Supporting Information

One-pot Catalyst-switching Synthesis of Thermoresponsive Amphiphilic Diblock Copolymers Consisting of Poly(*N*,*N*-diethylacrylamide) and Biodegradable Polyesters

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1. Table of PDEAm$_x$-OH, PDEAM$_x$-*b*-PTMC$_y$ and PDEAm$_x$-*b*-PLLA$_y$

Table S1. Preparation for a stock solution of PDEAm-OH in CH_2CL_2 by i) the equimolar hydrosilylation of MAm-OTBDMS and Me_2EtSiH using $B(C_6F_5)_3$[a] and ii) the GTP of DEAm using Me_3SiNTf_2,[b] followed by iii) the deprotection using TBAF [c]

PDEAm$_x$-OH	[DEAm]$_0$/[SKAm^{Me2Et}-OTBDMS]$_0$	Time / h	$M_{n,calcd}$ [d] / kg mol^{-1}	$M_{n,SEC}$ (M_w/M_n) [e] / kg mol^{-1}	T_{cp} [f]
PDEAm$_{30}$-OH	30	6	3.8	3.6 (1.07)	53.8
PDEAm$_{40}$-OH	40	6	5.1	4.8 (1.08)	52.5
PDEAm$_{50}$-OH	50	6	6.4	6.2 (1.08)	51.9
PDEAm$_{60}$-OH	60	6	7.7	7.9 (1.07)	51.5
PDEAm$_{70}$-OH	70	6	8.9	8.7 (1.09)	51.0
PDEAm$_{80}$-OH	80	7	10.1	9.9 (1.10)	50.5
PDEAm$_{90}$-OH	90	8	11.4	10.5 (1.10)	49.9

[a] Solvent, CH_2Cl_2; room temperature; argon atmosphere; MAm-OTBDMS, 0.22 mmol; [MAm-OTBDMS]$_0$/[Me_2EtSiH]$_0$/[$B(C_6F_5)_3$]$_0$ = 1.1/1.0/0.25. [b] [DEAm]$_0$, 1.0 mol L^{-1}; SKAm^{Me2Et}-OTBDMS, 0.20 mmol; [SKAm^{Me2Et}-OTBDMS]$_0$/[Me_3SiNTf_2]$_0$, 1/0.05; monomer conversion determined by ^{1}H NMR spectra in $CDCl_3$, >99%. [c] Tetrabutylammonium fluoride (TBAF) solution, 1.0 mol L^{-1} in THF. [d] $M_{n,cacld}$ = (MW of PDEAm-OH) + [TMC]$_0$/[PDEAm-OH]$_0$ x (monomer conversion) x (MW of TMC) + (M.W. of H) x 2. [e] Determined by SEC equipped with a RI detector in DMF containing LiCl (0.01 mol L^{-1}) using PMMA standards. [f] Determined by UV-vis measurements in water (3 g L^{-1}).

Table S2. Synthesis of PDEAm-*b*-PTMC by the ring-opening polymerization (ROP) of trimethylene carbonate (TMC) using PDEAm-OH as the macroinitiator and *t*-Bu-P_2 as the organocatalyst [a]

Sample code	$[TMC]_0/[PDEAm\text{-}OH]_0$	$M_{n,calcd}$ [b] / kg mol^{-1}	$M_{n,SEC}$ (M_w/M_n) [c] / kg mol^{-1}
$PDEAm_{30}$-*b*-$PTMC_{70}$	70	11.0	11.5 (1.10)
$PDEAm_{40}$-*b*-$PTMC_{60}$	60	11.2	11.7 (1.18)
$PDEAm_{50}$-*b*-$PTMC_{50}$	50	11.5	11.2 (1.17)
$PDEAm_{60}$-*b*-$PTMC_{40}$	40	11.7	12.5 (1.10)
$PDEAm_{70}$-*b*-$PTMC_{30}$	30	12.0	12.2 (1.09)
$PDEAm_{80}$-*b*-$PTMC_{20}$	20	12.2	13.2 (1.09)
$PDEAm_{90}$-*b*-$PTMC_{10}$	10	12.5	13.5 (1.19)

[a] $[TMC]_0$, 1.0 mol L^{-1}; solvent, CH_2Cl_2; room temperature; argon atmosphere; polymerization time, 24 h; monomer conversion determined by ^1H NMR spectra in $CDCl_3$, >99%. [b] $M_{n,cacld}$ = (MW of PDEAm-OH) + $[TMC]_0/[PDEAm\text{-}OH]_0$ x (monomer conversion) x (MW of TMC) + (M.W. of H) x 2. [c] Determined by SEC equipped with a RI detector in DMF containing LiCl (0.01 mol L^{-1}) using PMMA standards.

