Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Rational Design, Synthesis and Evaluation of New Azido-Ester Structures as Green Energetic Plasticizers

Nasser Sheibani[a], Narges Zohari *[a], Reza Fareghi – Alamdari *[a]

a: Faculty of Chemistry and Chemical Engineering, Malek-Ashtar University of Technology, Iran.

E-mail: nargeszohari@gmail.com (N. Zohari), reza_fareghi@yahoo.com (R. Fareghi – Alamdari)

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1. Synthesize

1-1. Synthesize of GTAA:

30 mmol (2760 mg) of glycerol dissolved in 80 ml dry toluene, then 105 mmol (9920 mg) chloroacetic acid and 500 mg p-toluenesulfonic acid (PTSA) was added. The reaction mixture refluxed using a Dean-Stark apparatus until the completion of the reaction (7 h). Existing toluene extracted by vacuum distillation and the residue was dissolved in dichloromethane. Then, the solution has washed with saturated aqueous sodium bicarbonate. The organic layer extracted and dried using magnesium sulfate. Vaporization of the solvent gives corresponding chloroacetate (7820 mg, 24.30 mmol).

The obtained chloroacetate (7820 mg, 24.30 mmol) has dissolved in 100 mil DMSO. 85.05 mmol (5530 mg) of sodium azide gradually added to it in a water-ice bath. Then the reaction temperature was slowly raised to 40°C and carried out for 30 hours. Afterward, the reaction mixture added to 180 ml cold water and extracted by dichloromethane. The extracted organic layer was washed with brine and dried using magnesium sulfate. Evaporation of the solvent gave glyceryl tris(azidoacetate). The weight of the obtained azido-ester is 7050 mg (20.66 mmol).

1-2. Synthesize of TEGBAA:

30 mmol (4500 mg) of triethylene glycol dissolved in 60 ml dry toluene, then 63 mmol (5940 mg) chloroacetic acid and 450 mg p-toluenesulfonic acid (PTSA) was added. The reaction mixture refluxed using a Dean-Stark apparatus until the completion of the reaction (7 h). Existing toluene extracted by vacuum distillation and the residue was dissolved in dichloromethane. Then, the solution has washed with saturated aqueous sodium bicarbonate. The organic layer extracted and dried using magnesium sulfate. Vaporization of the solvent gives corresponding chloroacetate (7000 mg, 23.09 mmol).

The obtained chloroacetate (7000 mg, 23.09 mmol) has dissolved in 80 mil DMSO. 46.20 mmol (2961 mg) of sodium azide gradually added to it in a water-ice bath. Then the reaction temperature was slowly raised to 40°C and carried out for 24 hours. Afterward, the reaction mixture added to 160 ml cold water and extracted by dichloromethane. The extracted organic layer was washed with brine and dried using magnesium sulfate. Evaporation of the solvent gave triethylene glycol bis(azidoacetate). The weight of the obtained azido-ester is 5620 mg (17.77 mmol).

1-3. Synthesize of EGBAA:

The EGBAA azido-ester has synthesized according to reference [1].

1-4. Synthesize of DEGBAA:

The DEGBAA azido-ester has synthesized according to reference [1].

1-5. Synthesize of TEGDN:

The TEGDN nitrate-ester has synthesized according to reference [2].

1-6. Synthesize of GAP:

The glycidyl azide polymer (GAP) has synthesized according to reference [3].

2. Characterization

2-1. Characterization of GTAA

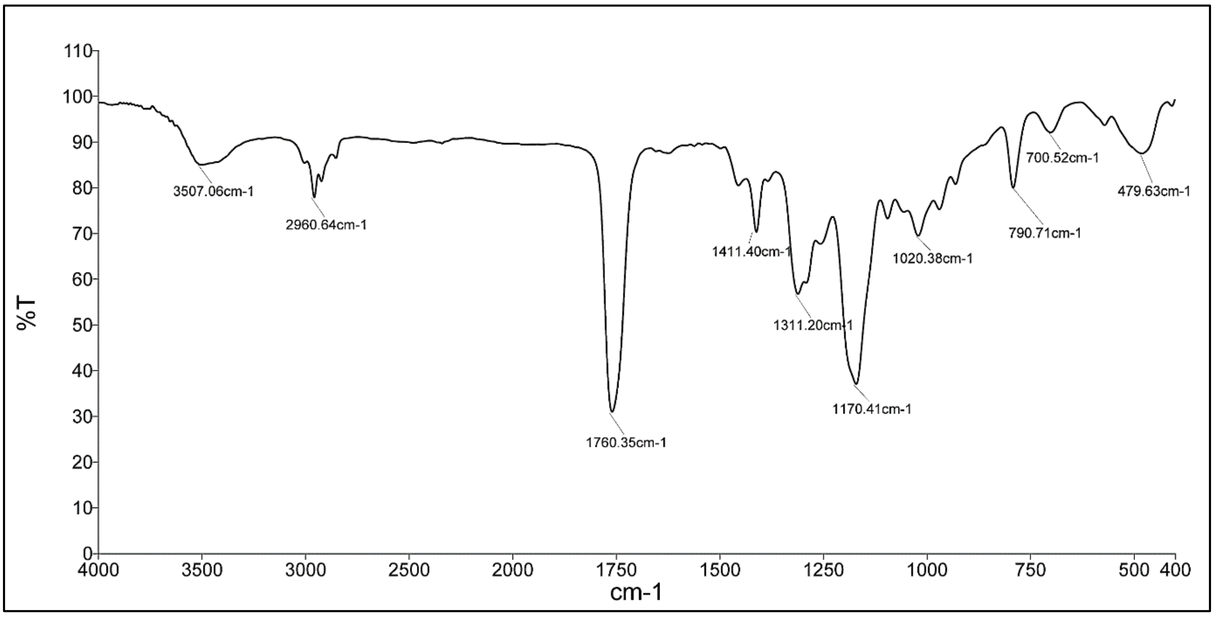


Figure S1. The IR spectra of the synthesized ester from glycerol and chloroacetic acid.

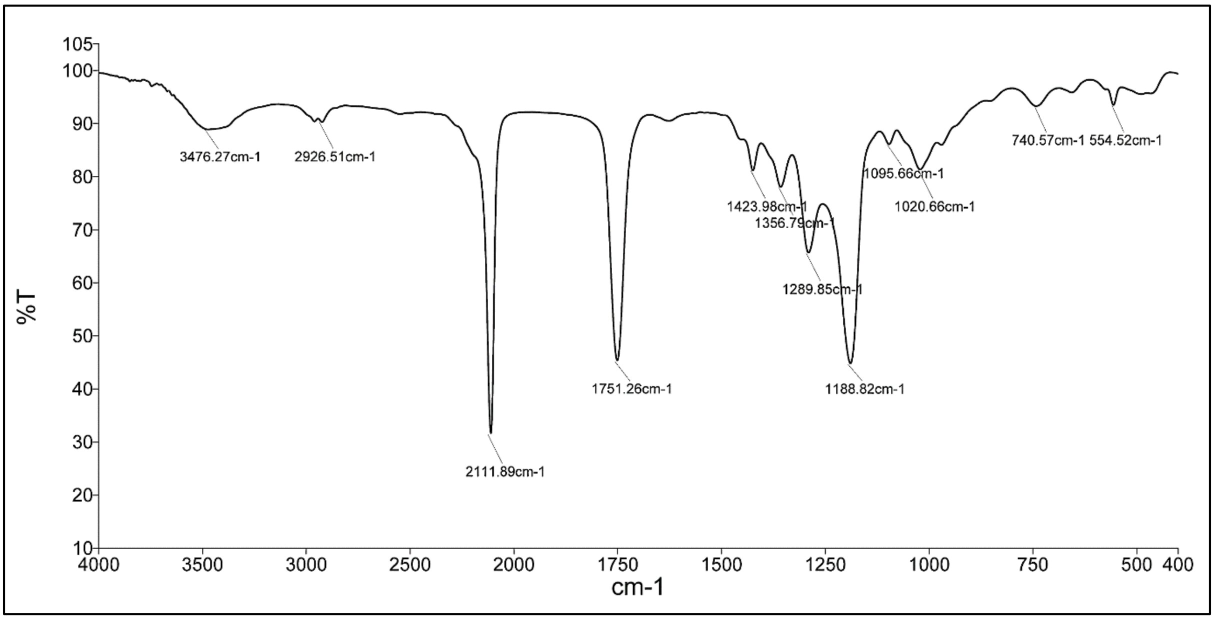


Figure S2. The IR spectra of GTAA azido-ester.

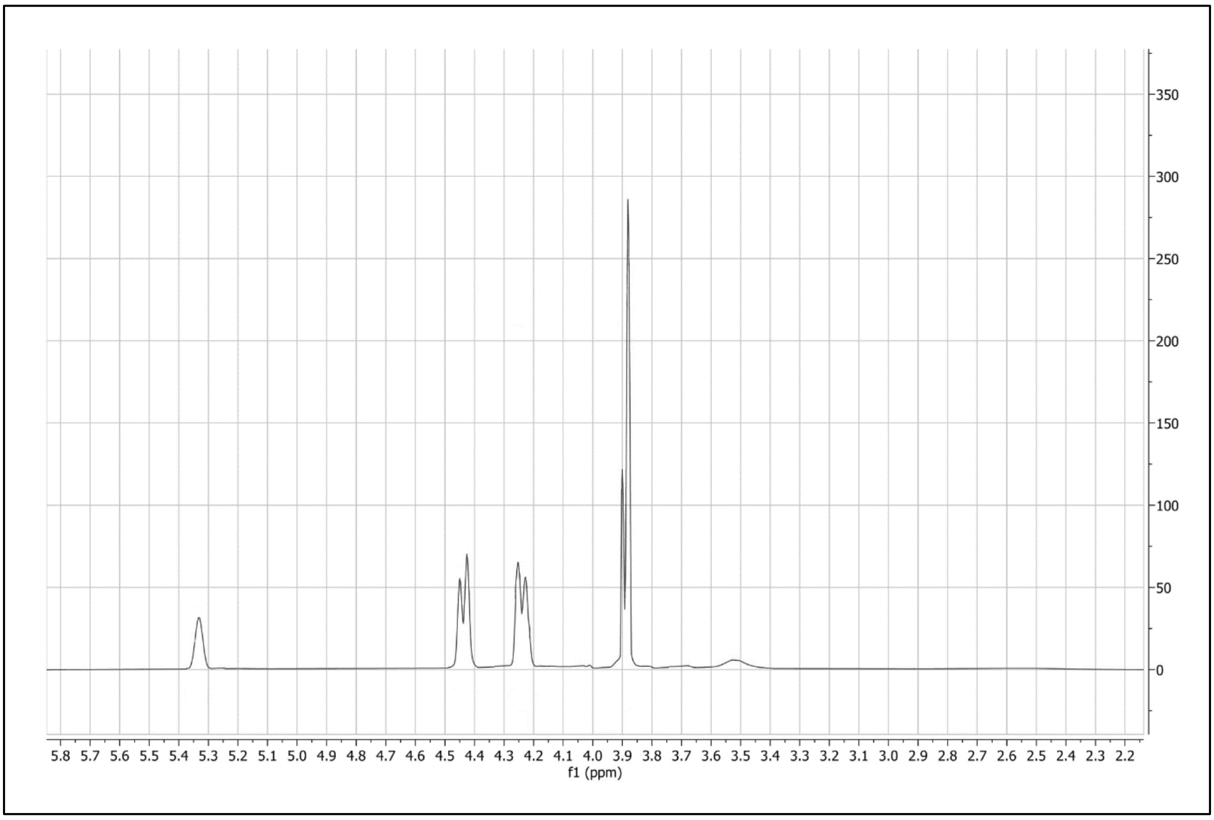


Figure S3. The ^{1}H NMR spectra of GTAA azido-ester.

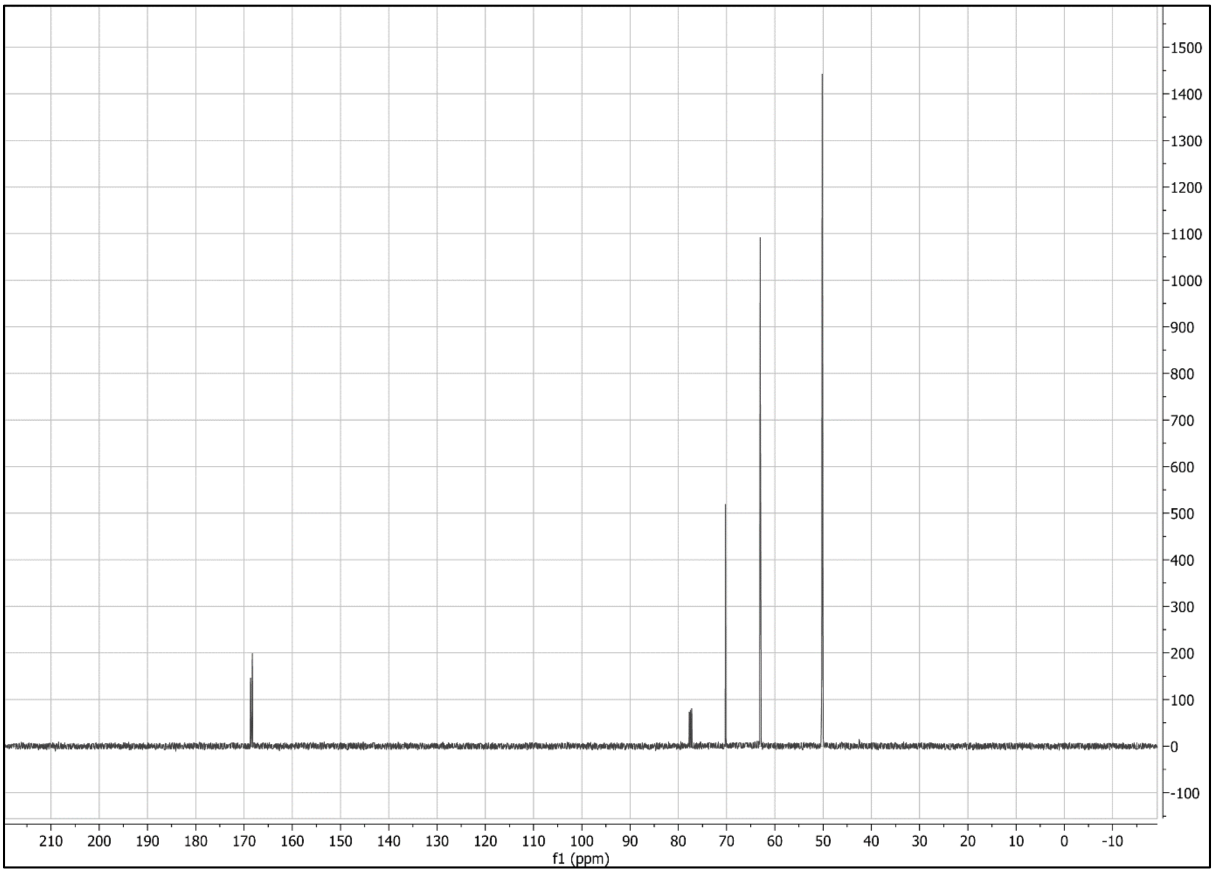


Figure S4. The ^{13}C NMR spectra of GTAA azido-ester.

