Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and Self-Assembly of Photoacid-Containing Block Copolymers based on 1-Naphthol

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Table S1: Optimization of RAFT terpolymerization with *t*NMAm or *t*VN.

Entry	Monomer	Solvent	CTA	T (°C)	I	M_n [a],SEC (kg mol^{-1})	$Đ$[a]	Overall Conversion[b] (%)
1	*t*NMAm	1,4-dioxane	CPADB	70	AIBN	9	1.24	25
2				90		9.5	1.20	27
3					ACHN	6	1.10	4
4			CEPTA			5	1.14	14
5		bulk	CPADB	70	AIBN	11	1.61	44
6		toluene				5	1.09	16
7	*t*VN	1,4-dioxane	CPADB	70	AIBN	5.5	1.23	24
8		bulk		90		10	1.33	46
9					ACHN	7	1.28	41
10		1,4-dioxane	CEPTA			5.5	1.31	24
11		bulk	CPADB	70	AIBN	8	1.22	46
12		Toluene				2	1.02	6

[a] SEC (DMAc/LiCl) (PMMA calibration), [b] ^{1}H-NMR (300 MHz, $CDCl_3$).

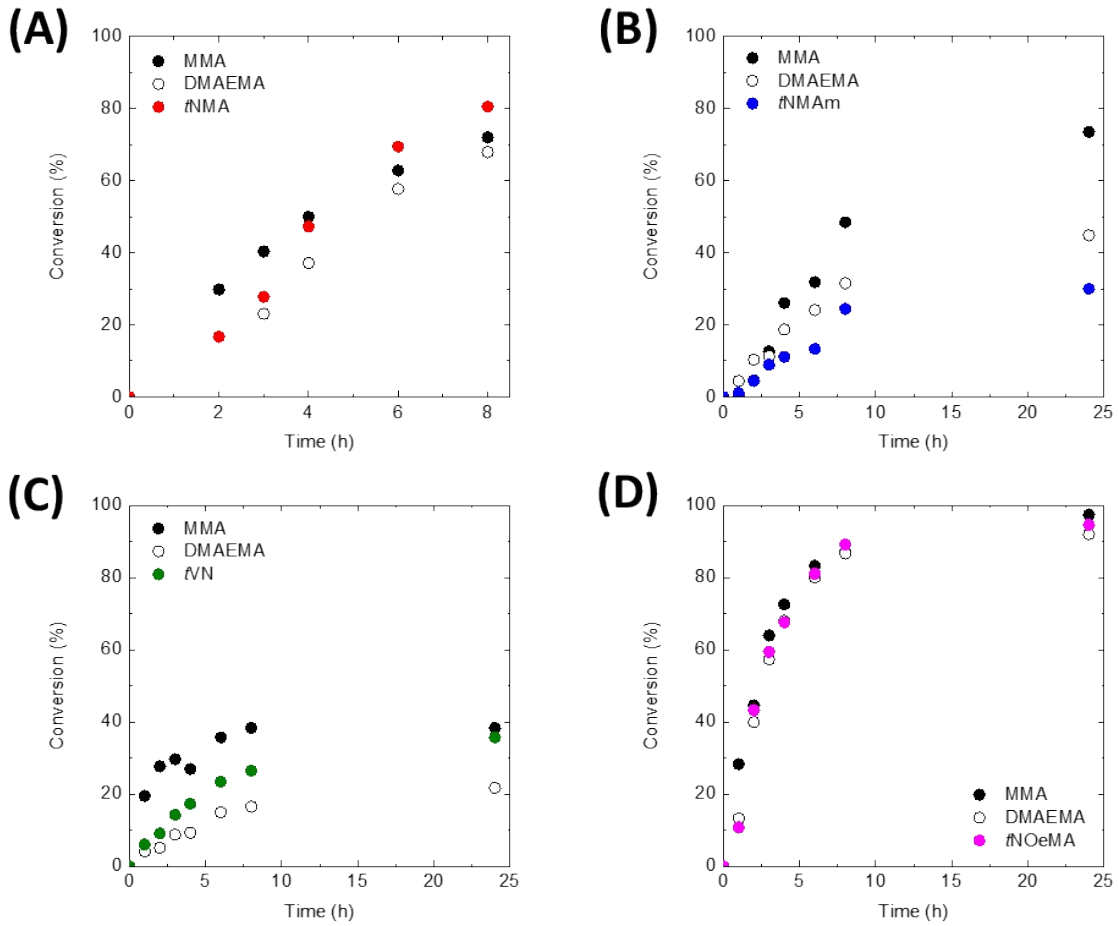

Figure S1: Monomer conversion *vs* time plot for (A) *t*NMA, (B) *t*NMAm, (C) *t*VN, and (D) *t*NOeMA, copolymerized with MMA and DMAEMA with a [monomer]:[CTA] = 125:1. TBS was used as an internal standard (IS) for (B) and (C).

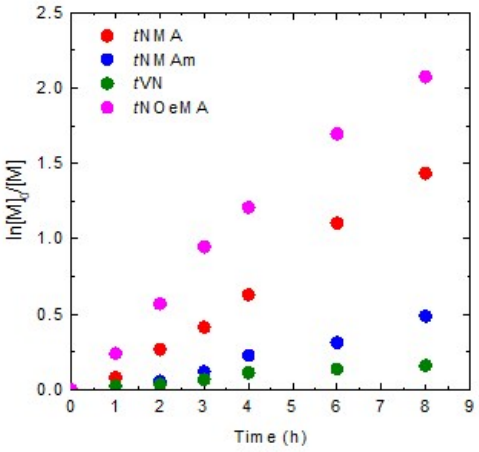

Figure S2: Semilogarithmic plot for *t*NMA, *t*NMAm, *t*VN, and *t*NOeMA, copolymerized with MMA and DMAEMA with a [monomer]:[CTA] = 125:1.

