Electronic Supplementary Material (ESI) for Polymer Chemistry.

Influence of Solvent on RAFT-mediated Polymerization of Benzyl Methacrylate (BzMA) and How to Overcome the Thermodynamic/Kinetic Limitation of Morphology Evolution during Polymerization-Induced Self-Assembly

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Synthesis of the Macro-RAFT Agent PEG_{45}-CPADB

PEG_{45}-OH (3.8 g, 2.0 mmol), CPADB (2.23 g, 8 mmol) and DMAP(98 mg, 0.8 mmol) were dissolved into 50 mL of dichloromethane (CH_2Cl_2) and then the solution was stirred in a low temperature reactor at 0 ℃ for 0.5 h. DCC(1.65 g, 8 mmol) was dissolved in 10 ml of dichloromethane, and then slowly dripped into the above cold solution. The reaction system was stirred for three days in the low temperature reactor at 0 ^{o}C. After removing the insoluble matter by filtration, most of the solvent was removed by a rotary evaporator. The concentrated solution was dropwise added into a large amount of cold diethyl ether to afford some pink precipitates. The precipitates were collected by filtration and then dissolved into the CH_2Cl_2 again. The procedure of precipitation was repeated three times, and the product was dried in vacuum to obtain a pink solid powder, which was characterized by ^{1}H NMR and GPC.

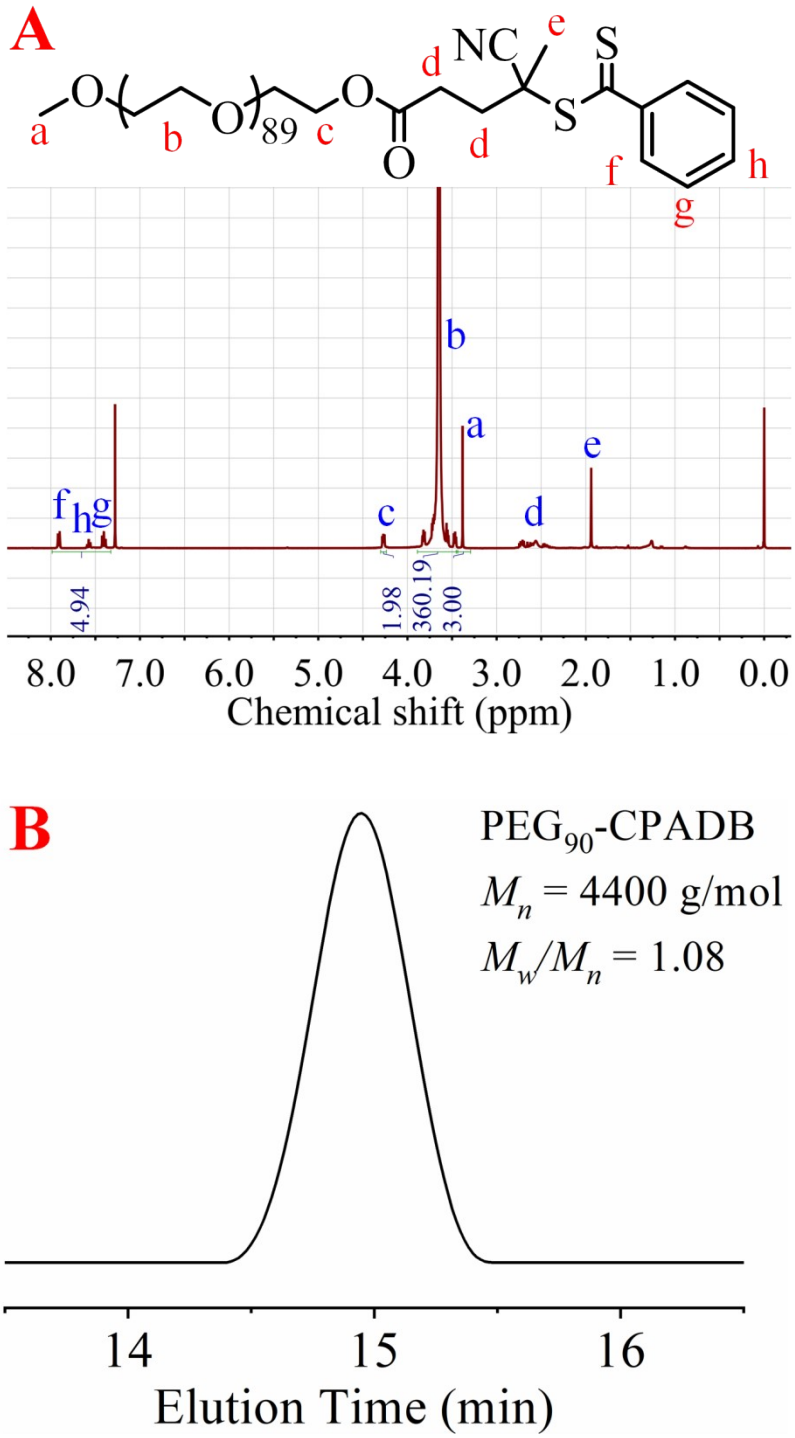


Figure S1. (A) The ^{1}H NMR spectrum and (B) GPC trace of the macro-CTA PEG_{90}-CPADB.