Table S3. Synthesis of PDEAm-*b*-PLLA by the ring-opening polymerization (ROP) of L-lactide (L-LA) using PDEAm-OH as the macroinitiator and *t*-Bu-P_2 as the organocatalyst [a]

Sample code	$[L\text{-}LA]_0/[PDEAm\text{-}OH]_0$	$M_{n,calcd}$ [b] / kg mol^{-1}	$M_{n,SEC}$ (M_w/M_n) [c] / kg mol^{-1}
$PDEAm_{30}$-*b*-$PLLA_{70}$	70	13.9	11.6 (1.13)
$PDEAm_{40}$-*b*-$PLLA_{60}$	60	13.7	11.2 (1.16)
$PDEAm_{50}$-*b*-$PLLA_{50}$	50	13.5	12.5 (1.17)
$PDEAm_{60}$-*b*-$PLLA_{40}$	40	13.4	11.8 (1.15)
$PDEAm_{70}$-*b*-$PLLA_{30}$	30	13.2	13.9 (1.19)
$PDEAm_{80}$-*b*-$PLLA_{20}$	20	13.0	12.9 (1.20)
$PDEAm_{90}$-*b*-$PLLA_{10}$	10	12.9	14.3 (1.14)

[a] $[L\text{-}LA]_0$, 1.0 mol L^{-1}; solvent, CH_2Cl_2; room temperature; argon atmosphere; polymerization time, 24 h; monomer conversion determined by ^{1}H NMR spectra in $CDCl_3$, >99%. [b] $M_{n,cacld}$ = (MW of PDEAm-OH) + $[L\text{-}LA]_0/[PDEAm\text{-}OH]_0$ x (monomer conversion) x (MW of L-LA) + (MW of H) x 2. [c] Determined by SEC equipped with a RI detector in DMF containing LiCl (0.01 mol L^{-1}) using PMMA standards.

2. SEC(RI) traces of PDEAM$_x$-*b*-PTMC$_y$ and PDEAm$_x$-*b*-PLLA$_y$

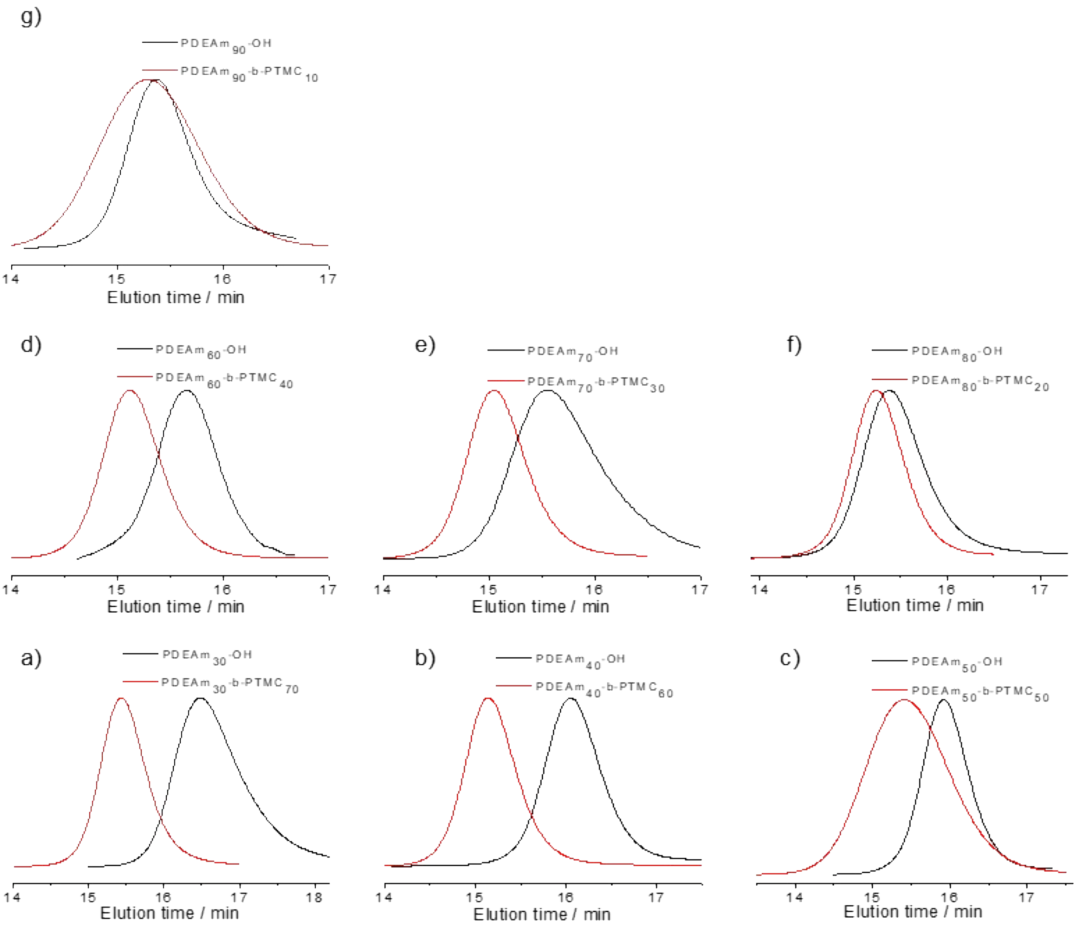


Figure S1. SEC traces of PDEAm and PDEAm-*b*-PTMC in $CDCl_3$.