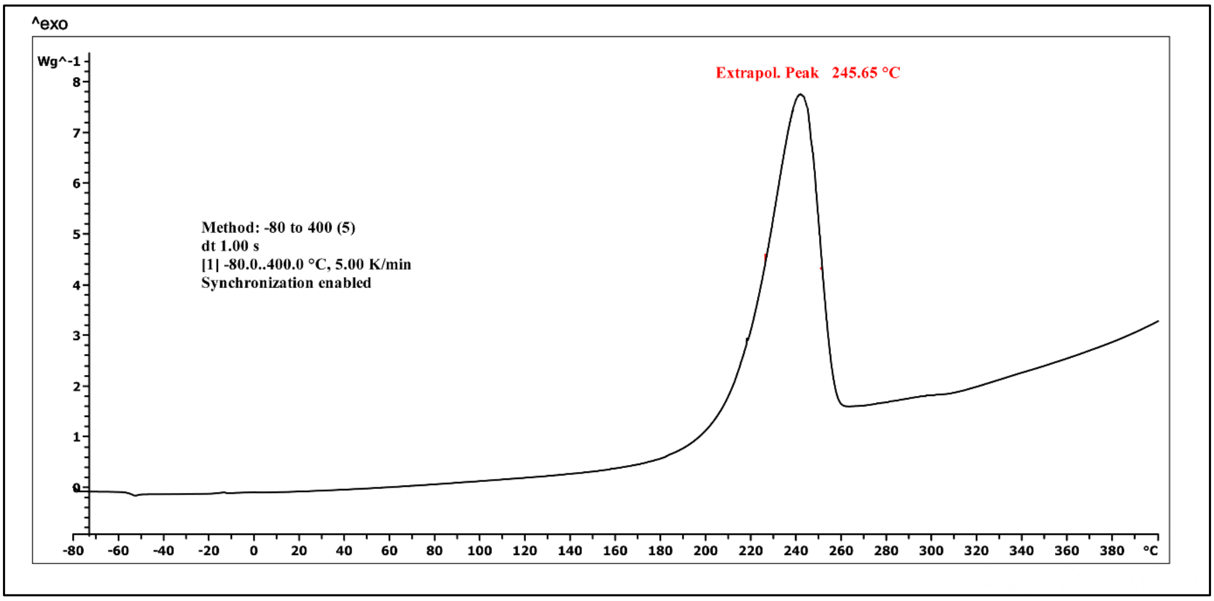


Figure S5. The thermal stability of GTAA azido-ester by DSC thermogram.

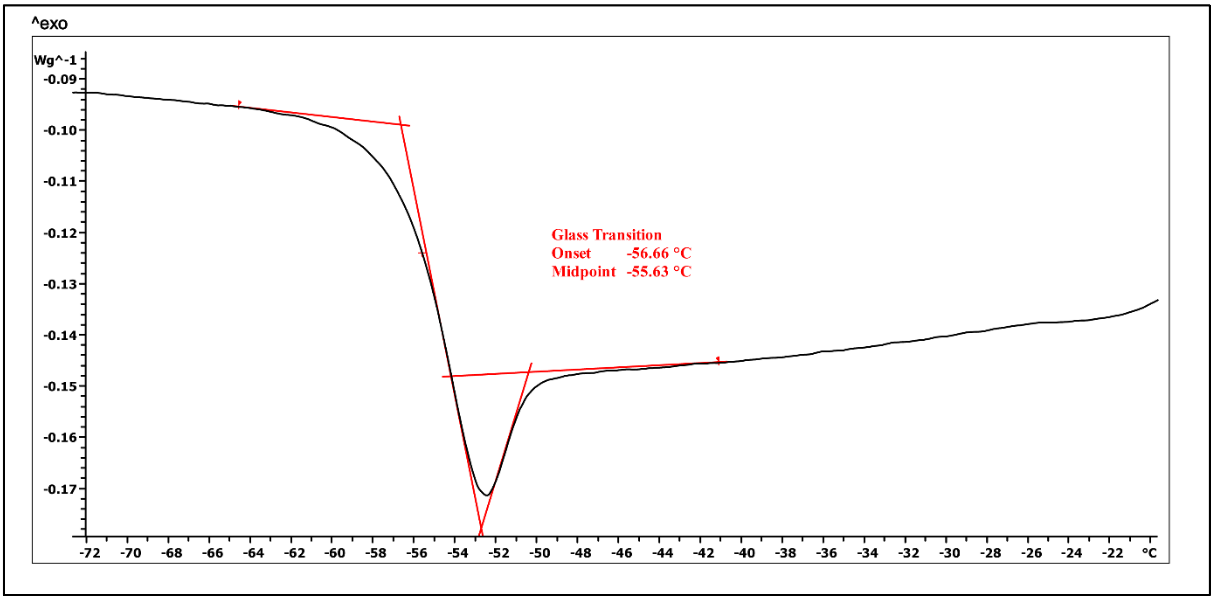


Figure S6. The glass transition temperature of GTAA azido-ester by DSC thermogram.

2-2. Characterization of TEGBAA

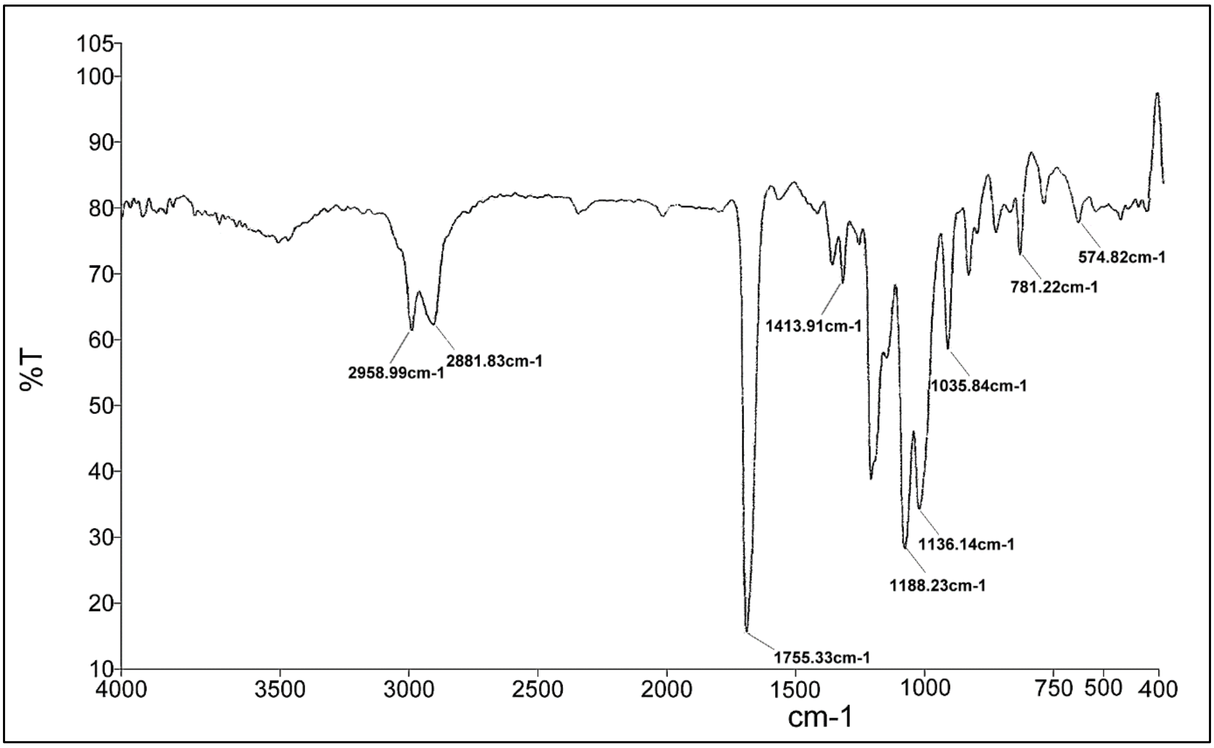


Figure S7. The IR spectra of the synthesized ester from triethylene glycol and chloroacetic acid.

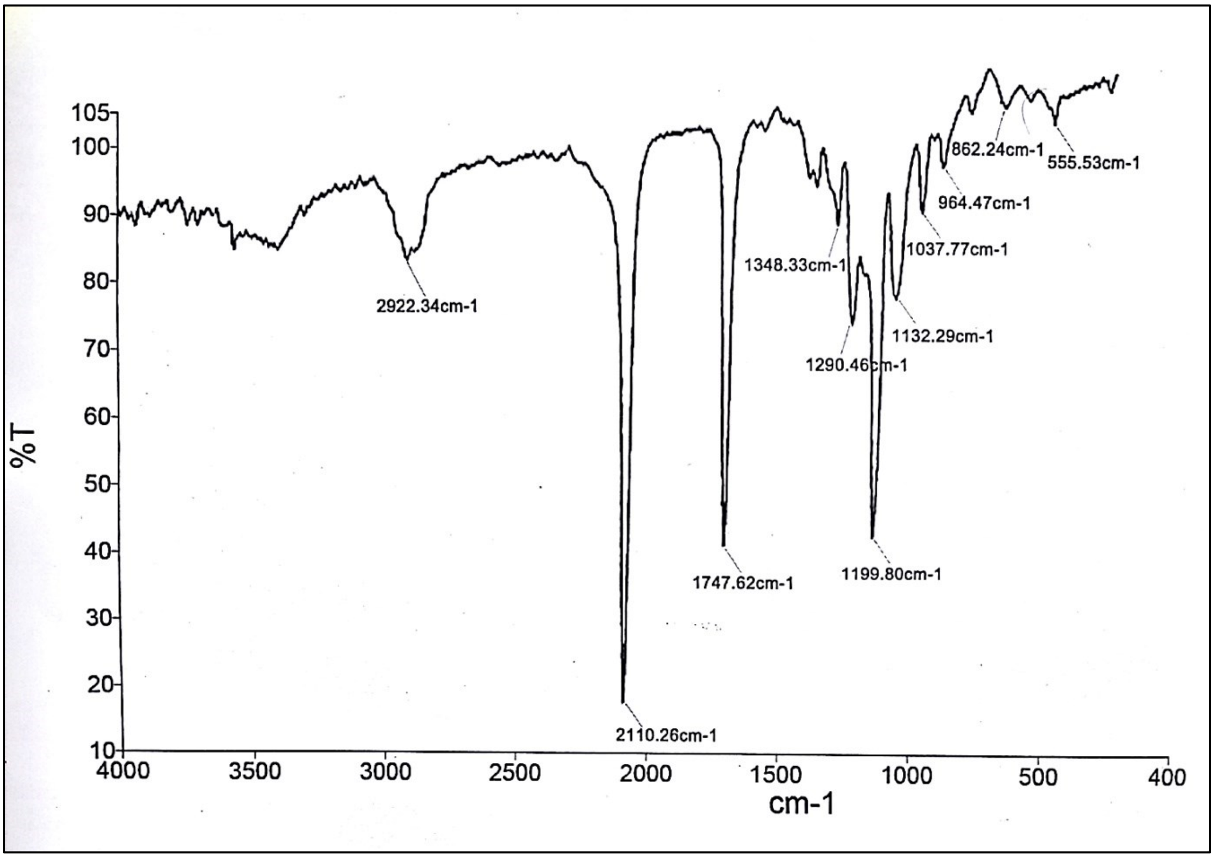


Figure S8. The IR spectra of TEGBAA azido-ester.

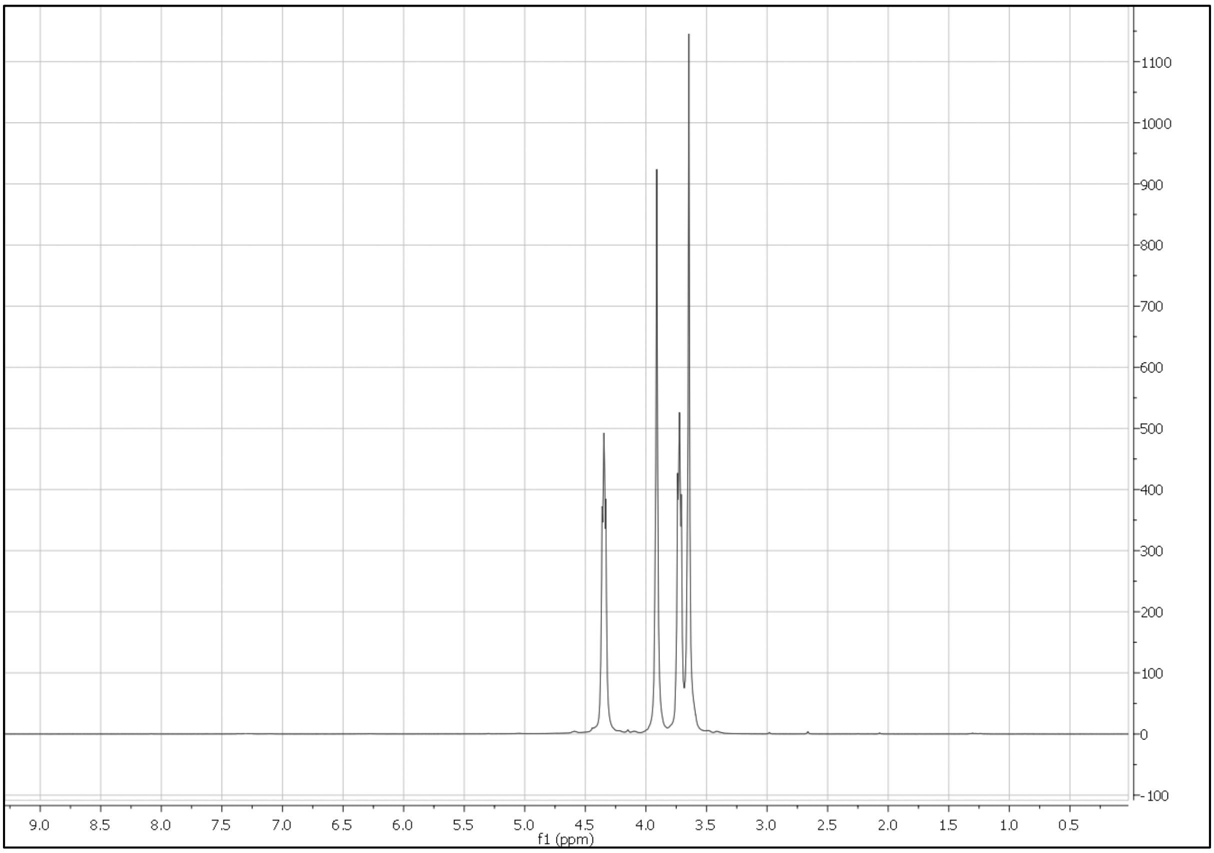


Figure S9. The ^{1}H NMR spectra of TEGBAA azido-ester.

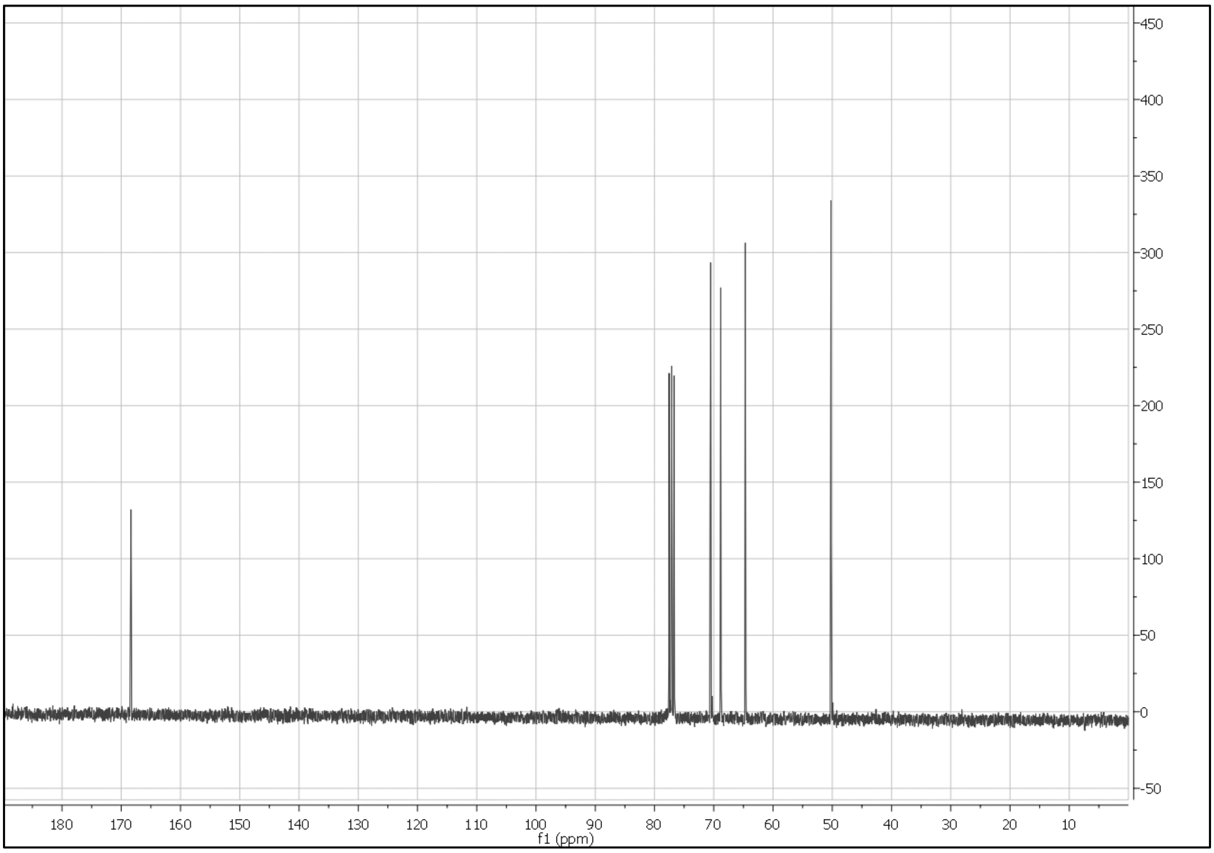


Figure S10. The ^{13}C NMR spectra of TEGBAA azido-ester.

