Precise Synthesis of Structurally Diverse Aggregation-Induced Emission-Active Polyacrylates by Cu(0)-Catalyzed SET-LRP with Macromolecular Structure-Correlated Emission

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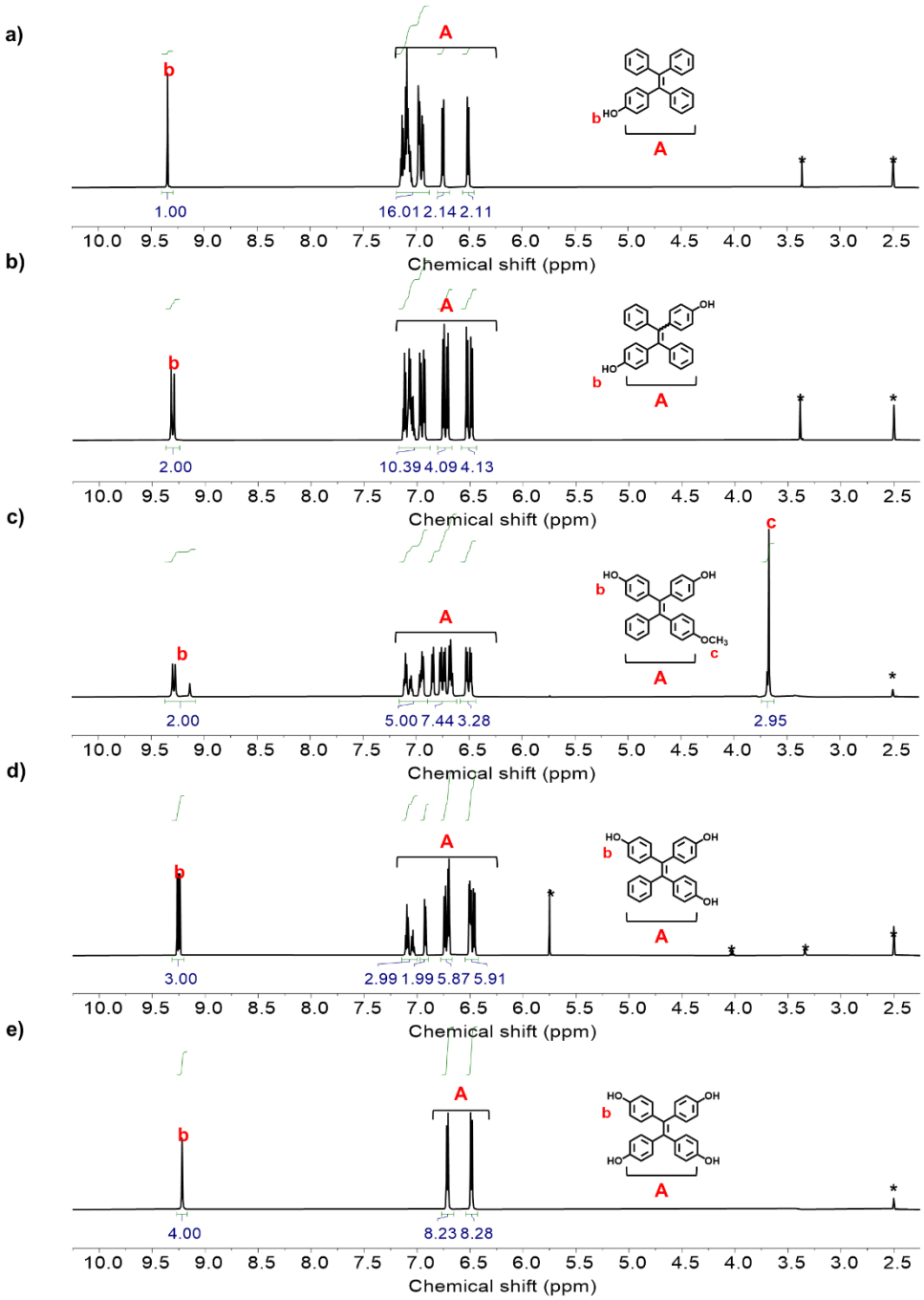

Figure S1. ^{1}H-NMR spectrum of (a) TPE-1OH, (b) TPE-2OH, (c) compound **1**, (d) TPE-3OH and (e) TPE-4OH in DMSO-d_6. ^{1}H NMR resonances from residual solvent in DMSO-d_6 are indicated by an asterisk (*).

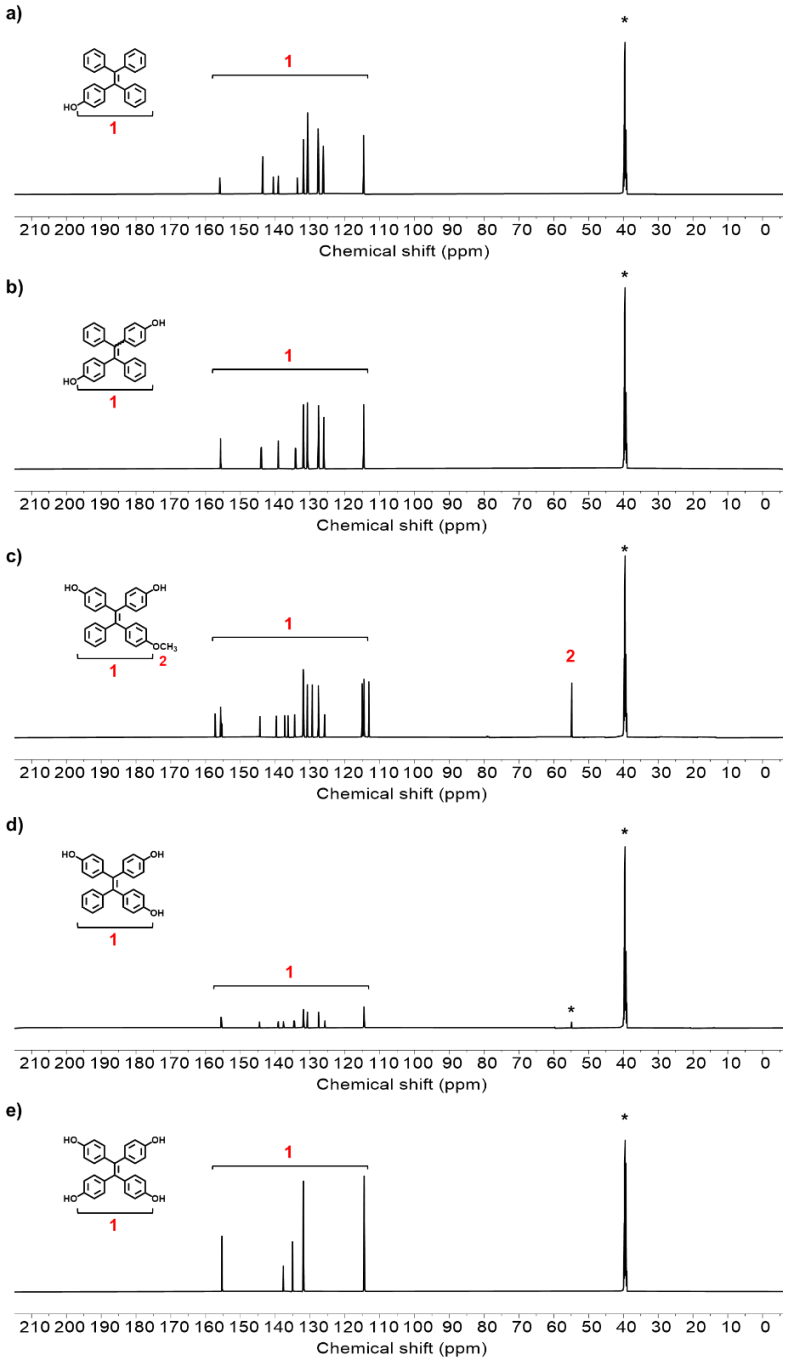

Figure S2. ^{13}C-NMR spectrum of (a) TPE-1OH, (b) TPE-2OH, (c) compound **1**, (d) TPE-3OH in DMSO-d_6 and (e) TPE-4OH in DMSO-d_6. ^{13}C NMR resonances from residual solvent in DMSO-d_6 are indicated by an asterisk (*).

