*Polymer Chemistry*

# Functional Glycidyl Triazolyl Polymers Exhibiting pH-Controllable and Time-Dependent Lower Critical Solution Temperature

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## Supporting Information

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## 1. Materials

PECH (Average molecular weight: 700 kg $mol^{-1}$) was purchased from Scientific Polymer Products. Propiolic acid and tri(ethylene glycol) monomethyl ether were purchased from Tokyo Chemical Industry. Propiolic acid was purified by distillation before use. Sodium azide ($NaN_3$), sodium hydroxide (NaOH), sodium hydrogen carbonate ($NaHCO_3$), anhydrous magnesium sulfate ($MgSO_4$), toluene, ethyl acetate, diethyl ether, Dulbecco's PBS without Ca and Mg [D-PBS(−)] and distilled water were purchased from Nacalai Tesque. Dry *N,N*-dimethylformamide (DMF) was purchased from Kanto Chemical. Sodium hydroxide solution (0.1 mol $L^{-1}$) and hydrochloric acid solution (0.1 mol $L^{-1}$) were purchased from Fujifilm Wako. Cation exchange resin Amberlite™ HPR2900 H hydrogen form was purchased from Merck. It was washed with distilled water and acetone, then dried under vacuum before use. The stock solution of GAP was prepared following a previously reported procedure.[1] An 80 g aliquot of the stock solution contains 5.1 g of GAP.

## 2. Methods

NMR spectra were recorded on a JEOL ECZ 400S (400 MHz and 100 MHz for $^{1}H$ and $^{13}C$ nuclei, respectively) with residual solvent as the internal standard. IR spectra were obtained using a Shimadzu IRSpirit-X with a KBr sample pellet. Size exclusion chromatography (SEC) was carried out at 50 °C with 0.01 M Li·$NTf_2$ in DMF as an eluent on a Shimadzu Nexera XR with a Shim-pack GPC-80MD column. Polystyrene standards (PStQuick A and B, Tosoh Bioscience) were used for molecular weight calibration. Sample concentration was 2 mg $mL^{-1}$. Differential scanning calorimetry (DSC) was performed on Shimadzu DSC-60 Plus at a heating/cooling rate of 10 °C $min^{-1}$ under $N_2$ flow. Thermogravimetric analysis (TGA) was performed with Shimadzu DTG-60 under $N_2$ flow. Aqueous solutions of GTPs were prepared by dissolving the polymer in a vial with continuous stirring overnight (16 h). The sample solution was stored in a temperature-controlled oven at 25°C. Transmittance change for LCST

characterization were recorded on a UV-2550 UV-Visible spectrophotometer (Wavelength: 500 nm) equipped with S-1700 thermoelectric single cell holder (Shimadzu) at a heating/cooling rate of 0.5 °C $min^{-1}$. The LCST is defined as the temperature at which the transmittance drops below 50% during the heating process. The pH values of the aqueous solutions were measured with a pH/Ion meter SevenCompact™ S220 (Mettler Toledo). Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer equipped with 633 nm laser. The sample solution was filtered with a hydrophilic polytetrafluoroethylene (PTFE) syringe filter (Whatman™ Puradisc™, pore size: 0.20 µm, diameter: 25 mm) three times before DLS measurement. The data were analyzed by regularized fitting (CONTIN).

## 3. IR spectra

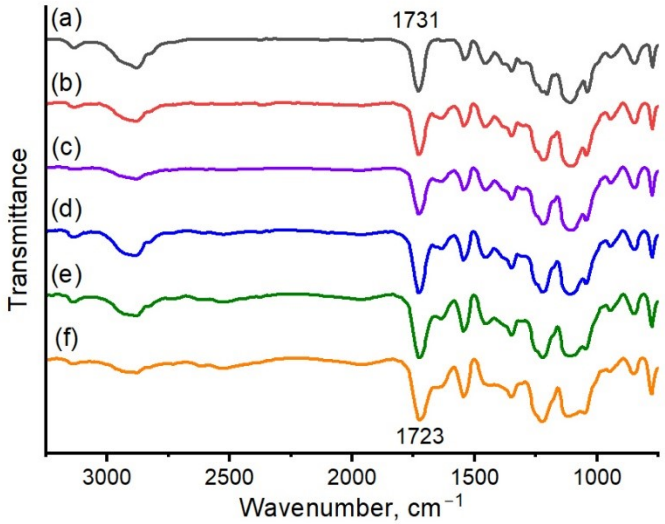


**Figure S1.** IR spectra of (a) GTP-EG3 homopolymer, (b) GTP-EG3-*co*-COOH20, (c) GTP-EG3-*co*-COOH30, (d) GTP-EG3-*co*-COOH40, (e) GTP-EG3-*co*-COOH60, (f) GTP-EG3-*co*-COOH80. KBr pellets.