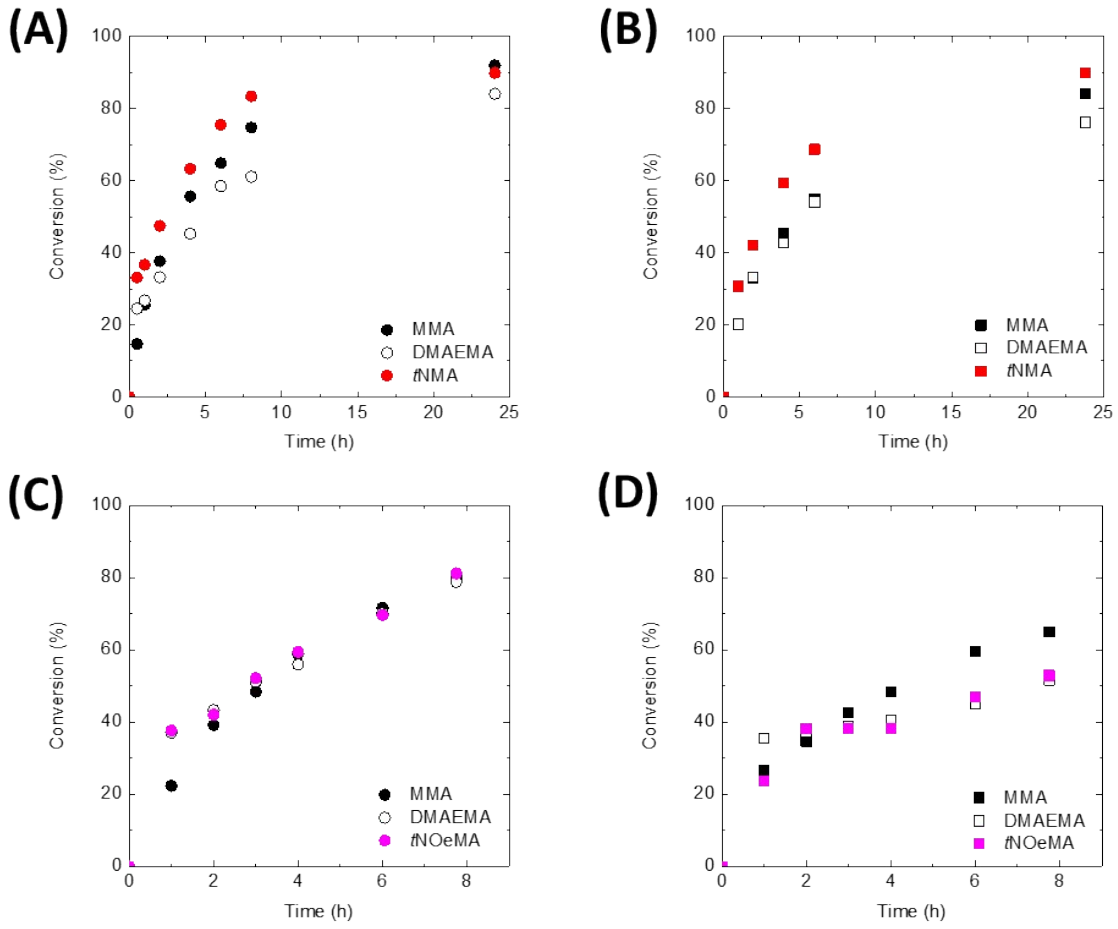

Figure S3: Monomer conversion *vs* time plot for *t*NMA with a [monomer]:[CTA] ratio of (A) 200:1 or (B) 500:1; and *t*NOeMA with a [monomer]:[CTA] ratio of (C) 200:1 or (D) 500:1, copolymerized with MMA and DMAEMA.

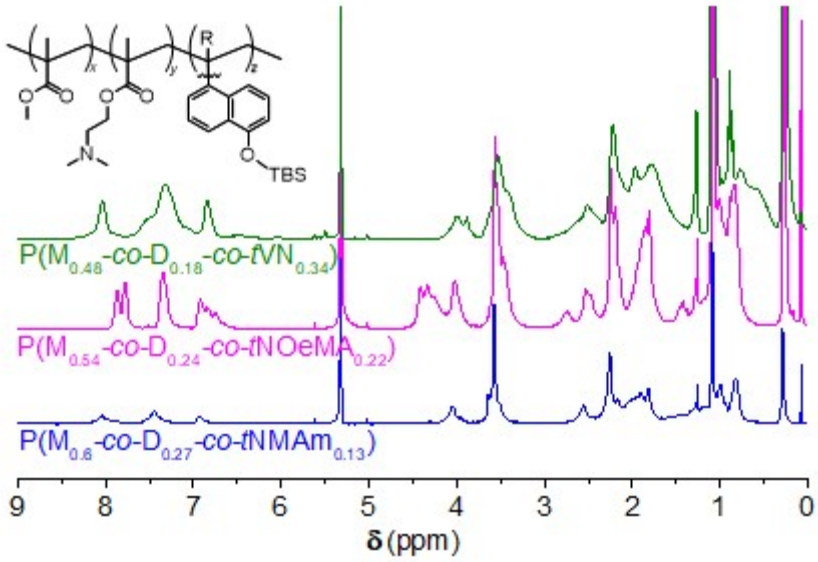