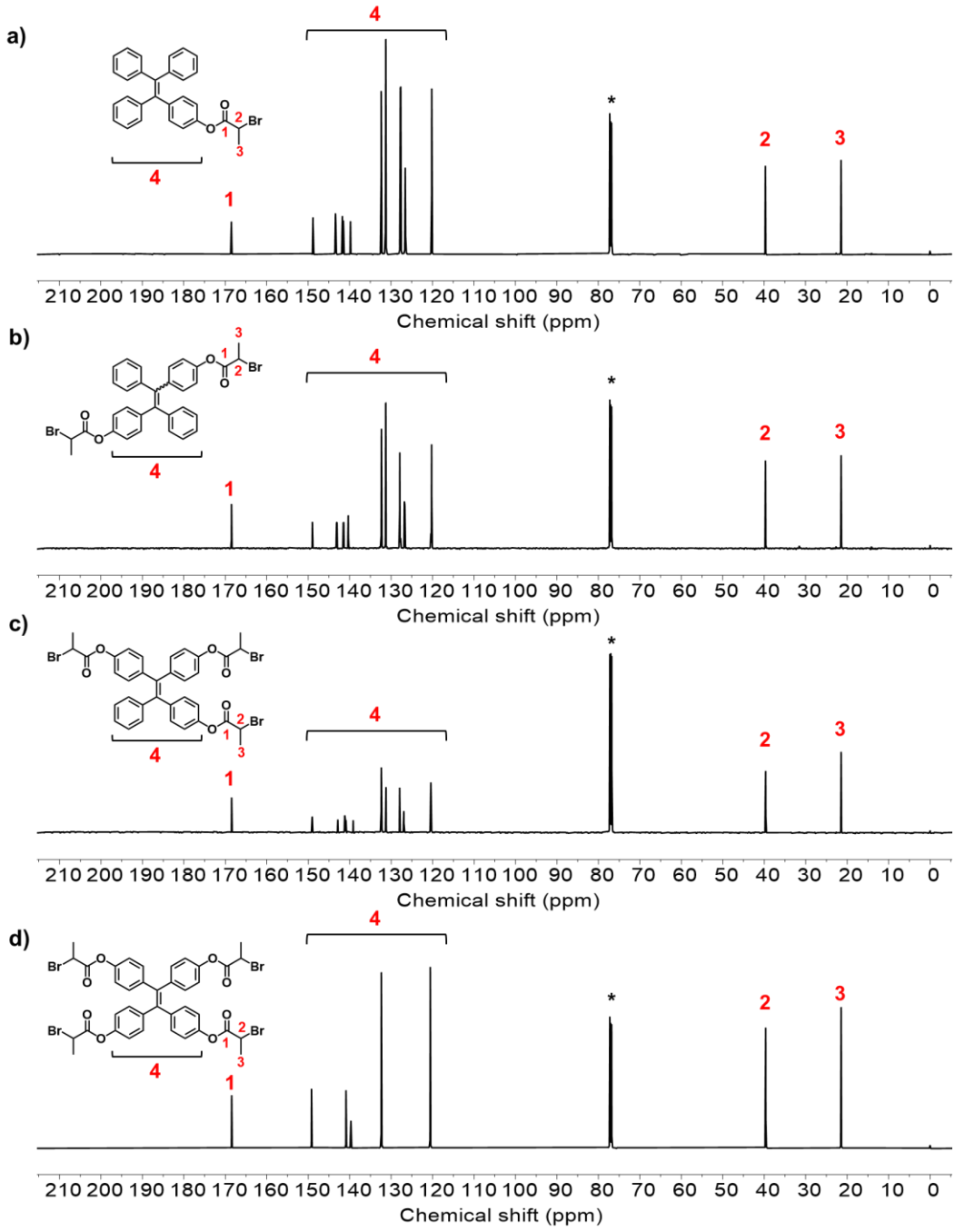

Figure S3. ^{13}C-NMR spectrum of (a) TPE-1Br, (b) TPE-2Br, (c) TPE-3Br and (d) TPE-4Br in $CDCl_3$. ^{13}C NMR resonances from residual solvent in $CDCl_3$ are indicated by an asterisk (*).

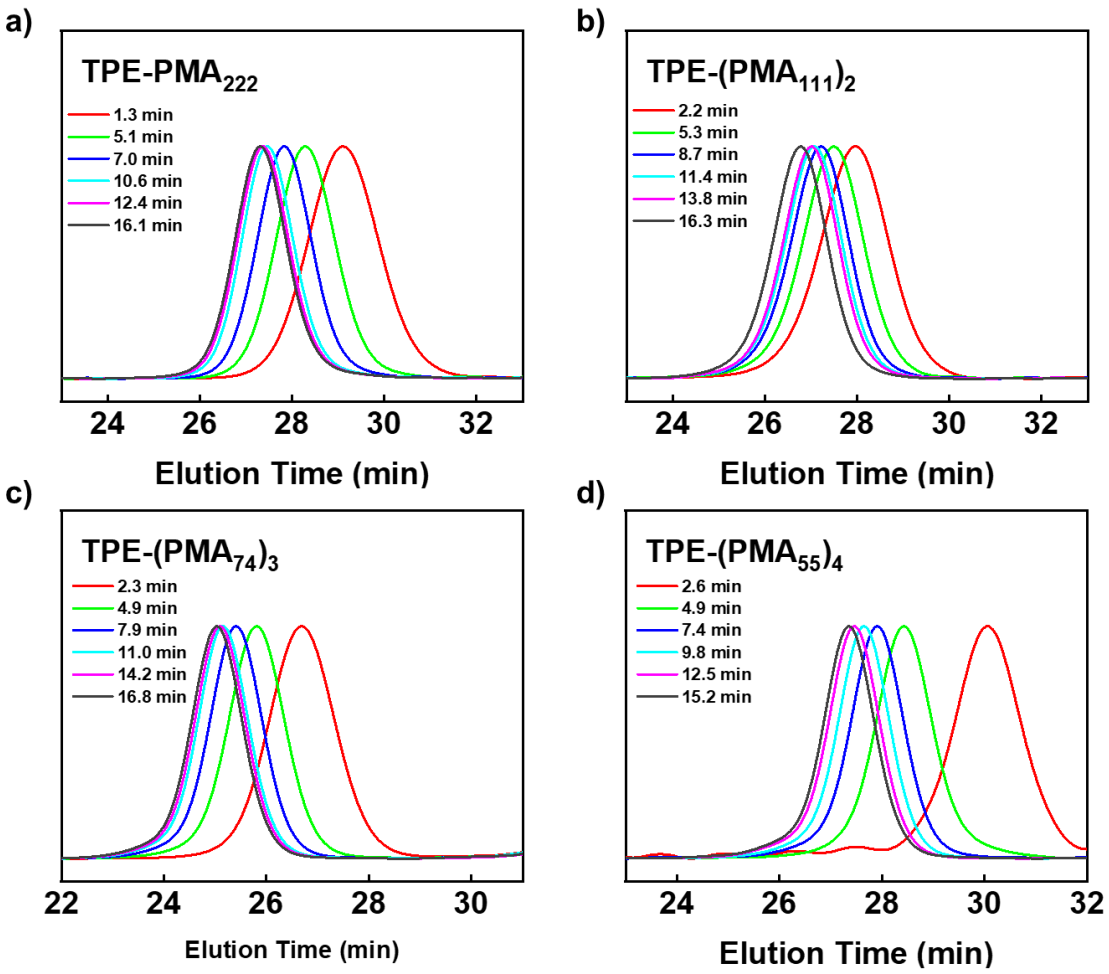

Figure S4. GPC traces of TPE-PMAs obtained by the SET-LRP of MA in DMSO initiated from (a) TPE-1Br, (b) TPE-2Br, (c) TPE-3Br and (d) TPE-4Br and catalyzed by the 12.5 cm nonactivated Cu(0) wire at 25 °C. Reaction conditions: MA = 1 mL, DMSO = 0.5 mL, $[MA]_0/[Initiator]_0/[Me_6\text{-TREN}]_0 = 222/1/0.1$.

