

Electronic Supplementary Information

Enzyme Mimetic-Catalyzed ATRP and Its Application in Block Copolymer Synthesis Combining with Enzymatic Ring-Opening Polymerization

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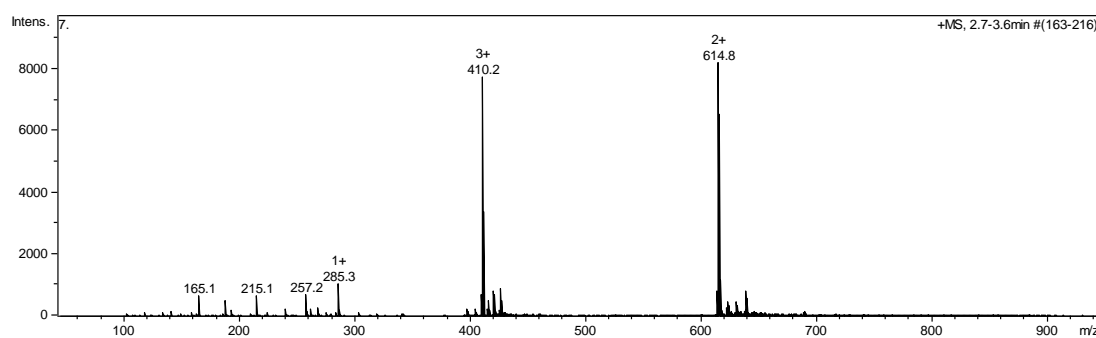


Figure S1. Mass spectrometry of DhHP-6 (molecular weight = 1229, performed on a liquid Chromatograph Mass Spectrometer, Agilent1290-microTOF Q II).

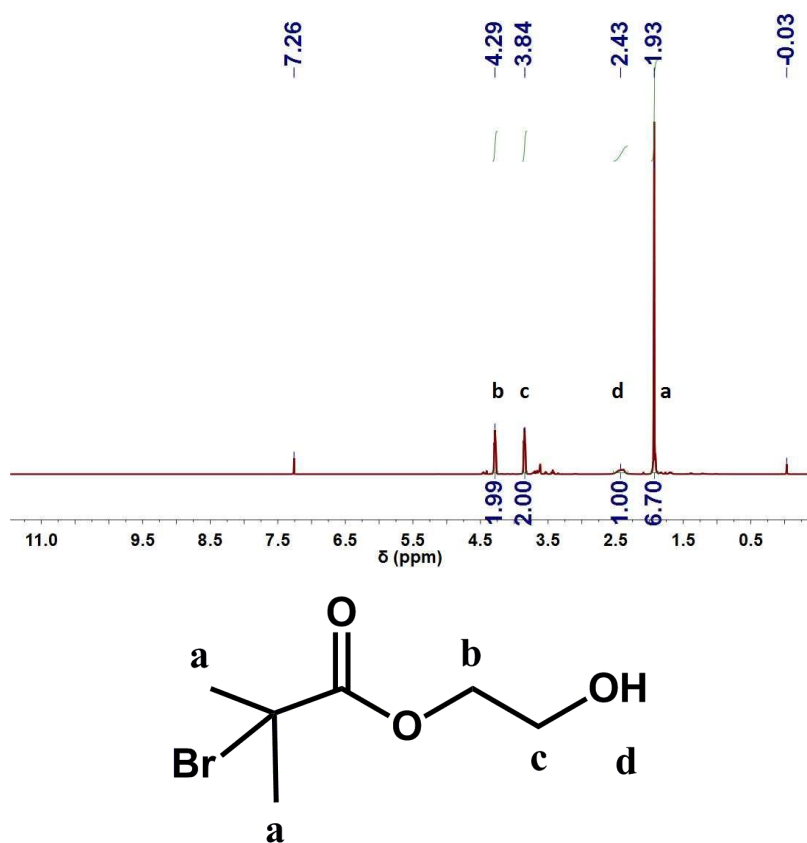


Figure S2. ^1H NMR spectrum (CDCl_3 , 400 MHz) of bifunctional initiator HEBiB.

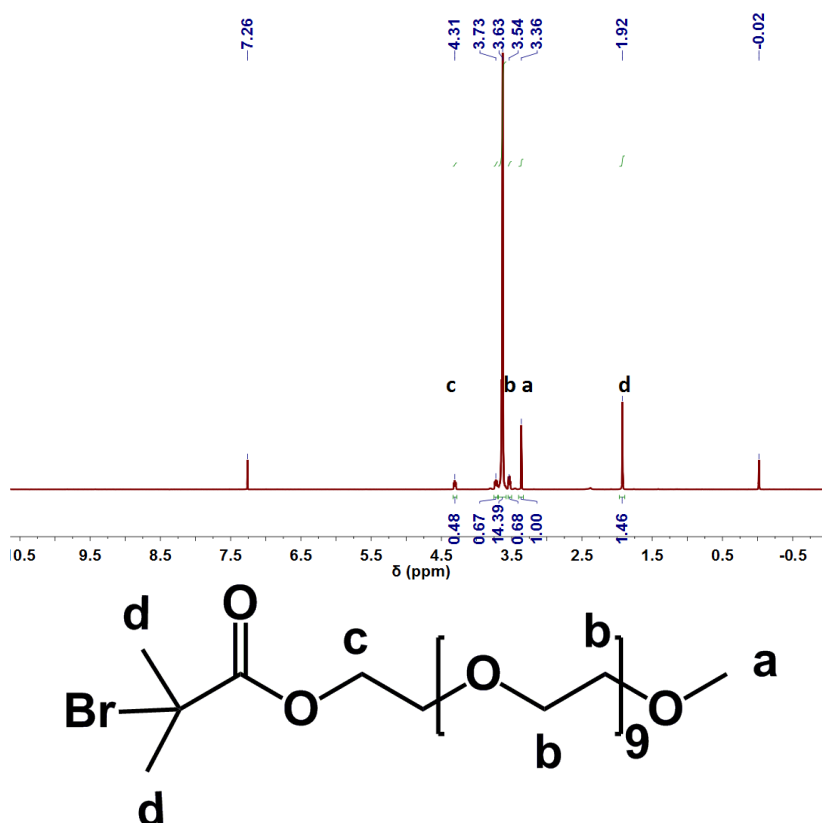


Figure S3. ¹H NMR spectrum (CDCl₃, 400 MHz) of the macroinitiator PEG-Br.

