Electronic Supplementary Information (ESI)

Systematic Study on Evolution of Self-Assembly Morphologies of CABC Tetrablock Terpolymers with Varied Segment Lengths

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1. Experimental Section

Materials. Methyl methacrylate (MMA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), 2-(2-ethoxyethoxy)ethyl acrylate (EEA) (>99.8%, TCI), and allyl methacrylate (AMA) (98%, Aldrich, US) were purified through an alumina column before use. Solketal methacrylate (SMA) (50 wt% in dichloromethane, Aldrich) was purified with rotary evaporator to remove dichloromethane before use. Tetra-*n*-octylammonium iodide (ONI) (>98.0%, TCI), 4,4'-azobis(4-cyanovaleric acid) (V501) (≥98%, Aldrich), hydrochloric acid (HCl) (1 mol/L, TCI), sodium hydroxide (NaOH) (2 mol/L in water, TCI), tetrahydrofuran (THF) (>99.5%, Kanto Chemical, Japan), *N,N*-dimethylformamide (DMF) (>99.5%, Kanto), hexane (>99%, International Scientific, Singapore), acetonitrile (HPLC grade, Anhui Fulltime Specialized Solvent & Reagent, China), acetone-d_6 (99.9%D, Cambridge Isotope Laboratories, US), and dialysis tubing (benzoylated, pore size: 2000 MWCO, Aldrich) were

used as received. Methyl 2-iodo-2-(4'-(2"-iodopropionyloxy)phenyl)acetate (I-MEPE-I) (>92.0%) was provided through the courtesy of Godo Shigen, Japan.

^{1}H NMR. The ^{1}H NMR spectra were recorded on a Bruker (Billerica, US) AV500 spectrometer (500 MHz) (ambient temperature); spectral width 5000.00 Hz, acquisition time 6.554 sec, and pulse delay 1.000 sec. Acetone-d_6 was used as a solvent for the NMR analysis, and the chemical shift was calibrated using the residual undeuterated solvent as the internal standard. The monomer conversions were determined with ^{1}H NMR.

GPC. The GPC analysis was performed on a Shimadzu (Kyoto, Japan) LC-2030C Plus liquid chromatograph equipped with two Shodex (Tokyo, Japan) LF-804 mixed gel columns (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å). The eluent was *N,N*-dimethyl formamide (DMF) (containing LiBr (10 mM)) at a flow rate of 0.5 mL/min (40 °C). The sample detection was conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard poly(methyl methacrylate)s (PMMAs). For the relatively low-molecular-weight I-PMMA-I samples (M_n ≤ 3700) (Table S1 (entry 1) and Table S2 (entry 1-1)), the chromatogram of the polymer overlapped with those of small molecules or LiBr-cluster in the DMF eluent in the low-molecular-weight region. To avoid the overlap, these I-PMMA-I samples (Table S1 (entry 1) and Table S2 (entry 1-1)) were analyzed using tetrahydrofuran (THF) as an eluent at a flow rate of 0.7 mL/min (40 °C), for which the columns were a Shodex LF-804 mixed gel column (above) and a Shodex KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 μm; pore size = 1500 Å).

DLS Analysis. The DLS measurement was carried out using a Malvern Zetasizer Nano ZSP (Worcestershire, UK). A temperature-controlled quartz cell was employed. The test angle for the DLS analysis was 173° (backscattering detection). The sample was equilibrated at each temperature for 5 min.

TEM. The TEM images were obtained on a JEOL (Tokyo, Japan) JEM-1400 transmission electron microscope operated at 100 kV. The TEM grid was carbon-coated on 200 mesh (copper) (Ted Pella, Redding, US). The TEM samples at 4 °C (Figure 3b (E') and Figure 4b (I')) were prepared by freeze-drying. A micelle solution, a TEM grid in a vial, and a micropipette tip were placed in a fridge at 4 °C. A 100 mL flask was placed in a dry ice/acetone mixture bath. Then, the micelle solution was quickly dropped on the TEM grid in the vial using the micropipette, the TEM grid in the vial was quickly placed in the flask in the dry ice/acetone mixture bath, and the droplet was frozen. The sample in the flask was vacuumed with a pump overnight and lyophilized.

AFM. The AFM analysis was performed on a Bruker Multimode 8 atomic force microscope (Billerica, US) equipped with a SuperSharpSilicon SSS-NCH probe (tip radius, 2 nm) (Neuchâtel, Sweden). A micelle solution (sample F in Figure 2) and a mica in a vial were placed in an oil bath at 60 °C. Then, the solution (ca. 10 μL) was dropped on the mica in the vial and dried under N_2 in the oil bath (60 °C). The AFM image was taken in the air at ambient temperature.

Synthesis of Polymers. CABC tetrablock terpolymers were prepared according to our previous work.[1] The examples (Table S1 (entries 1, 2, and 3-1)) are described below.

Preparation of I-PMMA-I (Table S1 (entry 1)). A mixture of MMA (1.00 g, 8000 mM), I-MEPE-I (0.0947 g, 160 mM), and ONI (0.0593 g, 80 mM) in a Schlenk tube was heated at 60 °C for 2 h under argon atmosphere with magnetic stirring, yielding an I-ME-PMMA-I polymer with M_n = 2900 and $Đ$ = 1.11 (monomer conversion = 57%), where $Đ$ (= M_w/M_n) is dispersity, and M_n and M_w are the number- and weight-average molecular weights, respectively. The reaction mixture was diluted with THF (2 mL). Then, the polymer was

reprecipitated in hexane (20 mL) twice, giving a purified I-ME-PMMA-I with M_n = 3000 and $Đ$ = 1.10.

Preparation of I-PMMA-PSMA-I (Table S1 (entry 2)). A mixture of SMA (1.00 g, 8000 mM), I-ME-PMMA-I (0.300 g, 160 mM), and ONI (0.0593 g, 160 mM) in a Schlenk tube was heated at 60 °C for 1.5 h under argon atmosphere with magnetic stirring, yielding an I-PMMA-PSMA-I block copolymer with M_n = 5200 and $Đ$ = 1.17 (monomer conversion = 22%). The reaction mixture was diluted with THF (2 mL). Then, the polymer was reprecipitated in hexane (20 mL) twice, giving a purified I-ME-PMMA-PSMA-I with M_n = 5100 and $Đ$ = 1.16.

Preparation of I-PEEA-PMMA-PSMA-PEEA-I (Table S1 (entry 3-1)). A mixture of EEA (1.00 g, 8000 mM), I-ME-PMMA-PSMA-I (0.0452 g, 13 mM), and ONI (0.0210 g, 52 mM) in a Schlenk tube was heated at 110 °C for 13 h under argon atmosphere with magnetic stirring, yielding an I-PEEA-PMMA-PSMA-PEEA-I tetrablock terpolymer with M_n = 26000 and $Đ$ = 1.35 (monomer conversion = 20%). The reaction mixture was diluted with THF (3 mL). Then, the polymer was reprecipitated in hexane (30 mL) twice, giving a purified I-PEEA-PMMA-PSMA-PEEA-I with M_n = 27000 and $Đ$ = 1.35.

Preparation of I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entry 3-1)). A mixture of I-PEEA-PMMA-PSMA-PEEA-I (0.300 g), acetonitrile (4 mL), and an aqueous HCl solution (1 mol/L, 2 mL) in a 25 mL flask was stirred at room temperature for 12 h, yielding an I-PEEA-PMMA-PGLMMA-PEEA-I tetrablock terpolymer. Then, the polymer solution was neutralized with an aqueous NaOH solution (2 mol/L) and transferred to a dialysis tube (pore size: 2000 MWCO) to dialyze in water for 24 h, giving a purified I-PEEA-PMMA-PGLMMA-PEEA-I with M_n = 25000 and $Đ$ = 1.24.

Table S1. Synthesis of PEEA-PMMA-PGLMMA-PEEA tetrablock terpolymers with different DPs of PEEA.

Entry	Monomer	I-R-I	$[M]_0/[\text{I-R-I}]_0/[\text{ONI}]_0$ (mM)[a]	T (°C)	t (h)	conv (%)	M_n (GPC)[b] ($M_{n,\text{theo}}$[c]) (g mol^{-1})	DP (^{1}H NMR)[d]	$Đ$ (GPC)[b]
1	MMA	I-MEPE−I	8000/160/80	60	2	57	2900 (3000)		1.11
				After purification			3000	25	1.10
2	SMA	I-PMMA-I	8000/160/160	60	1.5	22	5200 (5000)		1.17
				After purification			5100	10	1.16
3-1	EEA	I-PMMA-PSMA-I	8000/13/52	110	13	20	26000 (30000)		1.35
				After purification			27000	132	1.35
				After deprotection			25000		1.24
3-2	EEA	I-PMMA-PSMA-I	8000/13/52	110	15	30	36000 (35000)		1.49
				After purification			37000	162	1.43
				After deprotection			33000		1.37
3-3	EEA	I-PMMA-PSMA-I	8000/10/40	110	18	30	43000 (40000)		1.57
				After purification			45000	184	1.45
				After deprotection			38000		1.63
3-4	EEA	I-PMMA-PSMA-I	8000/13/52	110	18	34	45000 (44000)		1.64
				After purification			46000	206	1.60
				After deprotection			38000		1.60
3-5	EEA	I-PMMA-PSMA-I	8000/13/52	110	19	35	47000 (47000)		1.88
				After purification			50000	224	1.81
				After deprotection			46000		1.76
3-6	EEA	I-PMMA-PSMA-I	8000/10/40	110	20	34	49000 (53000)		1.52
				After purification			50000	256	1.50
				After deprotection			47000		1.60
3-7	EEA	I-PMMA-PSMA-I	8000/10/40	110	21	37	51000 (58000)		1.61
				After purification			53000	280	1.49
				After deprotection			47000		1.69
3-8	EEA	I-PMMA-PSMA-I	8000/10/40	110	22	40	56000 (61000)		1.89
				After purification			57000	300	1.86
				After deprotection			51000		2.04
3-9	EEA	I-PMMA-PSMA-I	8000/8/32	110	24	40	64000 (69000)		2.01
				After purification			63000	340	1.95
				After deprotection			57000		1.88

[a] M = monomer. [b] PMMA-calibrated value by THF-GPC for entry 1 and DMF-GPC for the other entries. [c] Theoretical M_n calculated with $M_n = ([M]_0/[\text{I}−\text{R}−\text{I}]_0) \times$ conversion $\times$ (molecular weight of monomer) + (molecular weight of I-R-I). [d] DP obtained from the ^{1}H NMR peak areas of the initiating phenyl group and the monomer units (with ±10% experimental error).

Table S2. Synthesis of PEEA-PMMA-PGLMMA-PEEA tetrablock terpolymers with different DPs of PMMA and PEEA-PAMA-PGLMMA-PEEA.

Entry	Monomer	I-R-I	$[M]_0/[I\text{-}R\text{-}I]_0/[ONI]_0$ (mM)[a]	T (°C)	t (h)	conv (%)	M_n (GPC)[b] ($M_{n,theo}$[c]) (g mol⁻¹)	DP (¹H NMR)[d]	$Đ$ (GPC)[b]
1-1	MMA	I-MEPE-I	8000/160/80	60	2.5	68	3600 (3800)		1.11
				After purification			3700	33	1.10
1-2	SMA	I-PMMA-I	8000/160/160	60	1.3	20	5400 (5800)		1.20
				After purification			5400	10	1.19
1-3	EEA	I-PMMA-PSMA-I	8000/8/32	110	20	27	60000 (62000)		1.93
				After purification			60000	300	1.92
				After deprotection			55000		2.17
2-1	MMA	I-MEPE-I	8000/160/80	60	3	60	5700 (5500)		1.18
				After purification			5800	50	1.15
2-2	SMA	I-PMMA-I	8000/100/100	60	1.6	11	7900 (7500)		1.31
				After purification			8100	10	1.28
2-3	EEA	I-PMMA-PSMA-I	8000/8/32	110	21	30	62000 (64000)		2.11
				After purification			63000	300	2.00
				After deprotection			58000		2.00
3-1	MMA	I-MEPE-I	8000/80/40	60	3.5	67	6800 (6500)		1.19
				After purification			6700	60	1.16
3-2	SMA	I-PMMA-I	8000/80/80	60	1.6	10	8300 (8500)		1.21
				After purification			8500	10	1.20
3-3	EEA	I-PMMA-PSMA-I	8000/5/20	110	26	25	58000 (69000)		2.24
				After purification			58000	322	2.05
				After deprotection			55000		2.02
4-1	MMA	I-MEPE-I	8000/53/53	60	3.5	70	10000 (10000)		1.17
				After purification			11000	98	1.17
4-2	SMA	I-PMMA-I	8000/53/53	60	1.6	6	13000 (12000)		1.38
				After purification			14000	10	1.38
4-3	EEA	I-PMMA-PSMA-I	8000/5/20	110	24	19	56000 (71000)		2.11
				After purification			58000	311	1.83
				After deprotection			51000		2.00
5-1	AMA	I-MEPE-I	8000/160/80	60	2.5	45	6100 (4300)		1.22
				After purification			6100	30	1.17
5-2	SMA	I-PAMA-I	8000/182/182	60	1.5	15	8300 (6100)		1.26
				After purification			8700	9	1.25
5-3	EEA	I-PAMA-PSMA-I	8000/4/16	110	20	17	67000 (63000)		2.21
				After purification			66000	300	2.38
				After deprotection			60000		2.02

[a] M = monomer. [b] PMMA-calibrated value by THF-GPC for entry 1-1 and DMF-GPC for the other entries. [c] Theoretical M_n calculated with $M_n = ([M]_0/[I{-}R{-}I]_0) \times$ conversion $\times$ (molecular weight of monomer) + (molecular weight of I-R-I). [d] DP obtained from the ¹H NMR peak areas of the initiating phenyl group and the monomer units (with ±10% experimental error).

^{1}H NMR Analysis of I-MEPE-I, I-ME-PMMA$_{25}$-I, I-ME-PMMA$_{25}$-PSMA$_{10}$-I, I-PEEA$_{66}$-PMMA$_{25}$-PSMA$_{10}$-PEEA$_{66}$-I and I-PEEA$_{66}$-PMMA$_{25}$-PGLMMA$_{10}$-PEEA$_{66}$-I.

Figure S1a shows the ^{1}H NMR spectrum of I-MEPE-I (initiator). Figure S1b shows the spectrum of I-ME-PMMA-I polymer. The PE-I site proton (I-C*H*, proton **d**, 5.89 ppm) completely disappeared, meaning 100% initiation from the PE-I site. 97% of the I-ME site remained unreacted, as calculated from the signal areas of the I-ME site (I-C*H*, proton **b**, 4.95 ppm) and the phenyl group in the initiator (-C$_6$*H*$_4$-, proton **c**, 7.42-7.13 ppm). The number of MMA units (25 units) was calculated from the signal areas of the MMA units (-OC*H*$_3$, protons **e** and **h**, 3.79-3.59 ppm) and the phenyl group in the initiator (-C$_6$*H*$_4$-, proton **c**, 7.42-7.13 ppm). Figure S1c shows the spectrum of I-ME-PMMA-PSMA-I (a trace amount of the monomer SMA remained). 91% of the I-ME site remained unreacted, as calculated in a similar manner. The number of the SMA units (10 units) was calculated from the signal areas of the SMA units (-C*H*, proton **l**, 4.45-4.34 ppm) and the phenyl group in the initiator (-C$_6$*H*$_4$-, proton **c**, 7.42-7.13 ppm). Figure S1d shows the spectrum of I-PEEA-PMMA-PSMA-PEEA-I. The I-ME site proton (I-C*H*, proton **b**, 4.95 ppm) completely disappeared, meaning 100% initiation from the I-ME site. The number of the EEA units (132 units) was calculated from the signal areas of the EEA units (-C*H* in the backbone, proton **o**, 2.56-2.34 ppm) and the SMA units (-C*H*, proton **l**, 4.45-4.34 ppm) (10 units). Figure S1e shows the spectrum of I-PEEA-PMMA-PGLMMA-PEEA-I. The SMA units (-C*H*, proton **l**, 4.45-4.34 ppm) completely disappeared, meaning a full conversion of the SMA units to the GLMMA units.