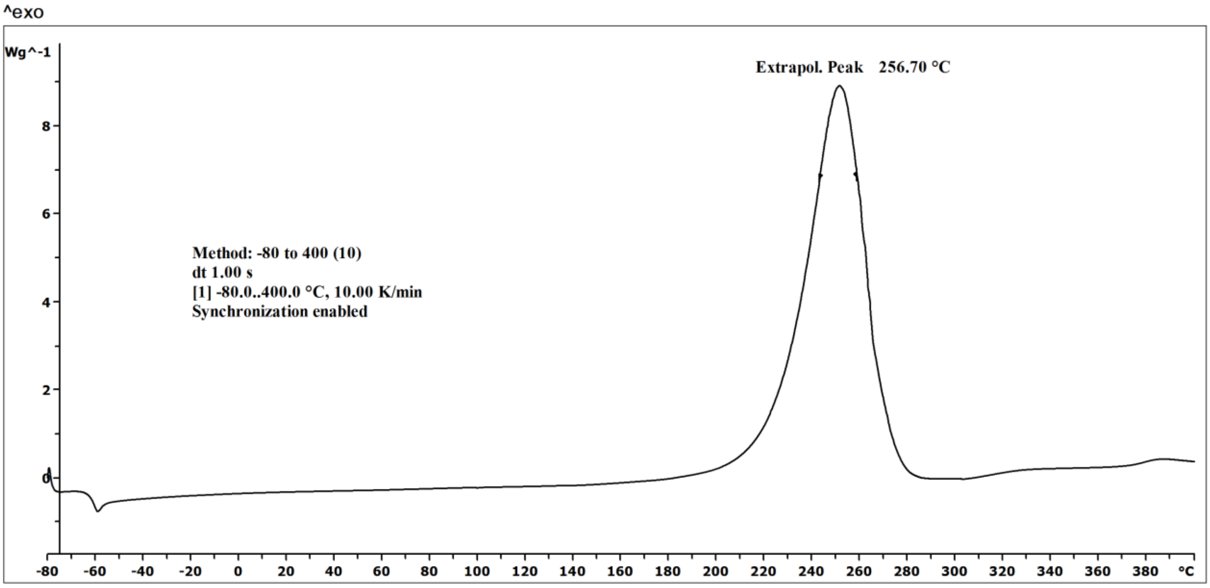


Figure S11. The thermal stability of TEGBAA azido-ester by DSC thermogram.

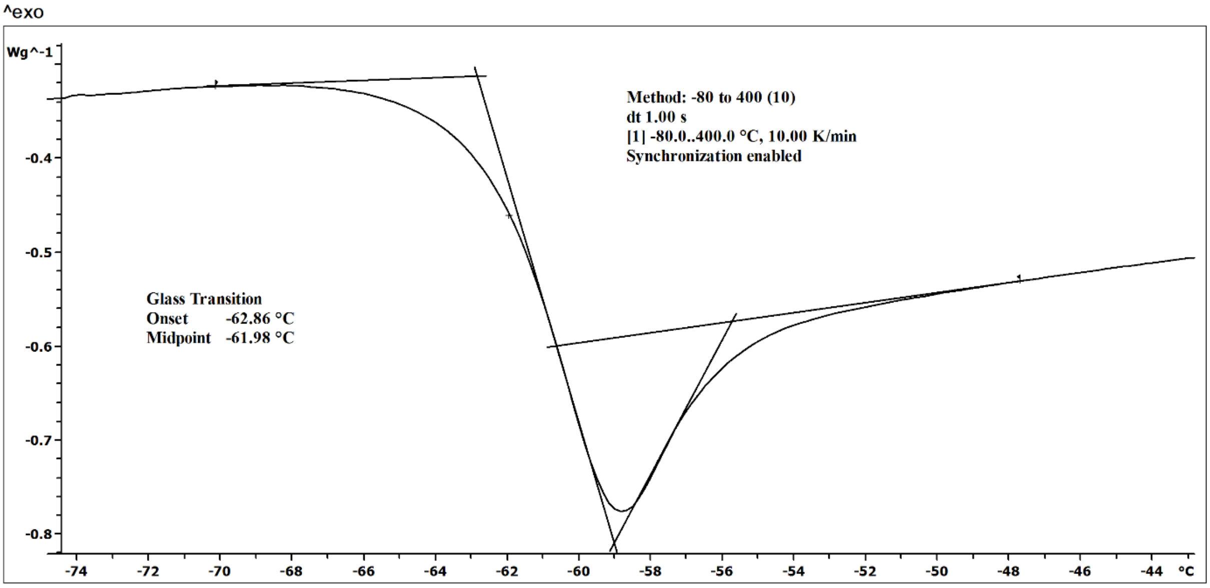


Figure S12. The glass transition temperature of TEGBAA azido-ester by DSC thermogram.

2-3. Characterization of EGBAA

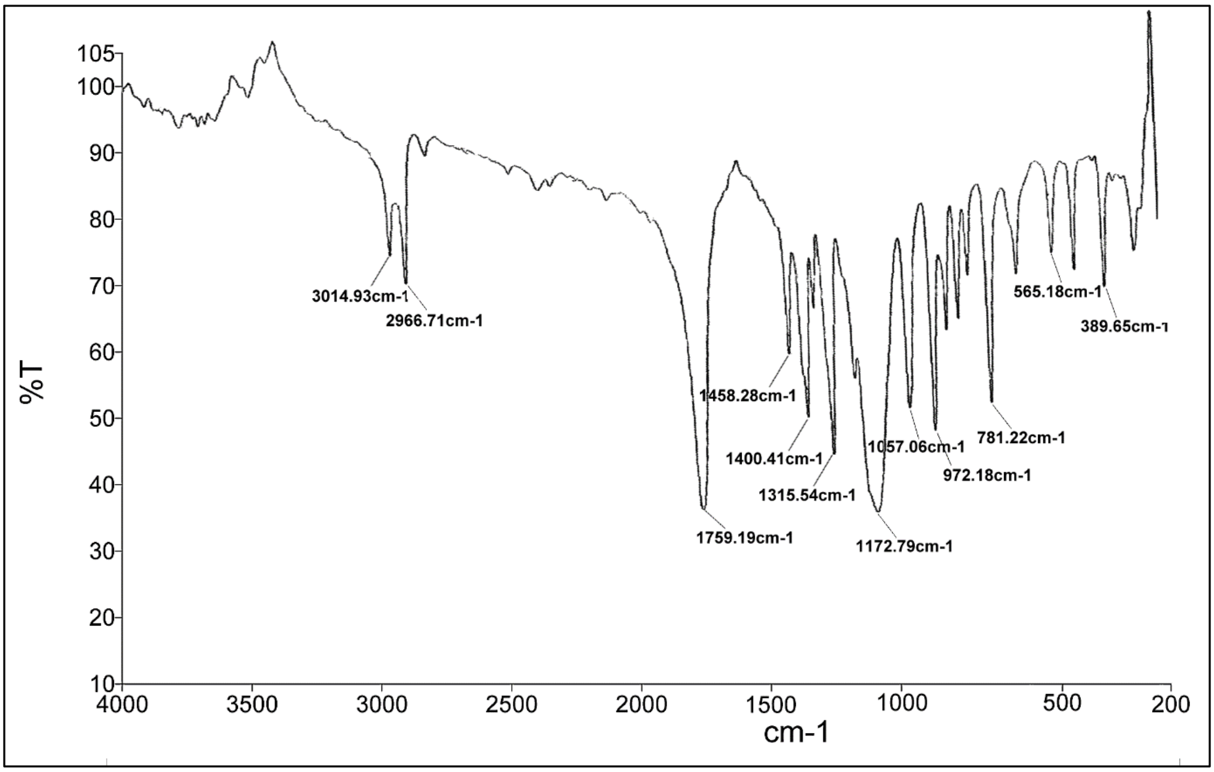


Figure S13. The IR spectra of the synthesized ester from ethylene glycol and chloroacetic acid.

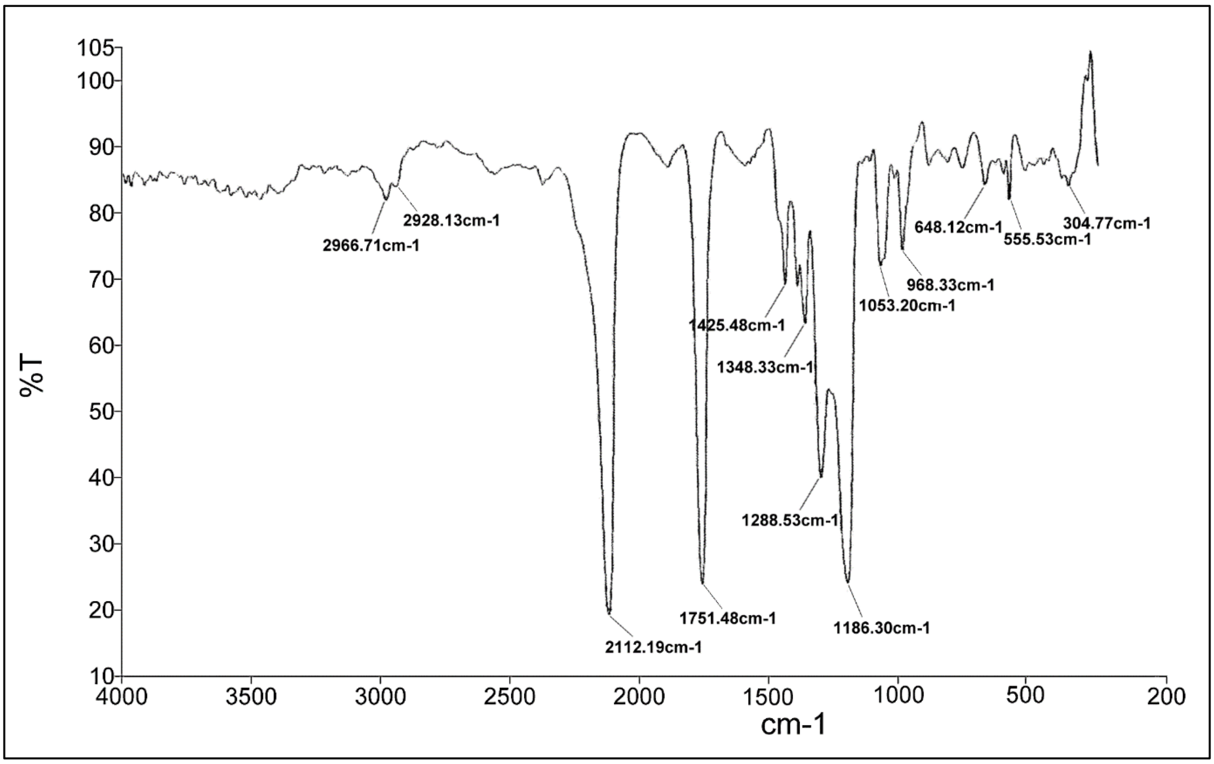


Figure S14. The IR spectra of EGBAA azido-ester.

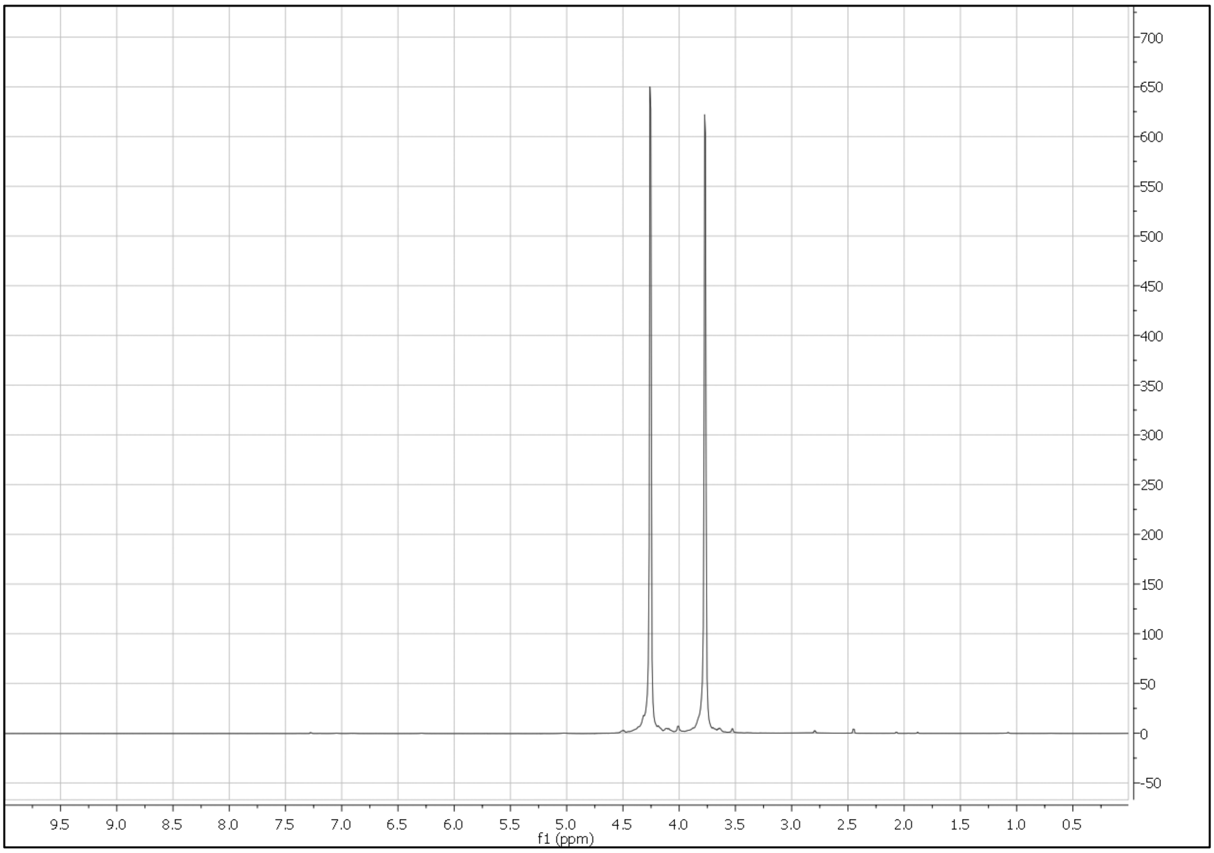


Figure S15. The ^{1}H NMR spectra of EGBAA azido-ester.

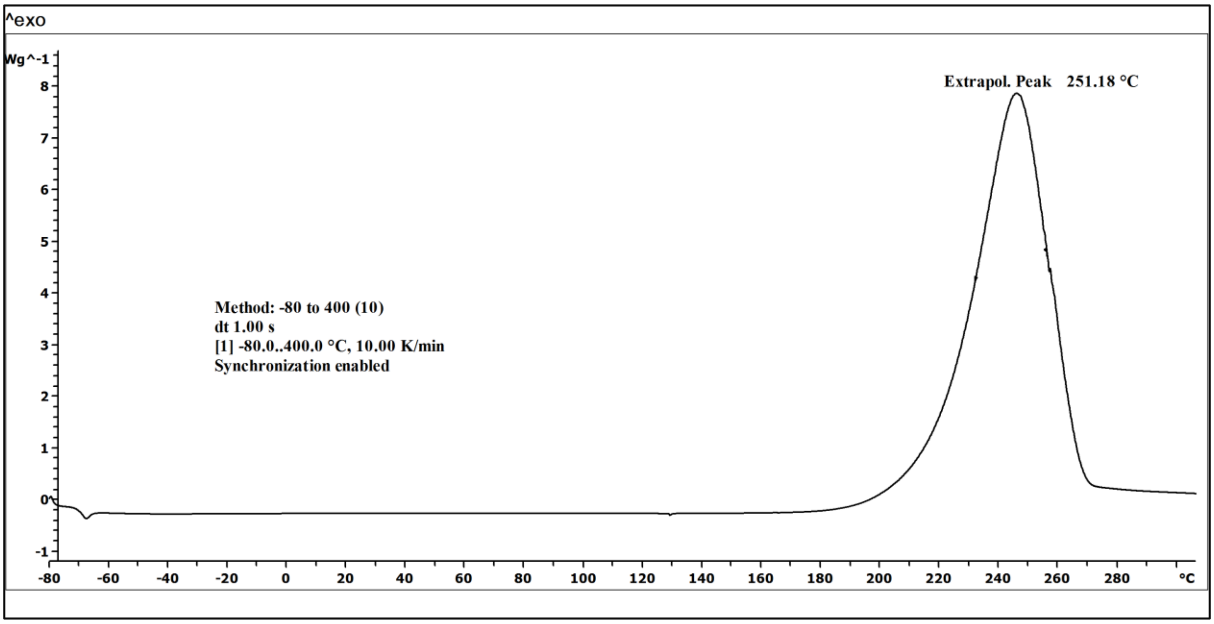


Figure S16. The thermal stability of EGBAA azido-ester by DSC thermogram.