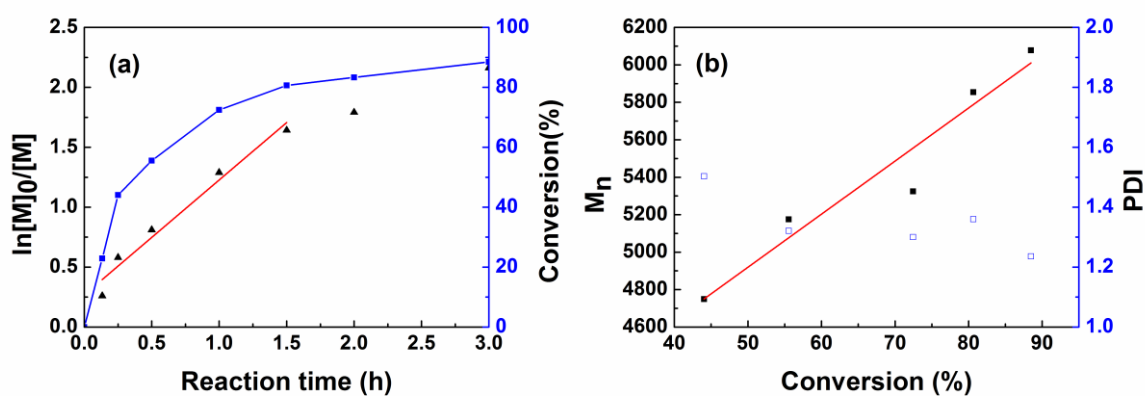


Figure S4. (a) First-order kinetic plot (▲) for DhHP-6 catalyzed ARGET ATRP of PEGMA₅₀₀ in PBS buffer (entry 2, pH = 7.0) and plot of monomer conversion vs. reaction time (■). (b) Number-average molecular weight (■) and PDI (□) of polyPEGMA vs. monomer conversion.

Note: [PEGMA₅₀₀]/[EBiB]/[DhHP-6]/[AscNa]/[KBr]=32/1/0.033/1/8 at 35 °C.

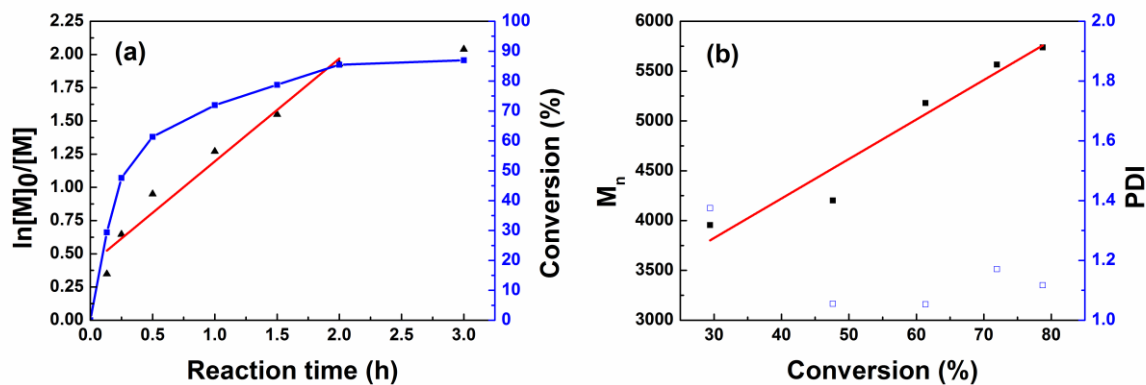


Figure S5. (a) First-order kinetic plot (▲) for DhHP-6 catalyzed ARGET ATRP of PEGMA₅₀₀ in PBS buffer (entry 3, pH = 7.5) and plot of monomer conversion vs. reaction time (■). (b) Number-average molecular weight (■) and PDI (□) of polyPEGMA vs. monomer conversion.

Note: [PEGMA₅₀₀]/[EBiB]/[DhHP-6]/[AscNa]/[KBr] = 32/1/0.033/1/8 at 35 °C.

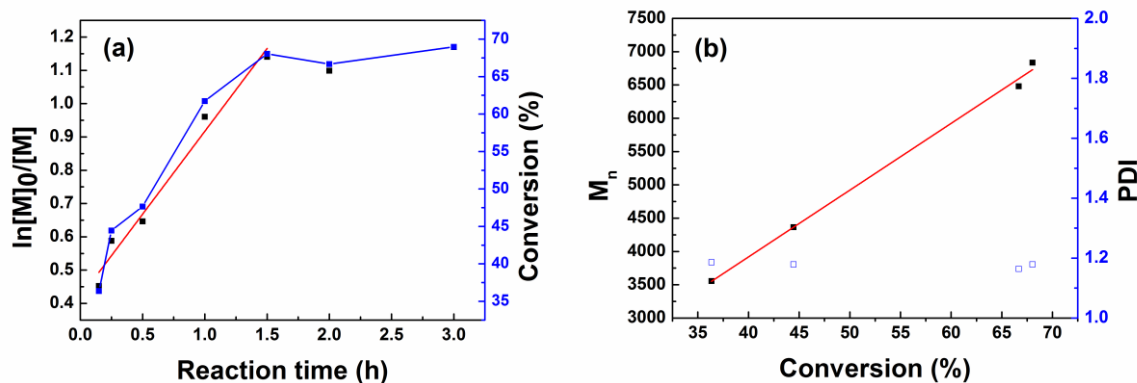


Figure S6. (a) First-order kinetic plot (▲) for DhHP-6 catalyzed ARGET ATRP of PEGMA₅₀₀ in PBS buffer (entry 4) and plot of monomer conversion vs. reaction time (■). (b) Number-average molecular weight (■) and PDI (□) of polyPEGMA vs. monomer conversion.