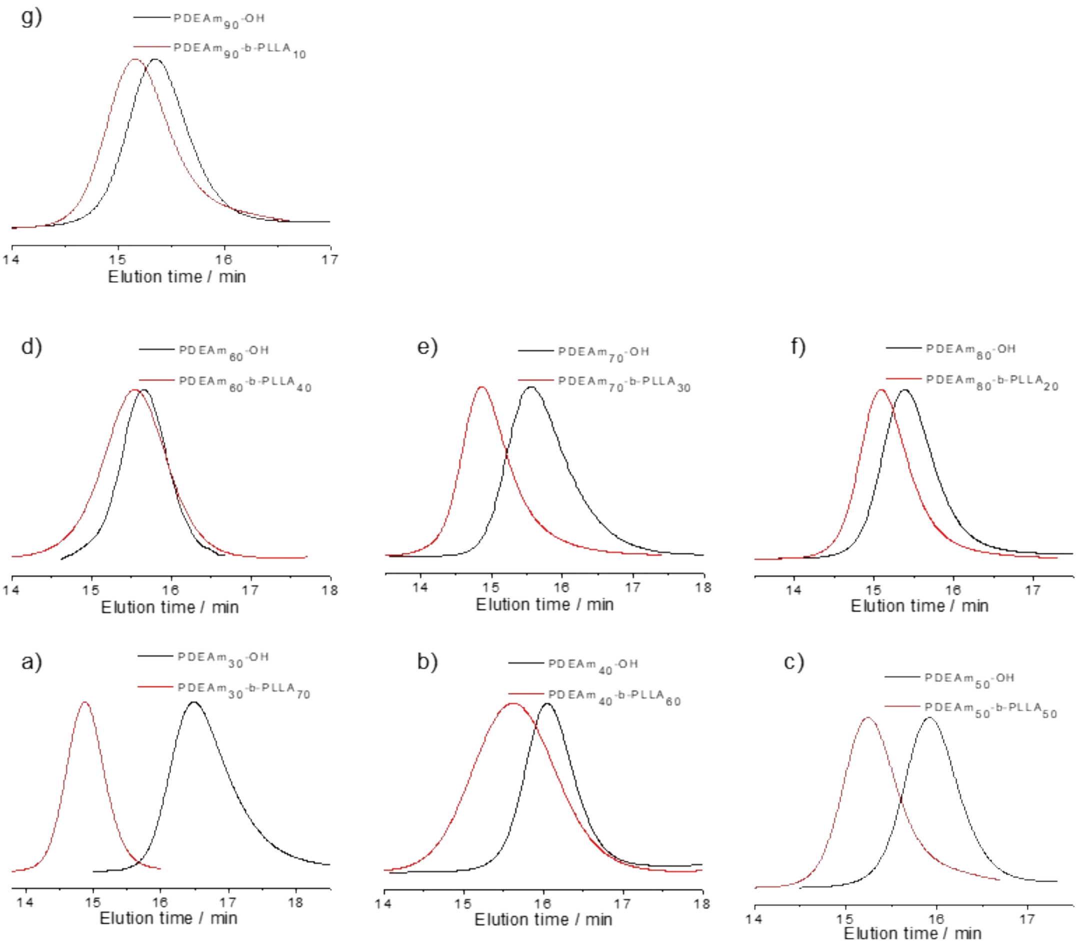


Figure S2. SEC traces PDEAm and of PDEAm-*b*-PLLA in $CDCl_3$.