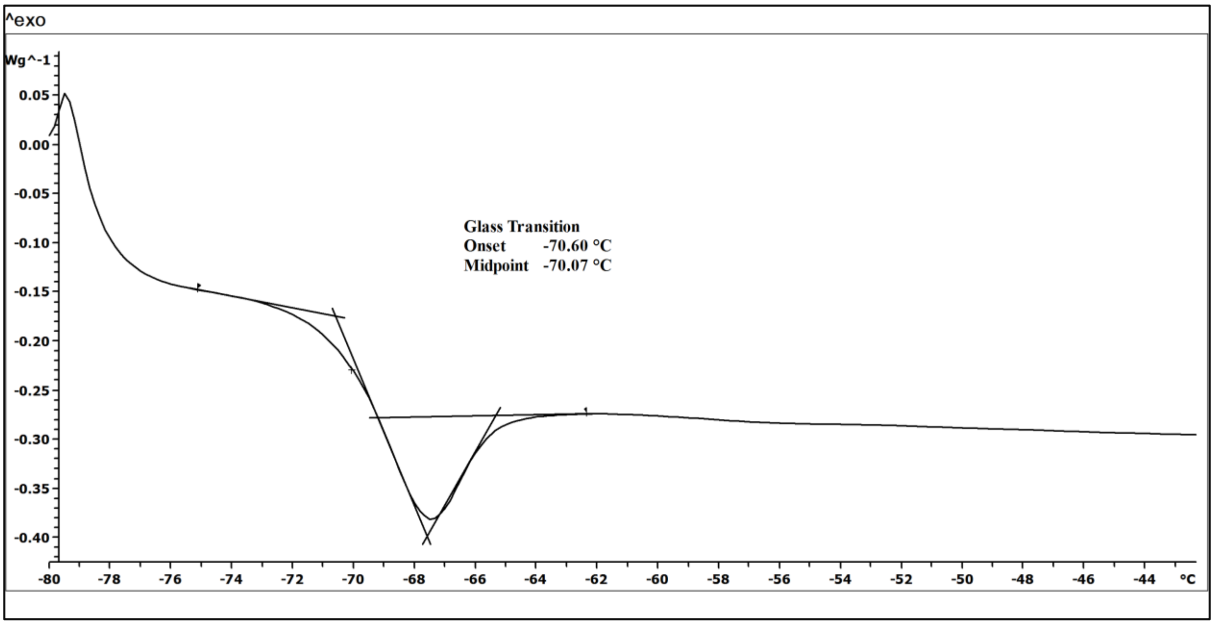


Figure S17. The glass transition temperature of EGBAA azido-ester by DSC thermogram.

2-4. Characterization of DEGBAA

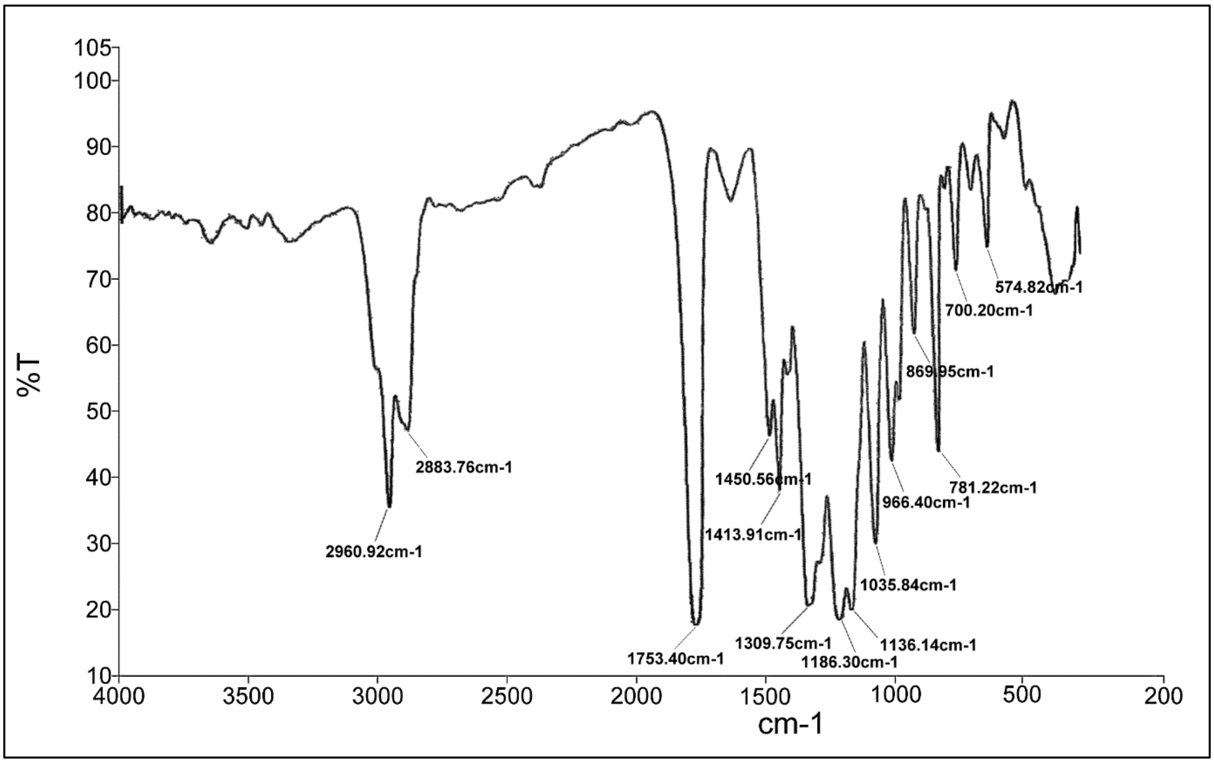


Figure S18. The IR spectra of the synthesized ester from diethylene glycol and chloroacetic acid.

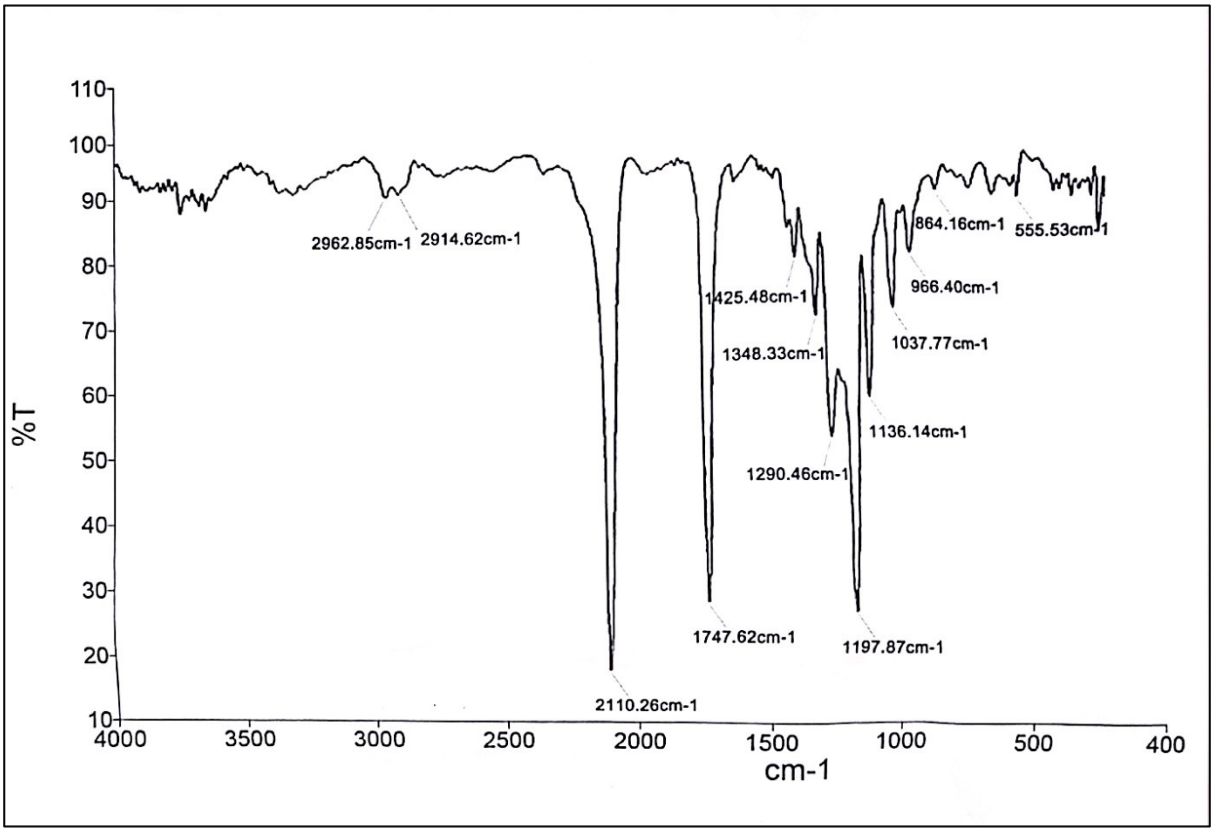


Figure S19. The IR spectra of DEGBAA azido-ester.

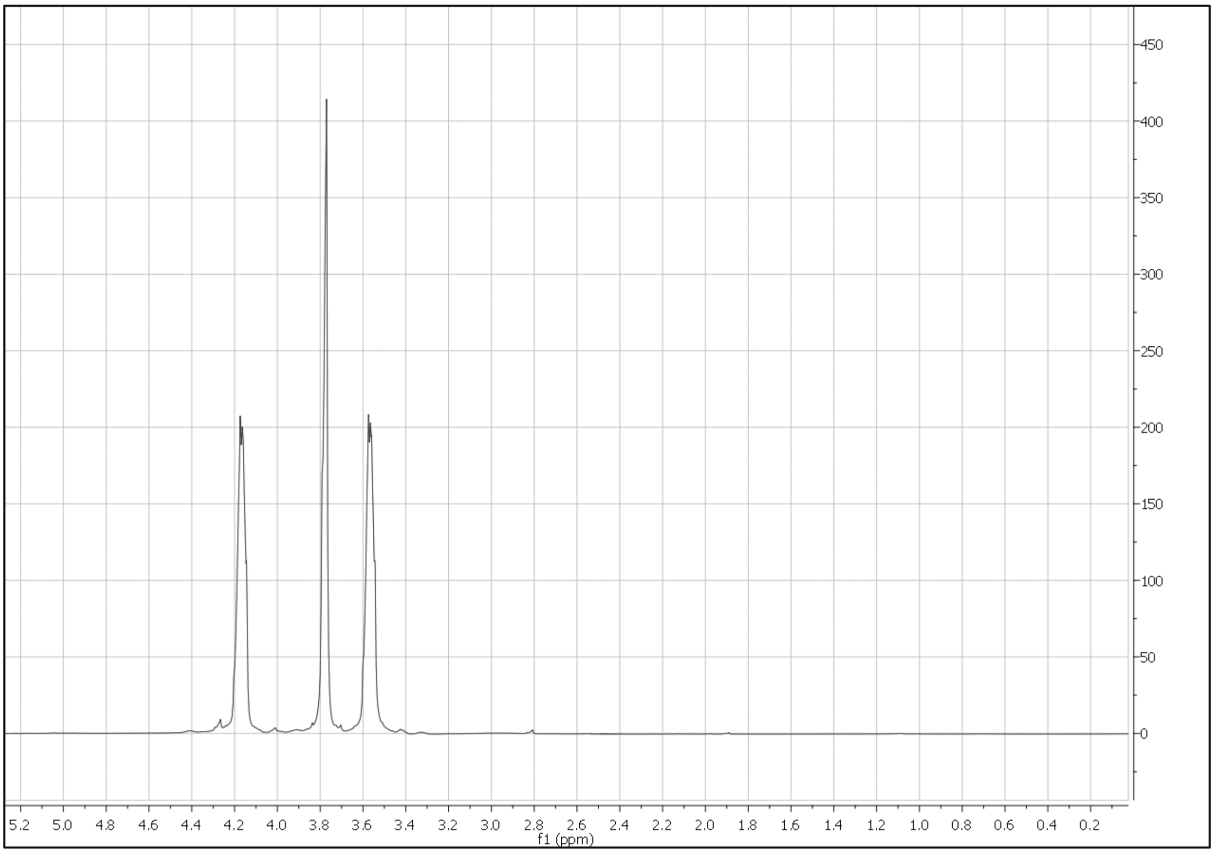


Figure S20. The ^1H NMR spectra of DEGBAA azido-ester.

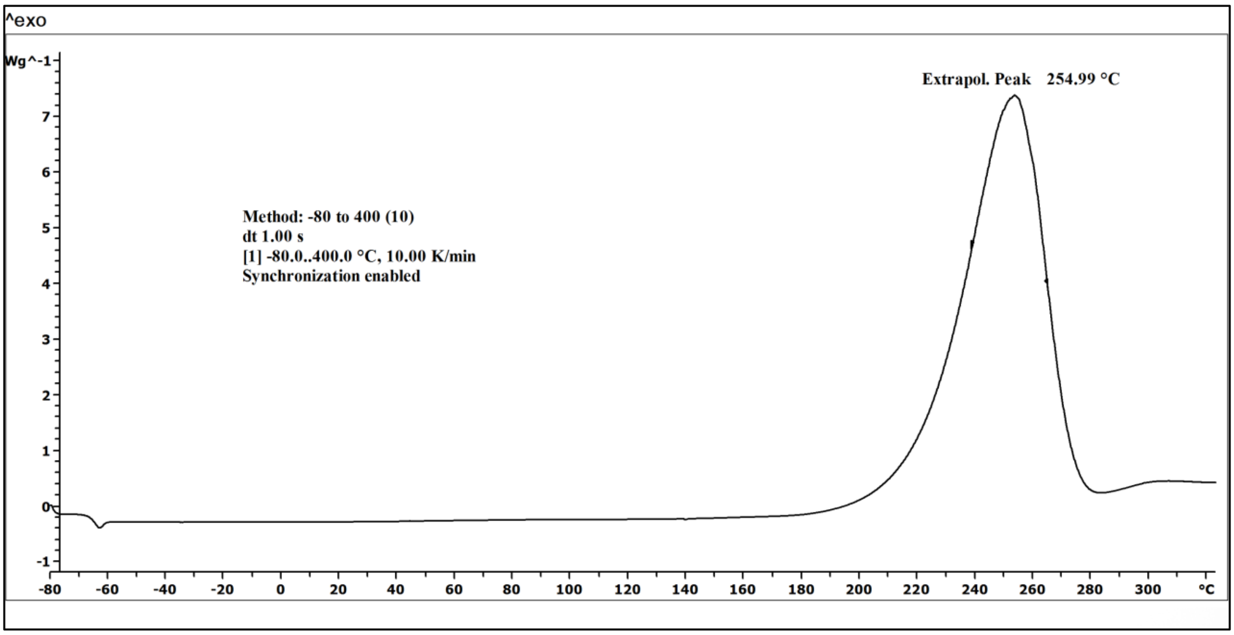


Figure S21. The thermal stability of DEGBAA azido-ester by DSC thermogram.

