Supporting Information

Poly[Glycidyl Oligo(oxyethylene)carbamate]s (PG_n-EO_mR' and R-PG_n-EO_mR'): Controlled Synthesis and Effects of Molecular Parameters (*n* and *m*), Side Group (R'), and End-Group (R) on Thermoresponsive Property

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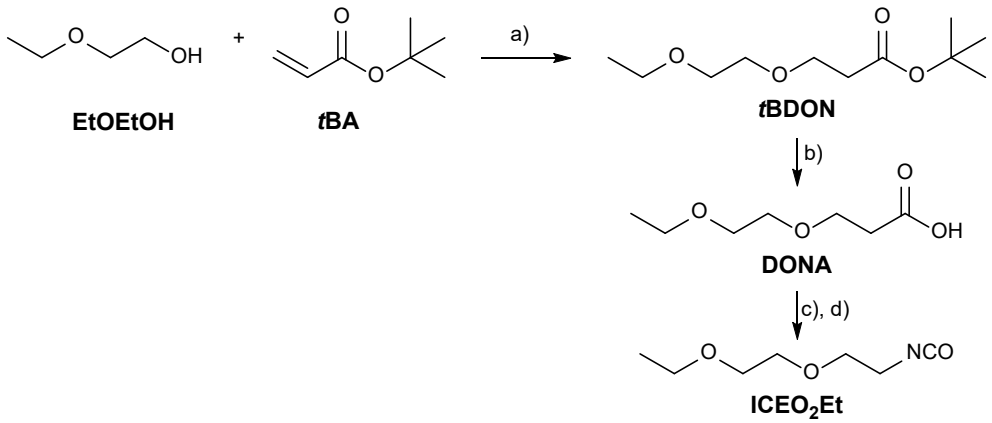
Contents

1. Synthesis of 3,6-dioxaoctyl isocyanate ($ICEO_2Et$)



Scheme S1. Reagents and conditions:[1)] a) NaH, in THF at room temp for 48 h under N_2, b) TFA, in dichloromethane at room temp. under N_2 for 42 h, c) DPPA, TEA, in toluene for 2 h under N_2 at room temperature d) heating at 70 °C for 3 h.

2-Ethoxyethanol (EtOEtOH) (20 g, 222 mmol) and *tert*-butyl acrylate (*t*BA) (29.0 mL, 200 mmol) were added to sodium hydride (NaH; 53.3 mg, 2.22 mmol) in dry THF (130 mL). After stirring at room temperature for 48 h under N_2 atmosphere, the solvent was removed by rotary evaporation, then the remaining product was purified by column chromatography using ethyl acetate to afford 3-(2-ethoxyethoxy)propionic acid (DONA) as a colorless oily liquid. Yield, 40 g (82.6%). Trifluoroacetic acid (TFA; 62.8 g, 500 mmol) was added to *t*BDON (40 g, 183 mmol) in dichloromethane (116 mL), and the reaction mixture was stirred at room temperature under N_2 for 42 h. After removing the solvent, the residual product was distilled under reduced pressure to give a colorless and transparent liquid of 3-(2-ethoxyethoxy) propionic acid (DONA). Yield, 20.8 g (70.1%).[2)]

Triethylamine (TEA; 17.6 mL, 127 mmol) and diphenyl phosphoryl azide (DPPA; 27.3 mL, 127 mmol) was added to a solution of DONA (20.8 g, 127 mmol) in dry toluene (160 mL). The whole reaction mixture was stirred for 2 h under N_2 at room temperature, then heated to 70 °C for 3 h. After removing the solvent, the obtained product was distilled under reduced pressure to give a colorless and transparent liquid of $ICEO_2Et$.[2)] Yield, 54.7 %; ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 3.69–3.58 (m, 6H, $–OCH_2–$ and $–\underline{CH_2}CH_2NCO$), 3.52 (q, 2H, J = 7.25Hz, $–O\underline{CH_2}CH_3$), 3.40 (t, 2H, J = 6.49 Hz, $–\underline{CH_2}NCO$), 1.21 (t, 3H, J = 7.23 Hz, $–OCH_2\underline{CH_3}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 125.0, 70.71, 70.32, 69.86, 66.71, 43.10, 15.24.