^{1}H NMR Analysis of I-PEEA$_x$-PMMA$_{25}$-PSMA$_{10}$-PEEA$_x$-I (2x = 162, 184, 206, 224, 256, 280, 300, and 340) and I-PEEA$_x$-PMMA$_{25}$-PGLMMA$_{10}$-PEEA$_x$-I. Figures S2a, S3a, S4a, S5a, S6a, S7a, S8a, and S9a show the ^{1}H NMR spectra of I-PEEA$_x$-PMMA$_{25}$-PSMA$_{10}$-PEEA$_x$-I (2x = 162, 184, 206, 224, 256, 280, 300, and 340) tetrablock terpolymers, respectively. The number of the EEA units were calculated from the signal areas of the EEA

units (-C*H* in the backbone, protons **o**, 2.56-2.34 ppm) and the SMA units (-C*H*, proton **l**, 4.45-4.34 ppm) (10 units). Figures S2b, S3b, S4b, S5b, S6b, S7b, S8b, and S9b show the spectra of I-PEEA$_x$-PMMA$_{25}$-PGLMMA$_{10}$-PEEA$_x$-I (2x = 162, 184, 206, 224, 256, 280, 300, and 340) tetrablock terpolymers, respectively.

^{1}H NMR Analysis of I-ME-PMMA$_{33}$-I, I-ME-PMMA$_{33}$-PSMA$_{10}$-I, I-PEEA$_{150}$-PMMA$_{33}$-PSMA$_{10}$-PEEA$_{150}$-I and I-PEEA$_{150}$-PMMA$_{33}$-PGLMMA$_{10}$-PEEA$_{150}$-I. Figure S10a shows the spectrum of I-ME-PMMA-I polymer. The PE-I site proton (I-C*H*, proton **d**, 5.89 ppm) completely disappeared, meaning 100% initiation from the PE-I site. 94% of the I-ME site remained unreacted, as calculated from the signal areas of the I-ME site (I-C*H*, proton **b**, 4.95 ppm) and the phenyl group in the initiator (-C$_6$*H*$_4$-, proton **c**, 7.42-7.13 ppm). The number of MMA units (33 units) was calculated from the signal areas of the MMA units (-OC*H*$_3$, protons **e** and **h**, 3.79-3.59 ppm) and the phenyl group in the initiator (-C$_6$*H*$_4$-, proton **c**, 7.42-7.13 ppm). Figure S10b shows the spectrum of I-ME-PMMA-PSMA-I (a trace amount of the monomer SMA remained). 94% of the I-ME site remained unreacted, as calculated in a similar manner. The number of the SMA units (10 units) was calculated from the signal areas of the SMA units (-C*H*, proton **l**, 4.45-4.34 ppm) and the phenyl group in the initiator (-C$_6$*H*$_4$-, proton **c**, 7.42-7.13 ppm). Figure S10c shows the spectrum of I-PEEA-PMMA-PSMA-PEEA-I. The I-ME site proton (I-C*H*, proton **b**, 4.95 ppm) completely disappeared, meaning 100% initiation from the I-ME site. The number of the EEA units (300 units) was calculated from the signal areas of the EEA units (-C*H* in the backbone, proton **o**, 2.56-2.34 ppm) and the SMA units (-C*H*, proton **l**, 4.45-4.34 ppm) (10 units). Figure S10d shows the spectrum of I-PEEA-PMMA-PGLMMA-PEEA-I. The SMA units (-C*H*, proton **l**, 4.45-4.34 ppm) completely disappeared, meaning a full conversion of the SMA units to the GLMMA units.

^{1}H NMR Analysis of I-ME-PMMA$_{50}$-I, I-ME-PMMA$_{50}$-PSMA$_{10}$-I, I-PEEA$_{150}$-PMMA$_{50}$-PSMA$_{10}$-PEEA$_{150}$-I and I-PEEA$_{150}$-PMMA$_{50}$-PGLMMA$_{10}$-PEEA$_{150}$-I. Figure S11a shows the spectrum of I-ME-PMMA-I polymer. The PE-I site proton (I-CH, proton **d**, 5.89 ppm) completely disappeared, meaning 100% initiation from the PE-I site. 98% of the I-ME site remained unreacted, as calculated from the signal areas of the I-ME site (I-CH, proton **b**, 4.95 ppm) and the phenyl group in the initiator (-C$_6H_4$-, proton **c**, 7.42-7.13 ppm). The number of MMA units (50 units) was calculated from the signal areas of the MMA units (-OCH_3, protons **e** and **h**, 3.79-3.59 ppm) and the phenyl group in the initiator (-C$_6H_4$-, proton **c**, 7.42-7.13 ppm). Figure S11b shows the spectrum of I-ME-PMMA-PSMA-I (a trace amount of the monomer SMA remained). 95% of the I-ME site remained unreacted, as calculated in a similar manner. The number of the SMA units (10 units) was calculated from the signal areas of the SMA units (-CH, proton **l**, 4.45-4.34 ppm) and the phenyl group in the initiator (-C$_6H_4$-, proton **c**, 7.42-7.13 ppm). Figure S11c shows the spectrum of I-PEEA-PMMA-PSMA-PEEA-I. The I-ME site proton (I-CH, proton **b**, 4.95 ppm) completely disappeared, meaning 100% initiation from the I-ME site. The number of the EEA units (300 units) was calculated from the signal areas of the EEA units (-CH in the backbone, proton **o**, 2.56-2.34 ppm) and the SMA units (-CH, proton **l**, 4.45-4.34 ppm) (10 units). Figure S11d shows the spectrum of I-PEEA-PMMA-PGLMMA-PEEA-I. The SMA units (-CH, proton **l**, 4.45-4.34 ppm) completely disappeared, meaning a full conversion of the SMA units to the GLMMA units.

^{1}H NMR Analysis of I-ME-PMMA$_{60}$-I, I-ME-PMMA$_{60}$-PSMA$_{10}$-I, I-PEEA$_{161}$-PMMA$_{60}$-PSMA$_{10}$-PEEA$_{161}$-I and I-PEEA$_{161}$-PMMA$_{60}$-PGLMMA$_{10}$-PEEA$_{161}$-I. Figure S12a shows the spectrum of I-ME-PMMA-I polymer. The PE-I site proton (I-CH, proton **d**, 5.89 ppm) completely disappeared, meaning 100% initiation from the PE-I site. 97% of the I-ME site remained unreacted, as calculated from the signal areas of the I-ME site (I-CH,

proton **b**, 4.95 ppm) and the phenyl group in the initiator (-C$_6$H$_4$-, proton **c**, 7.42-7.13 ppm). The number of MMA units (60 units) was calculated from the signal areas of the MMA units (-OCH$_3$, protons **e** and **h**, 3.79-3.59 ppm) and the phenyl group in the initiator (-C$_6$H$_4$-, proton **c**, 7.42-7.13 ppm). Figure S12b shows the spectrum of I-ME-PMMA-PSMA-I (a trace amount of the monomer SMA remained). 97% of the I-ME site remained unreacted, as calculated in a similar manner. The number of the SMA units (10 units) was calculated from the signal areas of the SMA units (-CH, proton **l**, 4.45-4.34 ppm) and the phenyl group in the initiator (-C$_6$H$_4$-, proton **c**, 7.42-7.13 ppm). Figure S12c shows the spectrum of I-PEEA-PMMA-PSMA-PEEA-I. The I-ME site proton (I-CH, proton **b**, 4.95 ppm) completely disappeared, meaning 100% initiation from the I-ME site. The number of the EEA units (322 units) was calculated from the signal areas of the EEA units (-CH in the backbone, proton **o**, 2.56-2.34 ppm) and the SMA units (-CH, proton **l**, 4.45-4.34 ppm) (10 units). Figure S12d shows the spectrum of I-PEEA-PMMA-PGLMMA-PEEA-I. The SMA units (-CH, proton **l**, 4.45-4.34 ppm) completely disappeared, meaning a full conversion of the SMA units to the GLMMA units.

^{1}H NMR Analysis of I-ME-PMMA$_{98}$-I, I-ME-PMMA$_{98}$-PSMA$_{10}$-I, I-PEEA$_{156}$-PMMA$_{98}$-PSMA$_{10}$-PEEA$_{156}$-I and I-PEEA$_{156}$-PMMA$_{98}$-PGLMMA$_{10}$-PEEA$_{156}$-I. Figure S13a shows the spectrum of I-ME-PMMA-I polymer. The PE-I site proton (I-CH, proton **d**, 5.89 ppm) completely disappeared, meaning 100% initiation from the PE-I site. 94% of the I-ME site remained unreacted, as calculated from the signal areas of the I-ME site (I-CH, proton **b**, 4.95 ppm) and the phenyl group in the initiator (-C$_6$H$_4$-, proton **c**, 7.42-7.13 ppm). The number of MMA units (98 units) was calculated from the signal areas of the MMA units (-OCH$_3$, protons **e** and **h**, 3.79-3.59 ppm) and the phenyl group in the initiator (-C$_6$H$_4$-, proton **c**, 7.42-7.13 ppm). Figure S13b shows the spectrum of I-ME-PMMA-PSMA-I (a trace amount of the monomer SMA remained). 92% of the I-ME site remained unreacted, as

calculated in a similar manner. The number of the SMA units (10 units) was calculated from the signal areas of the SMA units (-CH, proton **l**, 4.45-4.34 ppm) and the phenyl group in the initiator (-C$_6H_4$-, proton **c**, 7.42-7.13 ppm). Figure S13c shows the spectrum of I-PEEA-PMMA-PSMA-PEEA-I. The I-ME site proton (I-CH, proton **b**, 4.95 ppm) completely disappeared, meaning 100% initiation from the I-ME site. The number of the EEA units (311 units) was calculated from the signal areas of the EEA units (-CH in the backbone, proton **o**, 2.56-2.34 ppm) and the SMA units (-CH, proton **l**, 4.45-4.34 ppm) (10 units). Figure S13d shows the spectrum of I-PEEA-PMMA-PGLMMA-PEEA-I. The SMA units (-CH, proton **l**, 4.45-4.34 ppm) completely disappeared, meaning a full conversion of the SMA units to the GLMMA units.

^{1}H NMR Analysis of I-ME-PAMA$_{30}$-I, I-ME-PAMA$_{30}$-PSMA$_9$-I, I-PEEA$_{154}$-PAMA$_{30}$-PSMA$_9$-PEEA$_{154}$-I, and I-PEEA$_{154}$-PAMA$_{30}$-PGLMMA$_9$-PEEA$_{154}$-I. Figure S14a shows the spectrum of I-ME-PAMA-I polymer. The PE-I site proton (I-CH, proton **d**, 5.89 ppm) completely disappeared, meaning 100% initiation from the PE-I site. 95% of the I-ME site remained unreacted, as calculated from the signal areas of the I-ME site (I-CH, proton **b**, 4.95 ppm) and the phenyl group in the initiator (-C$_6H_4$-, proton **c**, 7.42-7.13 ppm). The number of AMA units (30 units) was calculated from the signal areas of the AMA units (-CH, proton **v**, 6.06-5.94 ppm) and the phenyl group in the initiator (-C$_6H_4$-, proton **c**, 7.42-7.13 ppm). Figure S14b shows the spectrum of I-ME-PAMA-PSMA-I. 95% of the I-ME site remained unreacted, as calculated in a similar manner. The number of the SMA units (9 units) was calculated from the signal areas of the SMA units (-CH, proton **l**, 4.45-4.34 ppm) and the phenyl group in the initiator (-C$_6H_4$-, proton **c**, 7.42-7.13 ppm). Figure S14c shows the spectrum of I-PEEA-PAMA-PSMA-PEEA-I. The I-ME site proton (I-CH, proton **b**, 4.95 ppm) completely disappeared, meaning 100% initiation from the I-ME site. The number of the EEA units (308 units) was calculated from the signal areas of the EEA units (-CH in the

backbone, proton **o**, 2.56-2.34 ppm) and the AMA units (-C*H*, proton **v**, 6.06-5.94 ppm) (30 units). Figure S14d shows the spectrum of I-PEEA-PAMA-PGLMMA-PEEA-I. The SMA units (-C*H*, proton **l**, 4.45-4.34 ppm) completely disappeared, meaning a full conversion of the SMA units to the GLMMA units.

Preparation of Micelles. To a pre-warmed DMF solution (0.2 mL) of a CABC tetrablock terpolymer (0.0110 g) in an oil bath (60 ^{o}C), warm water (2 mL, 60 ^{o}C) was added slowly under stirring at 60 ^{o}C (water/DMF = 10/1 (v/v)). The obtained micellar solutions were studied with DLS at prescribed temperatures using temperature controllers.

Preparation of crosslinked micelles. The micellar solution was transferred to a reaction tube contained the 4,4'-azobis(4-cyanovaleric acid) (V501) (1 equiv to 30 AMA units (30 vinyl groups)). The reaction was conducted under argon atmosphere with magnetic stirring for 2 h at 60 ^{o}C.