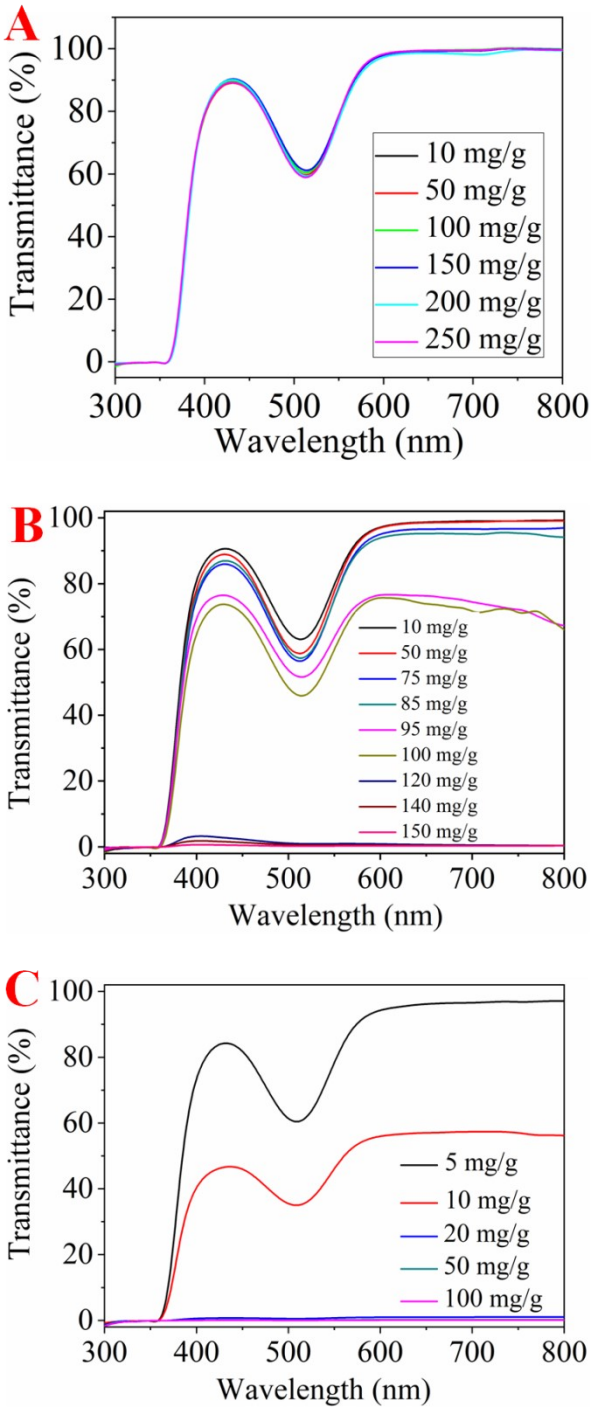
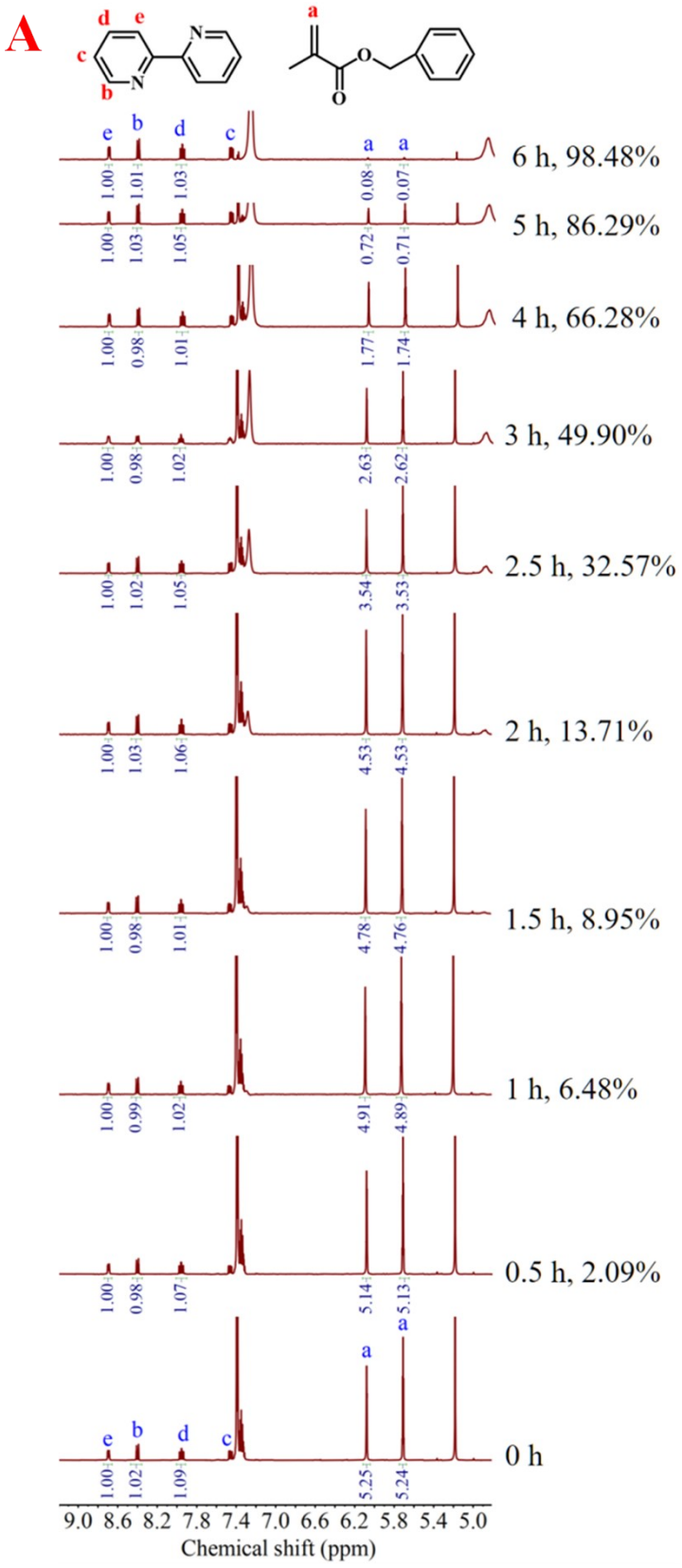
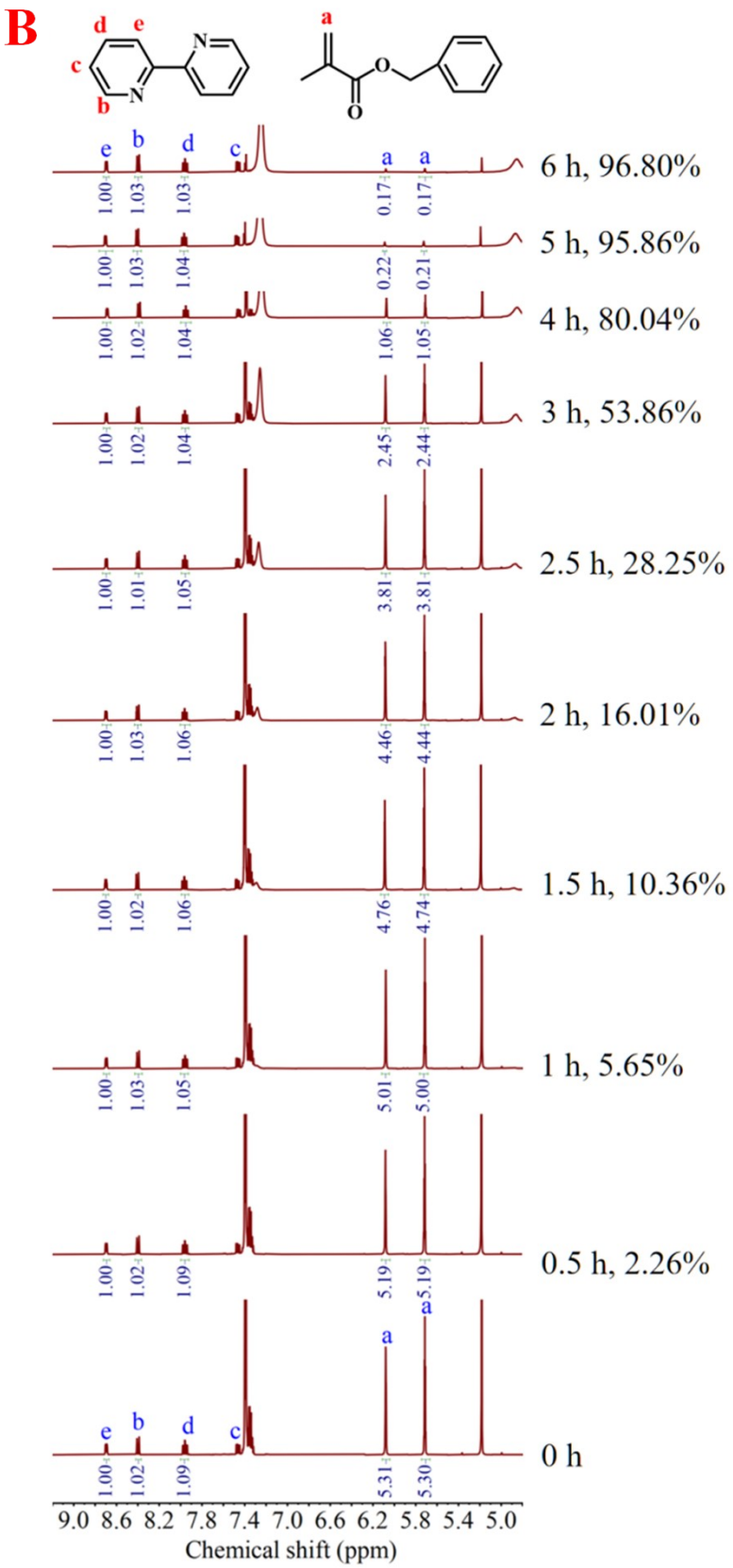


Figure S2. Transmittance versus wavelength plots recorded under different concentrations of BzMA at 70 °C in different ethanol/water mixture: (A) ethanol/water (7/3, w/w); (B) ethanol/water (5/5, w/w); (C) ethanol/water (3/7, w/w). The transmittance versus concentration of BzMA plots at λ = 700 nm in different ethanol/water mixture are summarized in Figure 2. The transmittance at λ = 700 nm was chosen to avoid the absorption bands of the dithiobenzoate chain-ends at approximate 300 and 507 nm.

Figure S3. The images of the initial reaction mixtures (before polymerization) of PEG_{90}-CPADB-mediataed RAFT polymerization of BzMA (BzMA/PEG_{90}-CPADB = 120) at 20 % solid content in different solvents, Sample 1: ethanol/water (7/3, w/w); Sample 2: ethanol/water (5/5, w/w) and Sample 3: ethanol/water (3/7, w/w).


A
d e
c
b
N
N
a
O
O
e b d c a a
1.00 1.01 1.03 0.08 0.07
6 h, 98.48%
1.00 1.03 1.05 0.72 0.71
5 h, 86.29%
1.00 0.98 1.01 1.77 1.74
4 h, 66.28%
1.00 0.98 1.02 2.63 2.62
3 h, 49.90%
1.00 1.02 1.05 3.54 3.53
2.5 h, 32.57%
1.00 1.03 1.06 4.53 4.53
2 h, 13.71%
1.00 0.98 1.01 4.78 4.76
1.5 h, 8.95%
1.00 0.99 1.02 4.91 4.89
1 h, 6.48%
1.00 0.98 1.07 5.14 5.13
0.5 h, 2.09%
e b d c a a
1.00 1.02 1.09 5.25 5.24
0 h
9.0 8.6 8.2 7.8 7.4 7.0 6.6 6.2 5.8 5.4 5.0
Chemical shift (ppm)


B
d e
c
b
N
N
a
O
O
e b d c a a
1.00 1.03 1.03 0.17 0.17
6 h, 96.80%
1.00 1.03 1.04 0.22 0.21
5 h, 95.86%
1.00 1.02 1.04 1.06 1.05
4 h, 80.04%
1.00 1.02 1.04 2.45 2.44
3 h, 53.86%
1.00 1.01 1.05 3.81 3.81
2.5 h, 28.25%
1.00 1.03 1.06 4.46 4.44
2 h, 16.01%
1.00 1.02 1.06 4.76 4.74
1.5 h, 10.36%
1.00 1.03 1.05 5.01 5.00
1 h, 5.65%
1.00 1.02 1.09 5.19 5.19
0.5 h, 2.26%
a
a
e b d c
1.00 1.02 1.09 5.31 5.30
0 h
9.0 8.6 8.2 7.8 7.4 7.0 6.6 6.2 5.8 5.4 5.0
Chemical shift (ppm)