References

1) N. Sakai, M. Jin, S. Sato, T. Satoh and T. Kakuchi, *Polym. Chem*., 2014, **5**, 1057–1062.
2) T. R. Yerramreddy, M. Milewski, N. R. Penthala, A. L. Stinchcomb and P. A. Crooks, *Bioorg. Med. Chem. Lett*., 2010, **20**, 3280–3283.

2. SEC traces of *t*BBA-PBnGE$_n$, R-PBnGE$_n$, PG$_n$, R-PG$_n$, PG$_n$-EO$_m$R', and R-PG$_n$-EO$_m$R'

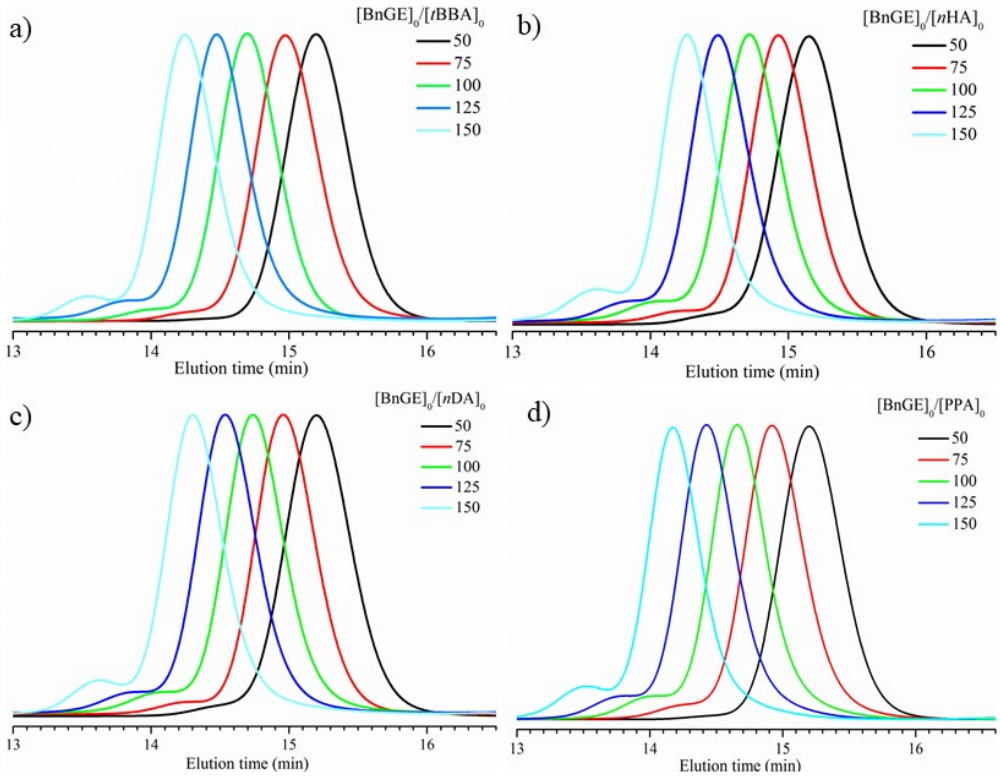


Fig. S1. SEC traces of a) *t*BBA-PBnGE$_n$, b) *n*HA-PBnGE$_n$, c) *n*DA-PBnGE$_n$, and d) PPA-PBnGE$_n$ obtained by the organocatalytic ROP of BnGE using *t*BBA, *n*HA, *n*DA, and PPA, respectively (eluent, THF; flow rate, 1 mL min^{-1}; PS standard).