## 4. $^{1}H$ and $^{13}C$ NMR spectra

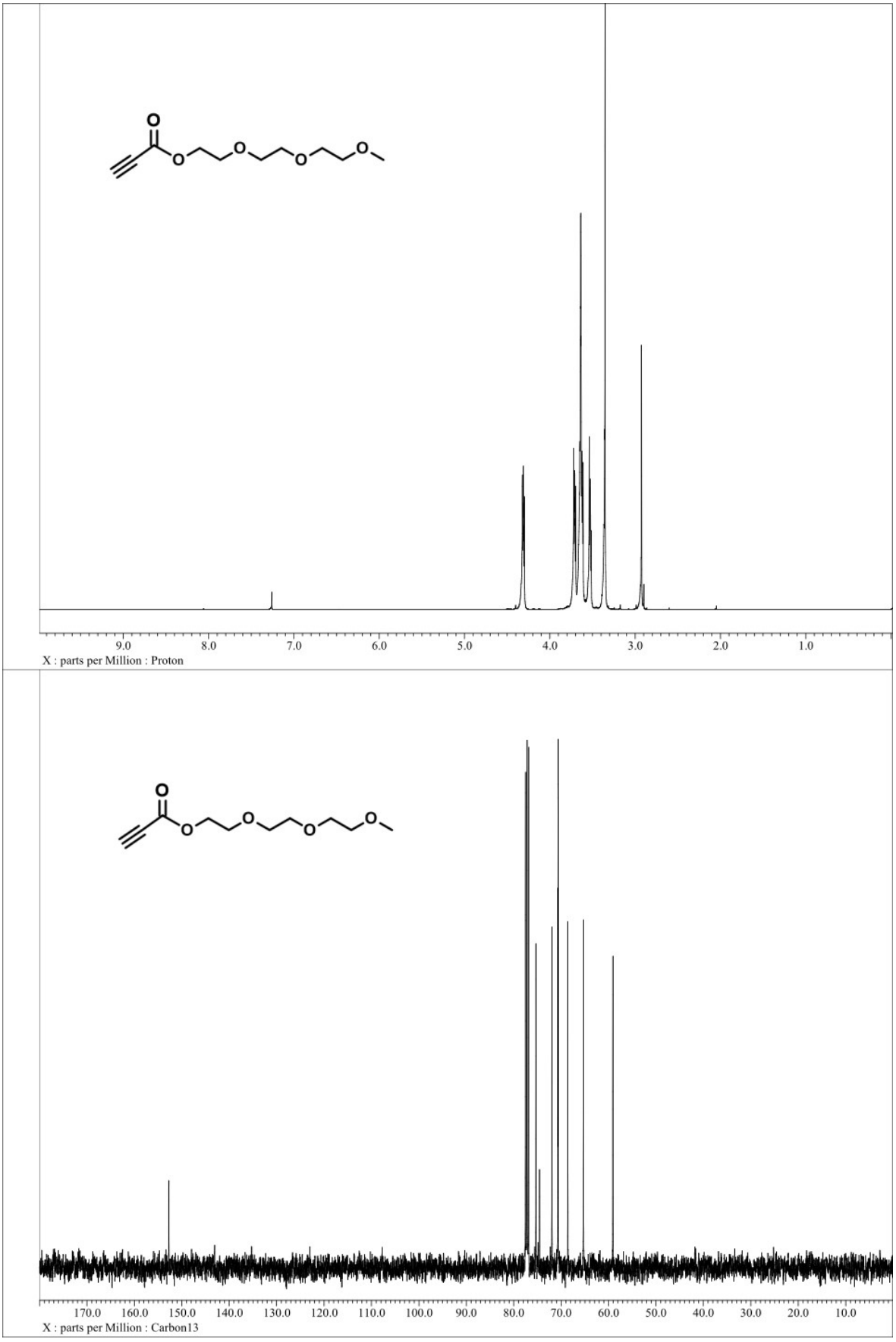


**Figure S2**. $^{1}H$ and $^{13}C$ NMR spectra of Compound **1** (Solvent: $CDCl_3$).

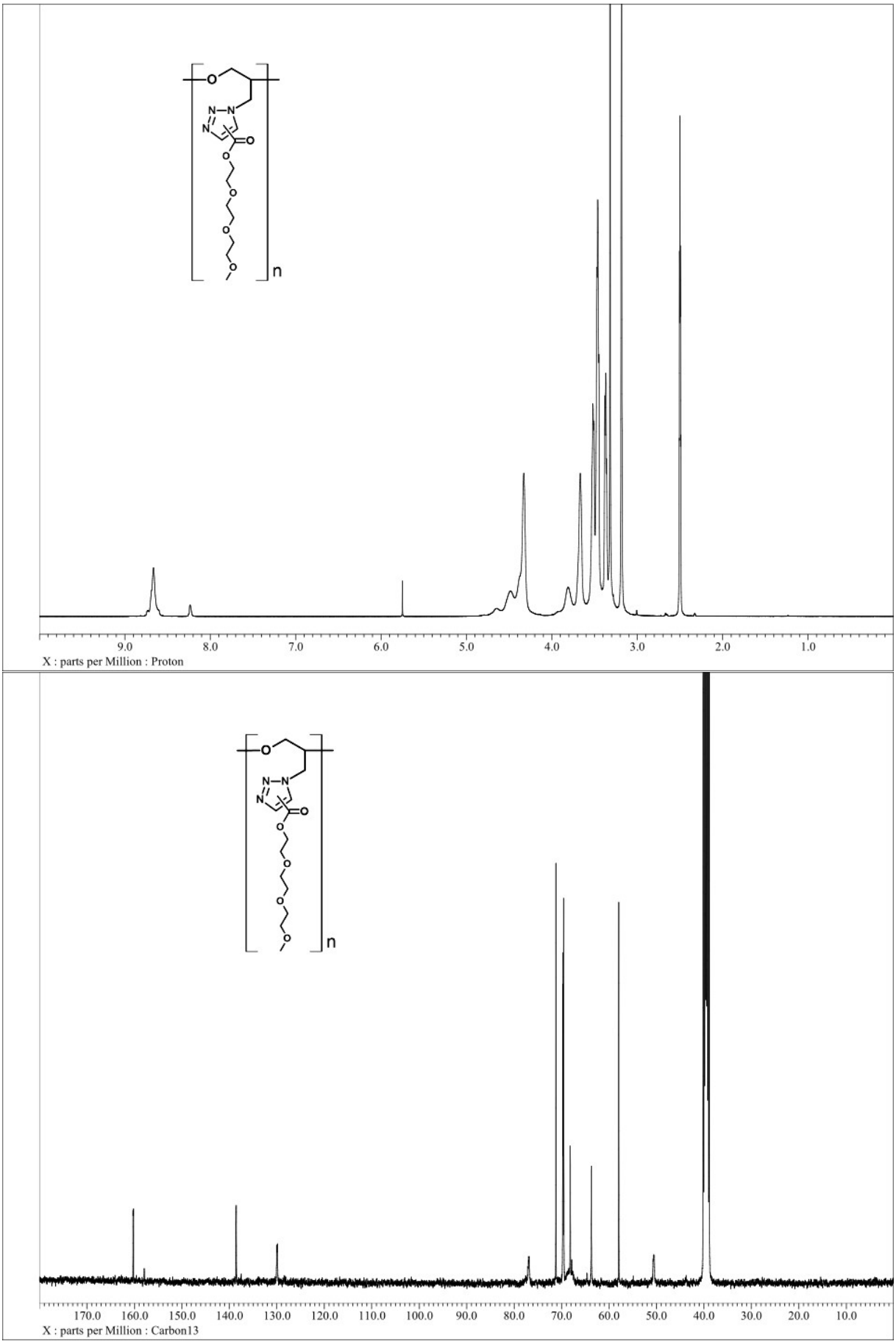


**Figure S3**. $^{1}H$ and $^{13}C$ NMR spectra of GTP-EG3 (Solvent: DMSO-$d_6$).

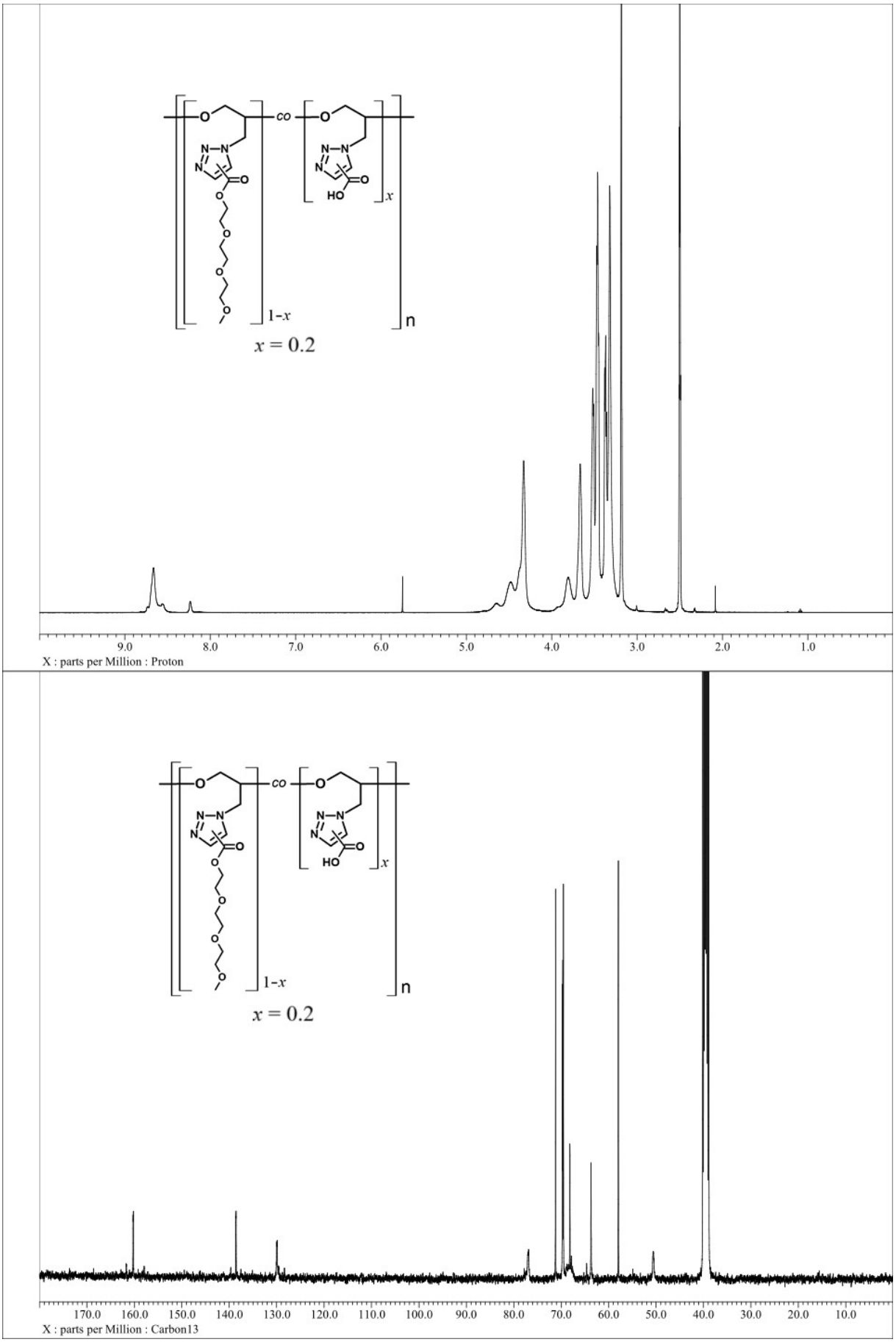


**Figure S4**. $^{1}H$ and $^{13}C$ NMR spectra of GTP-EG3-*co*-COOH20 (Solvent: DMSO-$d_6$).

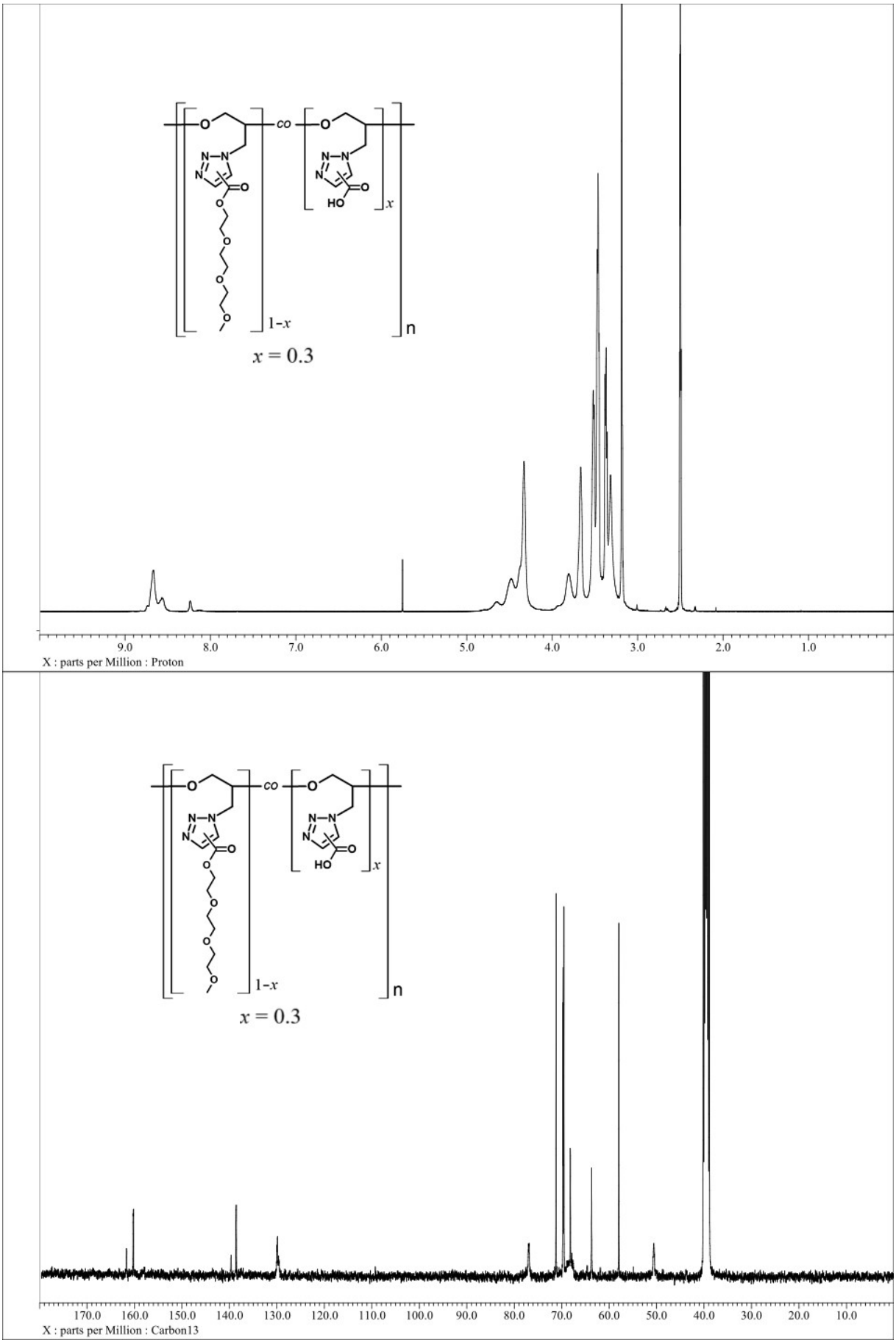