Figure S4: ^{1}H-NMR spectra of P($M_{0.6}$-*co*-$D_{0.27}$-*co*-*t*$NMAm_{0.13}$), P($M_{0.54}$-*co*-$D_{0.24}$-*co*-*t*$NOeMA_{0.22}$) and P($M_{0.48}$-*co*-$D_{0.18}$-*co*-*t*$VN_{0.34}$).

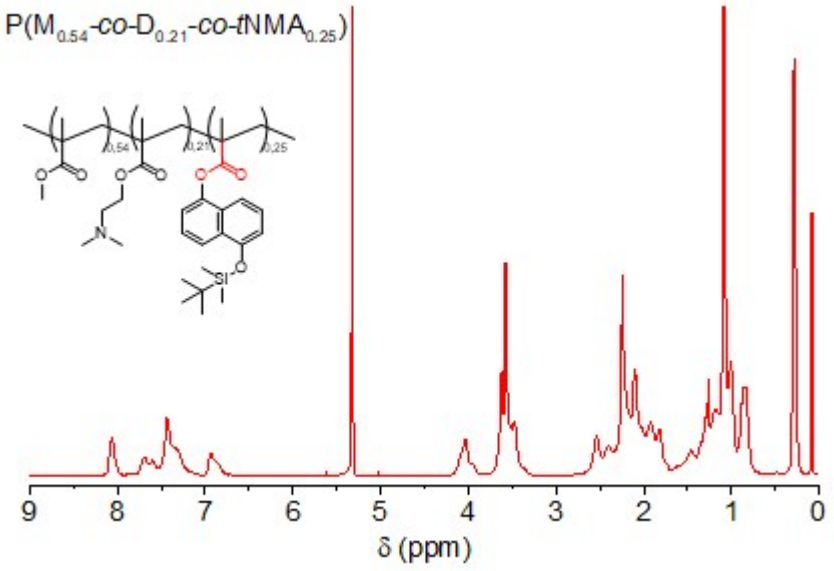

Figure S5: ^{1}H-NMR spectrum of P($M_{0.54}$-*co*-$D_{0.21}$-*co*-*t*$NMA_{0.25}$).