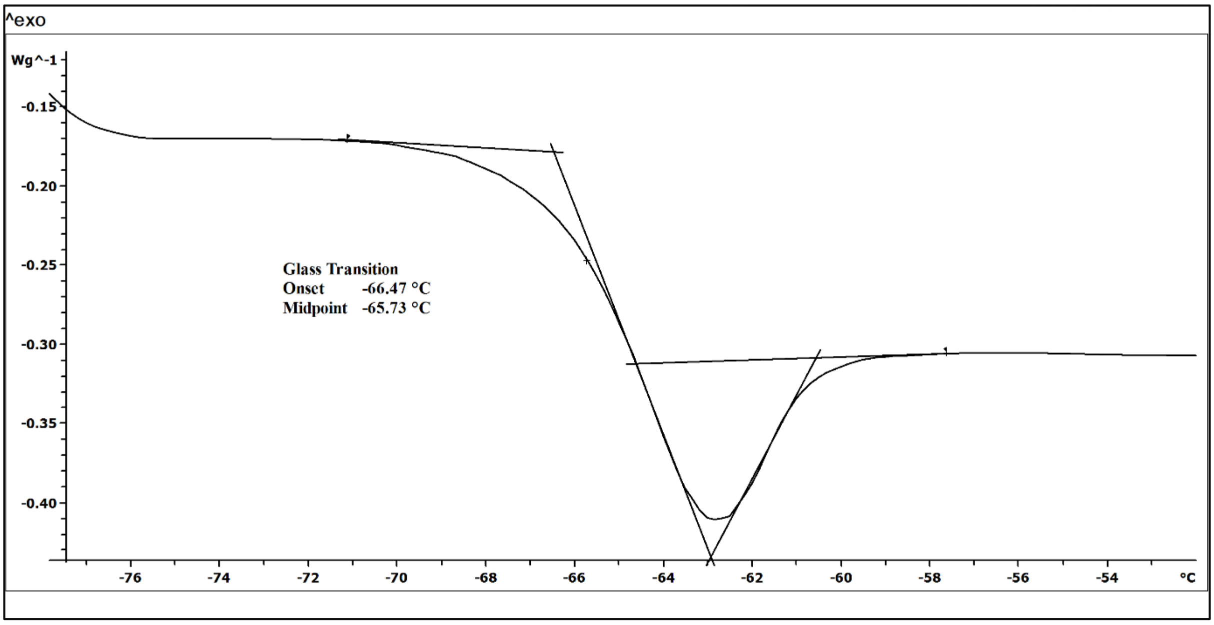


Figure S22. The glass transition temperature of DEGBAA azido-ester by DSC thermogram.

2-5. Characterization of TEGDN

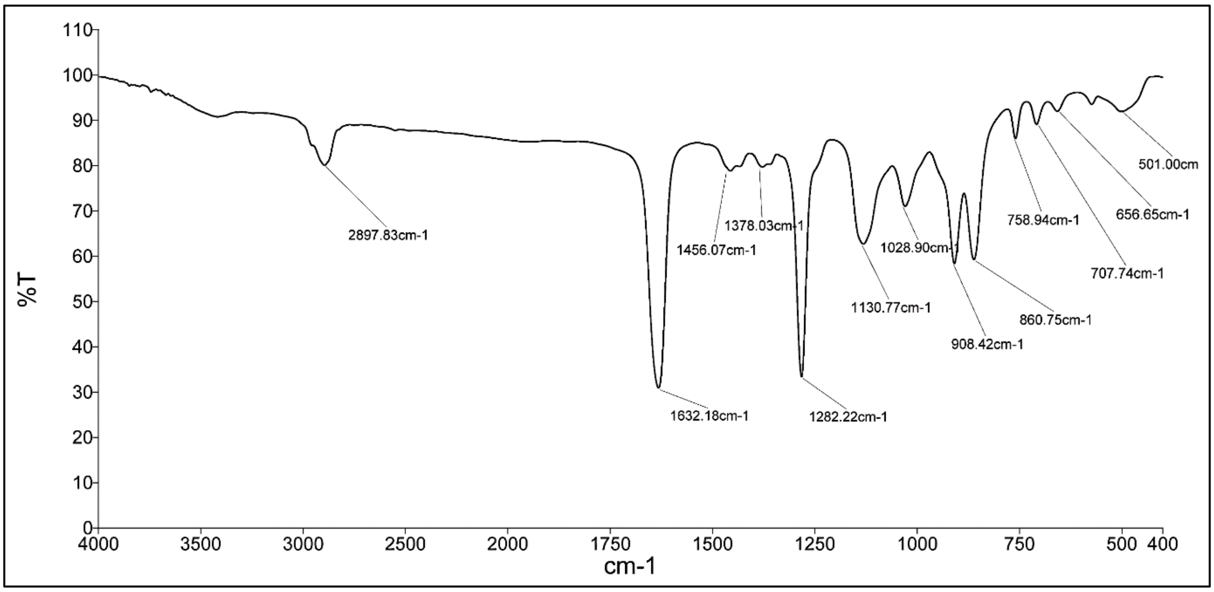


Figure S23. The IR spectra of the synthesized triethylene glycol dinitrate (TEGDN).

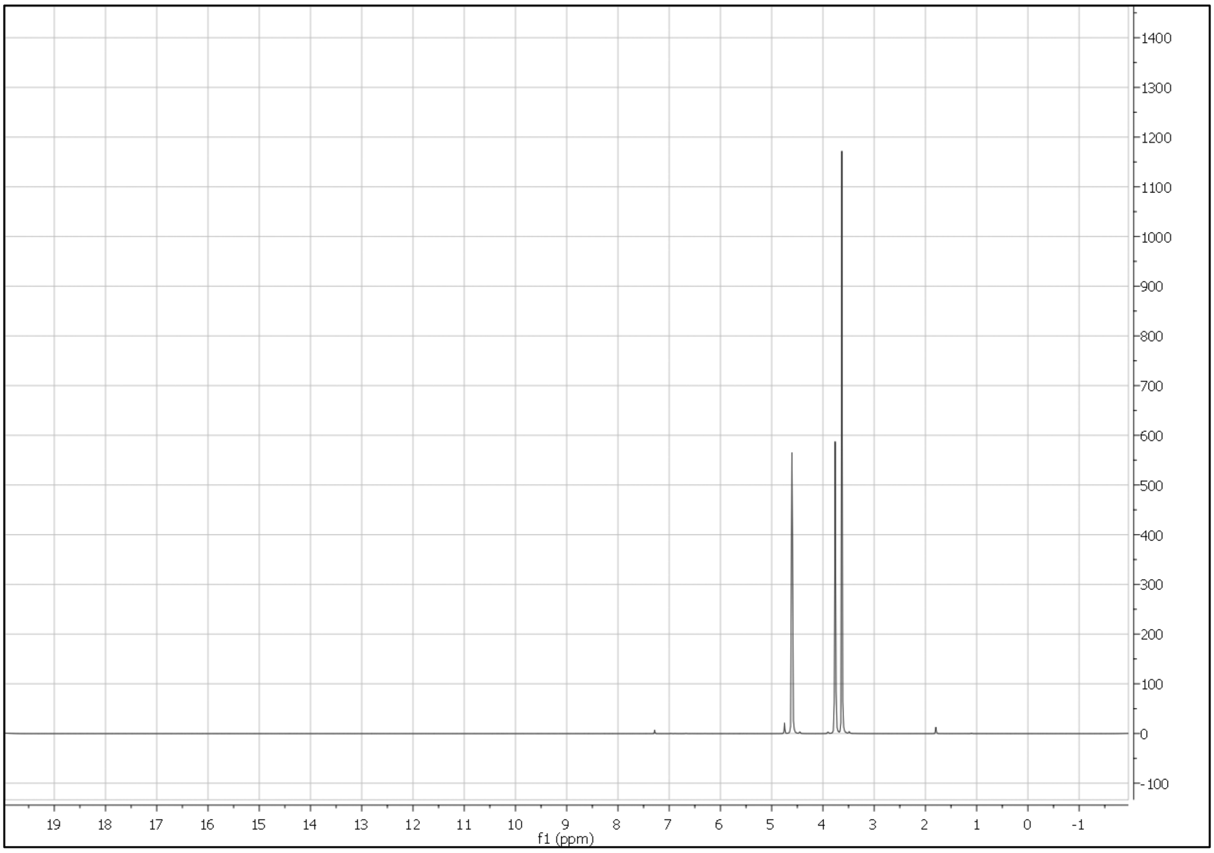


Figure S24. The ^{1}H NMR spectra of TEGDN.

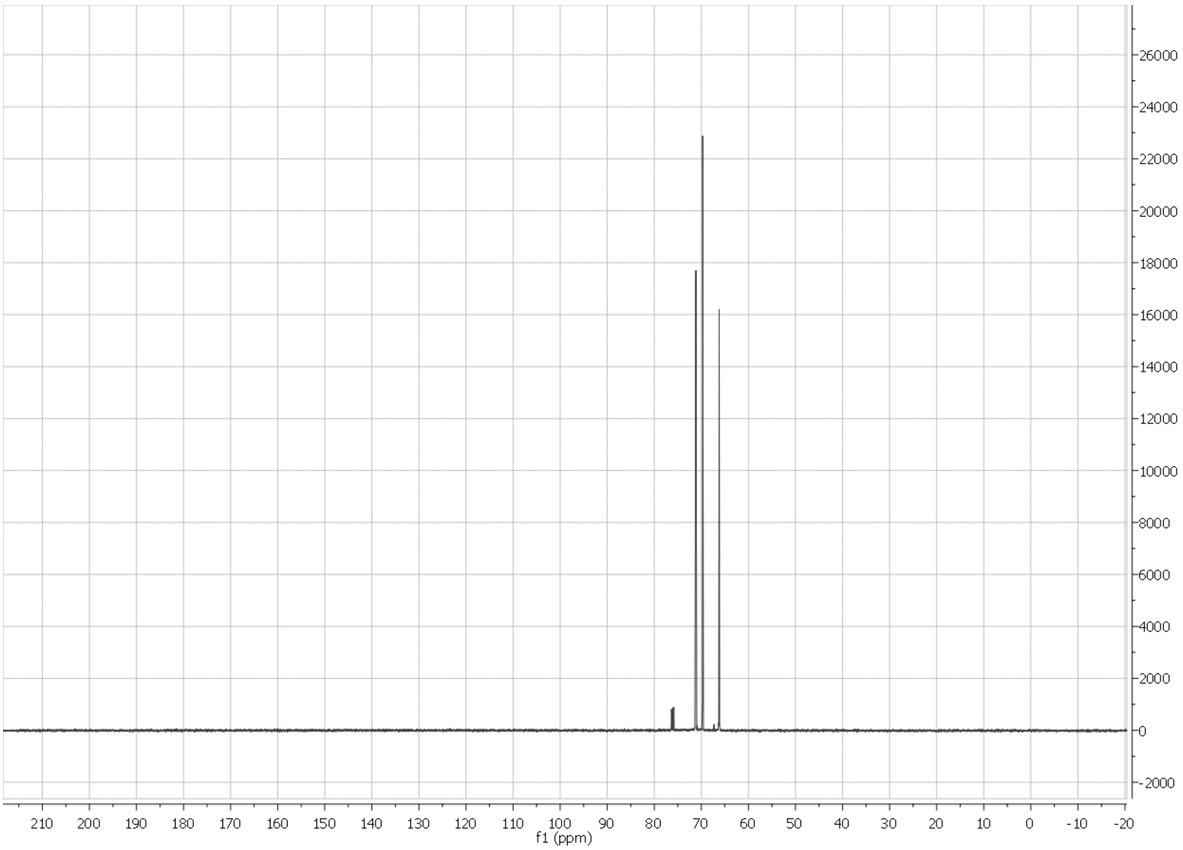


Figure S25. The ^{13}C NMR spectra of TEGDN.

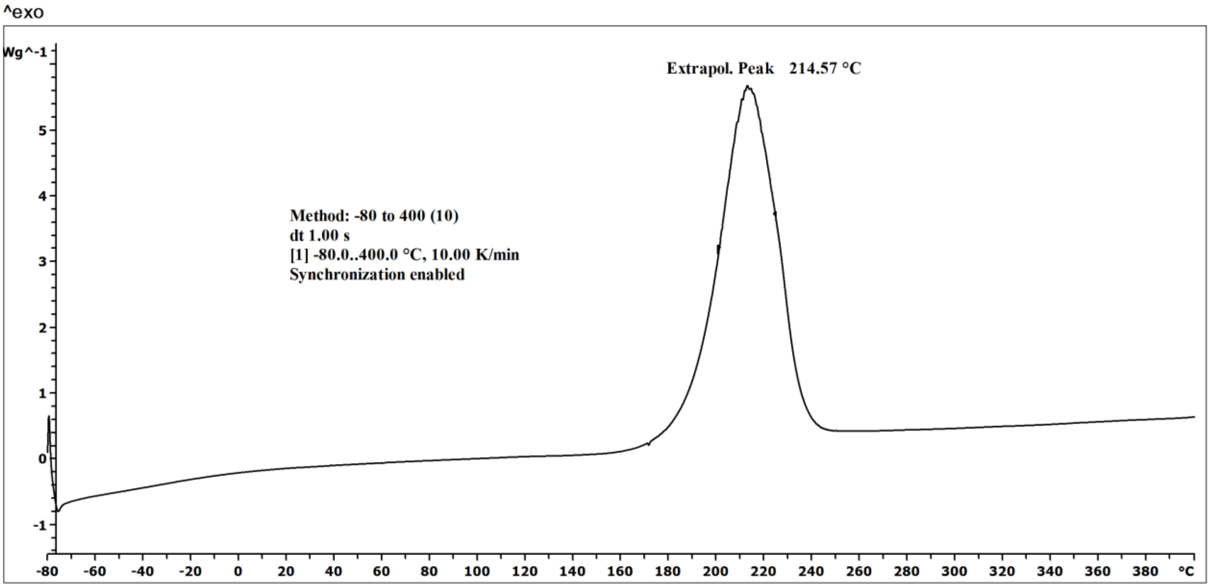


Figure S26. The thermal stability of TEGDN by DSC thermogram.

2-6. Characterization of GAP

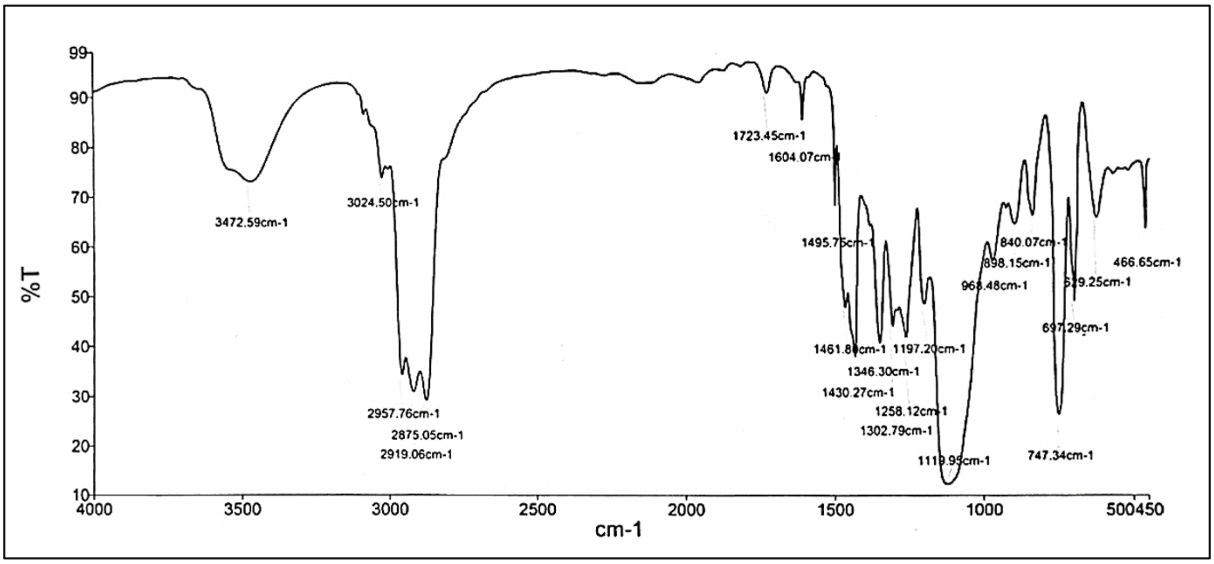


Figure S27. The IR spectra of the synthesized PECH.