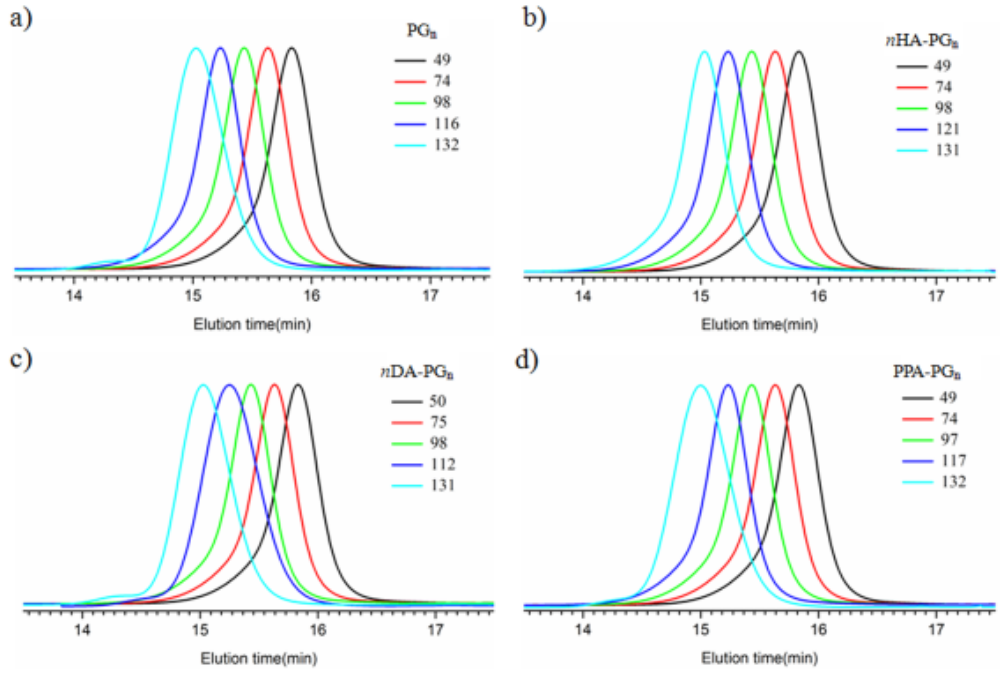


Fig. S2. SEC traces of a) PG$_n$, b) *n*HA-PG$_n$, c) *n*DA-PG$_n$, and d) PPA-PG$_n$ (eluent, H_2O in the presence of 0.05 % NaN_3; flow rate, 1 mL min^{-1}; PEG standard).

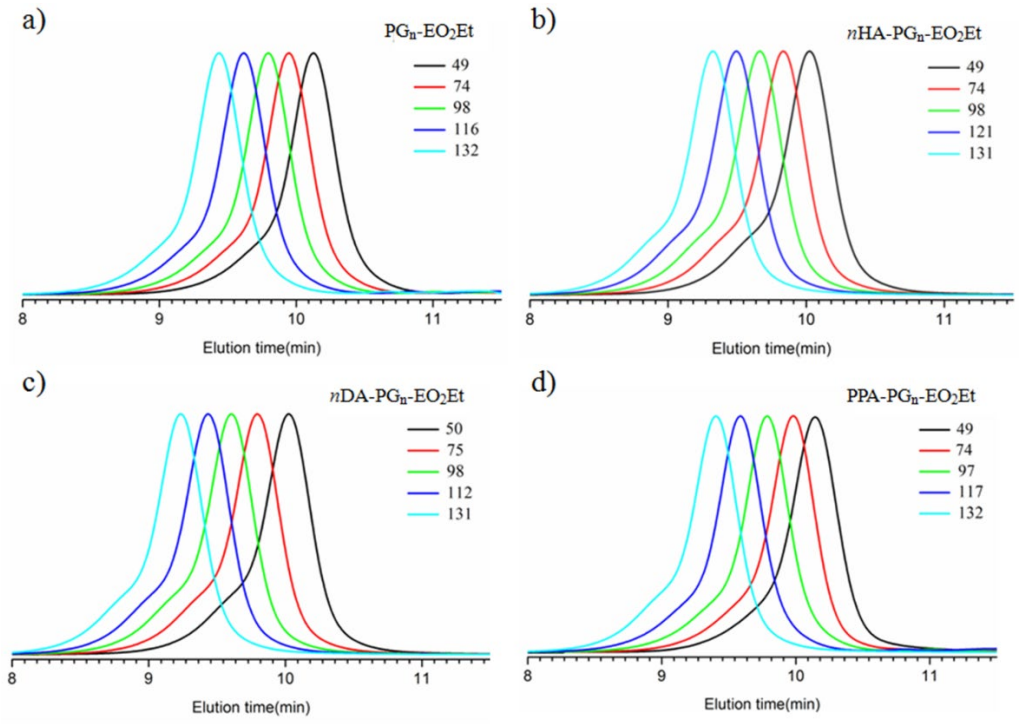


Fig. S3. SEC traces of a) PG_n-EO_2Et, b) *n*HA-PG_n-EO_2Et, c) *n*DA-PG_n-EO_2Et, and d) PPA-PG_n-EO_2Et (eluent, H_2O in the presence of 0.05 % NaN_3; flow rate, 1 mL min^{-1}; PEG standard).

