**Supplementary Materials**

# Reactive energetic plasticizers utilizing Cu-free azide-alkyne 1,3-dipolar cycloaddition for in-situ preparation of poly(THF-co-GAP)-based polyurethane energetic binders

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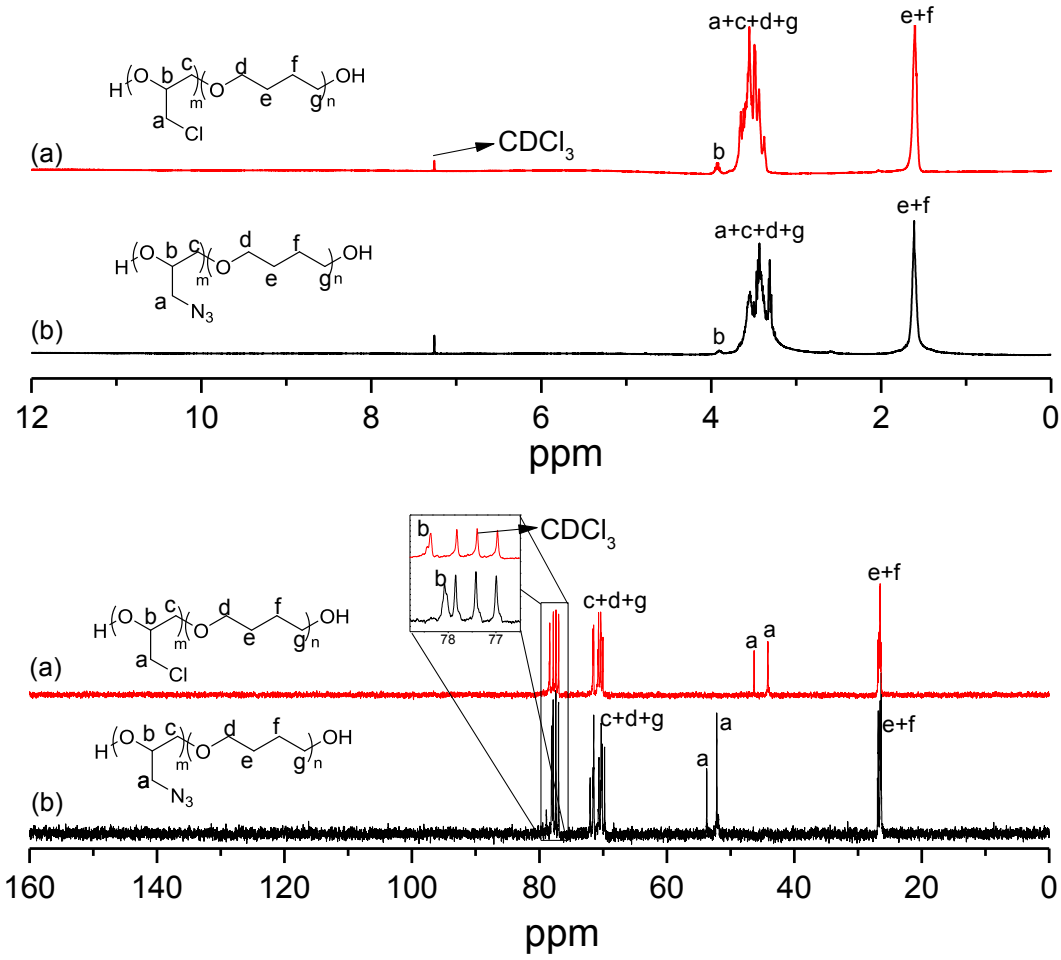