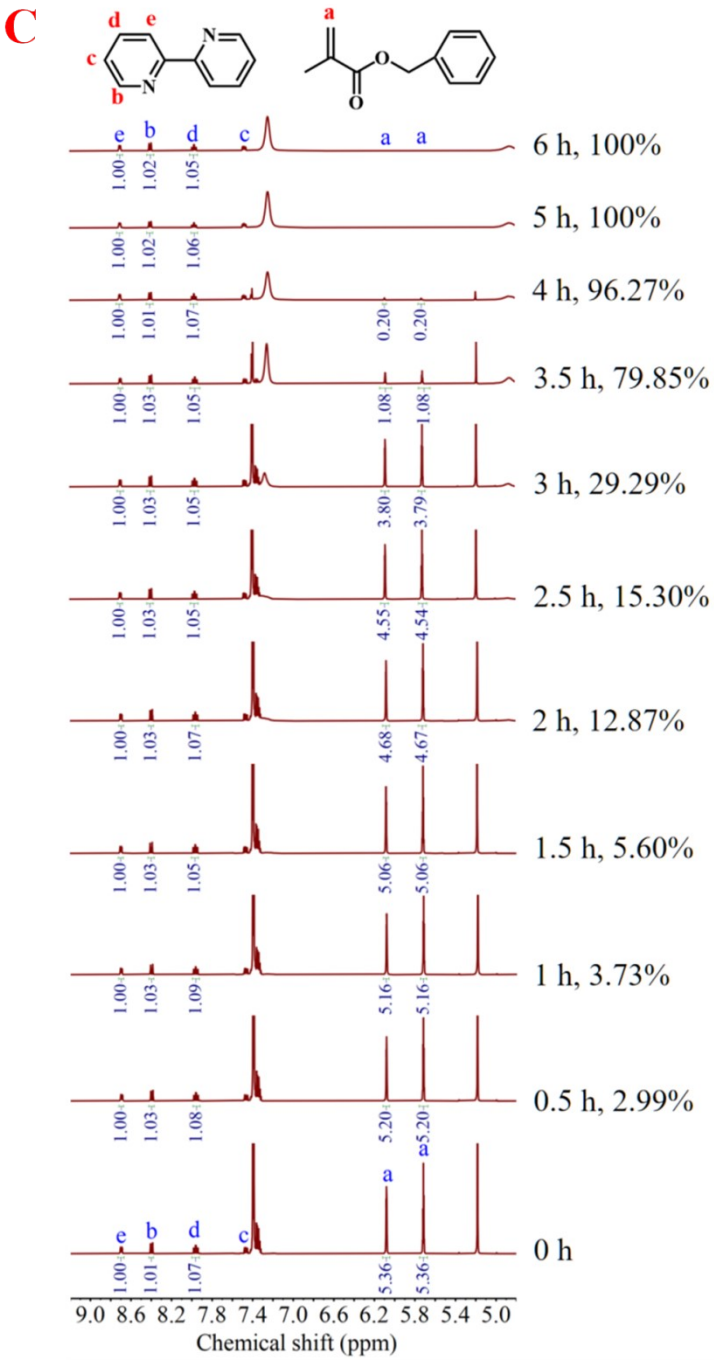


Figure S4. ^{1}H NMR spectra of the reaction mixture (RAFT polymerization of BzMA targeted to PEG_{90}-*b*-$PBzMA_{120}$ at different polymerization times. 2,2'- bipyridine was used as an internal standard to calculate the conversion of the monomer BzMA) in different solvents, (A) ethanol/water (7/3, w/w); (B) ethanol/water (5/5, w/w); (C) ethanol/water (3/7, w/w). 50 μL of the reaction mixture was taken out for ^{1}H NMR (DMSO-d_6) characterization at specific time of polymerization. The monomer BzMA conversions at different polymerization time were calculated according to the following equation:

Conversion $(\%)_{BzMA} = (1 - a_t / a_0) \times 100\%$

The integral value of vinyl protons of BzMA (a) at 0 h and t h of polymerization is denoted as a_0 and a_t, respectively.

Table S1. Summary of results obtained by RAFT polymerization of BzMA in different solvents (varying mass ratio of ethanol/water), monomer conversion, M_n and M_w/M_n of the resultant polymers, morphology of the resultant nano-objects.

Samples	Solvent Composition	Conv. of BzMA[a](%)	$M_{n,NMR}$[b] (kg/mol)	Actual DP_{PBzMA}[b]	$M_{n,GPC}$[c] (kg/mol)	M_w/M_n[c]	Morphology[d]
PEG_{90}-*b*-$PBzMA_{60}$	Ethanol/Water (7/3,w/w)	99	14.6	59	14.4	1.11	S
PEG_{90}-*b*-$PBzMA_{80}$		99	18.4	80	17.7	1.12	S
PEG_{90}-*b*-$PBzMA_{100}$		99	21.9	99	21.5	1.13	S
PEG_{90}-*b*-$PBzMA_{120}$		99	25.4	119	24.1	1.13	S
PEG_{90}-*b*-$PBzMA_{60}$	Ethanol/Water (5/5,w/w)	100	14.8	60	14.9	1.14	S+W
PEG_{90}-*b*-$PBzMA_{80}$		100	18.3	79	18.0	1.14	W+V
PEG_{90}-*b*-$PBzMA_{100}$		100	21.9	100	21.4	1.20	V
PEG_{90}-*b*-$PBzMA_{120}$		100	25.1	118	24.9	1.15	V
PEG_{90}-*b*-$PBzMA_{60}$	Ethanol/Water (3/7,w/w)	100	14.8	60	15.2	1.22	S
PEG_{90}-*b*-$PBzMA_{80}$		100	18.4	80	18.6	1.24	S
PEG_{90}-*b*-$PBzMA_{100}$		100	21.9	100	20.3	1.28	S
PEG_{90}-*b*-$PBzMA_{120}$		100	25.3	119	22.5	1.31	S

[a] Monomer conversions were determined by ^{1}H NMR of the reacted solution;

[b] $M_{n,NMR}$ and Actual DP_{PBzMA} were determined by ^{1}H NMR of the resultant polymer as shown in Figure S5-S7;

[c] $M_{n,GPC}$ and M_w/M_n were determined by GPC;

[d] Morphologies of the nano-objects were identified by TEM, wherein S represents spherical micelles, W is worm-like micelles, V represents vesicles.

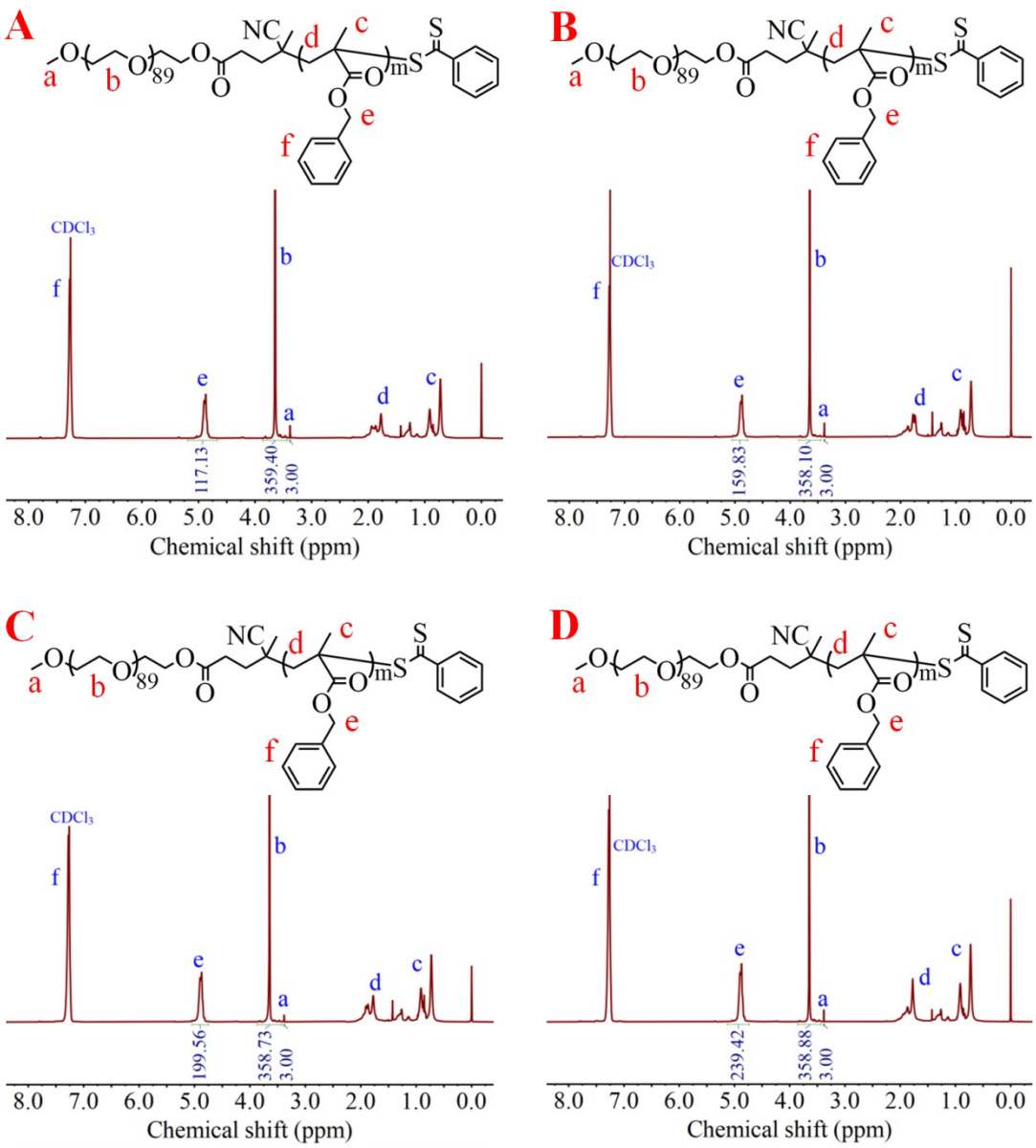


Figure S5. ^{1}H NMR spectra of the block copolymers (A) PEG_{90}-*b*-$PBzMA_{60}$, (B) PEG_{90}-*b*-$PBzMA_{80}$, (C) PEG_{90}-*b*-$PBzMA_{100}$, and (D) PEG_{90}-*b*-$PBzMA_{120}$ obtained by RAFT dispersion polymerization of BzMA in ethanol/water (7/3, w/w) with varying BzMA/PEG_{90}-CPADB (60~120).