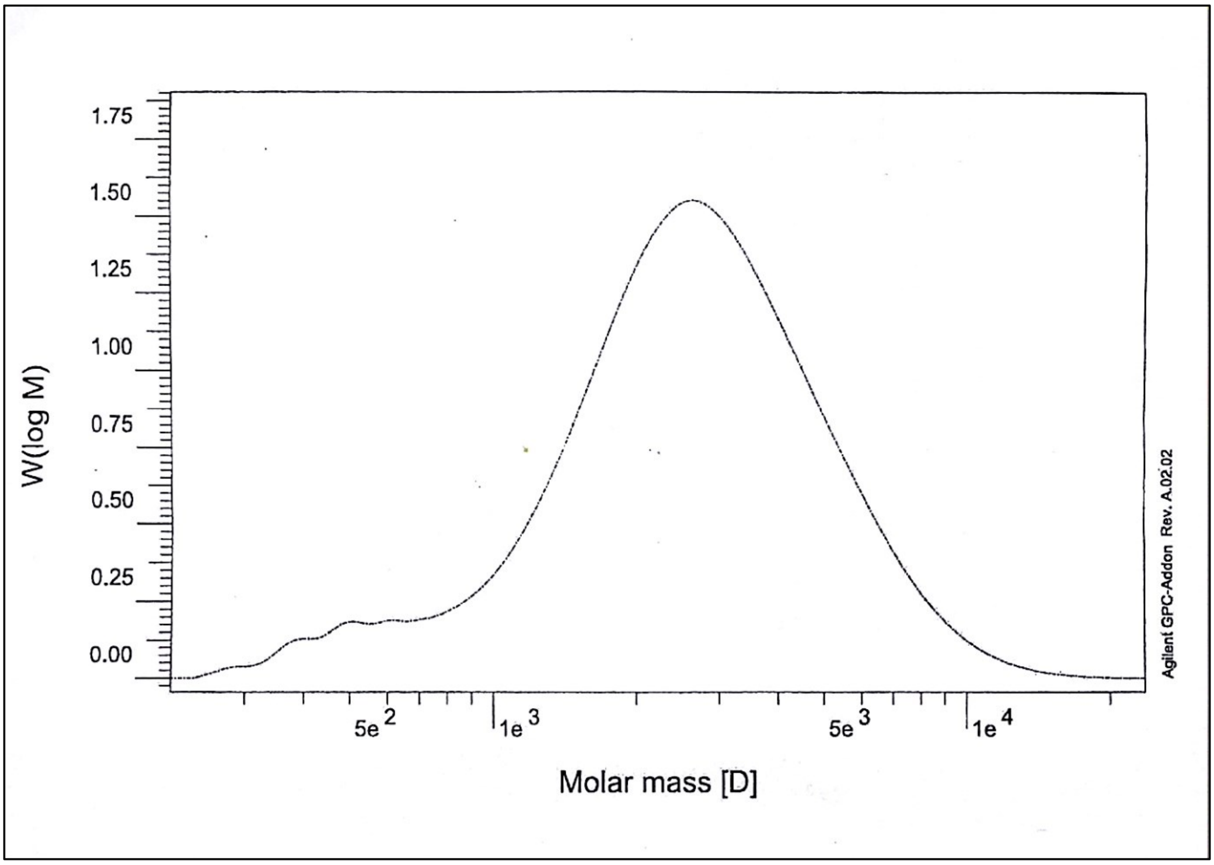


Figure S28. GPC curve of synthesized PECH.

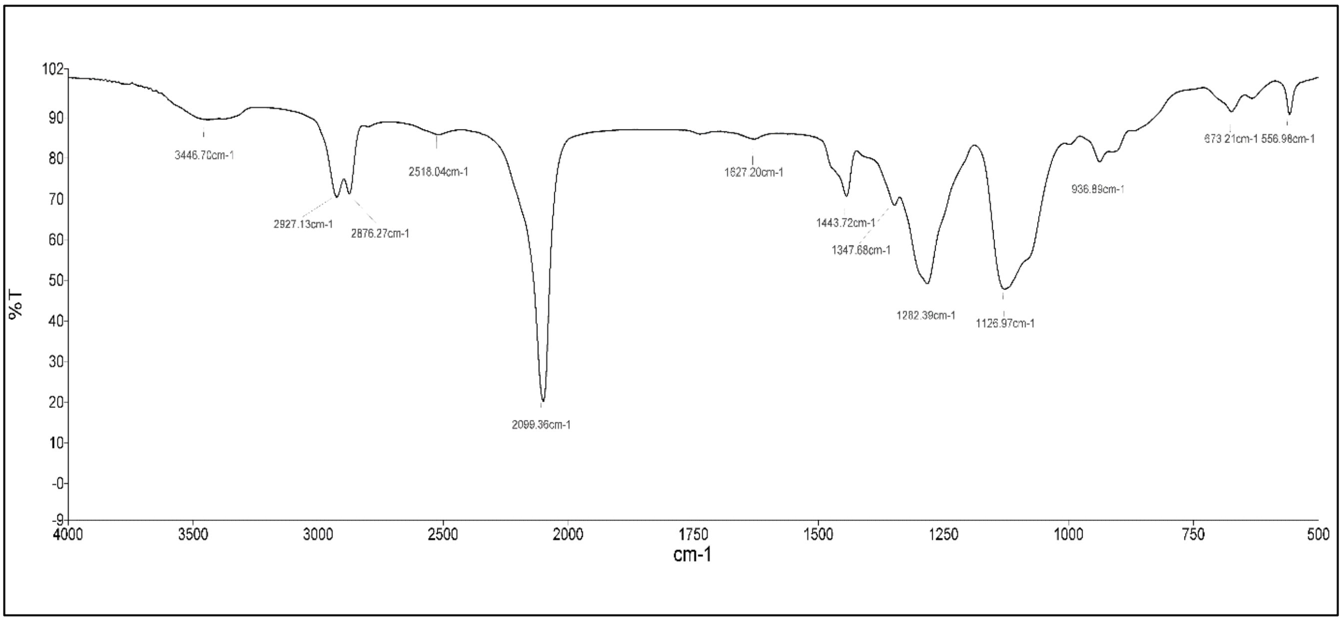


Figure S29. The IR spectra of the synthesized GAP.

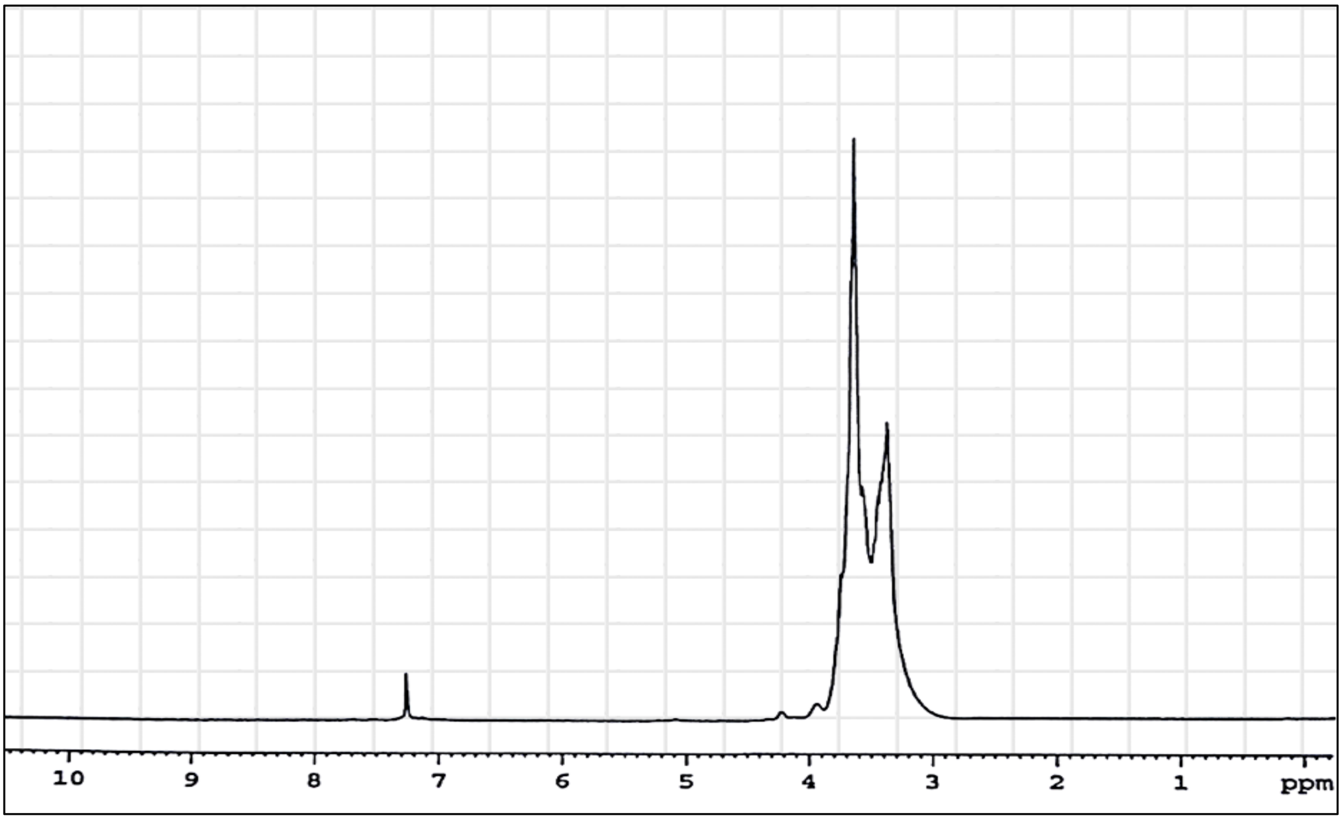


Figure S30. The ^{1}H NMR of the synthesized GAP.

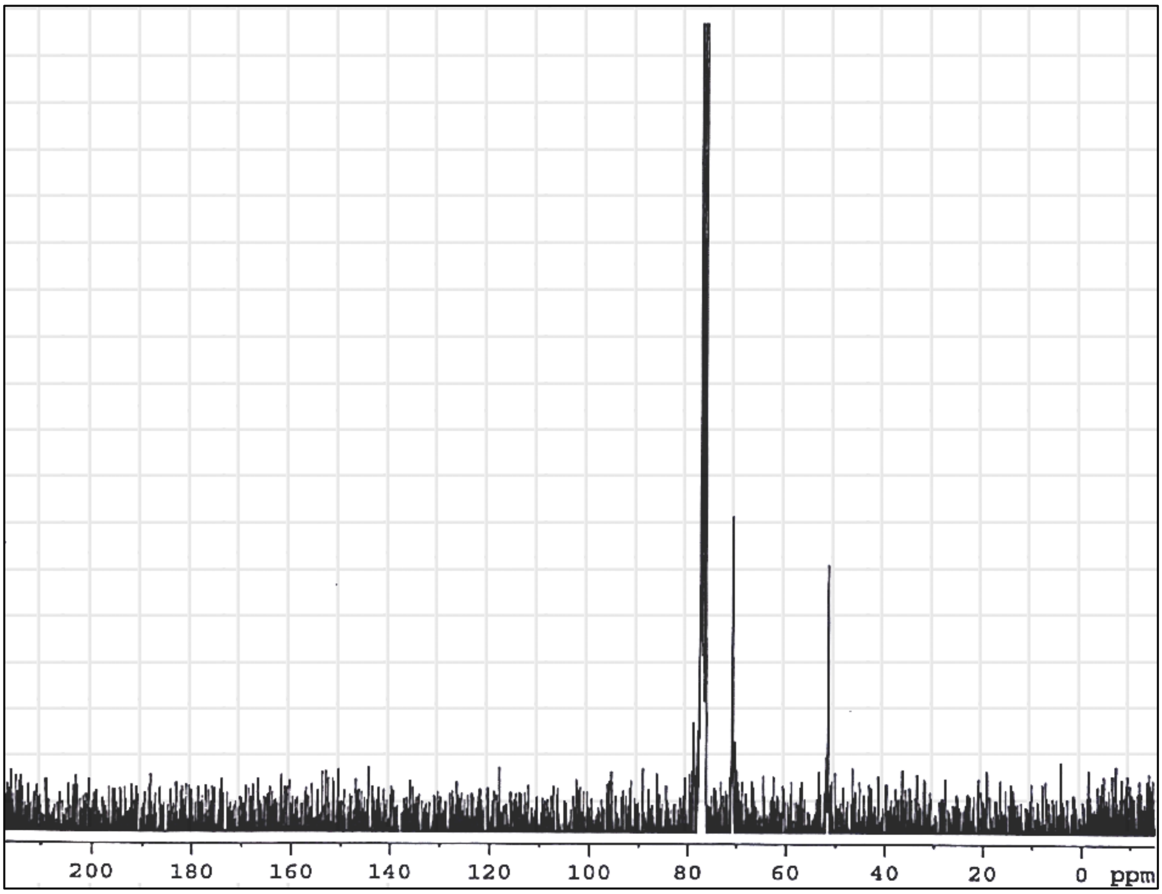


Figure S31. The ^{13}C NMR of the synthesized GAP.

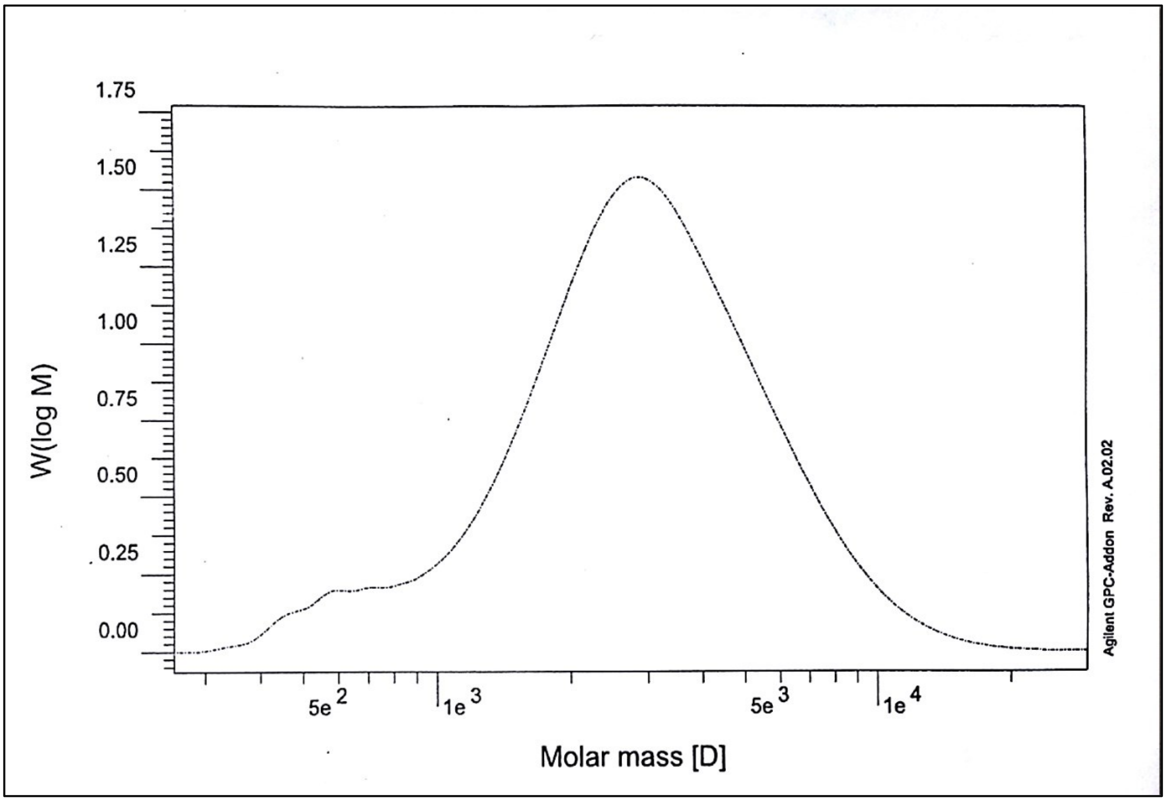


Figure S32. GPC curve of synthesized GAP.