Note : [PEGMA₅₀₀]/[EBiB]/[DhHP-6]/[AscNa]/[KBr]=64/1/0.033/1/8 at 35 °C.

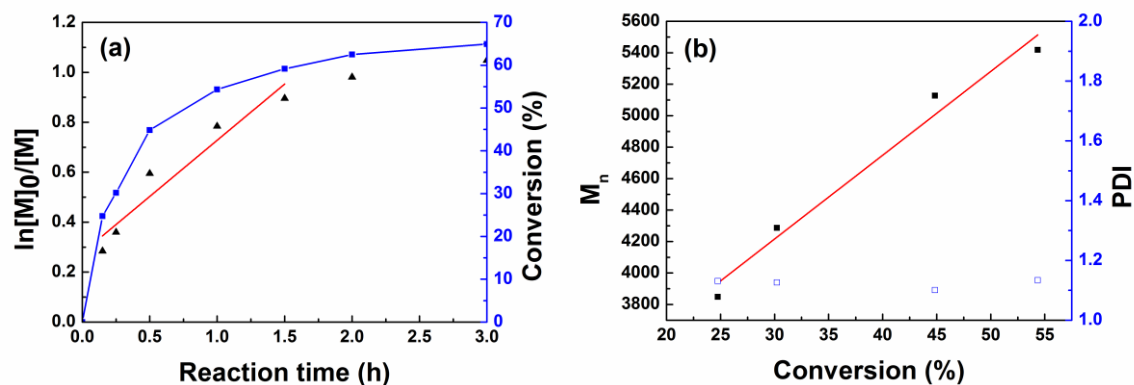


Figure S7. (a) First-order kinetic plot (\blacktriangle) for DhHP-6 catalyzed tARGET ATRP of PEGMA₅₀₀ in PBS buffer (entry 5) and plot of monomer conversion vs. reaction time (\blacksquare). (b) Number-average molecular weight (\blacksquare) and PDI (\square) of polyPEGMA vs. monomer conversion.

Note: [PEGMA₅₀₀]/[EBiB]/[DhHP-6]/[AscNa]/[KBr]=64/1/0.033/1/4 at 35 °C.

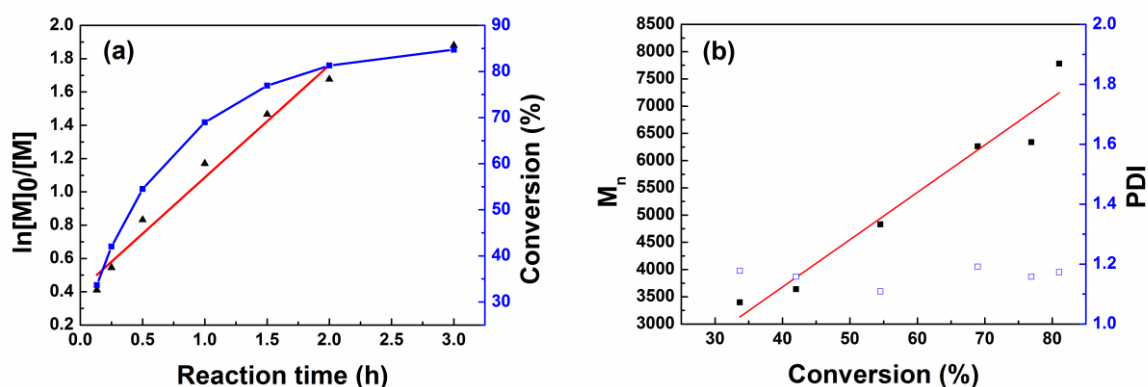


Figure S8. (a) First-order kinetic plot (\blacktriangle) for DhHP-6 catalyzed ATRP of PEGMA₅₀₀ in PBS buffer (entry 6) and plot of monomer conversion vs. reaction time (\blacksquare). (b) Number-average molecular weight (\blacksquare) and PDI (\square) of polyPEGMA vs. monomer conversion.

Note: [PEGMA₅₀₀]/[EBiB]/[DhHP-6]/[AscNa]/[KBr] =64/1/0.033/1/2 at 35 °C.

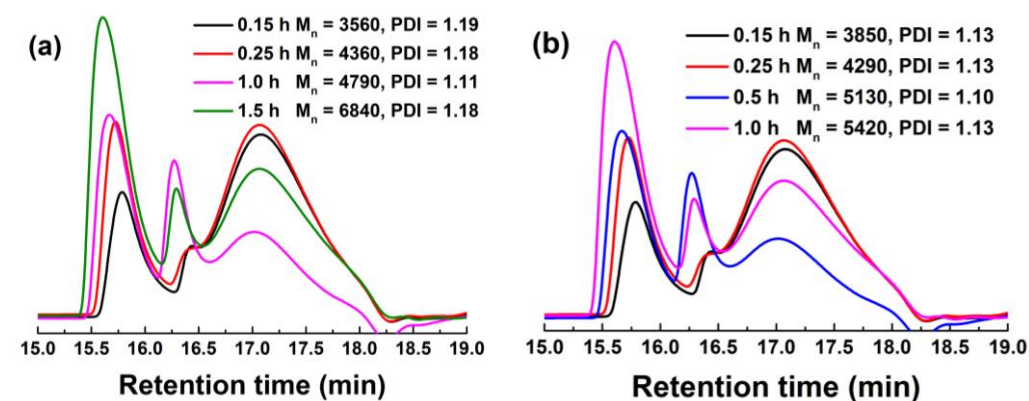


Figure S9. GPC traces of DhHP-6 catalyzed ARGET ATRP.

Note: (a) $[\text{PEGMA}_{500}]/[\text{EBiB}]/[\text{DhHP-6}]/[\text{AscNa}]/[\text{KBr}] = 64/1/0.033/1/8$ at $35\text{ }^{\circ}\text{C}$ (Table 1, entry 4); (b) $[\text{PEGMA}_{500}]/[\text{EBiB}]/[\text{DhHP-6}]/[\text{AscNa}]/[\text{KBr}] = 64/1/0.033/1/4$ at $35\text{ }^{\circ}\text{C}$ (Table 1, entry 5).

