Supplementary Information (SI) for Polymer Chemistry.

Supporting information for:

Control over membrane fluidity and biophysical properties of synthetic terpolymer stabilized complex coacervates

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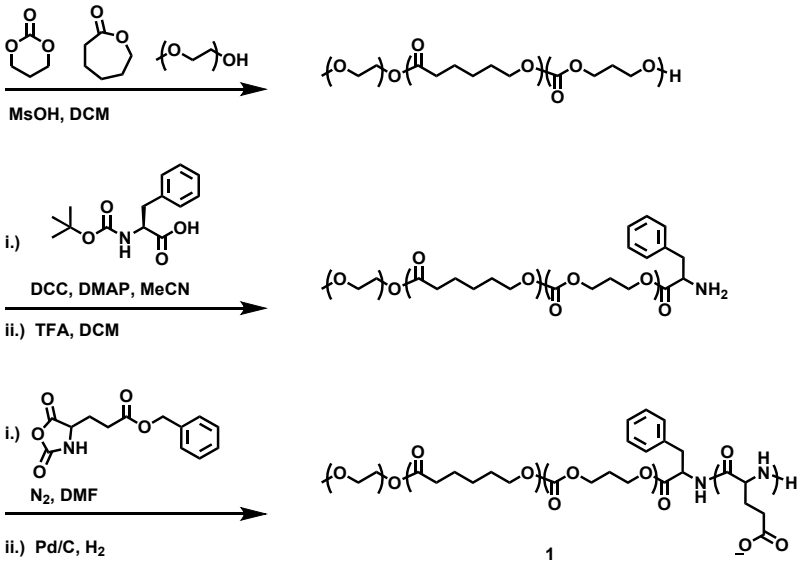
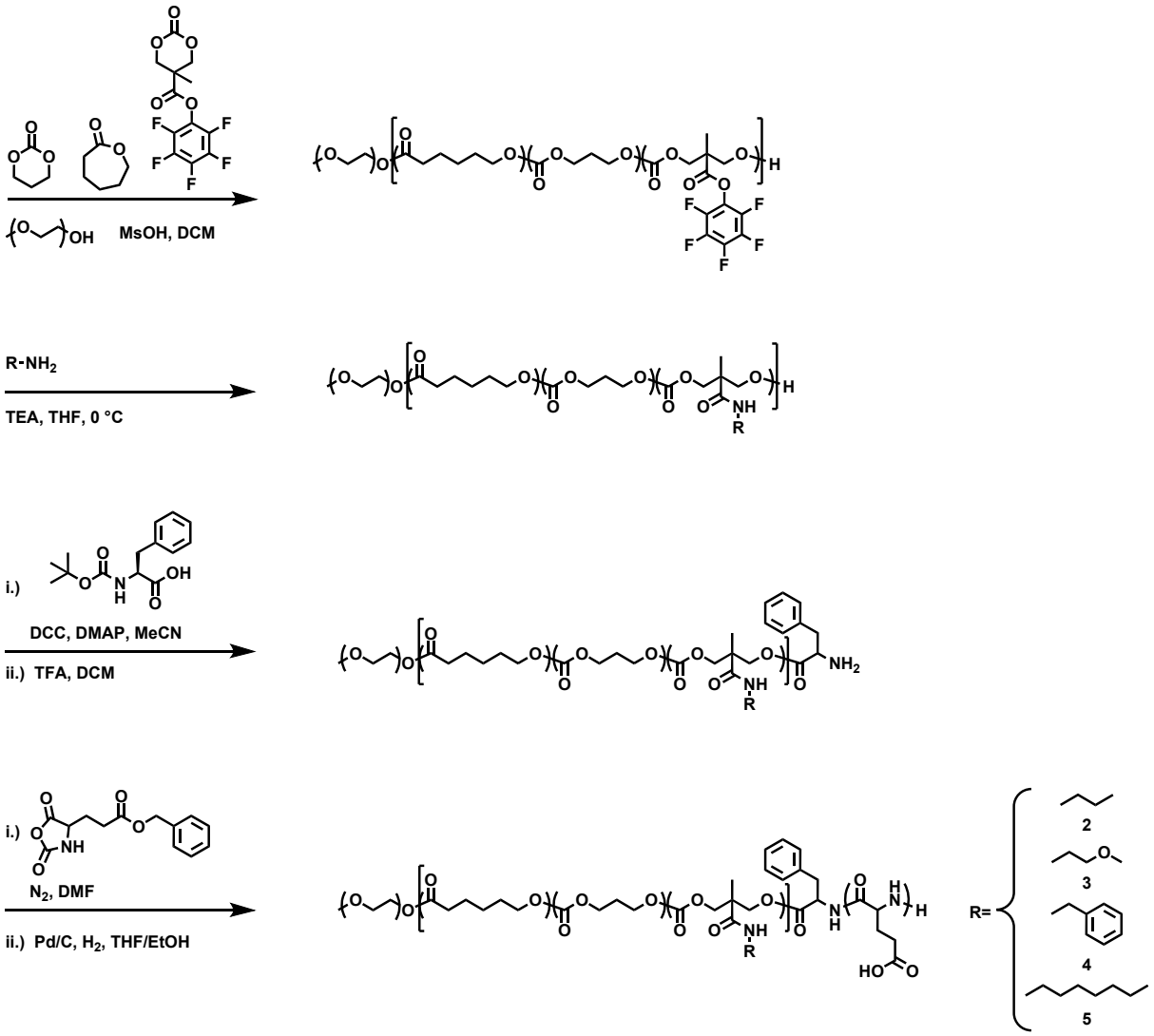
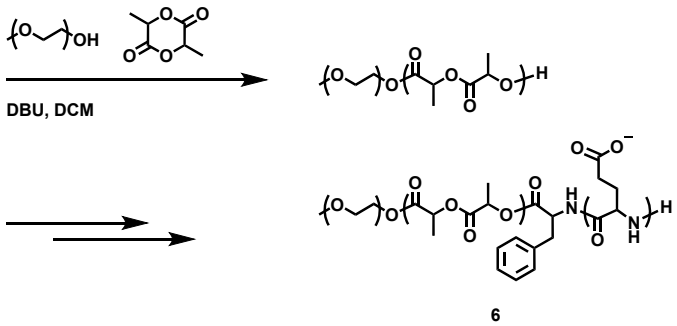