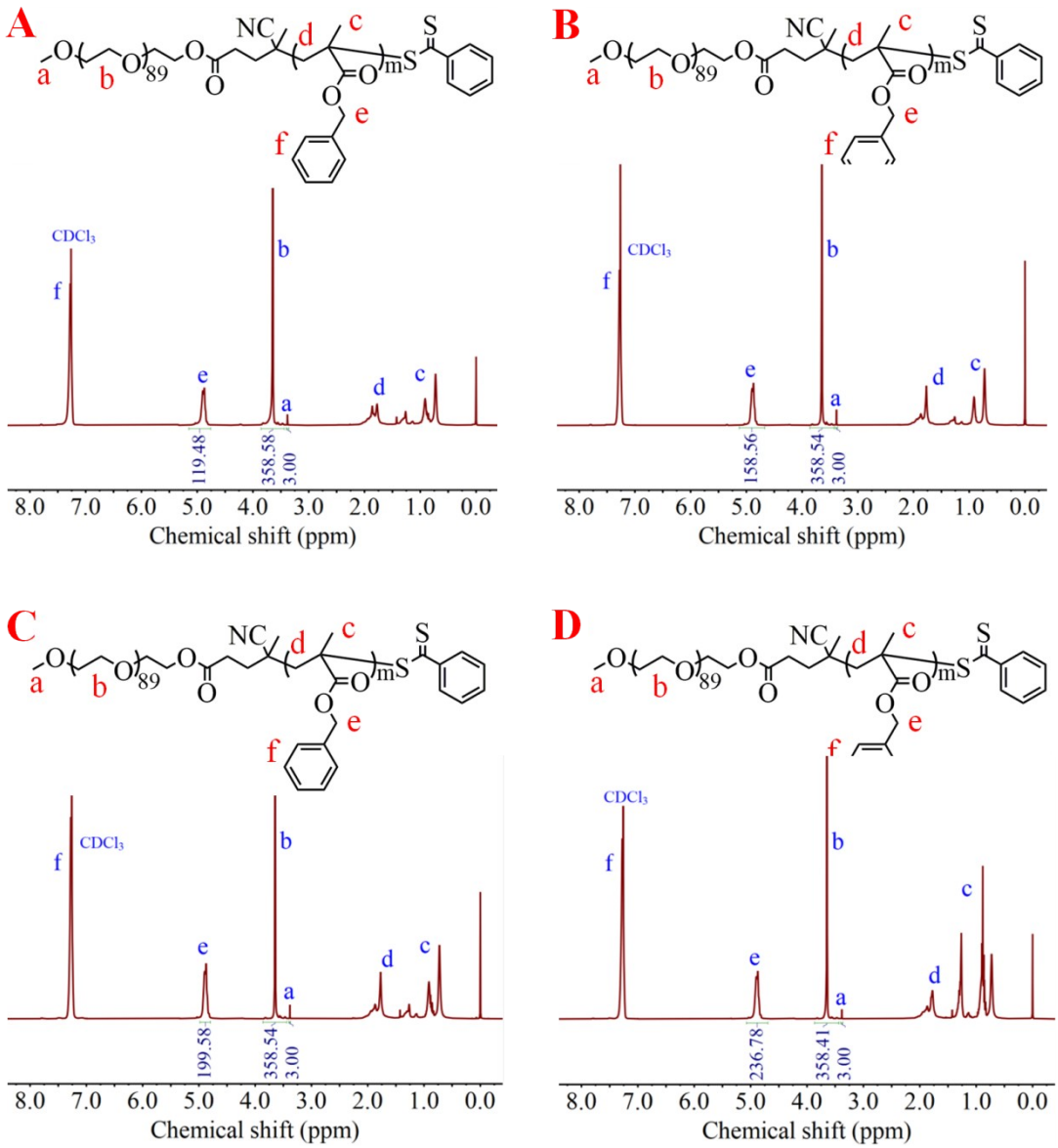


Figure S6. ^{1}H NMR spectra of the block copolymers (A) PEG_{90}-*b*-$PBzMA_{60}$, (B) PEG_{90}-*b*-$PBzMA_{80}$, (C) PEG_{90}-*b*-$PBzMA_{100}$, and (D) PEG_{90}-*b*-$PBzMA_{120}$ obtained by RAFT dispersion+emulsion polymerization of BzMA in ethanol/water (5/5, w/w) with varying BzMA/PEG_{90}-CPADB (60~120).

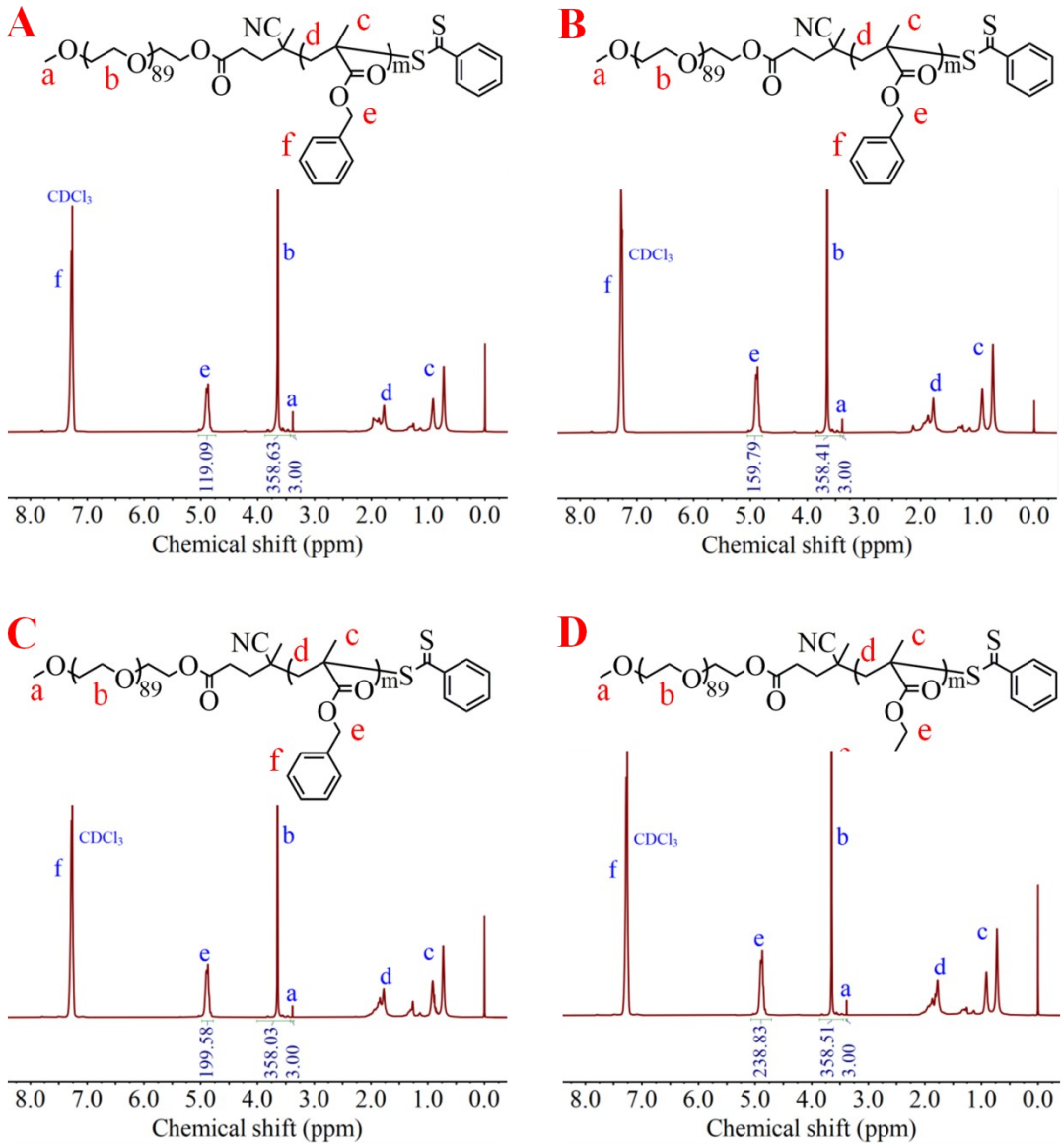


Figure S7. ^{1}H NMR spectra of the block copolymers (A) PEG_{90}-*b*-$PBzMA_{60}$, (B) PEG_{90}-*b*-$PBzMA_{80}$, (C) PEG_{90}-*b*-$PBzMA_{100}$, and (D) PEG_{90}-*b*-$PBzMA_{120}$ obtained by RAFT emulsion polymerization of BzMA in ethanol/water (3/7, w/w) with varying BzMA/PEG_{90}-CPADB (60~120).

