Electronic Supplementary Information

Synthesis of AB_x and AB_xC poly(ester-ether): polymer sequences and effects of B_x and B_xC units on thermal properties

Nattawat Jabprakon, Phongnarin Chumsaeng and Khamphee Phomphrai*

Department of Materials Science and Engineering, School of Molecular Science and Engineering,
Vidyasirimedhi Institute of Science and Technology (VISTEC), WangChan, Rayong 21210, Thailand.
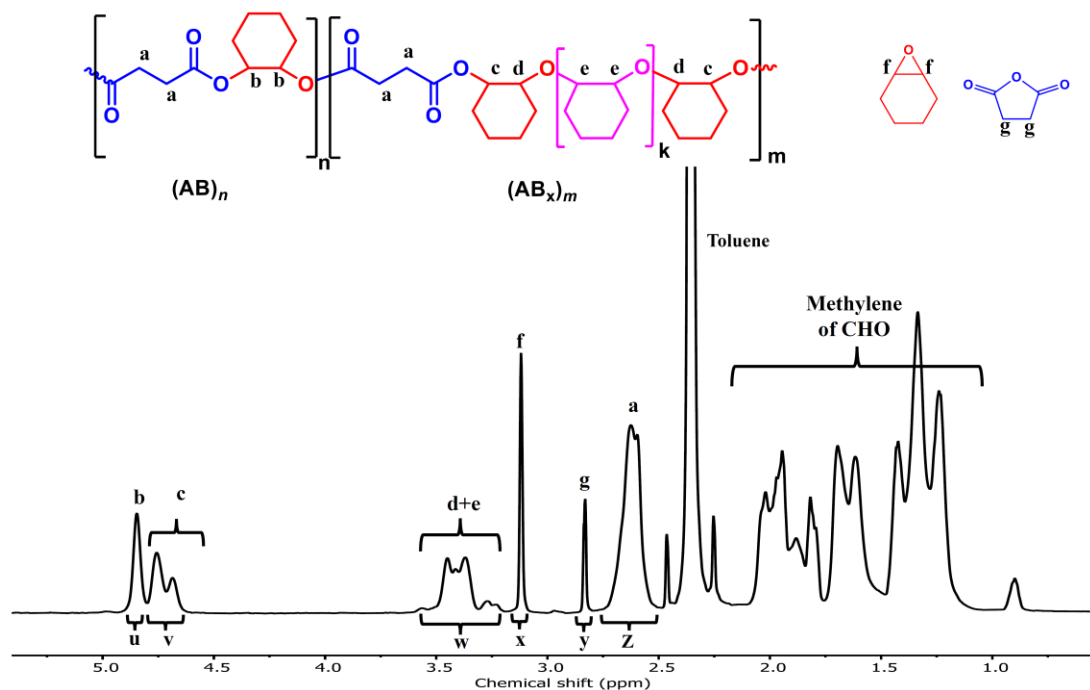
E-mail: khamphee.p@vistec.ac.th

1. Calculation of monomer conversion, degree polymerization and polymer Compositions

(With some modifications from R. W. F. Kerr and C. K. Williams, *J. Am. Chem. Soc.* **2022**, *144*, 6882-6893.)

1.1 Copolymers from CHO and cyclic anhydrides

Calculation of monomer conversion

From ^{1}H NMR of the crude mixture in CDCl$_3$ shown above, the SA conversion was determined from the integration of protons from the remaining and polymerized SA monomers as shown below.

$$SA\ conversion\ \% = \frac{z}{y+z} \times 100\%$$

Where *y* and *z* are the integration of protons *g* and *a*, respectively.

From ^{1}H NMR of the crude mixture in CDCl$_3$, the CHO conversion was determined from the integration of the methine protons from the remaining and polymerized CHO monomers as shown below.

$$CHO\ conversion\ \% = \frac{u + v + w}{x + u + v + w} \times 100\%$$

Where u, v, w, and x are the integration of protons b, c, $d+e$, and f, respectively. For other cyclic anhydrides, the monomer conversion can be calculated similarly.

Finally, the degree of polymerization (DP) of CHO and SA can be calculated as follows.

$$DP\ of\ SA = SA\ conversion(\%) \times \frac{[SA]_0}{[Sn]_0}$$

$$DP\ of\ CHO = CHO\ conversion(\%) \times \frac{[CHO]_0}{[Sn]_0}$$

Calculation of polymer compositions

S3
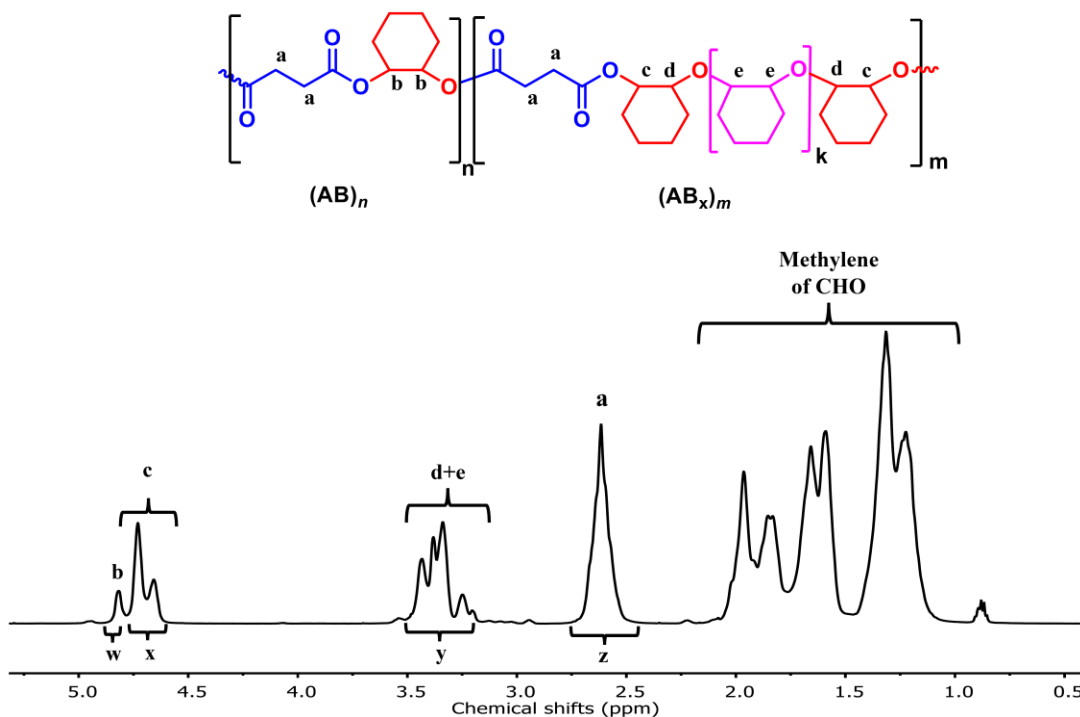
From ^{1}H NMR of the purified polymer in CDCl$_3$ shown above, the percentage compositions of (AB)$_n$ and (AB$_x$)$_m$ were defined as the percentage of cyclic anhydride (A) in (AB)$_n$ and in (AB$_x$)$_m$, respectively. Although the CH_2 protons of cyclic anhydrides (A) in (AB)$_n$ and (AB$_x$)$_m$ comes at the same chemical shift around 2.62 ppm (peak a), they can be traced back from different chemical shifts of CHO (peaks b and c, for example). ^{1}H NMR spectroscopy was used to analyze the resultant copolymers using the following equations.

For (AB)$_n$ polymer, the number of protons a is twice as many as protons b. Therefore, %(AB)$_n$ can be calculated as follows.

$$\%(\mathbf{AB})_{\boldsymbol{n}} = \frac{2\mathbf{w}}{\mathbf{z}} \times \mathbf{100\%}$$

$$\%(\mathbf{AB}_{\boldsymbol{x}})_{\boldsymbol{m}} = \mathbf{100\%} - \%(\mathbf{AB})_{\boldsymbol{n}}$$

$$\boldsymbol{x} \text{ (average number of B units in (AB}_{\text{x}})_{\boldsymbol{m}}) = \text{(x+y)/x}$$

Where w, x, y, and z are the integration of b, c, $d+e$, and a signals, respectively. Note that (AB)$_n$ and (AB$_x$)$_m$ polymers are treated as different polymer sequences. Therefore, the calculation of x values excludes B units in the (AB)$_n$ polymer. For other cyclic anhydrides, (AB)$_n$ and (AB$_x$)$_m$ can be calculated similarly.

Note: Protons c appeared to consist of two peaks (left and right) in the range of 4.6-4.8 ppm. The taller left peak at 4.73 ppm is syndiotactic (CHO)$_2$ units and the smaller right peak at 4.65 ppm is isotactic (CHO)$_2$ units. Please see our assignment in *Macromolecules* **2020**, *53*, 9869-9877 for more details.

1.2 Copolymers from CHO, cyclic anhydrides, and THF or 1,4-dioxane

Calculation of the degrees of polymerization for each monomer (in the presence of THF)

From ^{1}H NMR of crude mixture in CDCl$_3$, the SA conversion was measured by the integration ratio of protons from remaining and polymerized SA monomers as shown below.
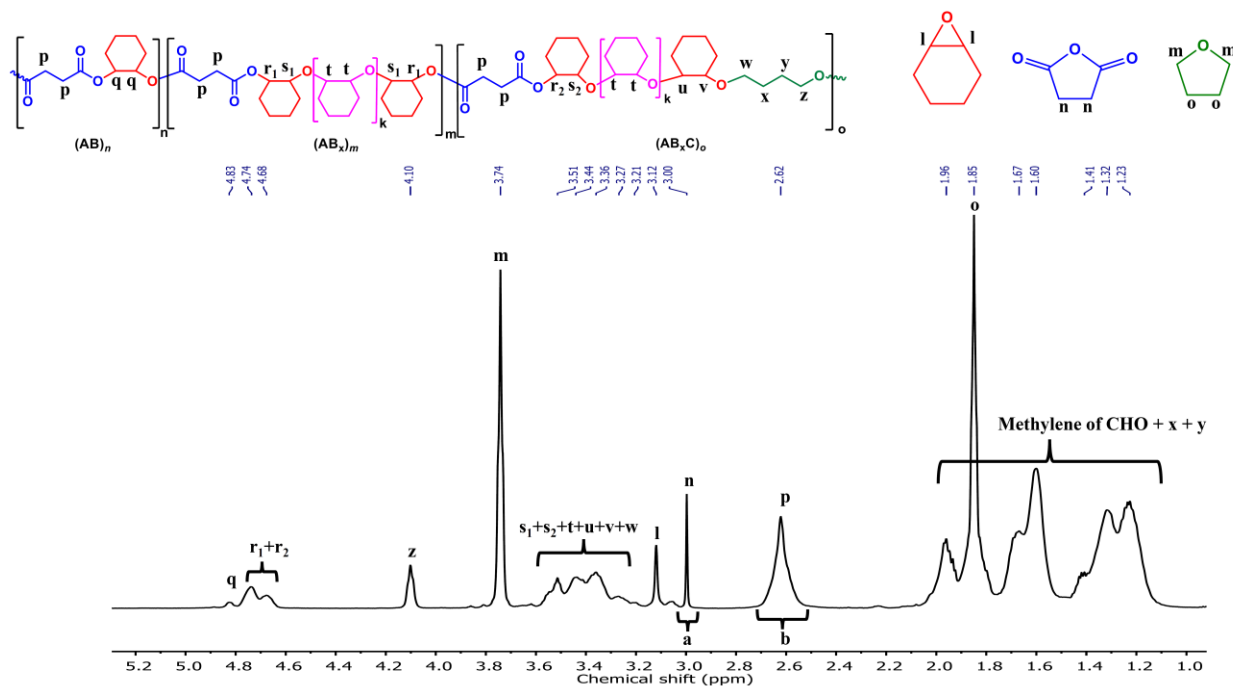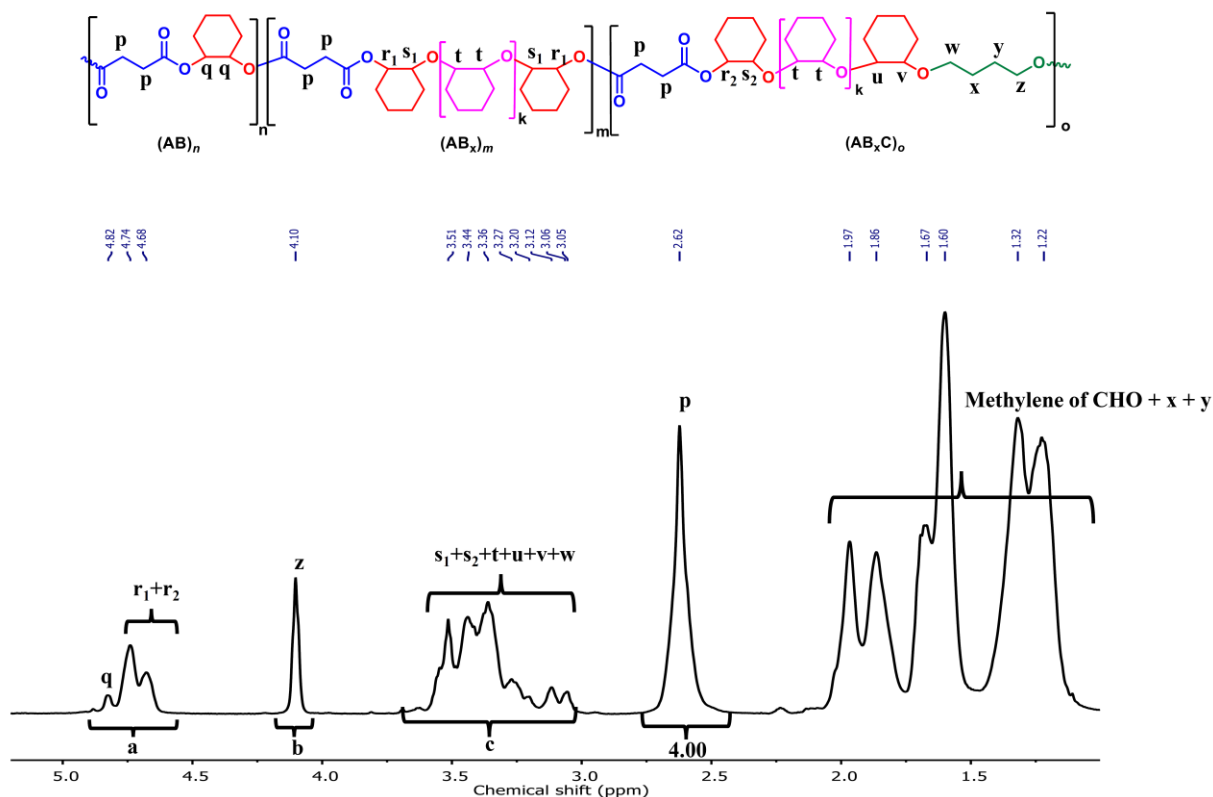

$$SA\ conversion\ \% = \frac{b}{a+b} \times 100\%$$

Where *a* and *b* are the integration of protons *n* and *p*, respectively.

From this, degree of polymerization (DP) for SA can be calculated as shown.

$$DP\ of\ SA = SA\ conversion(\%) \times \frac{[SA]_0}{[Sn]_0}$$

Because THF is highly volatile, conversion of THF cannot be calculated directly from unreacted THF. From ^{1}H NMR of the purified polymer in CDCl$_3$ shown above, to calculate DP for CHO and THF, the integration of SA protons (protons p at 2.62 ppm) was first set to 4 protons (4H/ one SA unit). Since protons w are hidden in the range 3.0-3.7 ppm, they must be subtracted to get the total integration of methine protons of CHO in the polymer. However, the number of protons w is equal to protons z. Therefore, the total integration of methine protons of CHO in the polymer can be calculated as follows.

$$\textbf{\textit{Total integration of methine protons of CHO in polymer}} = \textbf{\textit{(a+c)-b}}$$

There are two methine protons in CHO. Therefore, the equivalent of CHO (in relative to one SA) in the polymer can be calculated as follows.

$$\textbf{\textit{Equivalents of CHO in polymer}} = \frac{(\textbf{\textit{a}} + \textbf{\textit{c}}) - \textbf{\textit{b}}}{\textbf{2}}$$

The equivalents of THF (in relative to one SA) in polymer can also be calculated similarly as follows.

$$Equivalents\ of\ THF\ in\ polymer = \frac{b}{2}$$

Where a, b, and c are the integration protons $q+r_1+r_2$, z, and $s_1+s_2+t+u+v+w$, respectively.
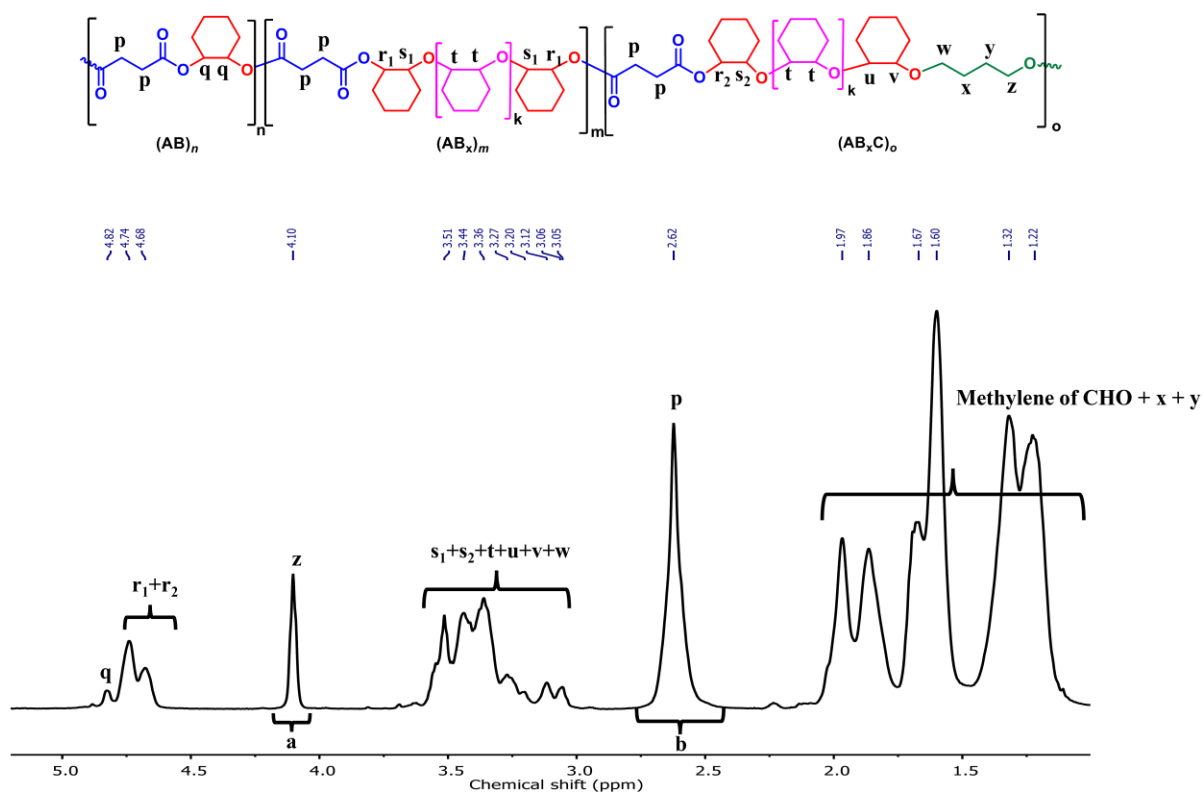
Finally, the DP of CHO and THF can be calculated in relative to the DP of SA as follows.

$$DP\ of\ CHO = DP\ of\ SA \times Equivalents\ of\ CHO\ in\ polymer$$

$$DP\ of\ THF = DP\ of\ SA \times Equivalents\ of\ THF\ in\ polymer$$

For MA and PA, the degrees of polymerization for each monomer can be calculated similarly.

Calculation of polymer selectivity for THF

From 2D NMR analysis, the ring-opened THF is always connected to SA. Therefore, the selectivity for THF can be calculated and defined in relative to SA. From ^{1}H NMR of the purified polymer in CDCl$_3$, polymer selectivity (%) for THF was defined and calculated using the integration ratio of protons z (2 protons/ THF unit) and protons p (4 protons/SA unit) as follows.

$$\textit{Polymer selectivity for THF } (\%) = \frac{\left(\dfrac{a}{2}\right)}{\left(\dfrac{b}{4}\right)} \times 100\%$$

Where a, and b are the integration ratio of protons z, and p, respectively. For MA and PA, polymer selectivity for THF (%) can be calculated similarly.

Calculation of polymer compositions (in the presence of THF)
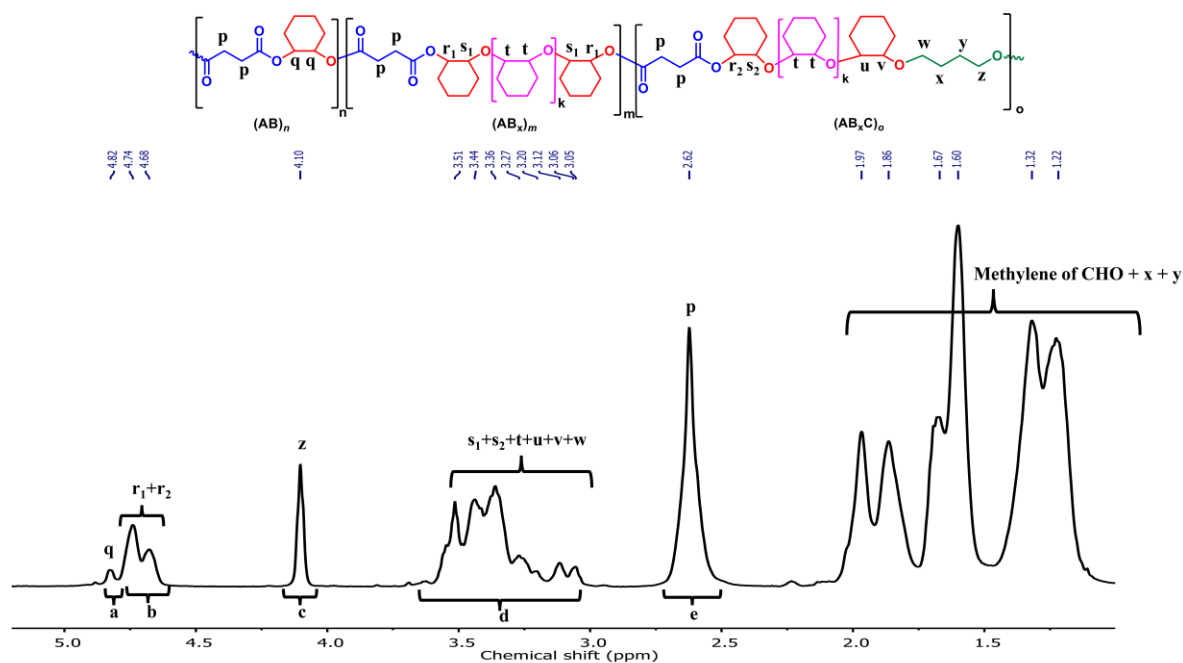
The percent compositions of $(AB)_n$, $(AB_x)_m$, and $(AB_xC)_o$ were defined as the percentage of cyclic anhydride (A) in $(AB)_n$, $(AB_x)_m$ and $(AB_xC)_o$, respectively. Although cyclic anhydrides (A) in $(AB)_n$, $(AB_x)_m$ and $(AB_xC)_o$ comes at the same chemical shift around 2.62 ppm (p peak), they can be derived from different chemical shifts of CHO and THF (peaks q, r_1 and z for example). ^{1}H NMR spectroscopy was used to analyze the resultant copolymers using the following equations.

$$\% \, (AB)_n = \frac{2a}{e} \times 100\%$$

Since the integration of protons $r_2 =$ proton $z \div 2$, the %$(AB_x)_m$ can be calculated as follows.

$$\%(AB_x)_m = \frac{2(b - \frac{c}{2})}{e} \times 100\%$$

$$\%(AB_xC)_o = \frac{2c}{e} \times 100\%$$

Because the B units in $(AB_x)_m$ and $(AB_xC)_o$ are indistinguishable, the ether lengths in both $(AB_x)_m$ and $(AB_xC)_o$ are averaged. Therefore, the x (average number of B units in $(AB_x)_m$ and $(AB_xC)_o$) can be calculated as the equivalents of CHO in relative to SA in $(AB_x)_m$ and $(AB_xC)_o$ as follows.

The integration of methine proton of CHO in $(AB_x)_m$ and $(AB_xC)_o = b+d\text{-}c$ (2 protons/unit)

The integration of SA in $(AB_x)_m$ and $(AB_xC)_o = e\text{-}2a$ (4 protons/unit)

$$x = \frac{(\frac{b + d - c}{2})}{(\frac{e - 2a}{4})}$$

Where a, $(b - \frac{c}{2})$, c, d and e are the integration of protons q, r_1, z, $s_1+s_2+t+u+v+w$, and p, respectively. For other cyclic anhydrides, $(AB)_n$, $(AB_x)_m$, $(AB_xC)_o$ and average x can be calculated similarly.

Calculation of the DP for each monomer (in the presence of 1,4-dioxane)

From ^{1}H NMR of the crude mixture, the PA conversion was measured by the integration ratio of protons from remaining and polymerized PA monomers as shown in the following.
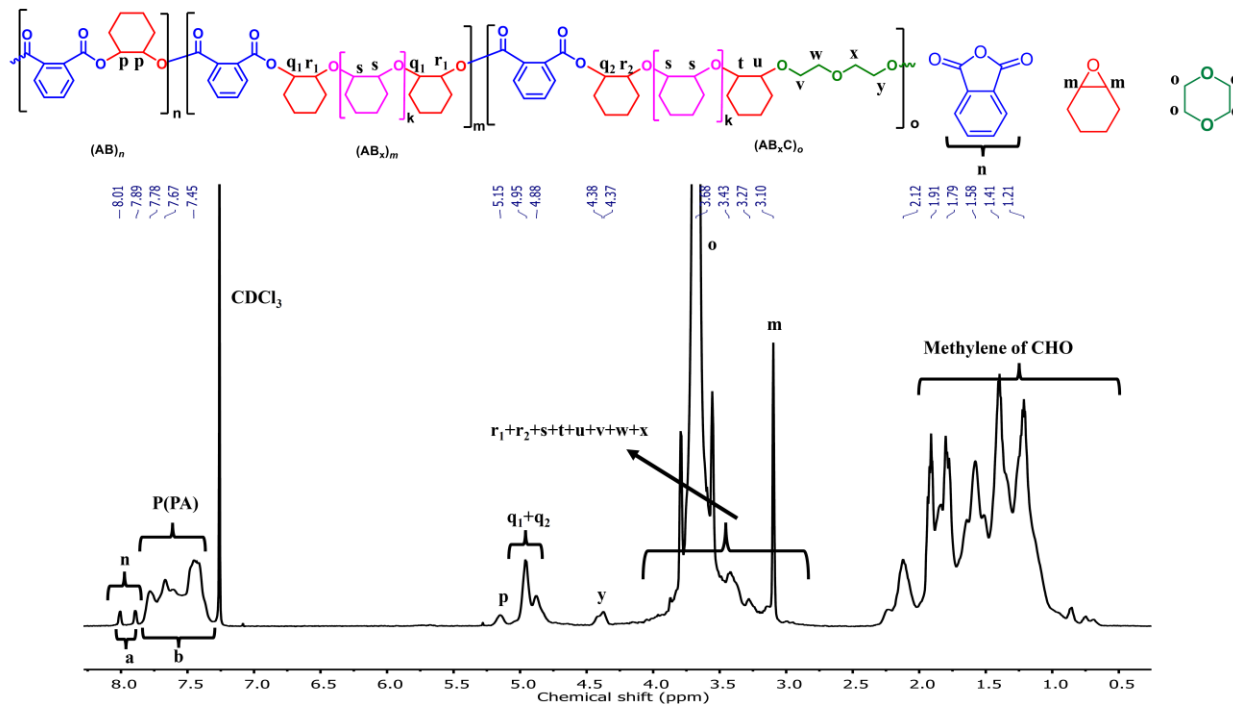
$$PA\ conversion\ \% = \frac{b}{a+b} \times 100\%$$

Where a and b are the integration of protons n and polymerized PA, respectively.

From this, DP for PA can be calculated as follows.

$$DP\ for\ PA = PA\ conversion(\%) \times \frac{[PA]_0}{[Sn]_0}$$
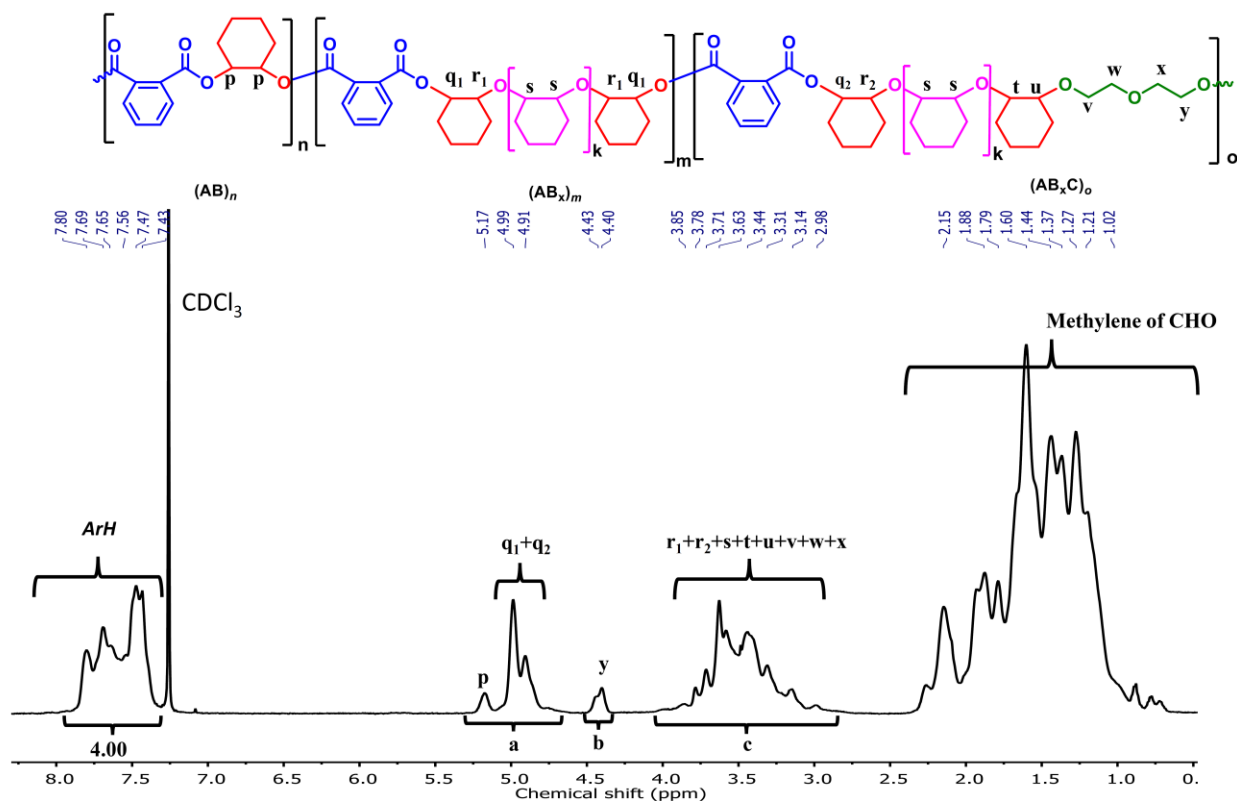
From ^{1}H NMR of the purified polymer shown above, to calculate DP for CHO and dioxane, the integration of PA protons (*ArH* protons at 7.43-7.80 ppm) was first set to 4 protons (4H/one PA unit). Since protons *v*, *w*, and *x* are hidden in the range 3.0-3.8 ppm, they must be subtracted to get the total integration of CHO in the polymer. However, the number of protons *v*, *w*, and *x* are equal to protons *y*. Therefore, the total integration of methine protons of CHO in the polymer can be calculated as follows.

$$\textbf{\textit{Total integration of methine protons of CHO}} = \textbf{(\textit{a+c})-3\textit{b}}$$

There are two methine protons in CHO. Therefore, the equivalent of CHO (in relative to one PA) in the polymer can be calculated as follows.

$$\textbf{\textit{Equivalents of CHO in polymer}} = \frac{\textbf{\textit{a}} + \textbf{\textit{c}} - 3\textbf{\textit{b}}}{\textbf{2}}$$

The equivalents of 1,4- dioxane (in relative to one PA) in polymer can also be calculated similarly as follows.

$$\textbf{\textit{Equivalents of }} \textbf{1,4} - \textbf{\textit{dioxane in polymer}} = \frac{\textbf{\textit{b}}}{\textbf{2}}$$

Where a, b, and c are the integration of protons $p+q_1+q_2$, y and $r_1+r_2+s+t+u+v+w+x$, respectively. Finally, the DP of CHO and 1,4-dioxane can be calculated in relative to the DP of PA as follows.

$$DP \ of \ CHO = DP \ of \ PA \ \times Equivalents \ of \ CHO \ in \ polymer$$

$$DP \ of \ 1,4-dioxane = DP \ of \ PA \ \times Equivalents \ of \ 1,4-dioxane \ in \ polymer$$

For SA, the degrees of polymerization for each monomer can be calculated similarly.