**Fig. S1.** $^{1}H$ (top) and $^{13}C$ NMR (bottom) spectra of (a) poly(ECH-co-THF) and (b) poly(GAP-co-THF).

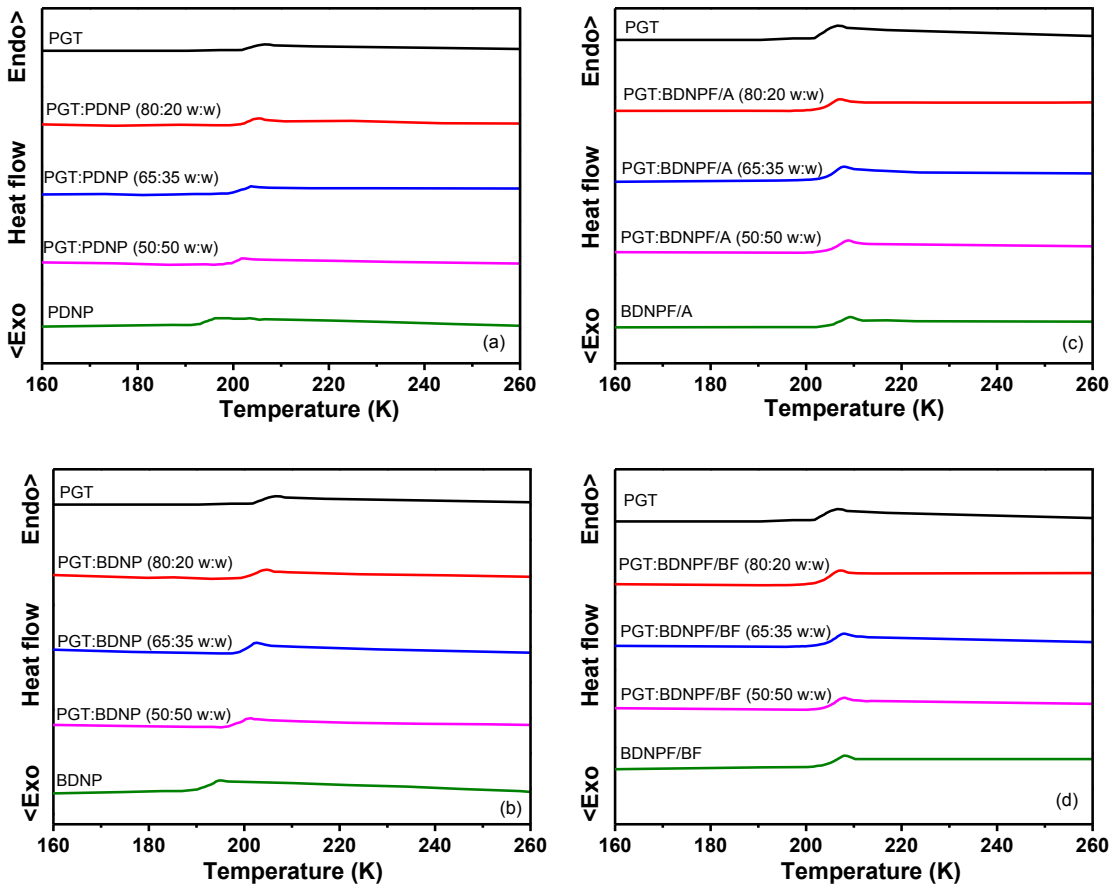


**Fig. S2.** DSC thermograms of (a) PGT:PDNP, (b) PGT:BDNP, (c) PGT:BDNPF/A, and (d) PGT:BDNPF/BF.

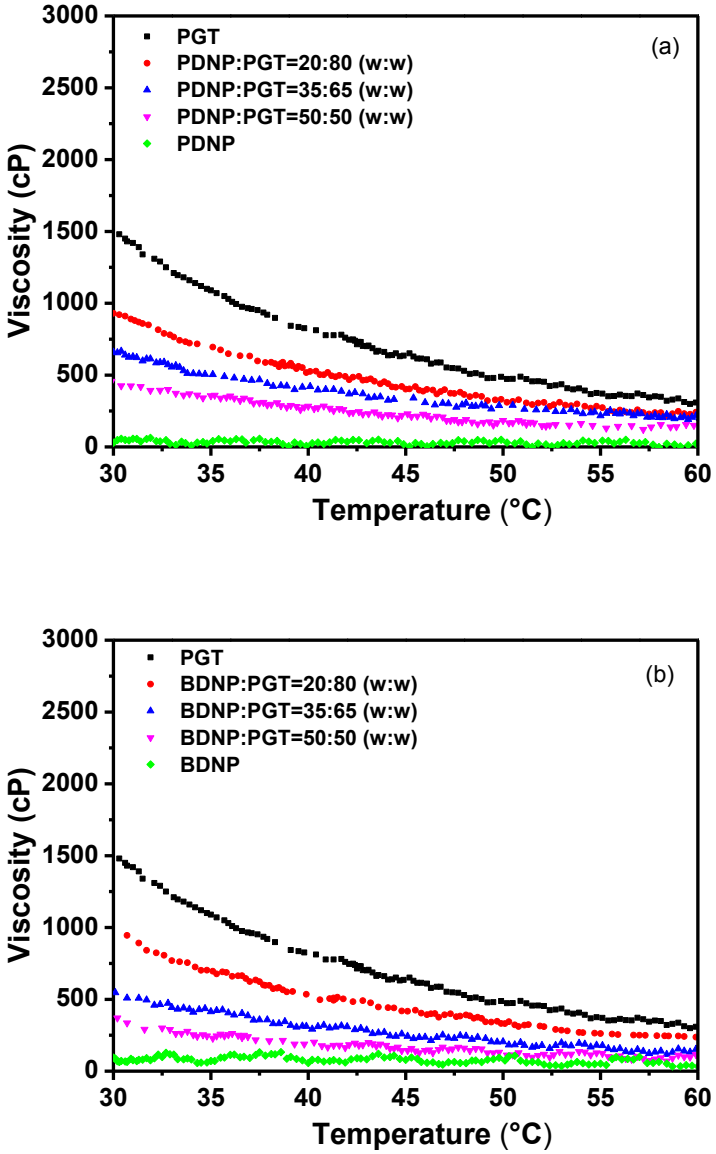