**Figure S5**. $^{1}H$ and $^{13}C$ NMR spectra of GTP-EG3-*co*-COOH30 (Solvent: DMSO-$d_6$).

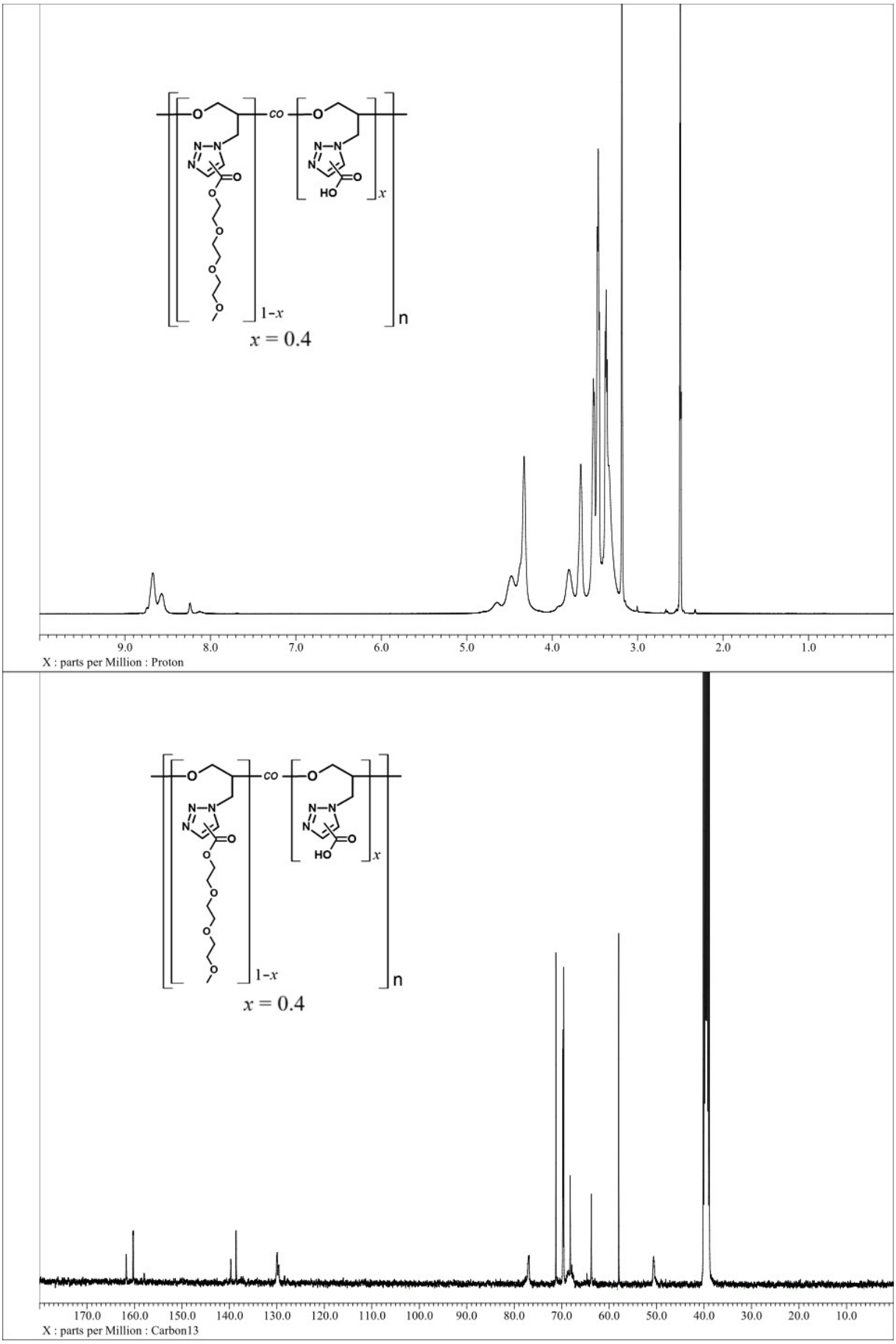


**Figure S6**. $^{1}H$ and $^{13}C$ NMR spectra of GTP-EG3-*co*-COOH40 (Solvent: DMSO-$d_6$).

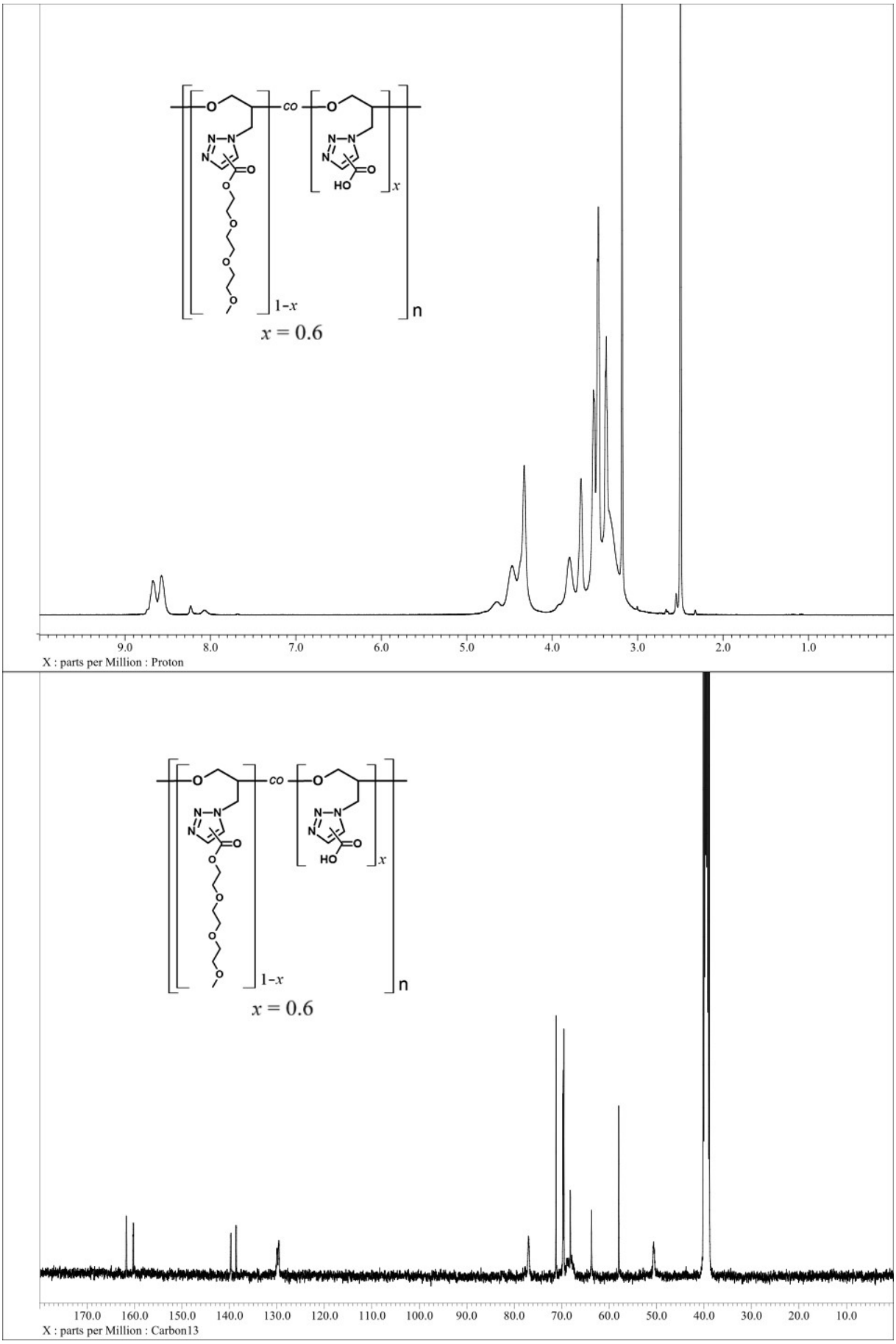


**Figure S7**. $^{1}H$ and $^{13}C$ NMR spectra of GTP-EG3-*co*-COOH60 (Solvent: DMSO-$d_6$).

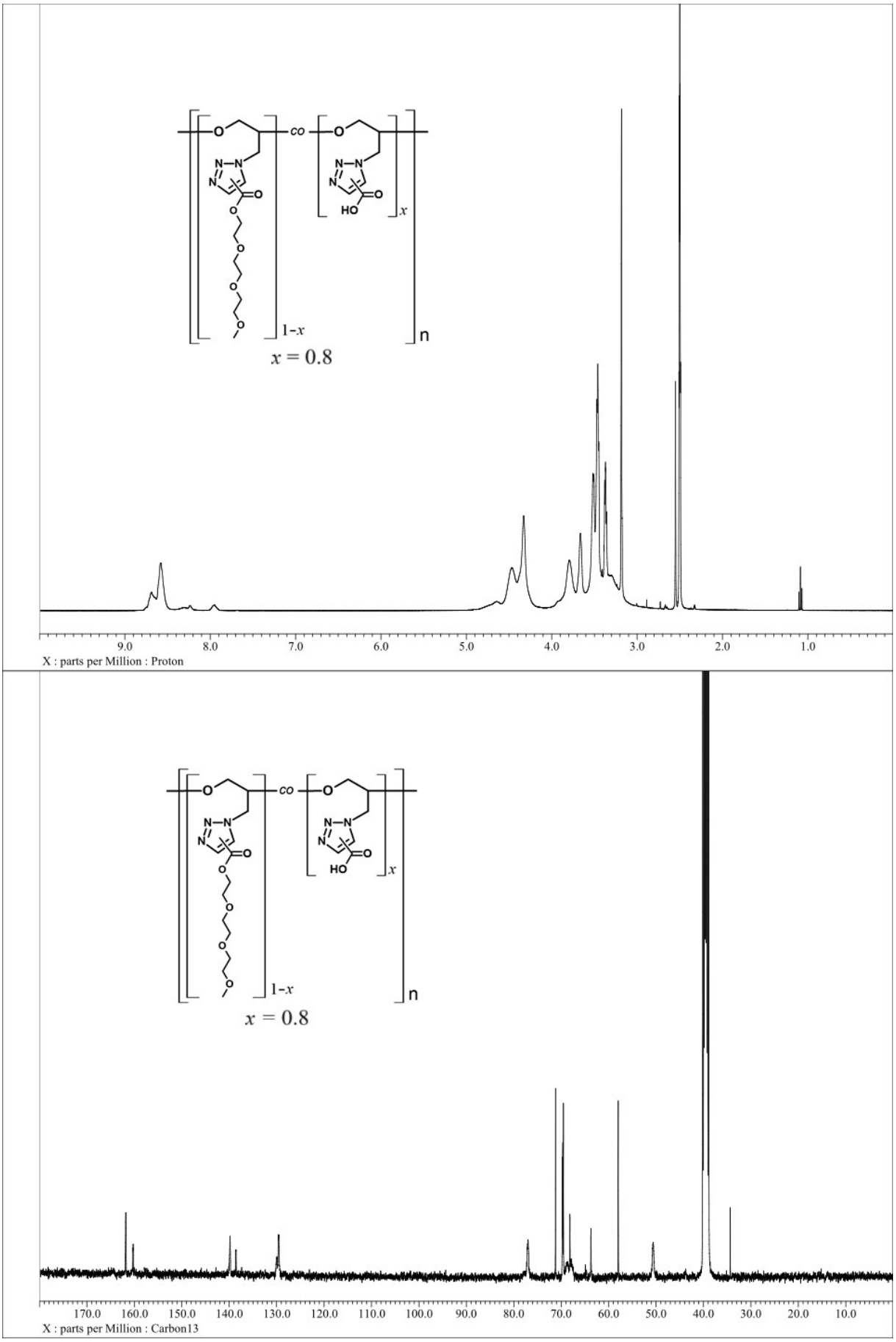