2. ¹H NMR Spectral Data
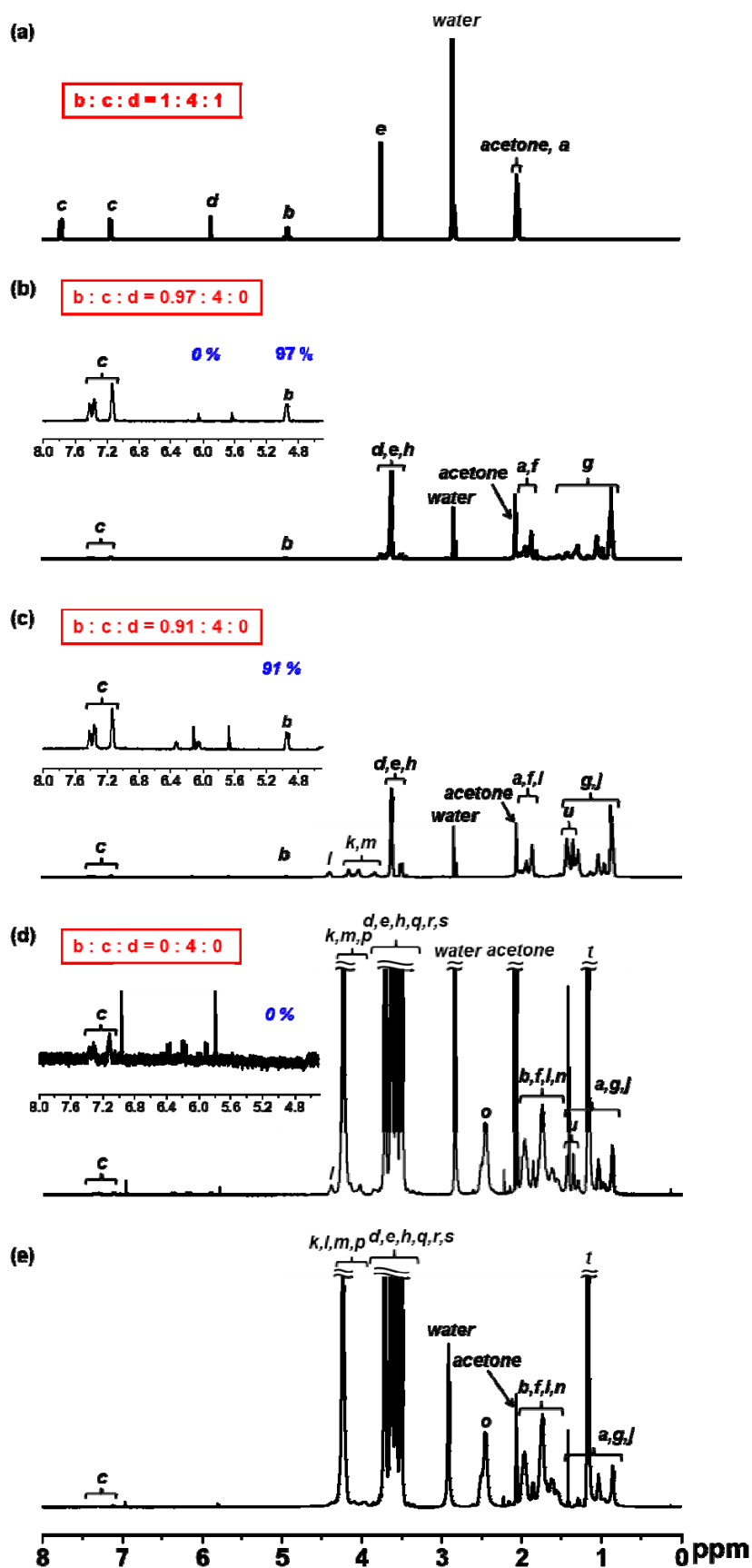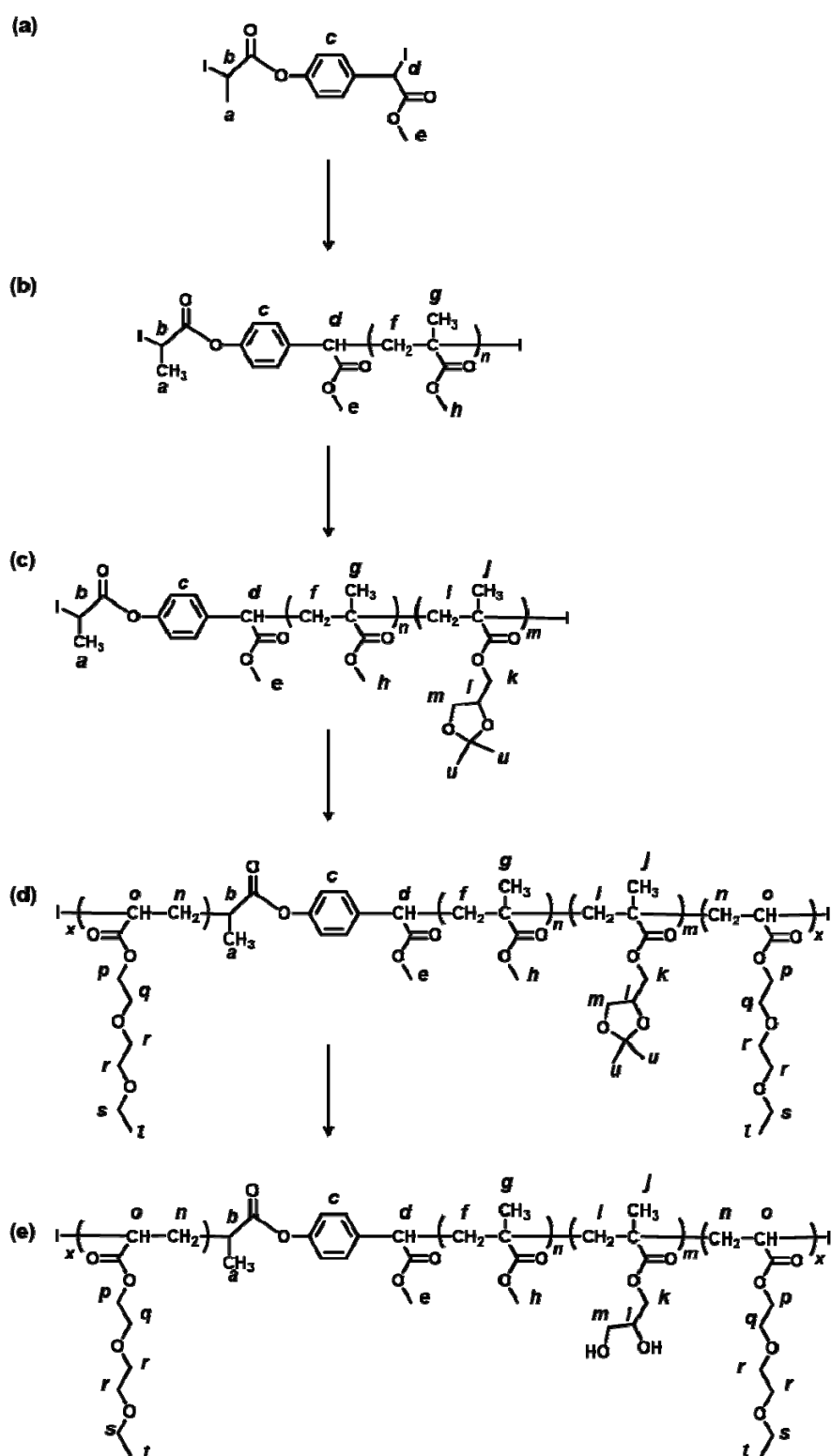
Figure S1. ^{1}H NMR spectra (acetone-d_6) of (a) I-MEPE-I, (b) I-ME-PMMA-I, (c) I-ME-PMMA-PSMA-I, (d) I-PEEA-PMMA-PSMA-PEEA-I, and (e) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entries 1, 2, and 3-1)).
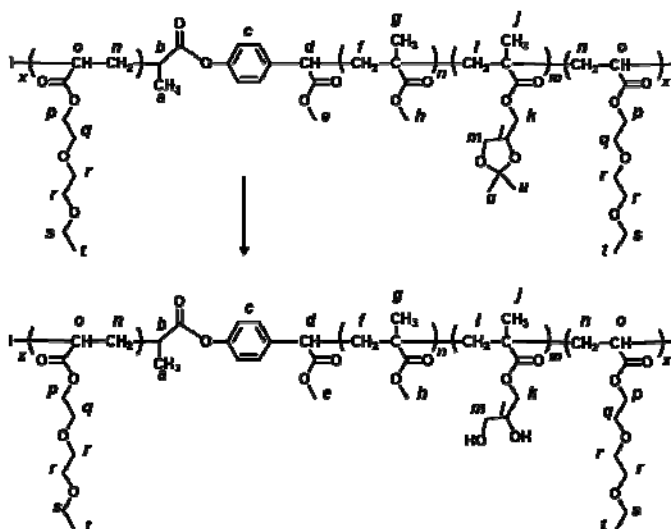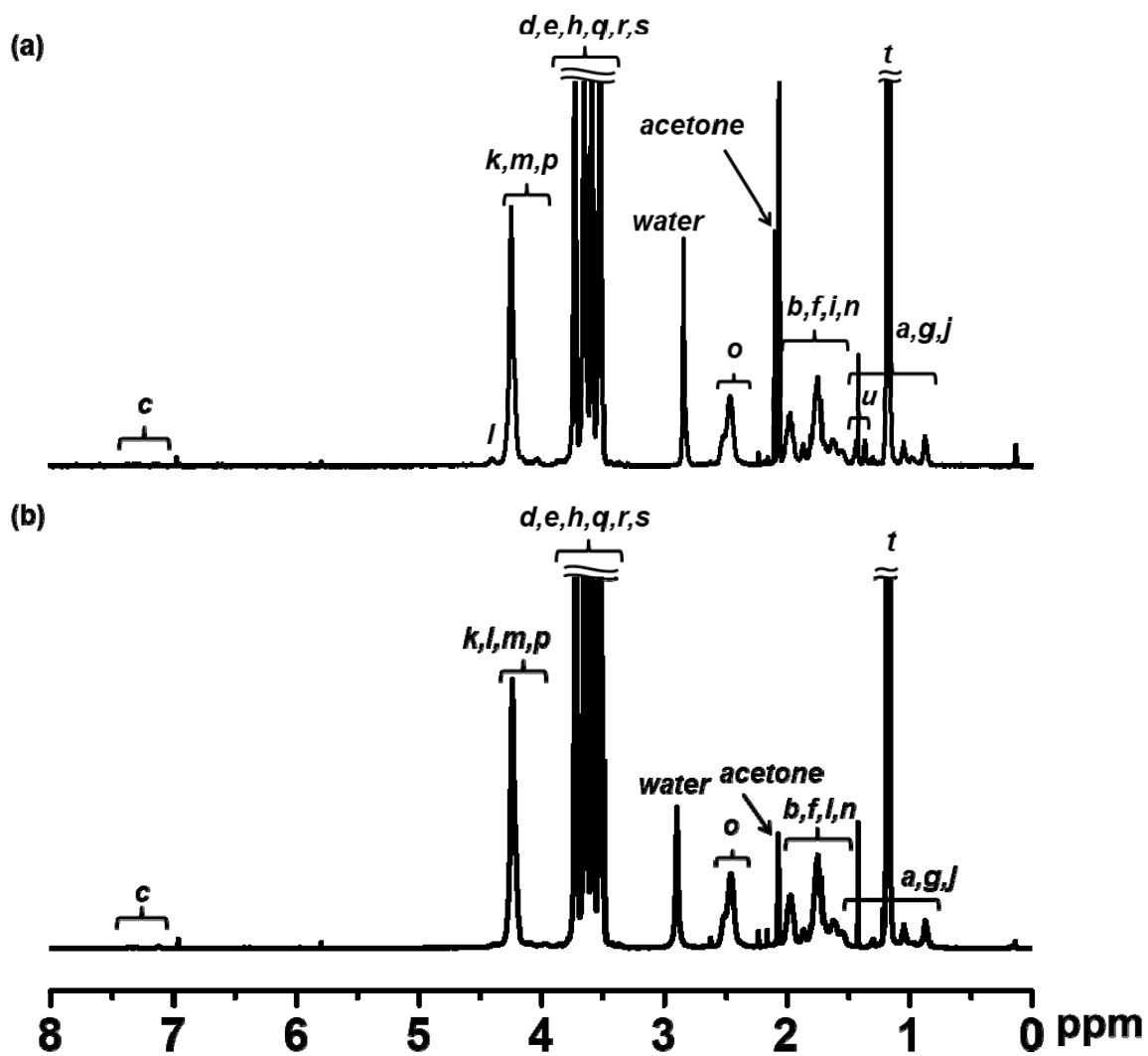
Figure S2. ^{1}H NMR spectra (acetone-d_6) of (a) I-PEEA-PMMA-PSMA-PEEA-I and (b) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entry 3-2)).
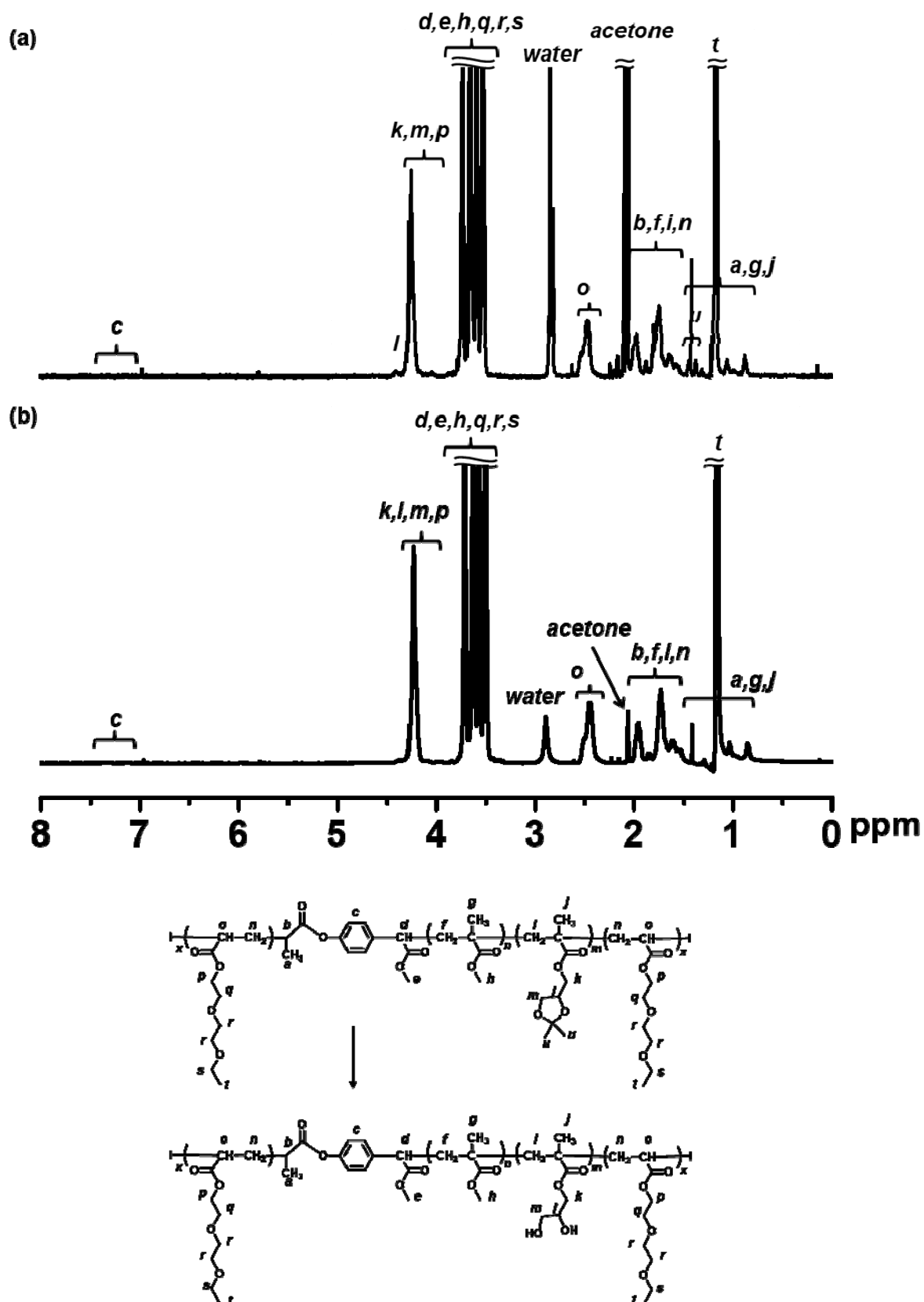