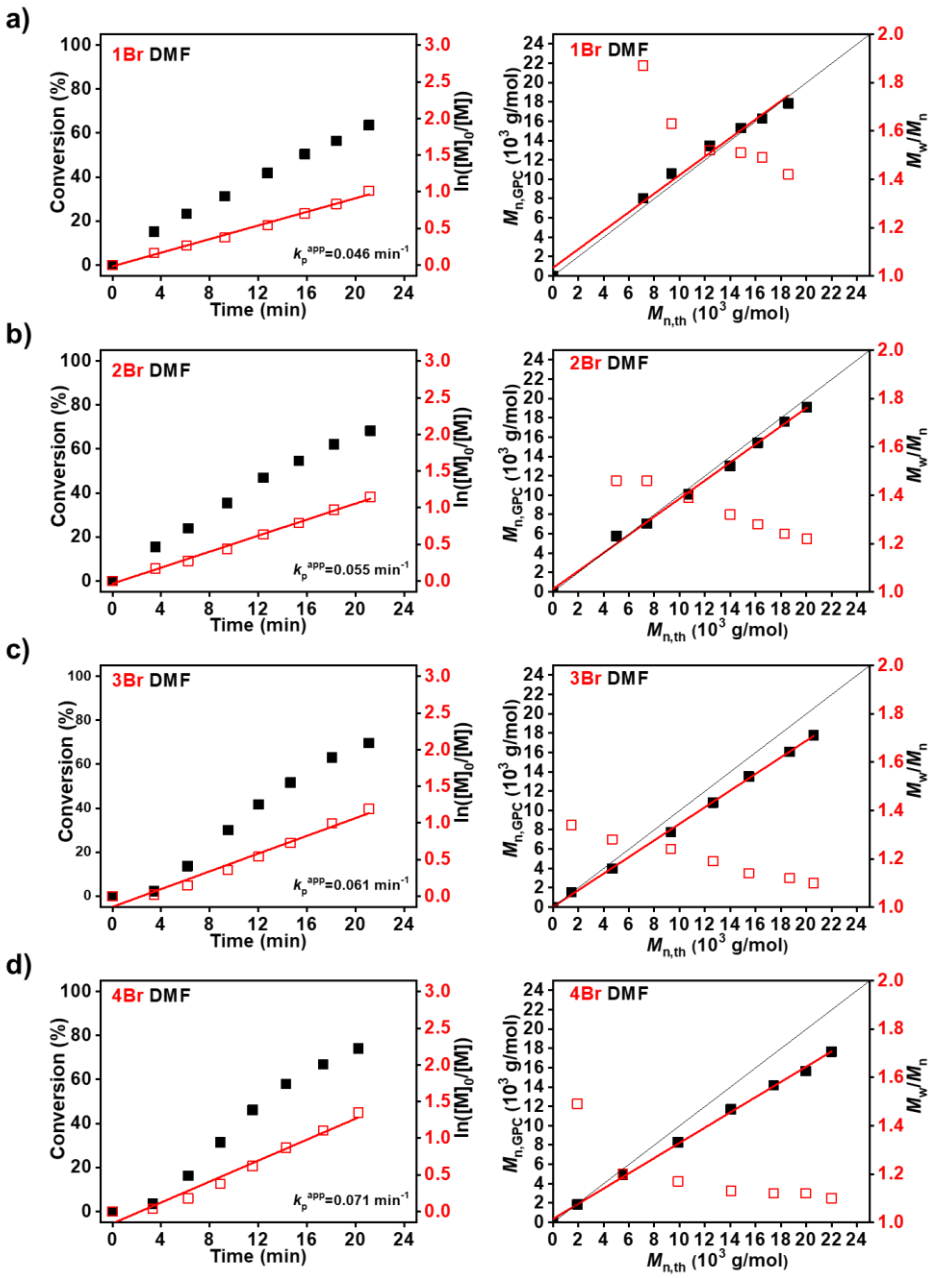

Figure S5. Monomer conversion, kinetic plots, and evolution of $M_{n,GPC}$ and $Đ$ (M_w/M_n) for the SET-LRP of *t*BA in DMF initiated from (a) TPE-1Br, (b) TPE-2Br, (c) TPE-3Br and (d) TPE-4Br and catalyzed by the 12.5 cm nonactivated Cu(0) wire at 25 °C. Reaction conditions: *t*BA = 1 mL, DMF = 0.5 mL, $[tBA]_0/[Initiator]_0/[Me_6\text{-TREN}]_0$ = 222/1/0.1.

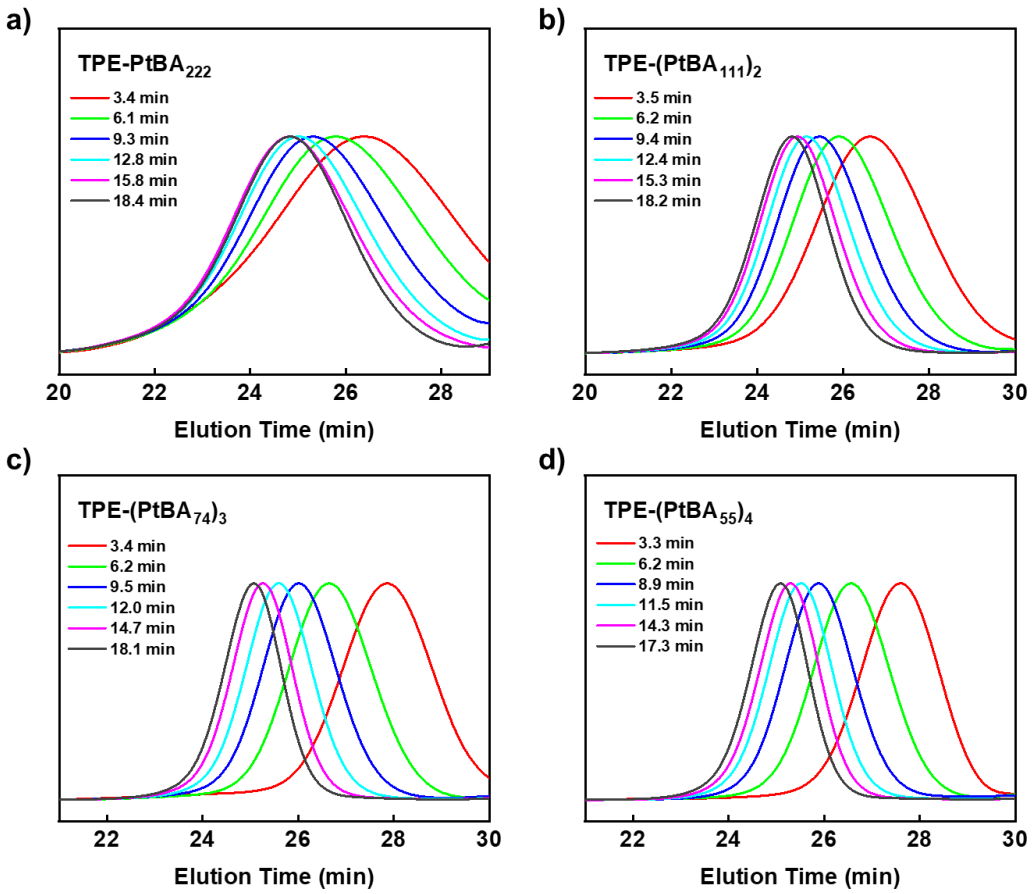

Figure S6. GPC traces of TPE-P*t*BA obtained by the SET-LRP of *t*BA in DMF initiated from (a) TPE-1Br, (b) TPE-2Br, (c) TPE-3Br and (d) TPE-4Br and catalyzed by the 12.5 cm nonactivated Cu(0) wire at 25 °C. Reaction conditions: *t*BA = 1 mL, DMF = 0.5 mL, $[tBA]_0/[Initiator]_0/[Me_6\text{-}TREN]_0 = 222/1/0.1$.