**Figure S8**. $^{1}H$ and $^{13}C$ NMR spectra of GTP-EG3-*co*-COOH80 (Solvent: DMSO-$d_6$).

## 5. $^1$H NMR spectra for COOH content determination

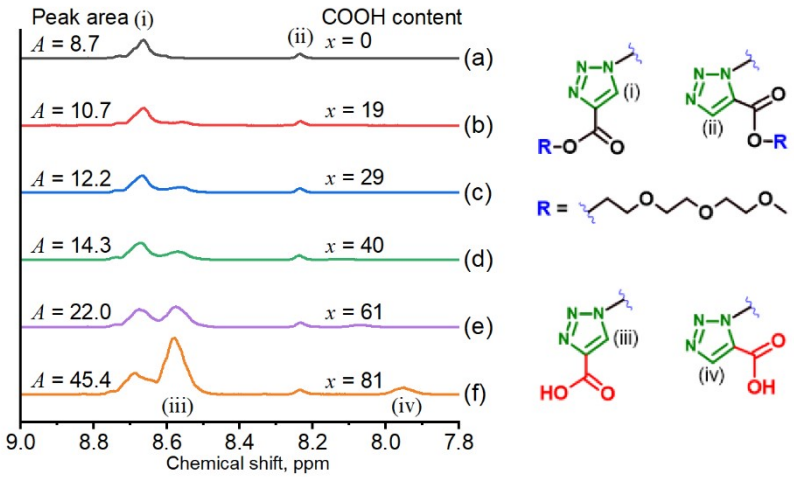


**Figure S9.** Partial $^1$H NMR spectra for COOH content determination (400 MHz, DMSO-$d_6$). (a) GTP-EG3 homopolymer; (b) GTP-EG3-*co*-COOH20; (c) GTP-EG3-*co*-COOH30; (d) GTP-EG3-*co*-COOH40; (e) GTP-EG3-*co*-COOH60; and (f) GTP-EG3-*co*-COOH80 copolymers. The labeling scheme for the triazole protons is shown on the right-hand side. The area of peak (ii) in each spectrum was normalized to 1.0. Consequently, the overlapping area of peaks (i) and (iii) consistently includes the 8.7 area units of peak (i). In spectrum (f), the COOH peak was subtracted from the original spectrum using the peak fitting function in OriginPro 2022b SR1 (Ver. 9.9.5.171).