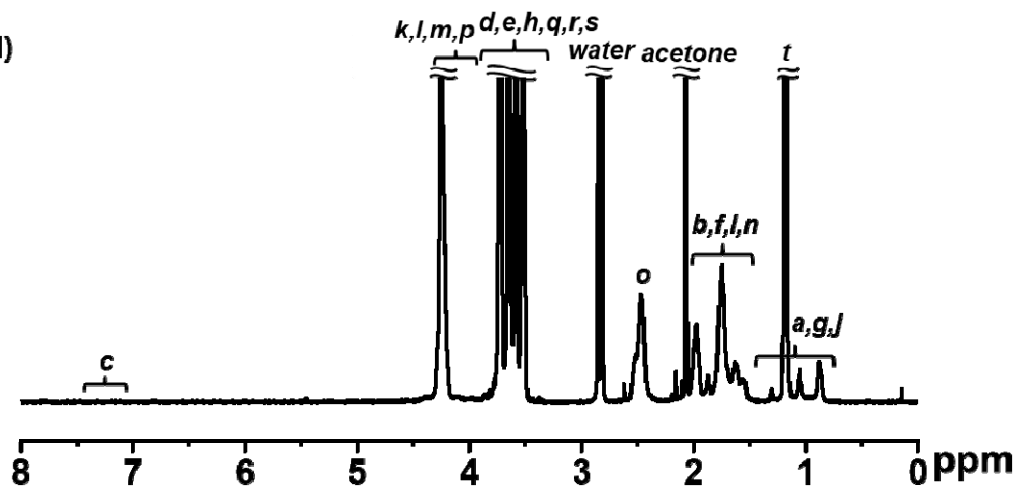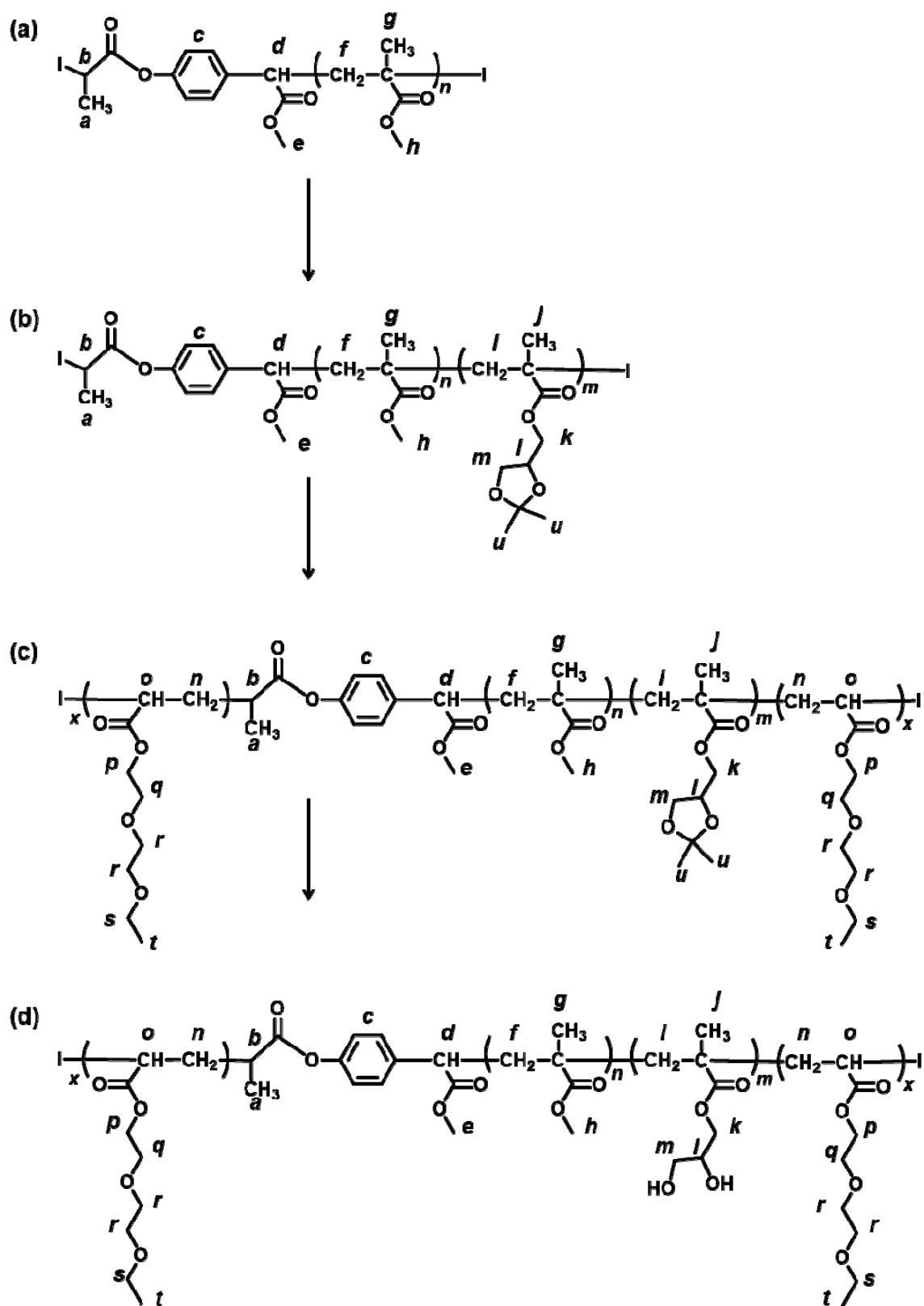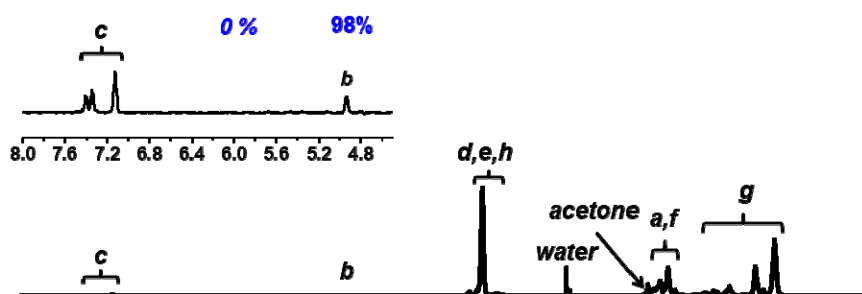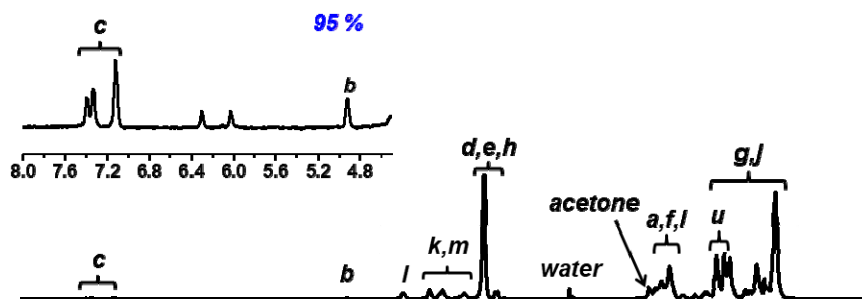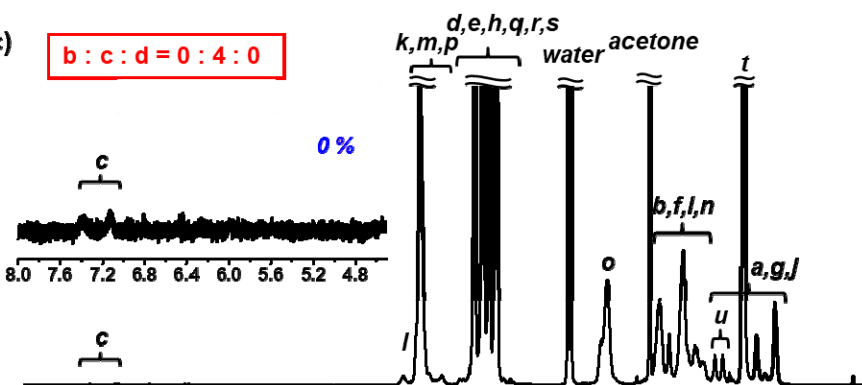**Figure S3.** ^{1}H NMR spectra (acetone-d_6) of (a) I-PEEA-PMMA-PSMA-PEEA-I and (b) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entry 3-3)).
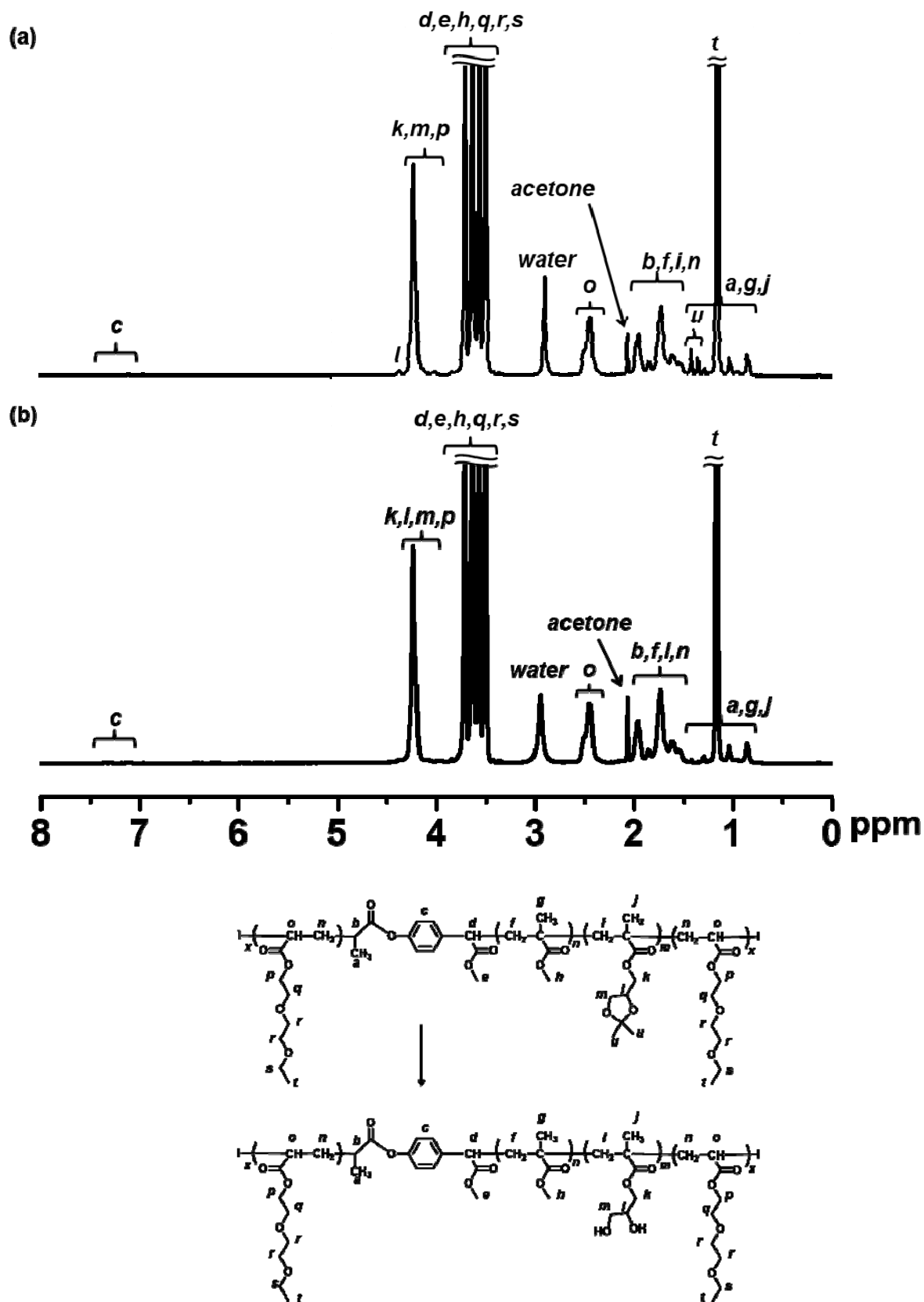
Figure S4. ^{1}H NMR spectra (acetone-d_6) of (a) I-PEEA-PMMA-PSMA-PEEA-I and (b) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entry 3-4)).
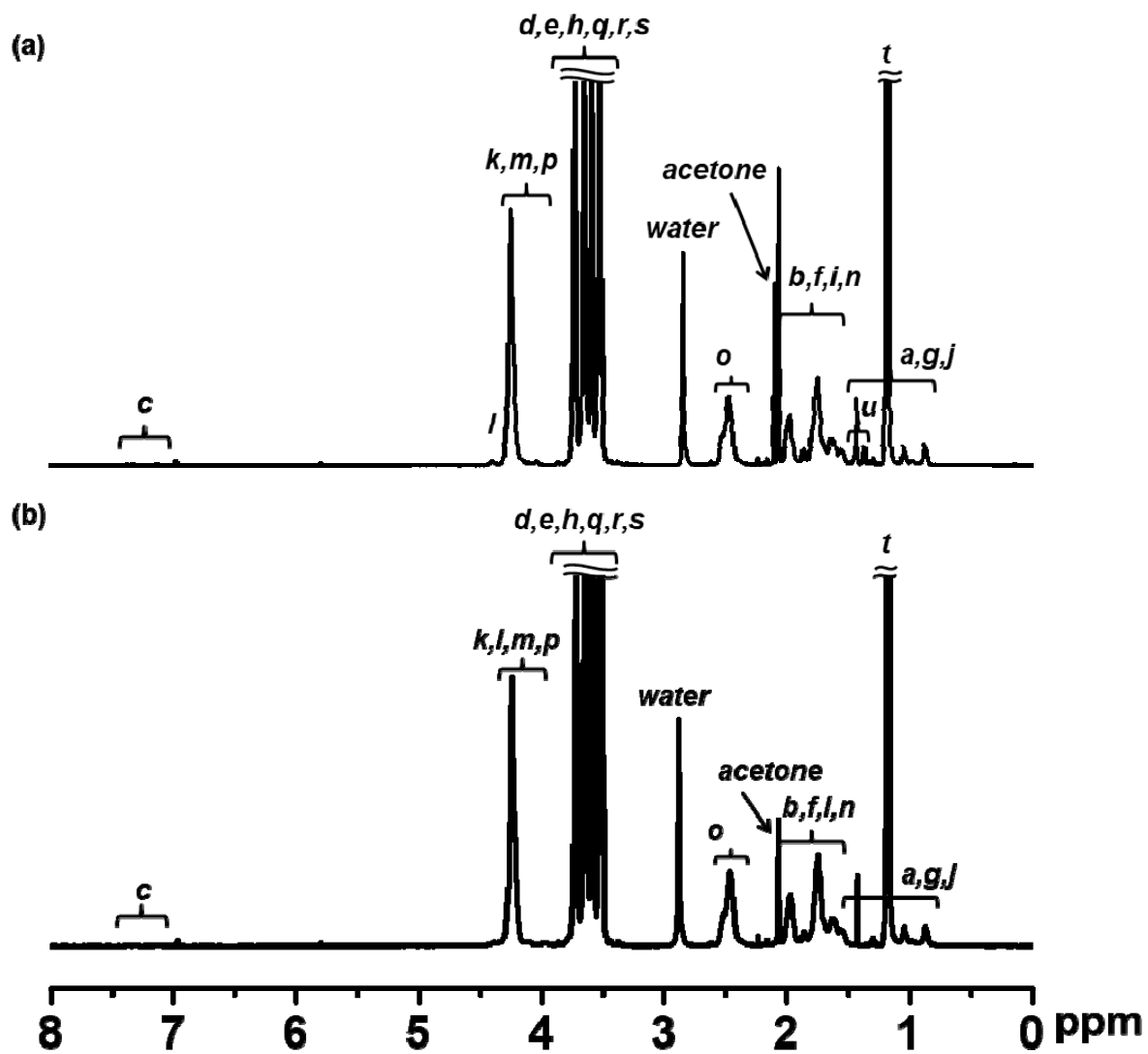
Figure S5. ^{1}H NMR spectra (acetone-d_6) of (a) I-PEEA-PMMA-PSMA-PEEA-I and (b) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entry 3-5)).
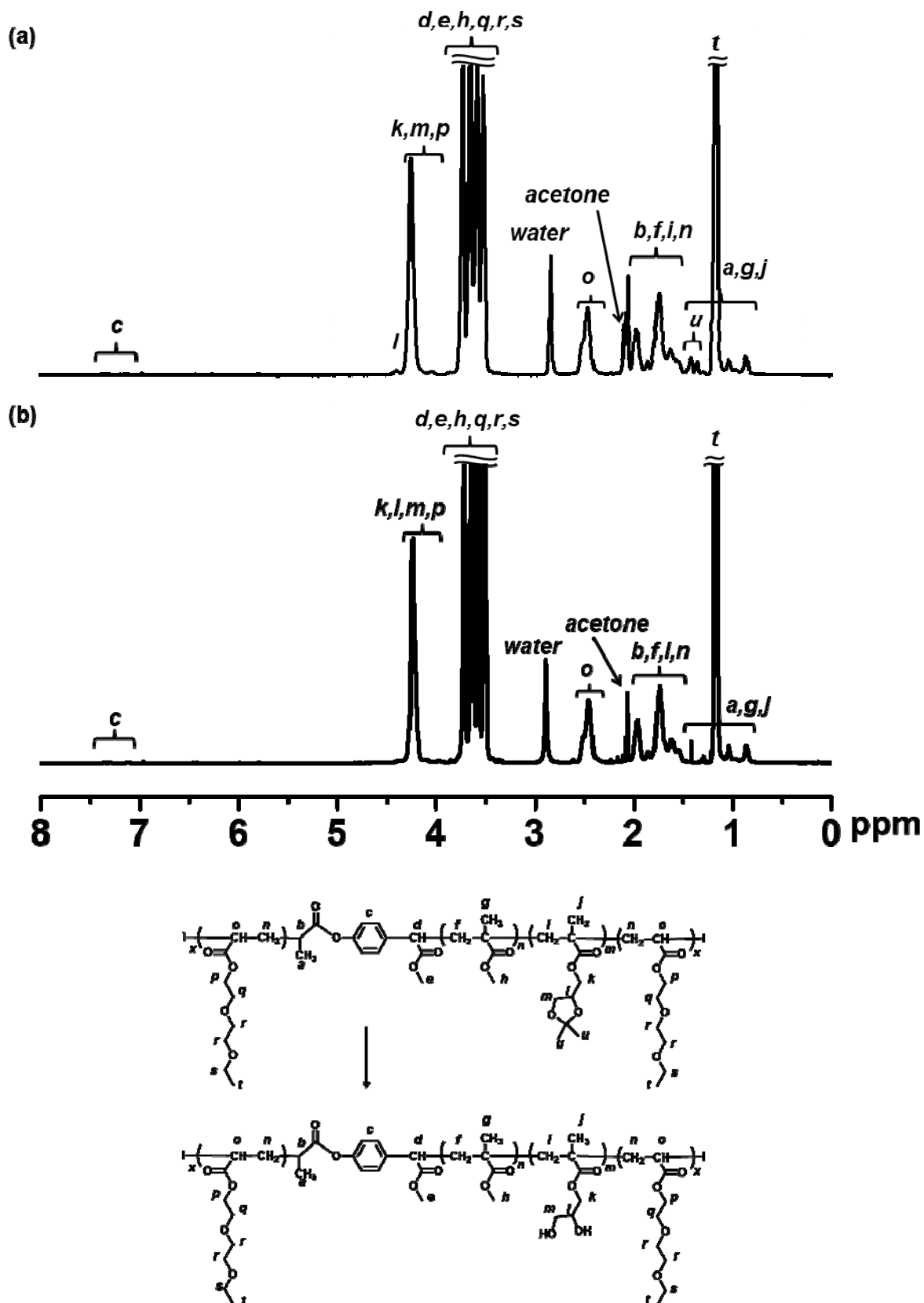