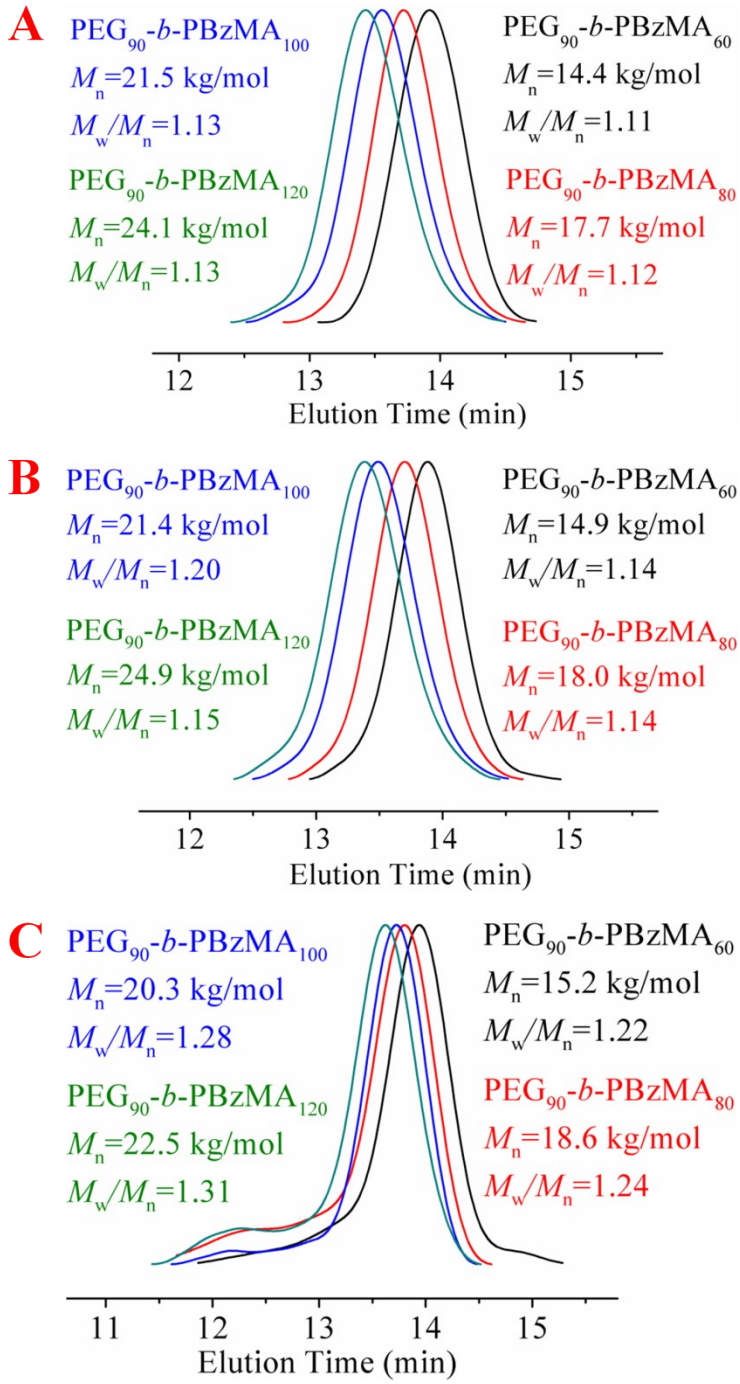


Figure S8. GPC curves of the block copolymers PEG_{90}-*b*-$PBzMA_{60\sim120}$ obtained by RAFT polymerization of BzMA with varying BzMA/PEG_{90}-CPADB (60~120) in different solvents, (A) ethanol/water (7/3, w/w); (B) ethanol/water (5/5, w/w); (C) ethanol/water (3/7, w/w).

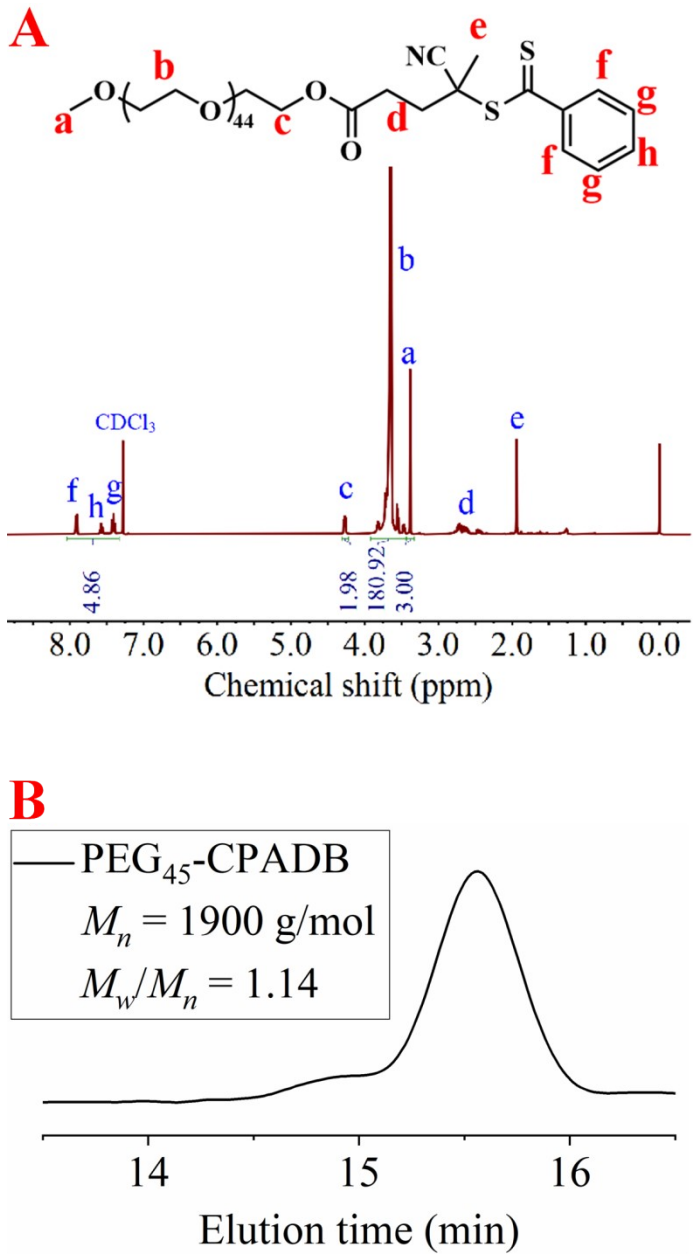


Figure S9. (A) The ^{1}H NMR spectrum and (B) GPC trace of the macro-CTA PEG_{45}-CPADB.

Table S2. Summary of results obtained by RAFT dispersion polymerization of BzMA, monomer conversion, M_n and M_w/M_n of the resultant polymers, morphology of the resultant nano-objects.

Samples[a]	Solvent composition	Conv. of monomer[a] (%)	$M_{n,NMR}$[b] (kg/mol)	Actual units of BzMA[b]	Actual units of HPMA[b]	$M_{n,GPC}$[c] (kg/mol)	M_w/M_n[c]	Morphology[d]
PEG_{45}-*b*-$PBzMA_{60}$	Ethanol/Water (7/3,w/w)	100	12.7	60	-	12.1	1.09	V
PEG_{45}-*b*-$PBzMA_{120}$		99	22.9	118	-	21.7	1.10	V
PEG_{45}-*b*-$PBzMA_{60}$	Ethanol/Water (3/7,w/w)	100	12.7	60	-	12.5	1.23	P
PEG_{45}-*b*-$PBzMA_{120}$		100	22.5	115	-	22.7	1.36	P
PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_{60}$	Ethanol/Water (7/3,w/w)	95	14.0	46	12	15.1	1.11	S
PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_{80}$		96	17.2	61	15	18.4	1.10	S
PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_{100}$		94	20.1	75	18	20.8	1.12	S
PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_{120}$		95	23.9	92	23	24.6	1.11	S
PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_{60}$	Ethanol/Water (3/7,w/w)	100	14.4	48	12	15.6	1.14	W
PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_{80}$		99	17.8	64	16	18.9	1.09	V
PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_{100}$		99	21.2	80	20	23.4	1.17	V
PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_{120}$		99	24.6	96	24	27.4	1.15	V

[a] The monomer conversions were calculated according to the ^{1}H NMR spectra of the reaction media.

[b] The $M_{n,NMR}$ of the block polymer, actual units of BzMA and HPMA in the resultant block polymers were calculated based on the ^{1}H NMR spectra as shown in Figure S10, S11, S14 and S16.

[c] The M_n and M_w/M_n of the resultant block polymer were determined by GPC.

[d] Morphologies of the nano-objects were identified by TEM, wherein S represents spherical micelles, W is worm-like micelles, and V denotes vesicles.