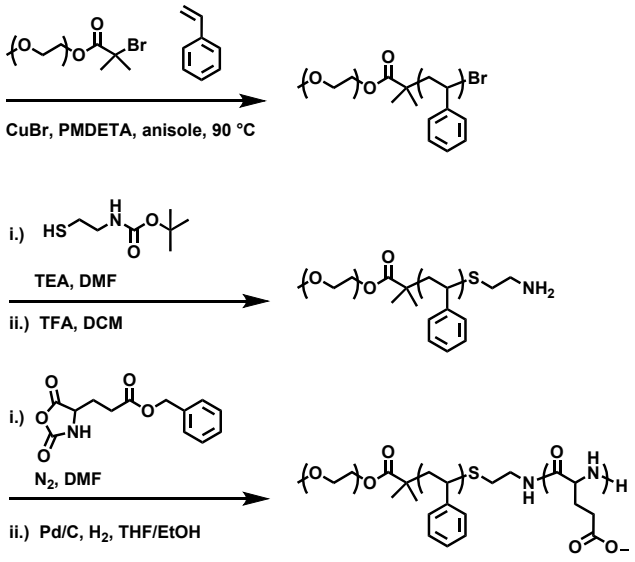
Supplementary scheme 1. *Schematic representation of PEG-PCLgTMC-PGA terpolymer synthesis. Poly(ethylene glycol) monomethyl ether initiated ring-opening polymerization of ε-caprolactone and trimethylene carbonate (step 1). Introduction of terminal amine was achieved via a Steglich esterification with Boc-L-Phe-OH and subsequent deprotection with TFA (step 2). The final poly(L-glutamic acid) block was introduced by the ring-opening polymerization of N-carboxyanhydride γ-benzyl-L-glutamate, followed by hydrogenation (step 3).*



Supplementary scheme 2. *Schematic representation of the synthesis of differently functionalised PEG-PCLgTMC-PGA terpolymers* ***2***-***5****. Formation of PEG-PCLgTMC by cationic ring opening polymerisation (step 1) was followed by amidation of the pentafluorophenyl activated ester side chains with respective amines (step 2). Introduction of the terminal amine was achieved via a Steglich esterification with Boc-L-Phe-OH and subsequent deprotection with TFA (step 3). The final poly(l-glutamic acid) block was introduced by the ring-opening polymerization of N-carboxyanhydride γ-benzyl-l-glutamate, followed by hydrogenation (step 4).*



Supplementary scheme 3. *Schematic representation for the synthesis of PEG-PDLLA-PGA terpolymer* ***6****. First, PEG-PDLLA copolymer was synthesized by DBU catalysed quasi-anionic ring-opening polymerization of D,L-Lactide. Subsequent steps encompassing the amine chain end modification with Phe-OH, a subsequent ring opening polymerisation of BLG-NCA and the respective deprotection step yielded terpolymer* ***6.***