Figure S6. ^{1}H NMR spectra (acetone-d_6) of (a) I-PEEA-PMMA-PSMA-PEEA-I and (b) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entry 3-6)).
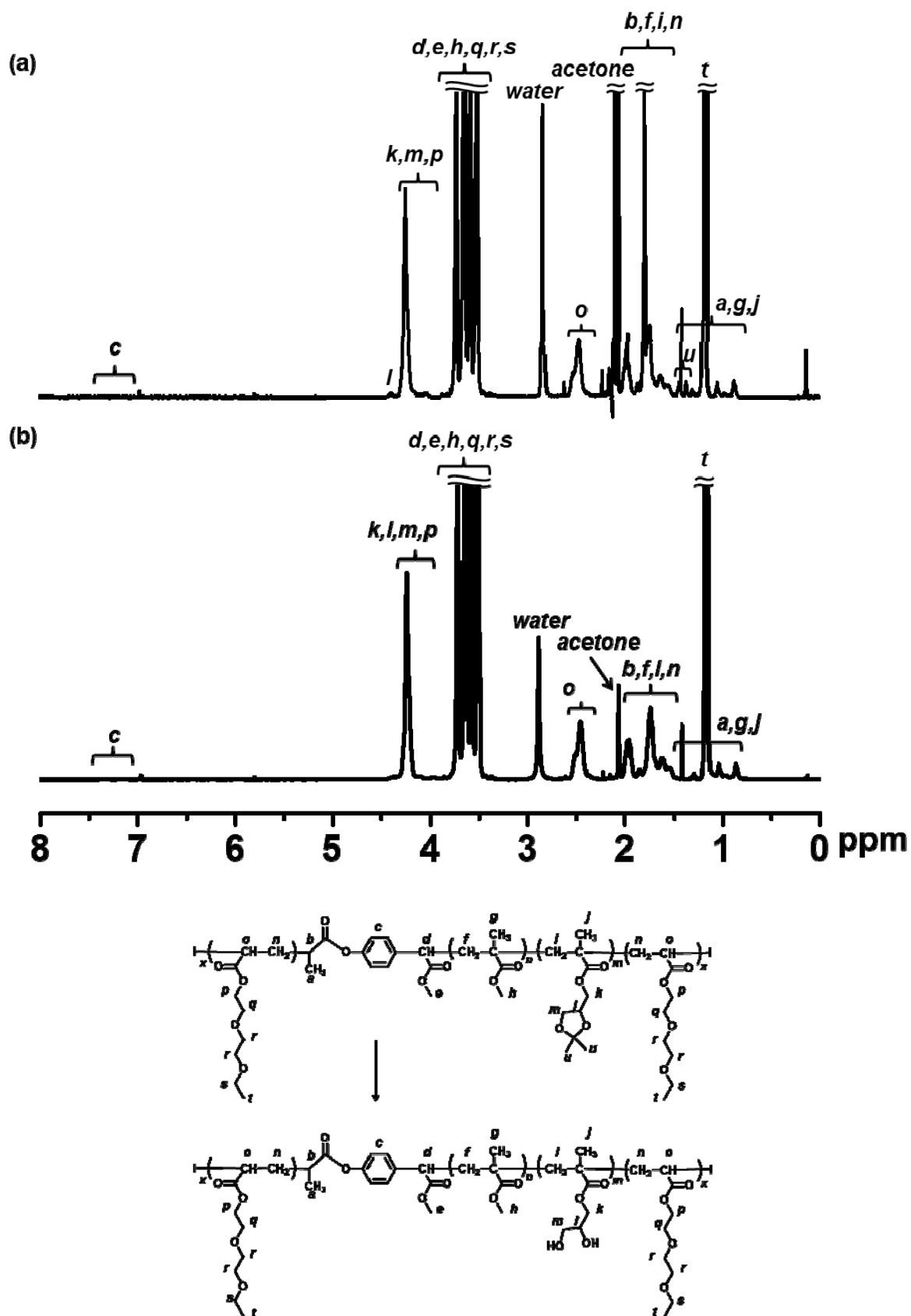
Figure S7. ^{1}H NMR spectra (acetone-d_6) of (a) I-PEEA-PMMA-PSMA-PEEA-I and (b) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entry 3-7)).
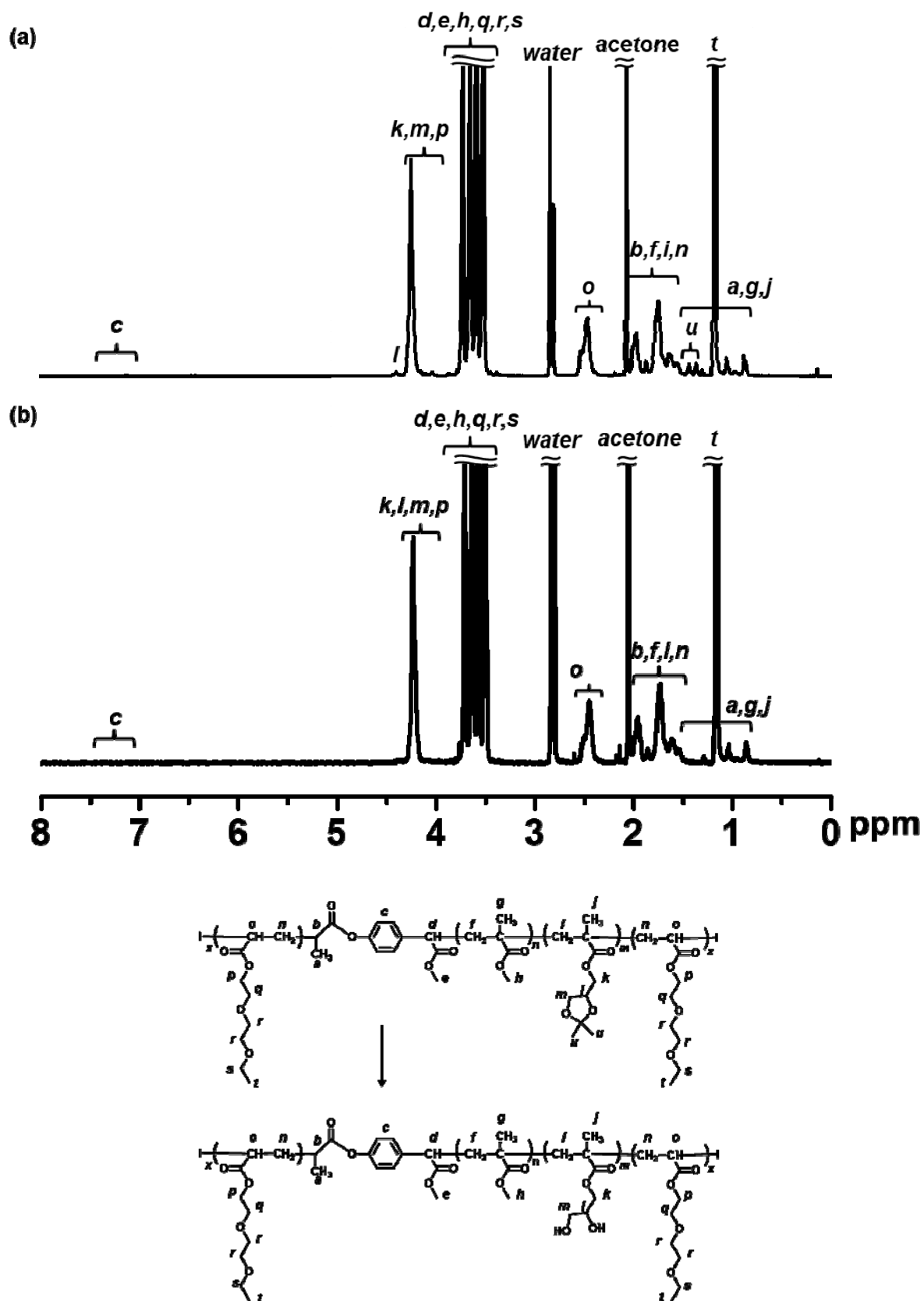
Figure S8. ^{1}H NMR spectra (acetone-d_6) of (a) I-PEEA-PMMA-PSMA-PEEA-I and (b) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entry 3-8)).
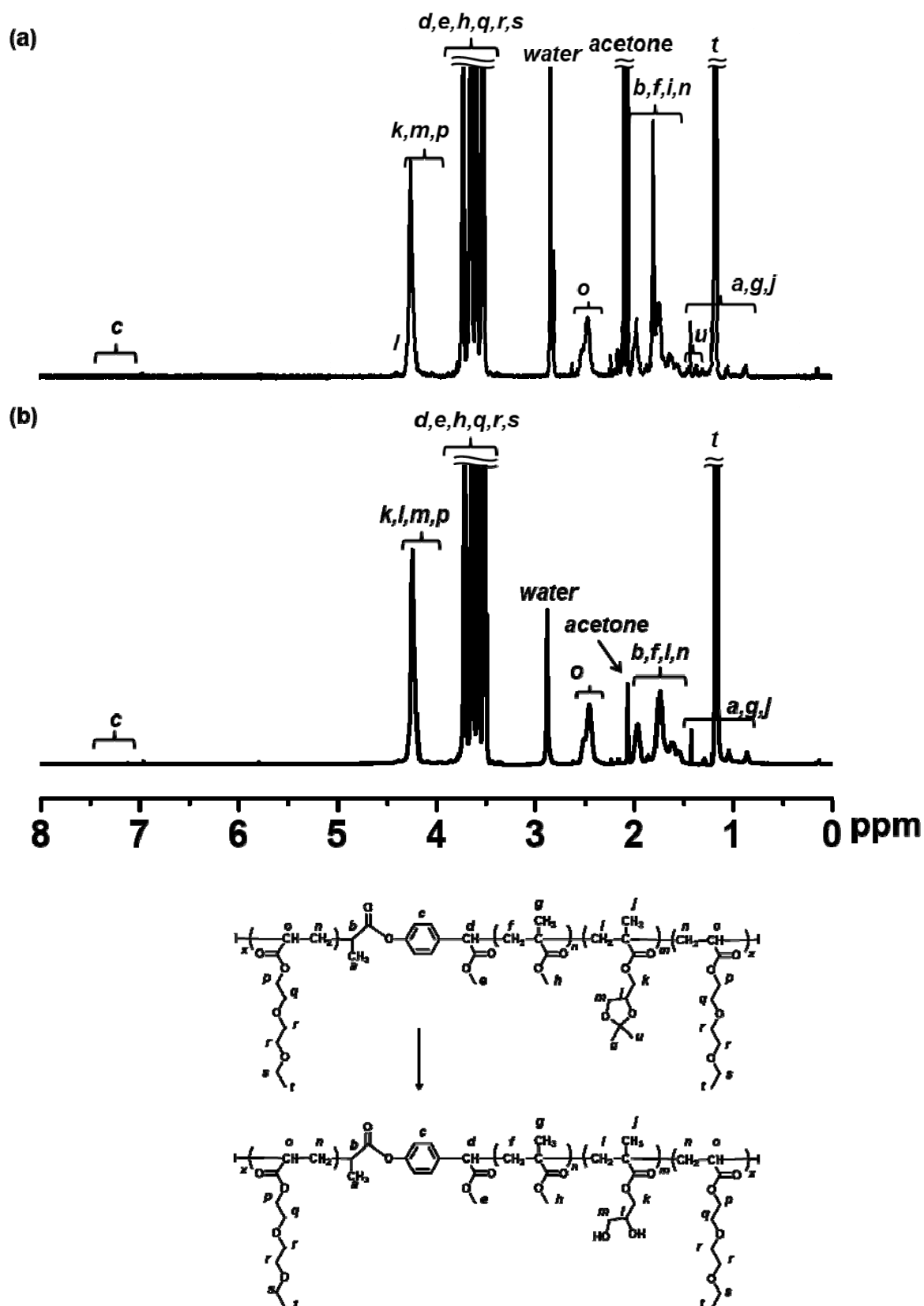
Figure S9. ^{1}H NMR spectra (acetone-d_6) of (a) I-PEEA-PMMA-PSMA-PEEA-I and (b) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S1 (entry 3-9)).