## 6. Size exclusion chlomrtography

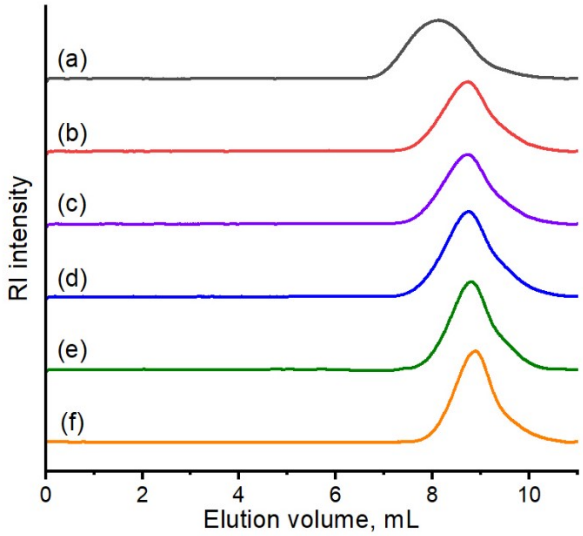


**Figure S10.** SEC traces of (a) GTP-EG3 homopolymer, (b) GTP-EG3-*co*-COOH20, (c) GTP-EG3-*co*-COOH30, (d) GTP-EG3-*co*-COOH40, (e) GTP-EG3-*co*-COOH60, and (f) GTP-EG3-*co*-COOH80 copolymers. Eluent: 0.01 M Li·$NTf_2$ in DMF.

## 7. DSC measurement

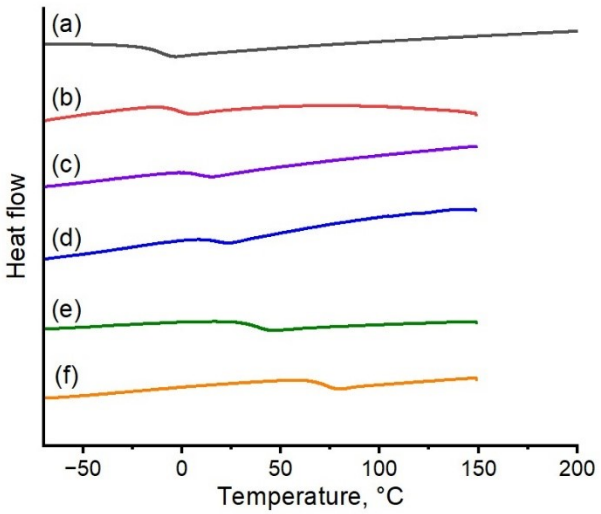


**Figure S11.** DSC traces of (a) GTP-EG3 homopolymer, (b) GTP-EG3-*co*-COOH20, (c) GTP-EG3-*co*-COOH30, (d) GTP-EG3-*co*-COOH40, (e) GTP-EG3-*co*-COOH60, (f) GTP-EG3-*co*-COOH80. Heating rate: 10 °C $min^{-1}$.

## 8. TGA measurement

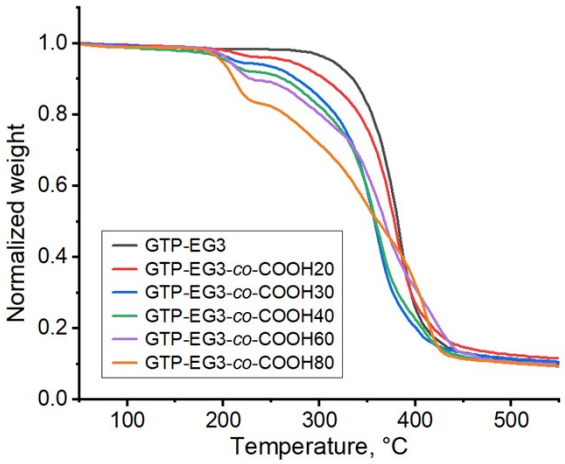


**Figure S12.** TGA traces of GTP-EG3-*co*-COOH copolymers. Heating rate: 10 °C $min^{-1}$. $N_2$ atmosphere.

## 9. Changes in titration curves and evidence for no hydrolysis

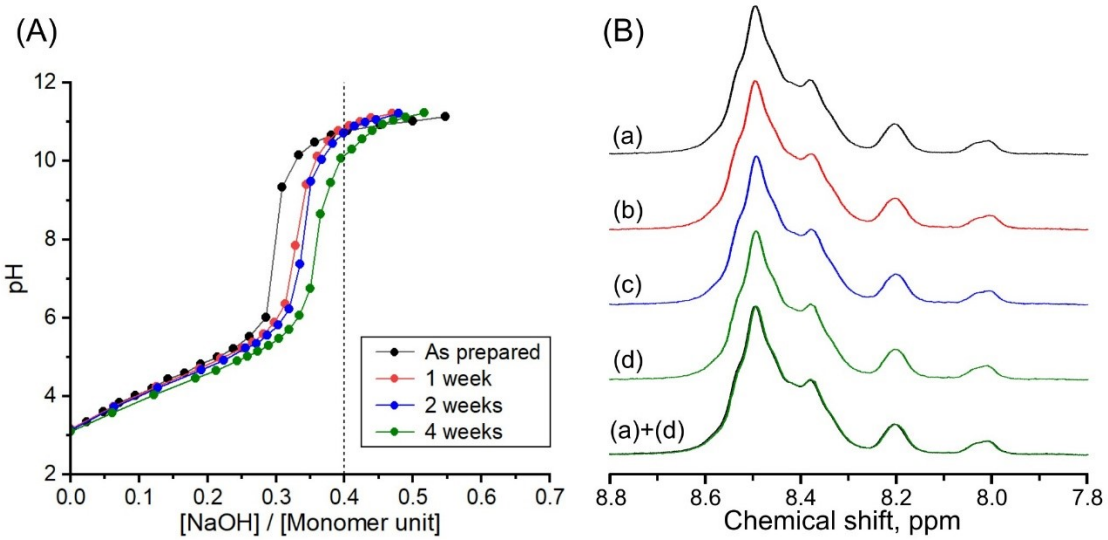


**Figure S13.** (A) Titration curves of 3 wt% GTP-EG3-*co*-COOH40 in distilled water. The solutions were stored at 25°C prior to titration. The theoretical equivalence point is indicated by a horizontal dashed line. The equivalence point of the titration curve gradually approached the theoretical value over time. (B) Changes in the triazole proton peaks in the $^{1}$H NMR spectra of 3 wt% GTP-EG3-*co*-COOH40 in $D_2O$. (a) As prepared; after storage at 25°C for (b) 1 week, (c) 2 weeks, and (d) 4 weeks. The bottom spectrum overlays spectra (a) and (d), showing no spectral change. This indicates that the shift in the titration curve was not due to hydrolysis of the ester group altering the COOH content.