Calculation of polymer selectivity for 1,4-dioxane
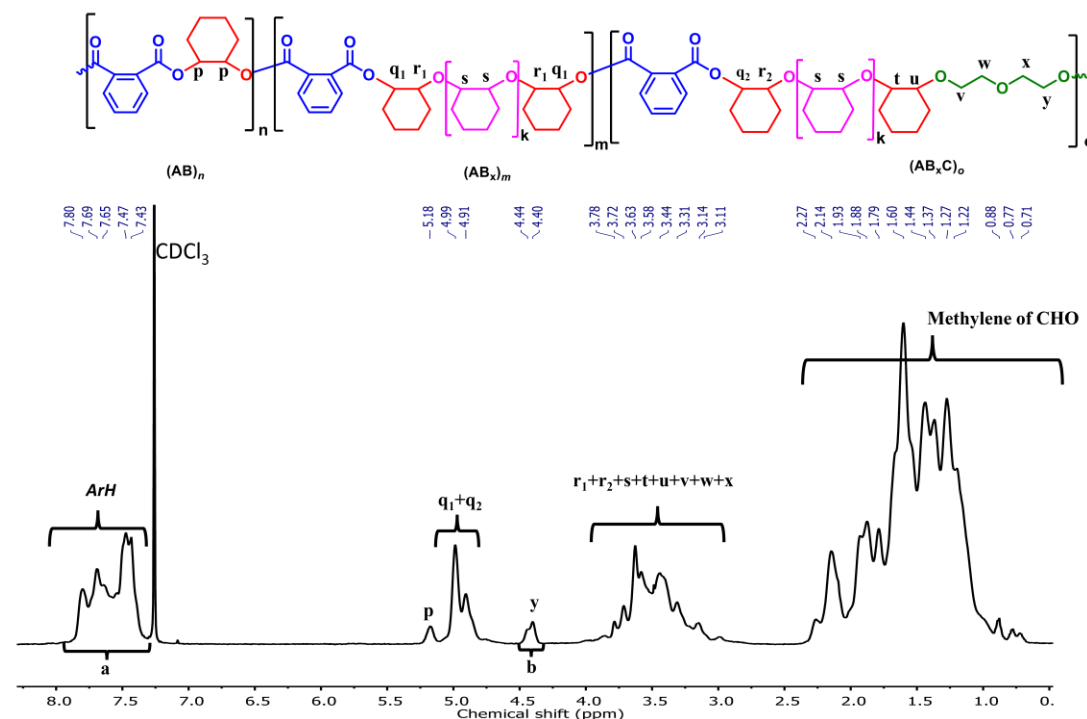
Similar to THF, the ring-opened 1,4-dioxane is always connected to PA. Therefore, the selectivity for 1,4-dioxane can be calculated and defined in relative to PA. From ^{1}H NMR of the purified polymer, polymer selectivity (%) for 1,4-dioxane was defined and calculated using the integration ratio of protons y (2 protons/unit) and protons ArH (4 protons/PA unit) as follows.

$$Polymer \ selectivity \ for \ 1,4-dioxane \ (\%) = \frac{\left(\frac{b}{2}\right)}{\left(\frac{a}{4}\right)} \times 100\%$$

S12

Where *a*, and *b* are the integration ratio of protons *ArH,* and y, respectively. For SA, polymer selectivity for 1,4-dioxane can be calculated similarly.

Calculation of polymer compositions (in the presence of 1,4-dioxane)
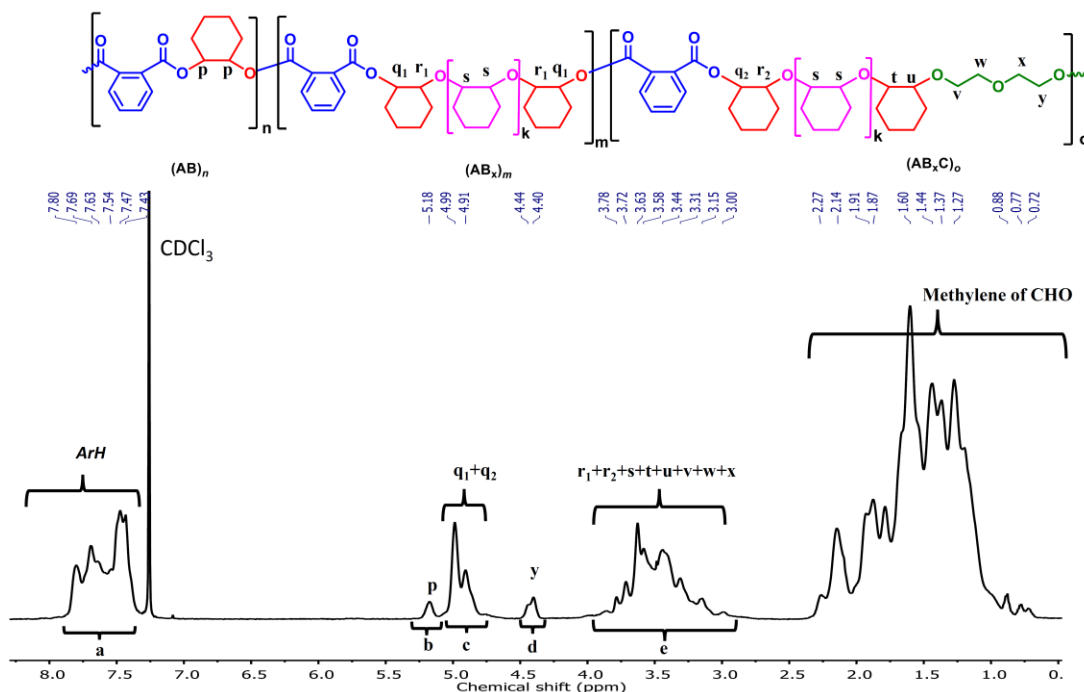
The percent compositions of $(AB)_n$, $(AB_x)_m$, and $(AB_xC)_o$ were defined as the percentage of cyclic anhydride (A) in $(AB)_n$, $(AB_x)_m$ and $(AB_xC)_o$ respectively. Although cyclic anhydrides (A) in $(AB)_n$, $(AB_x)_m$ and $(AB_xC)_o$ comes at the same chemical shift around 7.43-7.80 ppm (*ArH* peak), they can be derived from different chemical shifts of CHO and 1,4-dioxane (peaks *p, q_1* and *y* for example). Using similar analysis as in THF, ^{1}H NMR spectroscopy was used to analyze the resultant copolymers using the following equations.

$$\% \ (AB)_n = \frac{2b}{a} \times 100 \ \%$$

$$\%(AB_x)_m = \frac{2(c - \frac{d}{2})}{a} \times 100\%$$

$$\%(AB_xC)_o = \frac{2d}{a} \times 100\%$$

Because the B units in $(AB_x)_m$ and $(AB_xC)_o$ are indistinguishable, the ether lengths in both $(AB_x)_m$ and $(AB_xC)_o$ are averaged. Therefore, the x (average number of B units in $(AB_x)_m$ and $(AB_xC)_o$) can be calculated as the equivalents of CHO in relative to PA in $(AB_x)_m$ and $(AB_xC)_o$ as follows.

The integration of methine proton of CHO in $(AB_x)_m$ and $(AB_xC)_o = c+e\text{-}3d$ (2 protons/unit)

The integration of PA in $(AB_x)_m$ and $(AB_xC)_o = a\text{-}2b$ (4 protons/unit)

The average number of B (x) can then be calculated as follows.

$$x = \frac{\left(\dfrac{c+e-3d}{2}\right)}{\left(\dfrac{a-2b}{4}\right)}$$

Where a, b, $\left(c - \dfrac{d}{2}\right)$, d and e are the integration ratio of protons ArH, p, q_1, y and $r_1+r_2+s+t+u+v+w+x$, respectively. For other cyclic anhydrides, $(AB)_n$, $(AB_x)_m$, $(AB_xC)_o$ and average x can be calculated similarly.

2. Results

2.1 Copolymerization of epoxides and cyclic anhydrides by tin(II) octanoate
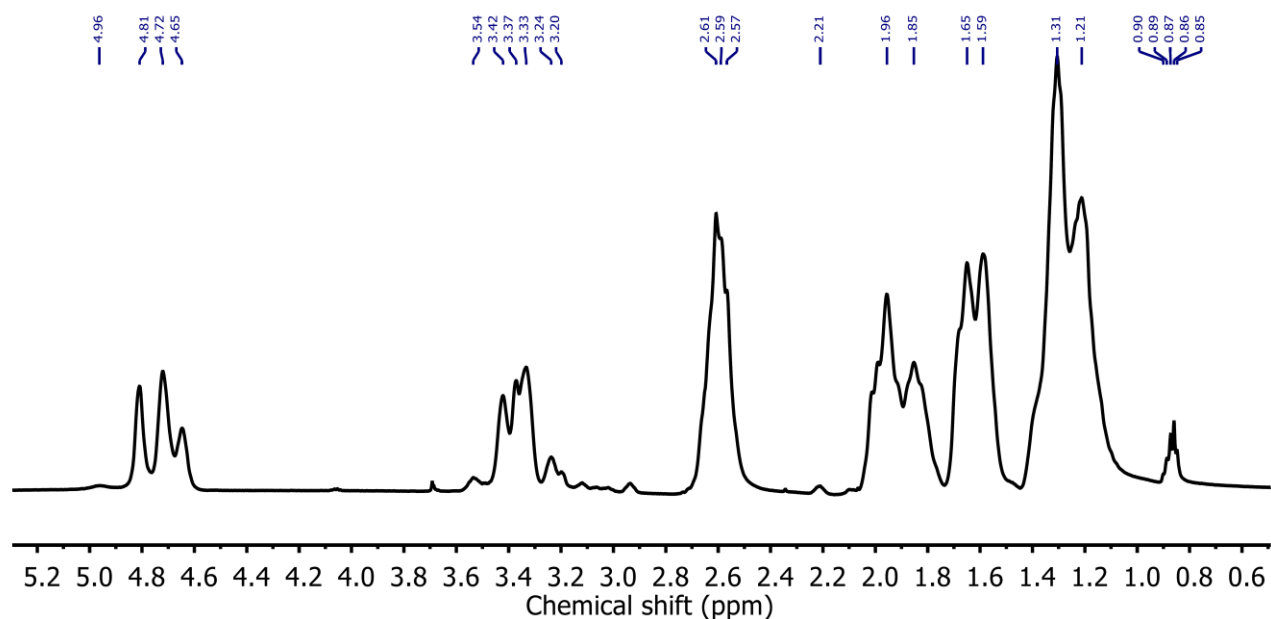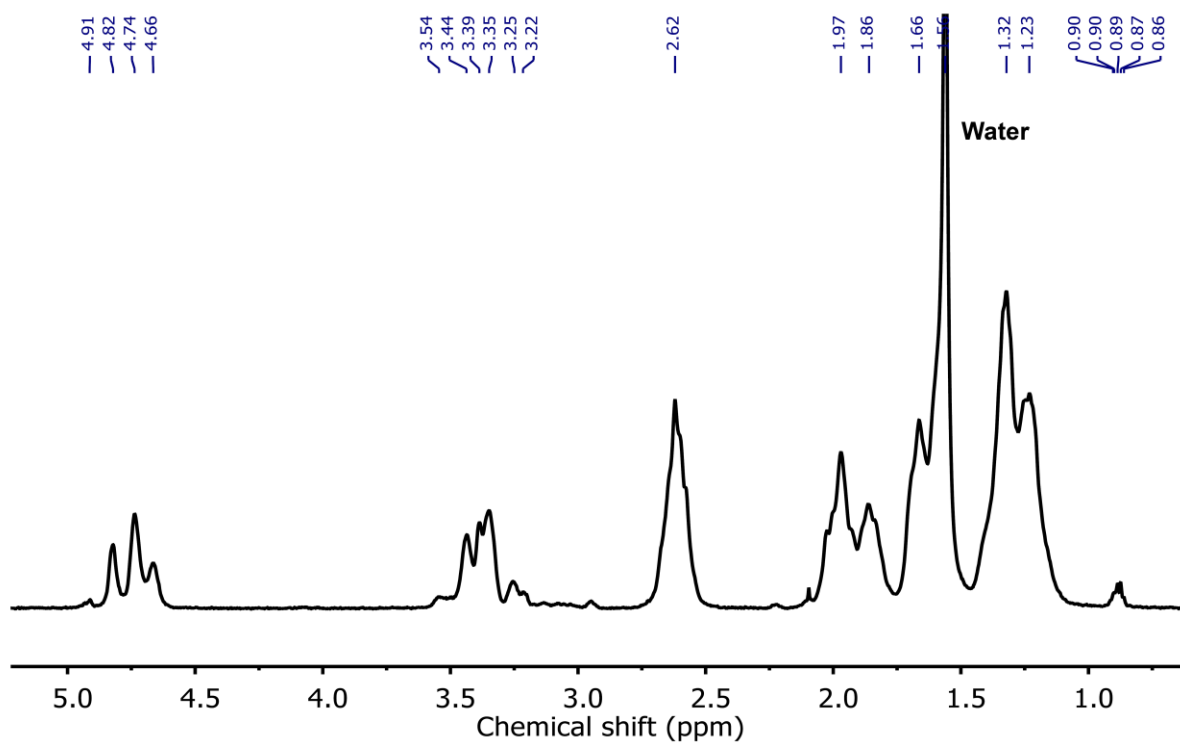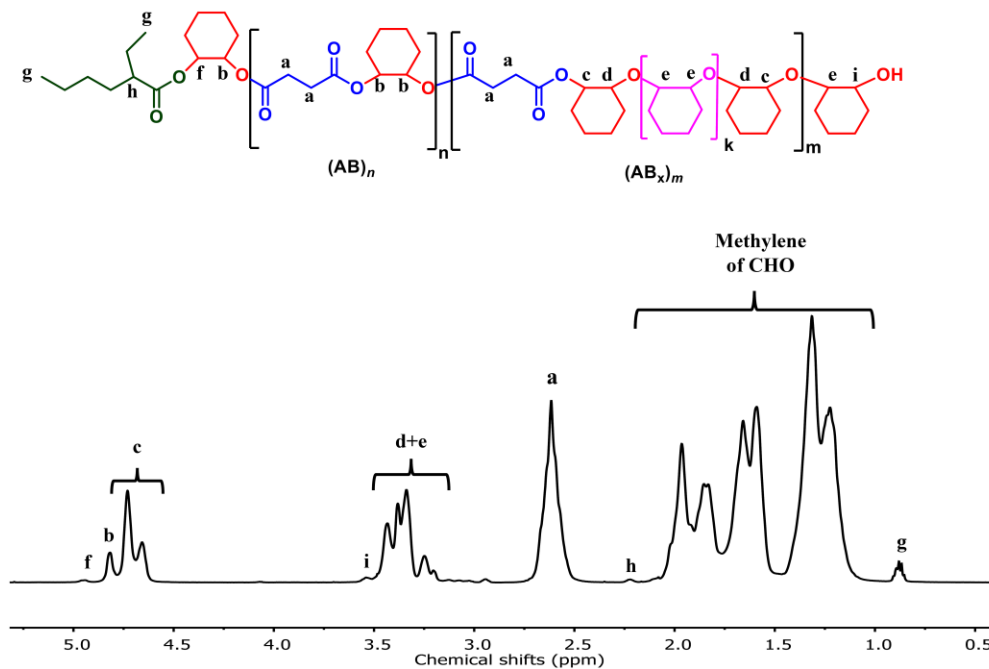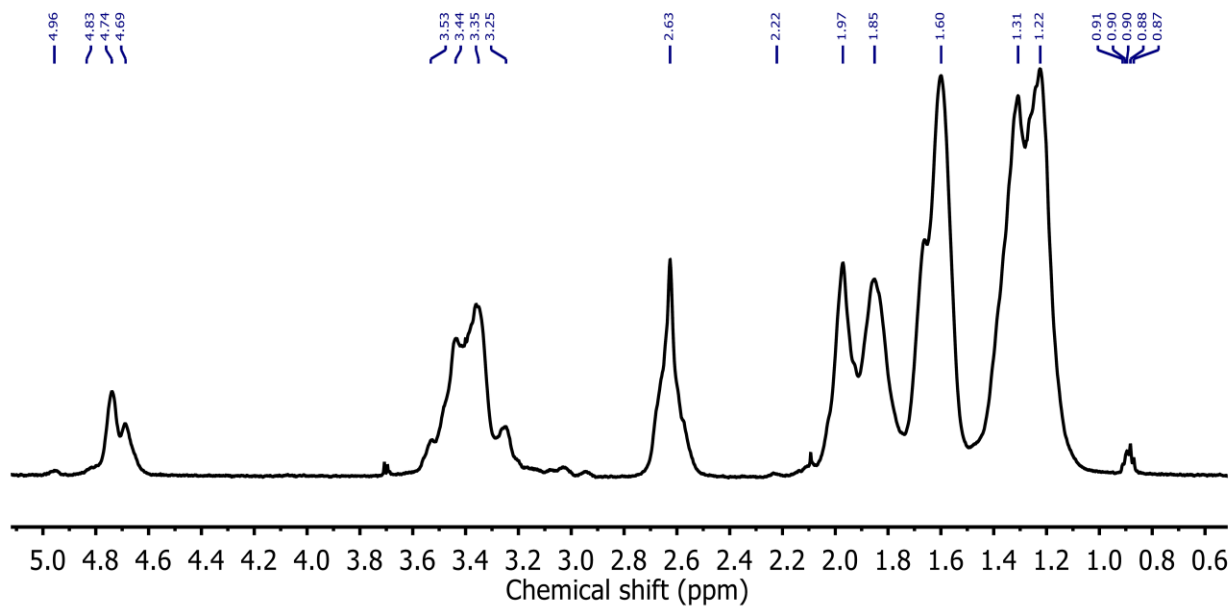
NMR spectrum of SA/CHO copolymers
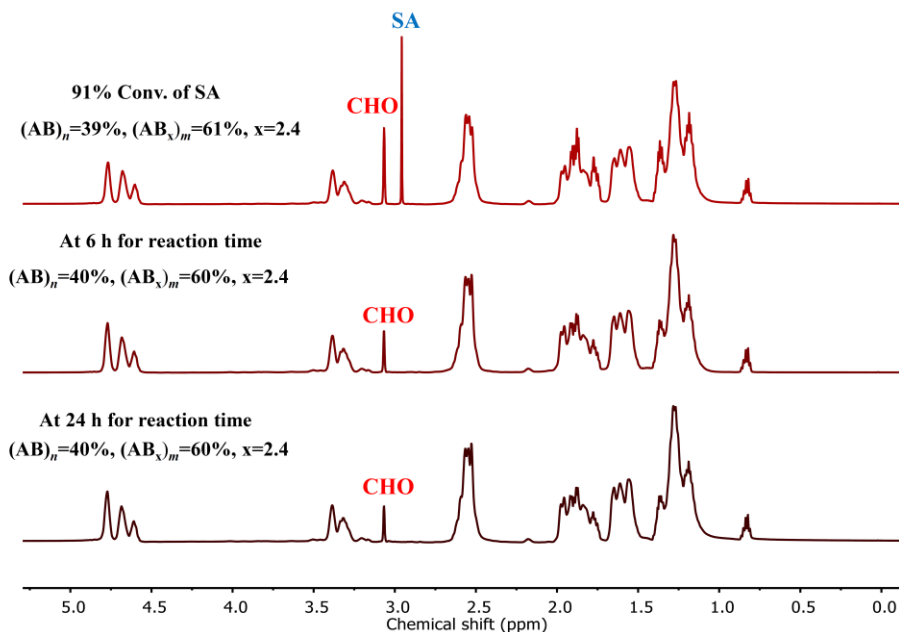
Figure S1 ^{1}H NMR spectra (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA and CHO using SA: CHO: SnOct$_2$ molar ratio of 50:100:1 and [CHO]$_0$ = 1.0 M at 80 °C with different polymerization time.
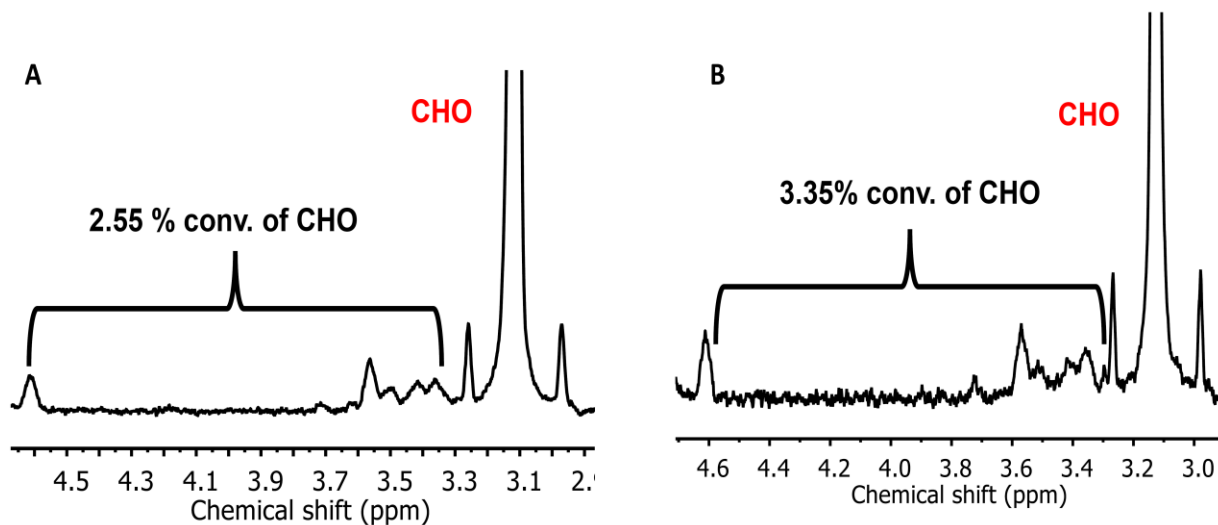
Figure S2 ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) from ROP of CHO using CHO: SnOct$_2$ molar ratio of 100:1 and [CHO]$_0$ = 1.0 M at 80 °C: (A) at 3 h and (B) at 24 h.
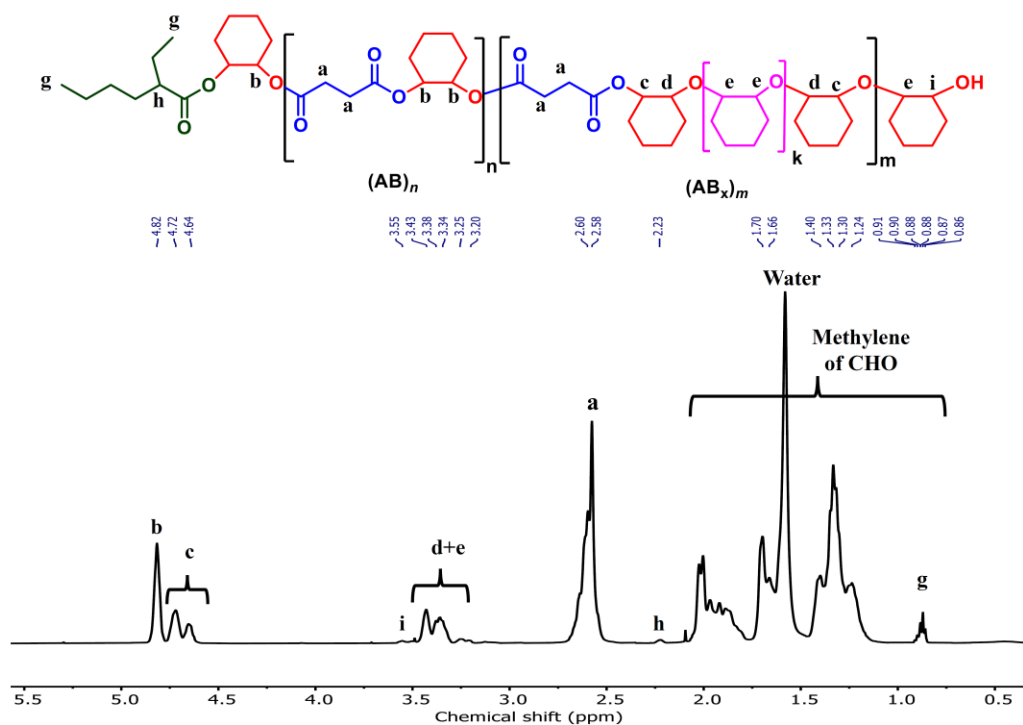
Figure S3. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the purified copolymer from ROCOP of SA and CHO using a SA:CHO:SnOct$_2$ molar ratio of 50:100:1, [CHO]$_0$ = 1.0 M at 110 °C (Table 1, entry 1).
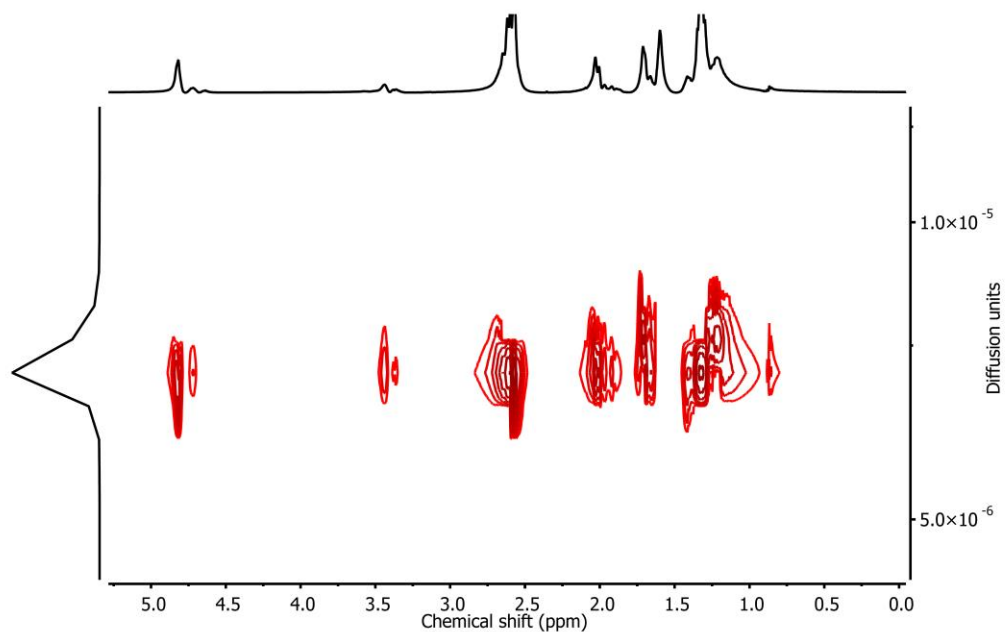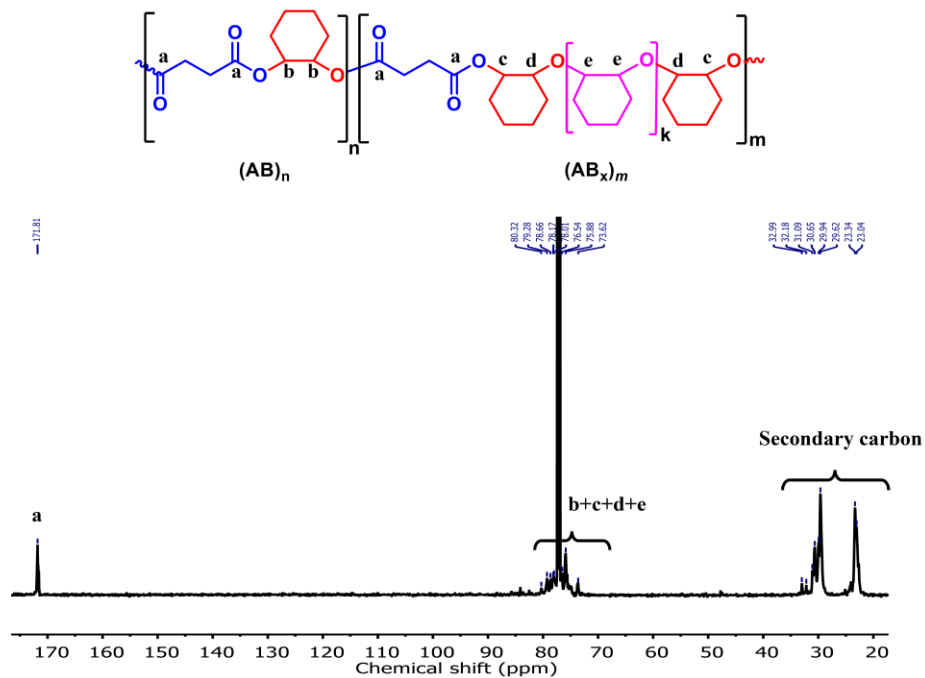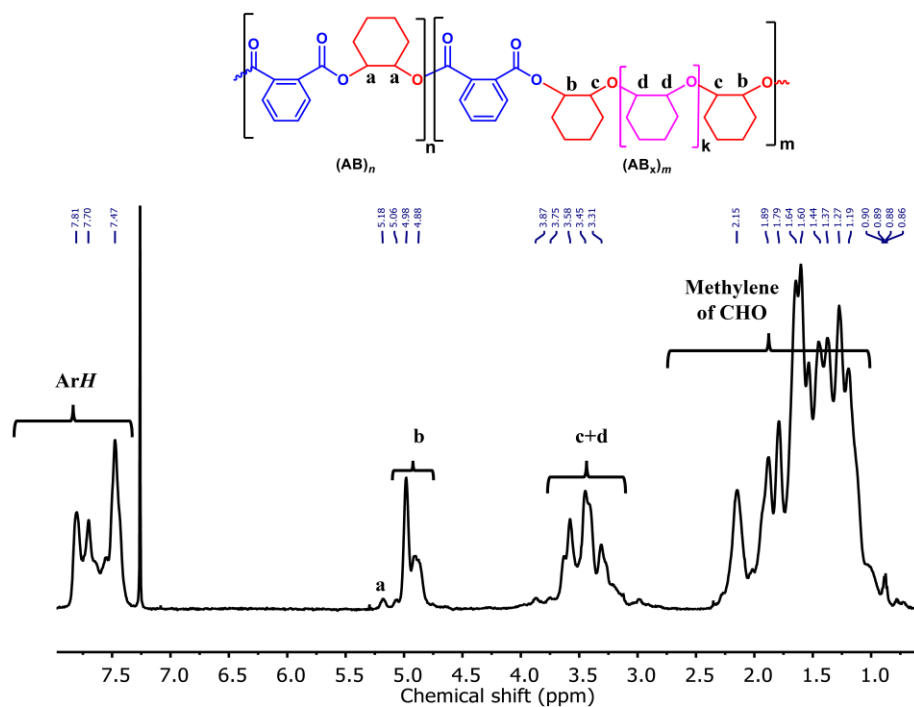

Figure S4. DOSY NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA and CHO using a SA/CHO/SnOct$_2$ molar ratio of 50:100:1 and [CHO]$_0$ = 1.0 M at 110 °C (Table 1, entry 1).