3. ^{1}H NMR spectrum for the polymerization mixture

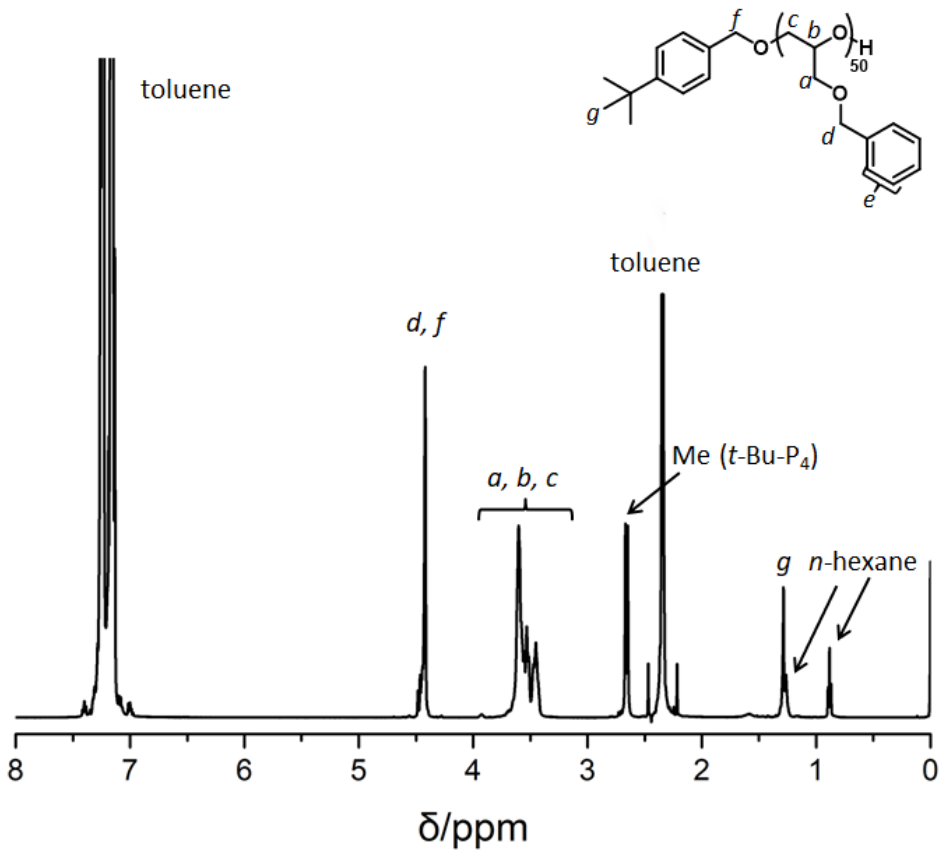


Fig. S4. ^{1}H NMR spectrum ($CDCl_3$) of the mixture after the polymerization of BnGE in toluene using *t*BBA as the initiator and *t*-Bu-P$_4$ (1.0 M solution in *n*-hexane) as the organocatalyst for 20 h ($[BnGE]_0/[tBBA]_0 = 50$).