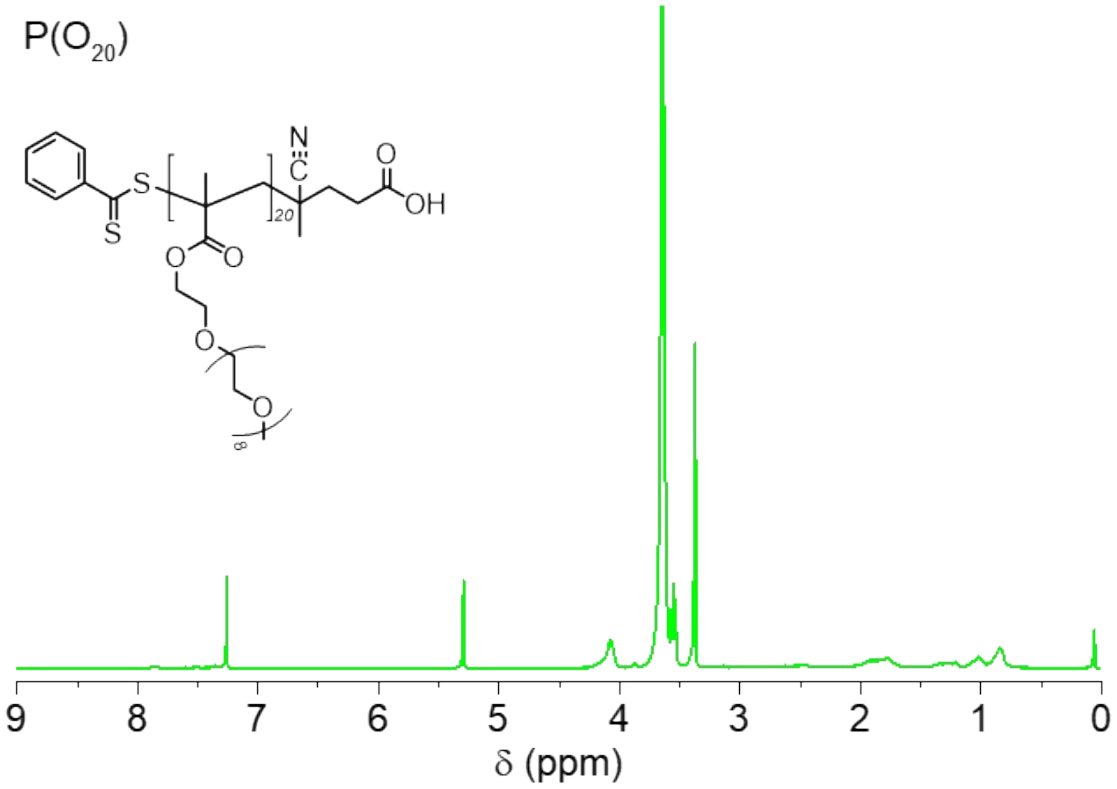

Figure S6: ^{1}H-NMR spectrum of P(O_{20}).