## 10. Change in LCST and titration curve over time

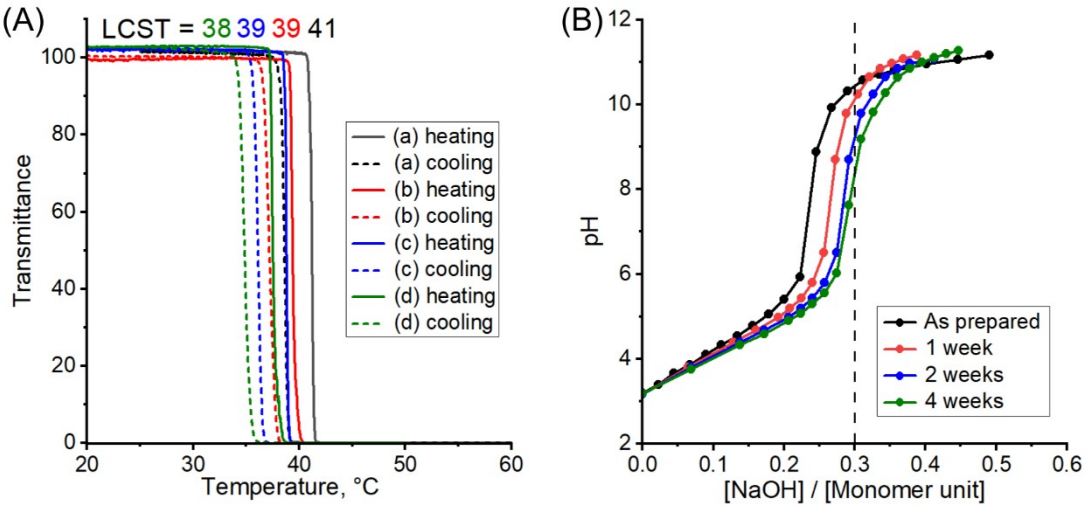


**Figure S14.** (A) Time-dependent LCST changes of 3 wt% GTP-EG3-*co*-COOH30 in distilled water. Heating and cooling were performed at a rate of 0.5 °C min$^{-1}$. (a) As-prepared solution. Solutions stored at 25 °C for (b) one week, (c) two weeks, and (d) four weeks. (B) Changes in the titration curves of GTP-EG3-*co*-COOH30 over a four-week period. A vertical dashed line indicates the theoretical equivalence point.

## 11. Hysteresis of transmittance change

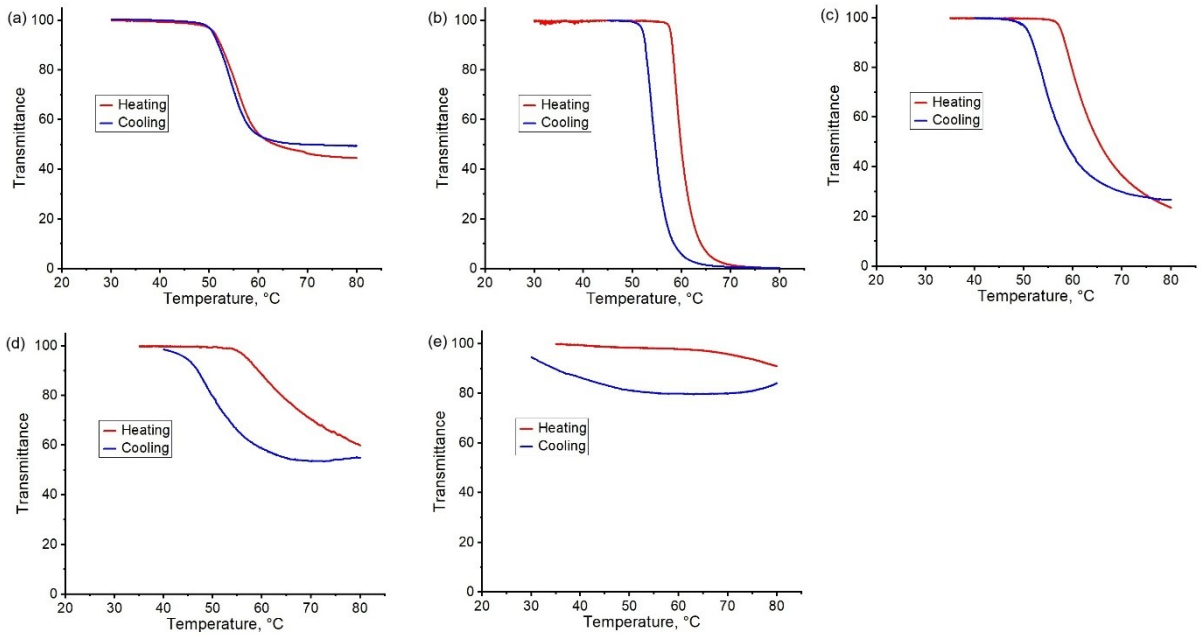


**Figure S15.** Transmittance change of 1 wt% GTP distilled water solutions in response to temperature. Heating/cooling rate: 0.5 °C min$^{-1}$. Optical path length: 1 cm. Wavelength: 500 nm. (a) GTP-EG3 homopolymer, (b) GTP-EG3-*co*-COOH20, (c) GTP-EG3-*co*-COOH30, (d) GTP-EG3-*co*-COOH40, (e) GTP-EG3-*co*-COOH60 copolymers.

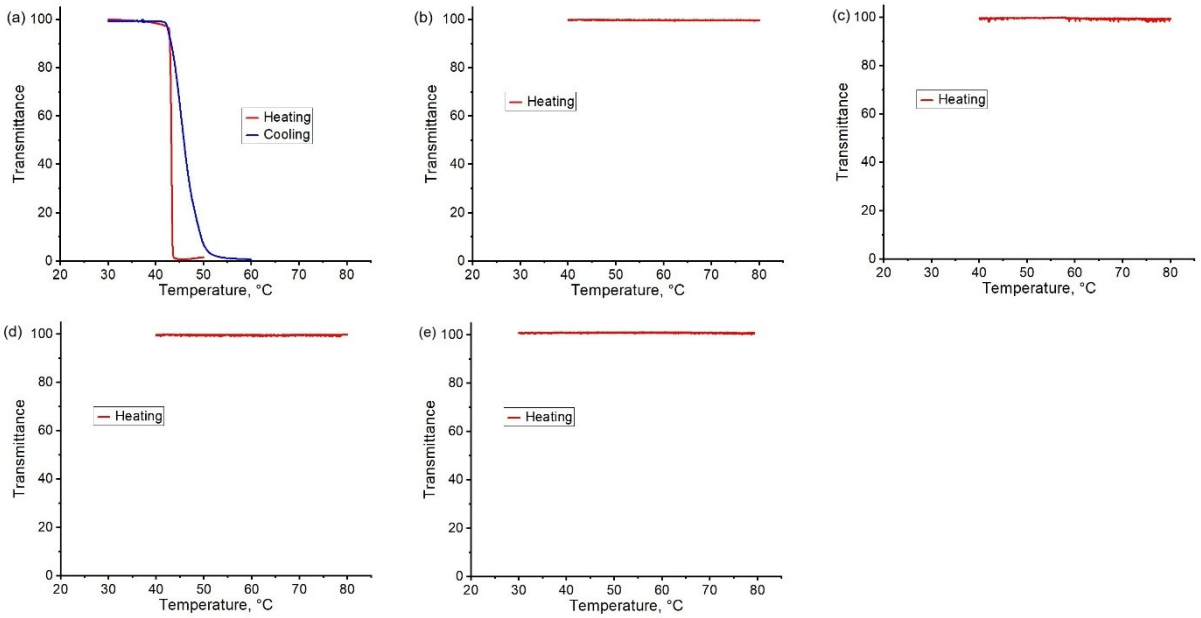


**Figure S16.** Transmittance change of 1 wt% GTP D-PBS(−) solutions in response to temperature. Heating/cooling rate: 0.5 °C min$^{-1}$. Optical path length: 1 cm. Wavelength: 500 nm. (a) GTP-EG3 homopolymer, (b) GTP-EG3-*co*-COOH20, (c) GTP-EG3-*co*-COOH30, (d) GTP-EG3-*co*-COOH40, (e) GTP-EG3-*co*-COOH60 copolymers.