3. ^{1}H NMR spectra of PDEAm-*b*-PTMC and PDEAm-*b*-PLLA

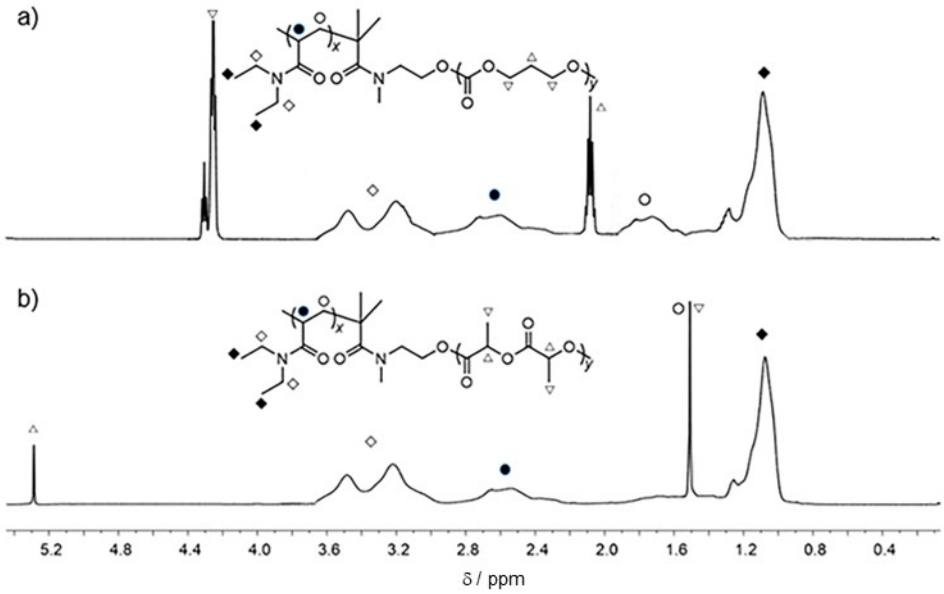
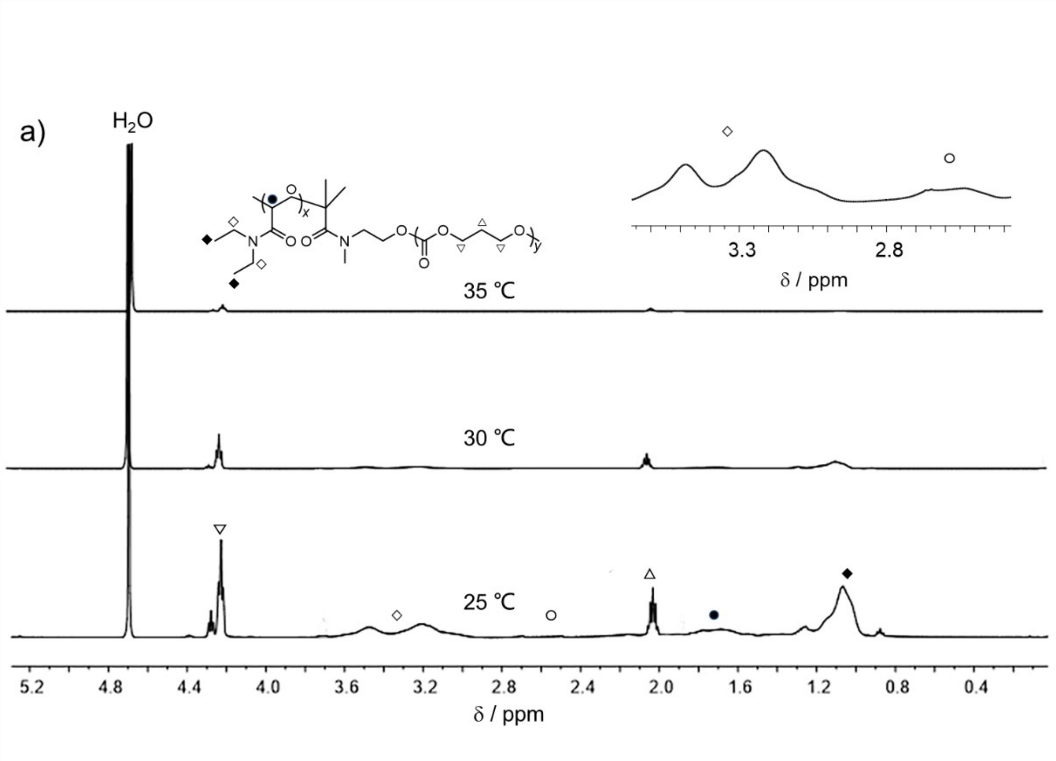


Figure S3. ^{1}H NMR spectra of a) PDEAm-*b*-PTMC and b) PDEAm-*b*-PLLA in $CDCl_3$.

4. Dynamic ^{1}H NMR spectroscopy of PDEAm$_{30}$-*b*-PTMC$_{70}$ and PDEAm$_{30}$-*b*-PLLA$_{70}$



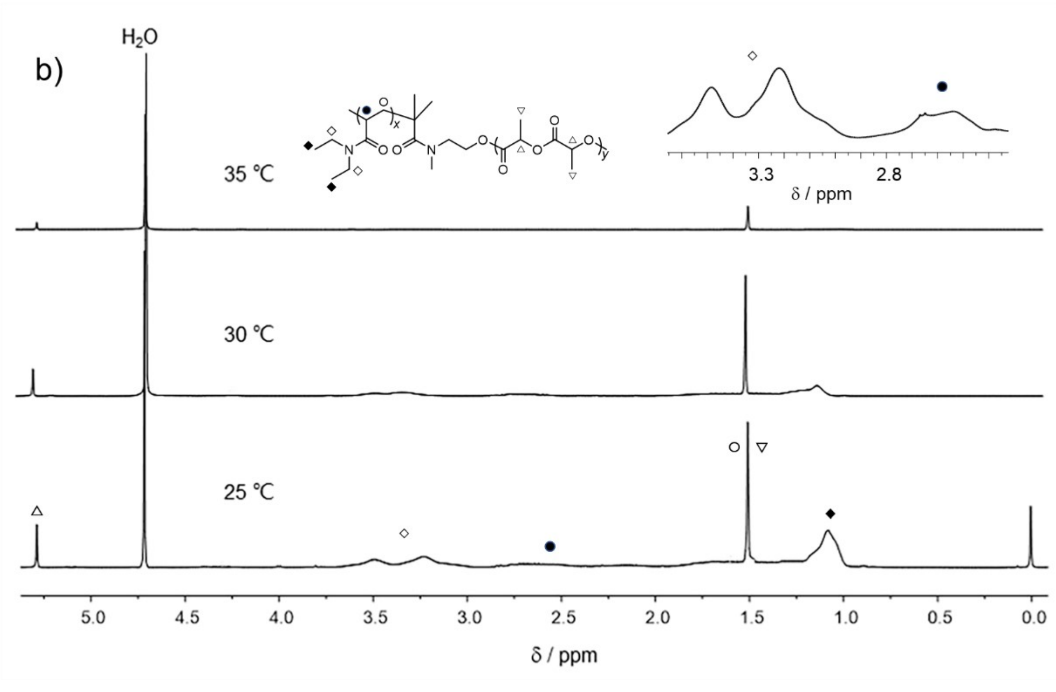


Figure S4. ^{1}H NMR spectra of a) PDEAm$_{30}$-*b*-PTMC$_{70}$ and b) PDEAm$_{30}$-*b*-PLLA$_{70}$ measured at 25, 30, 35 °C in D_2O.