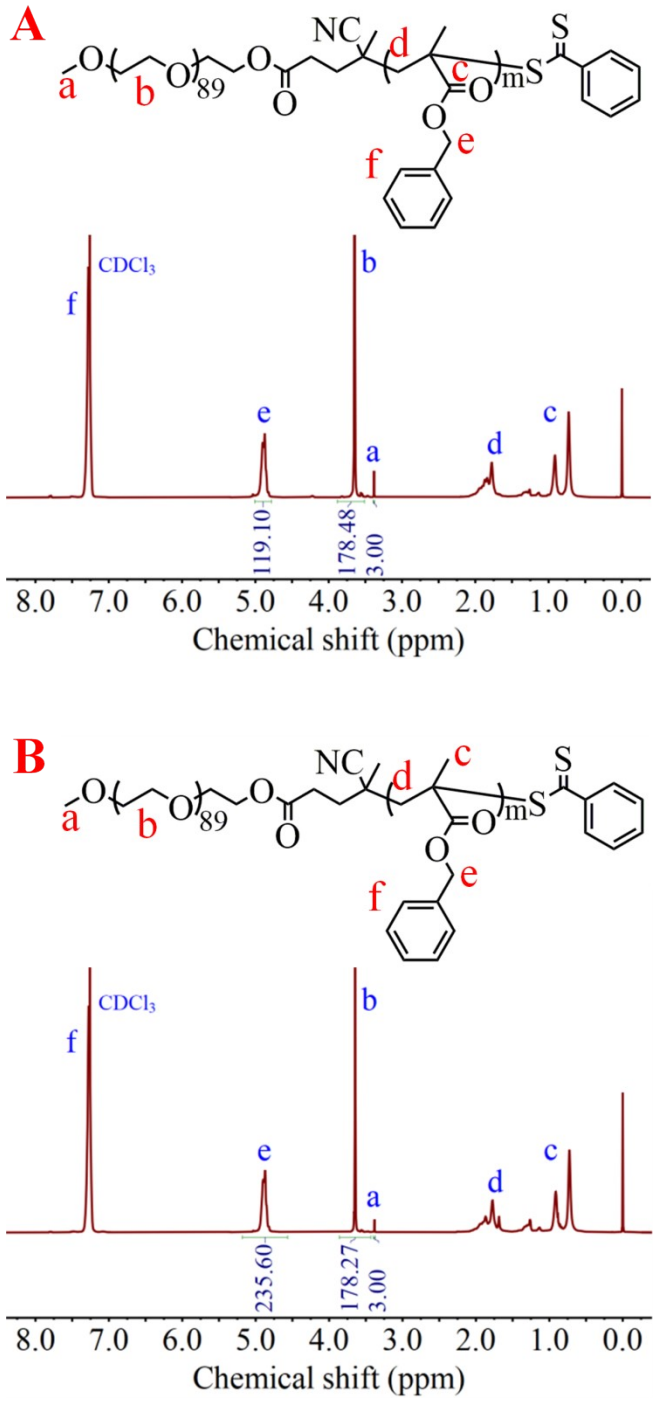


Figure S10. ^{1}H NMR spectra of the block copolymers (A) PEG_{45}-*b*-$PBzMA_{60}$ and (B) PEG_{45}-*b*-$PBzMA_{120}$ obtained by PEG_{45}-CPADB-mediated RAFT dispersion polymerization of BzMA in ethanol/water (7/3, w/w) with varying BzMA/PEG_{45}-CPADB (60 and 120).

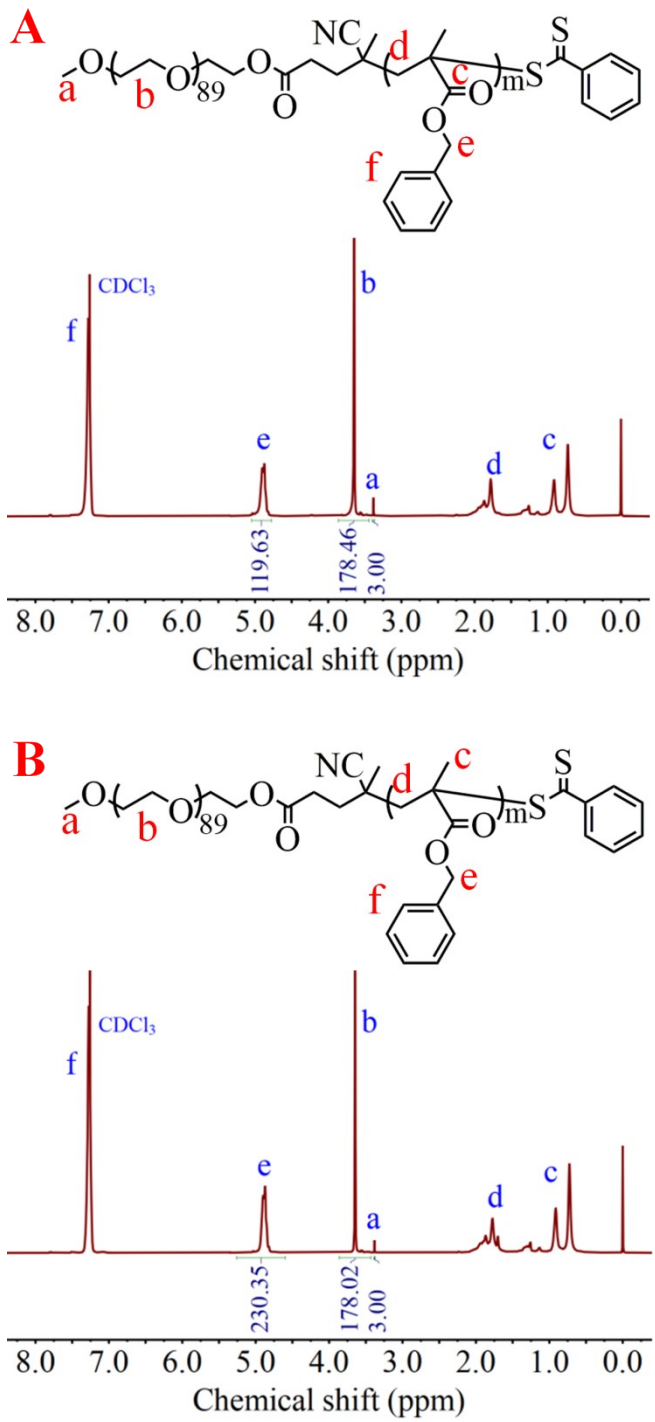


Figure S11. ^{1}H NMR spectra of the block copolymers (A) PEG_{45}-*b*-$PBzMA_{60}$ and (B) PEG_{45}-*b*-$PBzMA_{120}$ obtained by PEG_{45}-CPADB-mediated RAFT dispersion polymerization of BzMA in ethanol/water (3/7, w/w) with varying BzMA/PEG_{45}-CPADB (60 and 120).

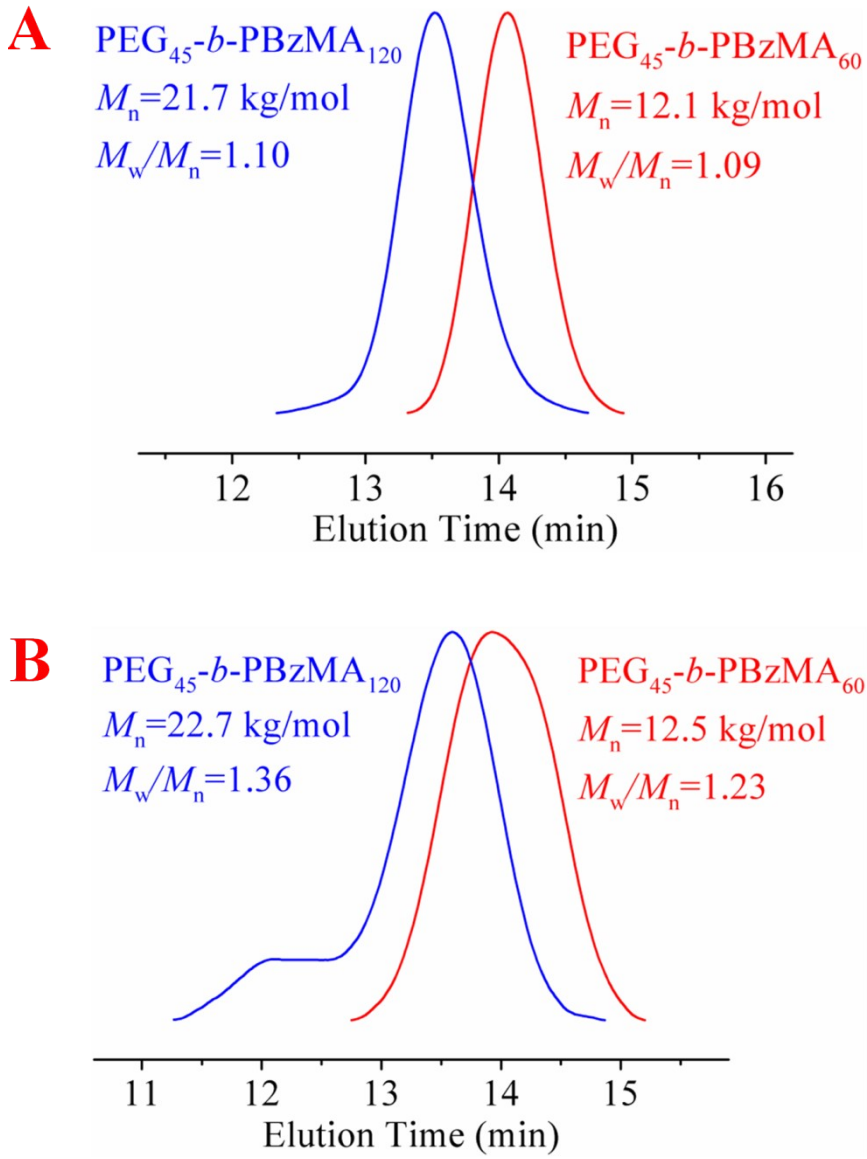


Figure S12. GPC curves of the block copolymers PEG_{45}-*b*-$PBzMA_{60}$ and PEG_{45}-*b*-$PBzMA_{120}$ obtained by RAFT polymerization of BzMA with varying BzMA/PEG_{45}-CPADB (60 and 120) in (A) ethanol/water (7/3, w/w); and (B) ethanol/water (3/7, w/w).

