SUPPORTING INFORMATION

Controllable Synthesis of Stereoregular Polyesters by Organocatalytic Alternating Copolymerizations of Cyclohexene oxide and Norbornene Anhydrides

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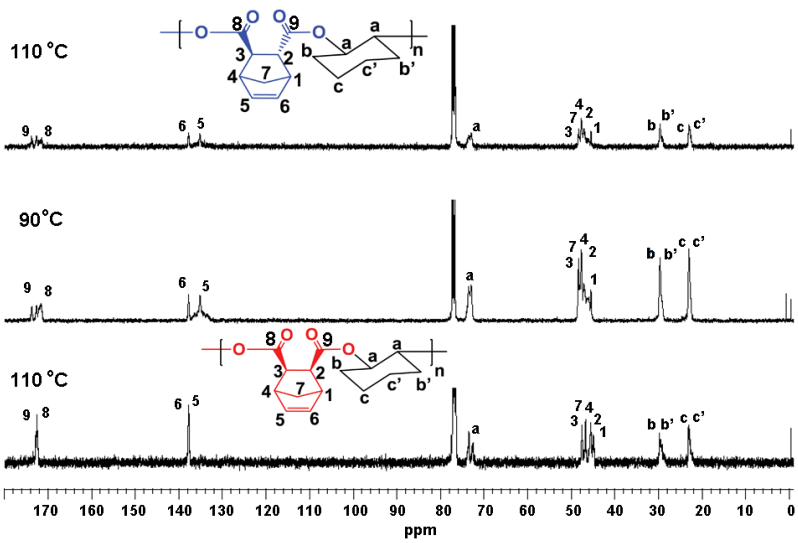


Figure S1. Representative ^{13}C NMR spectra of the obtained polyester (A) *endo*-NA/CHO=1:1(molar ratio) at 110^{o}C (entry7, Table1); (B) *endo*-NA/CHO=1:1(molar ratio) at 90 ^{o}C (entry 11, Table 1); and (C) *exo*-NA/CHO=1:1(molar ratio) 110 ^{o}C (entry 1, Table 1)

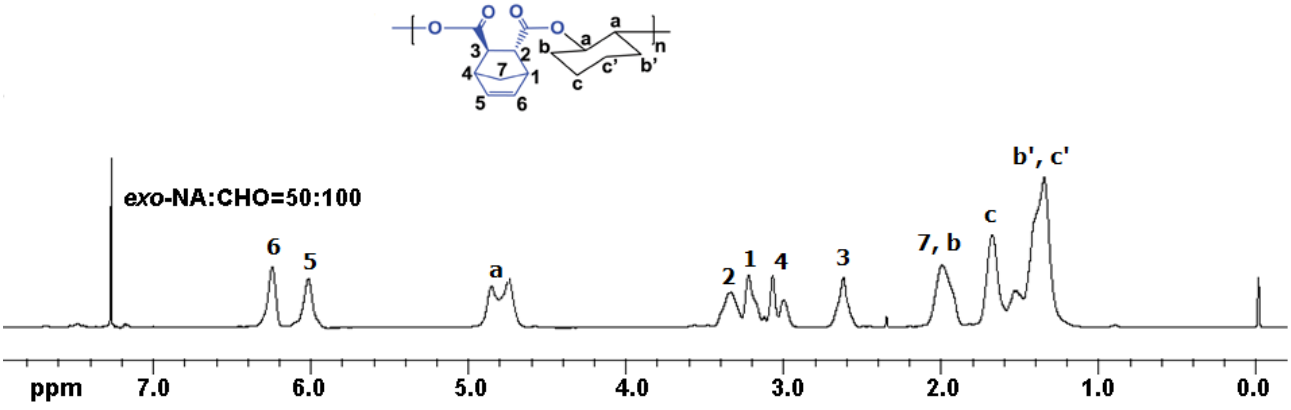


Figure S2.^{1}H NMR spectra of the obtained polyester (entry 4, Table 1) in $CDCl_3$