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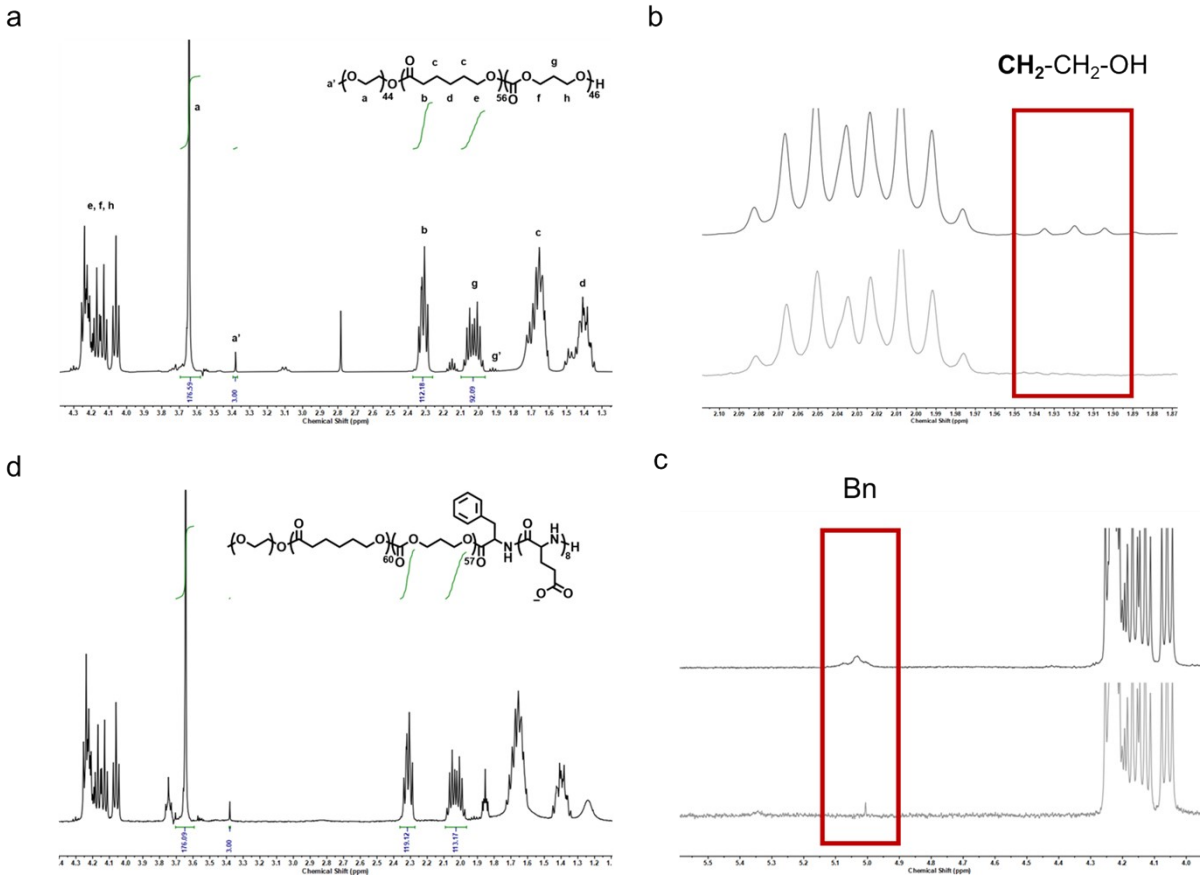
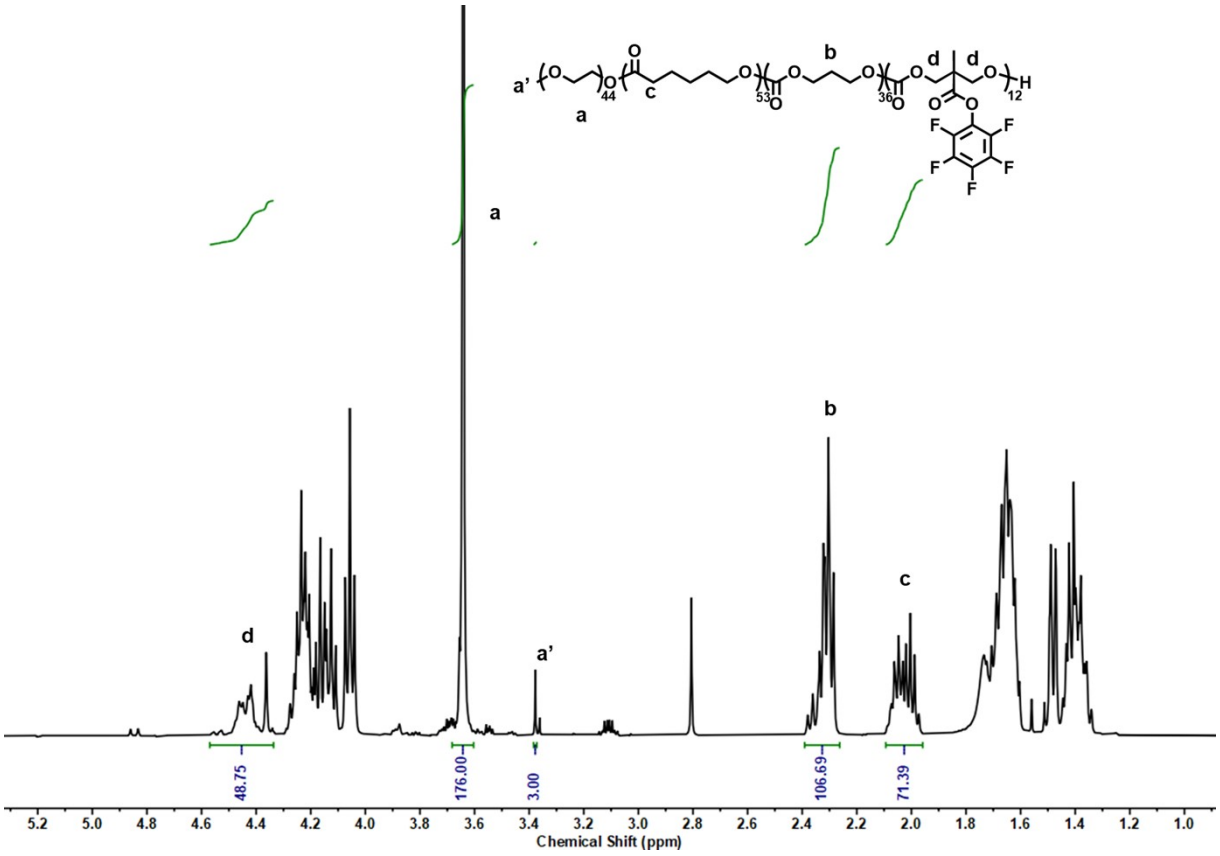
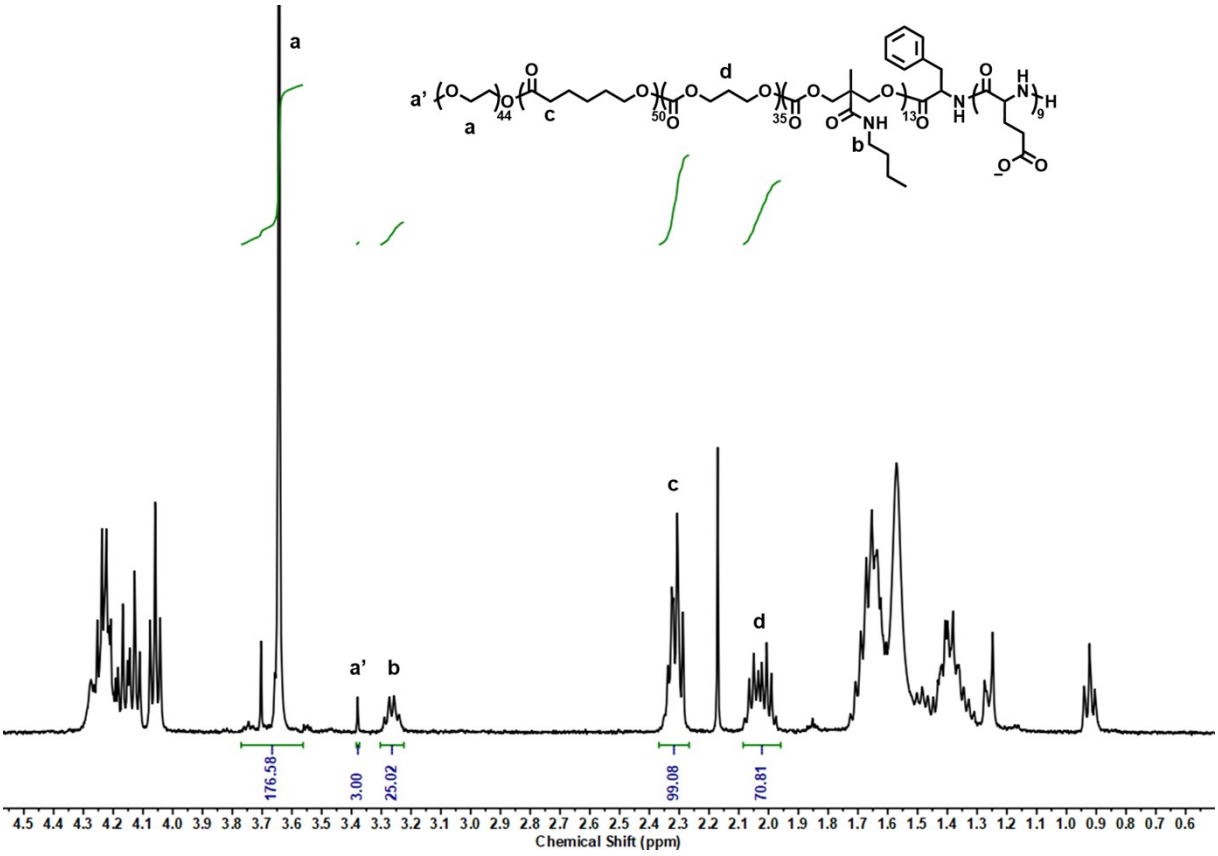
Supplementary scheme 4. *Schematic representation for the synthesis of PEG-PS-PGA terpolymer* ***7****. First, PEG-PS copolymer was synthesized via a bulk atom transfer radical polymerization (ATRP) of styrene catalysed with CuBr/PMDETA. Subsequent steps encompassing the amine chain end modification with Boc-protected 2- amino thiol followed by deprotection, a subsequent ring opening polymerisation of BLG-NCA and the respective deprotection step yielded terpolymer* ***7.***