Table S1 End-group fidelity of TPE-PMA[a]

	TPE-PMA_{50}	TPE-$(PMA_{25})_2$	TPE-$(PMA_{17})_3$	TPE-$(PMA_{12.5})_4$
F^{Br} /%[a]	98	99	99	100
F^{SPh} /%[b]	95	93	95	98

[a] End-group fidelity of TPE-PMA from the SET-LRP of MA in DMSO initiated with TPE-nBr (n = 1-4) and catalyzed by nonactivated Cu(0) wire at 25 °C: before (a) and after (b) the thio-bromo "click" reaction.

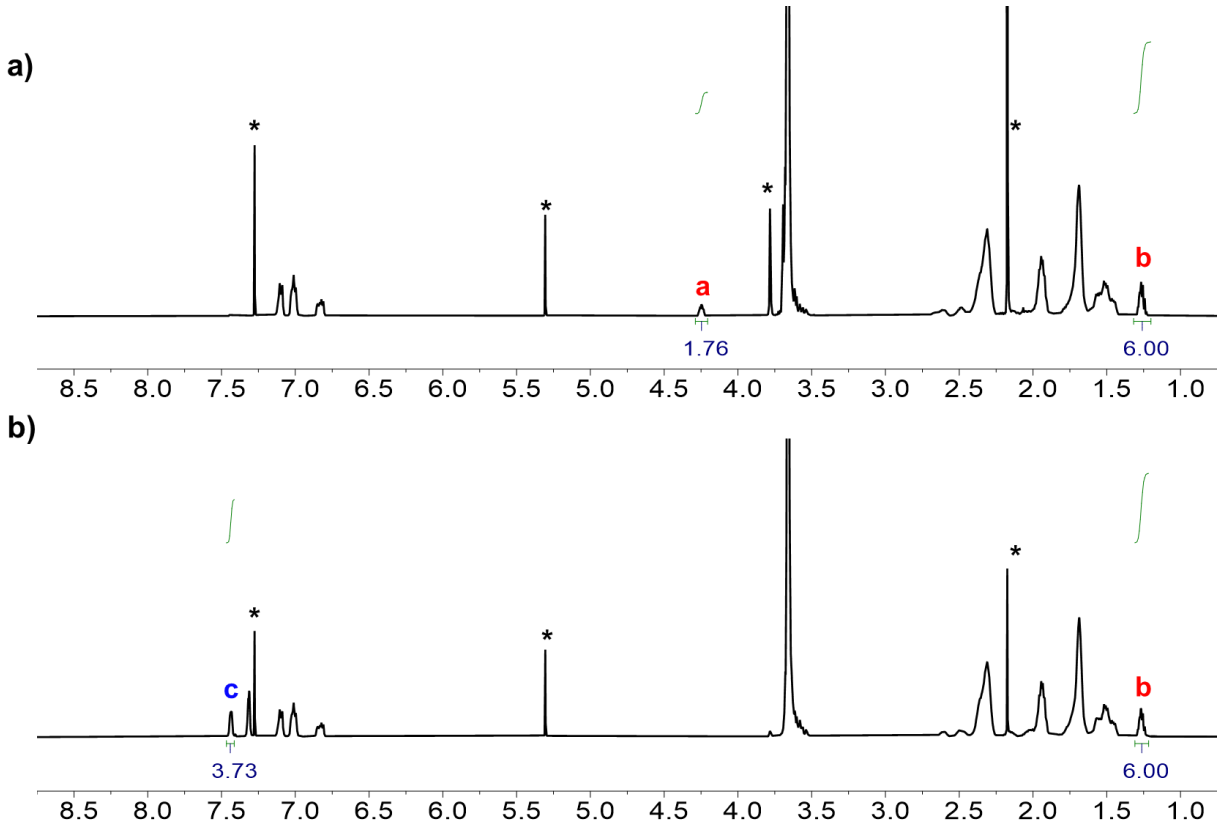

Figure S7. ^{1}H NMR spectra (600 MHz) of TPE-PMA at 88% conversion from the SET-LRP of MA in DMSO initiated with TPE-2Br and catalyzed by a nonactivated Cu(0) wire at 25 °C: before (a, F^{Br} = 1.76/1.78*100 = 99%) and after (b, F^{SPh} = 3.73/4*100 = 93%) the thio-bromo "click" reaction. Polymerization conditions: MA = 1 mL, DMSO = 0.5 mL, $[MA]_0/[TPE\text{-}2Br]_0/[Me_6\text{-}TREN]_0$ = 50/1/0.1, 12.5 cm of the Cu(0) wire. ^{1}H NMR resonances from residual solvents in $CDCl_3$ are indicated by an asterisk (*).