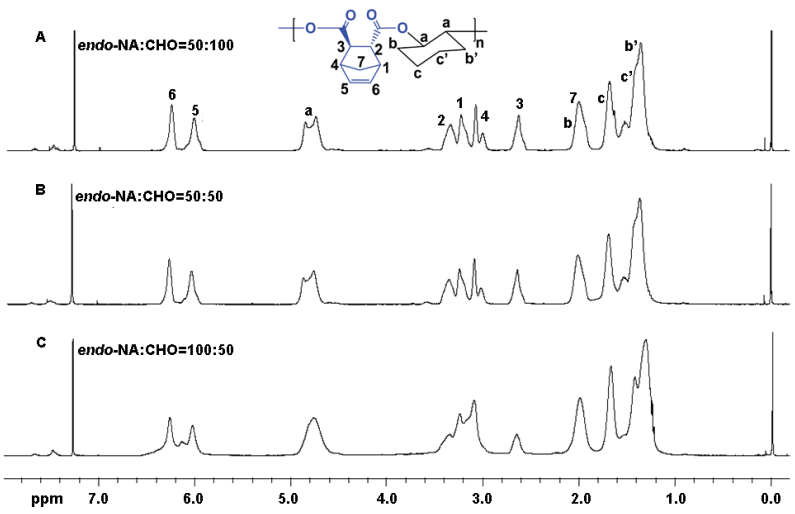
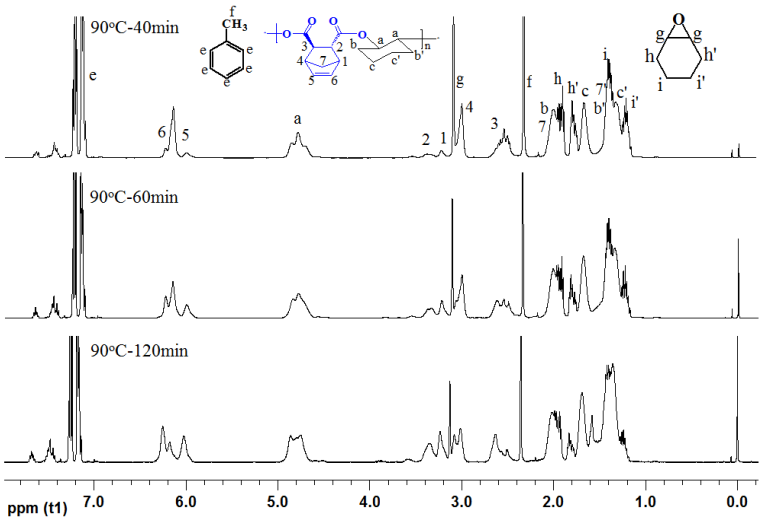
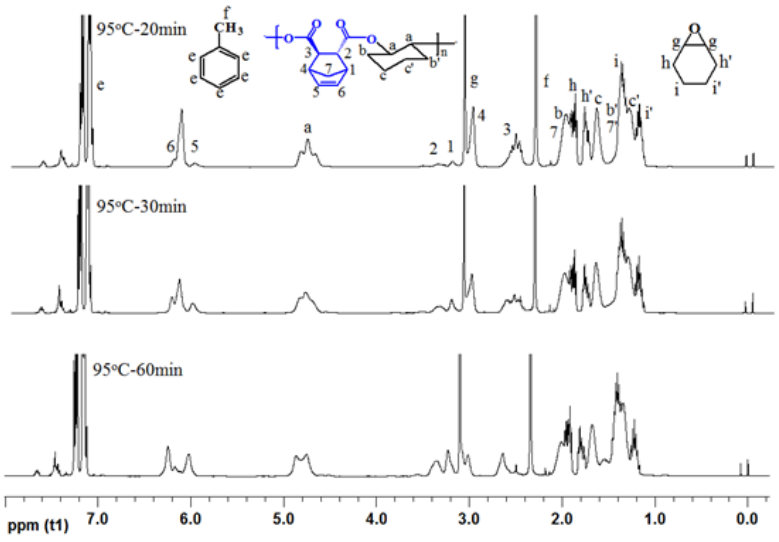


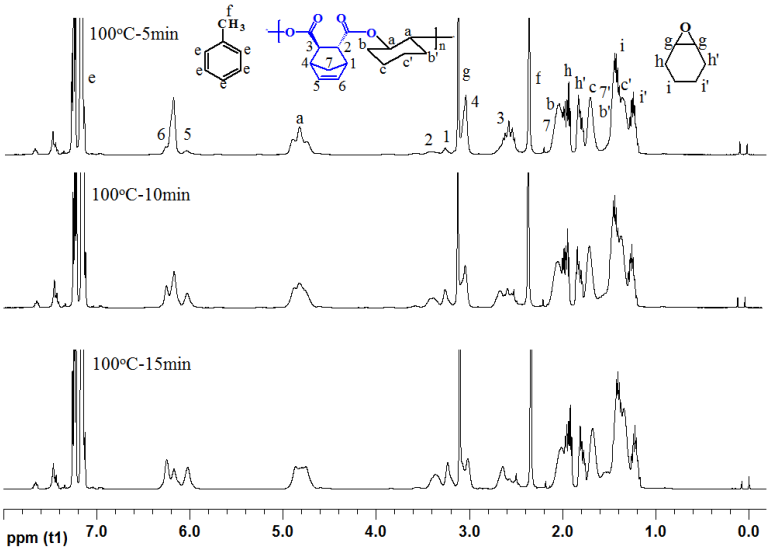
Figure S3. ^{1}H NMR spectra of the obtained polyesters (A) sample of entry 8 in Table 1); (B) sample of entry 7 in Table 1; and (C) sample of entry10 in Table 1) in $CDCl_3$