4. ^{1}H and ^{13}C NMR spectra of R-PBnGE$_n$ and R-PG$_n$-EO$_m$R'

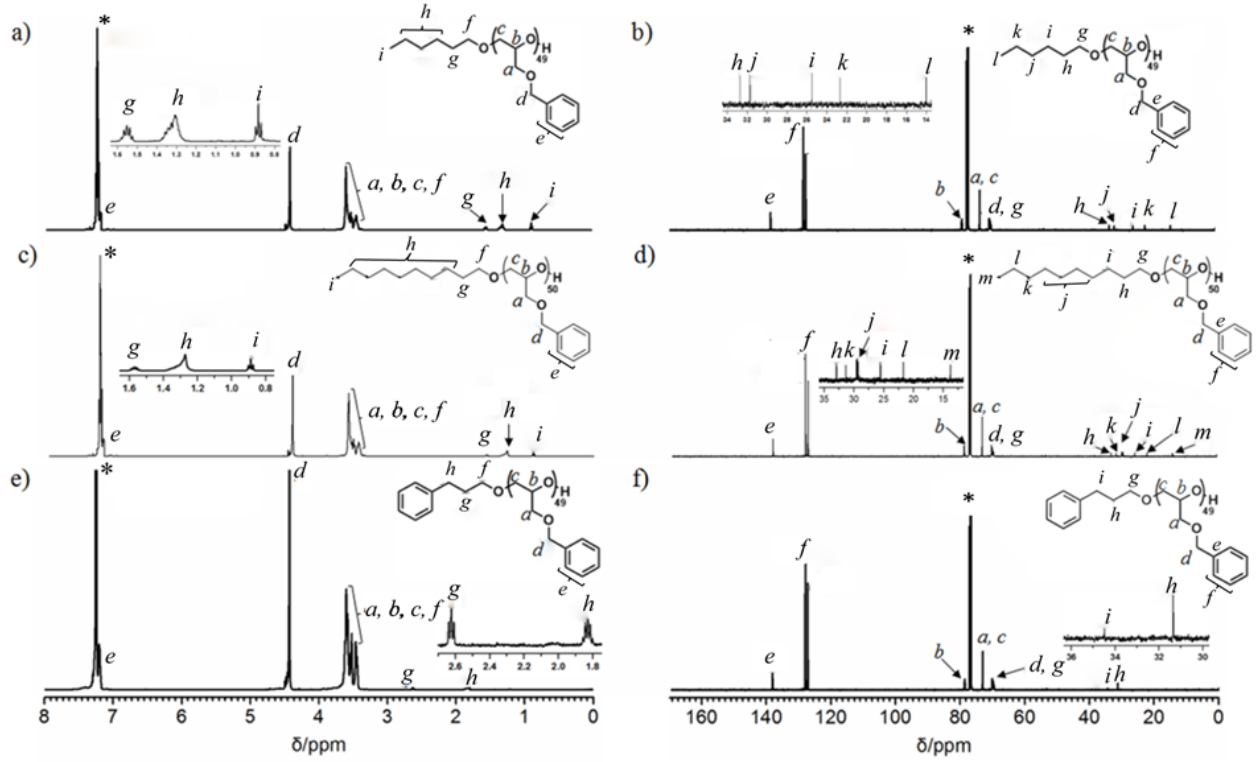


Fig. S5. ^{1}H NMR spectra ($CDCl_3$) of a) *n*HA-PBnGE$_{49}$, c) *n*DA-PBnGE$_{50}$, and e) PPA-PBnGE$_{49}$ and ^{13}C NMR spectra ($CDCl_3$) of b) *n*HA-PBnGE$_{49}$, d) *n*DA-PBnGE$_{50}$, and f) PPA-PBnGE$_{49}$. The symbol * refers to solvent peaks.