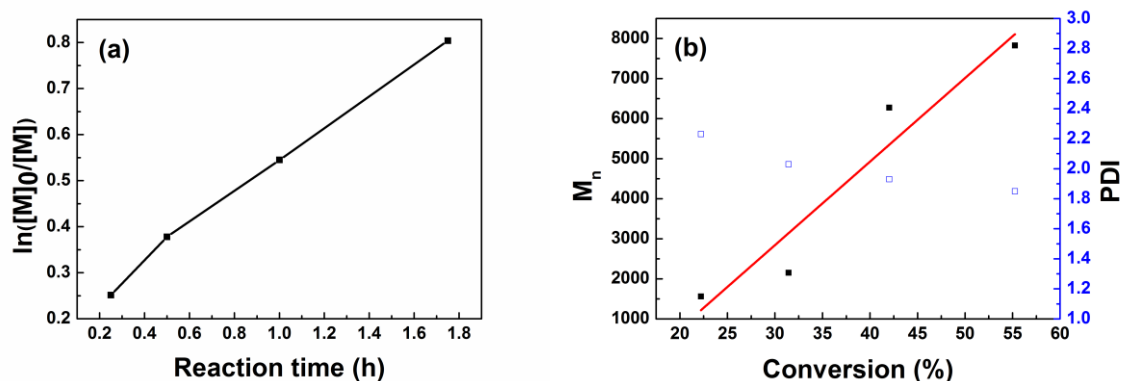


Figure S10. (a) First-order kinetic plot (■) for DhHP-6 catalyzed ARGET ATRP of GMA in DMF and (b) Number-average molecular weight (■) and PDI (□) of polyPEGMA vs. monomer conversion.

Note: $[\text{GMA}]_0/[\text{EBiB}]/[\text{DhHP-6}]/[\text{Asc}] = 100/1/0.03/2$ at $40\text{ }^{\circ}\text{C}$.

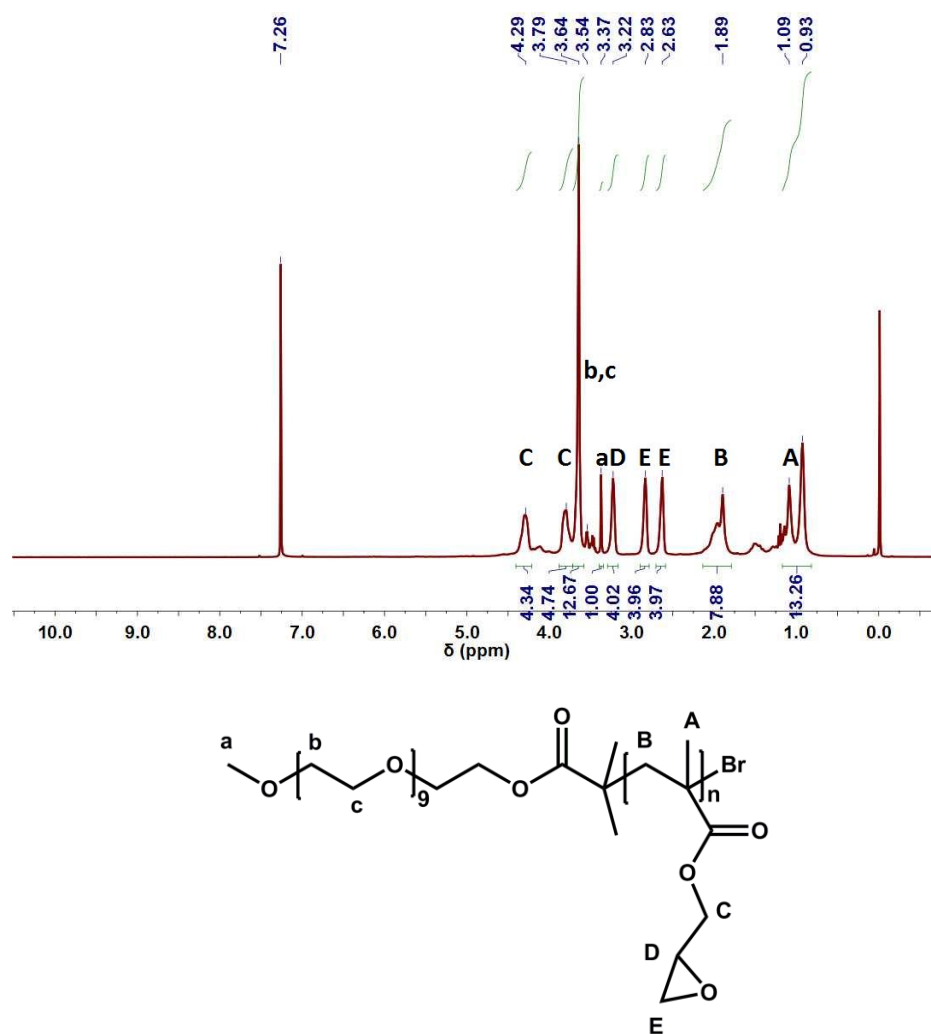


Figure S11. ¹H NMR spectrum (CDCl₃, 400 MHz) of purified PEG-PGMA sample obtained by DhHP-6 catalyzed ARGET ATRP using PEG-Br as macroinitiator.

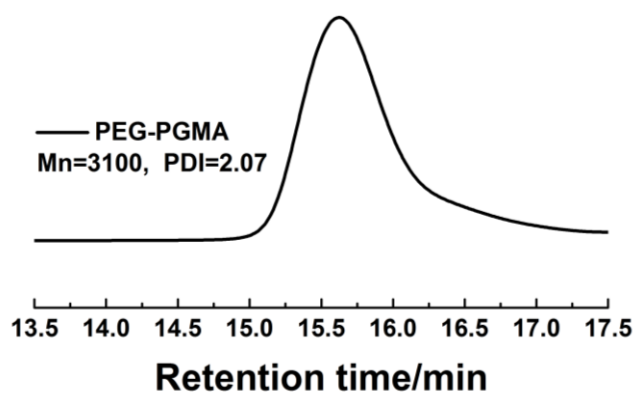


Figure S12. GPC trace of PEG-PGMA catalyzed by DhHP-6.