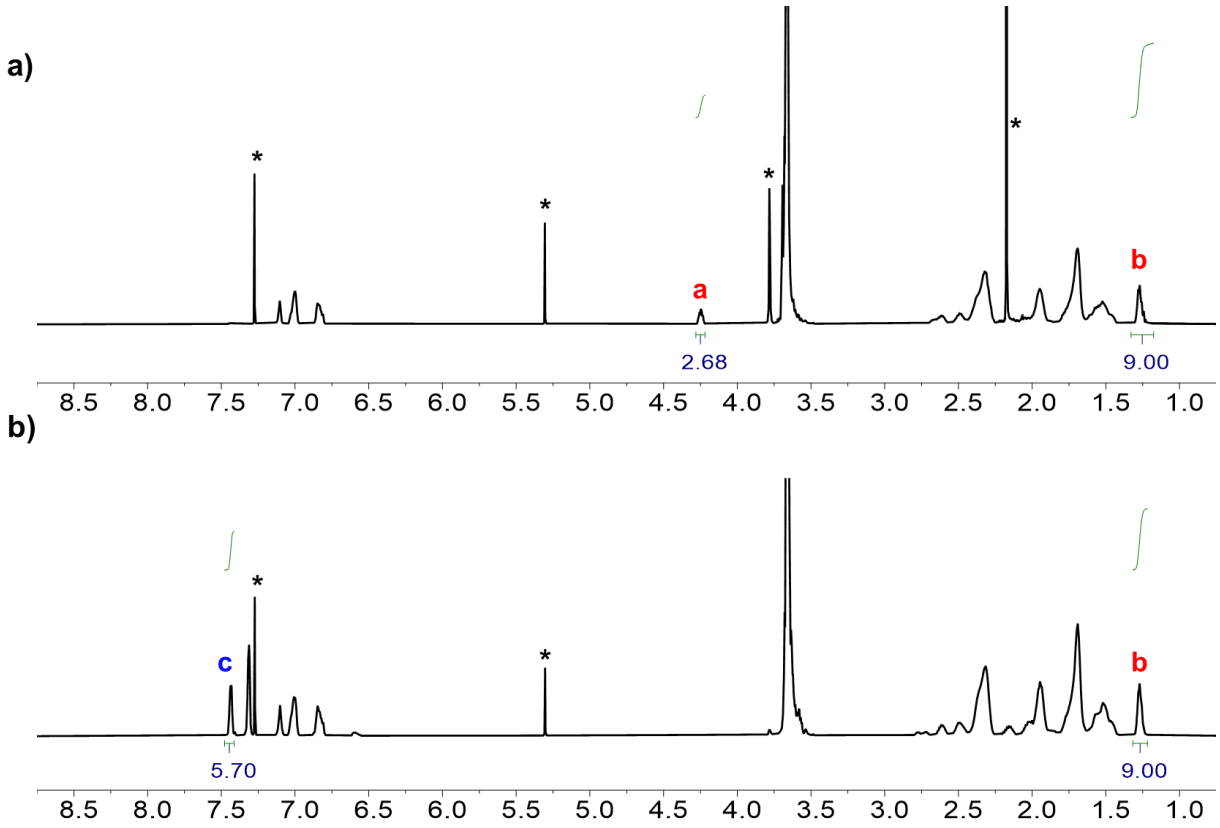

Figure S8. ^{1}H NMR spectra (600 MHz) of TPE-PMA at 90% conversion from the SET-LRP of MA in DMSO initiated with TPE-3Br and catalyzed by a nonactivated Cu(0) wire at 25 °C: before (a, F^{Br} = 2.68/2.71*100 = 99%) and after (b, F^{SPh} = 5.70/6*100 = 95%) the thio-bromo "click" reaction. Polymerization conditions: MA = 1 mL, DMSO = 0.5 mL, $[MA]_0/[TPE\text{-}3Br]_0/[Me_6\text{-}TREN]_0$ = 50/1/0.1, 12.5 cm of the Cu(0) wire. ^{1}H NMR resonances from residual solvents in $CDCl_3$ are indicated by an asterisk (*).

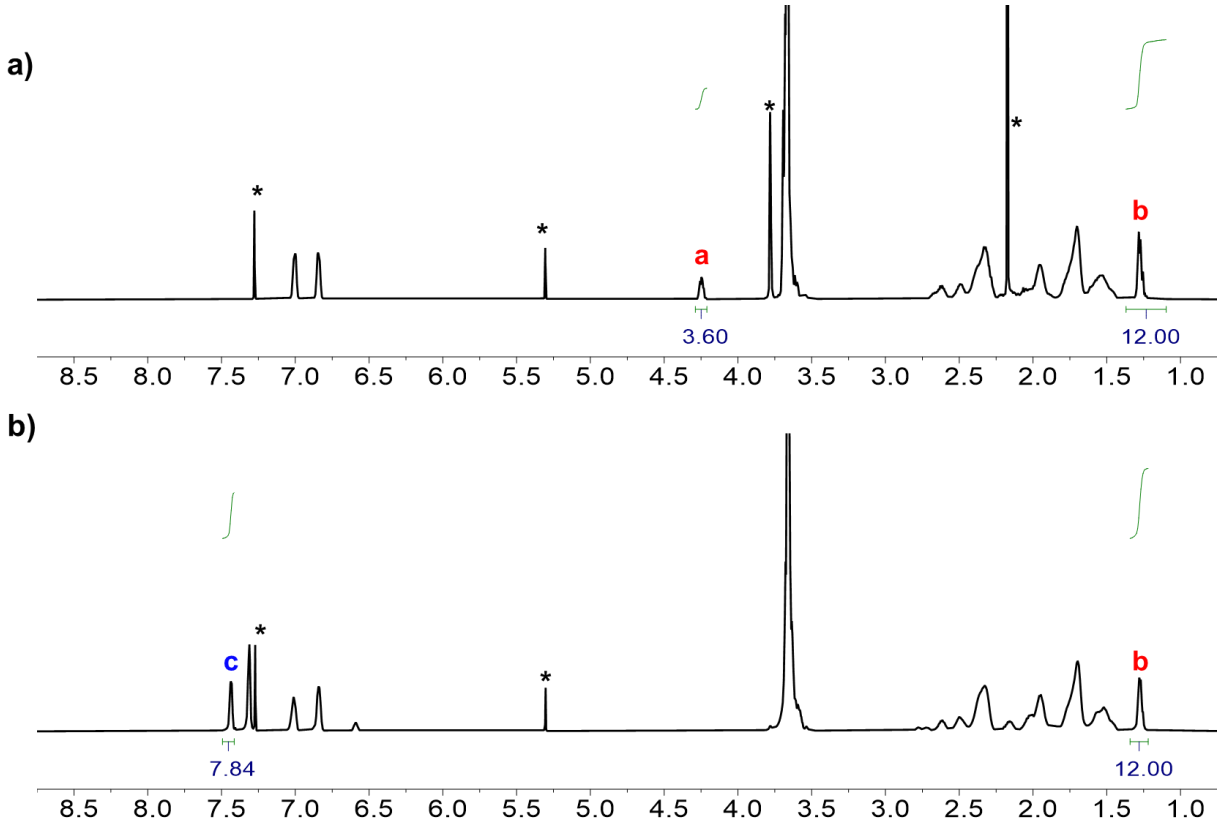

Figure S9. ^{1}H NMR spectra (600 MHz) of TPE-PMA at 90% conversion from the SET-LRP of MA in DMSO initiated with TPE-4Br and catalyzed by a nonactivated Cu(0) wire at 25 °C: before (a, F^{Br} = 3.60/3.60*100 = 100%) and after (b, F^{SPh} = 7.84/8*100 = 98%) the thio-bromo "click" reaction. Polymerization conditions: MA = 1 mL, DMSO = 0.5 mL, $[MA]_0/[TPE\text{-}4Br]_0/[Me_6\text{-}TREN]_0$ = 50/1/0.1, 12.5 cm of the Cu(0) wire. ^{1}H NMR resonances from residual solvents in $CDCl_3$ are indicated by an asterisk (*).