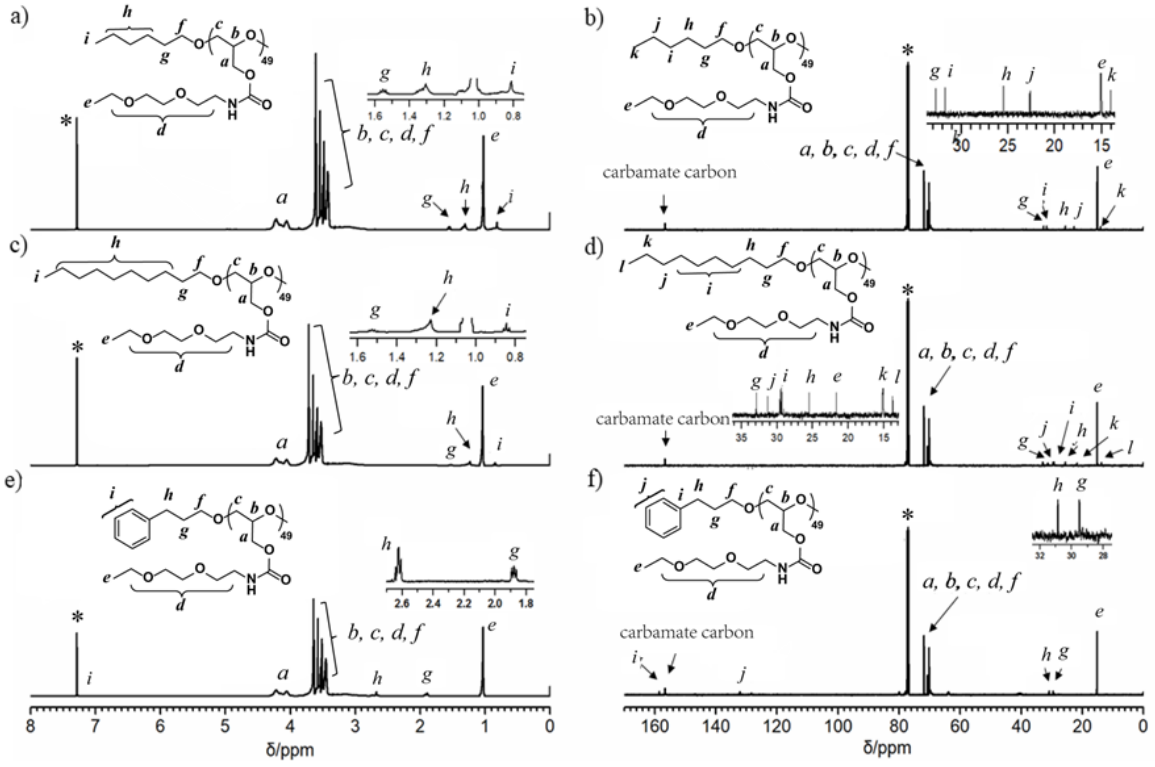


Fig. S6. ^{1}H NMR spectra ($CDCl_3$) of a) *n*HA-PG$_{49}$-EO$_2$Et, c) *n*DA-PG$_{49}$-EO$_2$Et, and e) PPA-PG$_{49}$-EO$_2$Et and ^{13}C NMR spectra ($CDCl_3$) of b) *n*HA-PG$_{49}$-EO$_2$Et, d) *n*DA-PG$_{49}$-EO$_2$Et, and f) PPA-PG$_{49}$-EO$_2$Et. The symbol * refers to solvent peaks.

5. Tables for the synthesis and characterization of PG, R-PG, PG-EO$_m$R', and R-PG-EO$_m$R'

Table S1. Synthesis and characterization of PG, *n*HA-PG$_n$, *n*DA-PG$_n$, and PPA-PG$_n$, which were obtained by the deprotection reactions of *t*BBA-PBnGE$_n$, *n*HA-PBnGE$_n$, *n*DA-PBnGE$_n$, and PPA-PBnGE$_n$, respectively