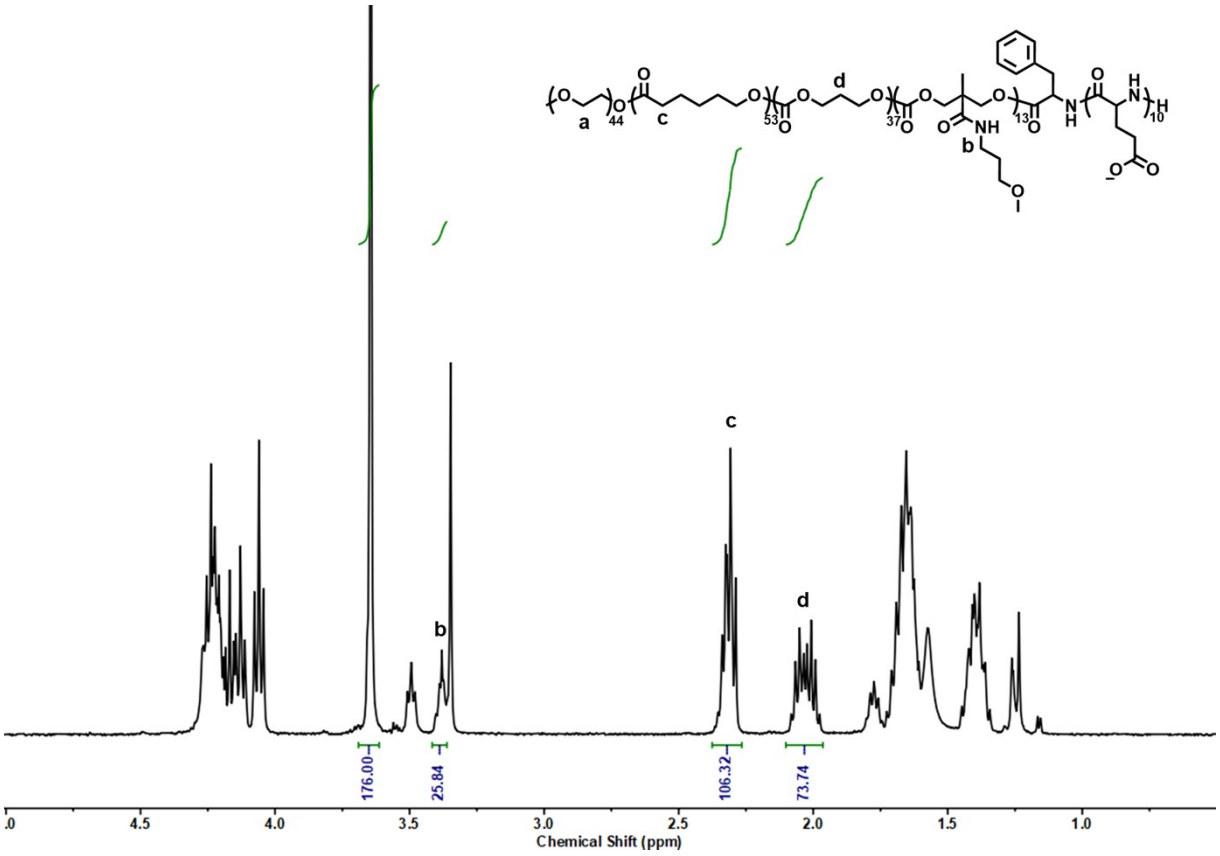
Supplementary Figure 1. *^{1}H NMR analysis of terpolymer TP **1**. a, Analysis of PEG-PCLgTMC. b, Demonstration of the complete chain-end modification of PEG-PCLgTMC with Boc-L-Phe using chain-end methylene protons (1.92 ppm). c, Specific evaluation of PGA content of the resulting terpolymer using benzylic protons (5.0-5.2 ppm), with lower spectrum showing successful deprotection by hydrogenation. d, analysis of the final terpolymer PEG-PCLgTMC-PGA.*