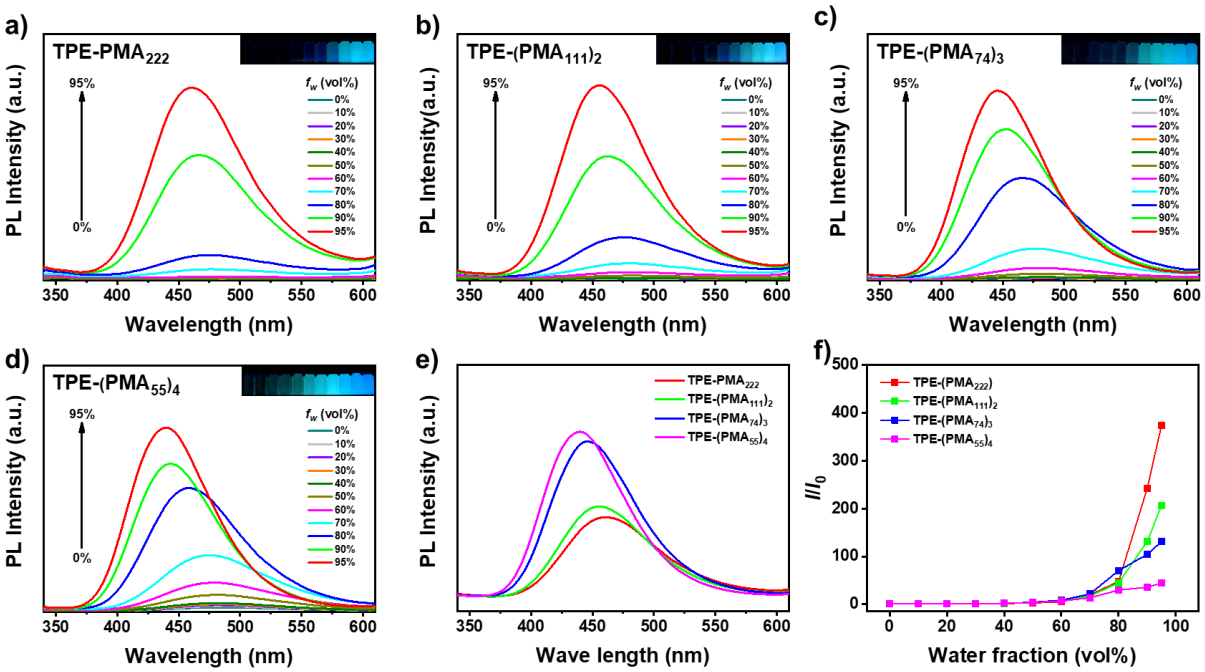

Figure S10. Photoluminescence (PL) spectra of (a) TPE-PMA$_{222}$, (b) TPE-(PMA$_{111}$)$_2$, (c) TPE-(PMA$_{74}$)$_3$ and (d) TPE-(PMA$_{55}$)$_4$ in THF/H_2O mixtures with different f_w. (e) PL intensity of TPE-(PMA)$_n$ (n = 1-4, [MA]$_0$/[TPE-nBr]$_0$ = 222/1) in THF/H_2O (f_w = 95%). (f) I/I_0 of TPE-(PMA)$_n$ (n = 1-4, [MA]$_0$/[TPE-nBr]$_0$ = 222/1). [TPE] = 10 μM; excitation wavelength: 320 nm; I_0: the PL intensity of the polymer in pure THF. The insets in panel (a)-(d) were taken under a hand-held UV lamp at 365 nm.

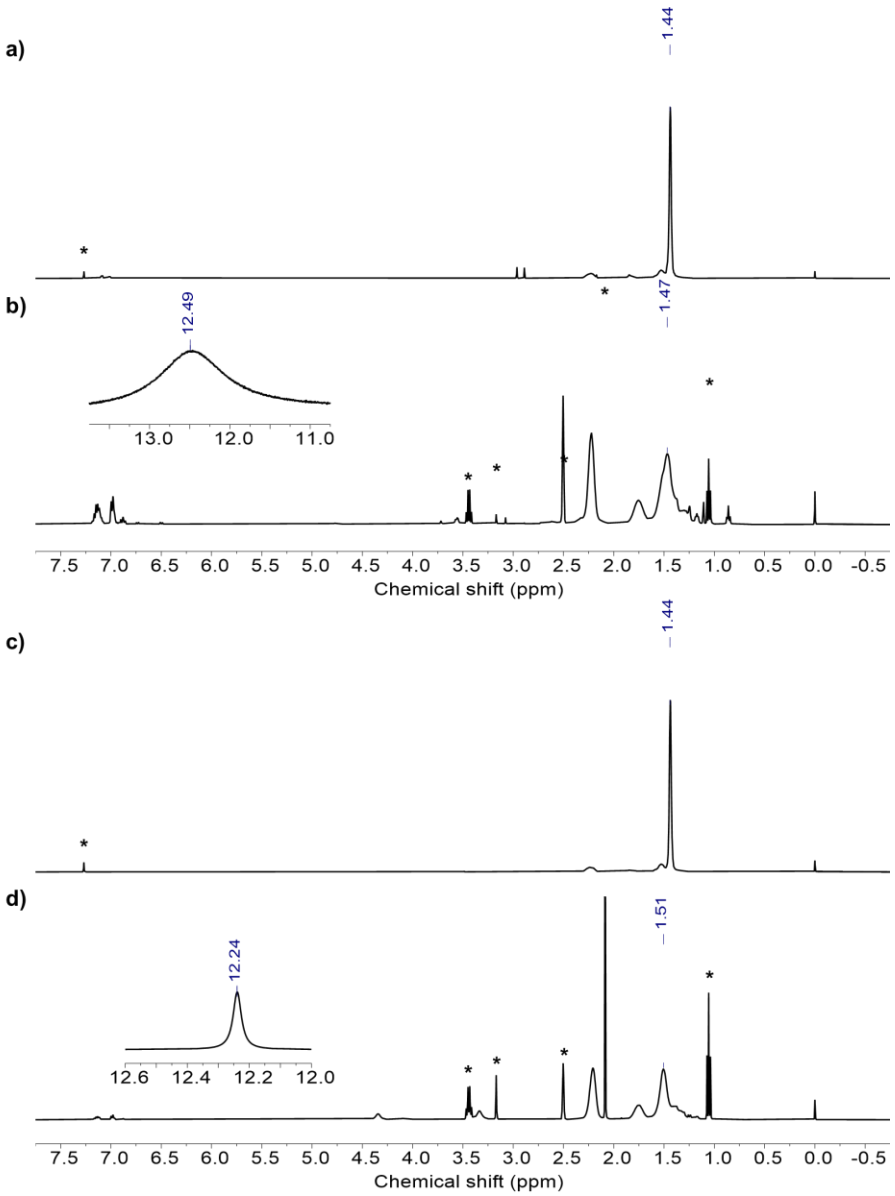

Figure S11. ^{1}H NMR spectra of (a)TPE-P*t*BA$_{50}$ and (c)TPE-P*t*BA$_{222}$ in $CDCl_3$ at 99% conversion from SET-LRP of *t*BA in DMF initiated with TPE-1Br and catalyzed by nonactivated Cu(0) wire at 25 °C. ^{1}H NMR of (b) TPE-PAA$_{50}$ and (d) TPE-PAA$_{222}$ in DMSO-d_6 obtained by hydrolysis of TPE-P*t*BA. Polymerization conditions: *t*BA = 1 mL, DMF = 0.5 mL, $[tBA]_0/[TPE\text{-}1Br]_0/[Me_6\text{-}TREN]_0$ = 50/1/0.1 and $[tBA]_0/[TPE\text{-}1Br]_0/[Me_6\text{-}TREN]_0$ = 222/1/0.1, 12.5 cm of Cu(0) wire. ^{1}H NMR resonances from residual solvents are indicated by an asterisk (*).