**Fig. S3.** Viscosity reduction of (a) PDNP : PGT, and (b) BDNP : PGT

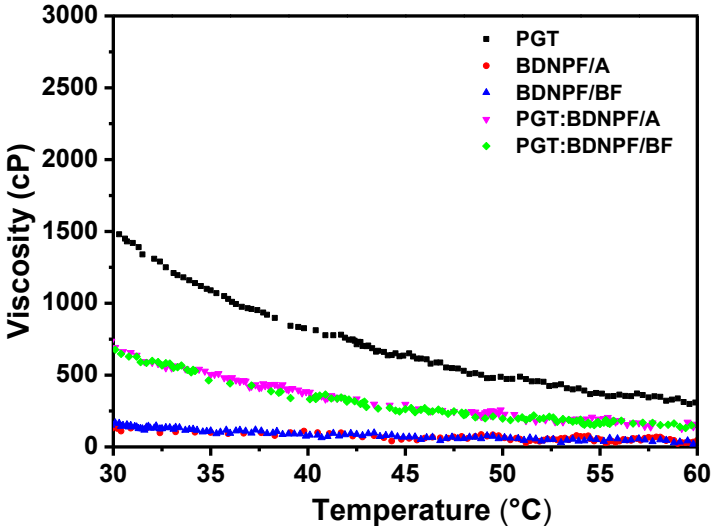


**Fig. S4.** Viscosity reduction of PGT prepolymer plasticized with 50 wt% of conventional EPs.

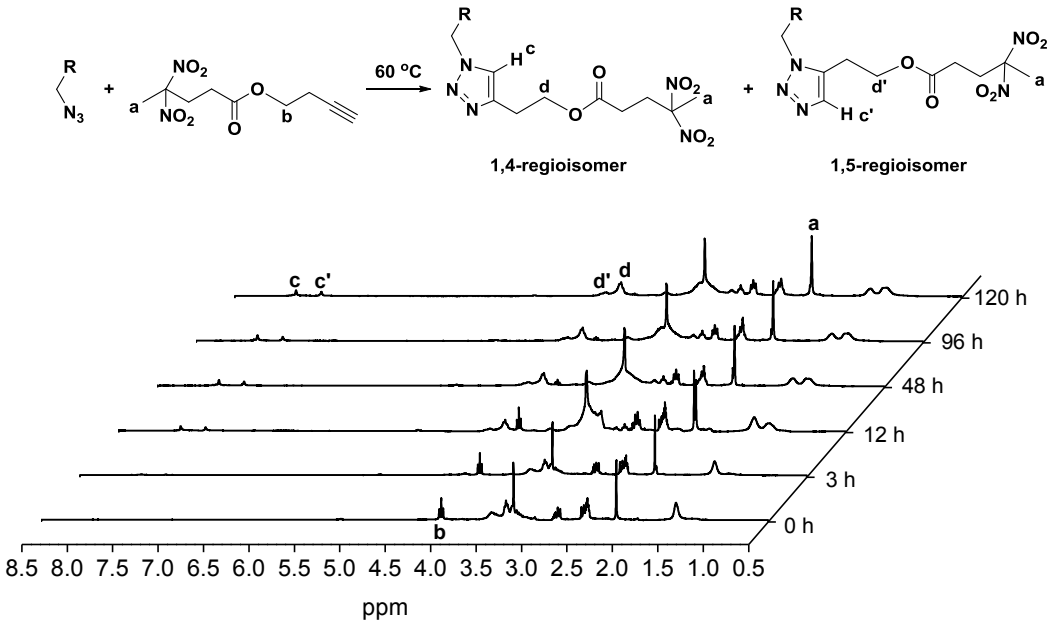


**Fig. S5.** $^{1}$H NMR spectra as a function of reaction time of Cu-free azide-alkyne 1,3-dipolar cycloaddition reaction