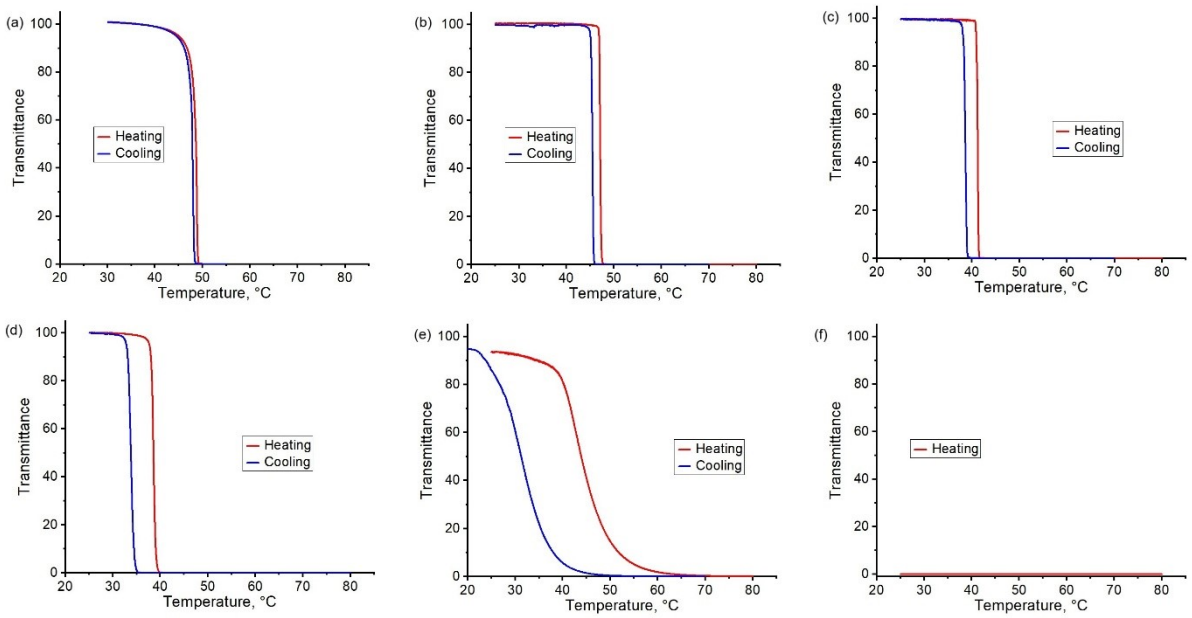


**Figure S17.** Transmittance change of 3 wt% GTP distilled water solutions in response to temperature. Heating/cooling rate: 0.5 °C min$^{-1}$. Optical path length: 1 cm. Wavelength: 500 nm. (a) GTP-EG3 homopolymer, (b) GTP-EG3-*co*-COOH20, (c) GTP-EG3-*co*-COOH30, (d) GTP-EG3-*co*-COOH40, (e) GTP-EG3-*co*-COOH60, (f) GTP-EG3-*co*-COOH80 copolymers.

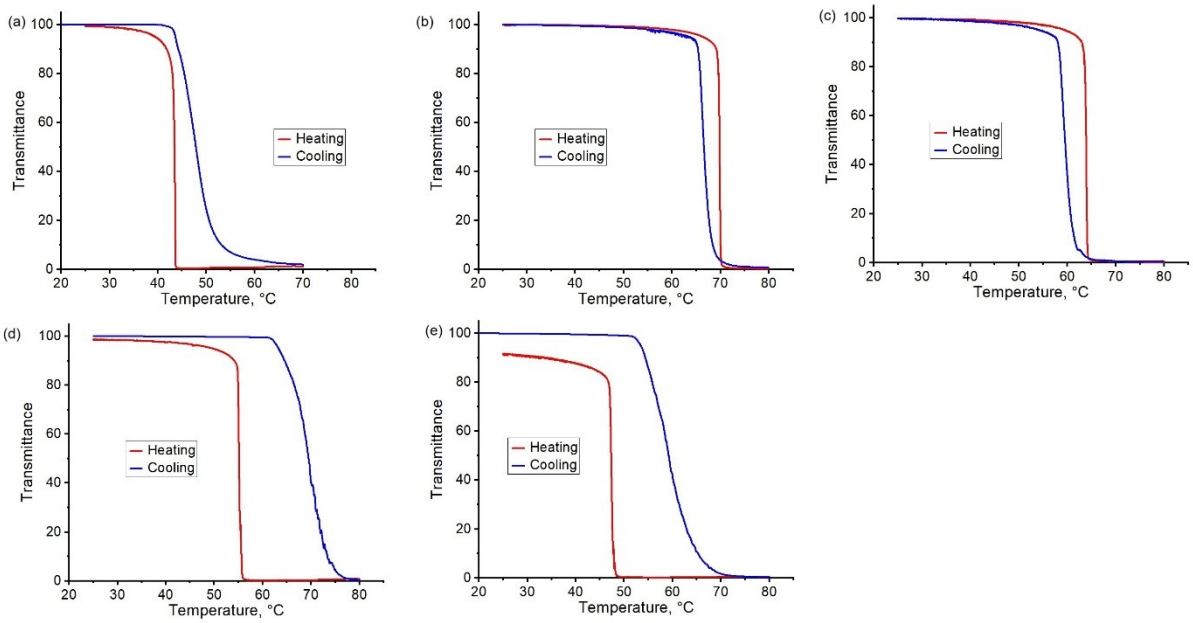


**Figure S18.** Transmittance change of 3 wt% GTP D-PBS(−) solutions in response to temperature. Heating/cooling rate: 0.5 °C min$^{-1}$. Optical path length: 1 cm. Wavelength: 500 nm. (a) GTP-EG3 homopolymer, (b) GTP-EG3-*co*-COOH20, (c) GTP-EG3-*co*-COOH30, (d) GTP-EG3-*co*-COOH40, (e) GTP-EG3-*co*-COOH60 copolymers.

## References

[1] Ikeda, T.; Hosoda, N. Facile, Efficient, and Safe Copper-Free Synthesis of Glycidyl Triazolyl Polymers. *J. Polym. Sci.* **2025**, *63*, 2568–2578.