S16

a)

Intens. [a.u.] ×10^4

■ Oct-(CHOSA)$_n$-(CHO$_x$SA)$_m$-CHO-H + Na$^+$, x > 1
▲ Oct-(CHOSA)$_n$-(CHO$_x$SA)$_m$-CHO-Na + Na$^+$, x > 1
● OH-(CHOSA)$_n$-(CHO$_x$SA)$_m$-CHO-H + Na$^+$, x > 1

1.2

1.0

0.8

0.6

0.4

0.2

0.0

1000   1500   2000   2500   3000   3500   m/z

b)

1551.583   1650.426   1749.313

98.89

1623.392

1673.543

1500   1800

■ **1650.426 (Obtained value)**

Oct-(CHO)$_9$-(SA)$_6$-H + Na$^+$

Theoretical value

M.W= Oct(143.1 g/mol)+(98.14 g/mol ×9)+(100.07 g/mol × 6)+1.01 g/mol + 22.99 g/mol =1650.78

● **1623.392 (Obtained value)**

HO-(CHO)$_9$-(SA)$_7$-H + Na$^+$

Theoretical value

M.W= HO(17.01 g/mol)+(98.14 g/mol ×9)+(100.07 g/mol × 7)+1.01 g/mol + 22.99 g/mol =1624.4

▲ **1673.543 (Obtained value)**

Oct-(CHO)$_9$-(SA)$_6$-Na + Na$^+$

Theoretical value

M.W= Oct(143.1 g/mol)+(98.14 g/mol ×9)+(100.07 g/mol × 6)+ 22.99 g/mol + 22.99 g/mol =1672.76

Figure S5. a) MALDI-TOF mass spectrum of poly(SA-*co*-CHO) obtained at low SA conversion (<50%) using [CHO]$_0$ /[SA]$_0$/[SnOct$_2$]$_0$ ratio of 100/50/1 at 110 °C and b) the expanded spectrum in the m/z 1500−1800 range and expected structures with theoretical molecular weights of the polymer.
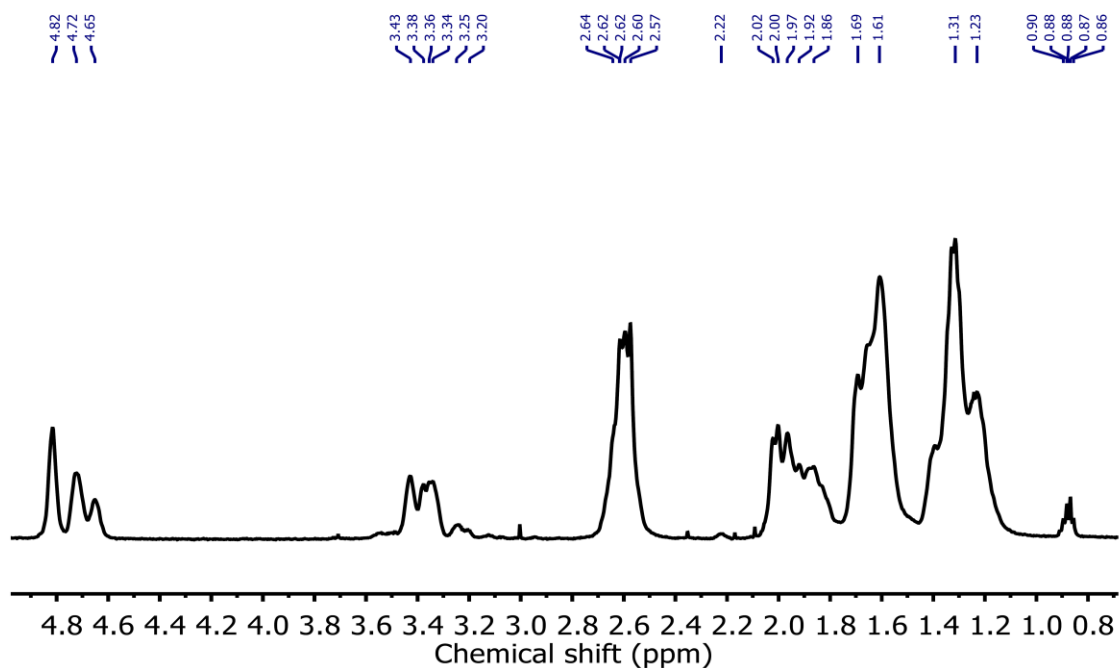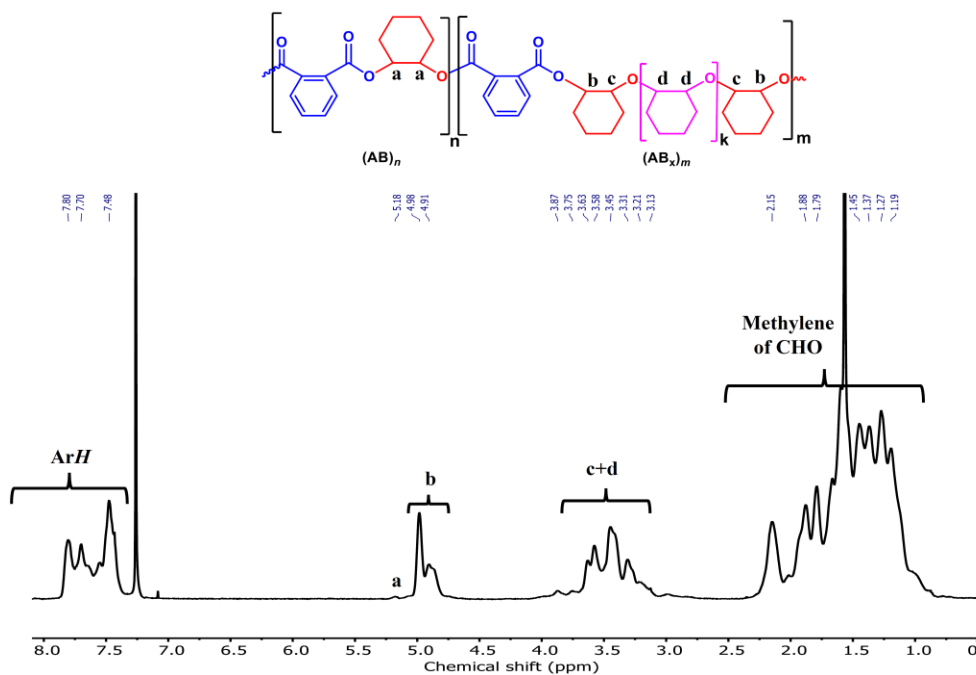
Figure S6. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA and CHO using SA: CHO: SnOct$_2$ molar ratio of 50:100:1 and [CHO]$_0$ = 1.0 M at 80 °C (Table 1, entry 2).
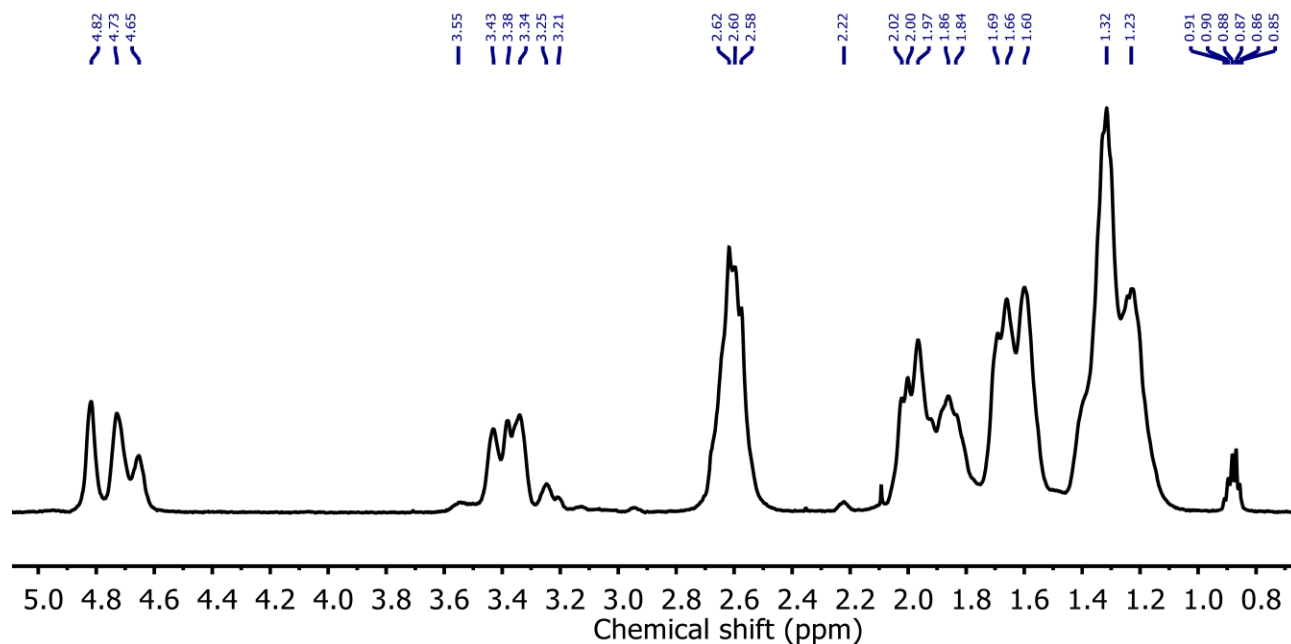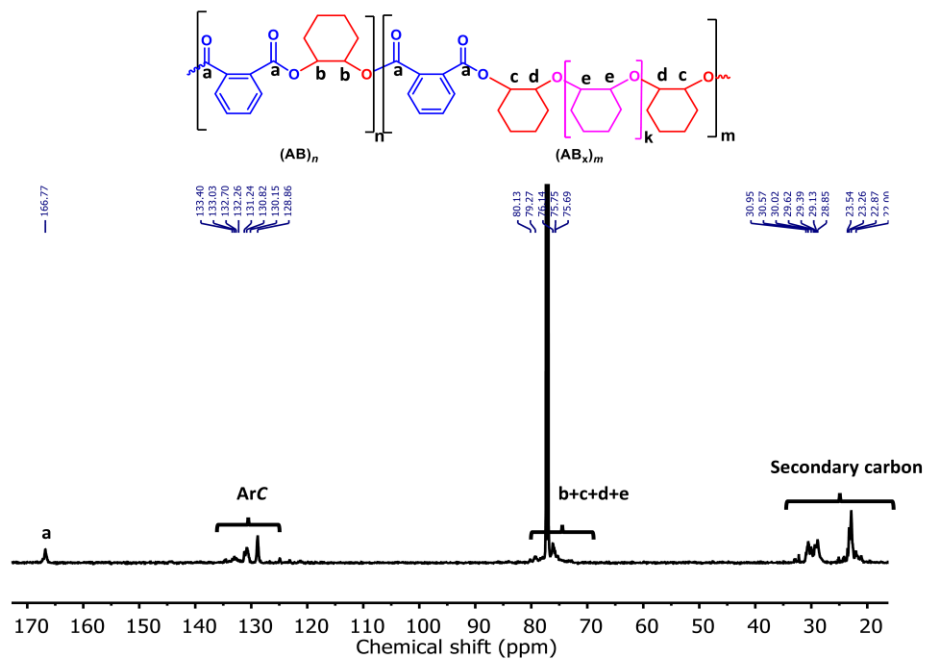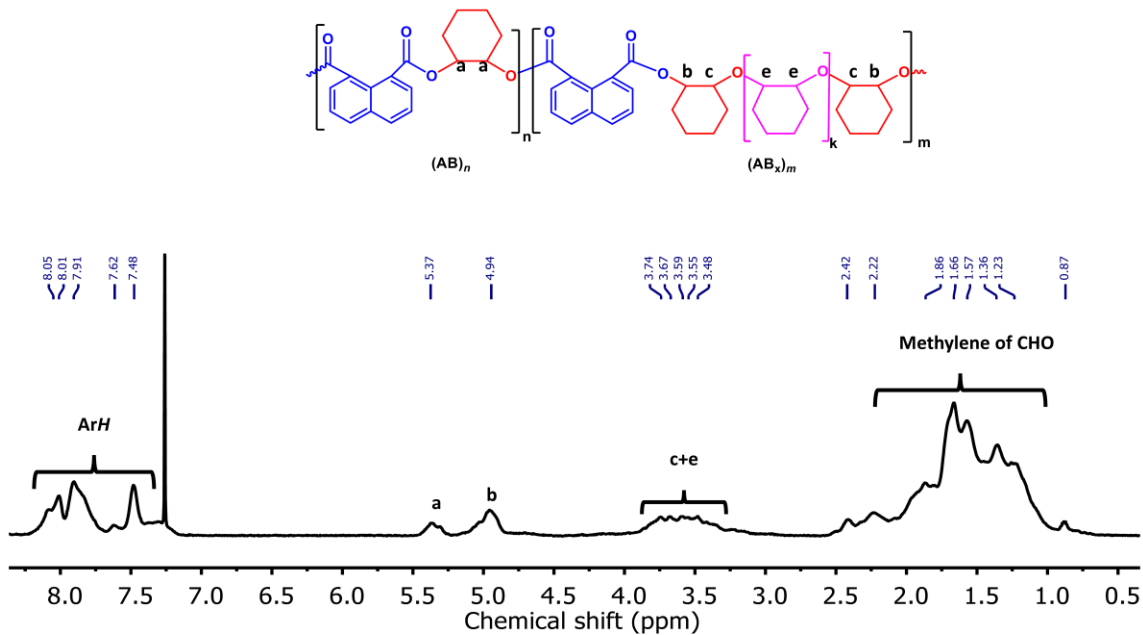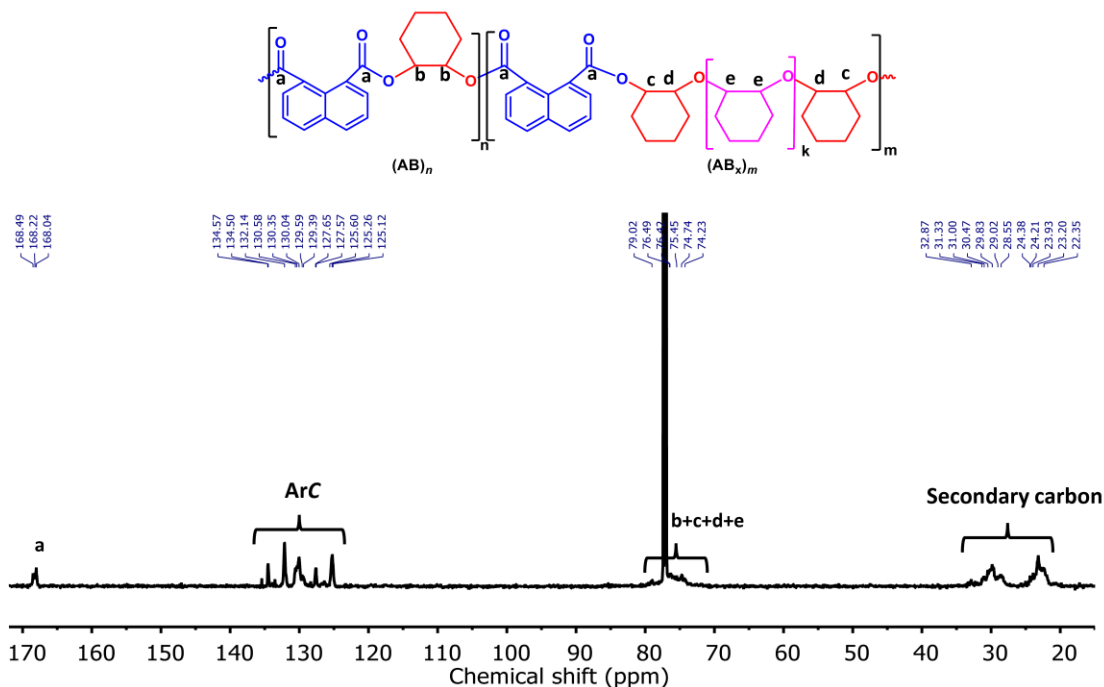

Figure S7. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA and CHO using SA: CHO: SnOct$_2$ molar ratio of 50:100:1 and [CHO]$_0$ = 1.0 M at 60 °C (Table 1, entry 3).
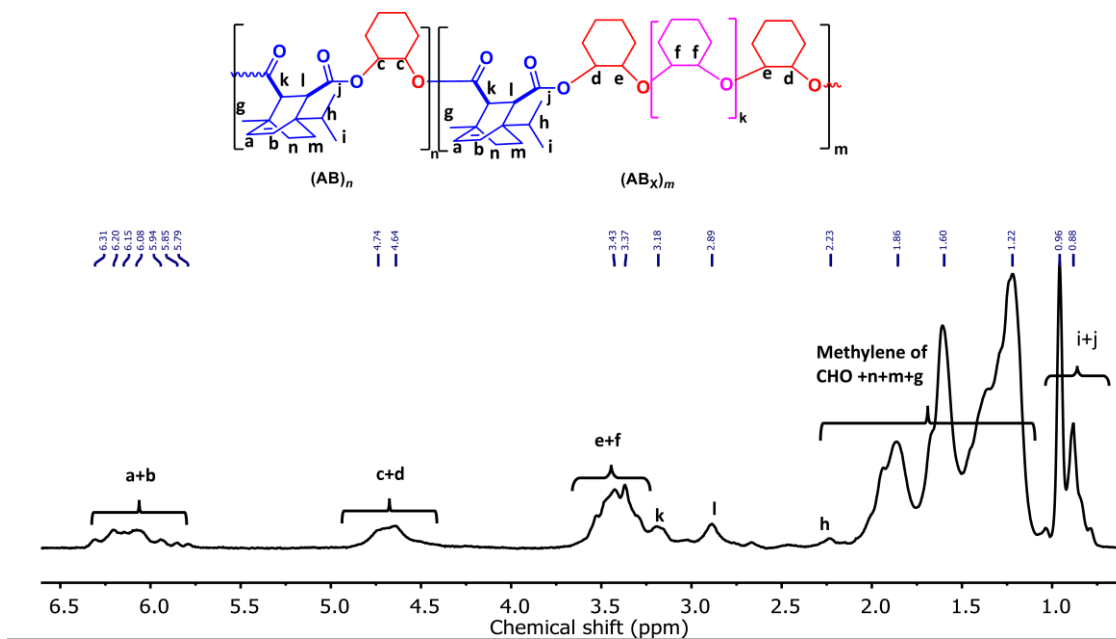
Figure S8. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA and CHO using SA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 1.0 M at 80 °C (Table 1, entry 4).

Figure S9. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of SA and CHO using SA: CHO: SnOct$_2$ molar ratio of 50:600:1 and [CHO]$_0$ = 1.0 M at 80 °C (Table 1, entry 5).

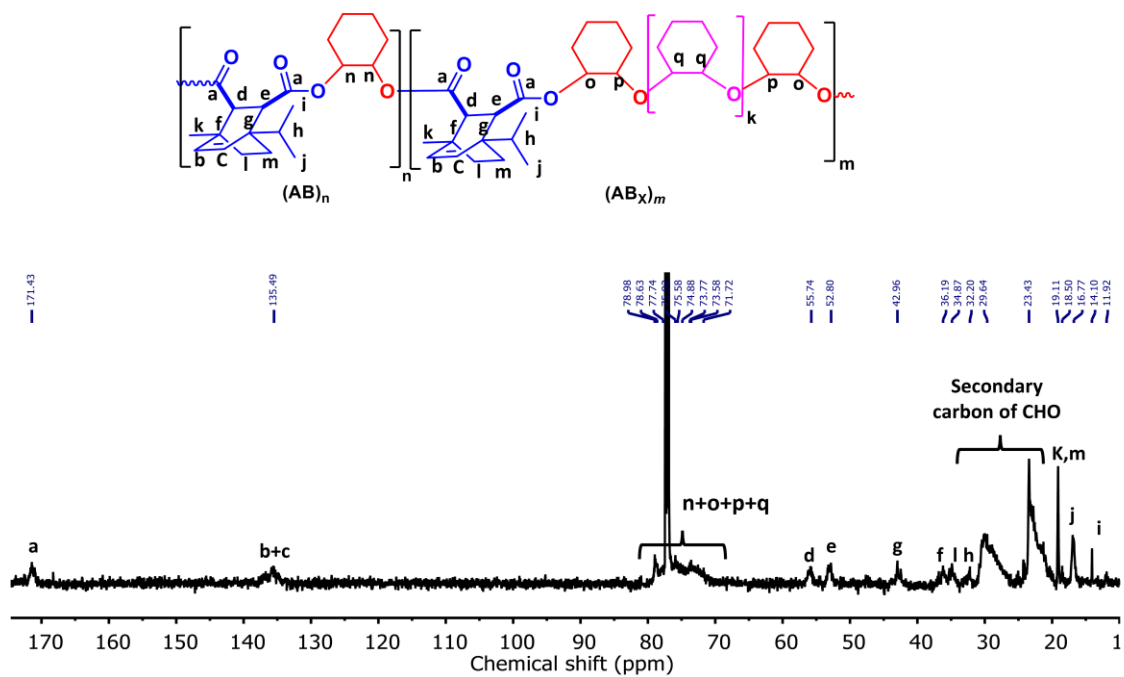**Figure S10**. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA and CHO using a SA/CHO/SnOct$_2$ molar ratio of 50:300:1 with CHO concentration of 2.0 M (Table 1, entry 6).

Figure S11. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA and CHO using SA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = neat condition at 80 °C (Table 1, entry 7).
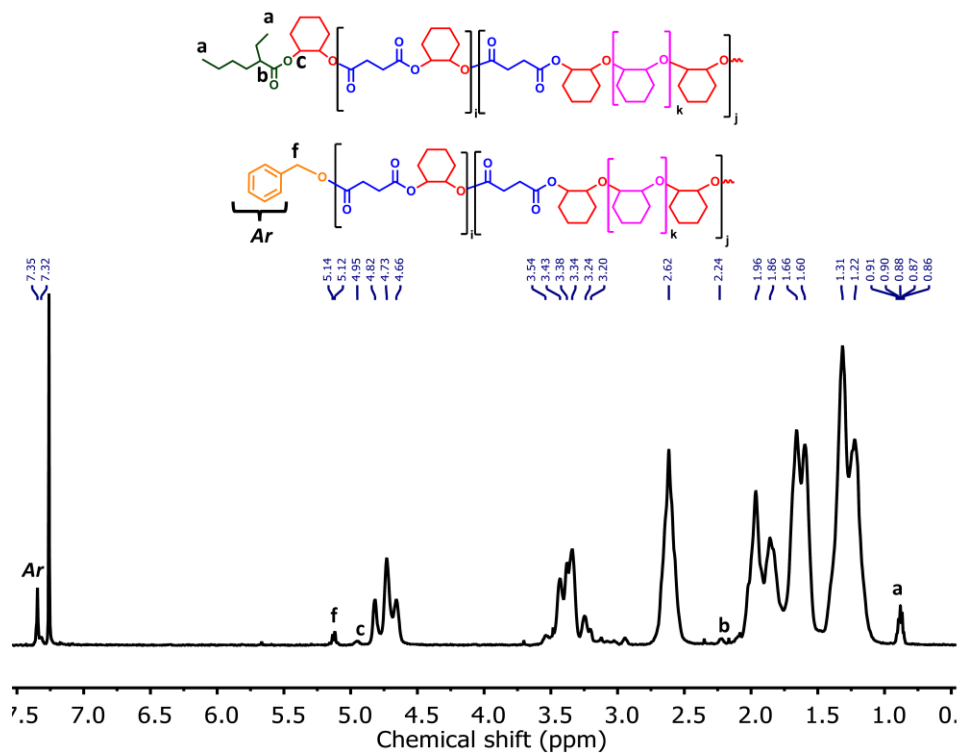
Figure S12. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of SA and CHO using SA: CHO: SnOct$_2$: BnOH molar ratio of 50:300:1:2 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 8).
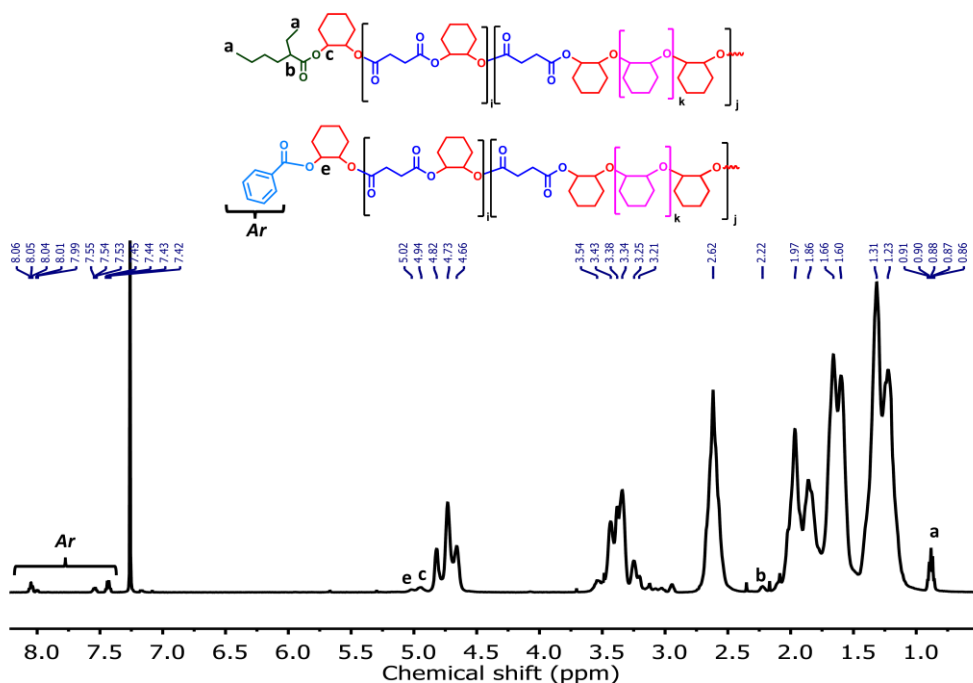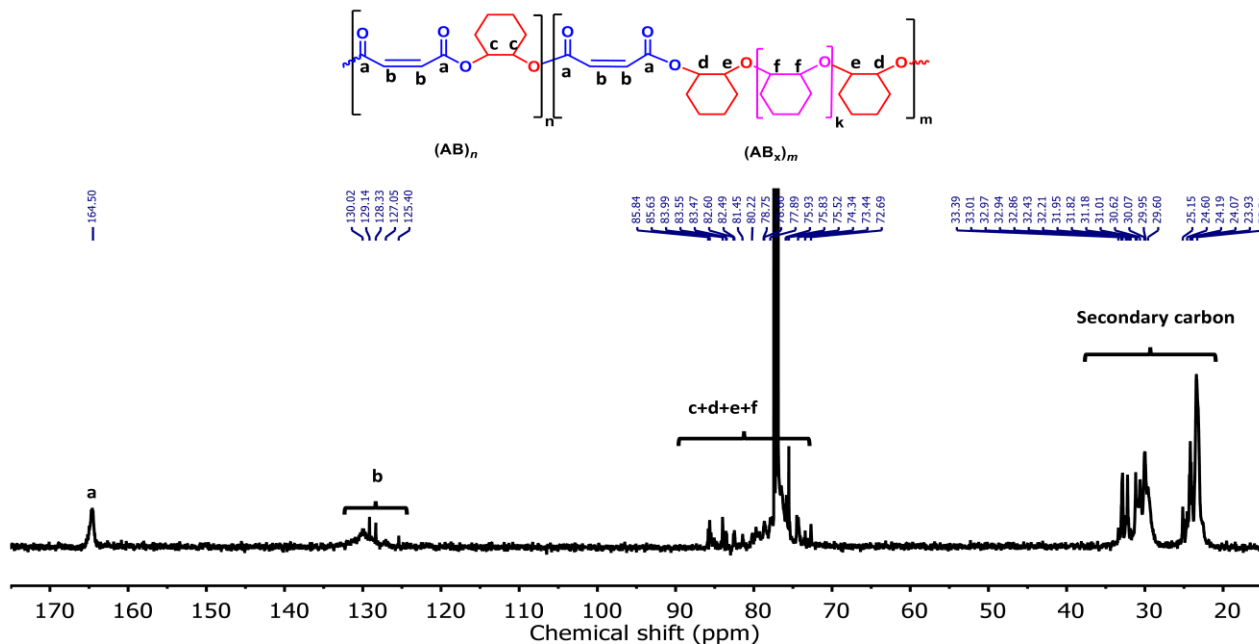

Figure S13. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of SA and CHO using SA: CHO: SnOct$_2$: PhCOOH molar ratio of 50:300:1:2 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 9).