of BDNP (n=2) and PGT prepolymer carried out in bulk condition at 60 °C. The R group in the reaction scheme above is the backbone of PGT prepolymer.

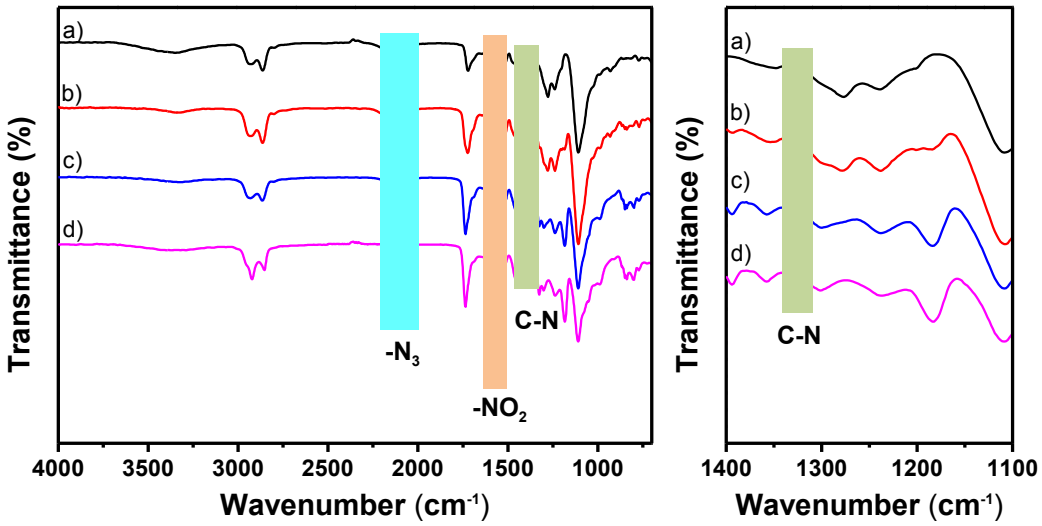


**Fig. S6.** FT-IR spectra of the BDNP/PGT-based PUs in terms of [C≡C]/[$N_3$] (mol/mol): a) 0/0.5, b) 0.1/0.5, c) 0.3/0.5 and d) 0.5/0.5.