Note: [GMA]/[PEG-Br]/[DhHP-6]/[Asc] = 58:1:0.05:1.25, reaction temperature = 40 °C in a mixed solvent of DMF-H₂O (DMF:H₂O=7.5:1).

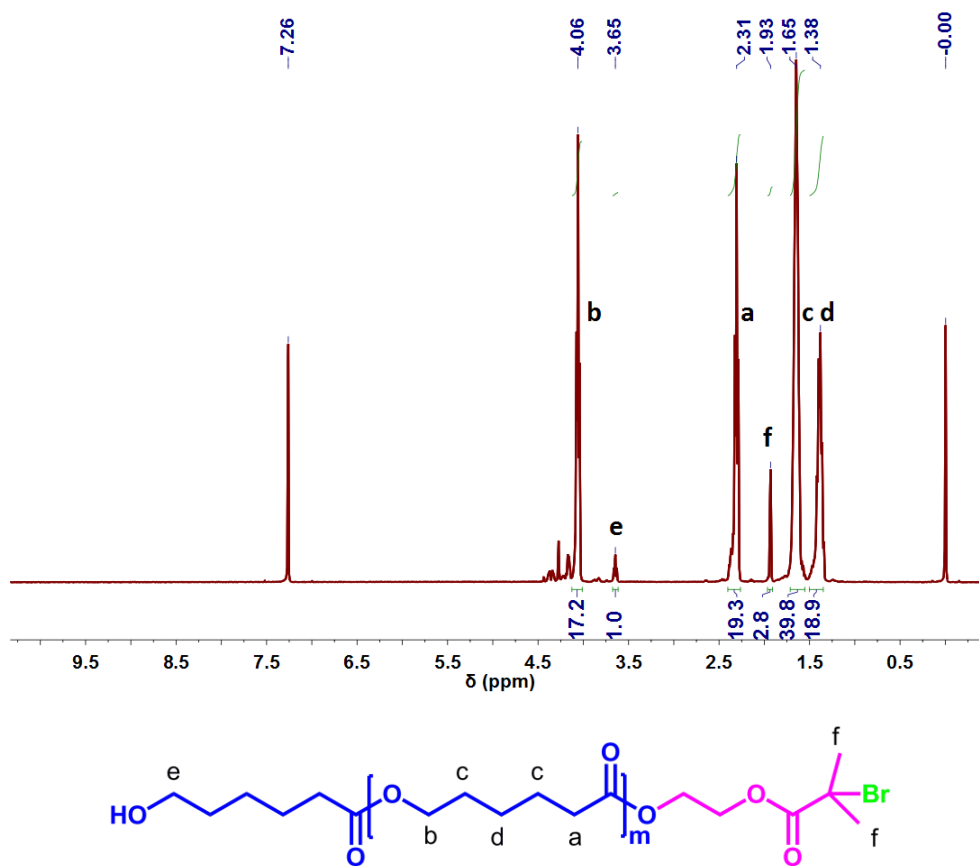


Figure S13. ^1H NMR spectrum (CDCl_3 , 400 MHz) of purified PCL-Br sample obtained by eROP using HEBiB as precursors.

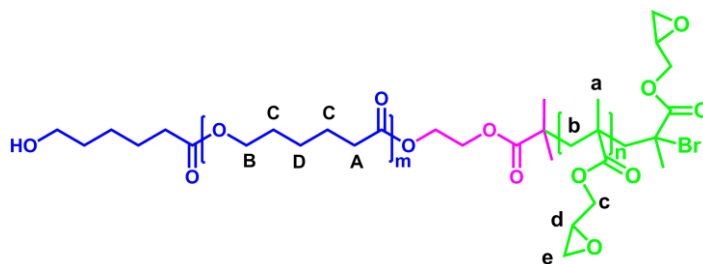
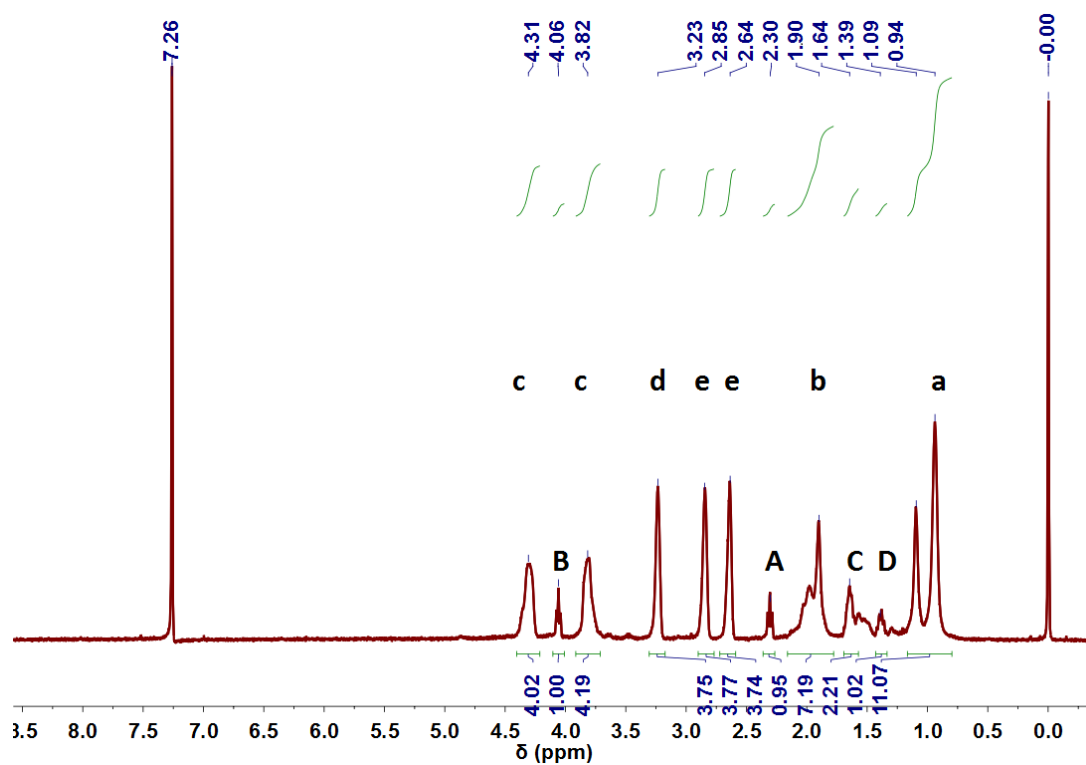