S21

Figure S14. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of SA and CHO using SA: CHO: SnOct$_2$: molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 6).
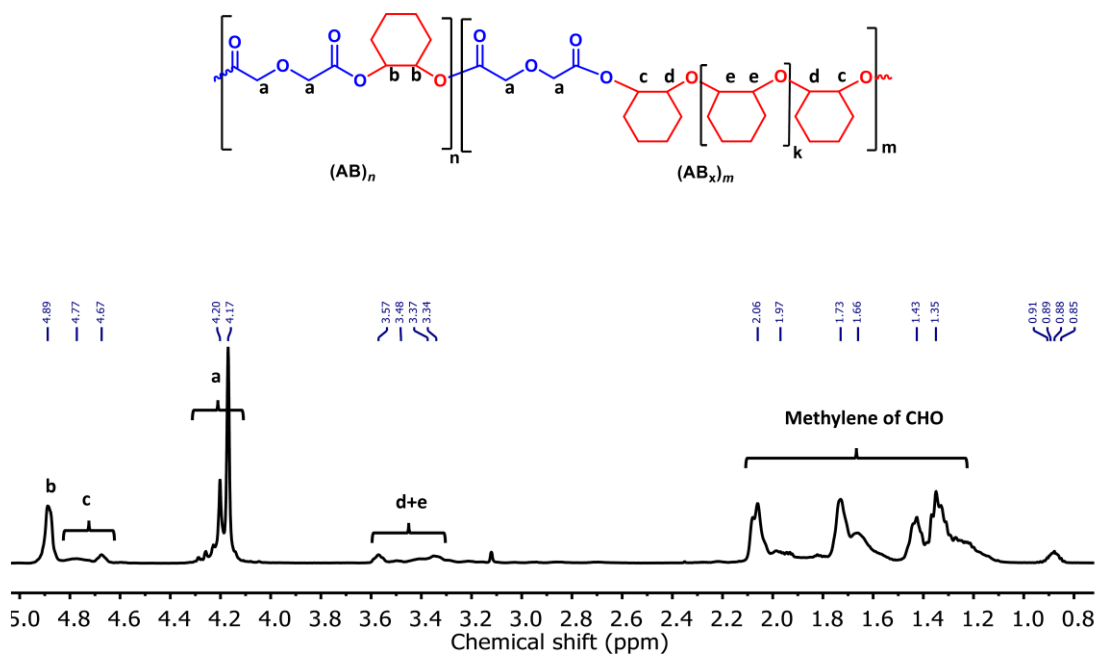
NMR spectrum of PA/CHO copolymers

Figure S15. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of PA and CHO using PA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 10).
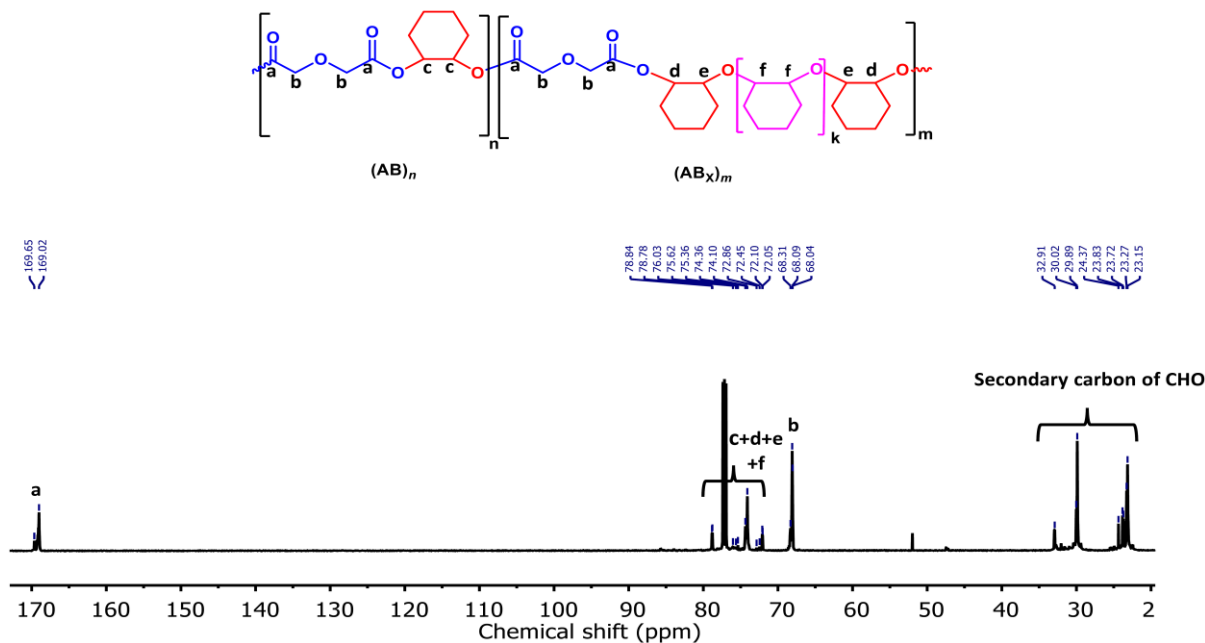

Figure S16. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of PA and CHO using PA: CHO: SnOct$_2$ molar ratio of 250:1500:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 15).

Figure S17. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of PA and CHO using PA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 10).
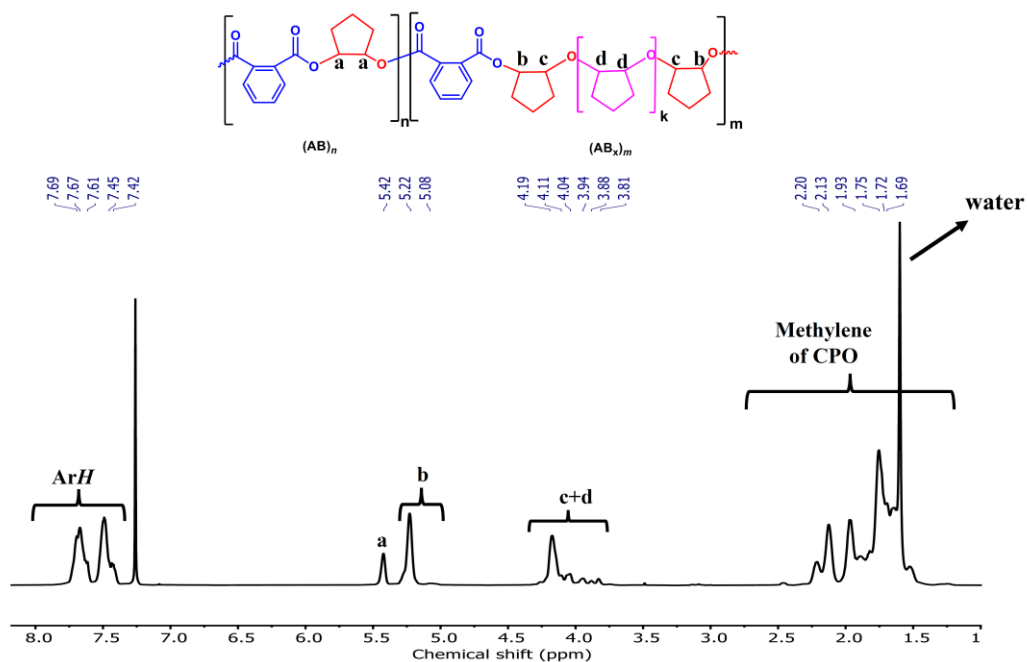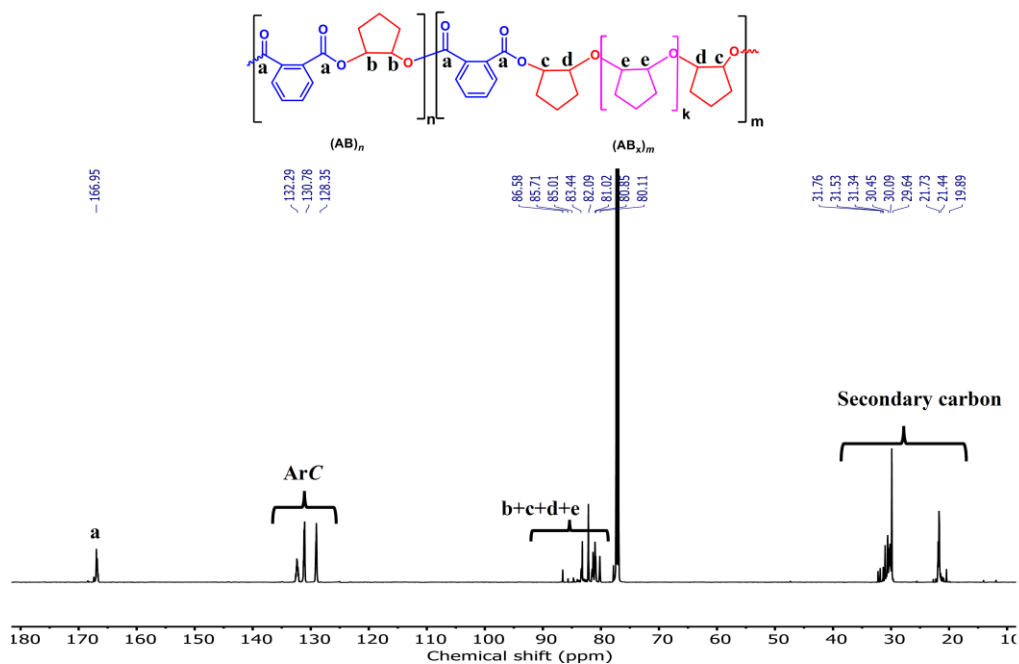
NMR spectrum of NA/CHO copolymers

Figure S18. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of NA and CHO using NA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 11).

Figure S19. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of NA and CHO using NA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 11).
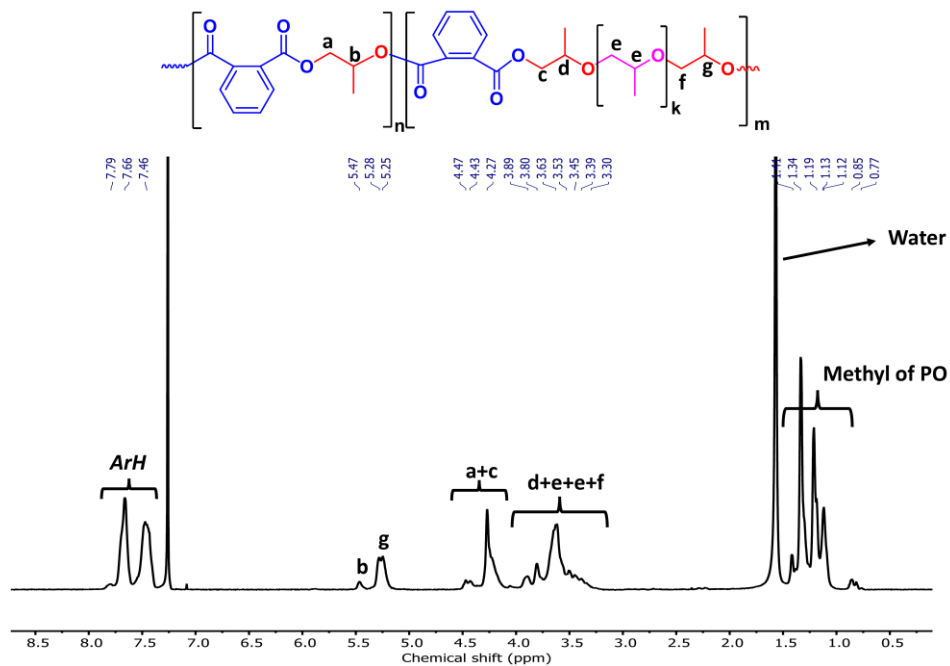
NMR spectrum of TBA/CHO copolymers

Figure S20. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of TBA and CHO using TBA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 14).
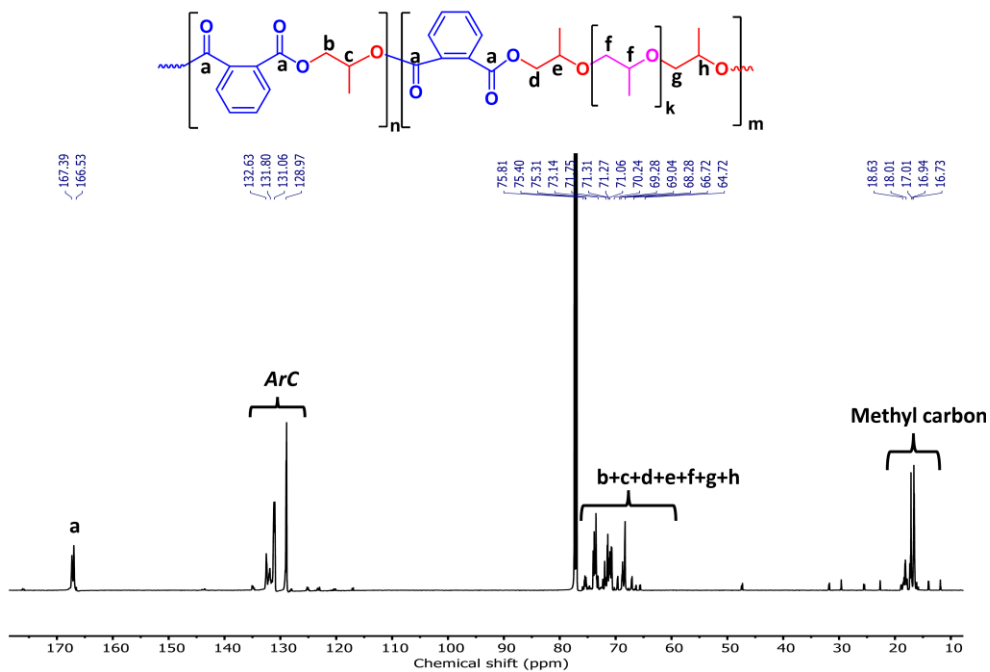

Figure S21. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of TBA and CHO using TBA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 14).
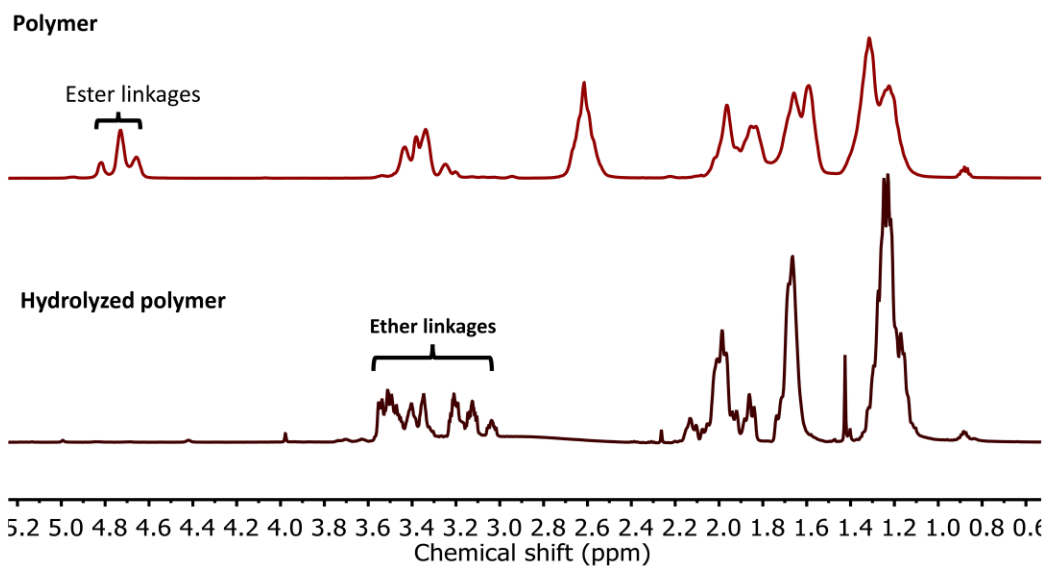
NMR spectrum of MA/CHO copolymers
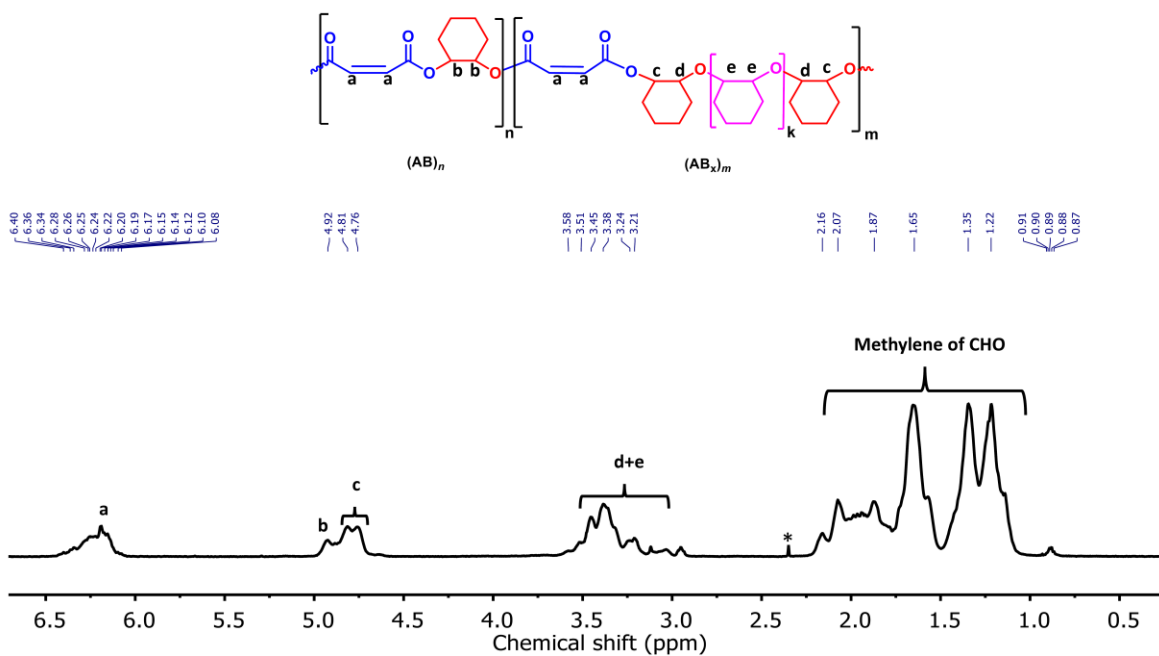
Figure S22. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C; Asterisk indicates residual toluene) of copolymer from ROCOP of MA and CHO using MA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 12).

Figure S23. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of MA and CHO using MA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 12).

NMR spectrum of DGA/CHO copolymers

Figure S24. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of DGA and CHO using DGA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 13).

Figure S25. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of DGA and CHO using DGA: CHO: SnOct$_2$ molar ratio of 50:300:1 and [CHO]$_0$ = 2.0 M at 80 °C (Table 1, entry 13).

NMR spectrum of PA/CPO copolymers

Figure S26. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of PA and CPO using PA: CPO: SnOct$_2$ molar ratio of 50:300:1 and [CPO]$_0$ = 2.0 M at 80 °C (Table 1, entry 16).

Figure S27. ^{13}C NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of PA and CPO using PA: CPO: SnOct$_2$ molar ratio of 50:300:1 and [CPO]$_0$ = 2.0 M at 80 °C (Table 1, entry 16).

NMR spectrum of PA/PO copolymers

Figure S28. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of PA and PO using PA: PO: SnOct$_2$ molar ratio of 50:300:1 and [PO]$_0$ = 2.0 M at 80 °C (Table 1, entry 17).

Figure S29. ^{13}C NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of copolymer from ROCOP of PA and PO using PA: PO: SnOct$_2$ molar ratio of 50:300:1 and [PO]$_0$ = 2.0 M at 80 °C (Table 1, entry 17).