A



B



C

Figure S4. ^{1}H NMR spectra of the mixture at different time. A) 90 ^{o}C; B) 95 ^{o}C; C) 100 ^{o}C

Reaction conditions: Solvent: toluene. First step: 110^{o}C, 3h, CHO/*exo*-NA/PPNCl=50:50:1

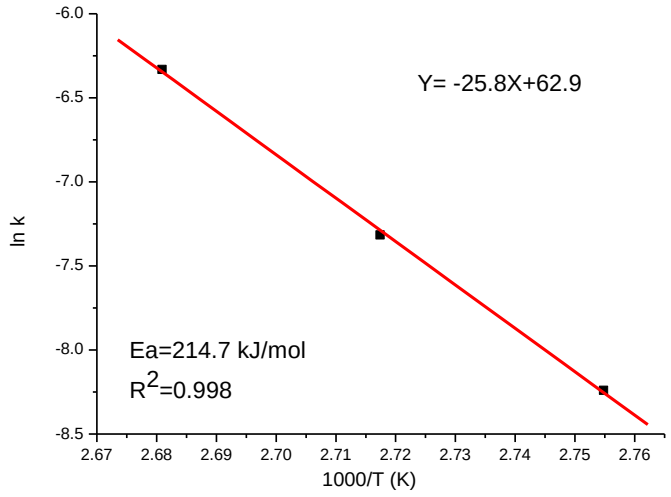


Figure S5. Arrhenius plots for the formation of trans-polyester. The equations for the linear fit are given in the top right corners, while the activation energies are given in the bottom left corners as insets.

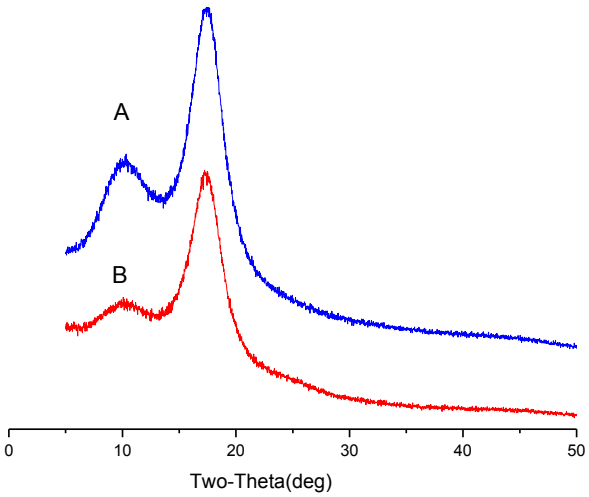
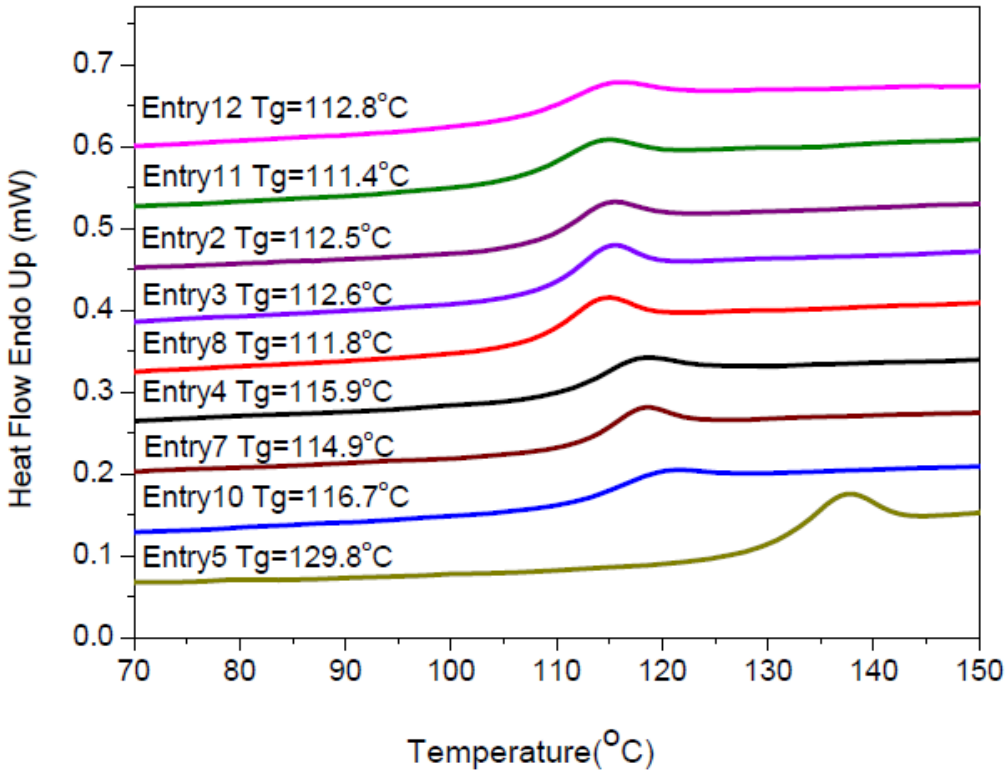
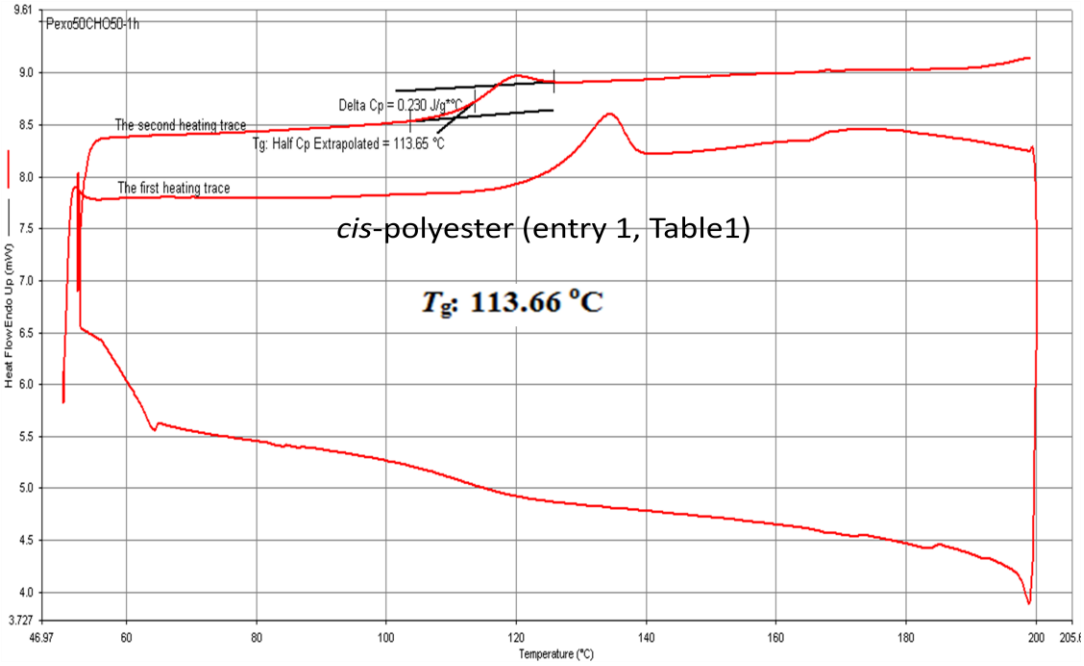