5. Distribution of hydrodynamic radius (Rh) of PDEAm$_x$-*b*-PCL$_y$, PDEAM$_x$-*b*-PTMC$_y$ and PDEAm$_x$-*b*-PLLA$_y$ at 25°C and 55°C

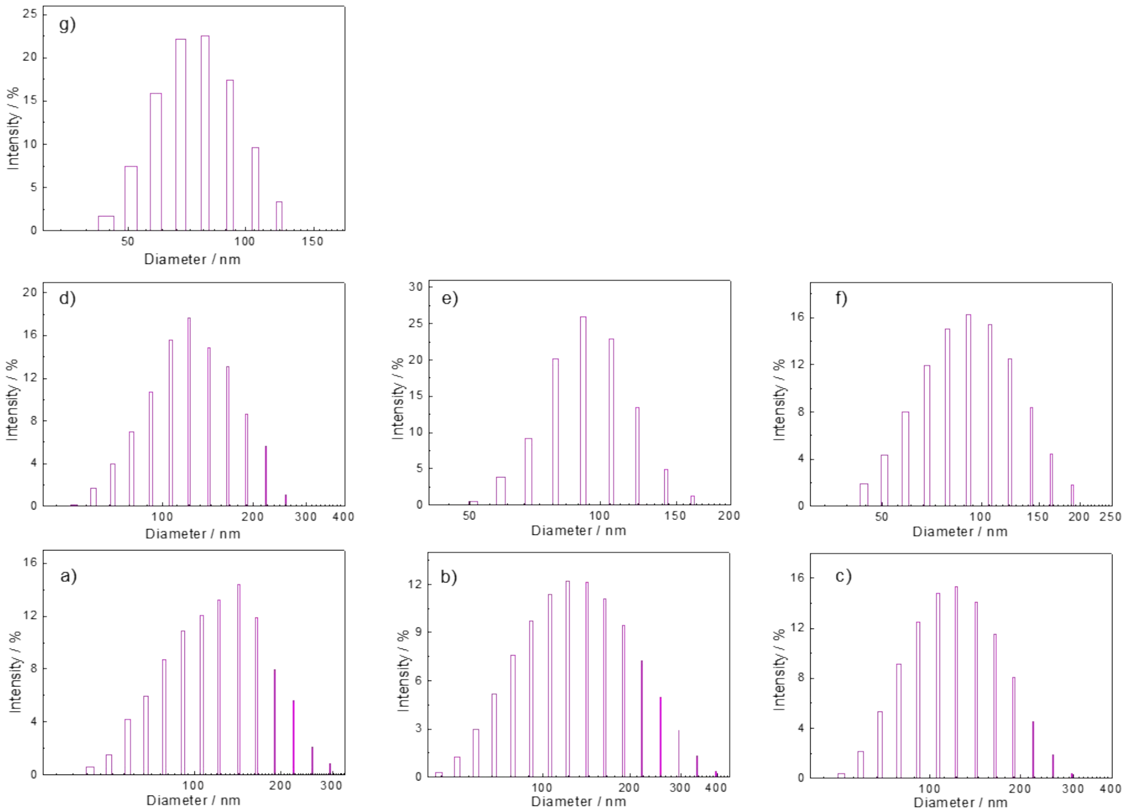


Figure S5. Distribution of hydrodynamic radii for PDEAm$_x$-*b*-PCL$_y$ with *x*/*y* ratios of (a) 30/70, (b) 40/60, (c) 50/50, (d) 60/40, (e) 70/30, (f) 80/20, and (g) 90/10 at 25°C.