Figure S14. ^1H NMR spectrum (CDCl_3 , 400 MHz) of PCL-PGMA copolymer obtained the combination of eROP and DhHP-6 catalyzed ARGET ATRP in $\text{DMF-H}_2\text{O}$.

Note: $[\text{GMA}]/[\text{PCL-Br}]/[\text{DhHP-6}]/[\text{Asc}] = 66:1:0.088:5.43$, 50°C .

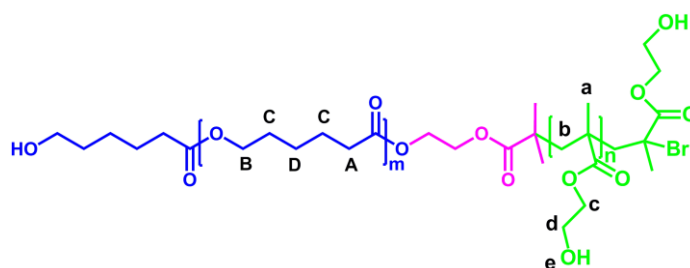
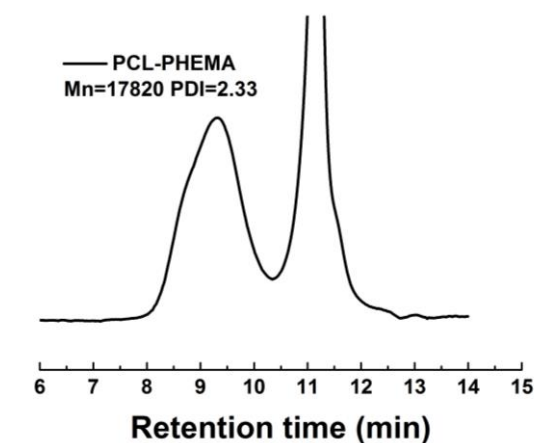
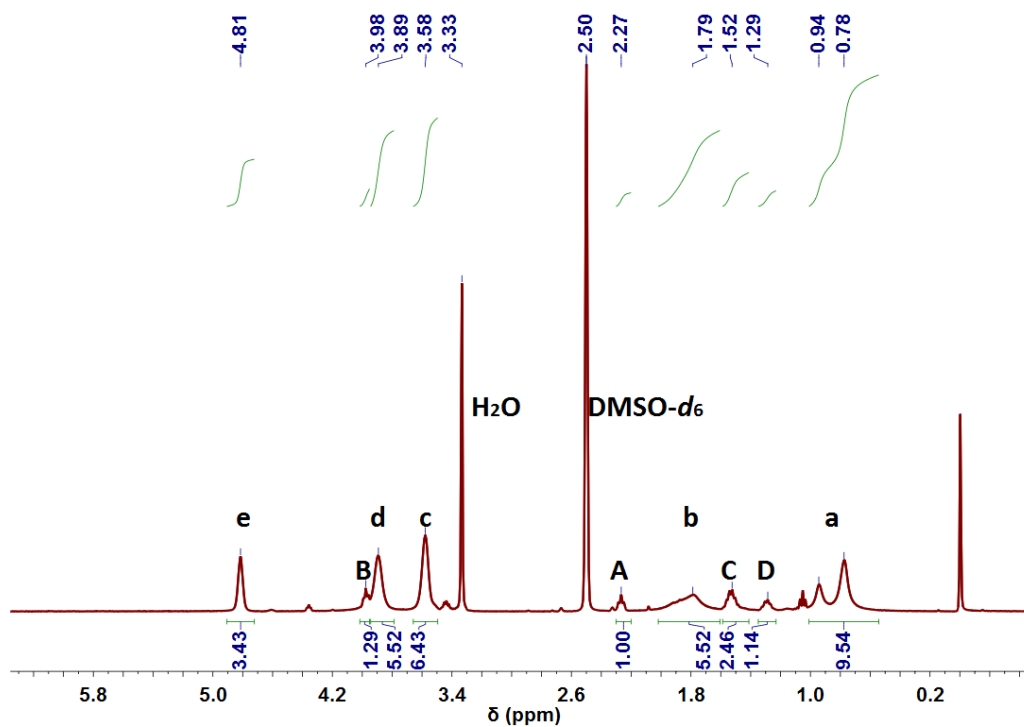


Figure S15. ^1H NMR spectrum ($\text{DMSO-}d_6$, 400 MHz) of amphiphilic copolymer, PCL-PHEMA, by the combination of eROP and DhHP-6 catalyzed ARGET ATRP in $\text{DMF-H}_2\text{O}$ and GPC trace of PCL-PHEMA.

Note: $[\text{HEMA}]/[\text{PCL-Br}]/[\text{DhHP-6}]/[\text{Asc}] = 87:1:0.08:3.23$, 50°C .