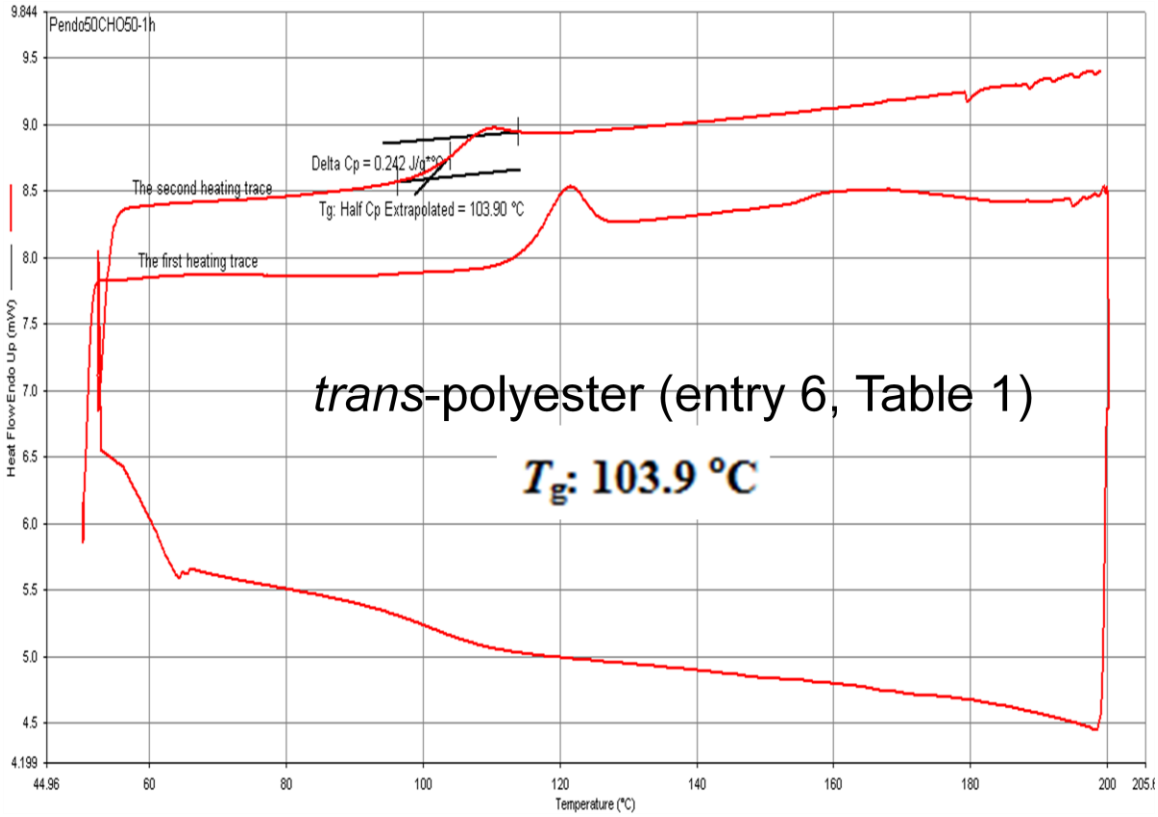
Figure S6.WAXD patterns of (A) *Cis*-polyester (M_n=6.89 ×10^3, PDI=1.57) and (B) *Trans*-polyester (M_n=6.20 ×10^3, PDI=2.31)