(a)

b : c : d = 0.94 : 4 : 0

c

0 %   94 %

b

8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8

d,e,h

acetone

a,f   *g*

c

water

b

(b)

b : c : d = 0.94 : 4 : 0

c

94 %

b

8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8

d,e,h

acetone

g,J

k,m   *a,f,l*   *u*

c   *water*

l   b

(c)

b : c : d = 0 : 4 : 0

k,m,p   *d,e,h,q,r,s*

water   *acetone*   *t*

c

0 %

8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8

o   *b,f,l,n*

u   *a,g,J*

c

l

(d)

k,l,m,p *d,e,h,q,r,s*

water *acetone*   *t*

o   *b,f,l,n*

a,g,J

c

8   7   6   5   4   3   2   1   0 ppm
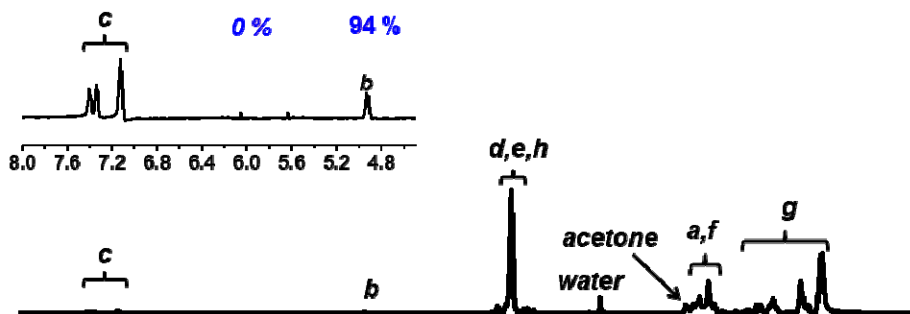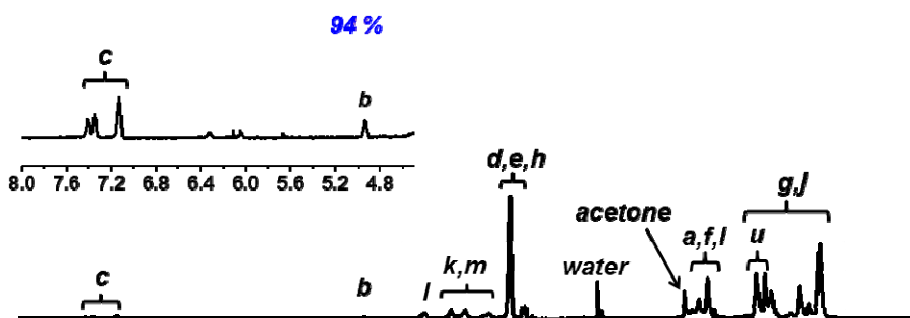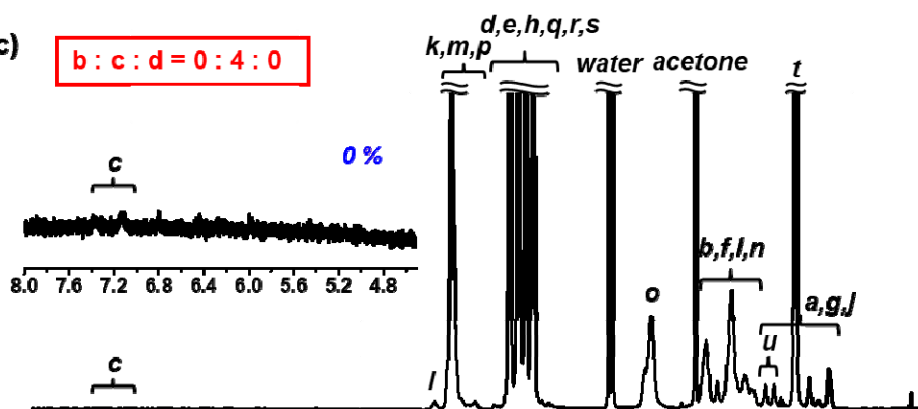
Figure S10. ^{1}H NMR spectra (acetone-d_6) of (a) I-ME-PMMA-I, (b) I-ME-PMMA-PSMA-I, (c) I-PEEA-PMMA-PSMA-PEEA-I, and (d) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S2 (entries 1-1, 1-2, and 1-3)).
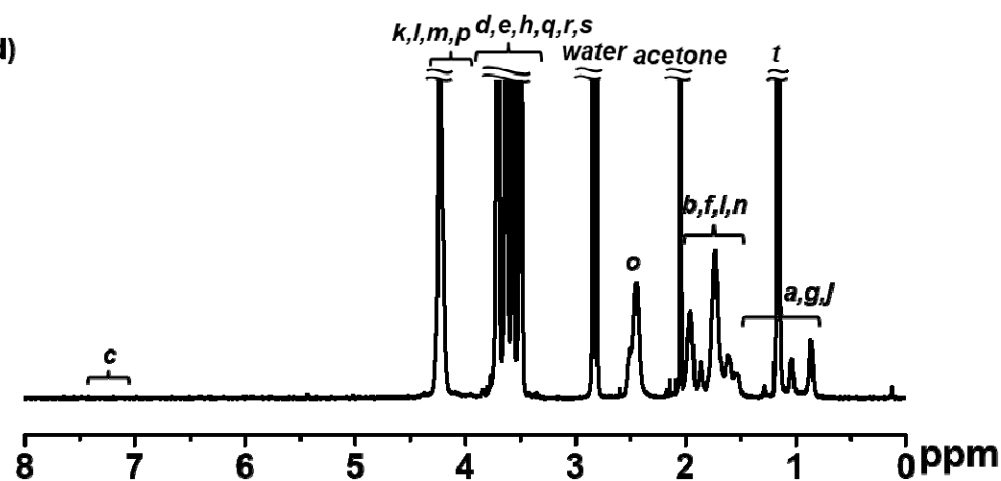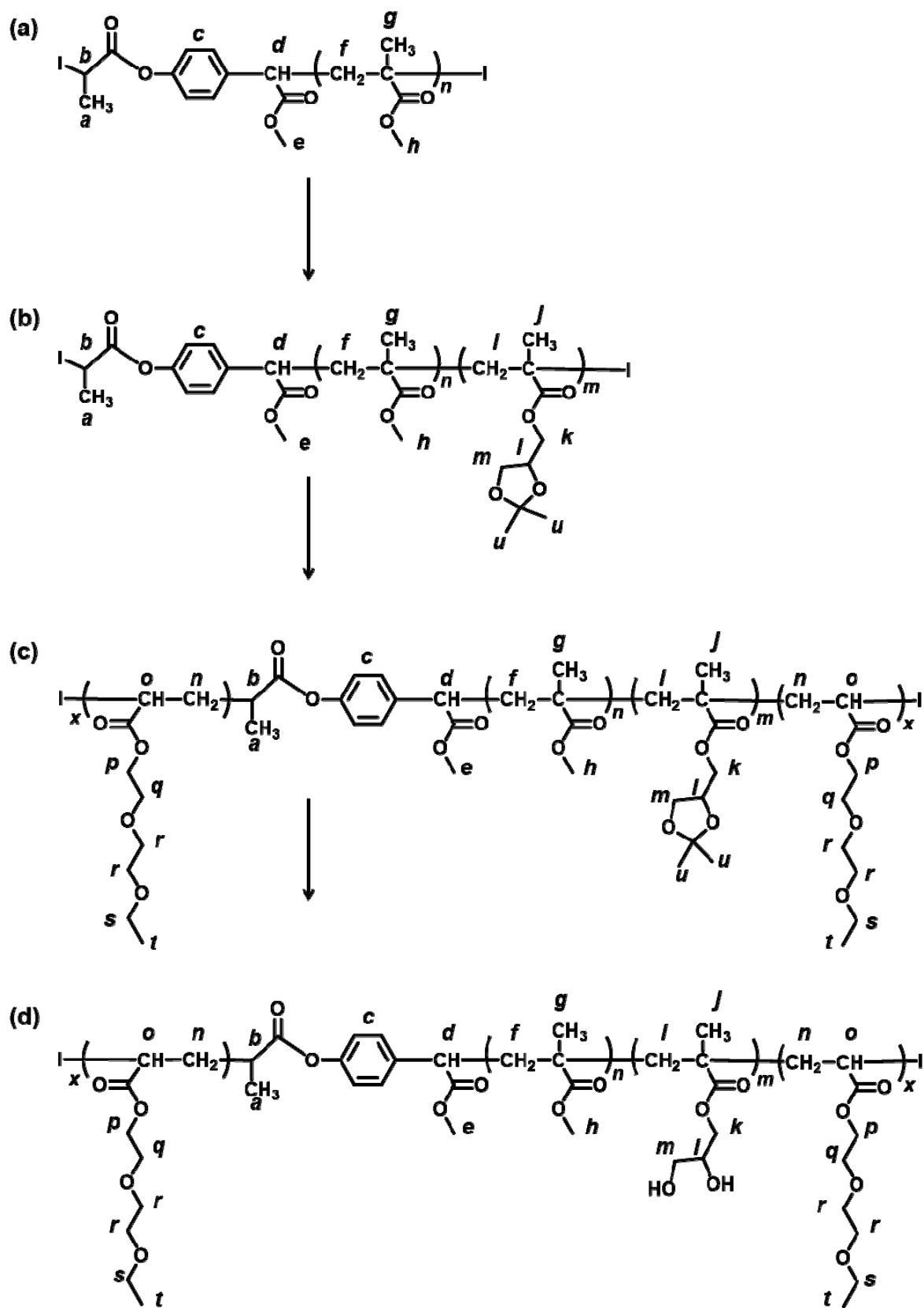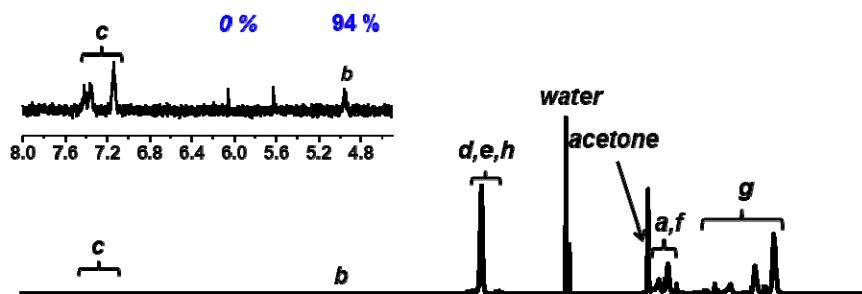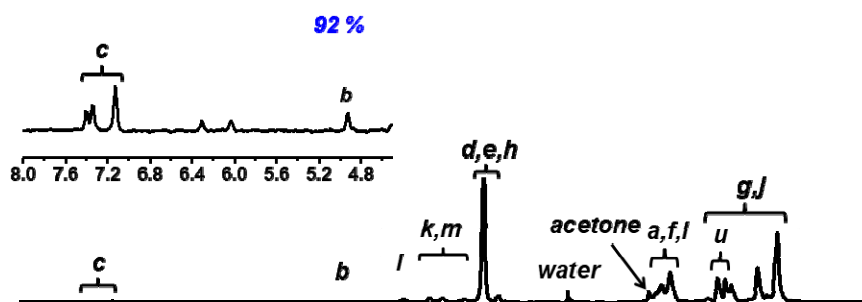
(a) b : c : d = 0.98 : 4 : 0

(b) b : c : d = 0.95 : 4 : 0

(c) b : c : d = 0 : 4 : 0

(d)
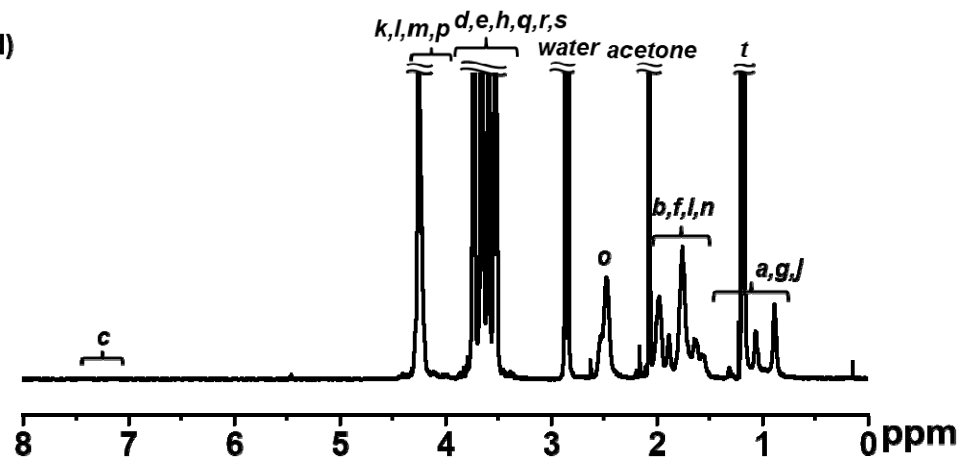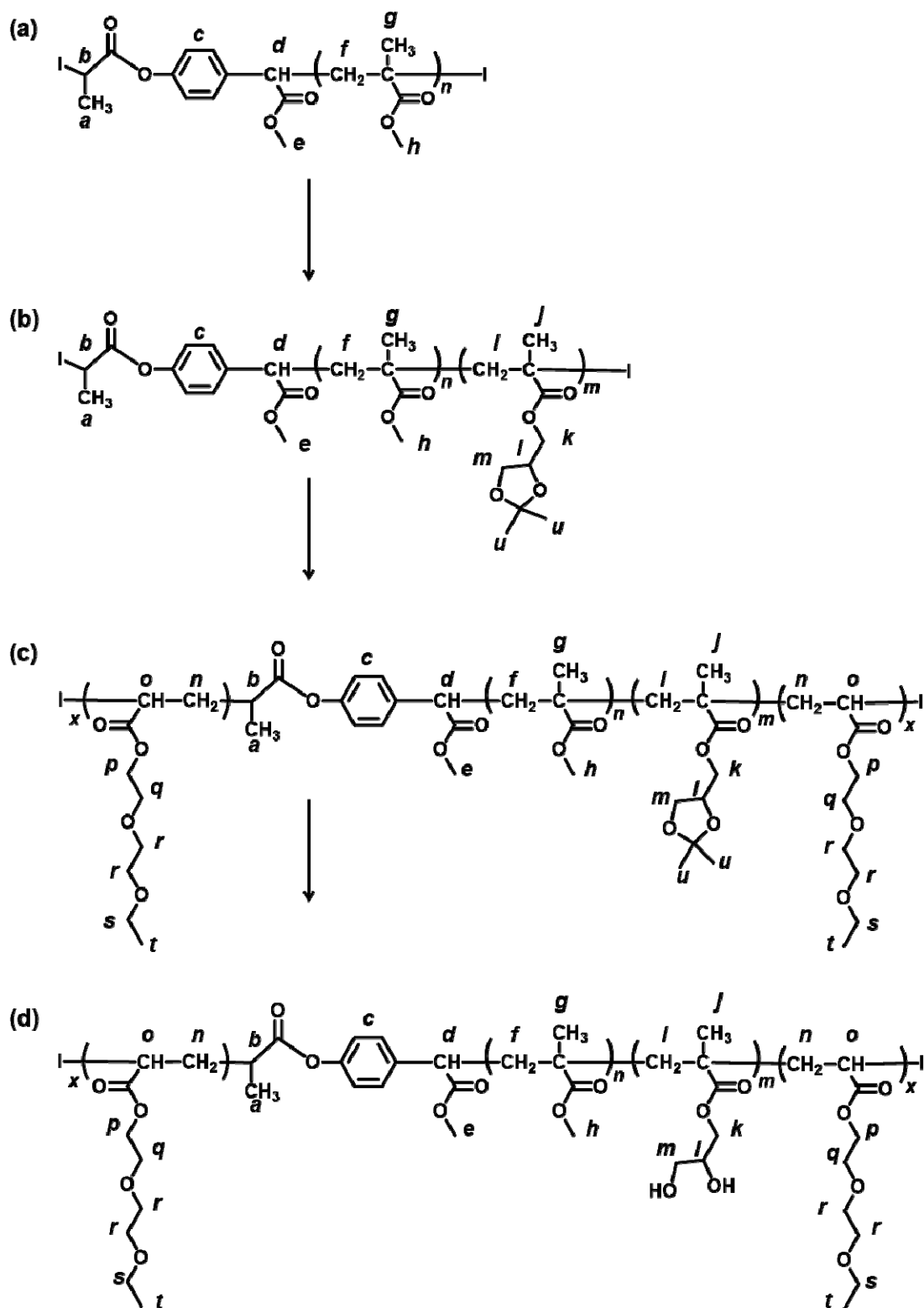
Figure S11. ^{1}H NMR spectra (acetone-d_6) of (a) I-ME-PMMA-I, (b) I-ME-PMMA-PSMA-I, (c) I-PEEA-PMMA-PSMA-PEEA-I, and (d) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S2 (entries 2-1, 2-2, and 2-3)).
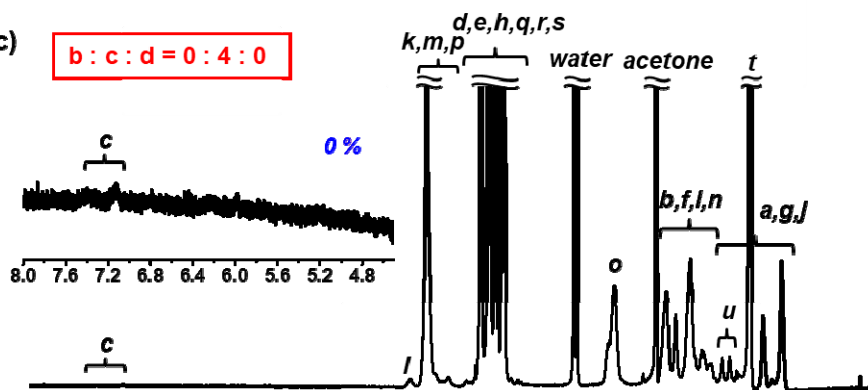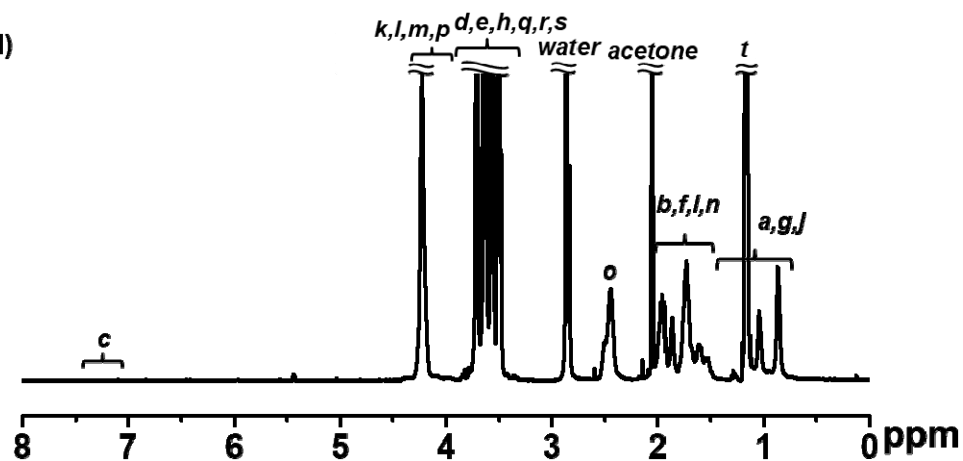
(a) b : c : d = 0.97 : 4 : 0