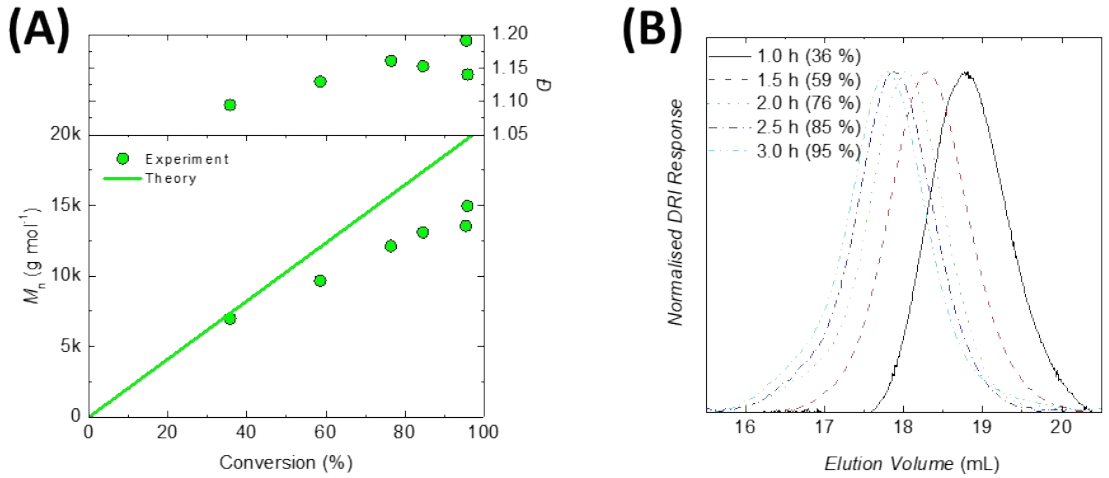

Figure S7: (A) Overall monomer conversion *vs* time plot for MEO_9MA homopolymerization with a [monomer]:[CTA] = 40:1; and the corresponding (B) SEC traces after different reaction times.

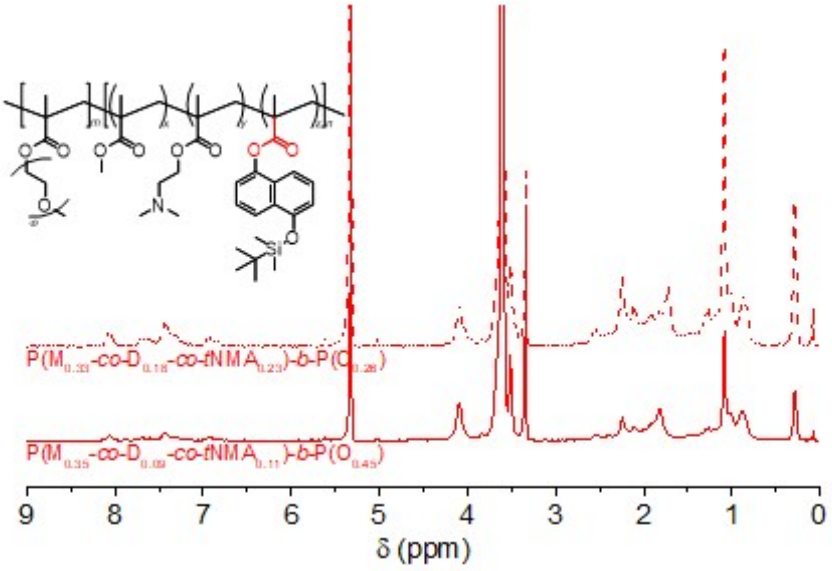

Figure S8: ^{1}H-NMR spectra of P($M_{0.35}$-*co*-$D_{0.09}$-*co*-*t*$NMA_{0.11}$)-*b*-P$(O)_{0.45}$ and P($M_{0.33}$-*co*-$D_{0.18}$-*co*-*t*$NMA_{0.23}$)-*b*-P$(O_{0.26})$.

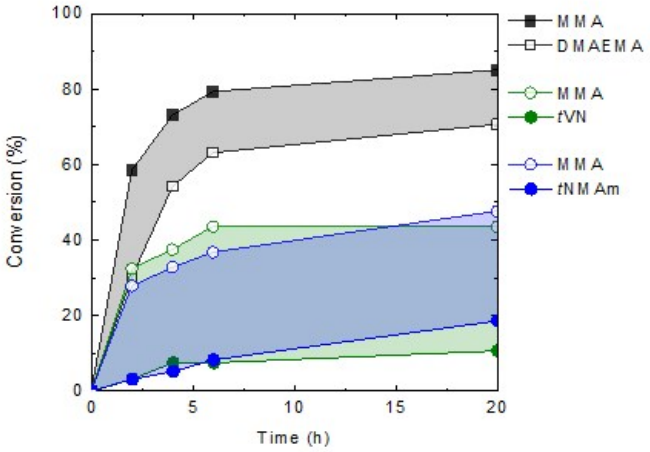

Figure S9: Monomer conversion *vs* time plot for copolymerization of various monomers (DMAEMA, *t*VN, and *t*NMAm) with MMA (reaction conditions: AIBN, 1,4-dioxane 70 °C).