Figure S30. ^{1}H NMR spectra (600 MHz, CDCl$_3$, 30 °C) of polymer (top) and hydrolyzed polymer (bottom) of poly(CHO-*co*-SA) (Table 1, entry 6).
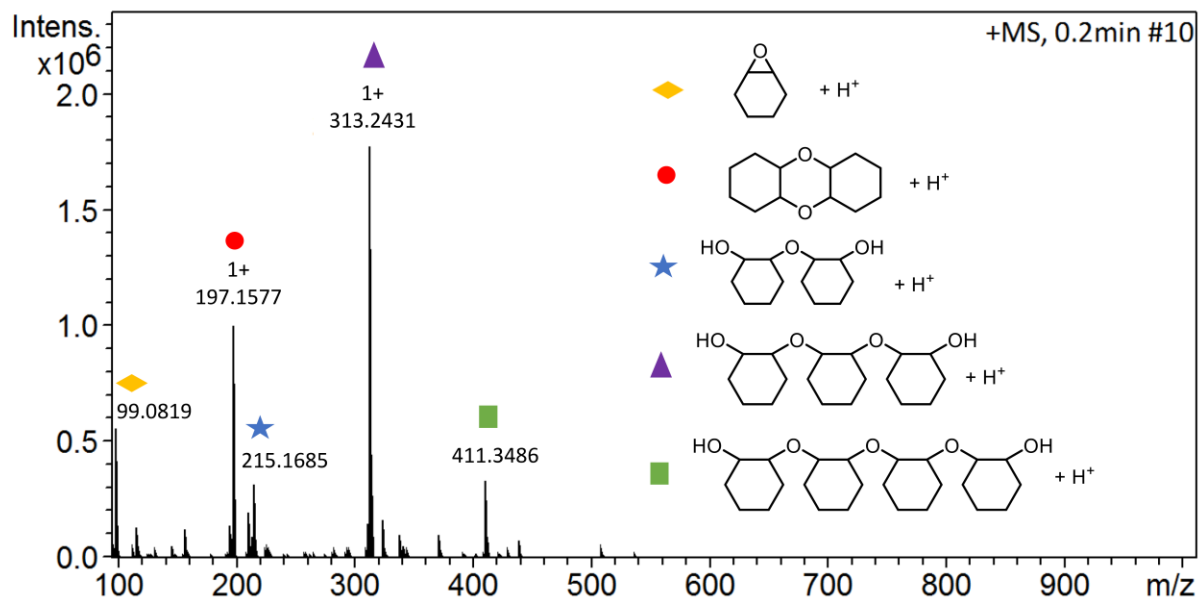
Figure S31. APCI mass spectrum of the hydrolyzed compositions of poly(CHO-*co*-SA) (from Table 1, entry 6) under basic condition at 80 °C for 3days.
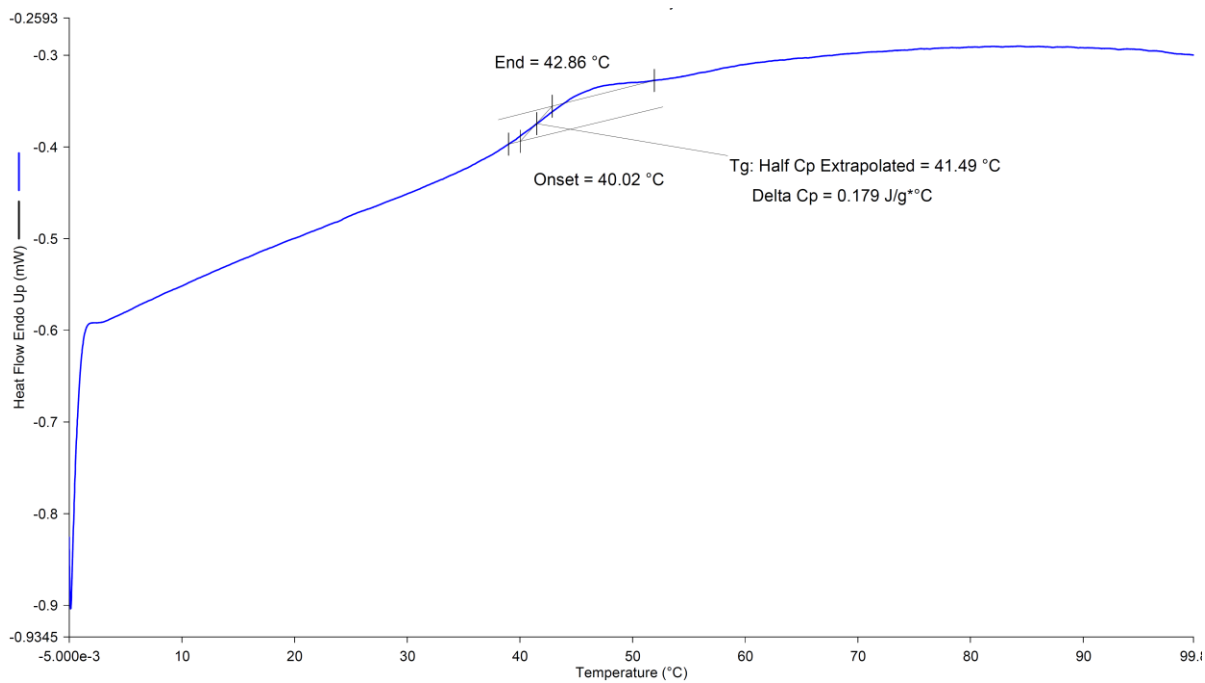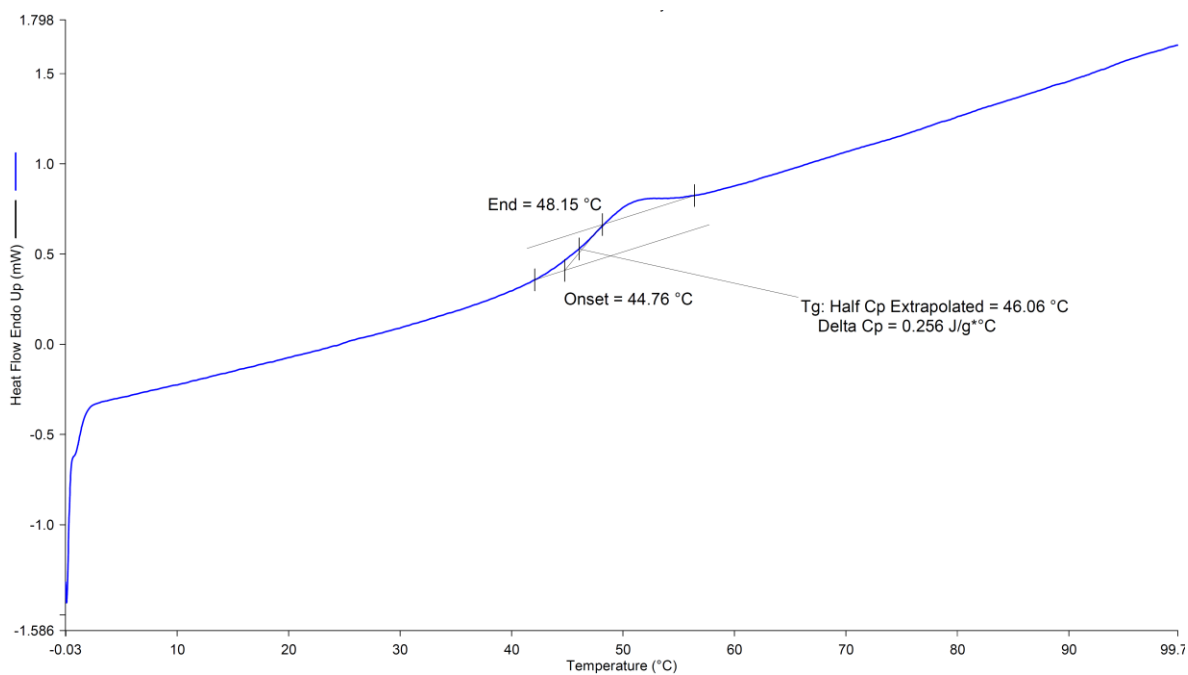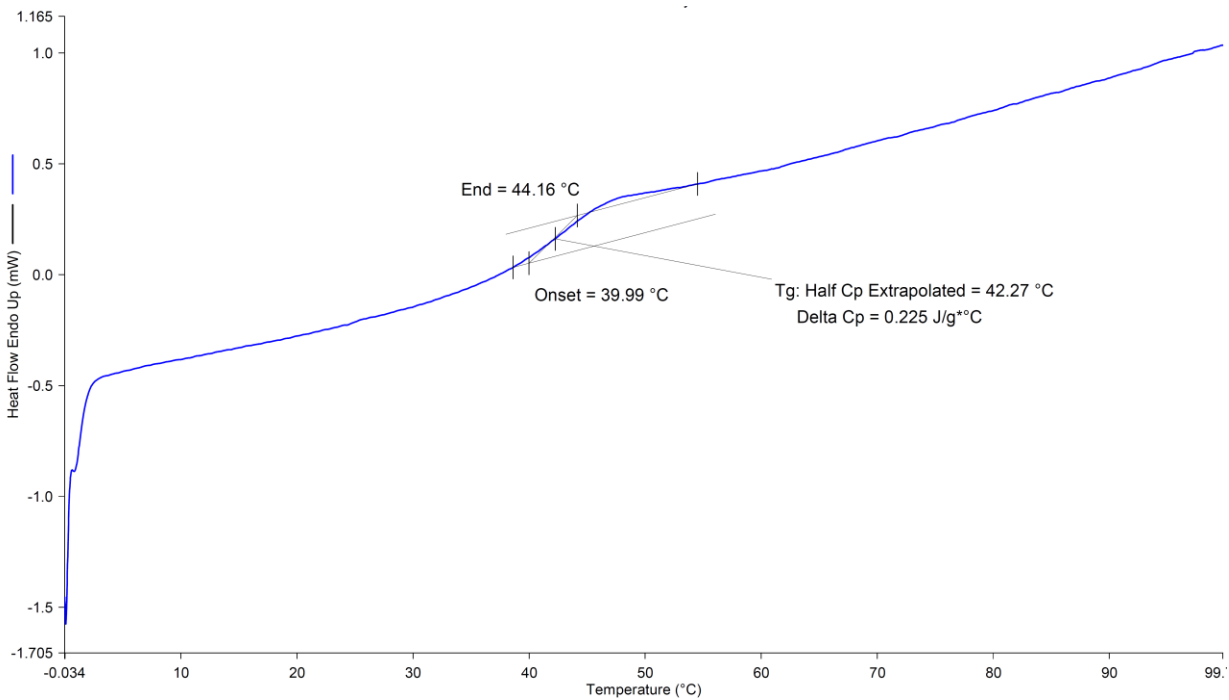
DSC measurements
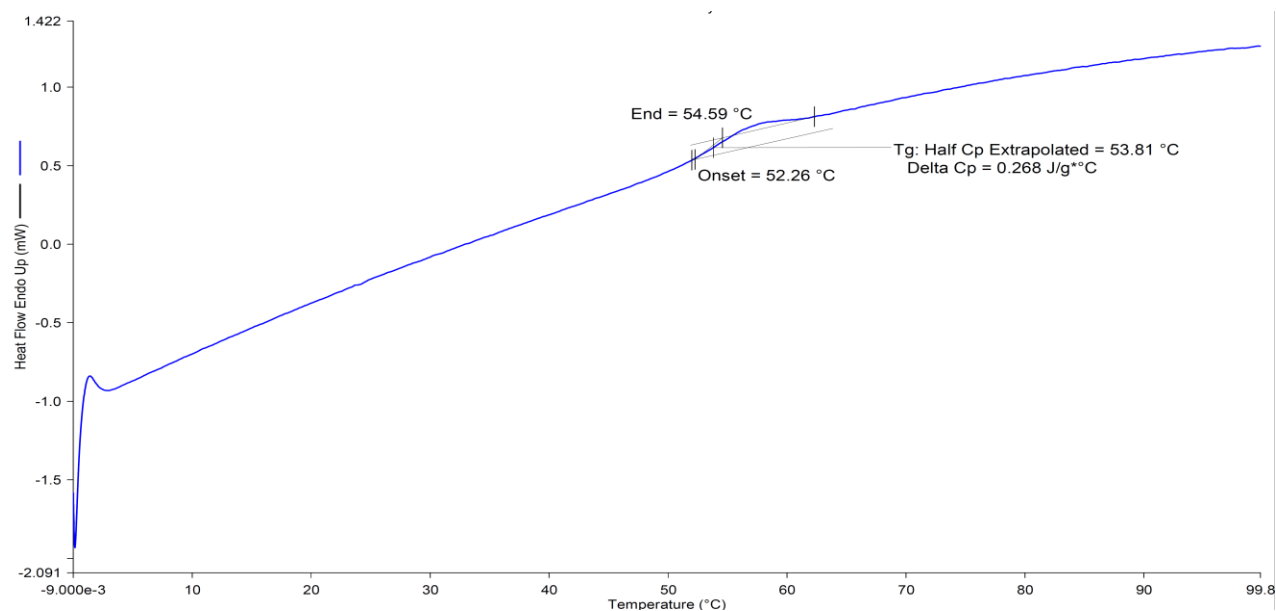
Figure S32. DSC data of polyester from copolymerization of CHO with SA (Table 1, entry 1).
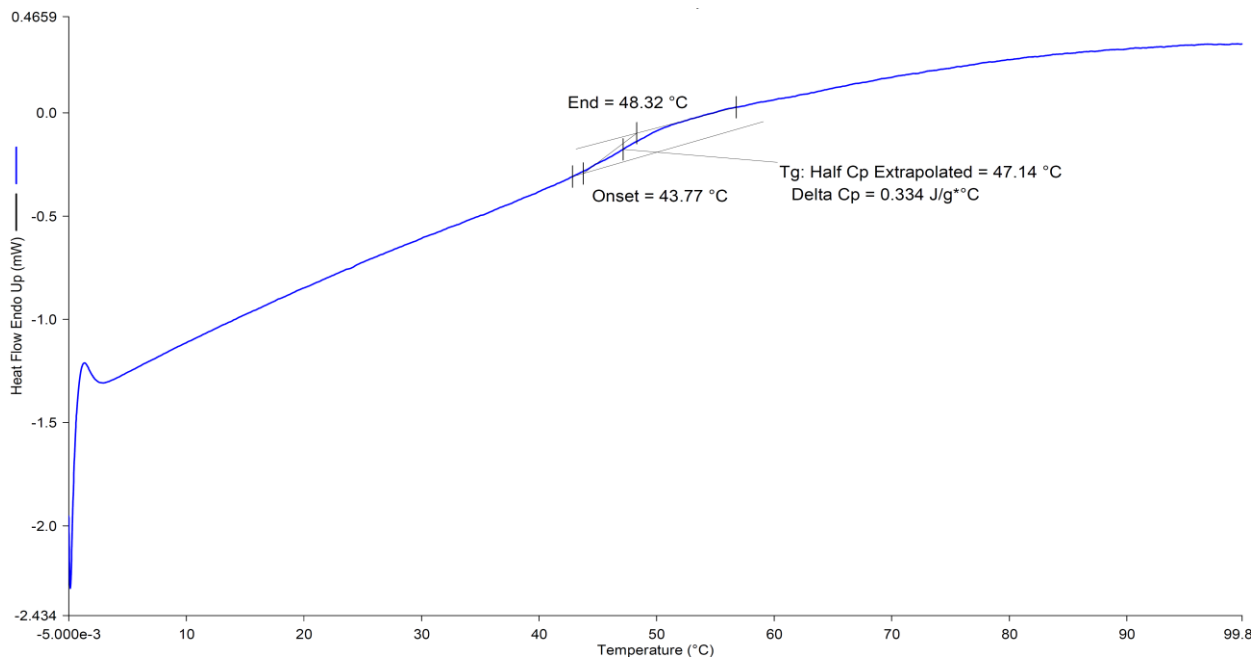
Figure S33. DSC data of polyester from copolymerization of CHO with SA (Table 1, entry 2).
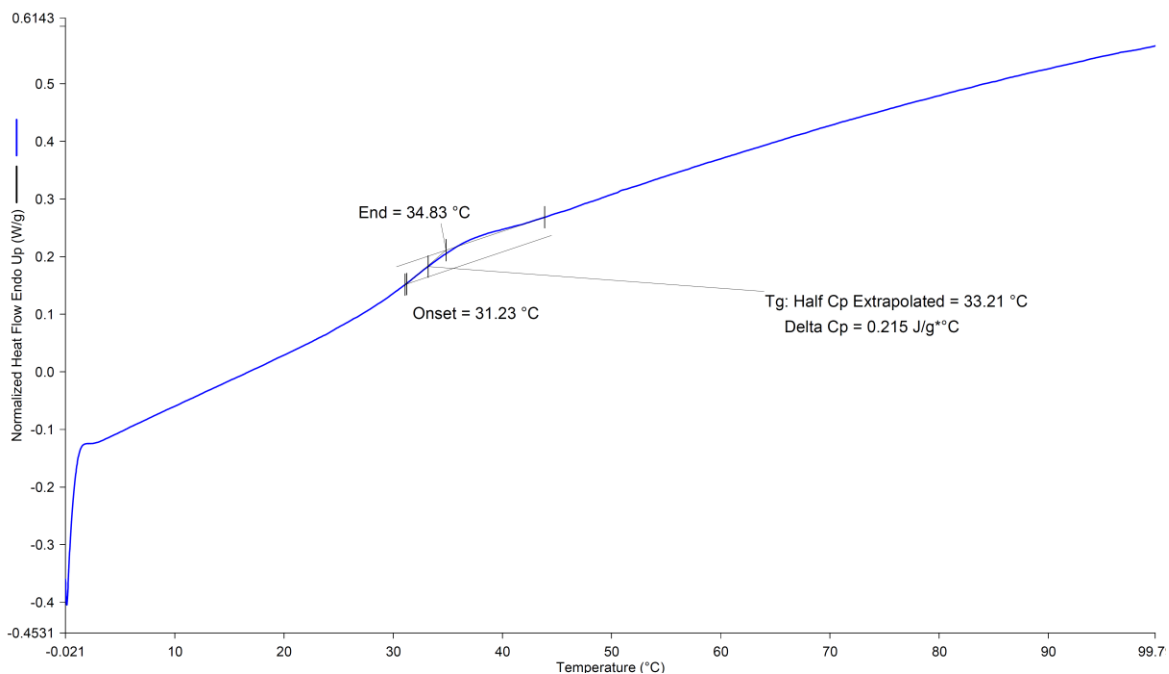
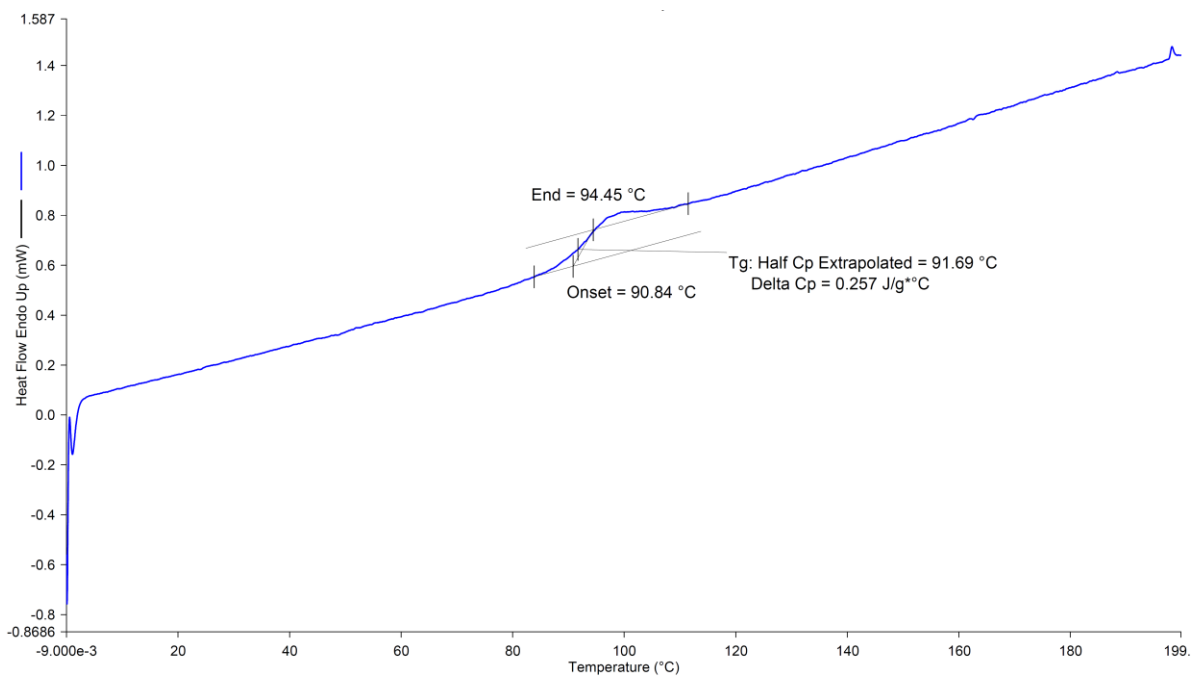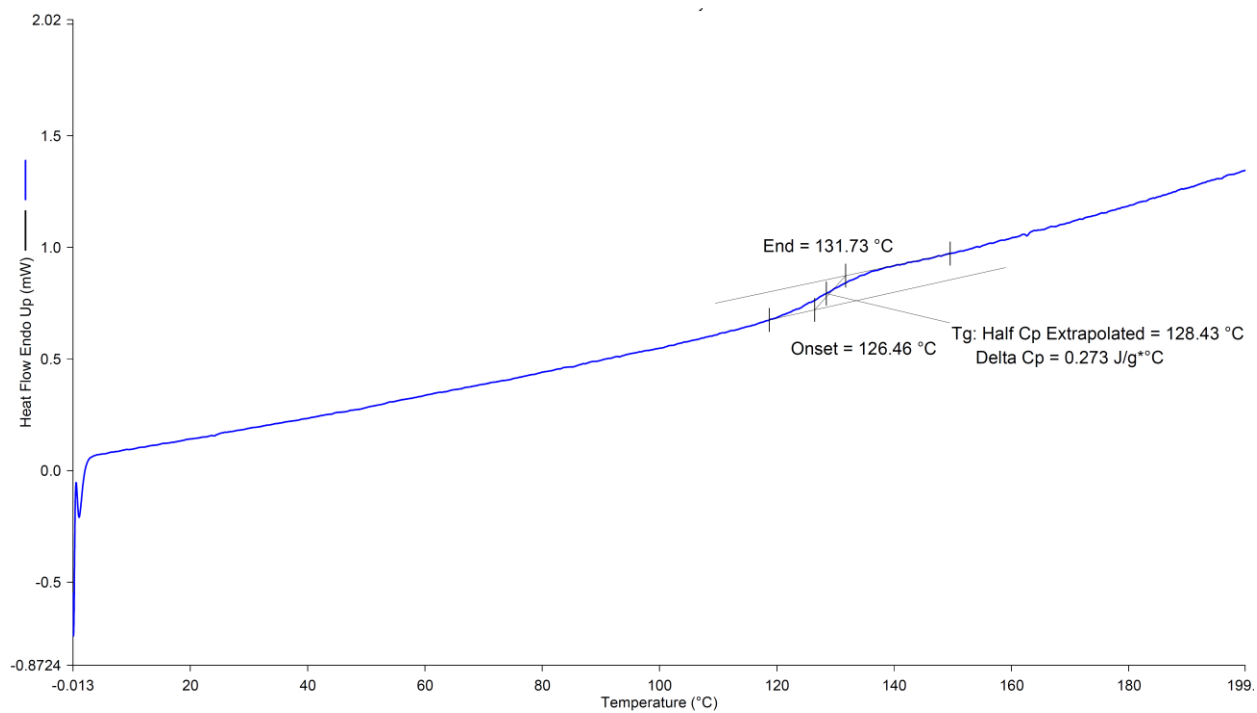**Figure S34**. DSC data of polyester from copolymerization of CHO with SA (Table 1, entry 3).
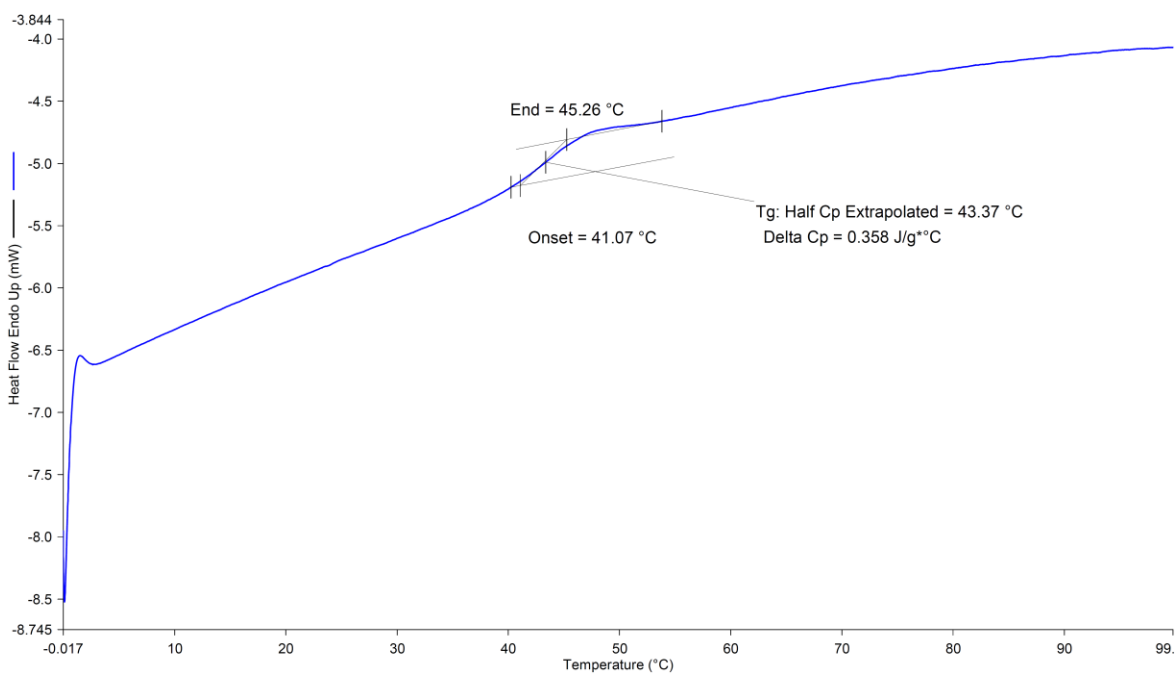
Figure S35. DSC data of polyester from copolymerization of CHO with SA (Table 1, entry 4).
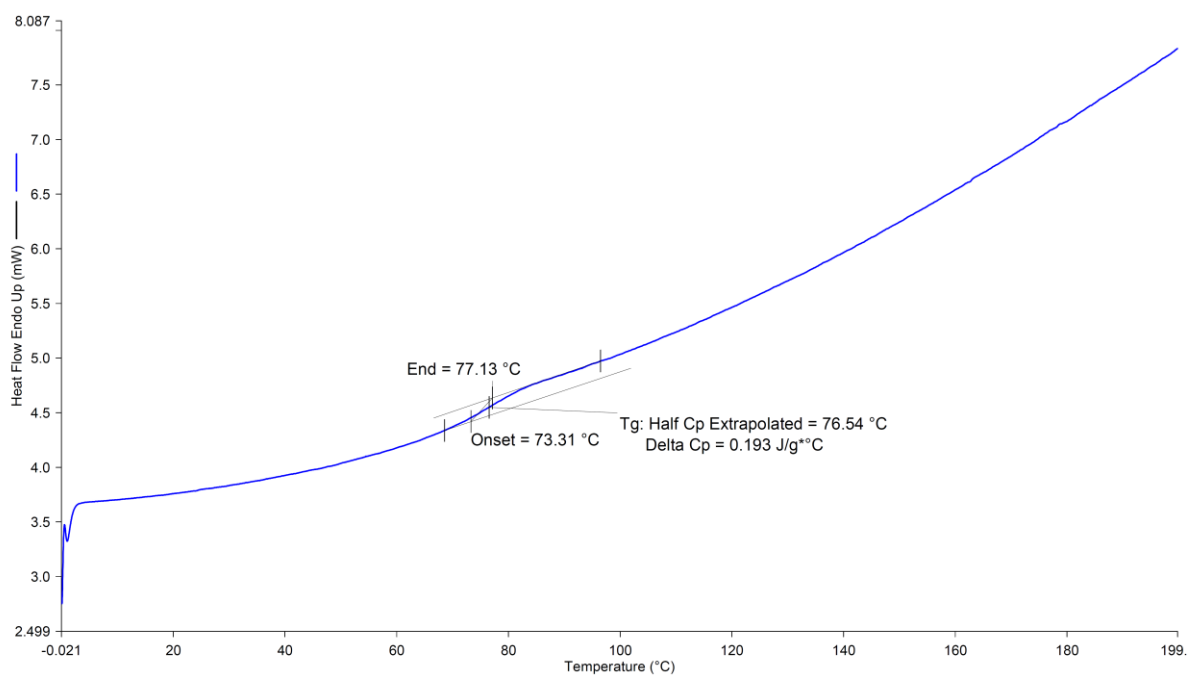
S33
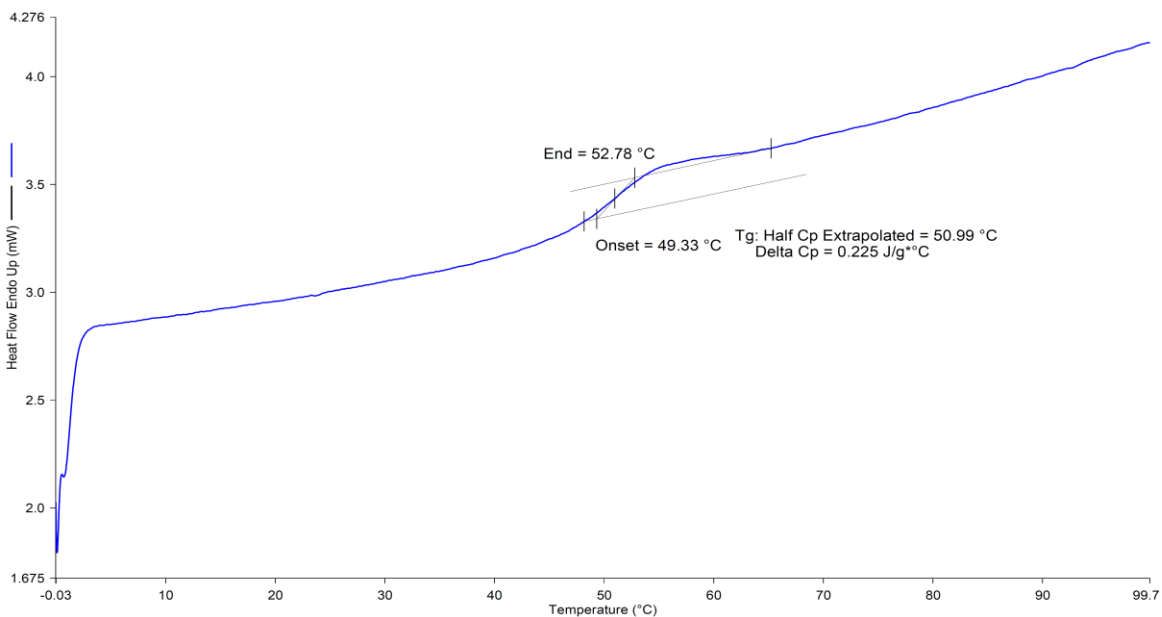
Figure S36. DSC data of polyester from copolymerization of CHO with SA (Table 1, entry 5).
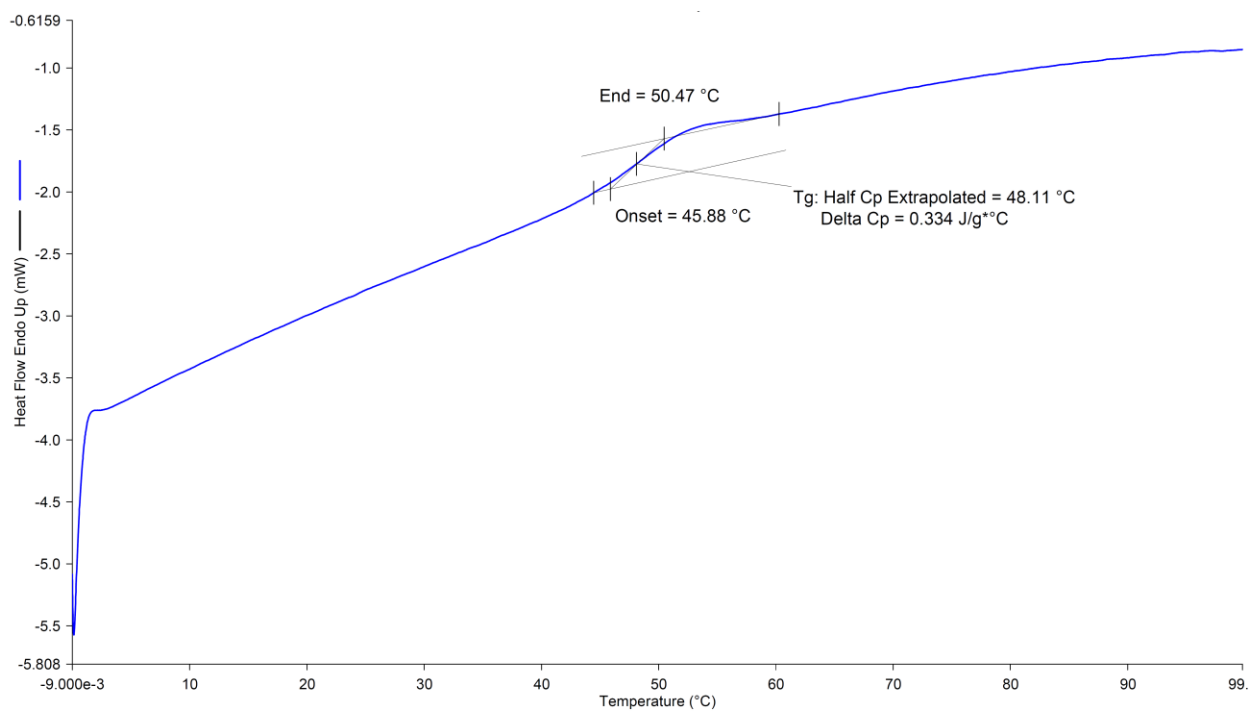
Figure S37. DSC data of polyester from copolymerization of CHO with SA (Table 1, entry 6).
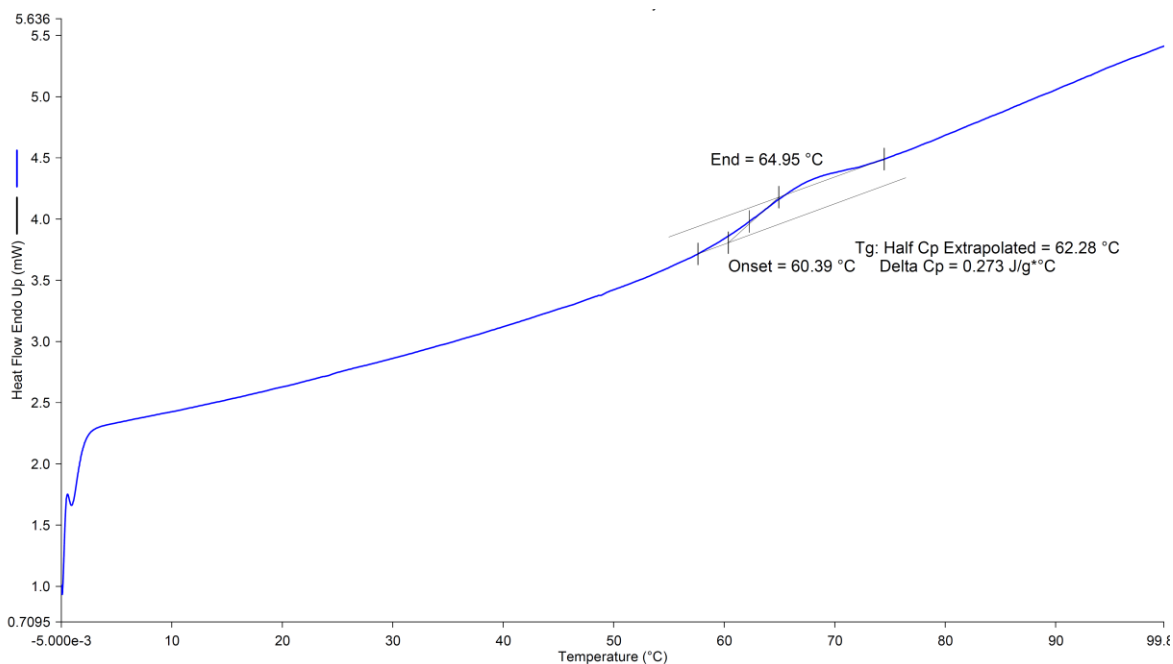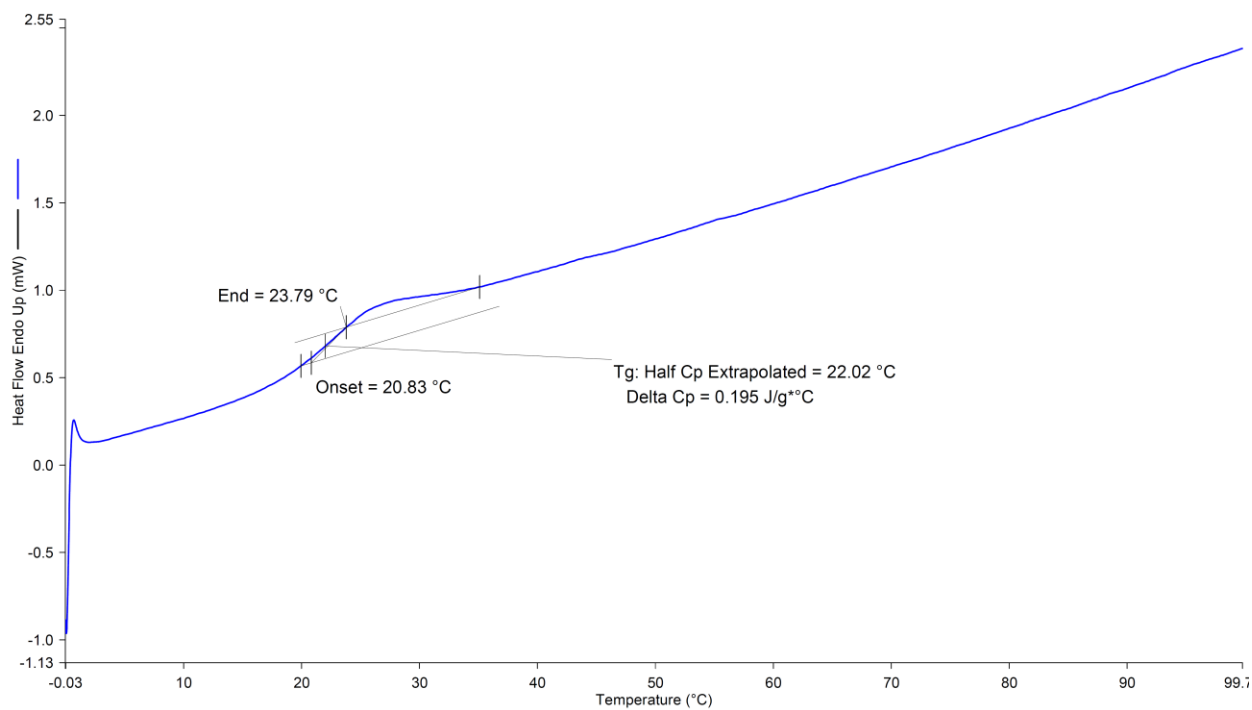
Figure S38. DSC data of polyester from copolymerization of CHO with SA (Table 1, entry 7).

Figure S39. DSC data of polyester from copolymerization of CHO with SA (Table 1, entry 8).

Figure S40. DSC data of polyester from copolymerization of CHO with SA (Table 1 entry 9).
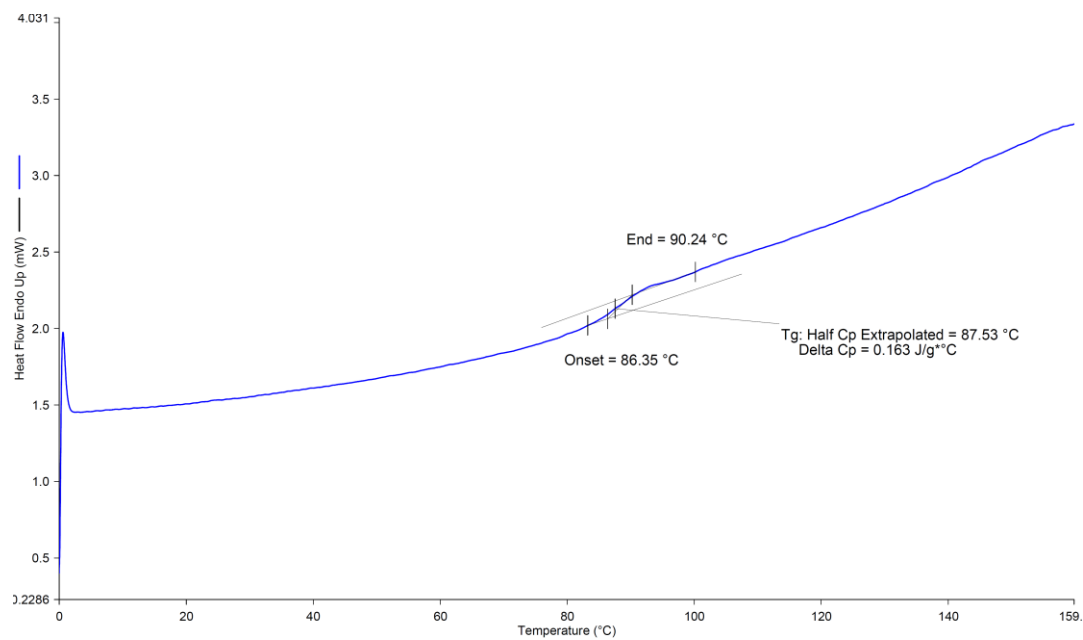

Figure S41. DSC data of polyester from copolymerization of CHO with PA (Table 1, entry 10).

Figure S42. DSC data of polyester from copolymerization of CHO with NA (Table 1, entry 11).

Figure S43. DSC data of polyester from copolymerization of CHO with TBA (Table 1, entry 14).
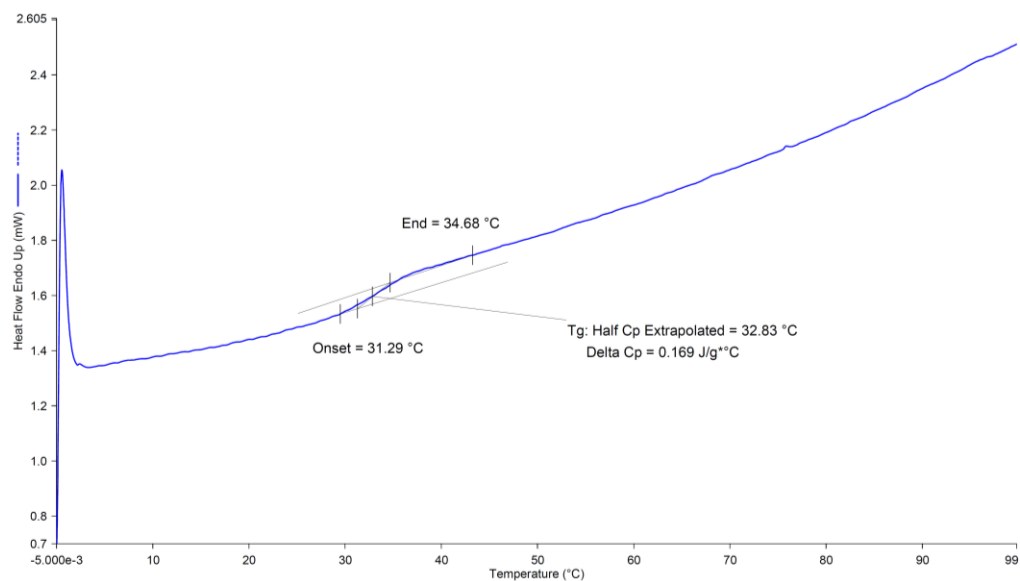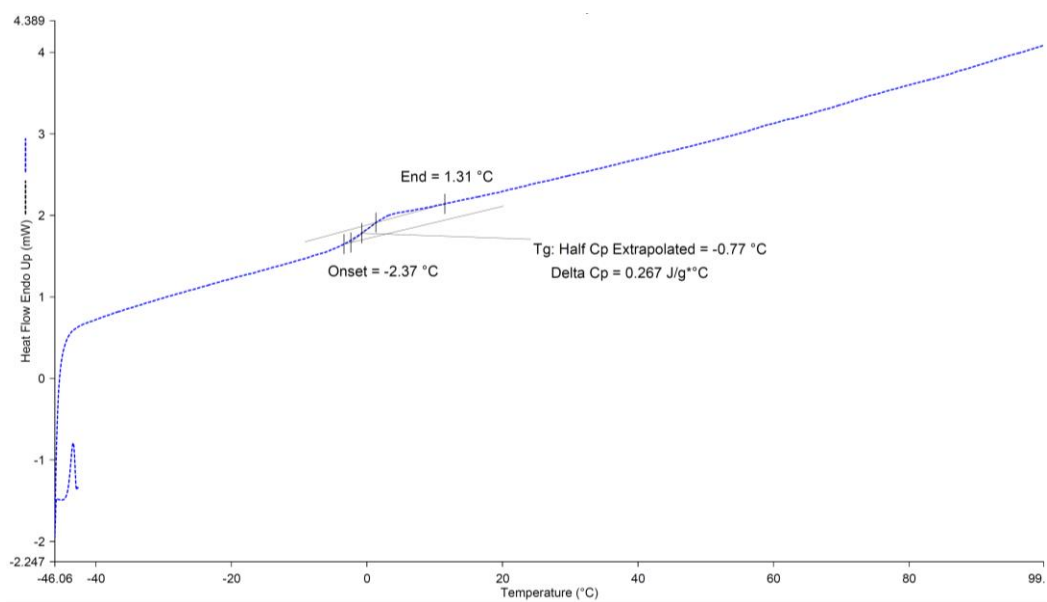
Figure S44. DSC data of polyester from copolymerization of CHO with MA (Table 1, entry 12).