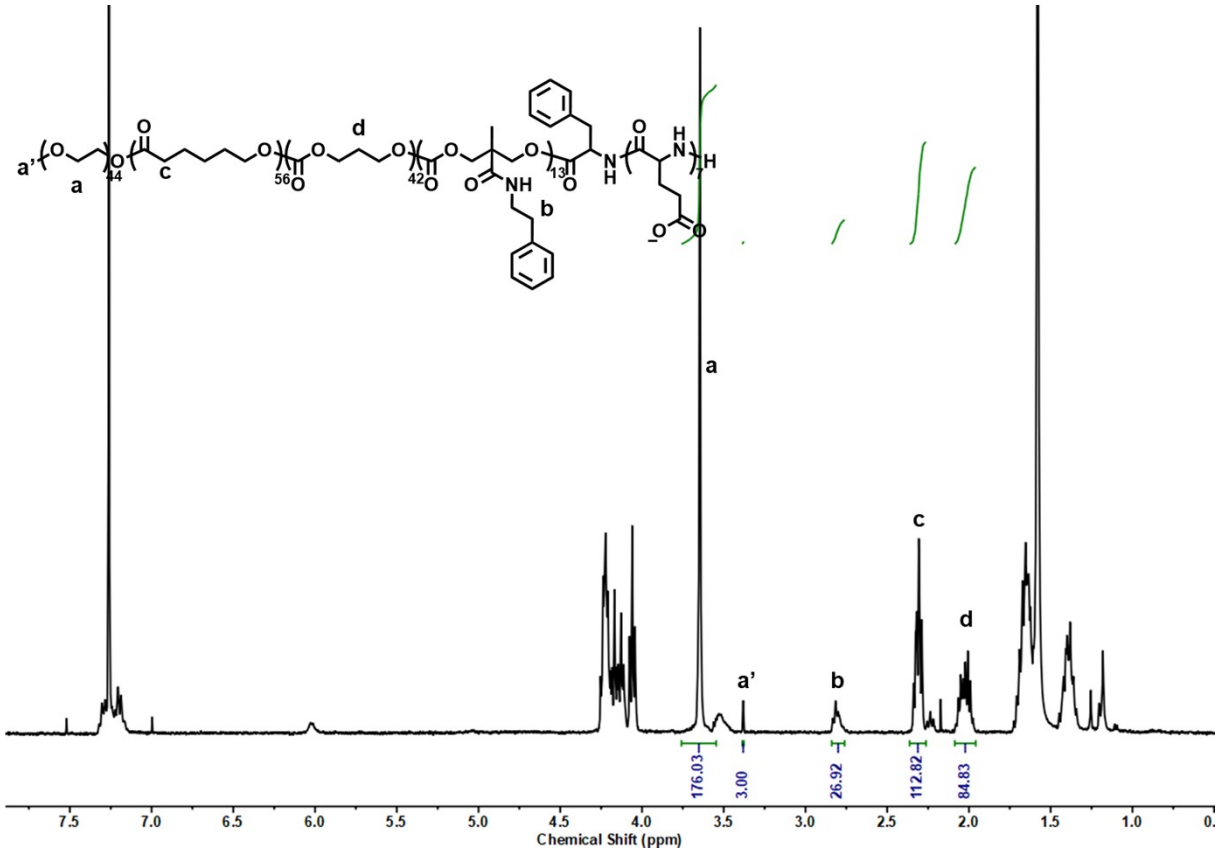
Supplementary Figure 2. *^{1}H NMR of PEGbPCLgTMCgPFPTMC.*



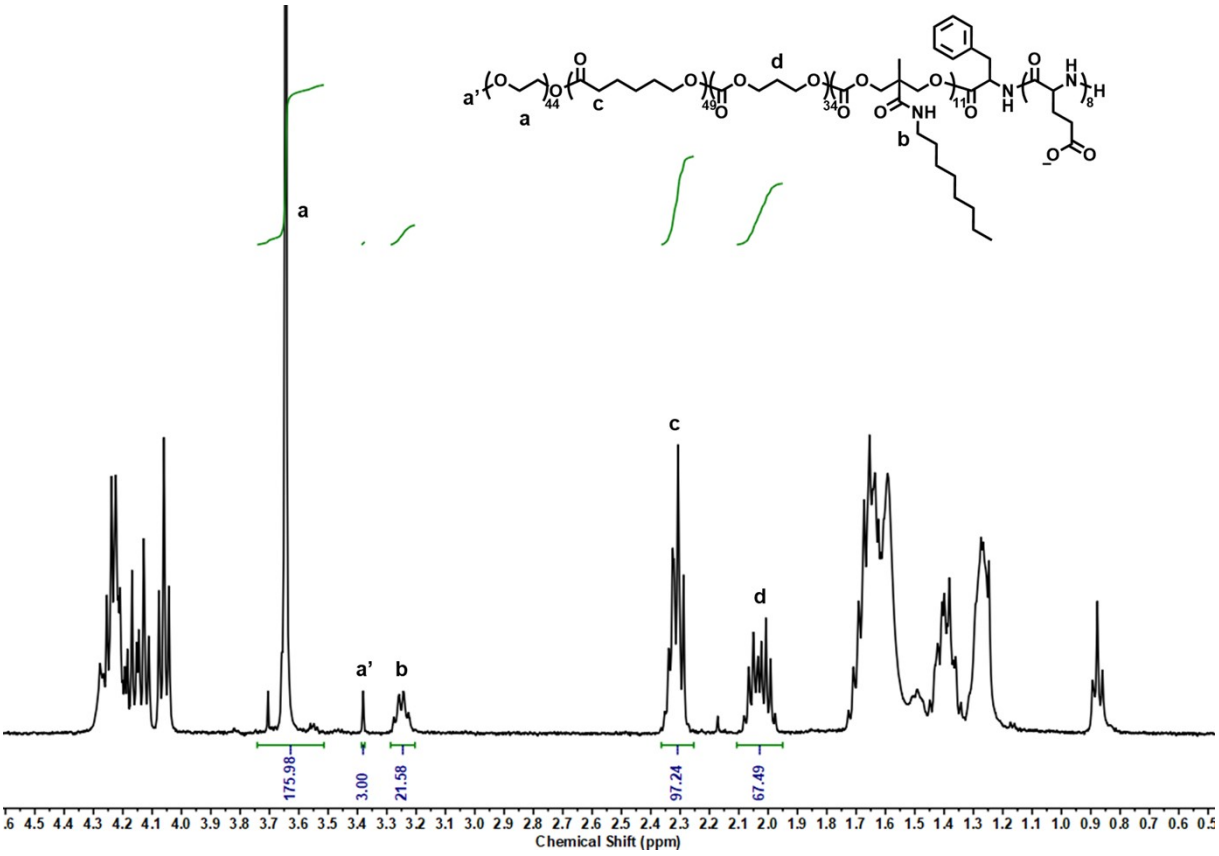
Supplementary Figure 3. *^{1}H NMR of terpolymer **2**.*