entry	starting material	yield in %	product	
			Code	$M_{n,NMR}$[a] (M_w/M_n[b])
38	*t*BBA-PBnGE$_{49}$	quant.	PG$_{49}$	3600[c] (1.11)
39	*t*BBA-PBnGE$_{74}$	quant.	PG$_{74}$	5500[c] (1.12)
40	*t*BBA-PBnGE$_{98}$	99.3	PG$_{98}$	7200 [c] (1.13)
41	*t*BBA-PBnGE$_{116}$	92.6	PG$_{116}$	8000 [c] (1.13)
42	*t*BBA-PBnGE$_{132}$	90.8	PG$_{132}$	8800 [c] (1.14)
43	*n*HA-PBnGE$_{49}$	quant.	*n*HA-PG$_{49}$	3700 (1.11)
44	*n*HA-PBnGE$_{74}$	quant.	*n*HA-PG$_{74}$	5500 (1.12)
45	*n*HA-PBnGE$_{98}$	quant.	*n*HA-PG$_{98}$	7300 (1.12)
46	*n*HA-PBnGE$_{121}$	96.5	*n*HA-PG$_{121}$	8700 (1.13)
47	*n*HA-PBnGE$_{131}$	91.7	*n*HA-PG$_{131}$	9700 (1.14)
48	*n*DA-PBnGE$_{50}$	quant.	*n*DA-PG$_{50}$	3800 (1.12)
49	*n*DA-PBnGE$_{75}$	quant.	*n*DA-PG$_{75}$	5700 (1.12)
50	*n*DA-PBnGE$_{98}$	quant.	*n*DA-PG$_{98}$	7400 (1.13)
51	*n*DA-PBnGE$_{112}$	98.1	*n*DA-PG$_{112}$	8200 (1.14)
52	*n*DA-PBnGE$_{131}$	90.3	*n*DA-PG$_{131}$	8800 (1.15)
53	PPA-PBnGE$_{49}$	quant.	PPA-PG$_{49}$	3700 (1.12)
54	PPA-PBnGE$_{74}$	quant.	PPA-PG$_{74}$	5600 (1.13)
55	PPA-PBnGE$_{97}$	98.2	PPA-PG$_{97}$	7100 (1.14)
56	PPA-PBnGE$_{117}$	92.9	PPA-PG$_{117}$	8000 (1.15)
57	PPA-PBnGE$_{132}$	90.5	PPA-PG$_{132}$	8900 (1.15)

[a]The number average molecular weight determined by ^{1}H NMR spectra in CD_3OD. [b]The molecular weight distribution determined by SEC in H_2O in the presence of 0.05 % NaN_3 using PEG standards. [c]The weight average molecular weight determined by the SEC equipped with a MALS ($M_{w,MALS}$) in DMF in the presence of 0.01 M LiCl.

Table S2. Synthesis and characterization of *n*HA-PG$_n$-EO$_2$Et, *n*DA-PG$_n$-EO$_2$Et, and PPA-PG$_n$-EO$_2$Et, which were obtained by the post-modification reactions of *n*HA-PG$_n$, *n*DA-PG$_n$, and PPA-PG$_n$ with ICEO$_2$Et, respectively

entry	starting material	yield in %	product				
			code	$M_{n,NMR}$[a] (M_w/M_n[b])	T_{cp}[c] in °C	R_h[d] in nm at 25 °C	R_h[d] in nm at T_{cp}
58	*n*HA-PG$_{49}$	81.5	*n*HA-PG$_{49}$-EO$_2$Et	11400 (1.14)	40.1	2.5	650
59	*n*HA-PG$_{74}$	81.1	*n*HA-PG$_{74}$-EO$_2$Et	17800 (1.16)	38.6	3.1	672
60	*n*HA-PG$_{98}$	78.6	*n*HA-PG$_{98}$-EO$_2$Et	22800 (1.19)	37.4	3.6	681
61	*n*HA-PG$_{121}$	79.4	*n*HA-PG$_{121}$-EO$_2$Et	24100 (1.20)	36.4	4.2	696
62	*n*HA-PG$_{131}$	70.1	*n*HA-PG$_{131}$-EO$_2$Et	31600 (1.22)	34.5	5.5	708
63	*n*DA-PG$_{50}$	79.6	*n*DA-PG$_{50}$-EO$_2$Et	11800 (1.16)	36.1	2.8	806
64	*n*DA-PG$_{75}$	80.4	*n*DA-PG$_{75}$-EO$_2$Et	18300 (1.17)	35.4	3.3	820
65	*n*DA-PG$_{98}$	72.5	*n*DA-PG$_{98}$-EO$_2$Et	22900 (1.19)	34.2	3.9	835
66	*n*DA-PG$_{112}$	73.9	*n*DA-PG$_{112}$-EO$_2$Et	27200 (1.21)	33.6	4.8	859
67	*n*DA-PG$_{131}$	68.4	*n*DA-PG$_{131}$-EO$_2$Et	31900 (1.24)	33.0	5.9	878
68	PPA-PG$_{49}$	78.5	PPA-PG$_{49}$-EO$_2$Et	11500 (1.15)	32.5	2.8	623
69	PPA-PG$_{74}$	72.5	PPA-PG$_{74}$-EO$_2$Et	17300 (1.17)	30.6	3.5	648
70	PPA-PG$_{97}$	71.0	PPA-PG$_{97}$-EO$_2$Et	22800 (1.18)	29.5	4.0	670
71	PPA-PG$_{117}$	73.2	PPA-PG$_{117}$-EO$_2$Et	28600 (1.20)	29.0	5.1	681
72	PPA-PG$_{132}$	67.5	PPA-PG$_{132}$-EO$_2$Et	31800 (1.22)	28.2	6.0	698