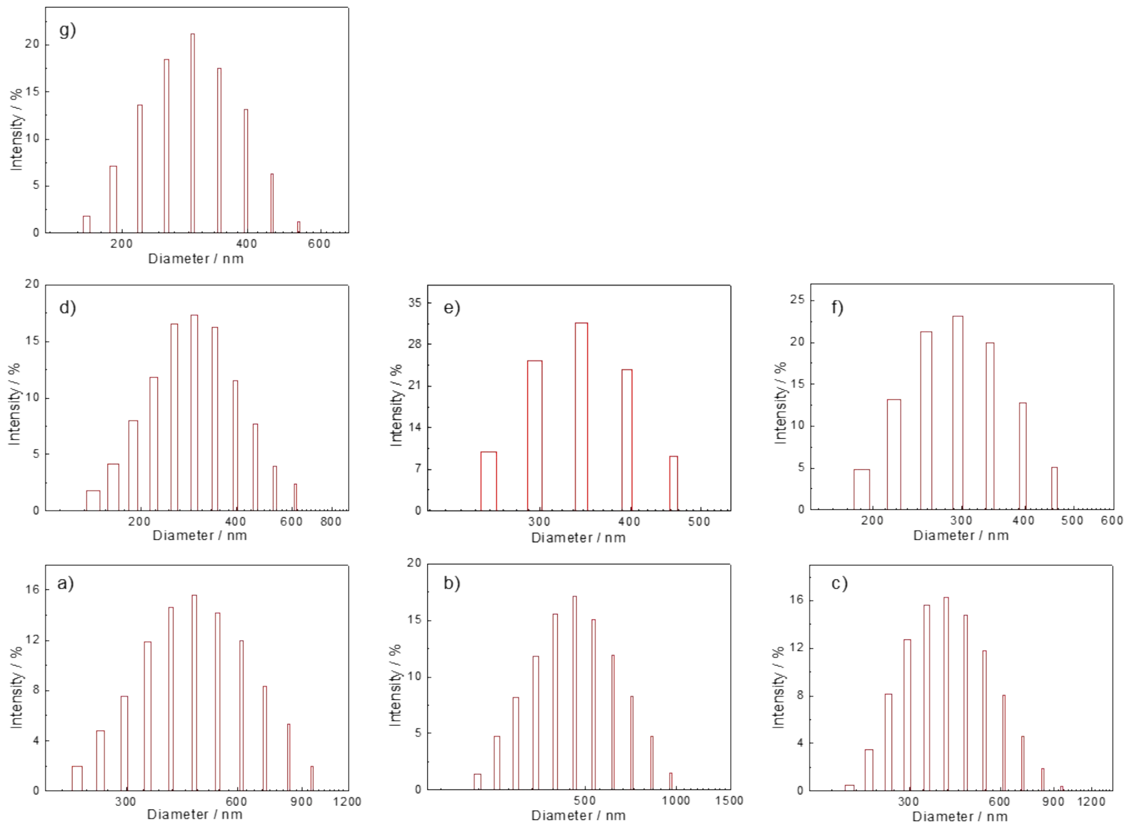


Figure S6. Distribution of hydrodynamic radii for PDEAm$_x$-*b*-PCL$_y$ with *x*/*y* ratios of (a) 30/70, (b) 40/60, (c) 50/50, (d) 60/40, (e) 70/30, (f) 80/20, and (g) 90/10 at 55°C.

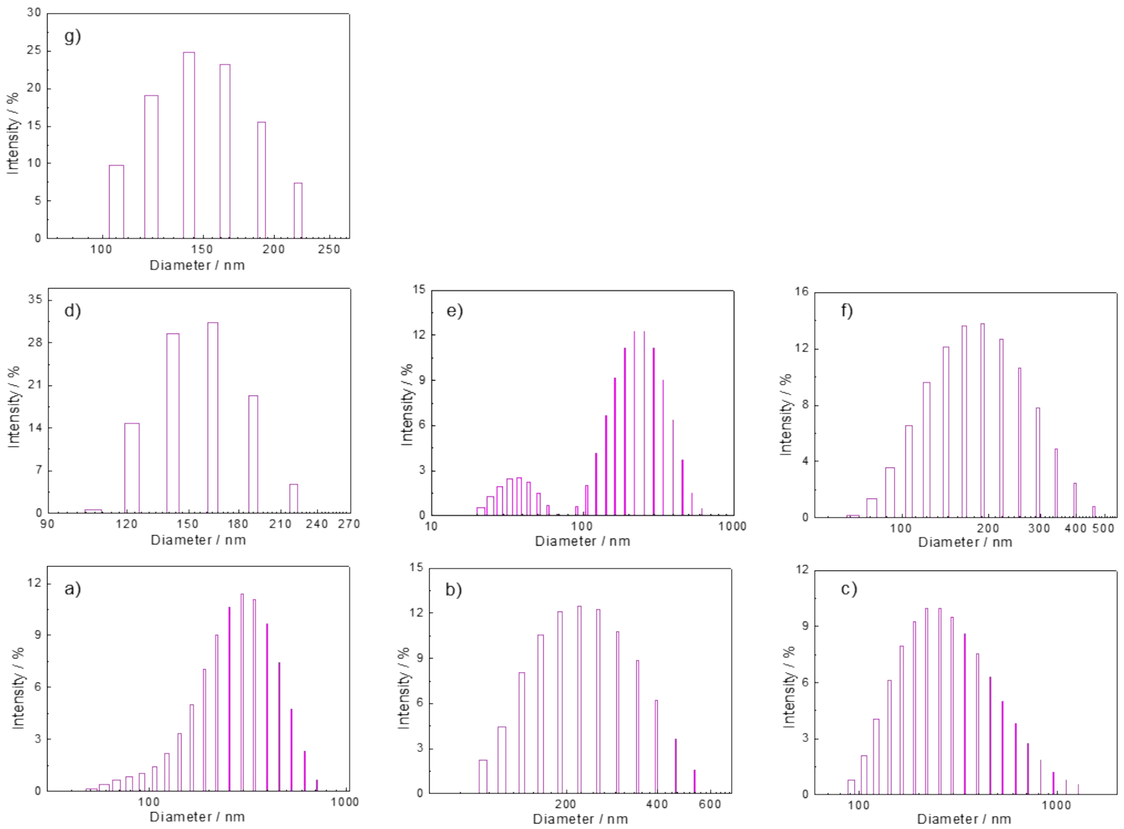


Figure S7. Distribution of hydrodynamic radii for PDEAm$_x$-*b*-PTMC$_y$ with x/y ratios of (a) 30/70, (b) 40/60, (c) 50/50, (d) 60/40, (e) 70/30, (f) 80/20, and (g) 90/10 at 25°C.