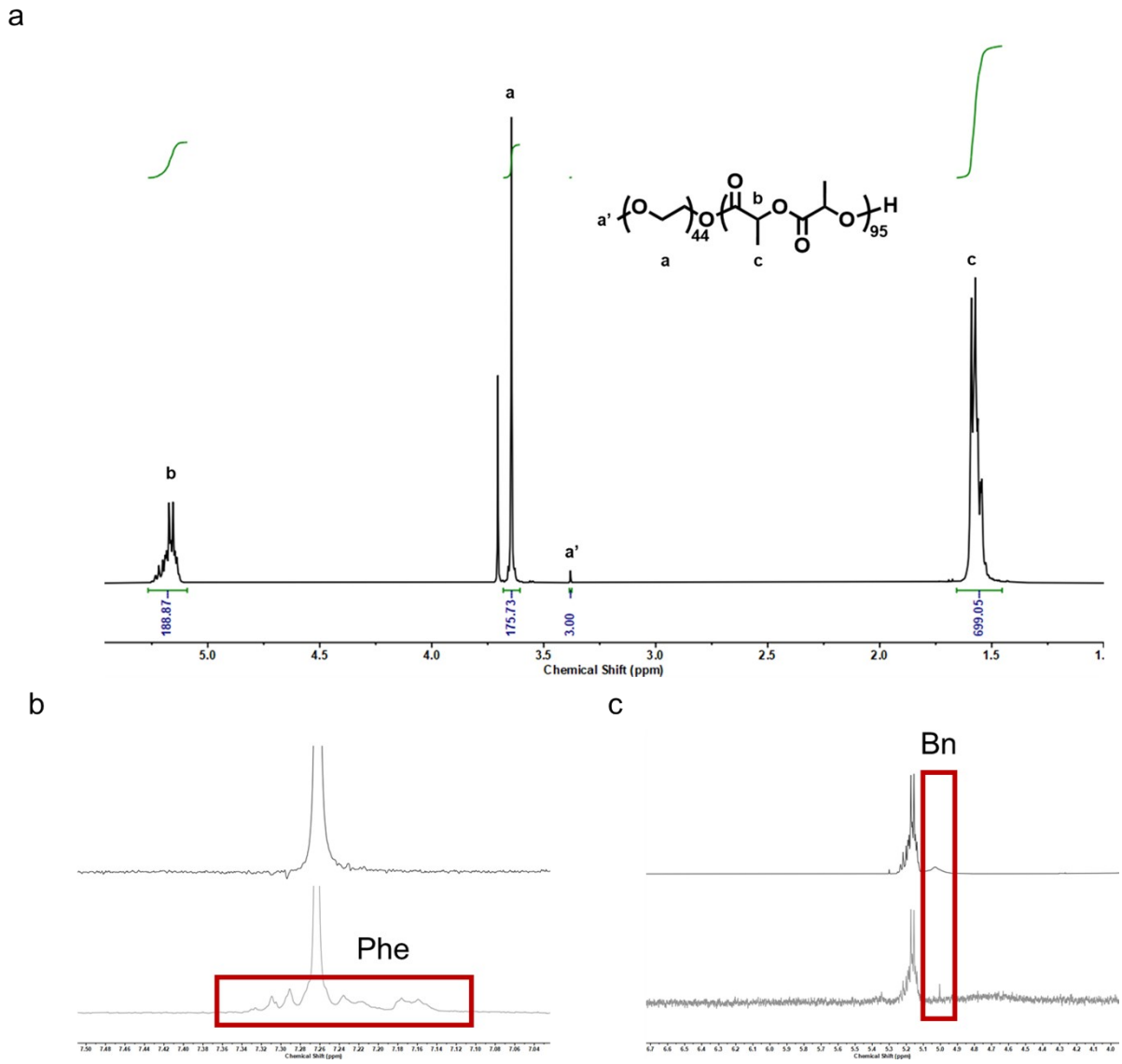
Supplementary Figure 4*. [1]H NMR of terpolymer* ***3****.*



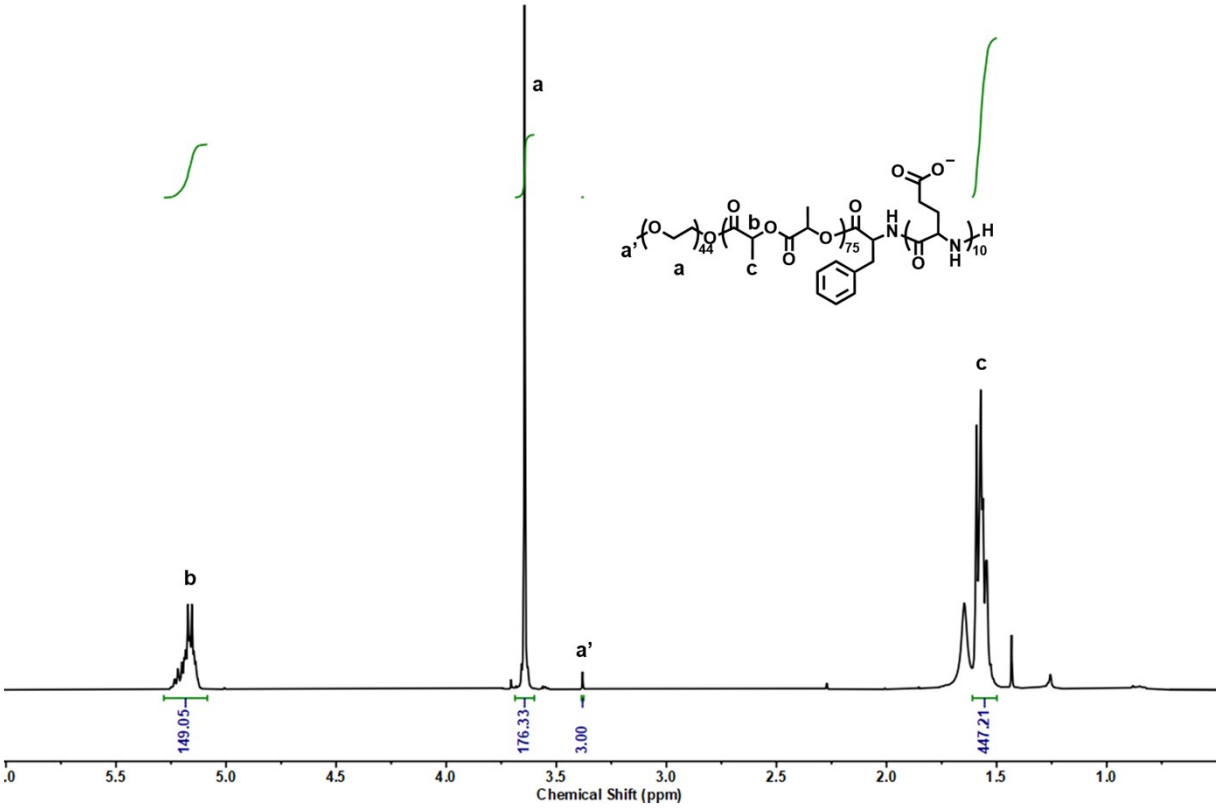
Supplementary Figure 5*. [1]H NMR of terpolymer* ***4****.*