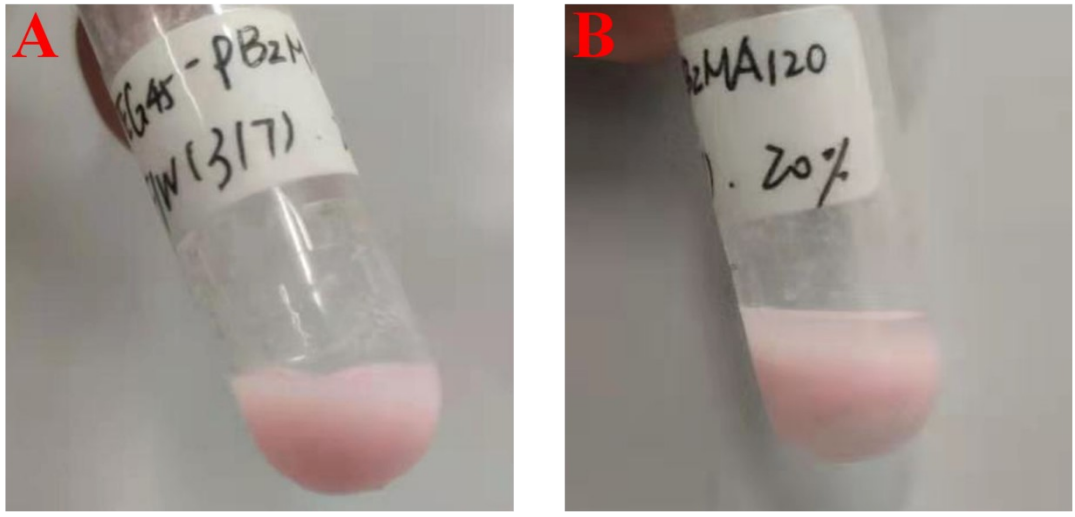


Figure S13. Images of PEG_{45}-*b*-$PBzMA_x$ precipitations obtained by RAFT emulsion polymerization of BzMA in ethanol/water (3/7, w/w) with varying feed molar ratio of BzMA/PEG_{45}-CPADB, (A) BzMA/PEG_{45}-CPADB = 60 and (B) BzMA/PEG_{45}-CPADB = 120.

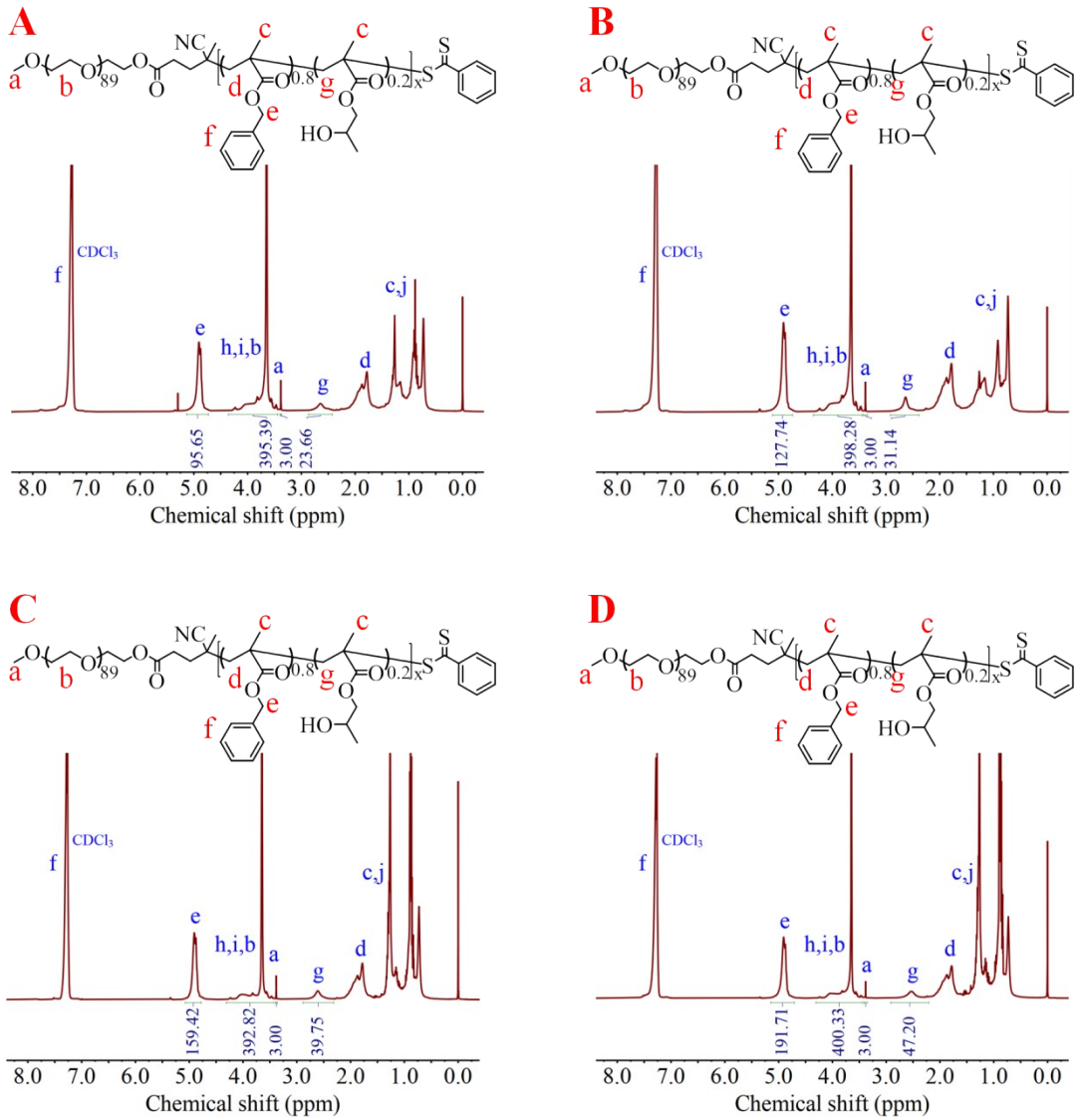


Figure S14. ^{1}H NMR spectra of the block copolymers (A) PEG_{90}-*b*-P($BzMA_{0.8}$-*co*-$HPMA_{0.2}$)$_{60}$, (B) PEG_{90}-*b*-P($BzMA_{0.8}$-*co*-$HPMA_{0.2}$)$_{80}$, (C) PEG_{90}-*b*-P($BzMA_{0.8}$-*co*-$HPMA_{0.2}$)$_{100}$, and (D) PEG_{90}-*b*-P($BzMA_{0.8}$-*co*-$HPMA_{0.2}$)$_{120}$ obtained by RAFT emulsion copolymerization of BzMA and HPMA in ethanol/water (3/7, w/w) with varying (BzMA+HPMA)/PEG_{90}-CPADB (60~120).