Figure S45. DSC data of polyester from copolymerization of CHO with DGA (Table 1, entry 13).

Figure S46. DSC data of polyester from copolymerization of CHO with PA (Table 1, entry 15).

Figure S47. DSC data of polyester from copolymerization of CPO with PA (Table 1, entry 16).

Figure S48. DSC data of polyester from copolymerization of PO with PA (Table 1, entry 17).

**Table S1**. A kinetic study of the ROCOP of CHO and SA using the condition in Table 1, entry 6.[a]

Time (h)	Average DP of CHO[b]	Average DP of SA[b]	Consumption ratio of CHO and SA[c]
1	24.8	9.4	2.64
2	64.6	23.8	2.72
3	91.1	32.7	2.78
4	106.0	38.0	2.79
5	115.7	41.1	2.81
6	120.0	43.1	2.78
7	125.0	44.6	2.80

[a] $([anh]_0/[CHO]_0/[SnOct_2]_0) = 50/300/1$; $[CHO] = 2.0$ M in toluene at 80 ° C. [b] Determined by ^{1}H NMR spectroscopy. [c] Calculated by DP of CHO/ DP of SA.

Table S2. Polymer molecular weight and dispersity for ROCOP using the condition in Table 1, entry 6.[a]

Time (h)	Conv. of SA (%)[b]	$M_{n,GPC}$ (Da)[c]	$M_{n,NMR}$ (Da)[b]	$Đ$[c]
1	17.0	1036	1340	1.58
2	48.2	1855	2844	1.48
3	68.1	2159	3912	1.52
4	77.5	2366	4290	1.52
5	85.8	2410	4524	1.53

[a] $([anh]_0/[CHO]_0/[SnOct_2]_0) = 50/300/1$; $[CHO] = 2.0$ M in toluene at 80 ° C. [b] Determined by ^{1}H NMR spectroscopy [c] Obtained from GPC analysis using refractive index (RI) detector.
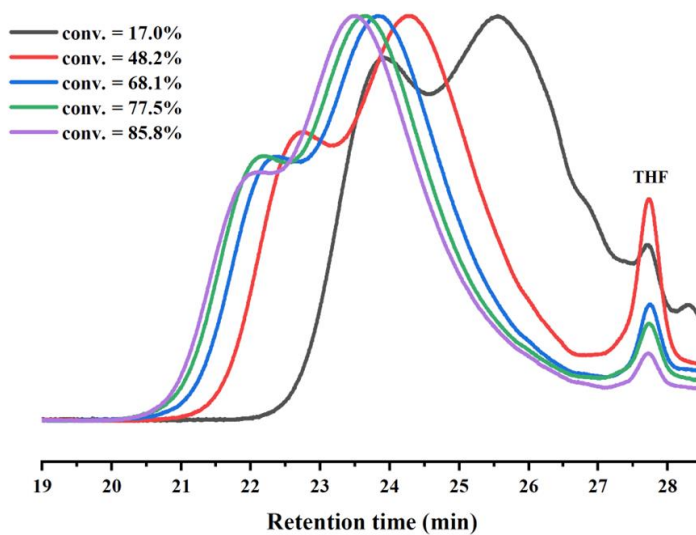
Figure S49 GPC traces of polymers at different conversions of SA reported in Table S2.

Kinetic analysis

- Rate dependence on cyclic anhydride

Table S3. Kinetic studies for determination of dependence on SA concentration.

Entry	[CHO] (M)	[SA] (M)	[Catalyst] (M)	Initial rates (mM s^{-1})
1	2.0	0.165	0.0067	0.00904
2	2.0	0.22	0.0067	0.01028
3	2.0	0.275	0.0067	0.01378
4	2.0	0.33	0.0067	0.01566

- Rate dependence on epoxide

Table S4. Kinetic studies for determination of dependence on CHO concentration.

Entry	[CHO] (M)	[SA] (M)	[Catalyst] (M)	Initial rates (mM s^{-1})	ln(Initial rates) (mM s^{-1})	ln([CHO]) (M)
1	1.33	0.33	0.0067	0.00774	-4.8614	0.285179
2	1.67	0.33	0.0067	0.01180	-4.4394	0.512824
3	2.00	0.33	0.0067	0.01566	-4.1569	0.693147
4	2.33	0.33	0.0067	0.02352	-3.7500	0.845868

- Rate dependence on catalyst

Table S5. Kinetic studies for determination of dependence on SnOct$_2$ concentration

Entry	[CHO] (M)	[SA] (M)	[Catalyst] M	Initial rates (mM s^{-1})
1	2.0	0.33	0.0033	0.00583
2	2.0	0.33	0.0067	0.01566
3	2.0	0.33	0.01	0.04531
4	2.0	0.33	0.0134	0.06714

Note: The aliquots of crude product were monitored by ^{1}H NMR spectroscopy to calculate a conversion. The initial rates were determined when conversions of SA were less than 20%.

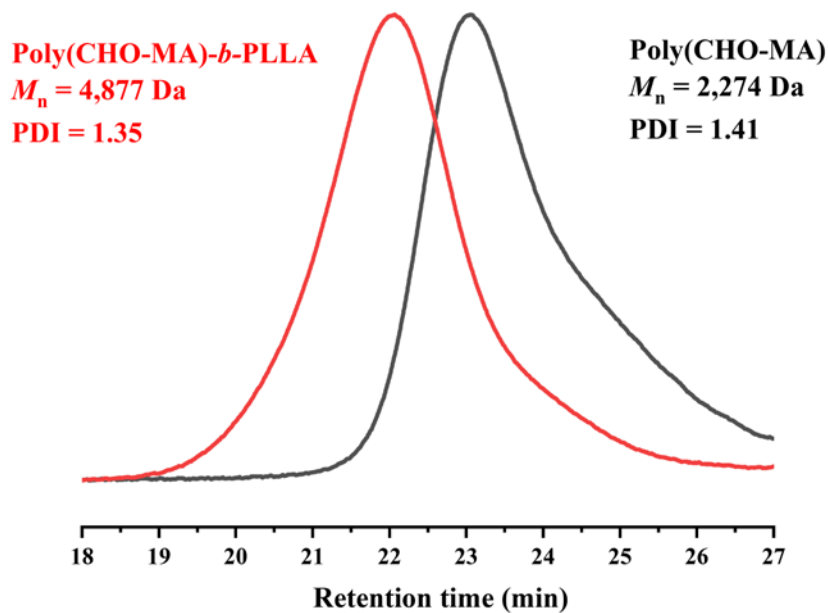## 2.2 Sequential terpolymerization with *L*-LA

Poly(CHO-MA)-*b*-PLLA
M_n = 4,877 Da
PDI = 1.35

Poly(CHO-MA)
M_n = 2,274 Da
PDI = 1.41

Figure 50. GPC traces (flow rate of 1.0 mL min^{-1} at 35 °C in THF) of poly(CHO-MA) and poly(CHO-MA)-*b*-PLLA from copolymerization of MA, CHO, and *L*-LA using refractometric (RI) detector.

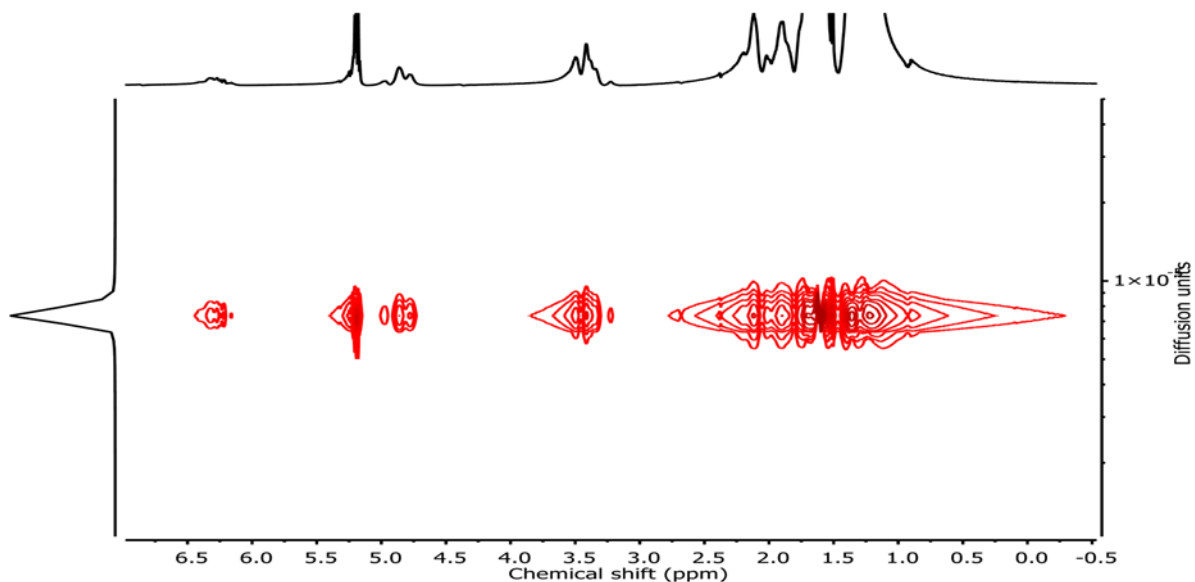**Figure 51**. DOSY NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of sequential terpolymerization of MA, CHO and *L*-LA using a SA/CHO/ *L*-LA /SnOct$_2$ molar ratio of 50:300:50:1 and [CHO]$_0$ = 2.0 M at 80 °C.
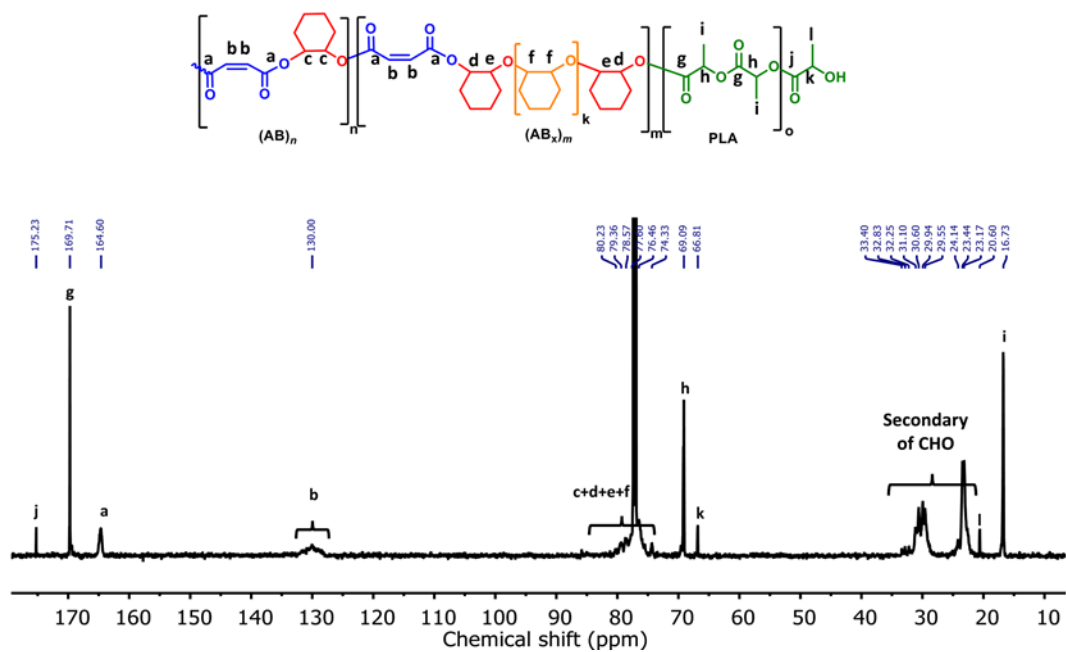
Figure S52. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of the terpolymer from ROCOP of MA and CHO followed by sequential addition of L-LA.
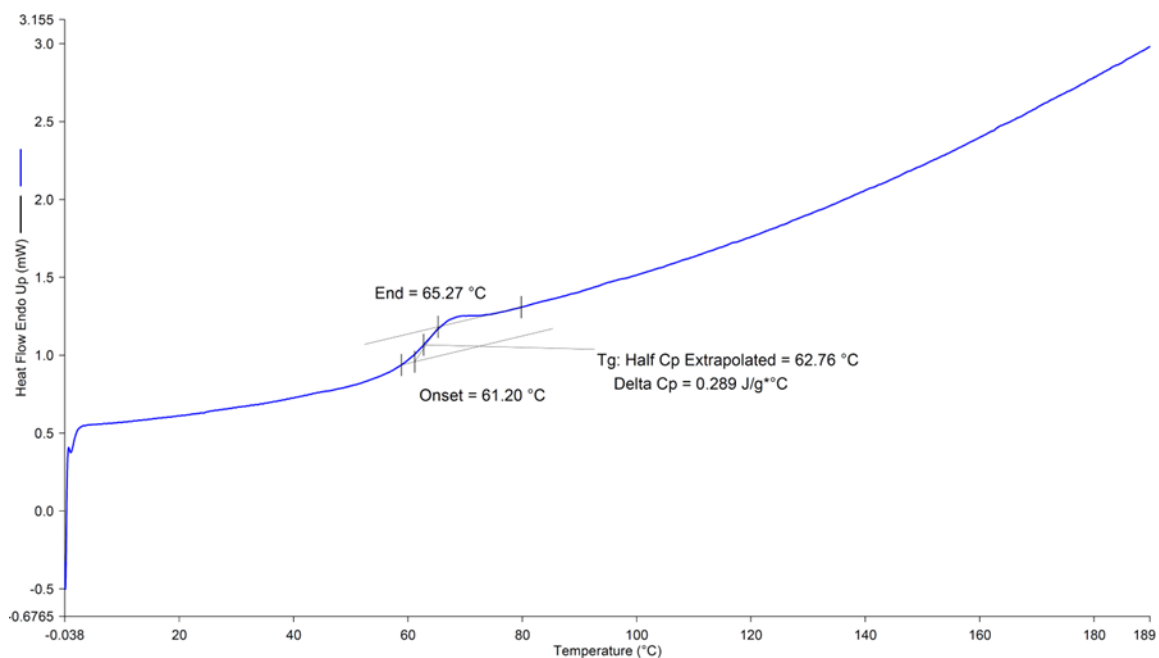
Figure S53. DSC data of the terpolymer from ROCOP of MA and CHO followed by sequential addition of L-LA.

2.3 The synthesis of poly(ester-ether)-based polyurethane
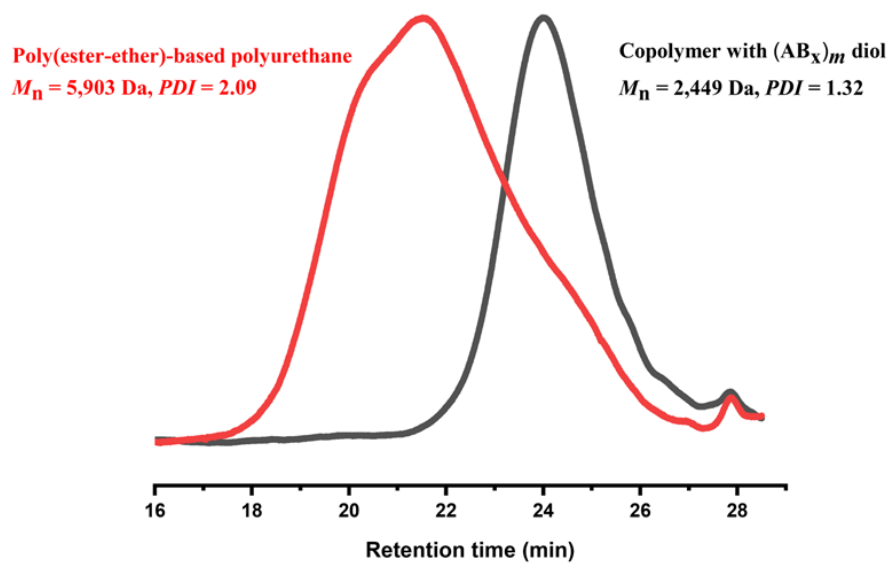
Figure S54. GPC traces (flow rate of 1.0 mL min^{-1} at 35 °C in THF) of copolymer with $(AB_x)_m$ diol and poly(ester-ether)-based polyurethane using refractometric (RI) detector.
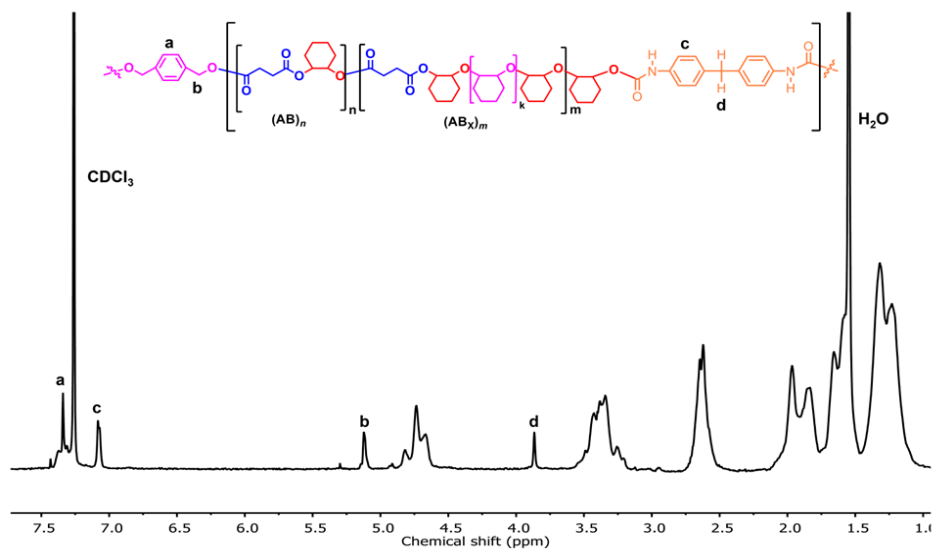
Figure S55. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the resulting poly(ester-ether)-based polyurethane
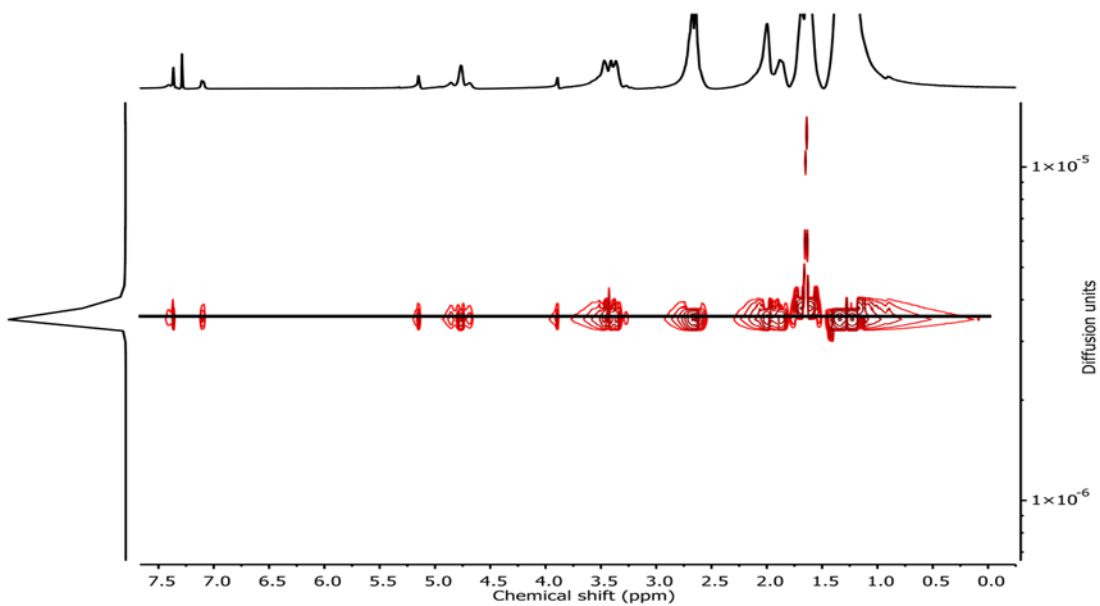
Figure 56. DOSY NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the resulting poly(ester-ether)-based polyurethane.
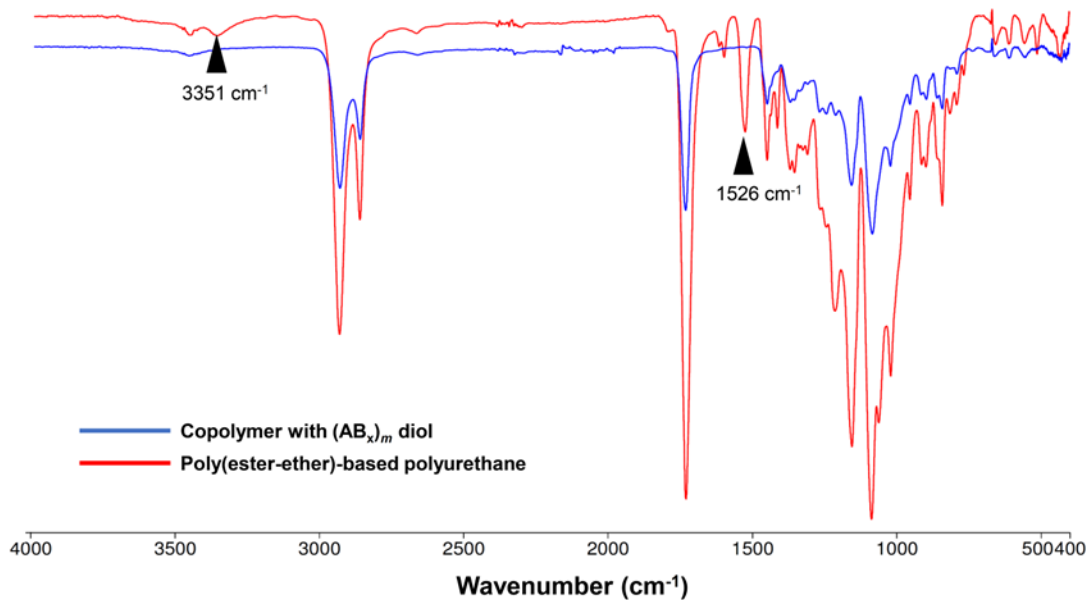
Figure S57. FT IR spectra of the copolymer with (AB$_x$)$_m$ diol (blue line) and the obtained poly(ester-ether)-based polyurethane (red line).

2.4 Copolymerization of CHO, cyclic anhydrides, and THF or 1,4-dioxane by tin(II) octanoate

Table S6. Starting molecular weight and components of poly(ester-ether) in the degradation test.

Entry	Polymers	Polymer selectivity for THF or OX (%) [a]	Component (%) [a]	$M_{n,GPC}$ (Da) [b]
			$(AB)_n/(AB_x)_m/(AB_xC)_o/ x_{av}$	
1	Poly(PA-*alt*-CHO)	-	100/-/-/-	6,100
2	Poly(PA-*co*-CHO);(AB$_{3.3}$)	-	3/97/-/3.3	6,578
3	Poly(PA/CHO/OX)	11	8/81/11/2.7	4,438
4	Poly(PA/CHO/THF)	73	4/23/73/2.5	6,200

[a]Determined by ^{1}H NMR spectroscopy (see ESI) [b]Obtained from GPC analysis using refractive index (RI) detector.
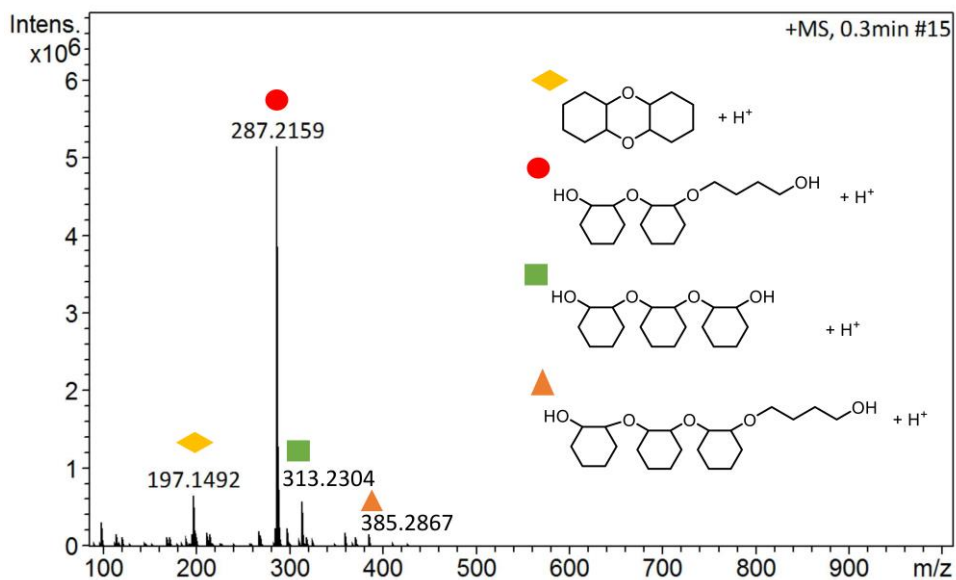
Figure S58. APCI mass spectrum of the hydrolyzed compositions of poly(PA/CHO/THF) (from Table S6, entry 4) under basic condition at 70 °C for 4 days.