Heat Flow Endo Up (mW)
Temperature(°C)
Entry12 Tg=112.8°C
Entry11 Tg=111.4°C
Entry2 Tg=112.5°C
Entry3 Tg=112.6°C
Entry8 Tg=111.8°C
Entry4 Tg=115.9°C
Entry7 Tg=114.9°C
Entry10 Tg=116.7°C
Entry5 Tg=129.8°C

(A)


Pexo50CHO50-1h
Delta Cp = 0.230 J/g*°C
The second heating trace
Tg: Half Cp Extrapolated = 113.65 °C
The first heating trace
cis-polyester (entry 1, Table1)
Tg: 113.66 °C
Heat Flow/Endo Up (mW)
Temperature (°C)

(B)



(C)

Figure S7. DSC curves of some polyesters (Table 1)

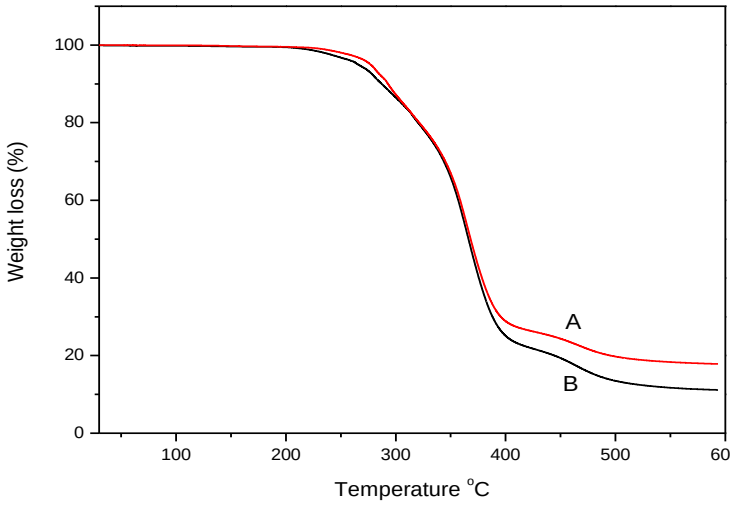
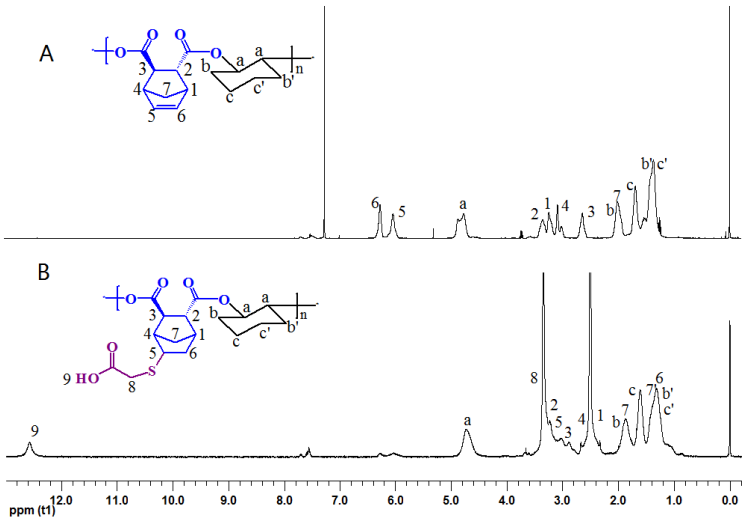


Figure S8.TGA curves of (A) *Cis*-polyester (M_n=6.89×10^3, PDI=1.57) and (B) *Trans*-polyester (M_n=6.20 ×10^3, PDI=2.31)



Fgure S9.^{1}H NMR spectra of *Trans*-polyester before (A) and after (B) modification with *thiol-ene* reaction (M_n=6.20 ×10^3, PDI=2.31)