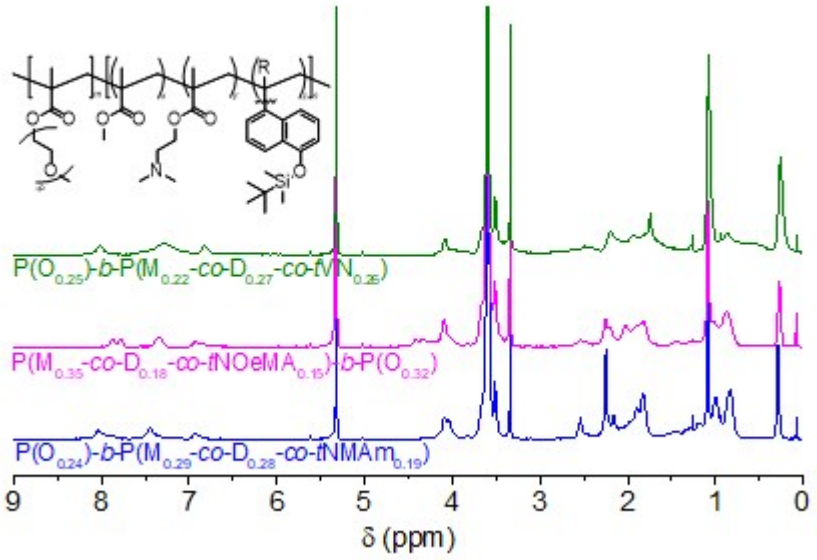

Figure S10: ^{1}H-NMR spectra of P($O_{0.24}$)-*b*-P($M_{0.29}$-*co*-$D_{0.28}$-*co*-*t*$NMAm_{0.19}$), P(M_{40}-*co*-D_9-*co*-*t*$NOeMA_{13}$)-*b*-P(O_{32}) and P($O_{0.25}$)-*b*-P($M_{0.22}$-*co*-$D_{0.27}$-*co*-*t*$VN_{0.26}$).

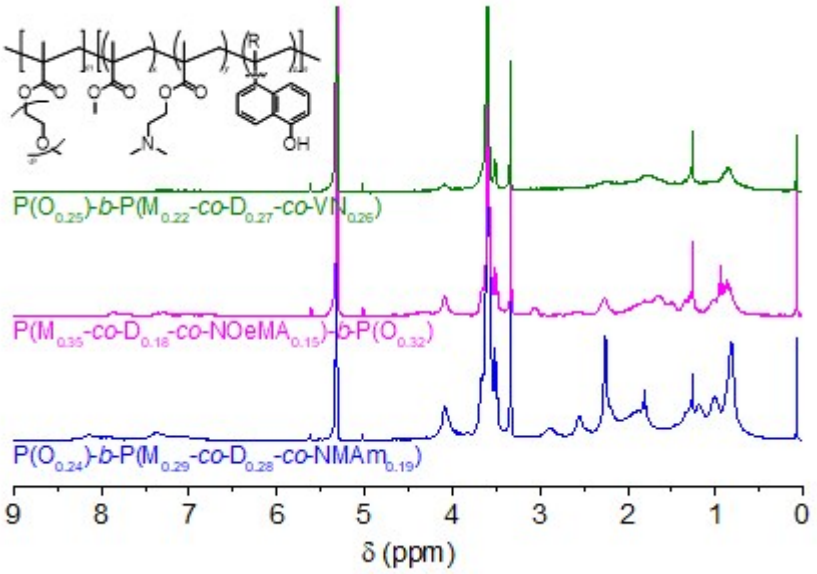

Figure S11: ^{1}H-NMR spectra of P($O_{0.24}$)-*b*-P($M_{0.29}$-*co*-$D_{0.28}$-*co*-$NMAm_{0.19}$), P(M_{40}-*co*-D_9-*co*-$NOeMA_{13}$)-*b*-P(O_{32}) and P($O_{0.25}$)-*b*-P($M_{0.22}$-*co*-$D_{0.27}$-*co*-$VN_{0.26}$).