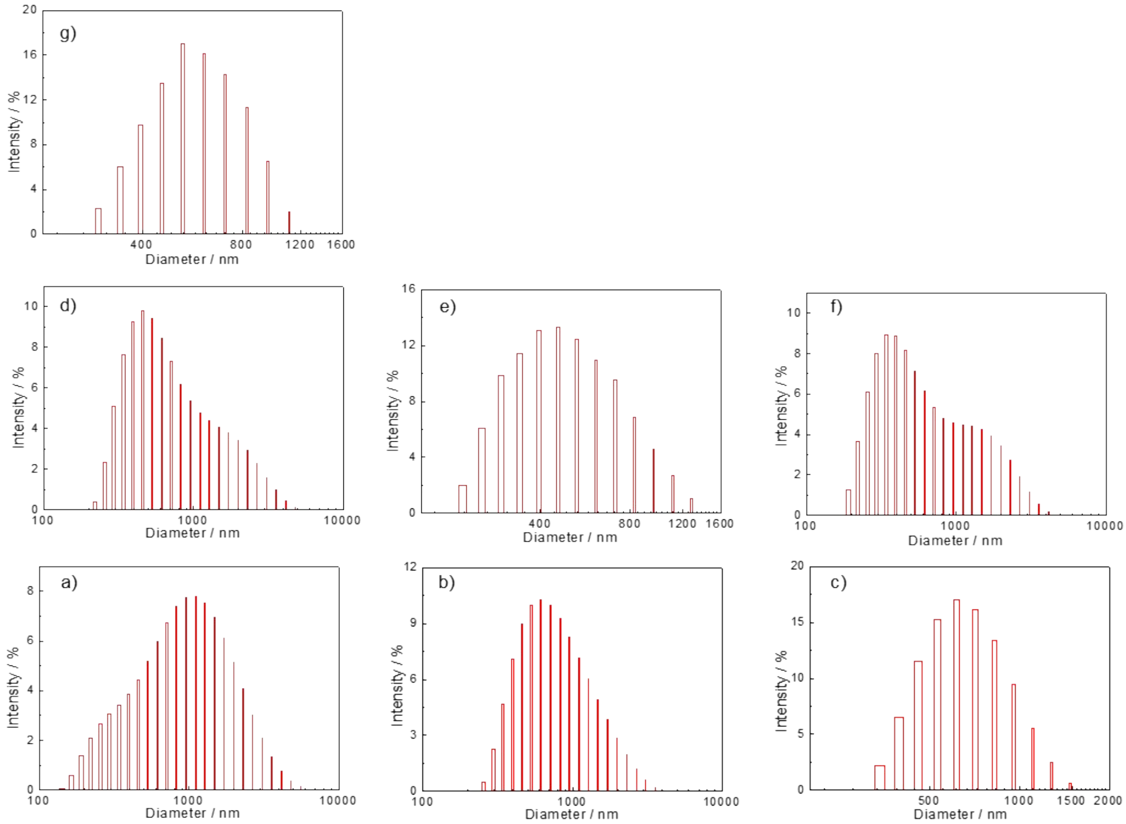


Figure S8. Distribution of hydrodynamic radii for PDEAm$_x$-*b*-PTMC$_y$ with *x*/*y* ratios of (a) 30/70, (b) 40/60, (c) 50/50, (d) 60/40, (e) 70/30, (f) 80/20, and (g) 90/10 at 55°C.