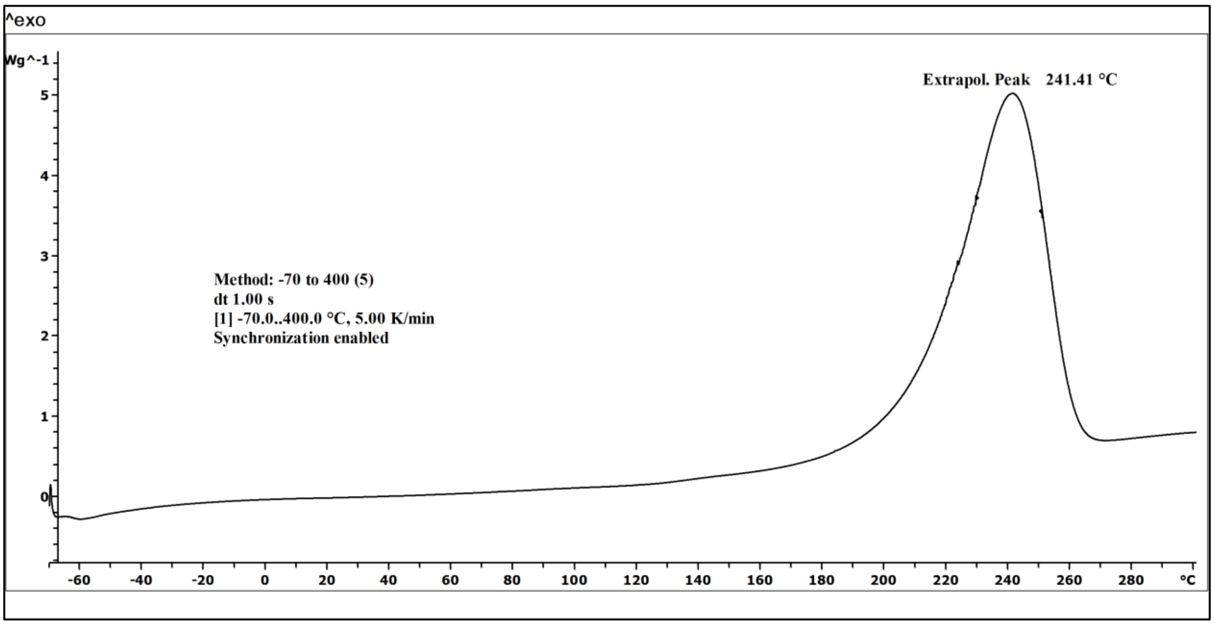


Figure S33. The thermal stability of synthesized GAP by DSC thermogram.

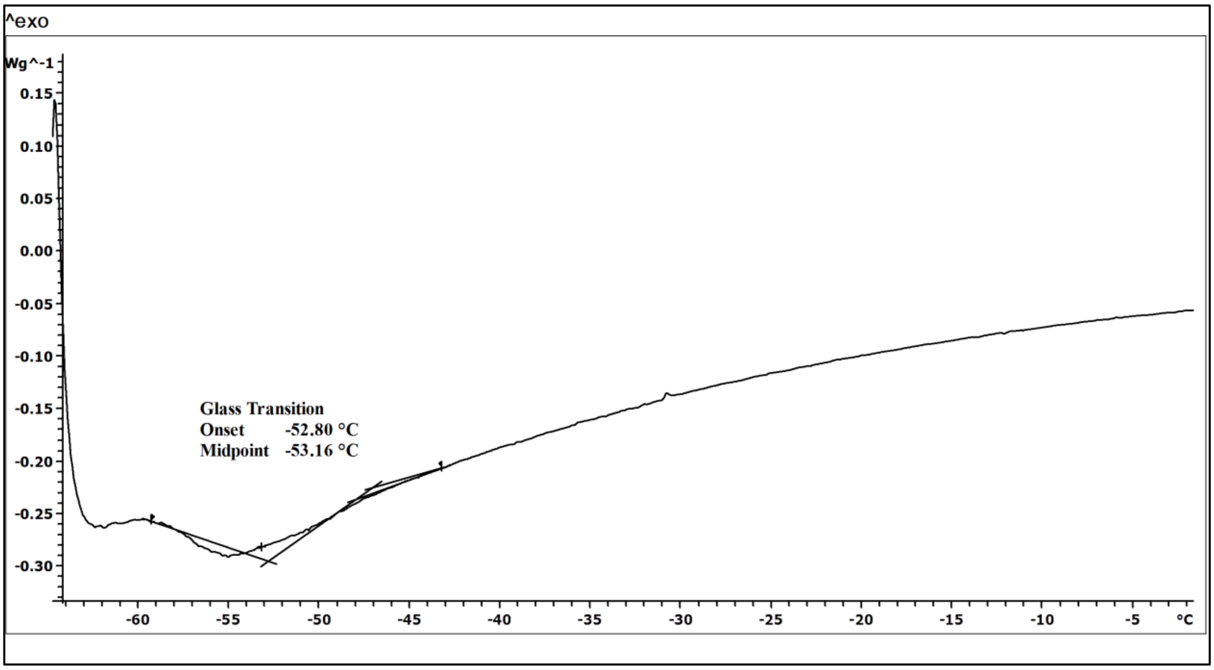


Figure S34. The glass transition temperature of synthesized GAP by DSC thermogram.

3. DSC thermogram of different GAP/plasticizer mixtures

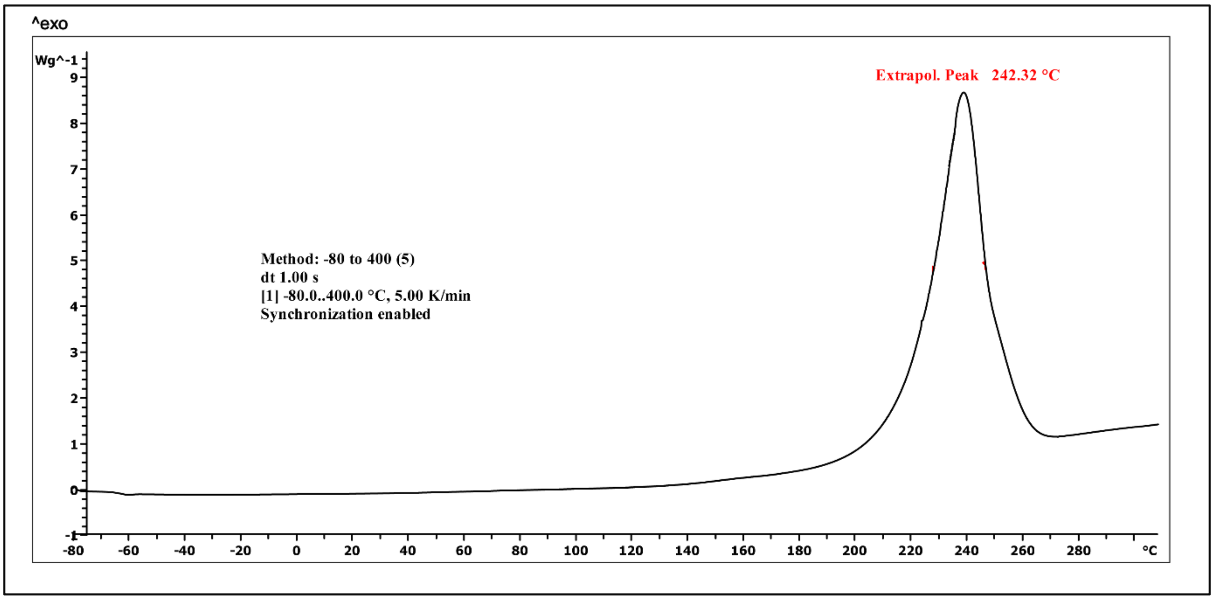


Figure S35. Thermal stability of GAP/GTAA composition.

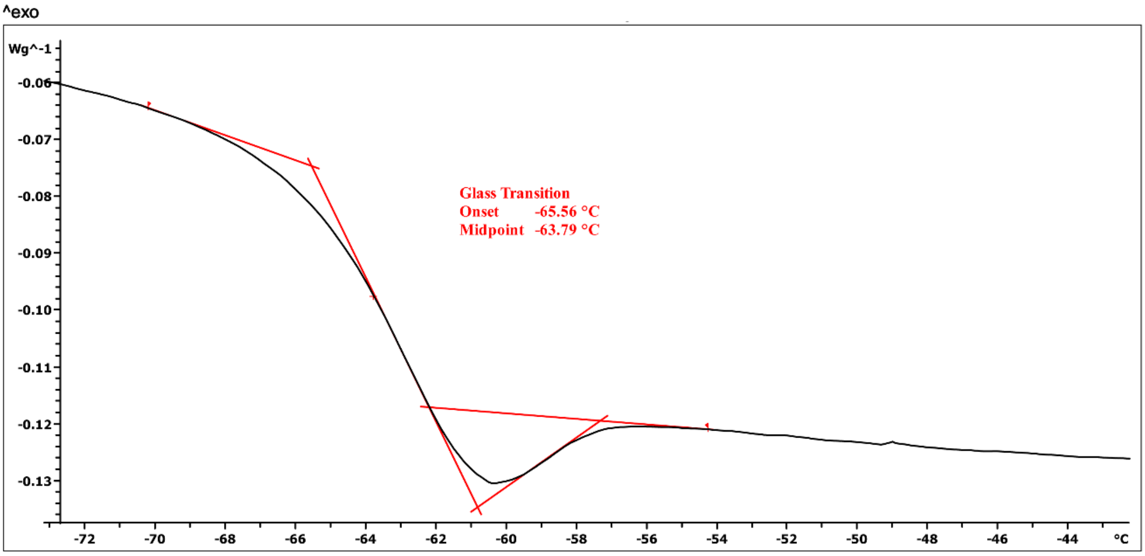


Figure S36. The glass transition temperature of GAP/GTAA composition.

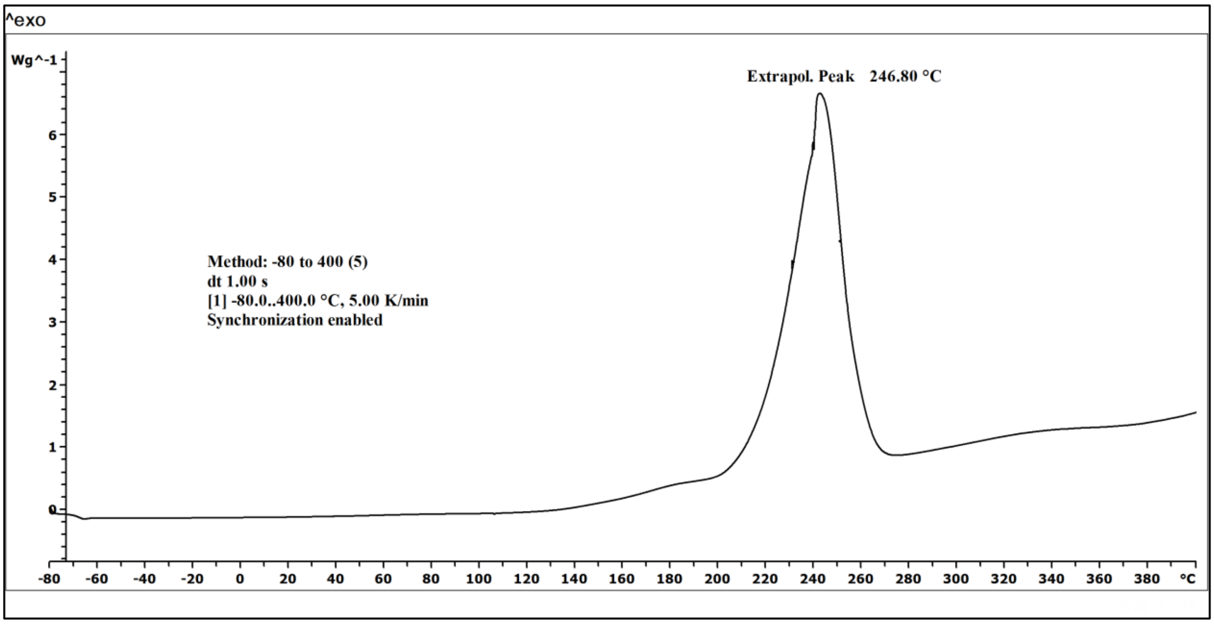


Figure S37. Thermal stability of GAP/TEGBAA composition.

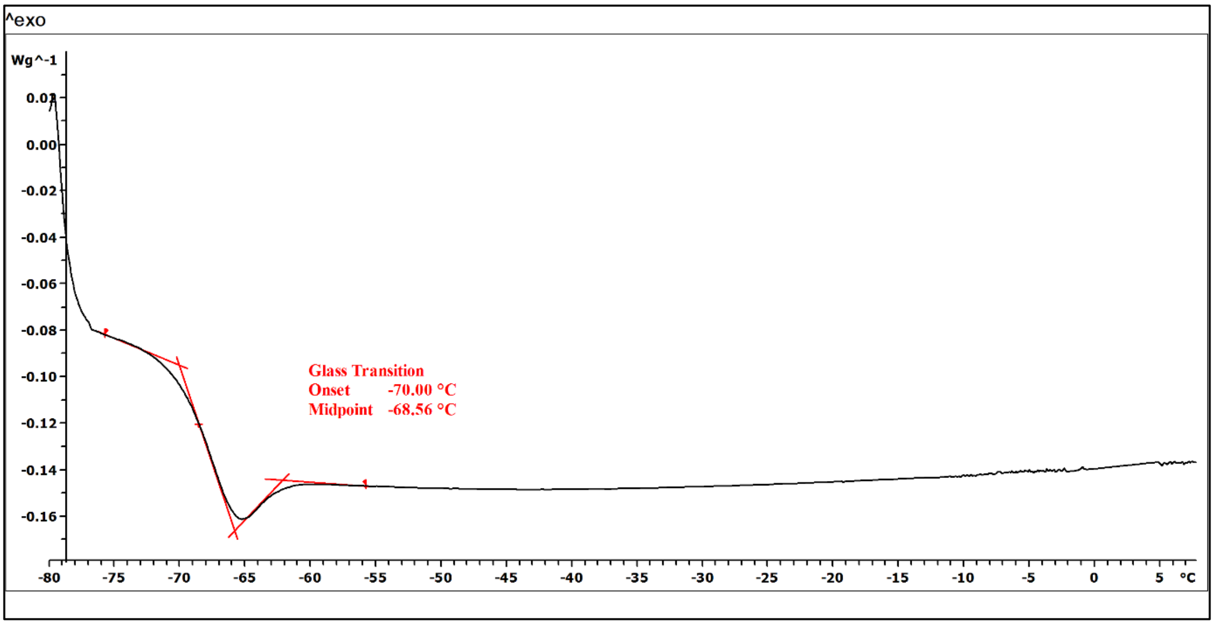


Figure S38. The glass transition temperature of GAP/TEGBAA composition.

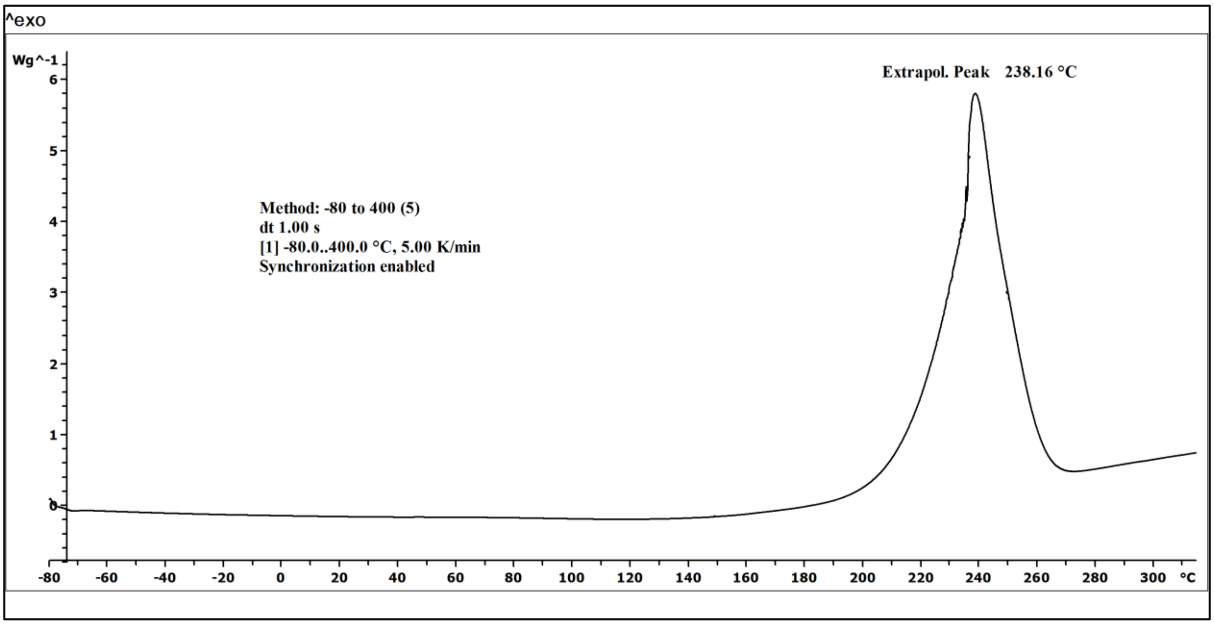


Figure S39. Thermal stability of GAP/EGBAA composition.

