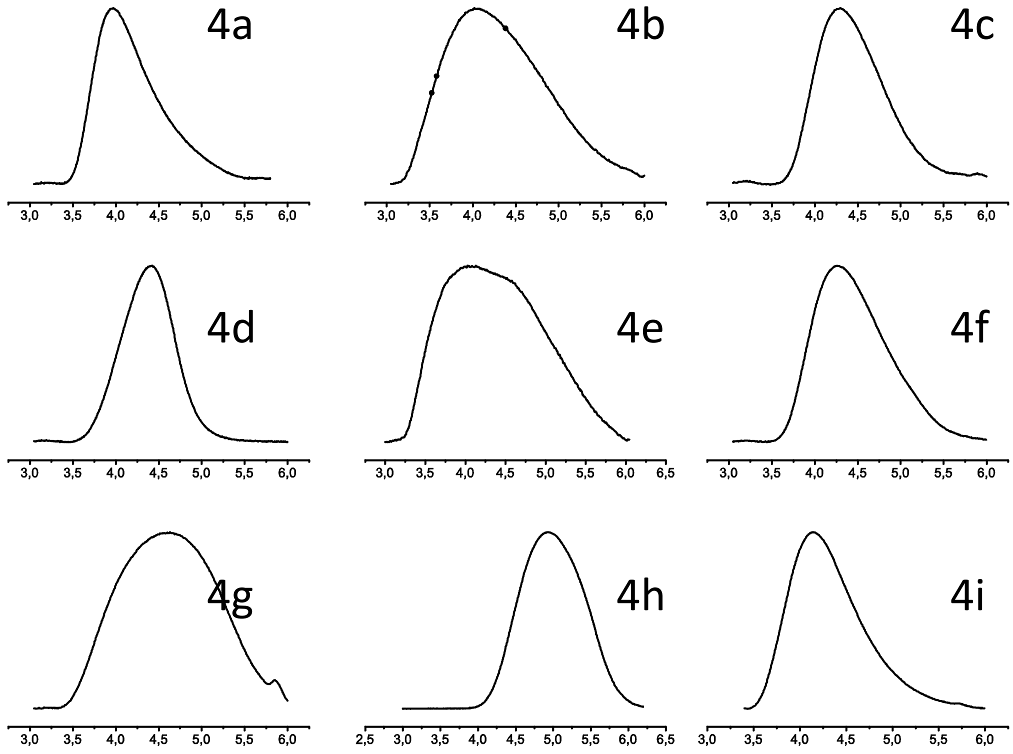


Figure S21. SEC (DMF) retention volume (ml) curves of polycarbonates **4a-i**.

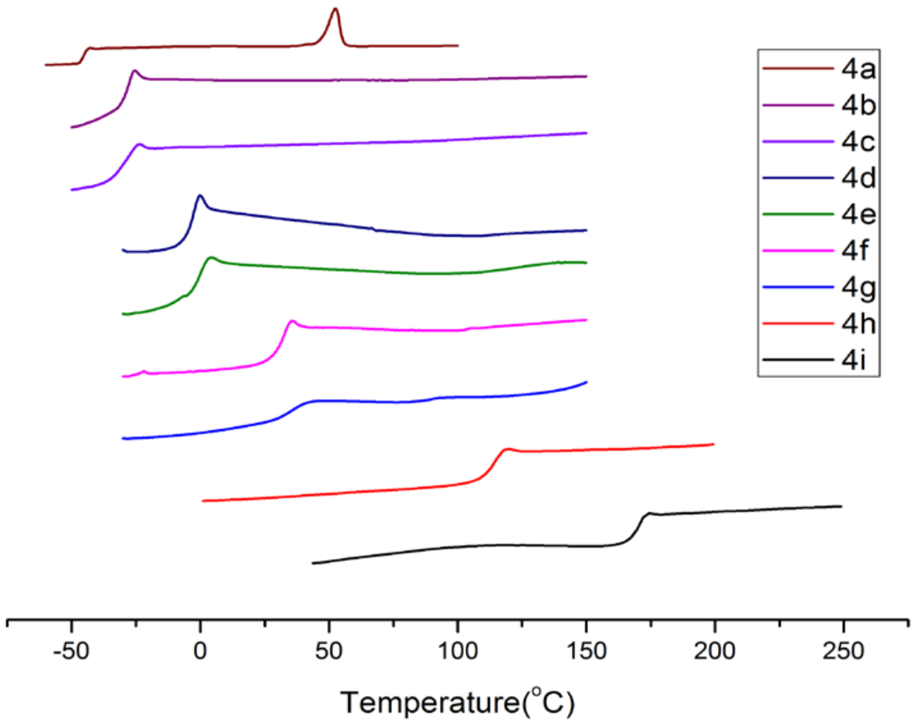


Figure S22. Second heating scan DSC curves of polycarbonates **4a-i**.

References

[1] H. Ihre, A. Hult, J. M. J. Frechet, I. Gitsov, *Macromolecules* **1998**, *31*, 4061-4068.

[2] J. V. Olsson, D. Hult, Y. Cai, S. Garcia-Gallego, M. Malkoch, *Polym. Chem.* **2014**, *5*, 6651-6655.

[3] S. Chatti, G. Schwarz, H. R. Kricheldorf, *Macromolecules* **2006**, *39*, 9064-9070.

[4] P. Loewenhielm, H. Claesson, A. Hult, *Macromol. Chem. Phys.* **2004**, *205*, 1489-1496.