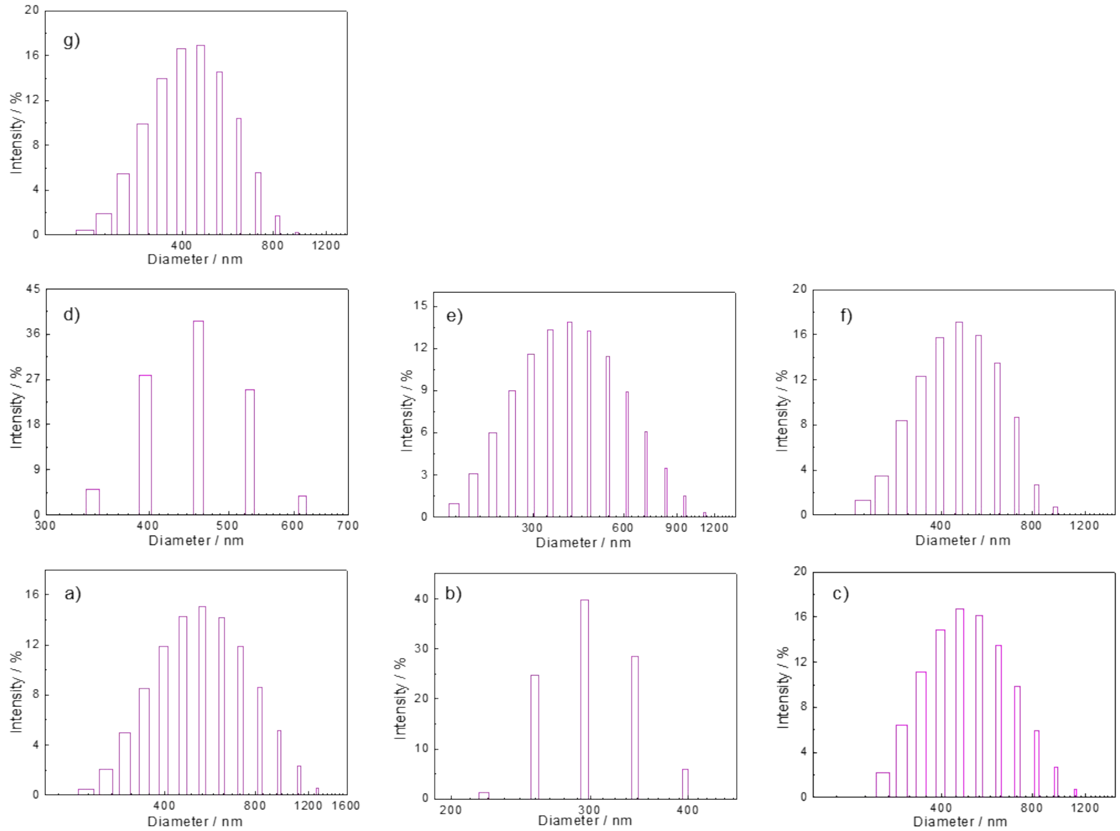


Figure S9. Distribution of hydrodynamic radii for PDEAm$_x$-*b*-PLLA$_y$ with x/y ratios of (a) 30/70, (b) 40/60, (c) 50/50, (d) 60/40, (e) 70/30, (f) 80/20, and (g) 90/10 at 25℃.

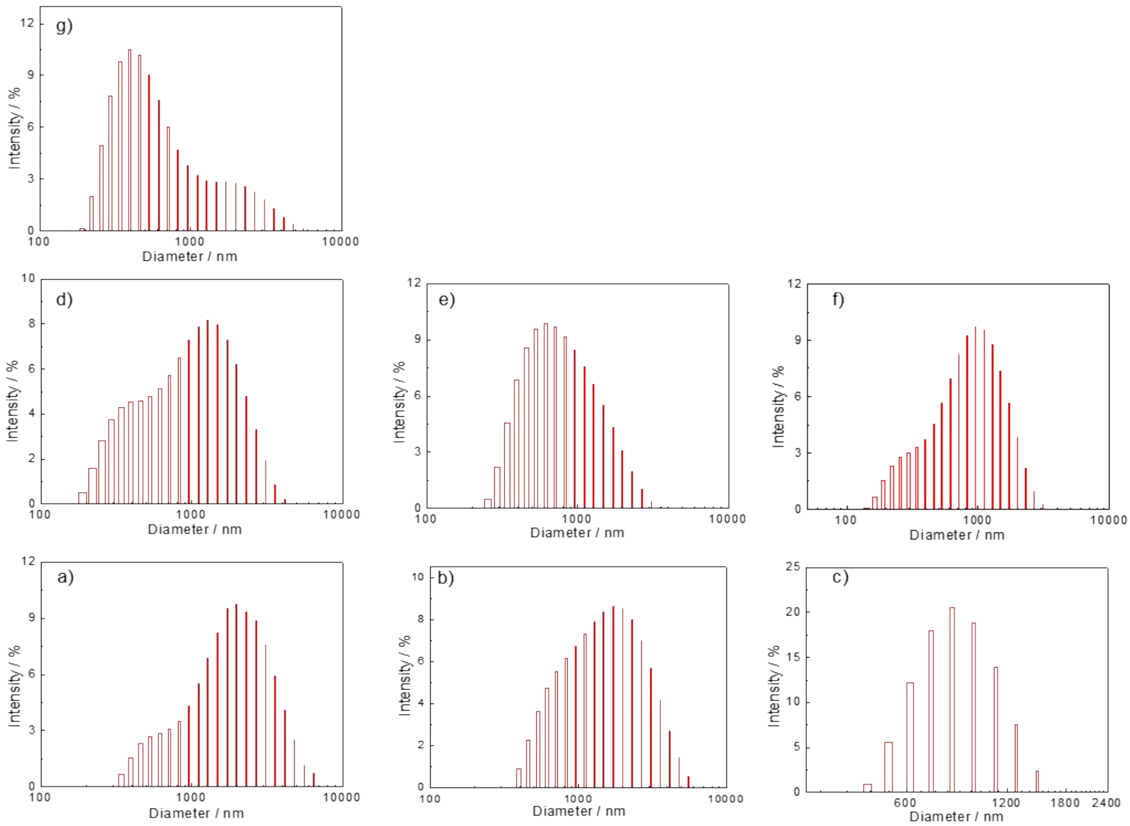


Figure S10. Distribution of hydrodynamic radii for PDEAm$_x$-*b*-PLLA$_y$ with x/y ratios of (a) 30/70, (b) 40/60, (c) 50/50, (d) 60/40, (e) 70/30, (f) 80/20, and (g) 90/10 at 55°C.