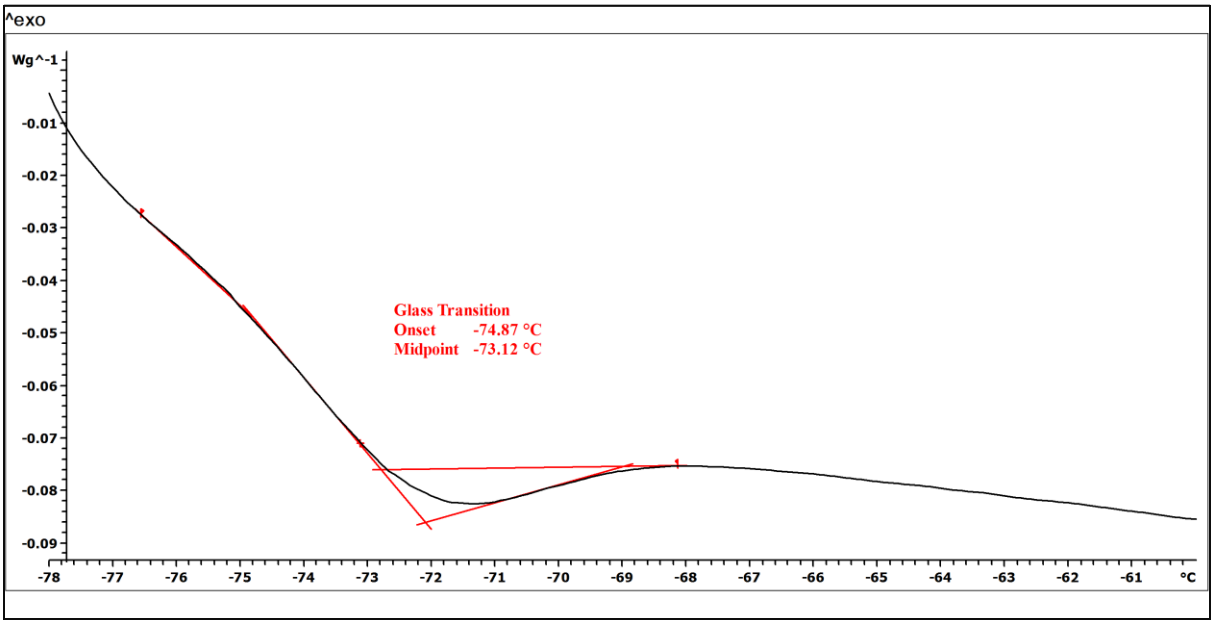


Figure S40. The glass transition temperature of GAP/EGBAA composition.

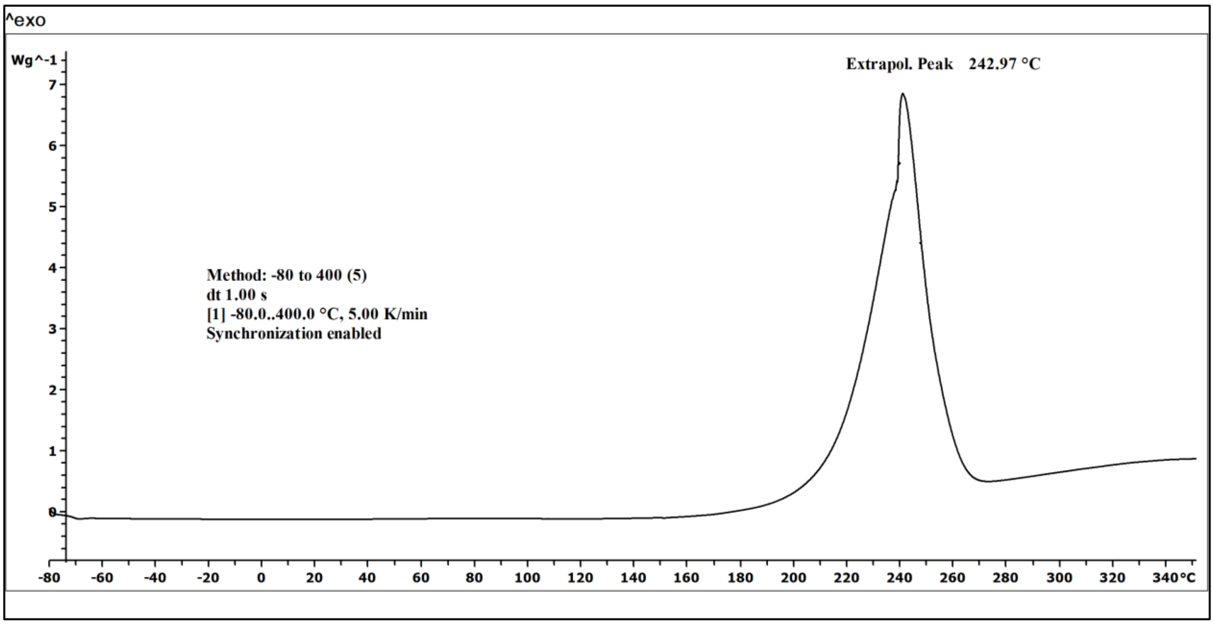


Figure S41. Thermal stability of GAP/DEGBAA composition.

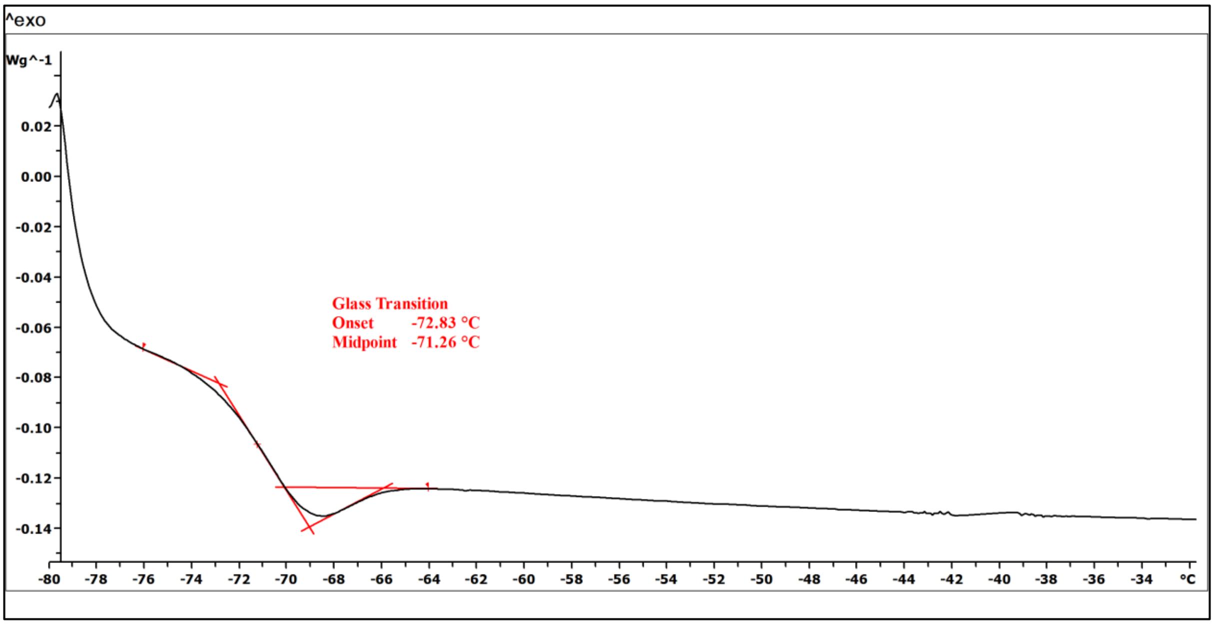


Figure S42. The glass transition temperature of GAP/DEGBAA composition.

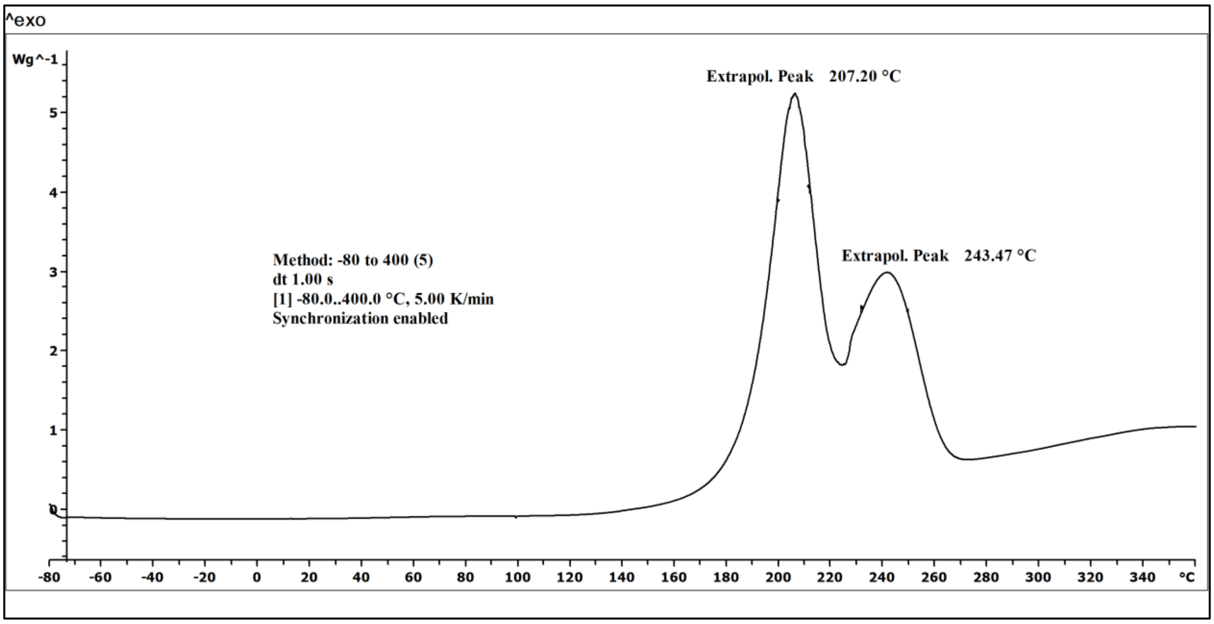
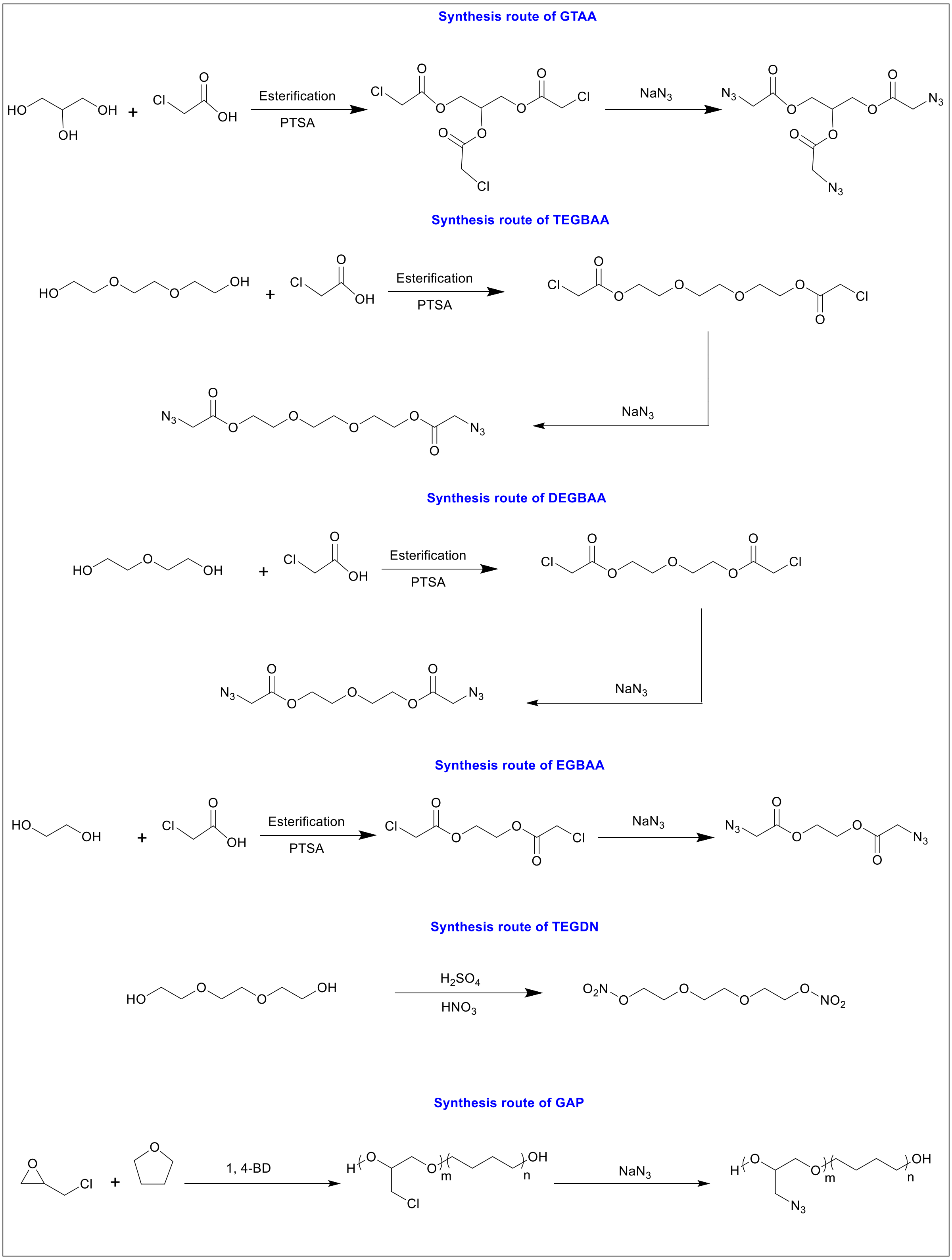


Figure S43. Thermal stability of GAP/TEGDN composition.

4. Details about calculation of the solubility parameter

Firstly, the 3D molecular structure of the azido-esters and GAP has drawn in atomistic space. Then, geometry optimization applied using Forcite modules and COMPASS force field. The temperature of 298 K and COMPASS force field has used for all MD calculations. The density of azido-esters has calculated by the theoretical method presented in reference [4]. A periodic cell for each azido-ester has created using the Amorphous Cell module in Materials Studio software package. As the primary amorphous structure is in a relatively high energy condition, 5000 energy minimization steps using the Smart Minimizer algorithm applied to initial configurations. Afterwards, cell relaxation performed for the energy minimized cell using NVT-MD simulations. For this purpose, the Forcite Dynamics using NVT ensemble by direct velocity scaling temperature control method with time step of 1 fs and duration of 100 ps performed. Then, the NVE-MD simulations of 250 ps carried out and finally cohesive energy density calculated using Forcite module. For all cases, the Atom-based summation method has applied for the van der Waals interactions with a cutoff distance of 9.5 Å, a spline width of 1.0 Å, and a buffer width of 0.5 Å. The Ewald summation method adopted for the electrostatic interactions.

5. The synthesis routes of the synthesized compounds



Synthesis route of GTAA

Synthesis route of TEGBAA

Synthesis route of DEGBAA

Synthesis route of EGBAA

Synthesis route of TEGDN

Synthesis route of GAP

Figure S44. The synthesis route of the synthesized plasticizers and polymers.

6. References

[1] D. Drees, D. Loffel, A. Messmer, K. Schmid, *Propellants Explos. Pyrotech.*, 1999, **24**,159–162.

[2] N. A. Straessler, A. J. Paraskos, M. P. Kramer, *Methods of producing nitrate esters*, 2012, US Patent US20120130115A1.

[3] M. B. Frankel, L. R. Grant, J. E. Flanagan, *J. Propul. Power*, 1992, **8**, 560–563.

[4] N. Zohari, N. Sheibani, *Z. Anorg. Allg. Chem.*, 2016, **642**, 1472–1479.