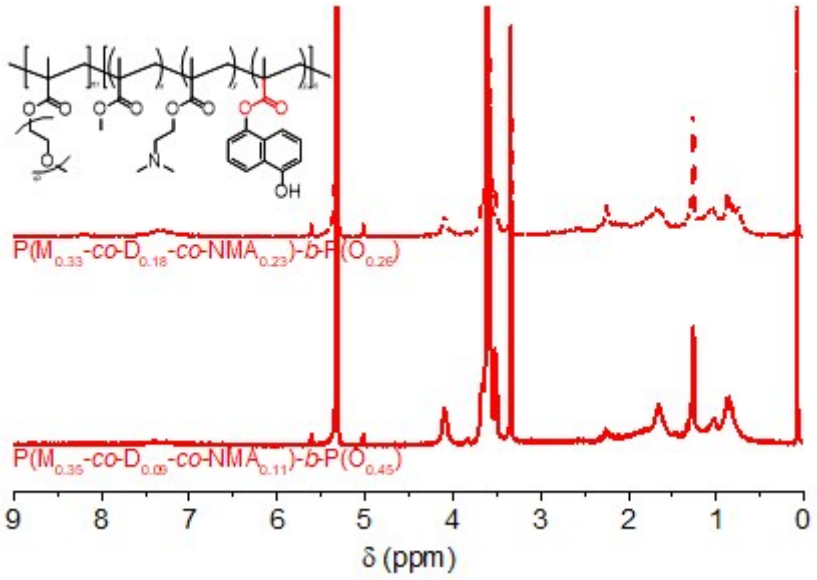

Figure S12: ^{1}H-NMR spectra of P($M_{0.35}$-*co*-$D_{0.09}$-*co*-$NMA_{0.11}$)-*b*-P($O_{0.45}$) and P($M_{0.33}$-*co*-$D_{0.18}$-*co*-$NMA_{0.23}$)-*b*-P($O_{0.26}$).

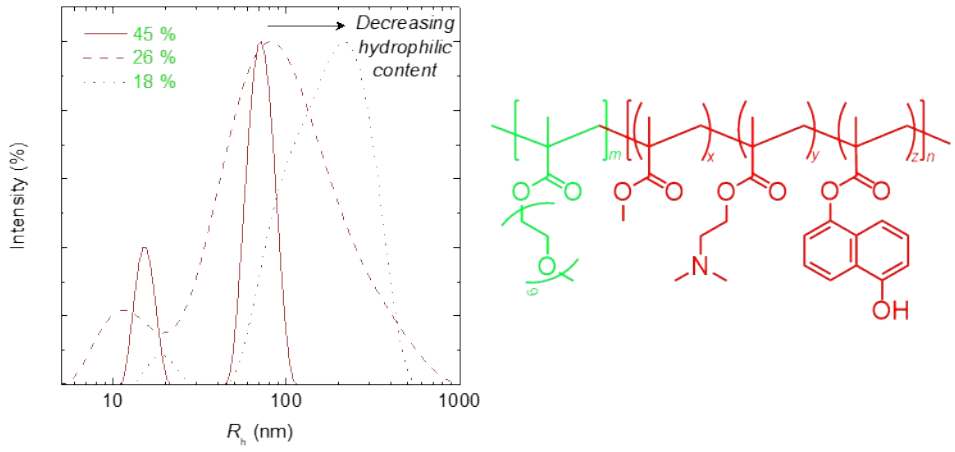

Figure S13: Intensity-weighted hydrodynamic radius of block tetrapolymers with varying hydrophilic contents: P($M_{0.35}$-*co*-$D_{0.09}$-*co*-$NMA_{0.11}$)-*b*-P($O_{0.45}$), (B) P($M_{0.33}$-*co*-$D_{0.18}$-*co*-$NMA_{0.23}$)-*b*-P($O_{0.26}$), and (C) P($M_{0.31}$-*co*-$D_{0.20}$-*co*-$NMA_{0.31}$)-*b*-P($O_{0.18}$) corresponding to 45, 26, and 18 %, respectively.