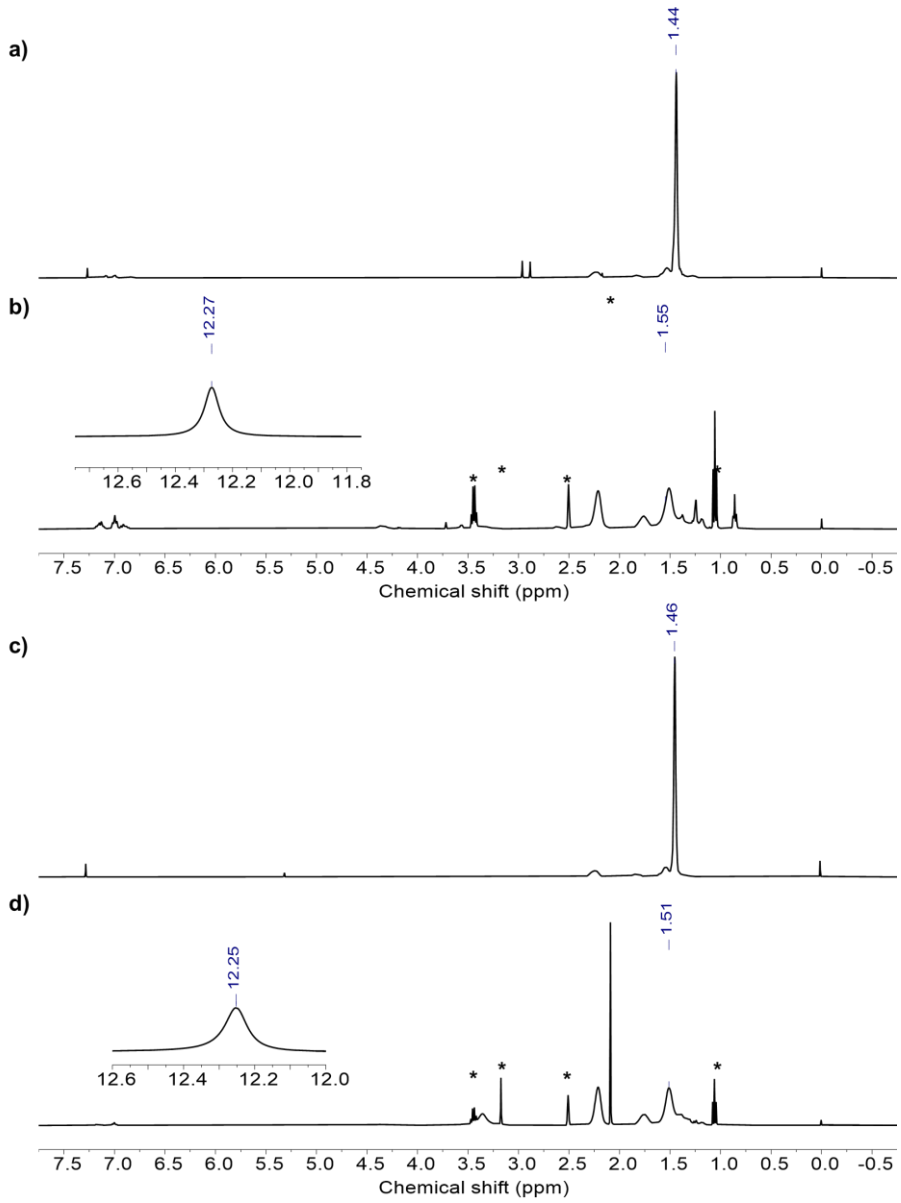

Figure S12. ^{1}H NMR spectra of (a) TPE-(P*t*BA$_{25}$)$_2$ and (c) TPE-(P*t*BA$_{111}$)$_2$ in $CDCl_3$ at 99% conversion from SET-LRP of *t*BA in DMF initiated with TPE-2Br and catalyzed by nonactivated Cu(0) wire at 25 °C. ^{1}H NMR of (b) TPE-(PAA$_{25}$)$_2$ and (d) TPE-(PAA$_{111}$)$_2$ in DMSO-d_6 obtained by hydrolysis of TPE-P*t*BA. Polymerization conditions: *t*BA = 1 mL, DMF = 0.5 mL, [*t*BA]$_0$/[TPE-2Br]$_0$/[Me$_6$-TREN]$_0$ = 50/1/0.1 and [*t*BA]$_0$/[TPE-2Br]$_0$/[Me$_6$-TREN]$_0$ = 222/1/0.1, 12.5 cm of Cu(0) wire. ^{1}H NMR resonances from residual solvents are indicated by an asterisk (*).

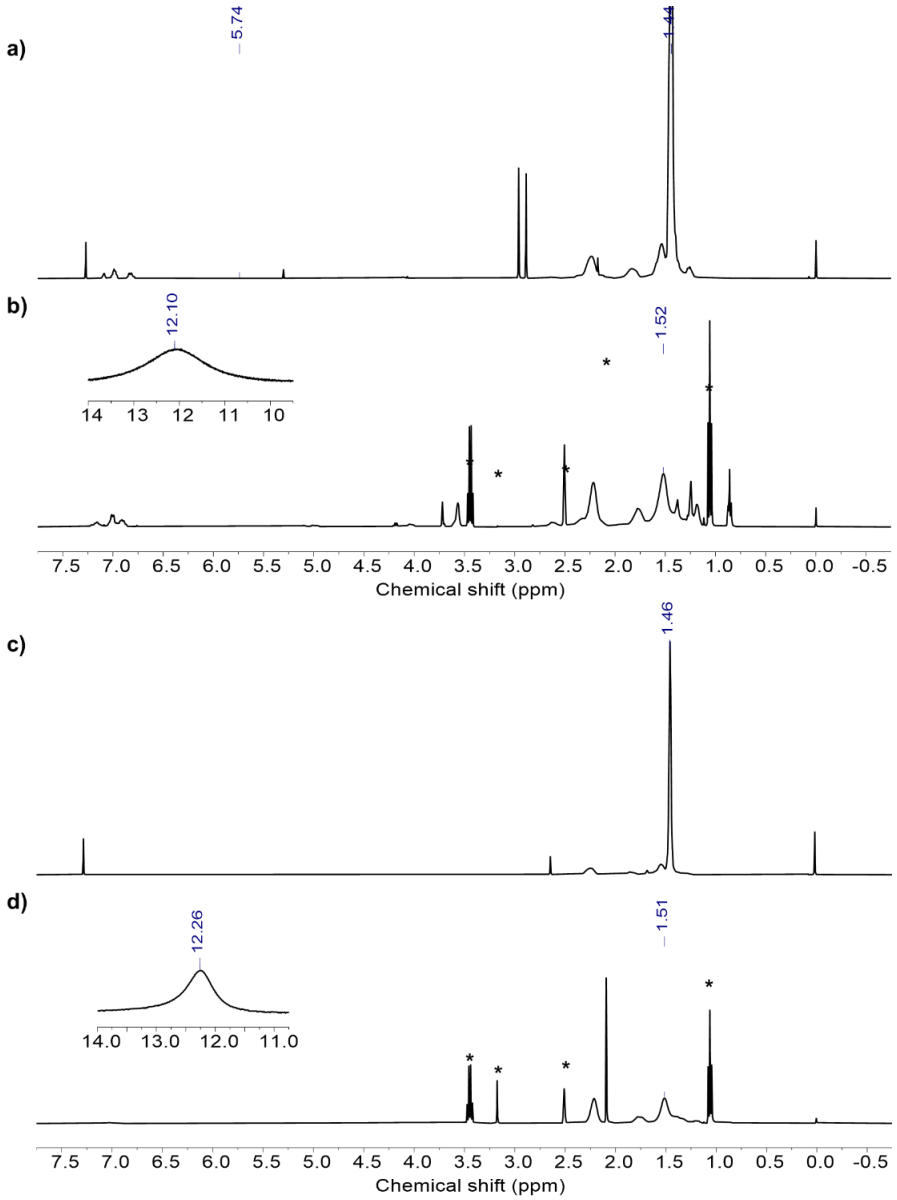

Figure S13. ^{1}H NMR spectra of (a) TPE-(P*t*BA$_{17}$)$_3$ and (c) TPE-(P*t*BA$_{74}$)$_3$ in $CDCl_3$ at 99% conversion from SET-LRP of *t*BA in DMF initiated with TPE-3Br and catalyzed by nonactivated Cu(0) wire at 25 °C. ^{1}H NMR of (b) TPE-(PAA$_{17}$)$_3$ and (d) TPE-(PAA$_{74}$)$_3$ in DMSO-d_6 obtained by hydrolysis of TPE-P*t*BA. Polymerization conditions: *t*BA = 1 mL, DMF = 0.5 mL, [*t*BA]$_0$/[TPE-3Br]$_0$/[Me$_6$-TREN]$_0$ = 50/1/0.1 and [*t*BA]$_0$/[TPE-3Br]$_0$/[Me$_6$-TREN]$_0$ = 222/1/0.1, 12.5 cm of Cu(0) wire. ^{1}H NMR resonances from residual solvents are indicated by an asterisk (*).