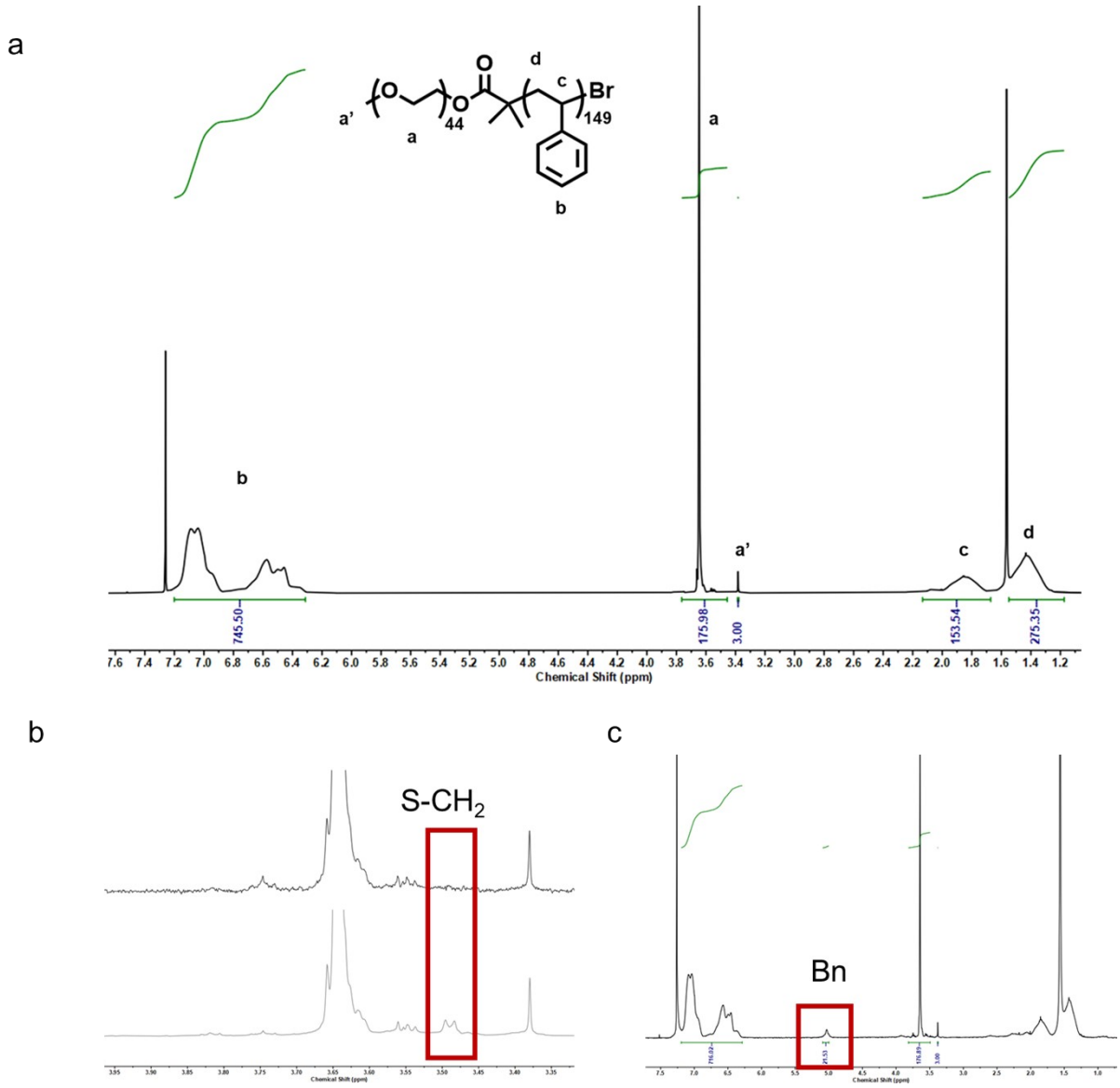
Supplementary Figure 6. *^{1}H NMR of terpolymer **5**.*



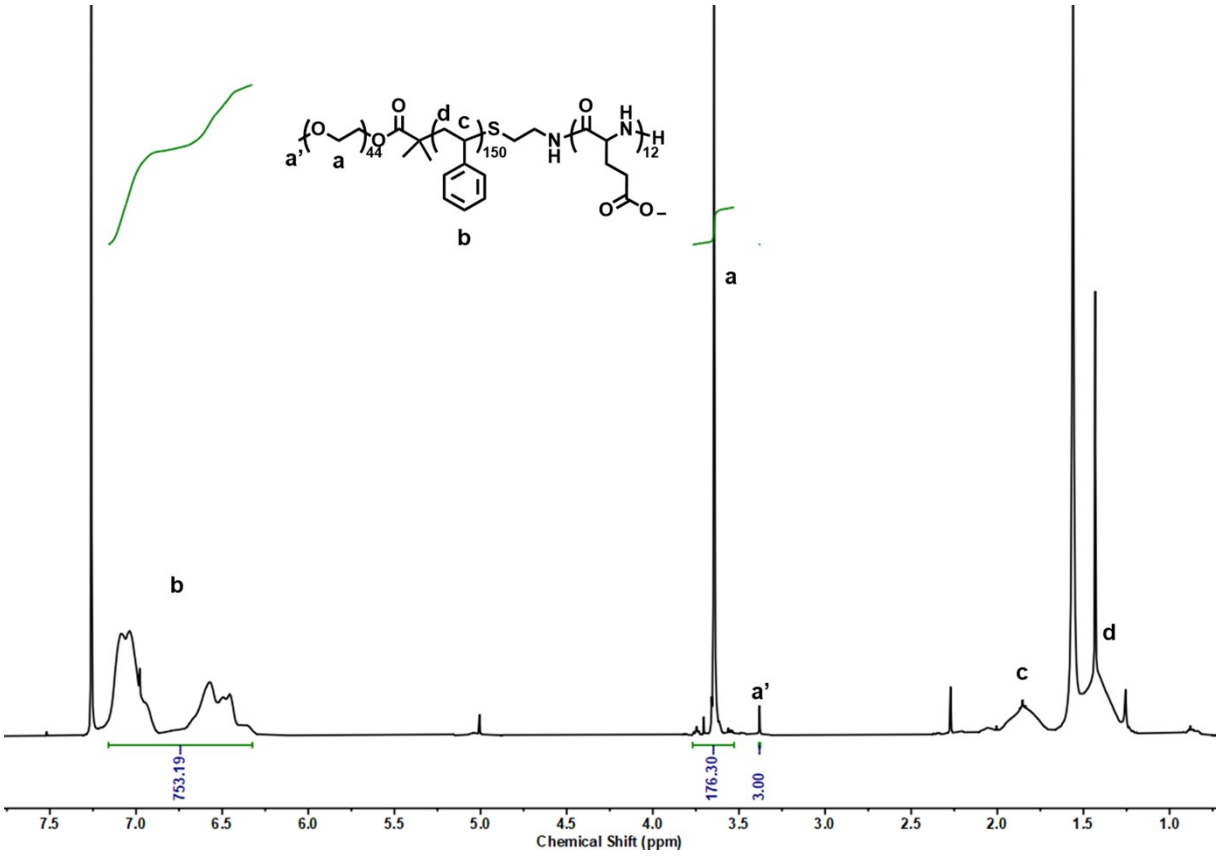
Supplementary Figure 7. *^{1}H NMR analysis of terpolymer synthesis for TP **6**. a, Analysis of PEG-PDLLA-PGA. b, Demonstration of the complete chain-end modification of PEG-PDLLA with Boc-L-Phe using chain-end aromatic protons (7.1-7.4 ppm). c, Specific evaluation of PGA content of the resulting terpolymer using benzylic protons (5.0-5.2 ppm), with lower spectrum showing successful deprotection by hydrogenation.*