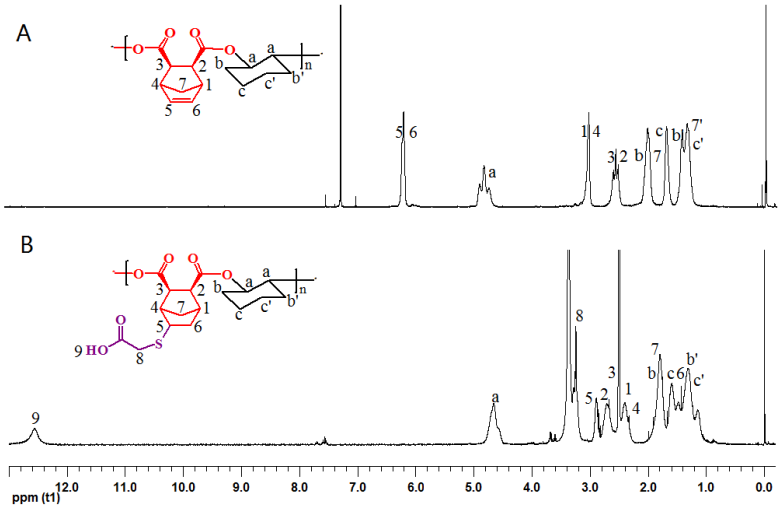


Figure S10. ^{1}H NMR spectra of *Cis*-polyester before (A) and after (B) modified by *thiol-ene* reaction with mercaptoacetic acid at 70 ^{o}C in THF with AIBN as initiator (M_n=6.89 ×10^3, PDI=1.57 for A).

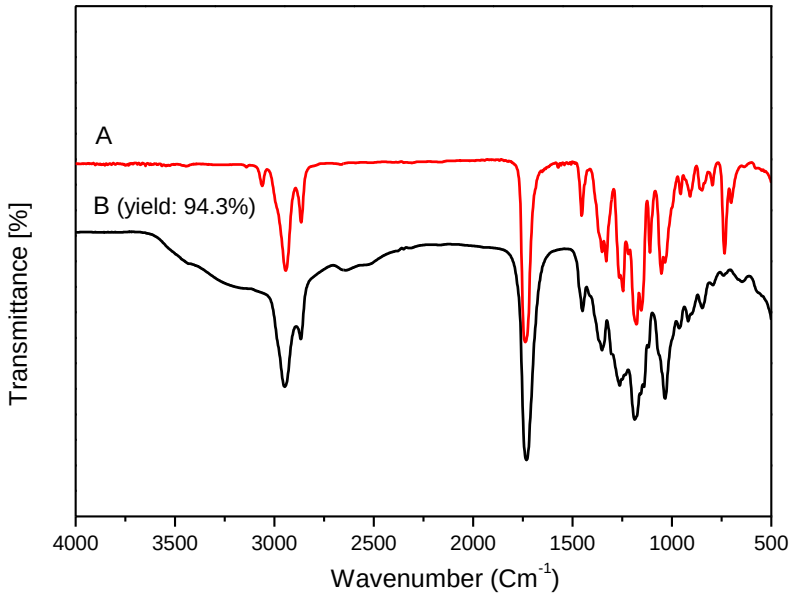


Figure S11. IR spectra of *Cis*-polyester before (A) and after (B) *thiol-ene* reaction at 70 ^{o}C in THF with AIBN as initiator (M_n=6.89 ×10^3, PDI=1.57 for A)

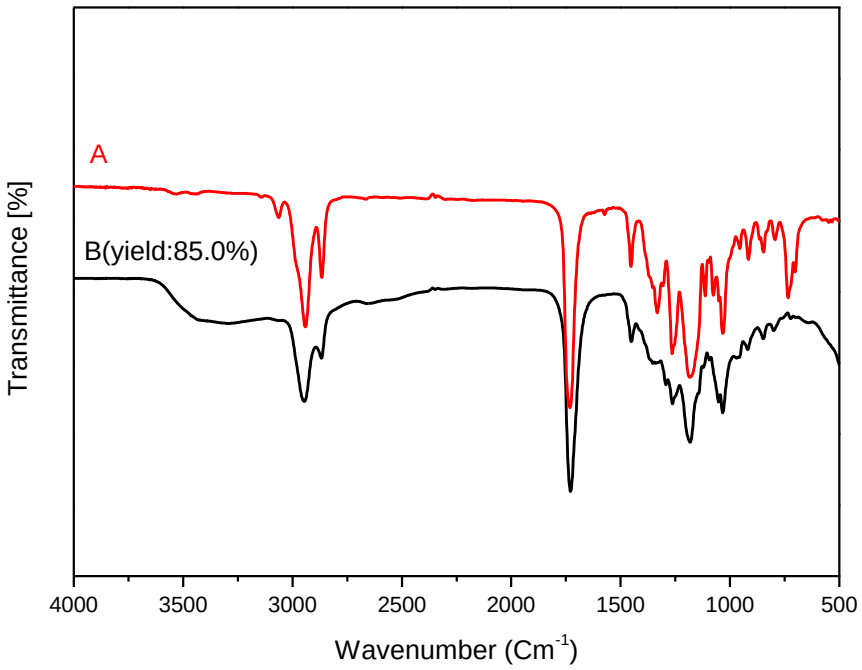


Figure S12. IR spectra of *Trans*-polyester before (A) and after (B) *thiol-ene* reaction at 70 ^{o}C in THF with AIBN as initiator (M_n=6.20 ×10^3, PDI=2.31 for A)