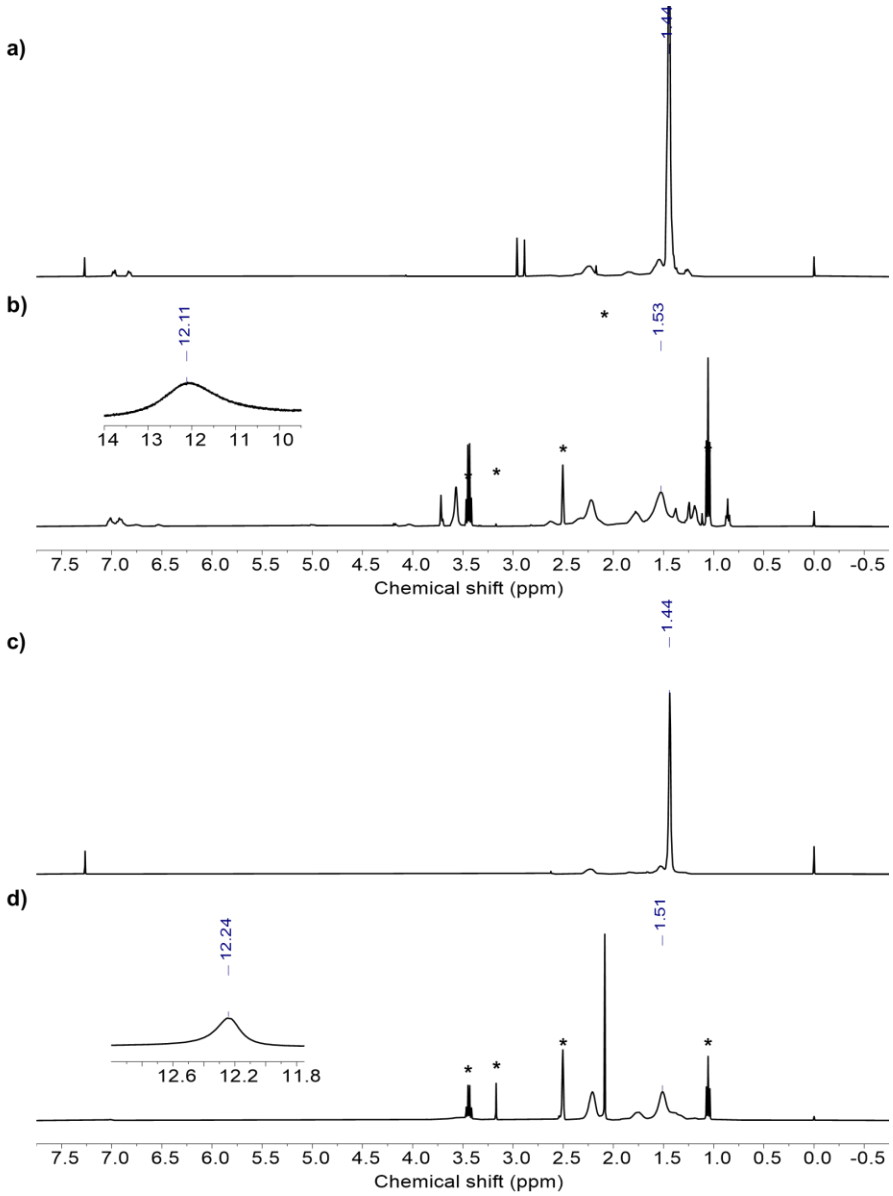

Figure S14. ^{1}H NMR spectra of (a) TPE-(P*t*BA$_{12}$)$_4$ and (c) TPE-(P*t*BA$_{55}$)$_4$ in $CDCl_3$ at 99% conversion from SET-LRP of *t*BA in DMF initiated with TPE-4Br and catalyzed by nonactivated Cu(0) wire at 25 °C. ^{1}H NMR of (b) TPE-(PAA$_{12}$)$_4$ and (d) TPE-(PAA$_{55}$)$_4$ in DMSO-d_6 obtained by hydrolysis of TPE-P*t*BA. Polymerization conditions: *t*BA = 1 mL, DMF = 0.5 mL, [*t*BA]$_0$/[TPE-4Br]$_0$/[Me$_6$-TREN]$_0$ = 50/1/0.1 and [*t*BA]$_0$/[TPE-4Br]$_0$/[Me$_6$-TREN]$_0$ = 222/1/0.1, 12.5 cm of Cu(0) wire. ^{1}H NMR resonances from residual solvents are indicated by an asterisk (*).

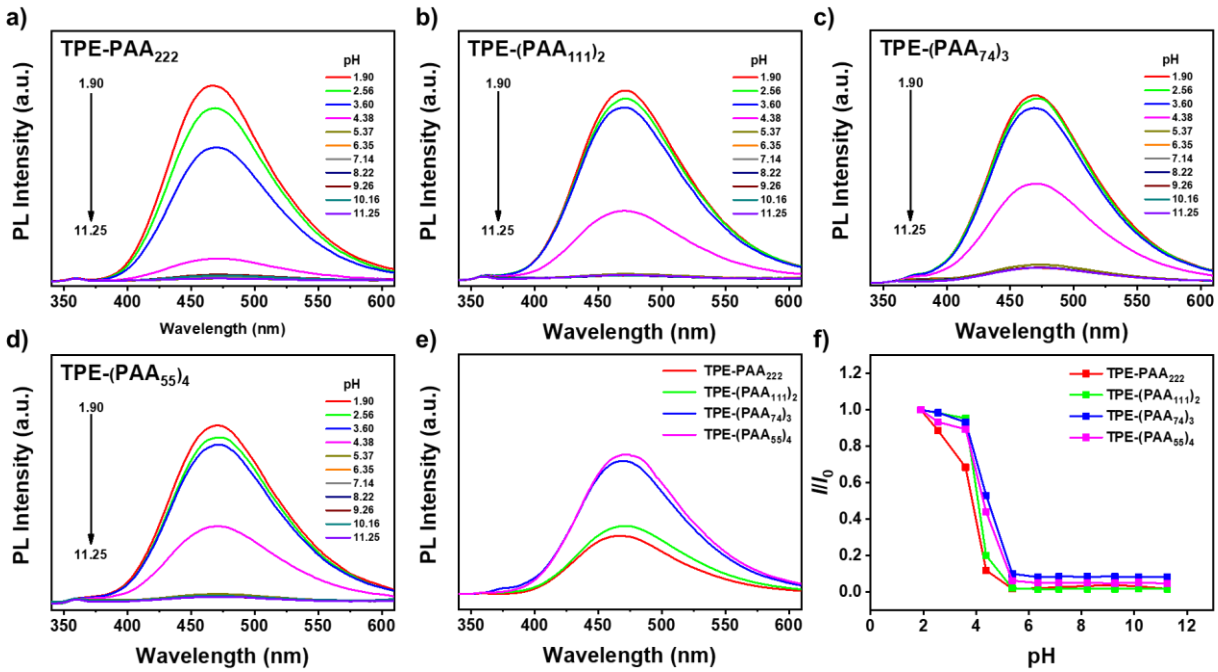

Figure S15. Photoluminescence (PL) spectra of (a) TPE-PAA_{222}, (b) TPE-$(PAA_{111})_2$, (c) TPE-$(PAA_{74})_3$ and (d) TPE-$(PAA_{55})_4$ in B-R buffer solutions of different pH values. (e) PL intensity of TPE-$(PMA)_n$ (n = 1-4, [AA]/[TPE-nBr] = 222/1) in B-R buffer solutions at pH = 1.90. (f) I/I_0 of TPE-$(PAA)_n$ (n = 1-4) at [AA]/[TPE-nBr] = 222/1. [TPE] = 20 μM; excitation wavelength: 320 nm; and I_0: the PL intensity of TPE-$(PAA)_n$ in B-R buffer solution at pH 1.90.