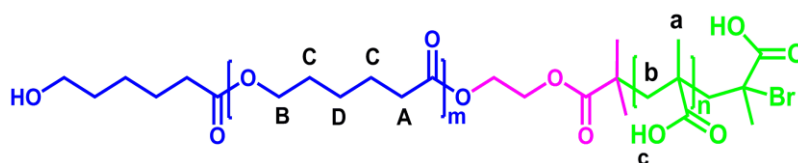
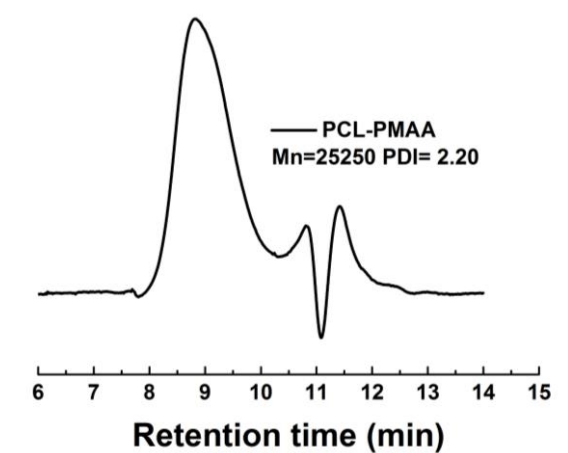
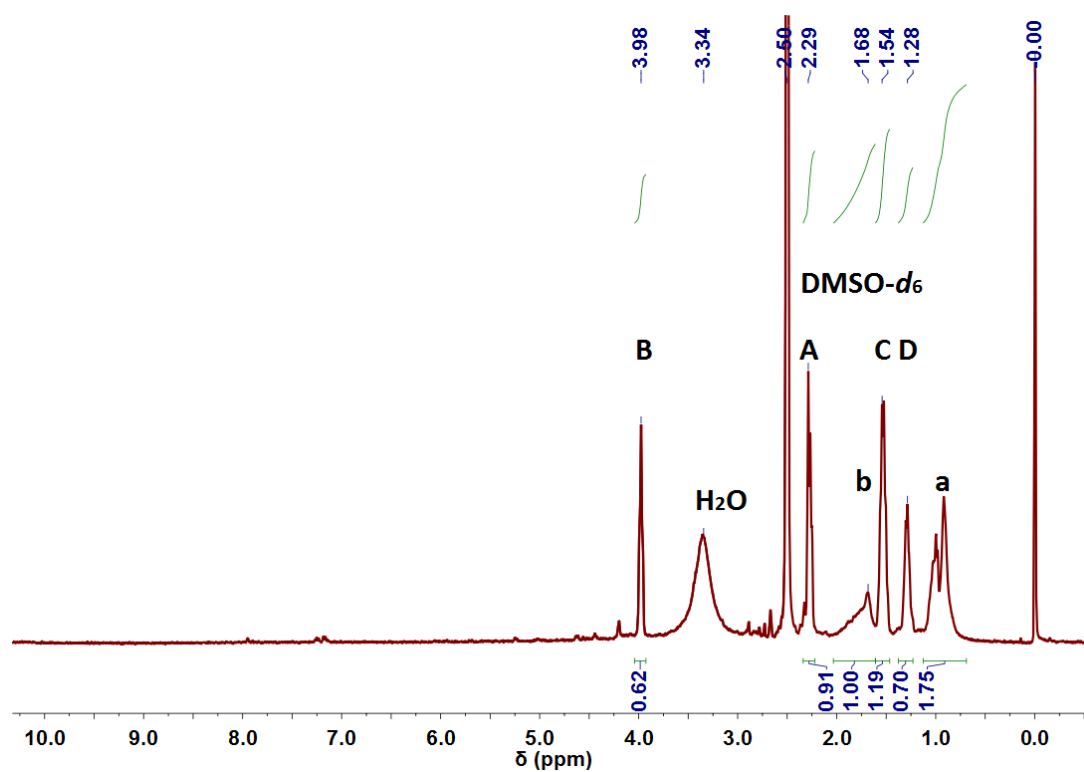


Figure S16. ^1H NMR spectrum ($\text{DMSO-}d_6$, 400 MHz) of amphiphilic copolymer, PCL-PMAA, by the combination of eROP and DhHP-6 catalyzed ARGET ATRP in $\text{DMF-H}_2\text{O}$ and GPC trace of PCL-PMAA.

Note: $[\text{MAA}]/[\text{PCL-Br}]/[\text{DhHP-6}]/[\text{Asc}] = 107:1:0.068:3.7$, $50\text{ }^\circ\text{C}$.