NMR spectrum of SA/CHO/THF copolymers
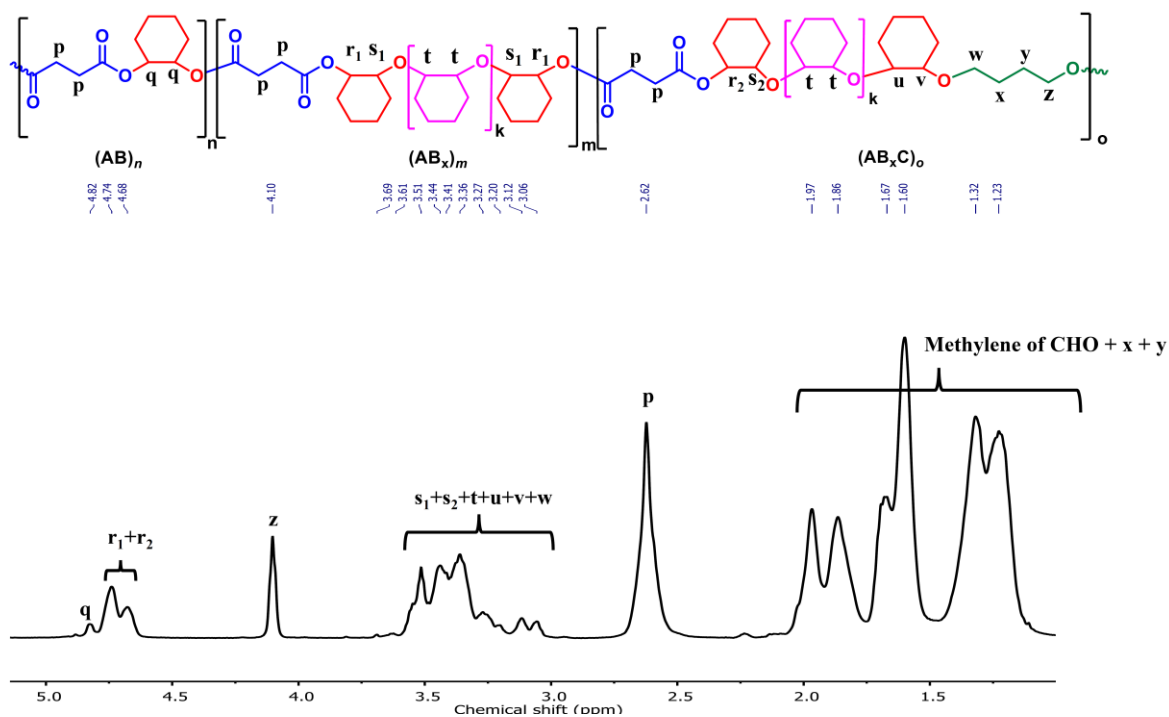
Figure S59. ¹H NMR spectrum (600 MHz, CDCl₃, 30 °C) of the copolymer from ROCOP of SA, CHO and THF using a SA/CHO/THF/SnOct₂ molar ratio of 50:150:150:1 (Table 2, entry 3).
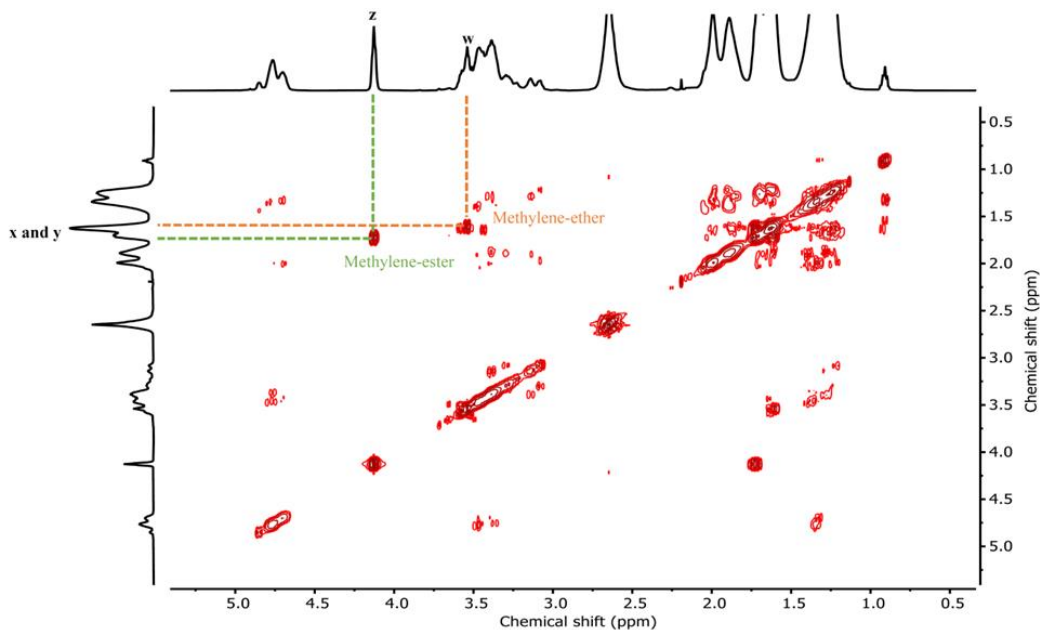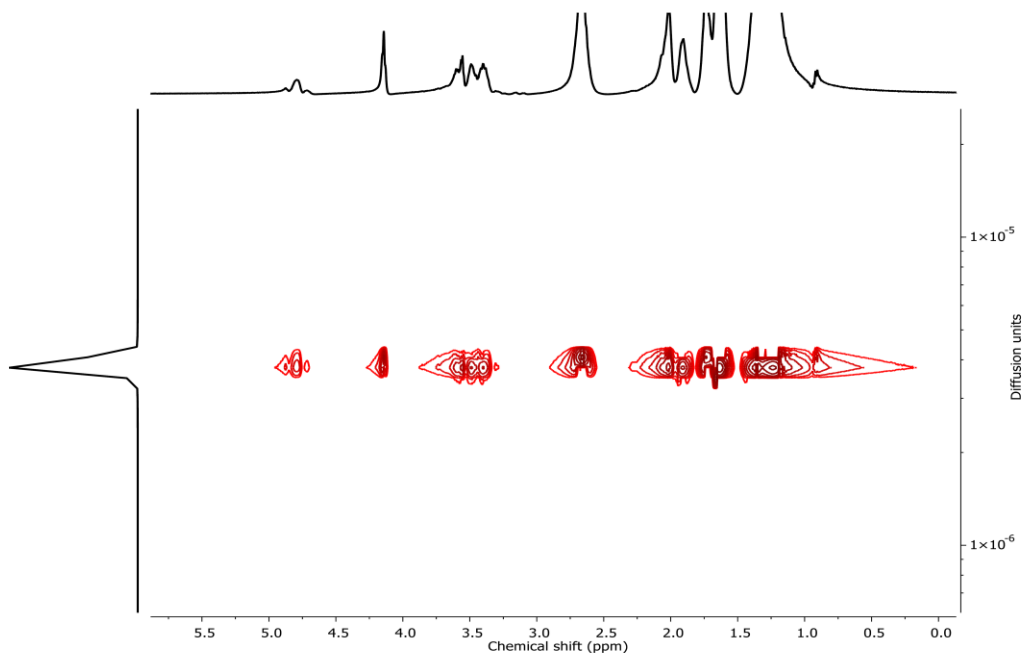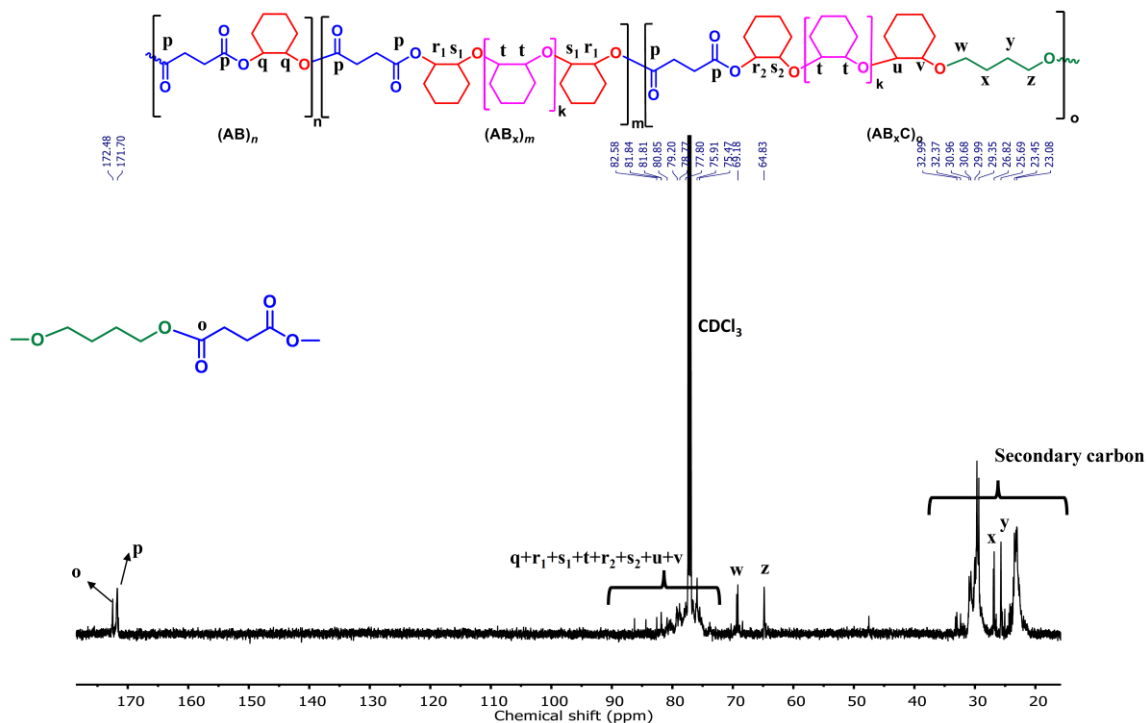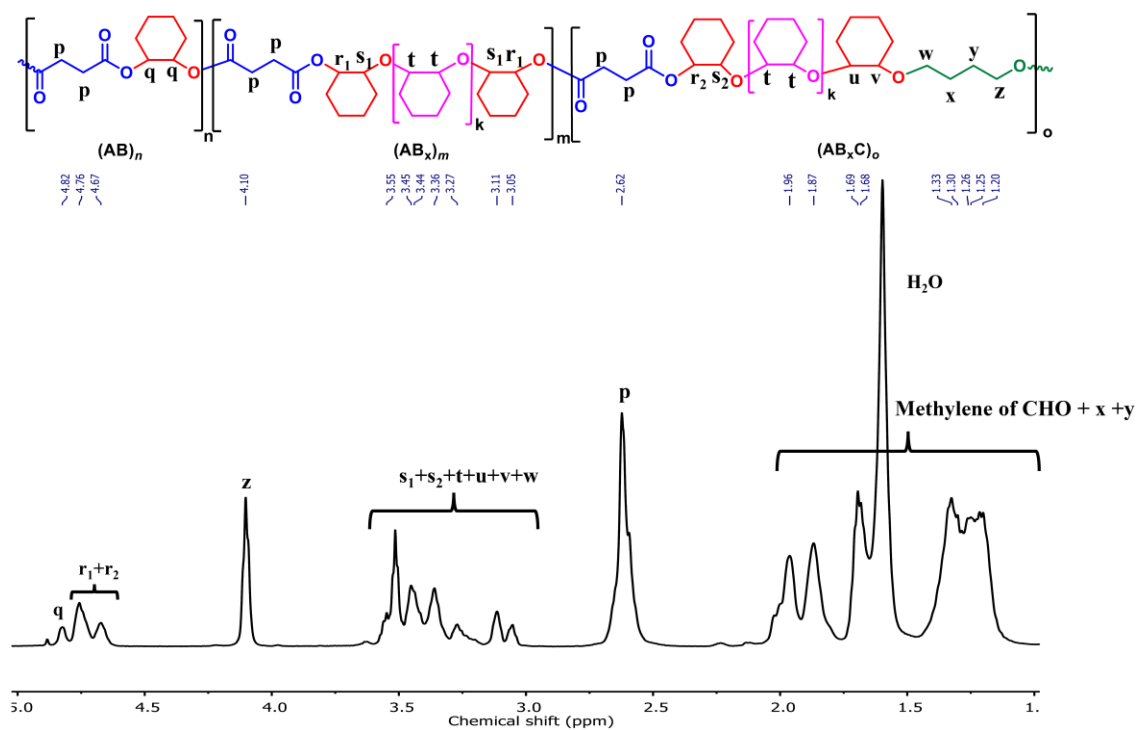

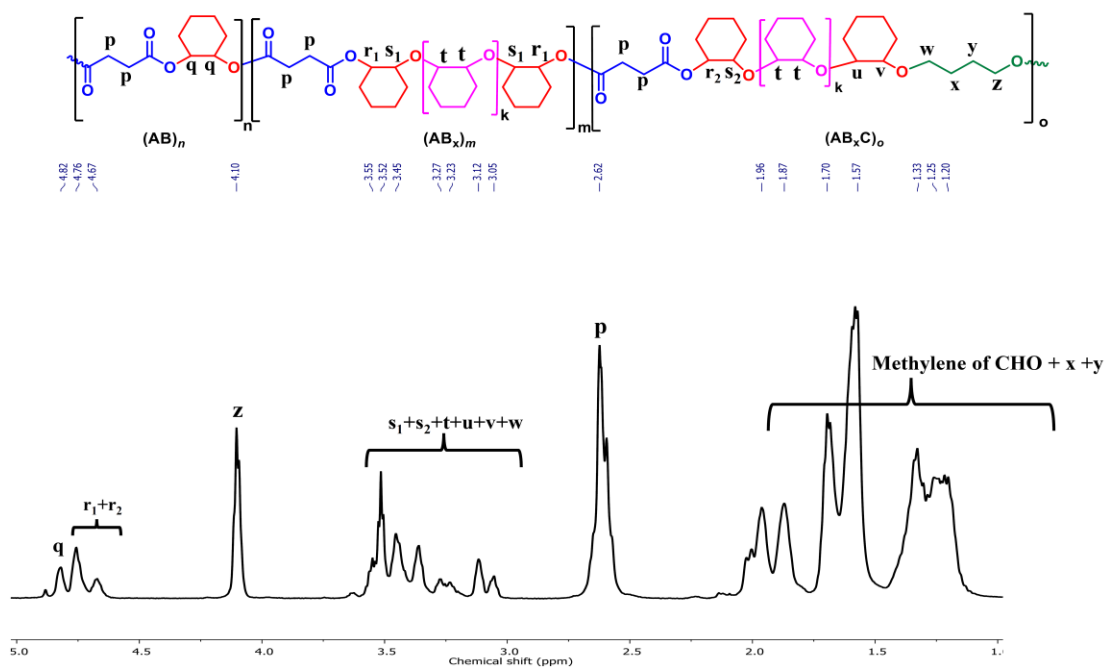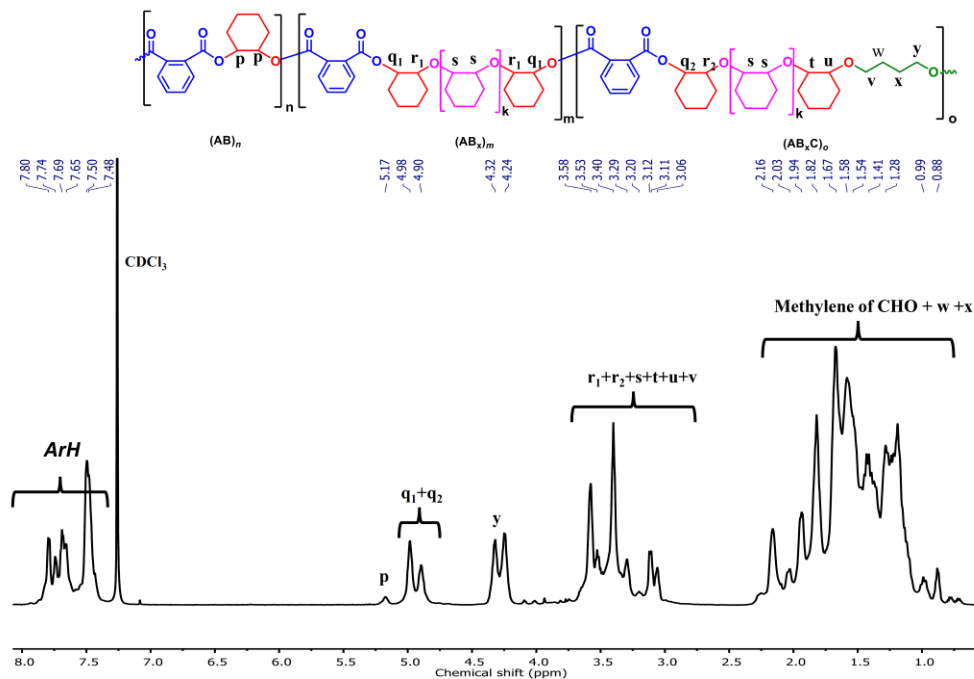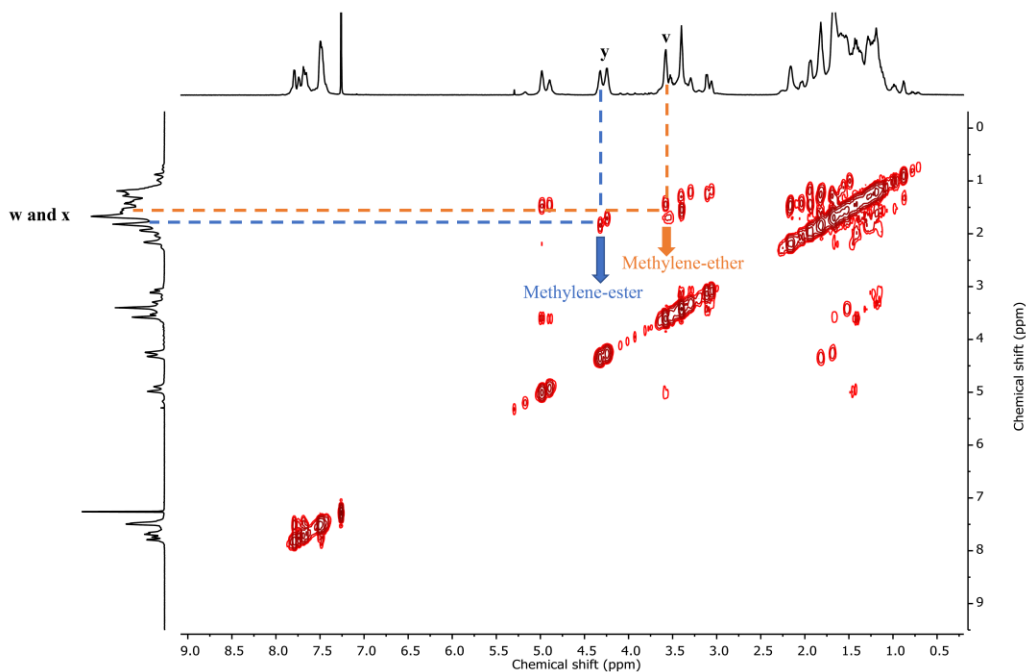**Figure S60**. COSY-NMR spectrum (600 MHz, CDCl₃, 30 °C) of the copolymer from ROCOP of SA, CHO and THF using a SA/CHO/THF/SnOct₂ molar ratio of 50:150:150:1 (Table 2, entry 3).

Figure S61. DOSY-NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA, CHO and THF using a SA/CHO/THF/SnOct$_2$ molar ratio of 50:150150:1 (Table 2, entry 3).

Figure S62. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA, CHO and THF using a SA/CHO/THF/SnOct$_2$ molar ratio of 50:150:150:1 (Table2, entry 3).

Figure S63. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA, CHO and THF using a SA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 4).
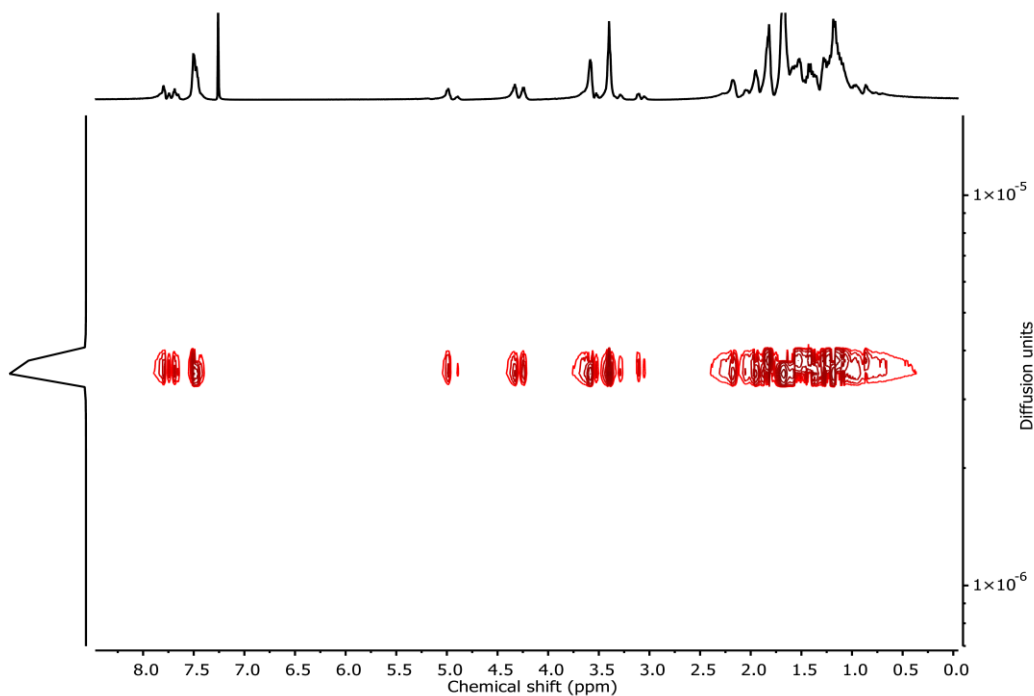

Figure S64. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA, CHO and THF using a SA/CHO/THF/SnOct$_2$ molar ratio of 50:150:3000:1 (Table 2, entry 5).
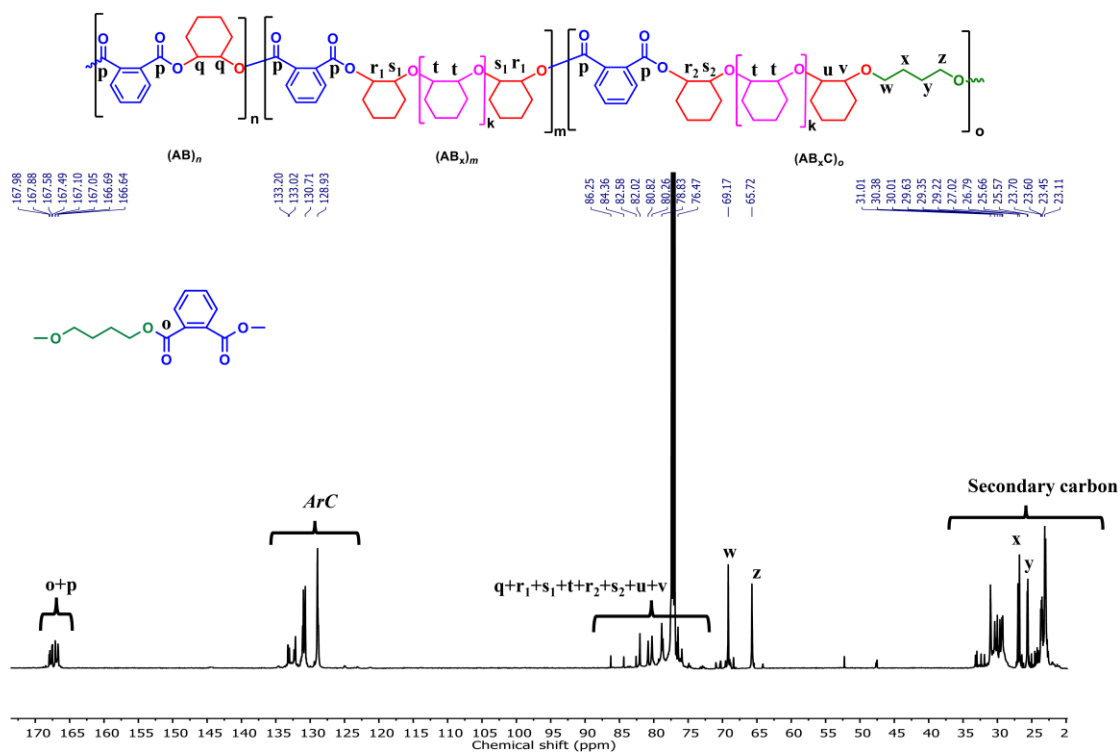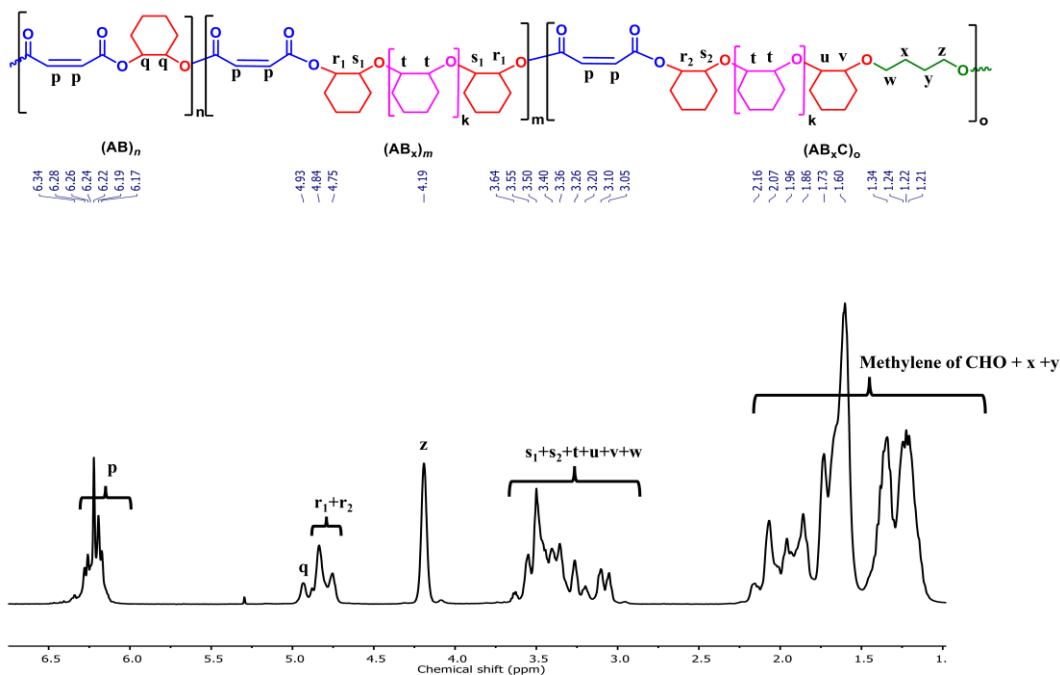
NMR spectrum of PA/CHO/THF copolymer

Figure S65. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of PA, CHO and THF using a PA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 6).

Figure S66. COSY-NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of PA, CHO and THF using a PA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 6).

Figure S67. DOSY-NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of PA, CHO and THF using a PA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 6).

Figure S68. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of PA, CHO and THF using a PA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 6).
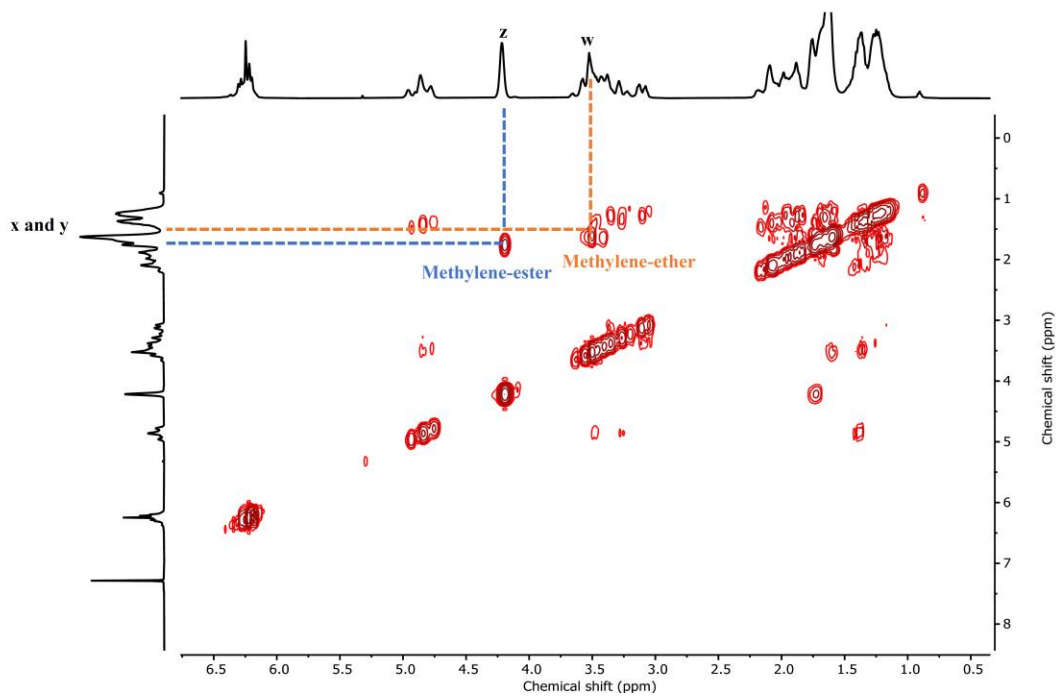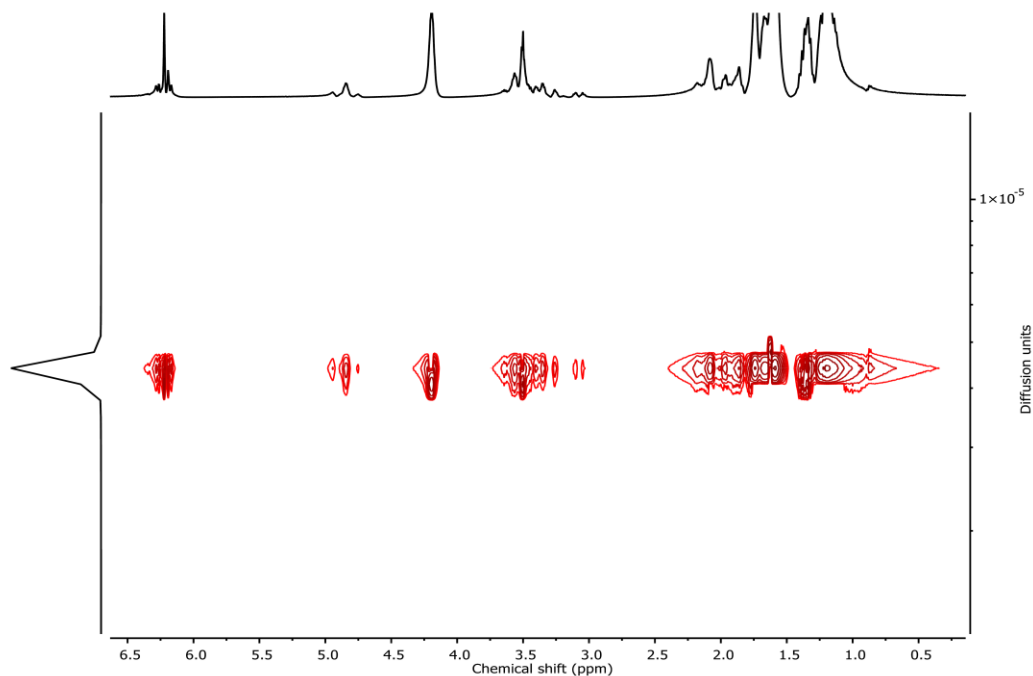
S52

NMR spectrum of MA/CHO/THF copolymer

Figure S69. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of MA, CHO and THF using a MA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 7).
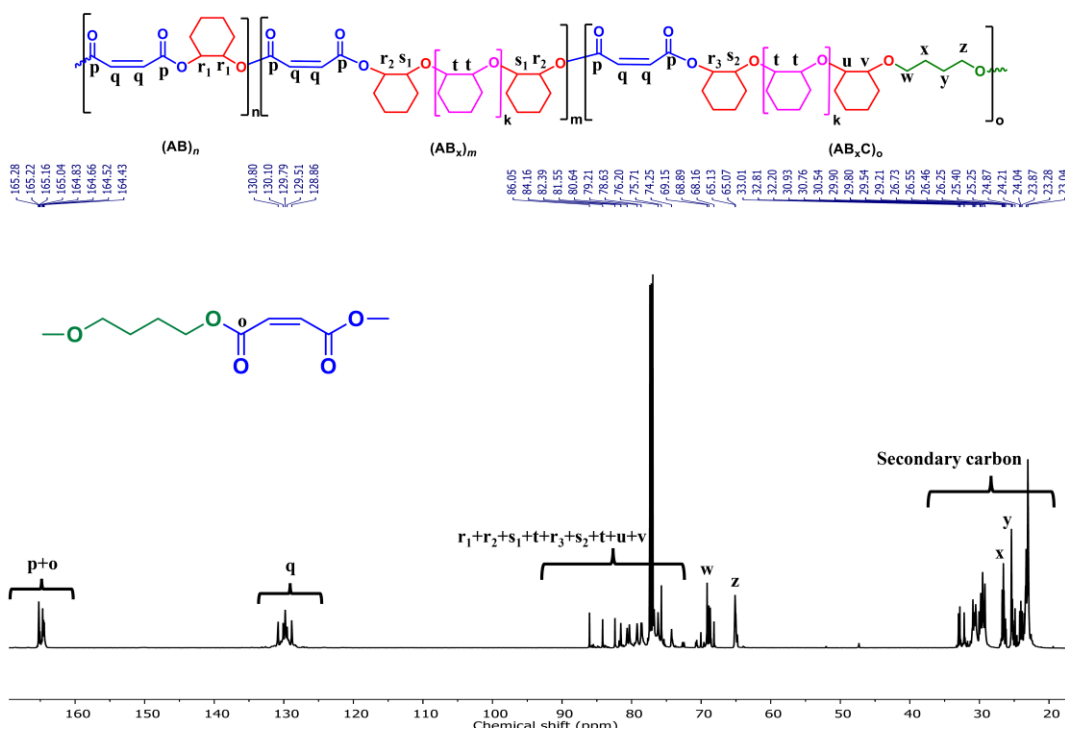

Figure S70. COSY-NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of MA, CHO and THF using a MA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 7).

Figure S71. DOSY-NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of MA, CHO and THF using a MA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 7).

.

Figure S72. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of MA, CHO and THF using a MA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 7).