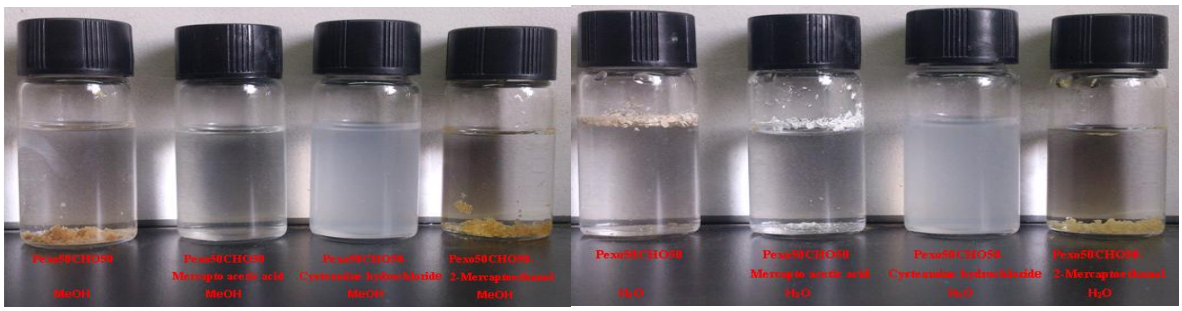


Figure S13. Solubility of polyesters in methanol or water before and after modification

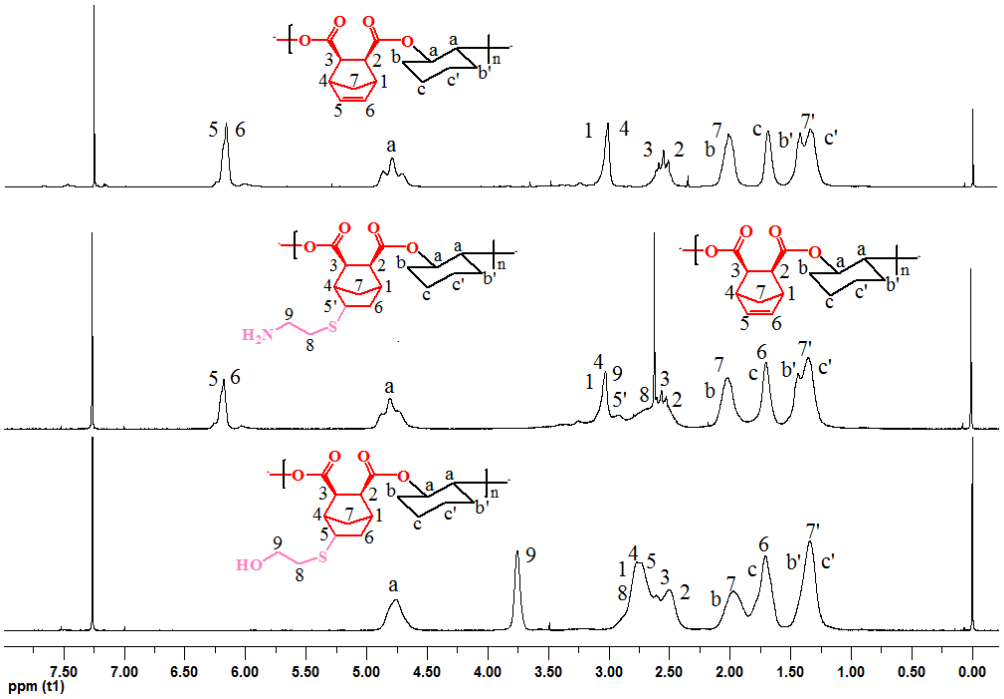


Figure S14. ^{1}H NMR spectra of *Cis*-polyester before and after modified by *thiol-ene* reaction with 2-mercaptoethanol and cysteamine at 70 ^{o}C in THF with AIBN as initiator, respectively (M_n=6.89 ×10^3, PDI=1.57 for *Cis*-polyester before modifications).