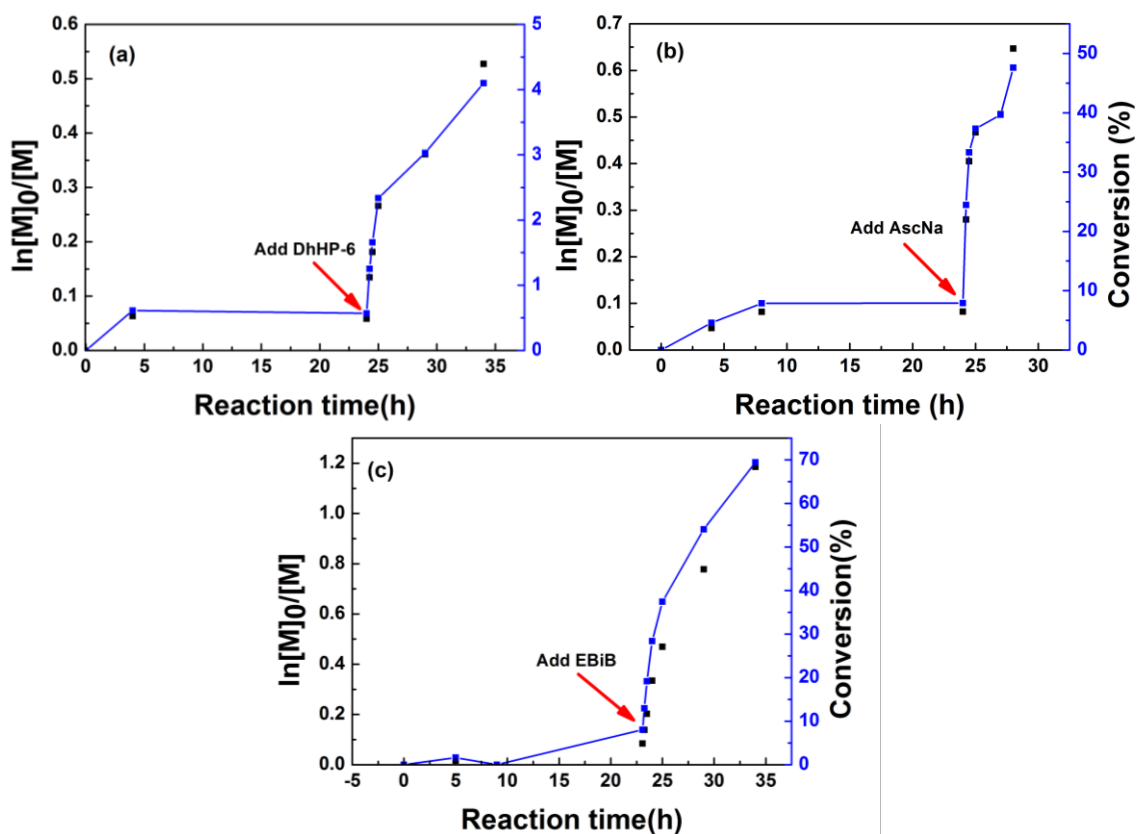


Figure S17. Control experiments and results (a) control experiment without the addition of DhHP-6; (b) control experiment without the addition of AscNa; (c) control experiment without the addition of EBiB (see Table 1, entries 8-10 for detailed conditions).

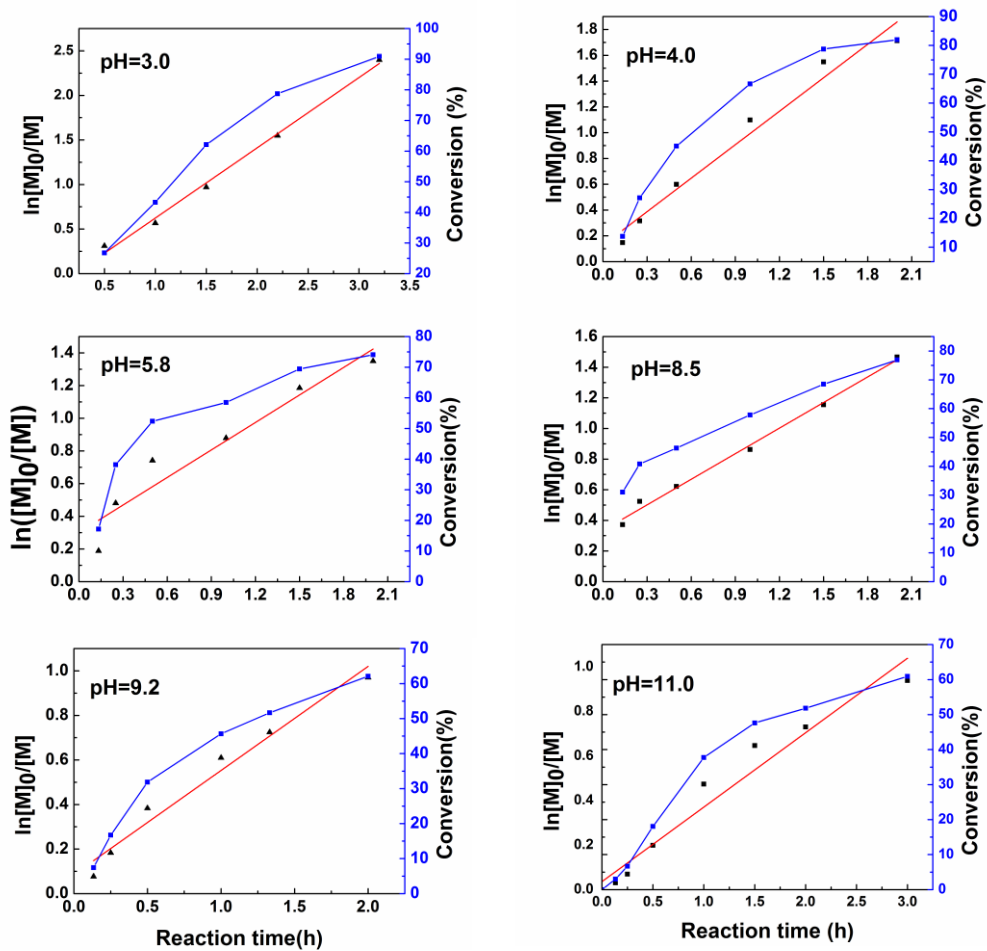


Figure S18. First-order kinetic plot (\blacktriangle) for enzyme mimic catalyzed ARGET ATRP of PEGMA₅₀₀ in PBS at different pHs (marked on each Figure), and plot of monomer conversion vs reaction time (\blacksquare).

Note: $[\text{PEGMA}_{500}]/[\text{EBiB}]/[\text{DhHP-6}]/[\text{AscNa}]/[\text{KBr}] = 32/1/0.033/1/8$ at 35 °C.

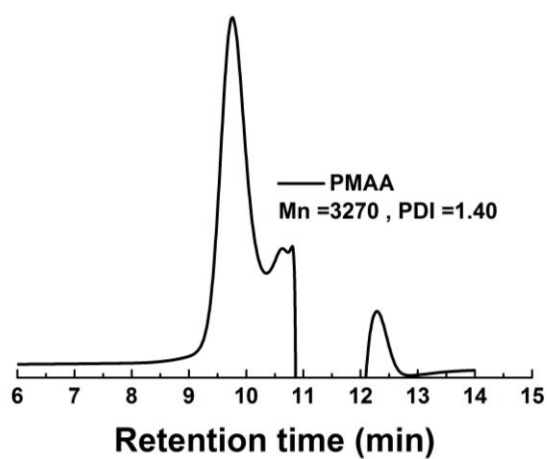


Figure S19. GPC trace of PMAA obtained by DhHP-6 catalyzed ARGET ATRP (THF as mobile phase, 1 mL min^{-1}).

Note: $[\text{MAA}]/[\text{EBiB}]/[\text{DhHP-6}]/[\text{Asc}] = 171/1/0.032/1.6$ at $50 \text{ }^\circ\text{C}$, in $\text{DMF:H}_2\text{O} = 7.5:1$.