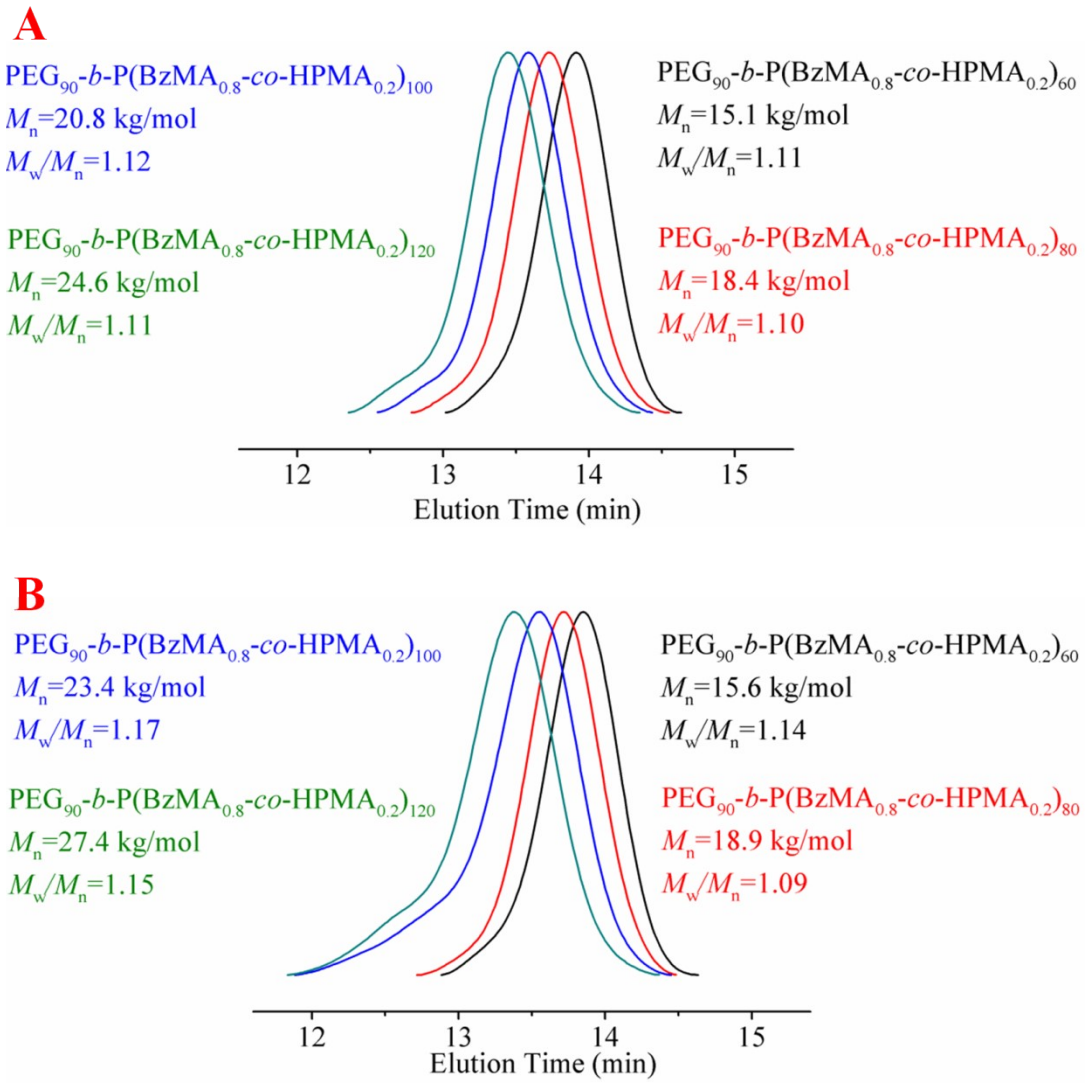


Figure S15. GPC curves of the block copolymers PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_{60\sim120}$ obtained by RAFT copolymerization of BzMA and HPMA with varying (BzMA+HPMA)/PEG_{45}-CPADB (60~120) in different solvents, (A) ethanol/water (7/3, w/w); (B) ethanol/water (3/7, w/w).

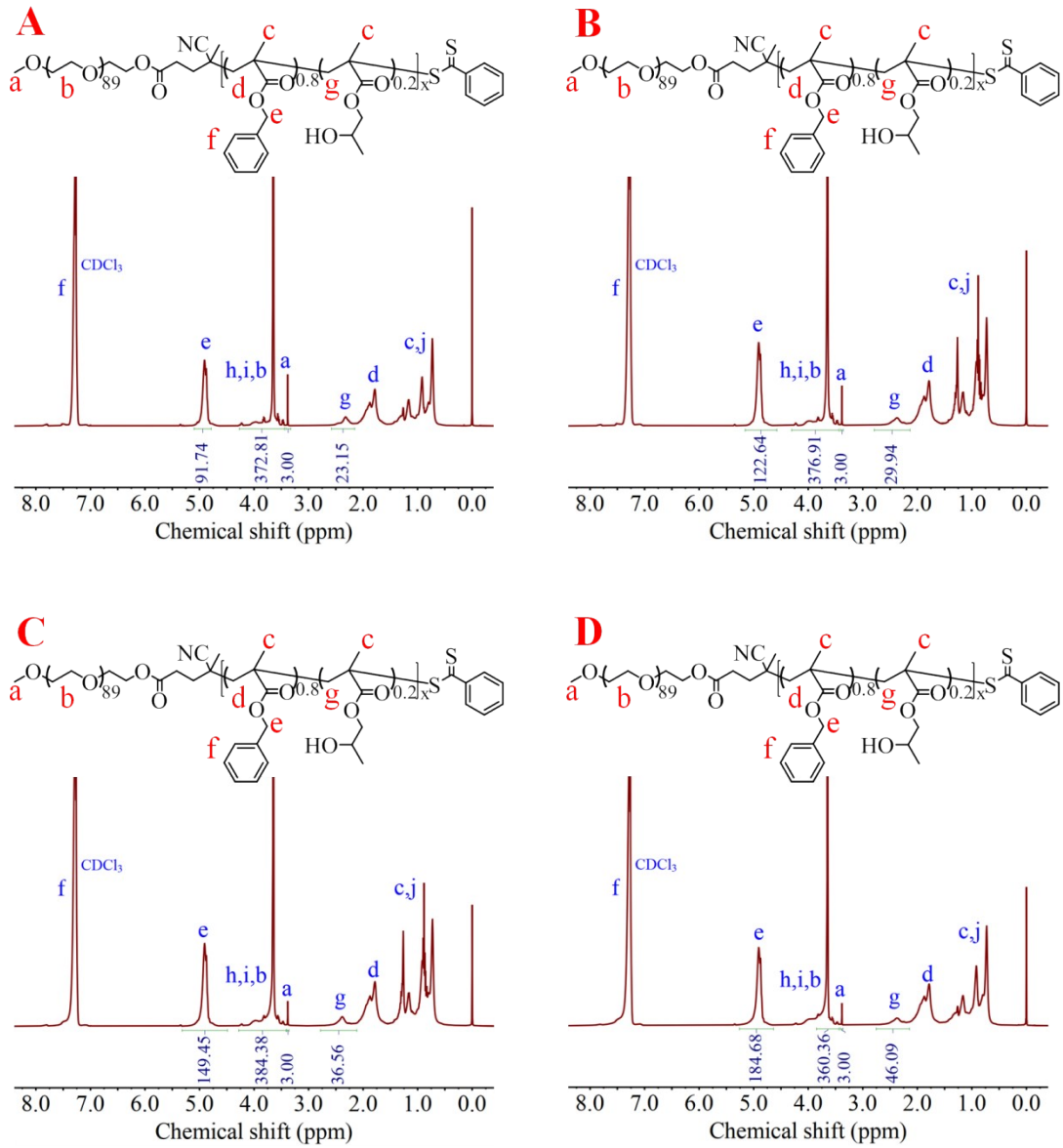


Figure S16. ^{1}H NMR spectra of the block copolymers (A) PEG_{90}-*b*-P($BzMA_{0.8}$-*co*-$HPMA_{0.2}$)$_{60}$, (B) PEG_{90}-*b*-P($BzMA_{0.8}$-*co*-$HPMA_{0.2}$)$_{80}$, (C) PEG_{90}-*b*-P($BzMA_{0.8}$-*co*-$HPMA_{0.2}$)$_{100}$, and (D) PEG_{90}-*b*-P($BzMA_{0.8}$-*co*-$HPMA_{0.2}$)$_{120}$ obtained by RAFT dispersion copolymerization of BzMA and HPMA in ethanol/water (7/3, w/w) with varying (BzMA+HPMA)/PEG_{90}-CPADB (60~120).

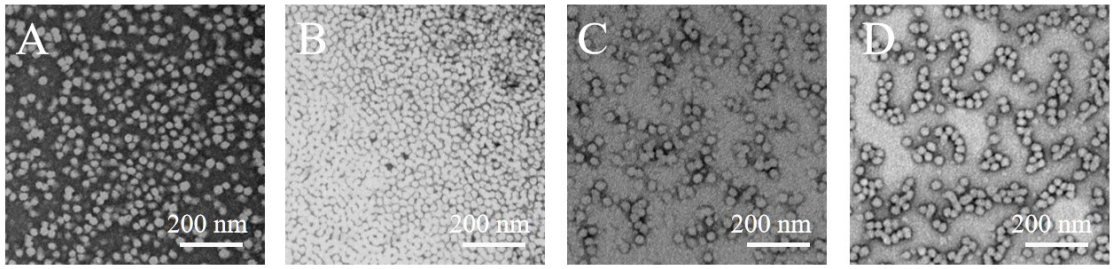


Figure S17. TEM images of PEG_{90}-*b*-$P(BzMA_{0.8}$-*co*-$HPMA_{0.2})_x$ nano-objects obtained by RAFT dispersion copolymerization of BzMA and HPMA in ethanol/water (7/3, w/w) with varying feed molar ratio of (BzMA+HPMA)/PEG_{90}-CPADB, (A) (BzMA+HPMA)/PEG_{90}-CPADB = 60, (B) (BzMA+HPMA)/PEG_{90}-CPADB = 80, (C) (BzMA+HPMA)/PEG_{90}-CPADB = 100 and (D) (BzMA+HPMA)/PEG_{90}-CPADB = 120.