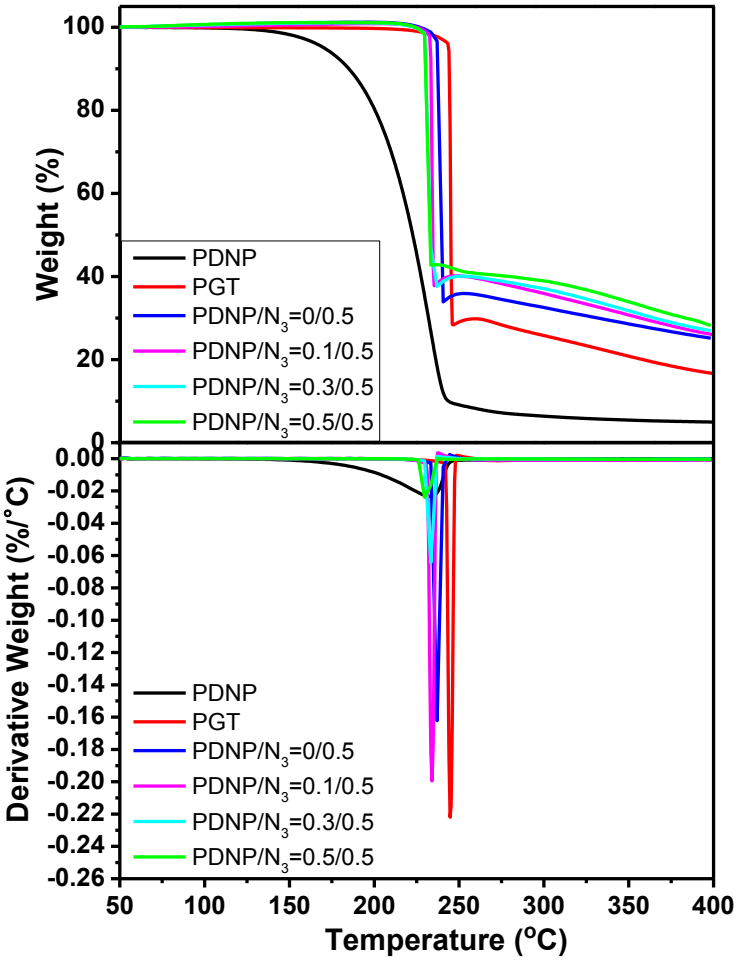


**Fig. S7.** TGA (top) and DTG (bottom) curves of the PDNP/PGT-based PUs.

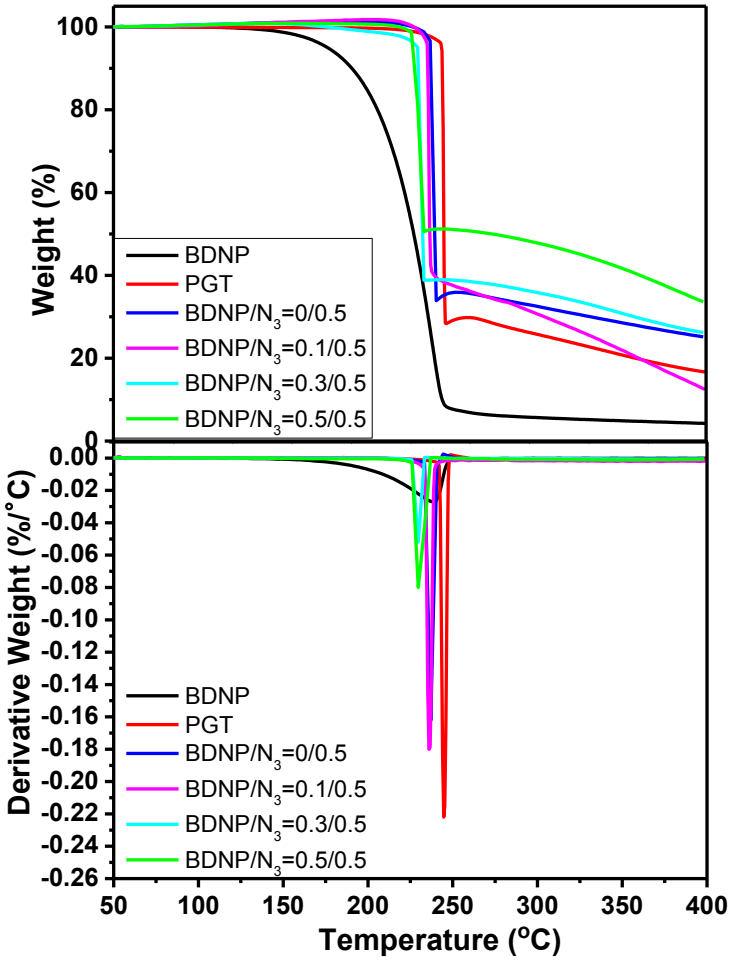


**Fig. S8.** TGA (top) and DTG (bottom) curves of the BDNP/PGT-based PUs.