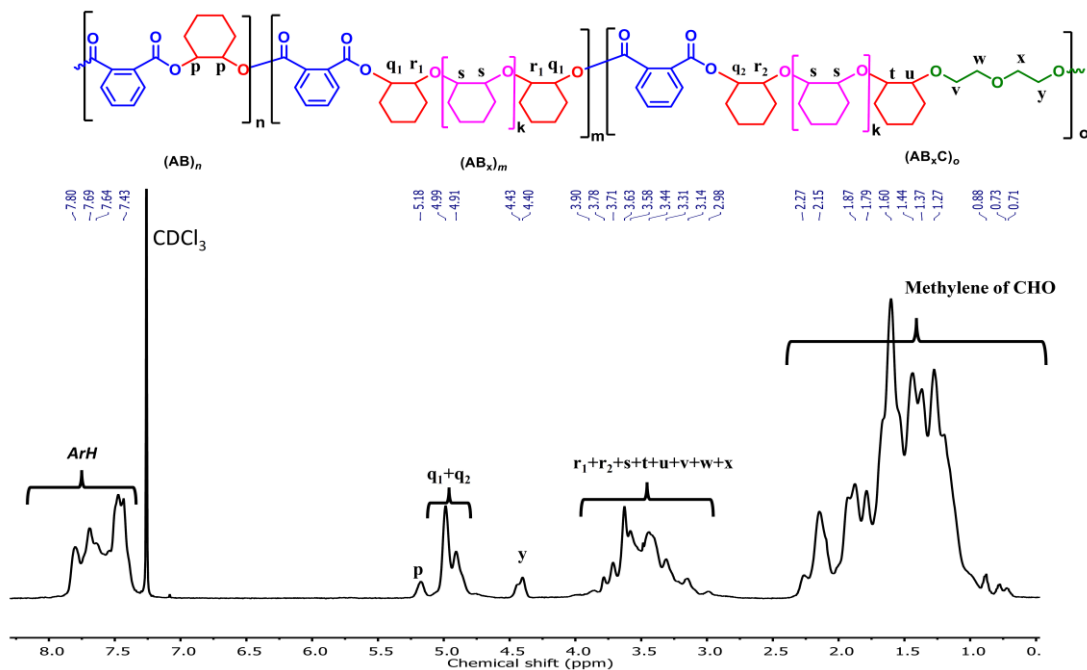# NMR spectrum of PA/CHO/1,4-dioxane copolymers

Figure S73. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of PA, CHO and 1,4-dioxane using a PA/CHO/1,4-dioxane/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 8).
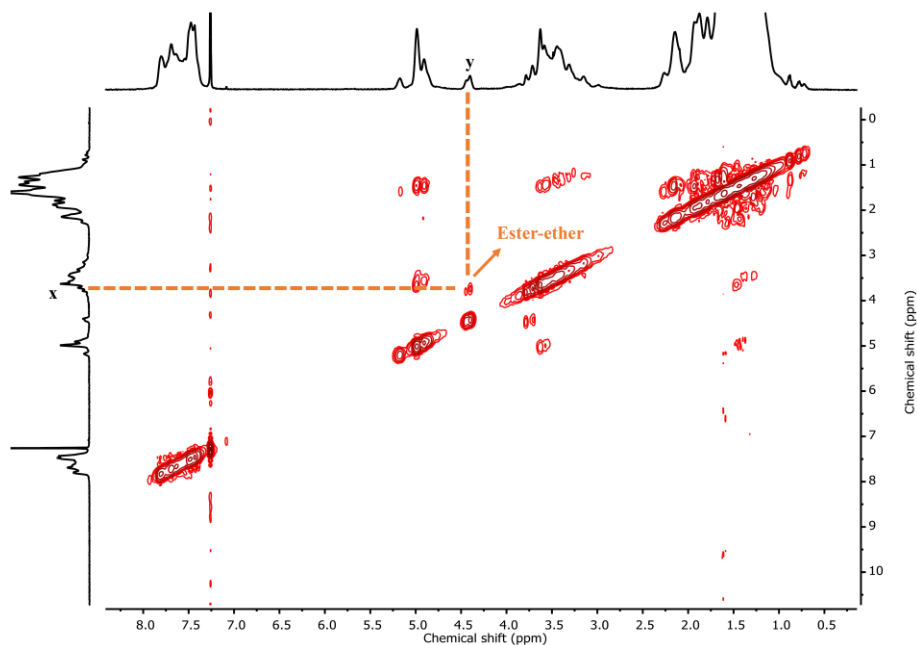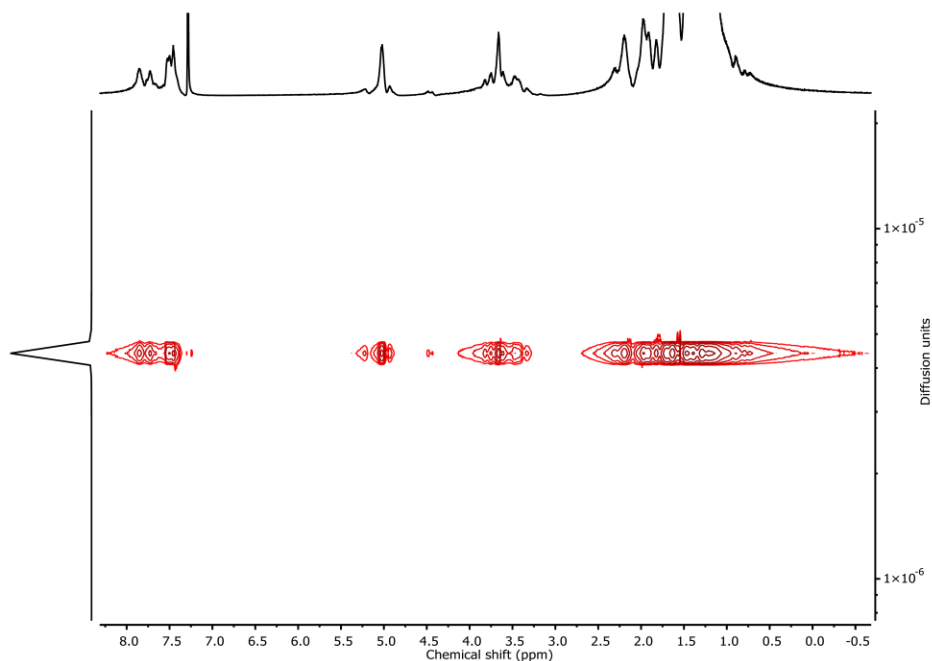

Figure S74. COSY-NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of PA, CHO and 1,4-dioxane using a PA/CHO/1,4-dioxane/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 8).
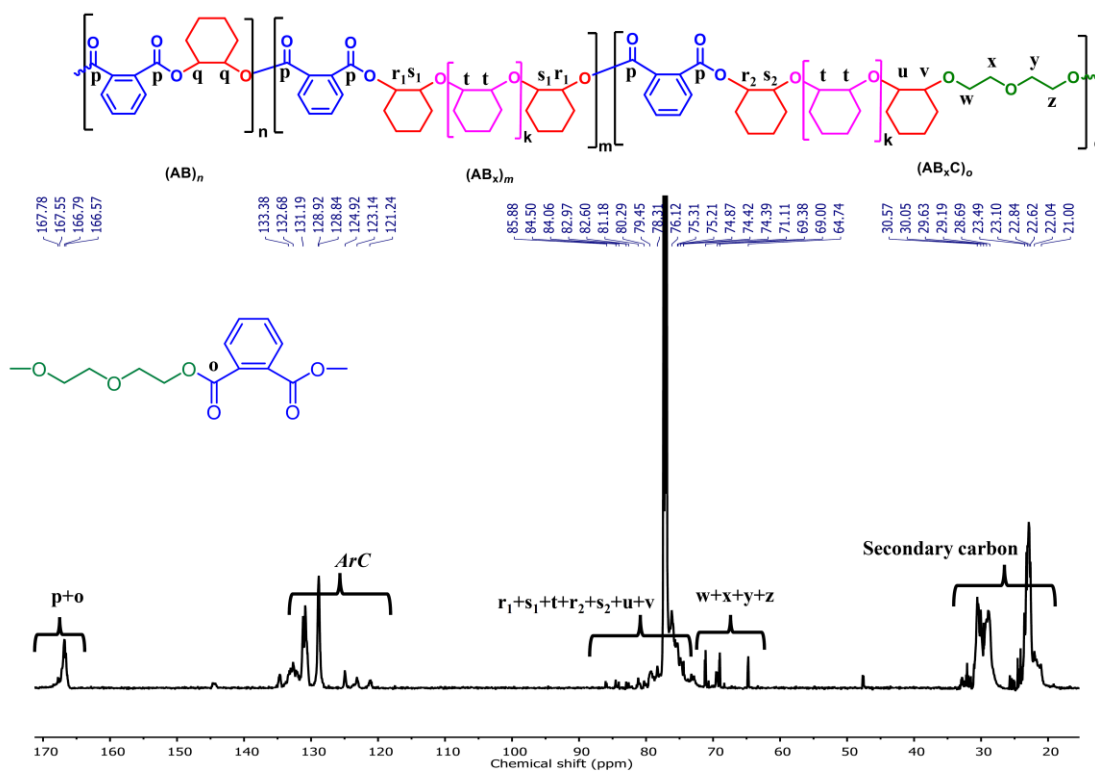
Figure S75. DOSY-NMR spectrum (600 MHz, CDCl₃, 30 °C) of the copolymer from ROCOP of PA, CHO and 1,4-dioxane using a PA/CHO/1,4-dioxane /SnOct₂ molar ratio of 50:150:800:1 (Table 2, entry 8).

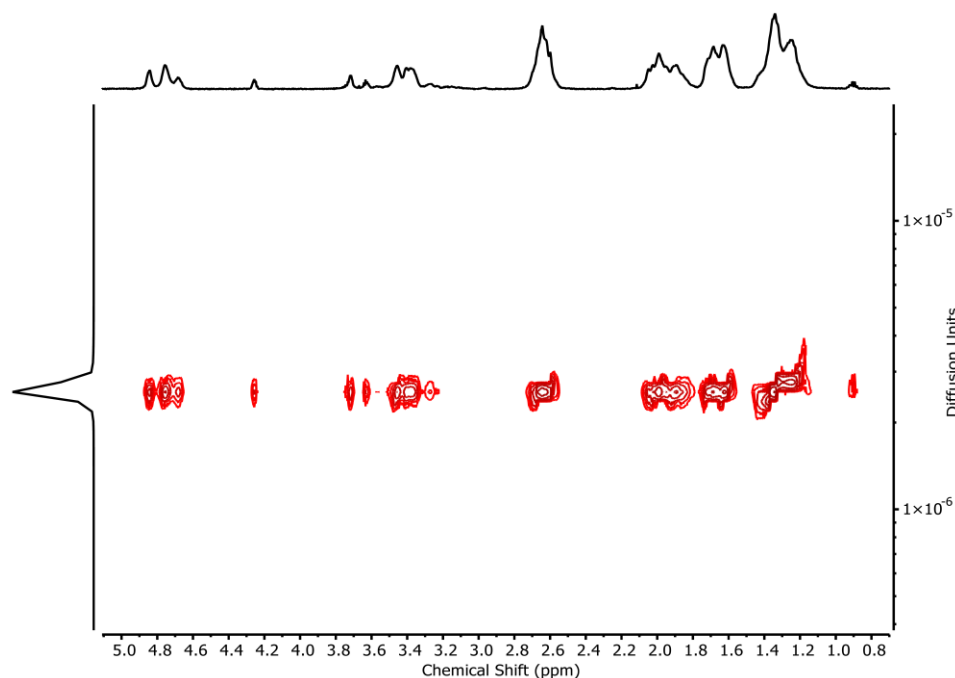**Figure S76**. ¹³C NMR spectrum (150 MHz, CDCl₃, 30 °C) of the copolymer from ROCOP of PA, CHO and 1,4-dioxane using a PA/CHO/1,4-dioxane /SnOct₂ molar ratio of 50:150:800:1 (Table 2, entry 8).

NMR spectrum of SA/CHO/1,4-dioxane copolymers

Figure S77. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA, CHO and 1,4-dioxane using a SA/CHO/1,4-dioxane/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 9).
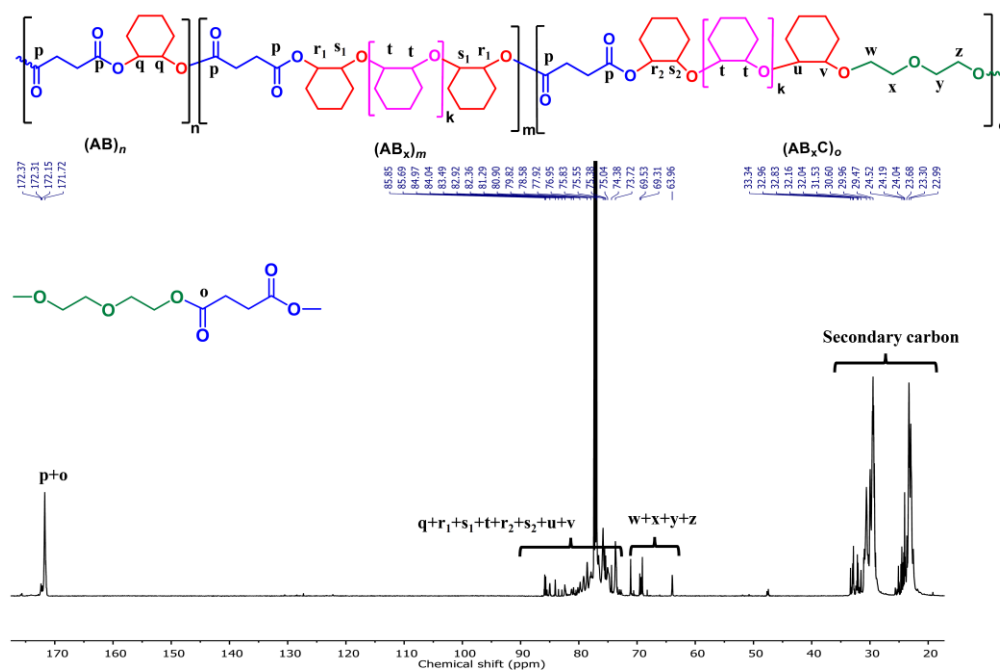

Figure S78. COSY-NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA, CHO and 1,4-dioxane using a SA/CHO/1,4-dioxane/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 9).

Figure S79. DOSY-NMR spectrum (600 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA, CHO and 1,4-dioxane using a SA/CHO/1,4-dioxane /SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 9).

Figure S80. ^{13}C NMR spectrum (150 MHz, CDCl$_3$, 30 °C) of the copolymer from ROCOP of SA, CHO and 1,4-dioxane using a SA/CHO/THF/SnOct$_2$ molar ratio of 50:150:800:1 (Table 2, entry 9).
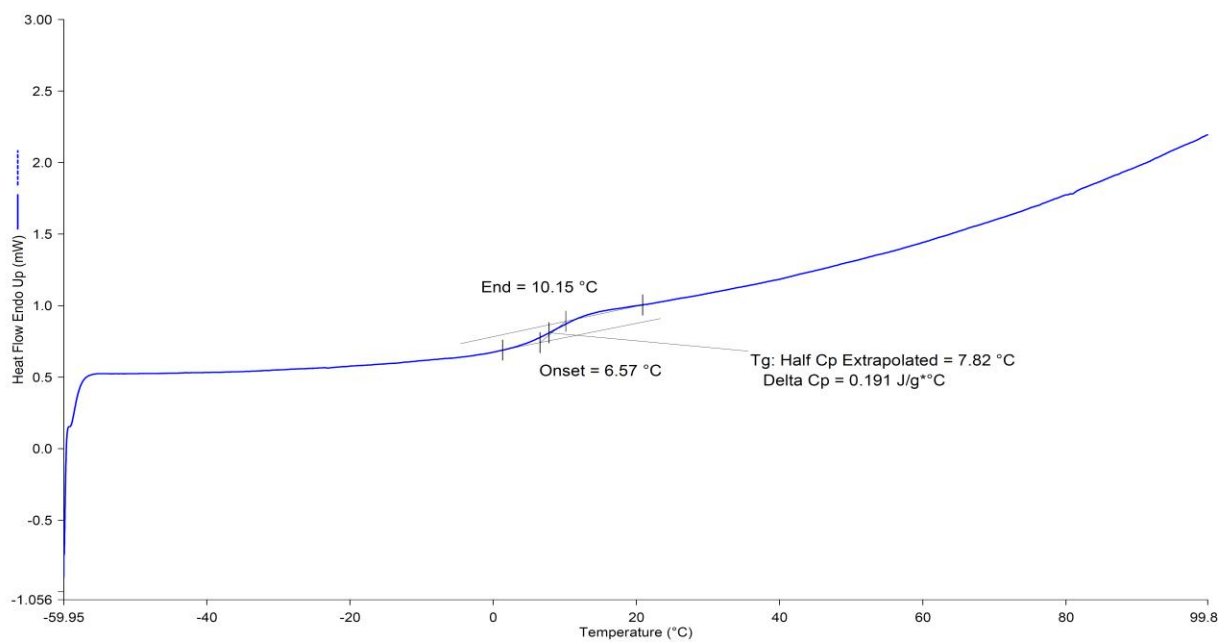
S58

DSC measurements

Figure S81. DSC data of polyester from copolymerization of CHO, SA and THF (Table 2, entry 3).
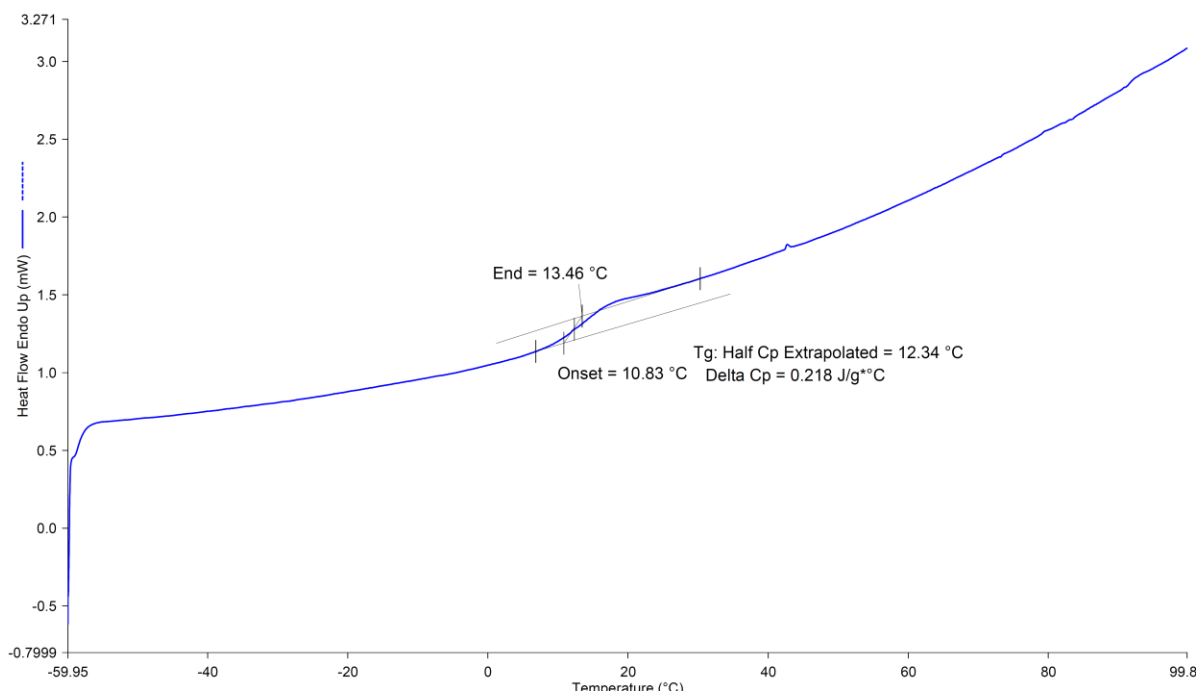

Figure S82. DSC data of polyester from copolymerization of CHO, SA and THF (Table 2, entry 4).
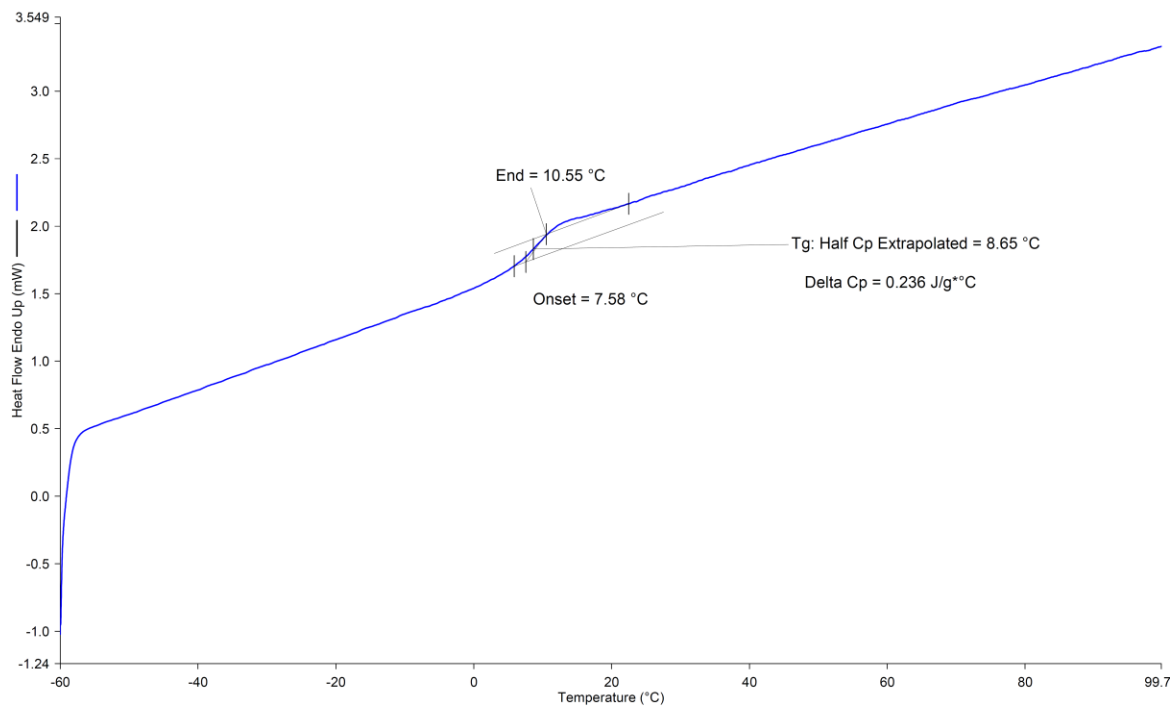
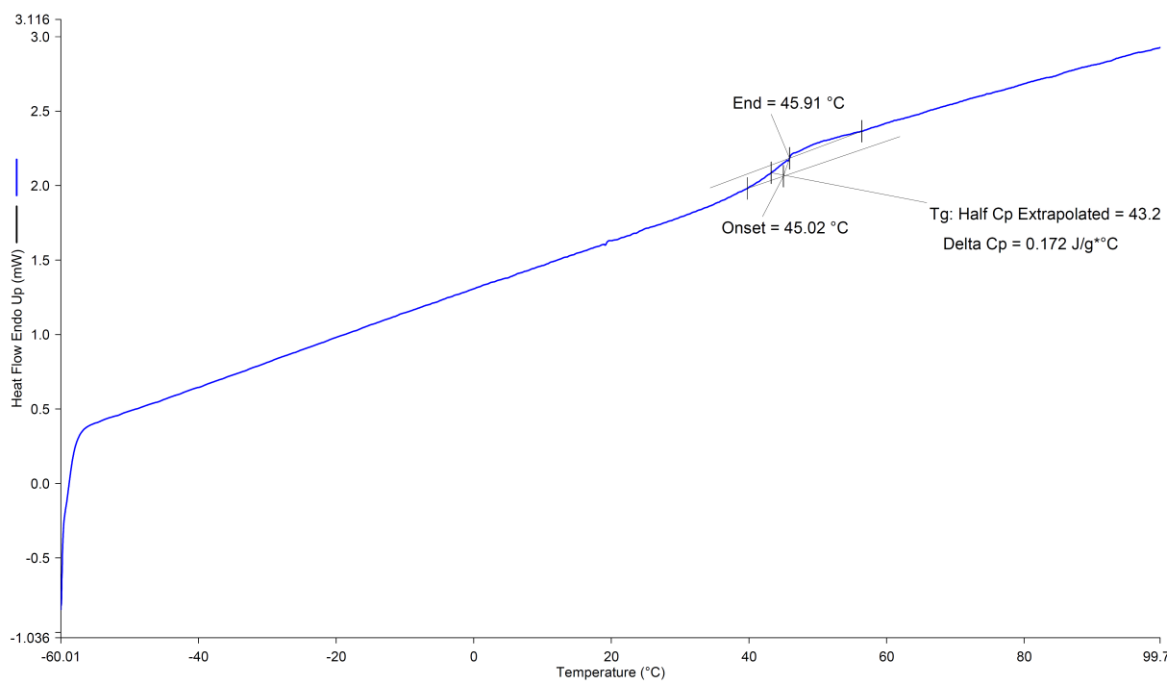**Figure S83**. DSC data of polyester from copolymerization of CHO, SA and THF (Table 2, entry 5).

Figure S84. DSC data of polyester from copolymerization of CHO, PA and THF (Table 2, entry 6).
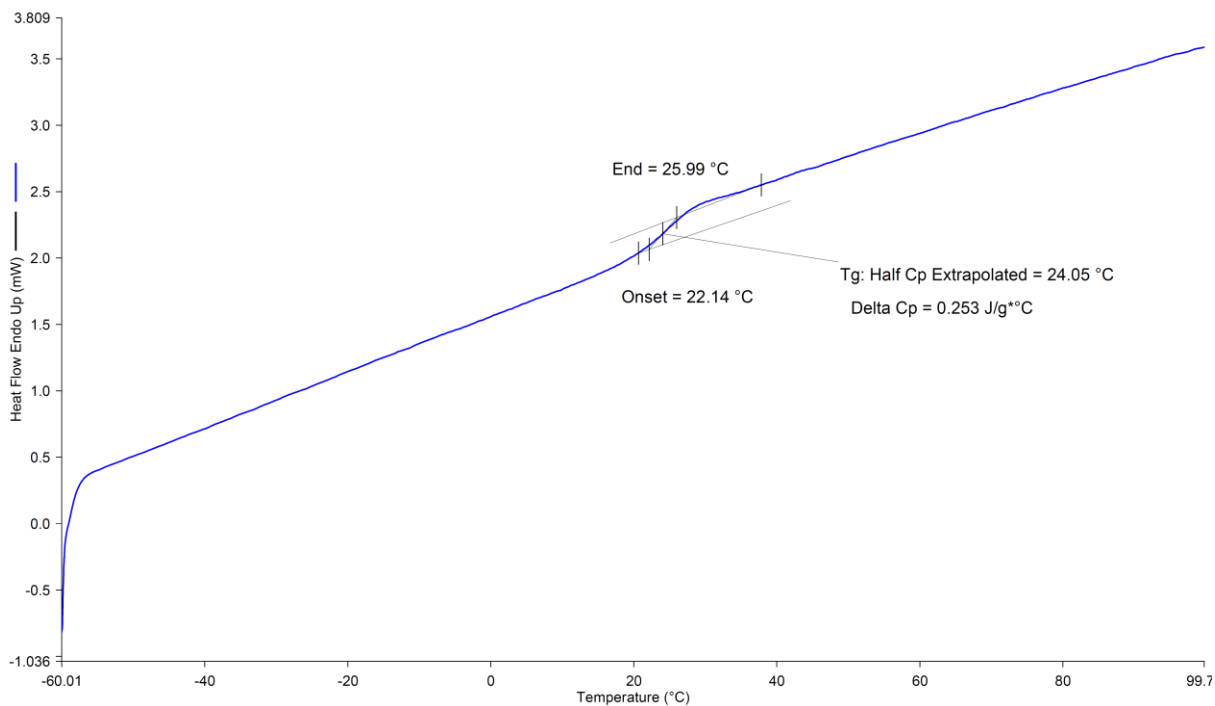
Figure S85. DSC data of polyester from copolymerization of CHO, MA and THF (Table 2, entry 7).
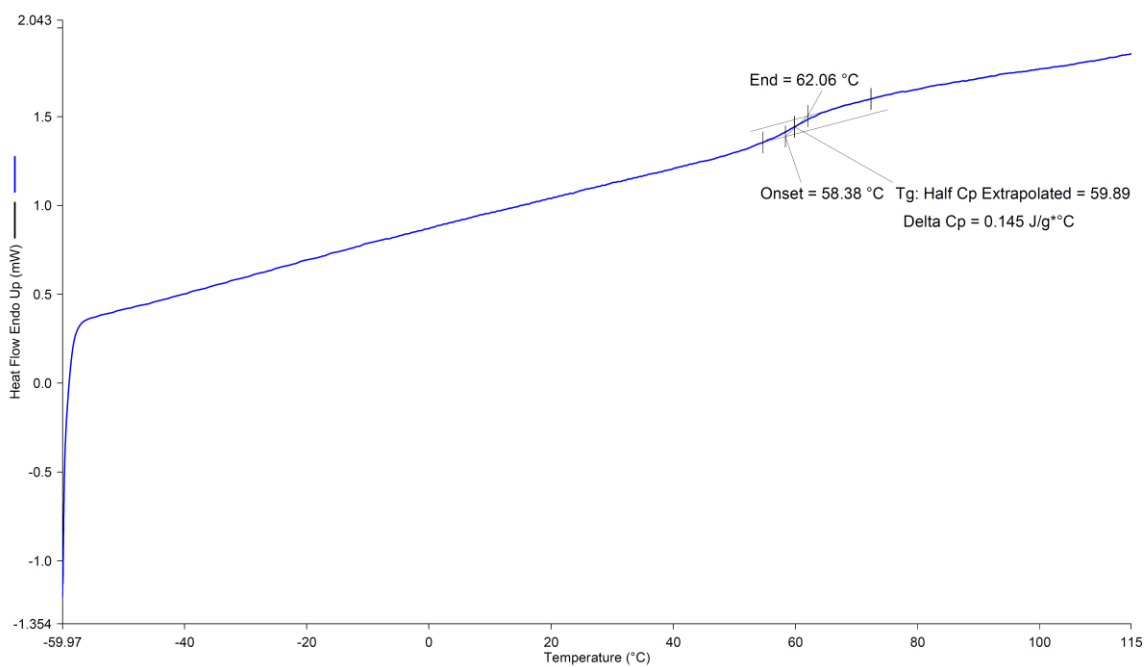

Figure S86. DSC data of polyester from copolymerization of CHO, PA and 1,4-dioxane (Table 2, entry 8).
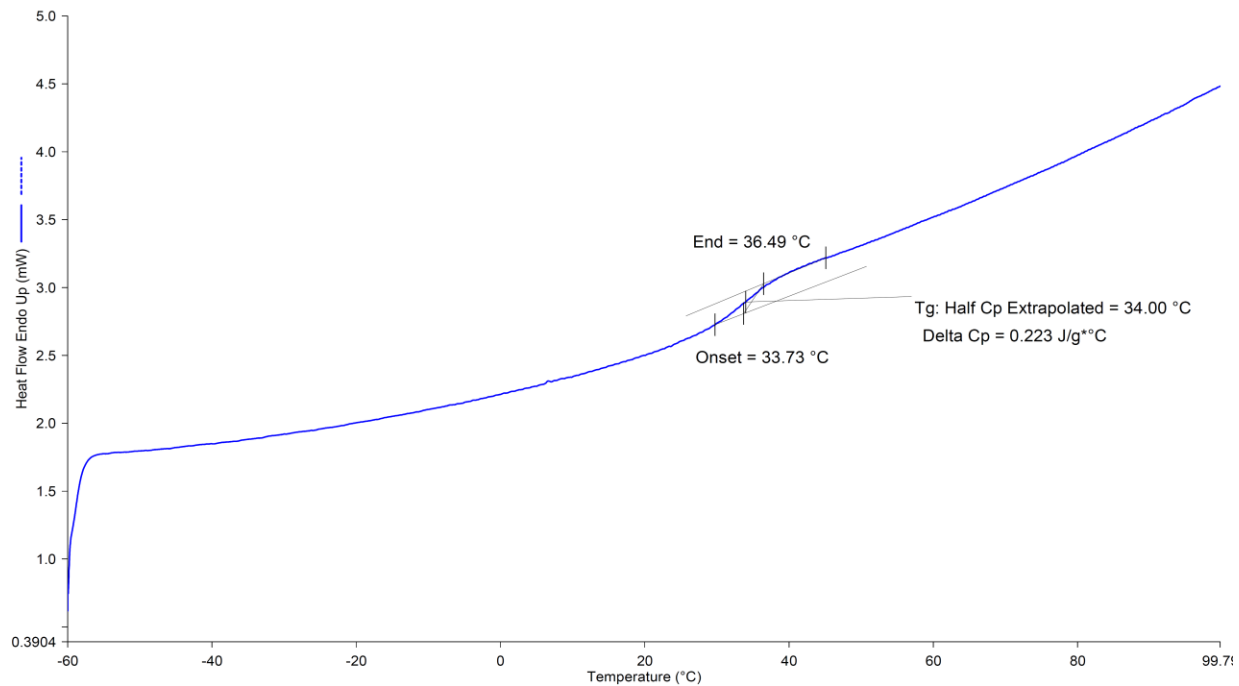
Figure S87. DSC data of polyester from copolymerization of CHO, SA and 1,4-dioxane (Table 2, entry 9).