0 % 97 %

c

b

d,e,h
acetone
water
a,f
g

c

b

(b) b : c : d = 0.97 : 4 : 0

97 %

c

b

d,e,h
acetone
water
a,f,l
g,J
u

c

b

l
k,m

(c) b : c : d = 0 : 4 : 0

0 %

c

c

k,m,p
d,e,h,q,r,s
water
acetone
t

b,f,l,n
o
a,g,J
u

l

(d)

k,l,m,p
d,e,h,q,r,s
water
acetone
t

b,f,l,n
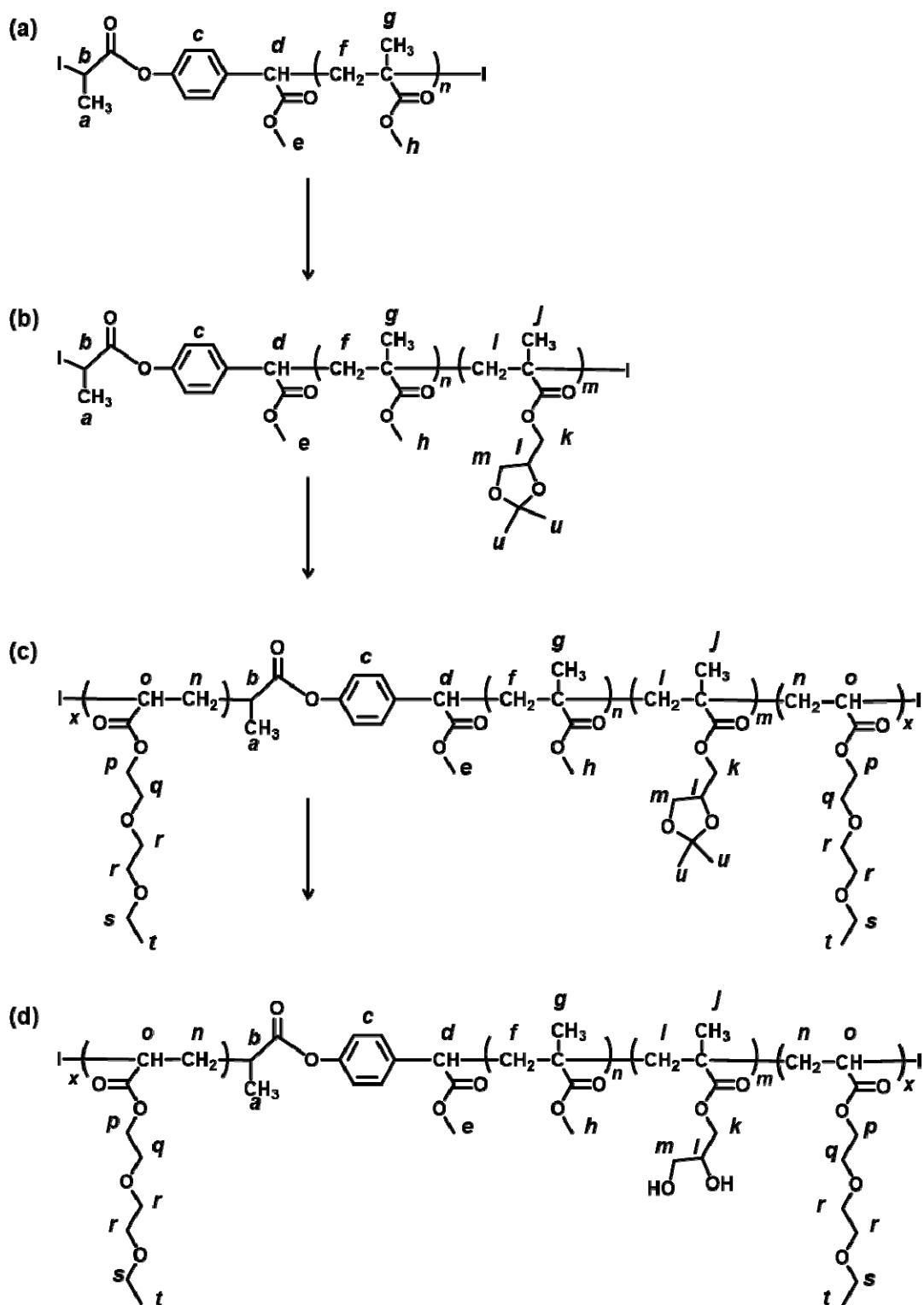o
a,g,J

c

8 7 6 5 4 3 2 1 0 ppm

S27
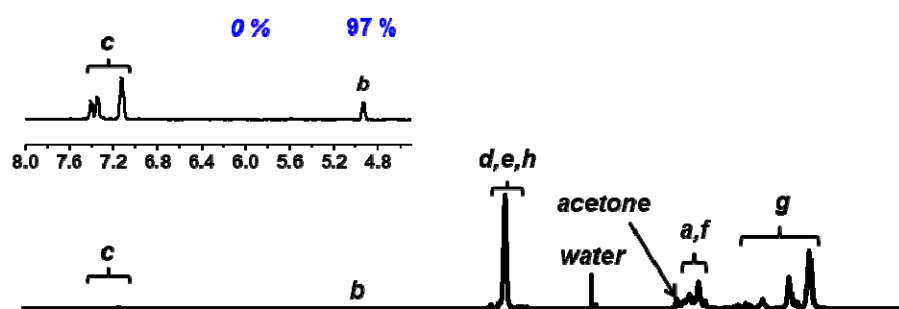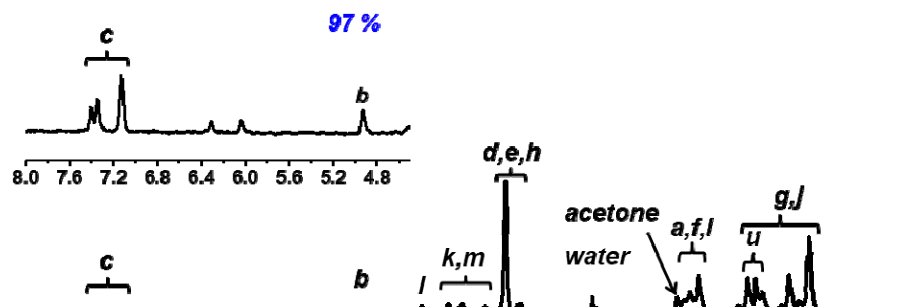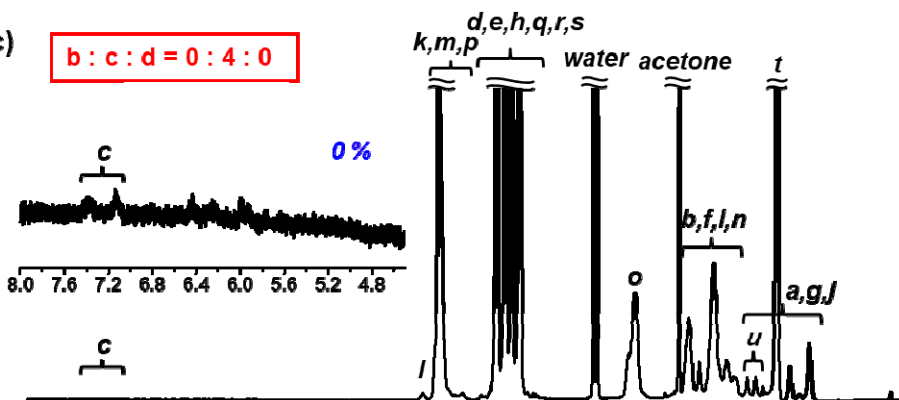
Figure S12. ^{1}H NMR spectra (acetone-d_6) of (a) I-ME-PMMA-I, (b) I-ME-PMMA-PSMA-I, (c) I-PEEA-PMMA-PSMA-PEEA-I, and (d) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S2 (entries 3-1, 3-2, and 3-3)).

(a) b : c : d = 0.94 : 4 : 0

0 %   94 %

c   *b*

8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8

d,e,h   water   acetone   *a,f*   *g*

c   *b*

(b) b : c : d = 0.92 : 4 : 0

92 %

c   *b*

8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8

d,e,h   *k,m*   acetone   *a,f,l*   *g,J*   water   *u*

c   *b*   *l*

(c) b : c : d = 0 : 4 : 0

k,m,p   *d,e,h,q,r,s*   water   acetone   *t*

0 %

c

8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8

b,f,l,n   *a,g,J*   *o*   *u*

c   *l*

(d)