[a]The number average molecular weight determined by ^{1}H NMR spectra in $CDCl_3$. [b]The molecular weight distribution determined by SEC in H_2O in the presence of 0.05 % NaN_3 using PEG standards. [c]The cloud point temperature determined by UV-vis measurements in water (10 g L^{-1}). [d]The average hydrodynamic radii determined by DLS measurements in water (10 g L^{-1}).

Table S3. Synthesis and characterization of *n*HA-PG$_n$-EO$_3$Et, *n*DA-PG$_n$-EO$_3$Et, and PPA-PG$_n$-EO$_3$Et, which were obtained by the post-modification reactions of *n*HA-PG$_n$, *n*DA-PG$_n$, and PPA-PG$_n$ with ICEO$_3$Et, respectively

entry	starting material	yield in %	product				
			code	$M_{n,NMR}$[a] (M_w/M_n[b])	T_{cp}[c] in °C	R_h[d] in nm at 25 °C	R_h[d] in nm at T_{cp}
73	*n*HA-PG$_{49}$	80.5	*n*HA-PG$_{49}$-EO$_3$Et	13500 (1.16)	57.4	4.0	905
74	*n*HA-PG$_{74}$	80.9	*n*HA-PG$_{74}$-EO$_3$Et	21100 (1.17)	56.6	5.4	924
75	*n*HA-PG$_{98}$	79.6	*n*HA-PG$_{98}$-EO$_3$Et	26900 (1.19)	55.1	6.2	953
76	*n*HA-PG$_{121}$	80.4	*n*HA-PG$_{121}$-EO$_3$Et	29400 (1.19)	54.5	6.8	983
77	*n*HA-PG$_{131}$	75.1	*n*HA-PG$_{131}$-EO$_3$Et	37300 (1.22)	53.8	7.4	1021
78	*n*DA-PG$_{50}$	80.6	*n*DA-PG$_{50}$-EO$_3$Et	14000 (1.17)	50.3	4.5	931
79	*n*DA-PG$_{75}$	79.4	*n*DA-PG$_{75}$-EO$_3$Et	21600 (1.17)	49.5	5.6	950
80	*n*DA-PG$_{98}$	79.5	*n*DA-PG$_{98}$-EO$_3$Et	27200 (1.18)	48.2	6.4	972
81	*n*DA-PG$_{112}$	74.9	*n*DA-PG$_{112}$-EO$_3$Et	32100 (1.19)	47.3	6.9	1027
82	*n*DA-PG$_{131}$	70.4	*n*DA-PG$_{131}$-EO$_3$Et	37600 (1.22)	46.5	7.6	1068
83	PPA-PG$_{49}$	79.5	PPA-PG$_{49}$-EO$_3$Et	13600 (1.18)	45.3	4.2	887
84	PPA-PG$_{74}$	72.5	PPA-PG$_{74}$-EO$_3$Et	20500 (1.19)	43.2	5.3	902
85	PPA-PG$_{97}$	70.5	PPA-PG$_{97}$-EO$_3$Et	27000 (1.21)	42.0	6.4	922
86	PPA-PG$_{117}$	71.2	PPA-PG$_{117}$-EO$_3$Et	33700 (1.21)	40.5	6.7	961
87	PPA-PG$_{132}$	68.5	PPA-PG$_{132}$-EO$_3$Et	37600 (1.23)	39.2	7.2	998

[a]The number average molecular weight determined by ^{1}H NMR spectra in $CDCl_3$. [b]The molecular weight distribution determined by SEC in H_2O in the presence of 0.05 % NaN_3 using PEG standards. [c]The cloud point temperature determined by UV-vis measurements in water (10 g L^{-1}). [d]The average hydrodynamic radii determined by DLS measurements in water (10 g L^{-1}).