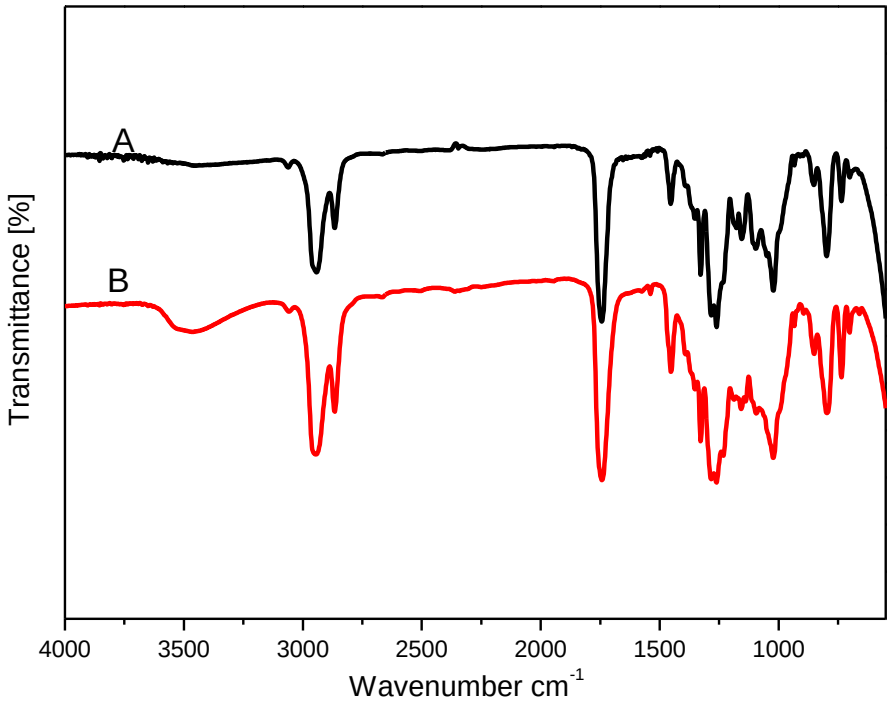


Figure S15. IR spectra of *Cis*-polyester before (A) and after (B) *thiol-ene* reaction with 2-mercaptoethanol at 70 ^{o}C in THF with AIBN as initiator (M_n=6.89 $\times 10^3$, PDI=1.57 for A, M_n=8.10 $\times 10^3$, PDI=1. 26 for B).

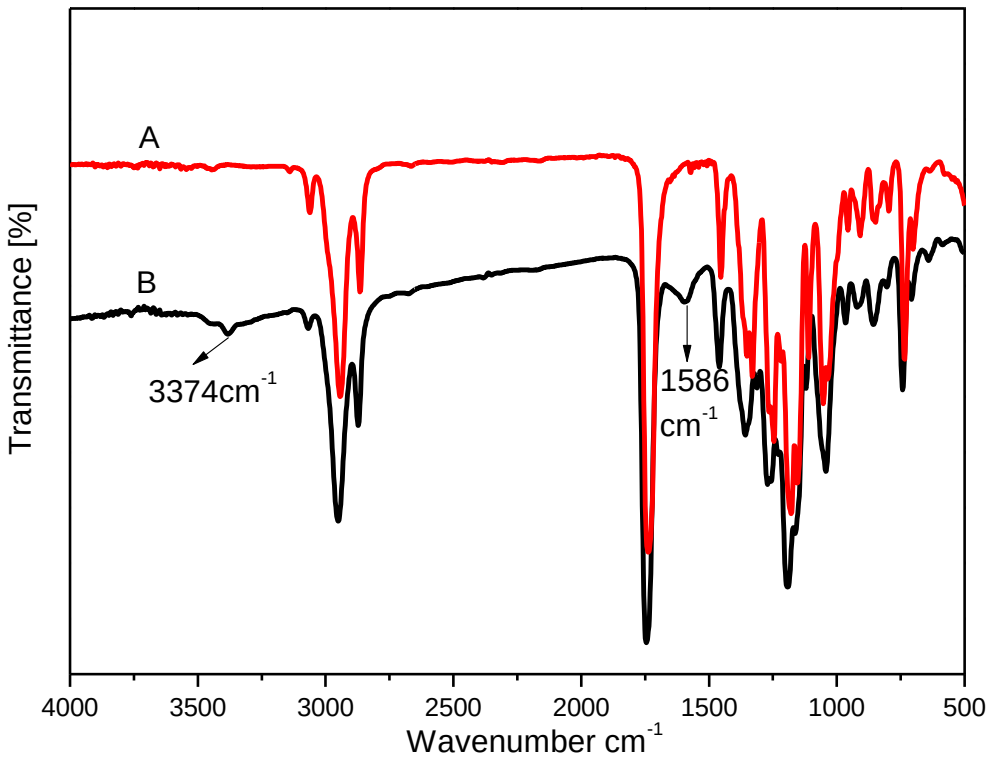


Figure S16. IR spectra of *Cis*-polyester before (A) and after (B) *thiol-ene* reaction with cysteamine at 70 ^{o}C in THF with AIBN as initiator (M_n=6.89 $\times10^3$, PDI=1.57 for A, M_n=7.06 $\times10^3$, PDI=1. 26 for B).