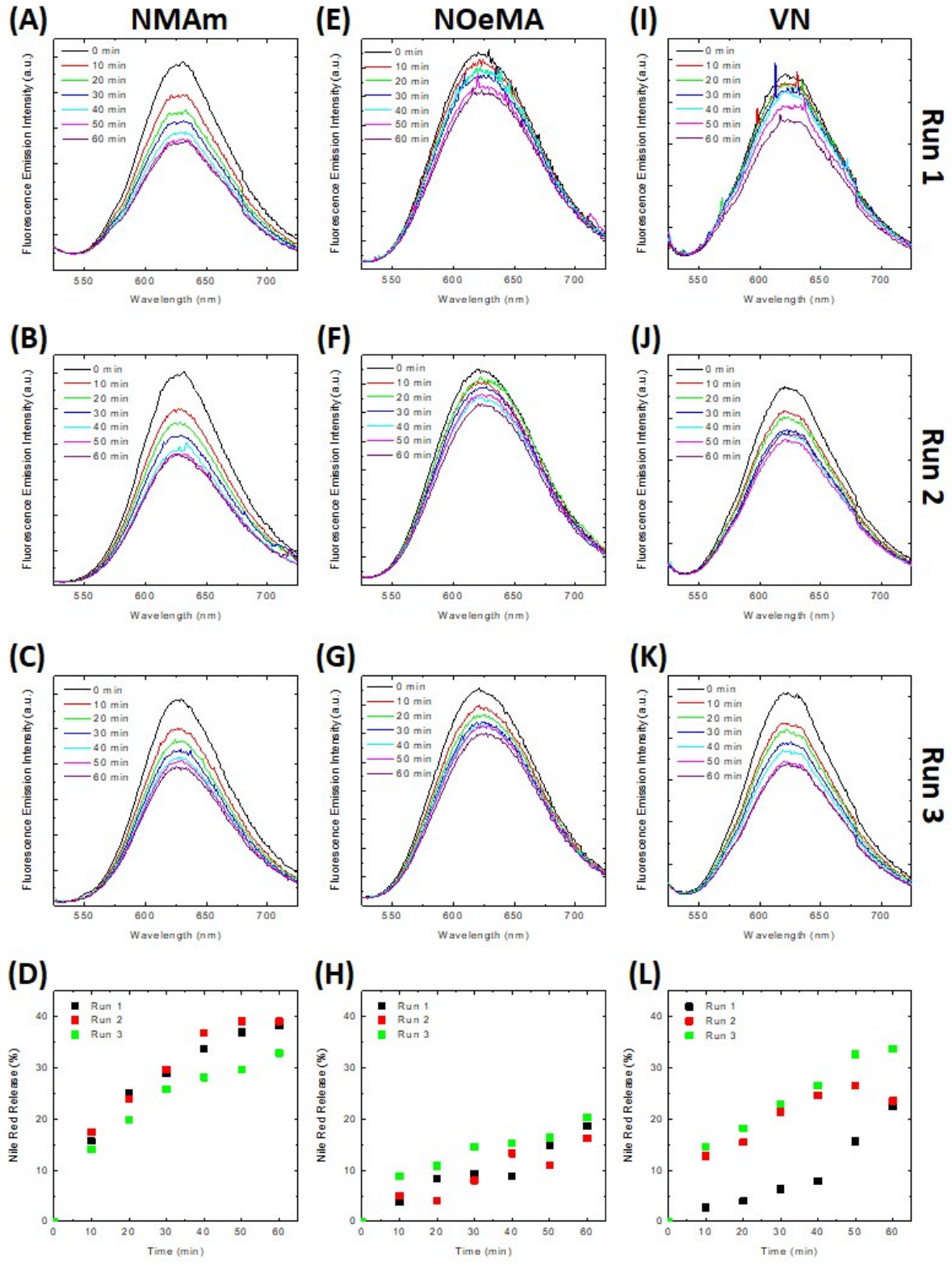

Figure S14: Fluorescence emission spectra of NR-loaded micelles of P[(M_x-*co*-D_y-*co*-"N"$_z$)$_n$-*b*-$(O)_m$] upon 365 nm light irradiation and corresponding NR release where "N" is NMAm (A)–(D), NOeMA (E)–(H), and VN (I)–(L).