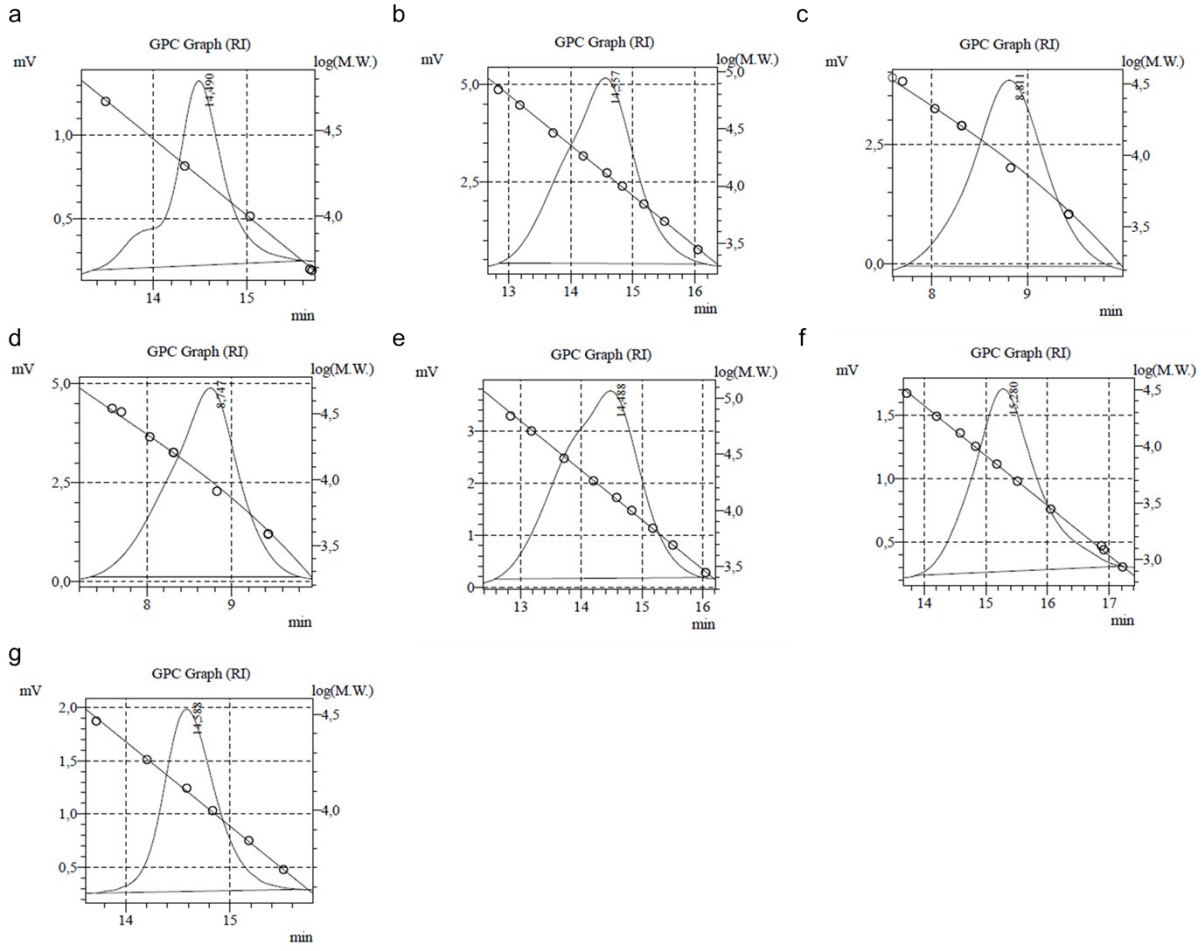
Supplementary Figure 8. *^{1}H NMR of PEG-PDLLA-PGA terpolymer **6**.*



Supplementary Figure 9. *^{1}H NMR analysis of PEG-PS terpolymer **7** synthesis. a, ^{1}H NMR of PEG-PS. b, Demonstration of the complete chain-end modification of PEG-PS with 2-(Boc-amino)ethanethiol using chain-end methylene protons (S-CH_2, 3.48 ppm), with lower spectrum showing successful chain-end modification. c, Specific evaluation of PBLG content of the resulting terpolymer using benzylic protons (5.0-5.2 ppm).*



***Supplementary Figure 10**.[1]H NMR of PEG-PS-PGA terpolymer **7**.*



Supplementary Figure 11. *SEC traces for terpolymer* ***a) 1****,* ***b) 2****,* ***c) 3****,* ***d) 4****,* ***e) 5****,* ***f) 6*** *and* ***g) 7****.*