k,l,m,p   *d,e,h,q,r,s*   water   acetone   *t*

b,f,l,n   *a,g,J*   *o*

c

8   7   6   5   4   3   2   1   0 **ppm**

Figure S13. ^{1}H NMR spectra (acetone-d_6) of (a) I-ME-PMMA-I, (b) I-ME-PMMA-PSMA-I, (c) I-PEEA-PMMA-PSMA-PEEA-I, and (d) I-PEEA-PMMA-PGLMMA-PEEA-I (Table S2 (entries 4-1, 4-2, and 4-3)).
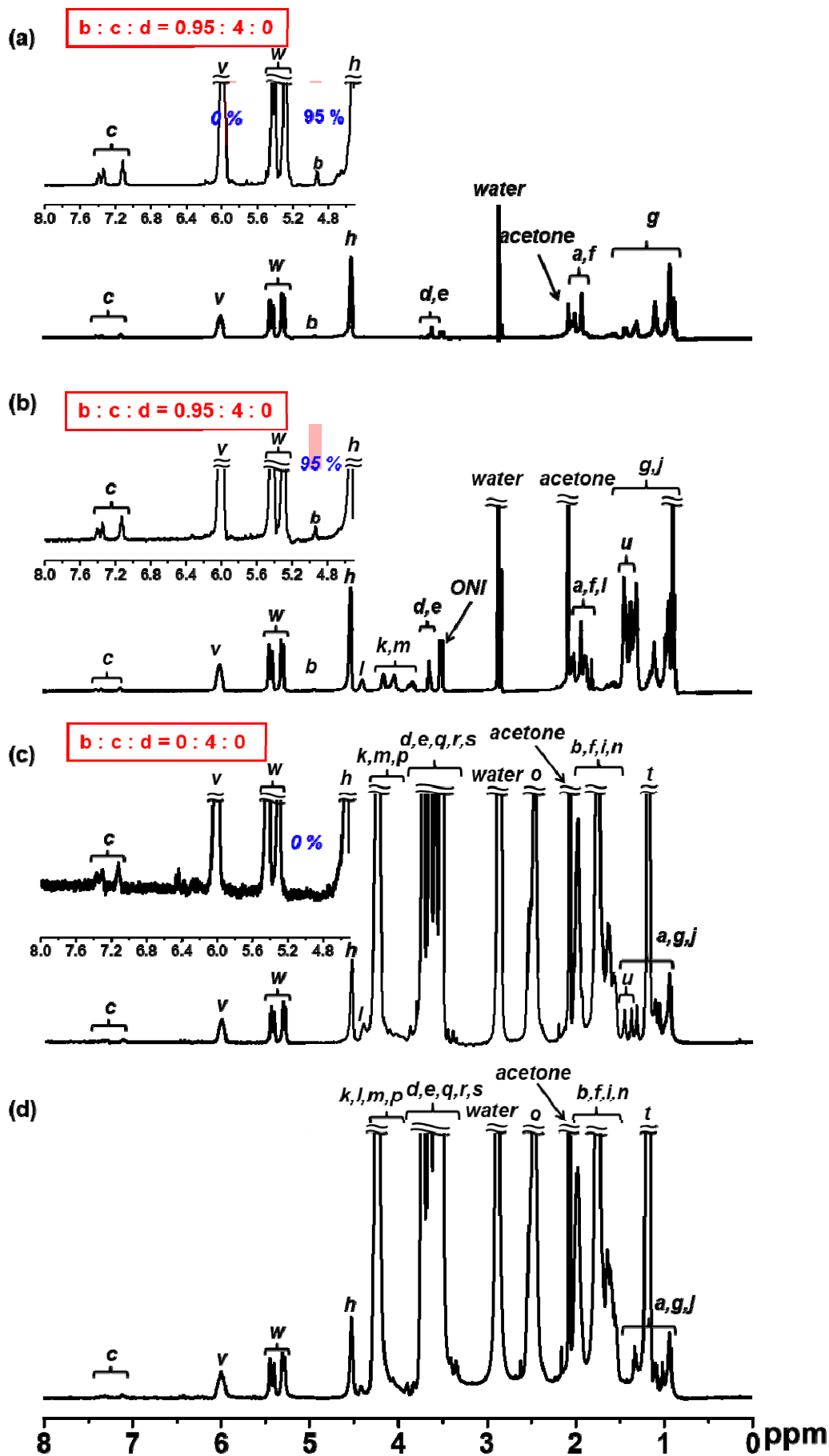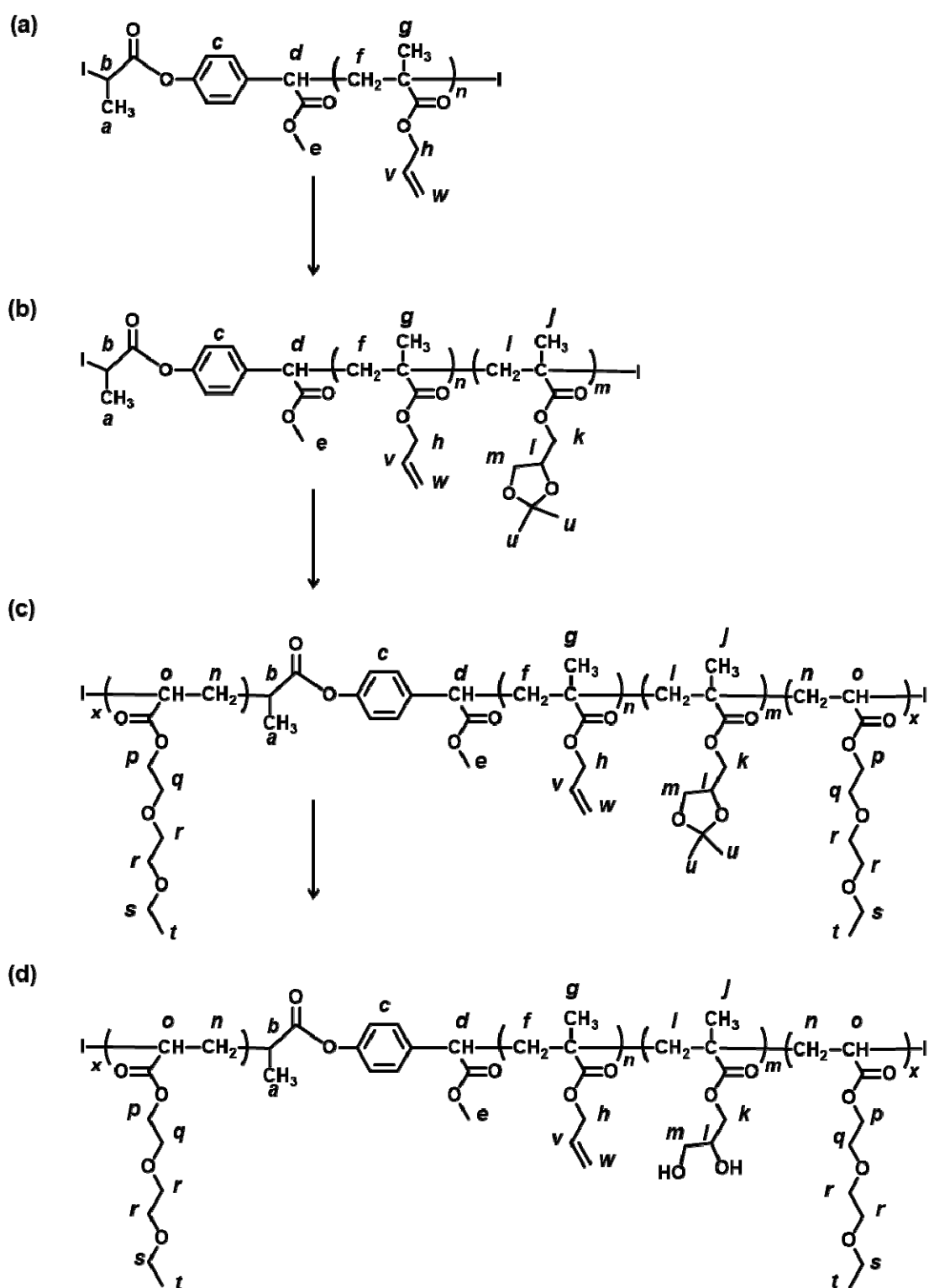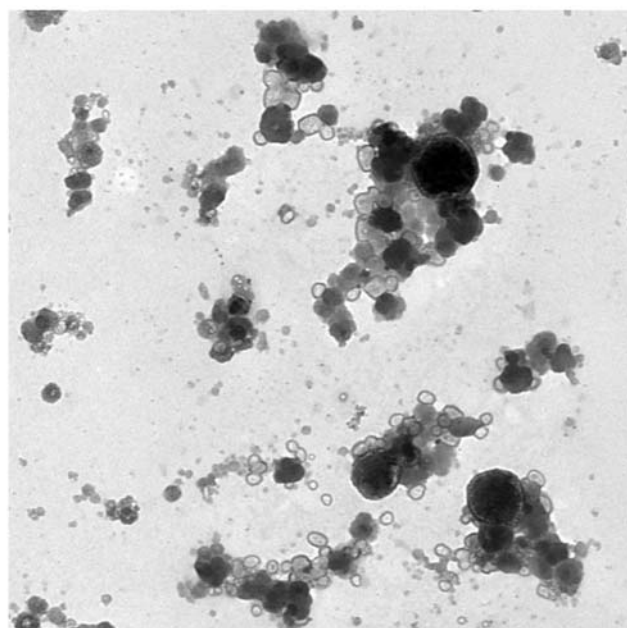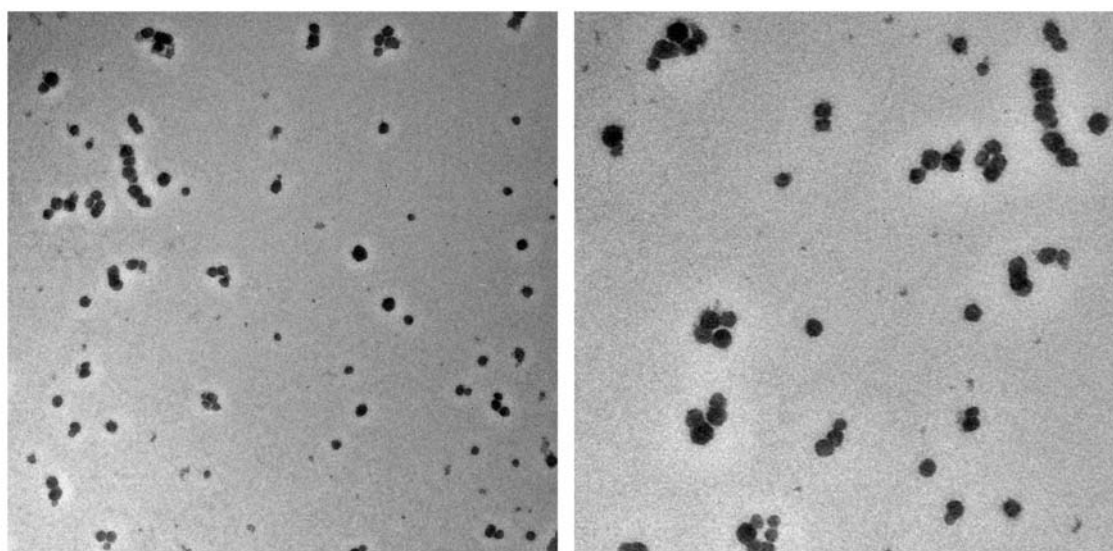
Figure S14. ^{1}H NMR spectra (acetone-d_6) of (a) I-ME-PAMA-I, (b) I-ME-PAMA-PSMA-I, (c) I-PEEA-PAMA-PSMA-PEEA-I, and (d) I-PEEA-PAMA-PGLMMA-PEEA-I (Table S2 (entries 5-1, 5-2, and 5-3)).

Figure S15. TEM images of the self-assemblies of sample E = PEEA$_{140}$-PMMA$_{25}$-PGLMMA$_{10}$-PEEA$_{140}$ tetrablock terpolymer (prepared at room temperature).

Figure S16. TEM images of the self-assemblies of sample D = PEEA$_{128}$-PMMA$_{25}$-PGLMMA$_{10}$-PEEA$_{128}$ tetrablock terpolymer (prepared at 60 ^{o}C).
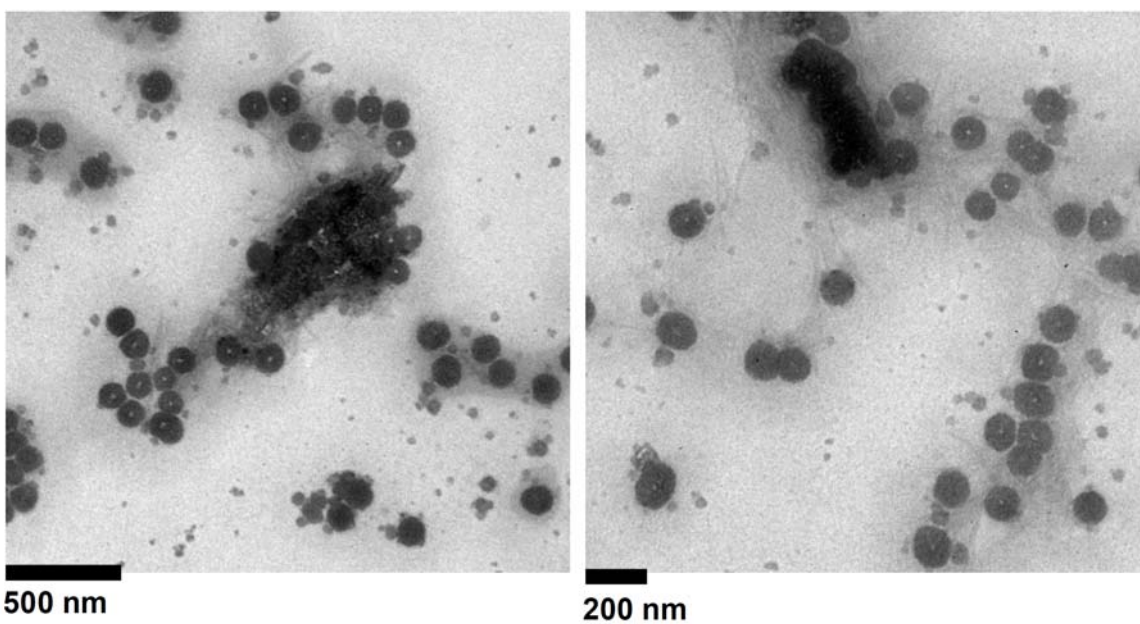
Figure S17. TEM images of the self-assemblies of E = $PEEA_{140}$-$PMMA_{25}$-$PGLMMA_{10}$-$PEEA_{140}$ tetrablock terpolymer (prepared at 60 ^{o}C).
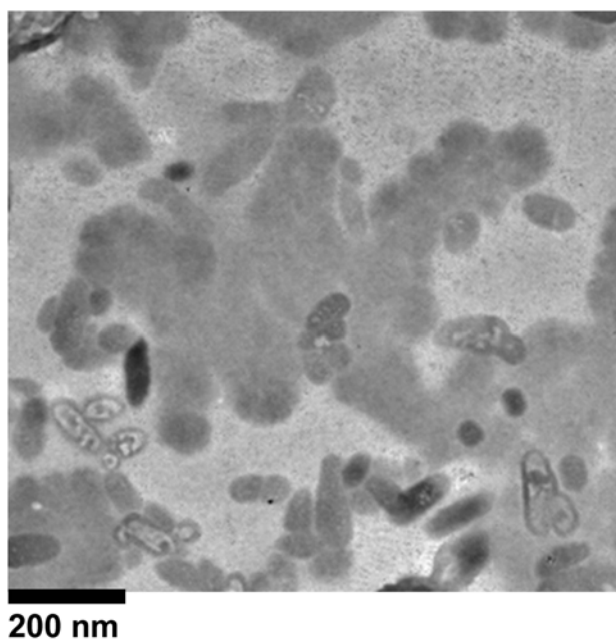
Figure S18. TEM images of the self-assemblies of sample G = $PEEA_{150}$-$PMMA_{50}$-$PGLMMA_{10}$-$PEEA_{150}$ tetrablock terpolymer (prepared at 60 ^{o}C).
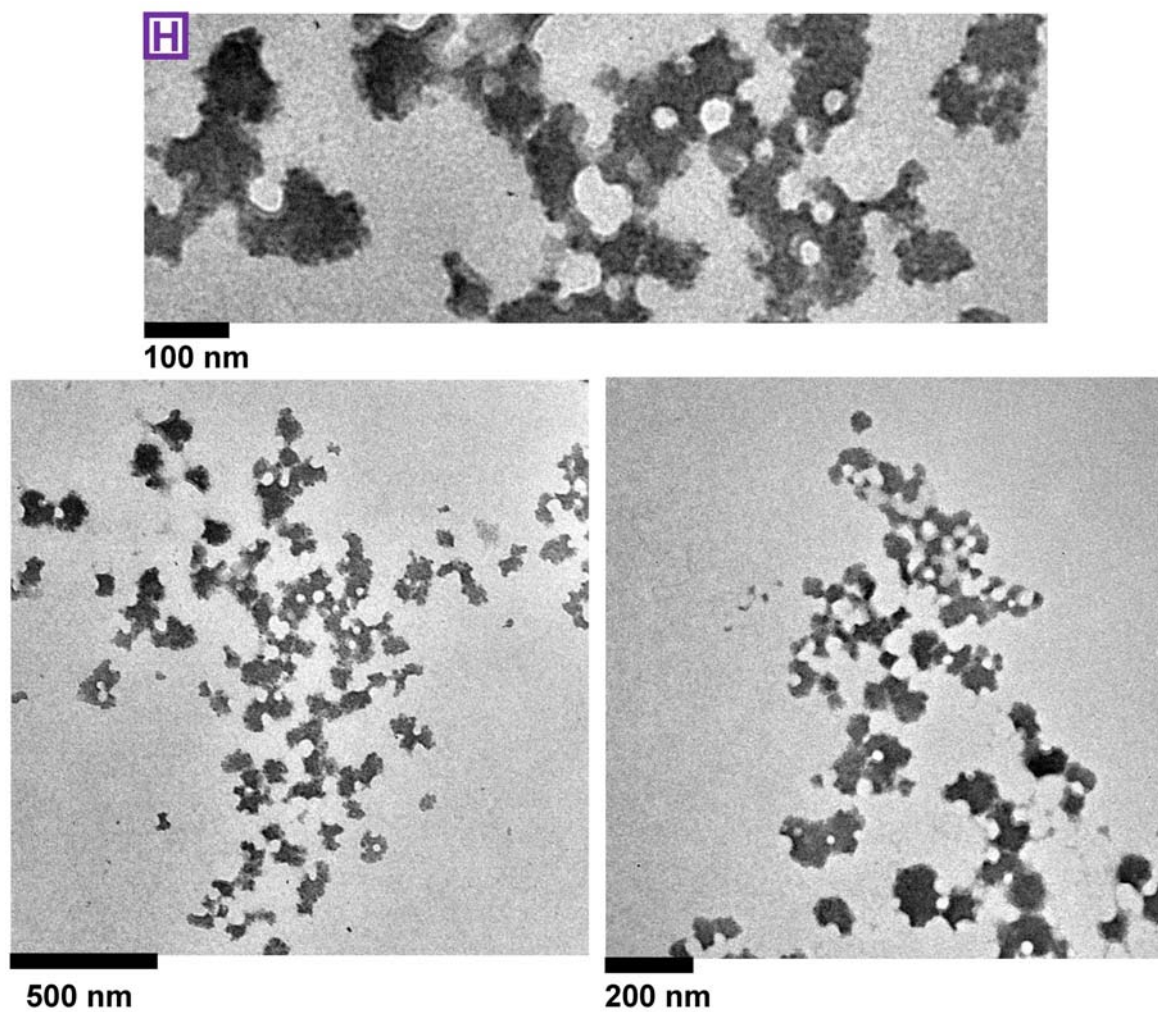
Figure S19. TEM images of the self-assemblies of sample H = PEEA$_{156}$-PMMA$_{98}$-PGLMMA$_{10}$-PEEA$_{156}$ tetrablock terpolymer (prepared at 60 ^{o}C).

3. Reference

(1) J. Zheng, C. Chen and A. Goto, *Angew. Chem. Int. Ed.*, 2020, **59**, 1941-1949.