Electronic Supplementary Information

A novel reactive phosphonium-containing polyelectrolyte with multiple reactivities: monomer synthesis, RAFT polymerization and post-polymerization modifications

Jian Sun [a], *Chang Wang* [a], *Zhi-Wei Tan*[b], *Cheng-Mei Liu* [a †]

[a] Key Laboratory of Materials Chemistry for Energy Conversion and Storage, Ministry of Education (HUST), School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China

[b] School of Chemical and Environmental Engineering, Hubei Minzu University, Enshi 445000, China

[†]Corresponding authors. E-mail: liukui@mail.hust.edu.cn; tanzw1112@sohu.com

Captions of ESI:

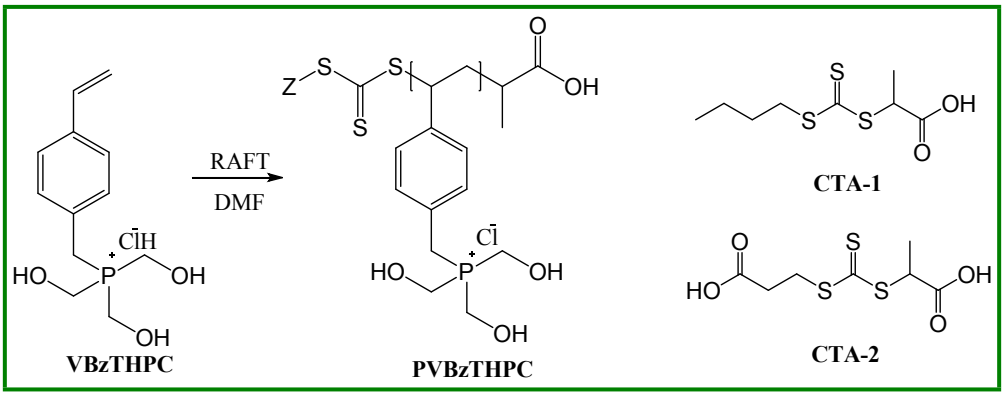

Table S1. Results of RAFT polymerization in DMF (entry A)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	14	0.1499	6,030	46,570	1.06
1	31	0.3764	13,070	68,890	1.09
1.5	45	0.6068	18,870	86,490	1.10
2	55	0.8082	23,000	100,300	1.14
3	69	1.1794	28,800	117,200	1.15
4	73	1.2920	30,460	123,300	1.15
8	81	1.6527	33,770	124,800	1.20
24	88	2.1059	36,670	134,000	1.19

[a] RAFT polymerization condition: $[VBzTHPC]_0:[CTA\text{-}1]_0:[AIBN]_0=150:1:0.5$; CTA-1; 33wt% in DMF at 70℃. [b] As determined by UV-vis. [c] As determined by the equation: $Mn,th=DP*Conv.*M_{VBzTHPC}+MCTA$. [d] Aa determined by GPC (DMF containing 50mM LiBr).

Table S2. Results of RAFT polymerization in DMF (entry B)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	8	0.0801	3,550	50,510	1.08
1	26	0.3003	11,000	67,610	1.10
1.5	37	0.4596	15,560	85,200	1.10
2	48	0.6497	20,110	99,810	1.11
3	62	0.9690	25,910	121,700	1.12
4	68	1.1528	28,390	128,400	1.14
8	78	1.5285	32,530	134,600	1.16
24	84	1.8384	35,020	138,600	1.17

[a] RAFT polymerization condition: $[VBzTHPC]_0:[CTA\text{-}1]_0:[AIBN]_0=150:1:0.3$; CTA-1; 33wt% in DMF at 70℃. [b] As determined by UV-vis. [c] As determined by the equation: $Mn,th=DP*Conv.*M_{VBzTHPC}+MCTA$. [d] Aa determined by GPC (DMF containing 50mM LiBr).

Table S3. Results of RAFT polymerization in DMF (entry C)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	4	0.0356	1,900	45,830	1.07
1	11	0.1137	4,800	55,650	1.09
1.5	20	0.2293	8,520	67,090	1.10
2	28	0.3293	11,830	75,120	1.10
3	43	0.5598	18,040	96,200	1.10
4	51	0.7201	21,350	108,800	1.11
8	61	0.9421	25,490	120,500	1.12
24	74	1.3476	30,870	133,700	1.16

[a] RAFT polymerization condition: $[VBzTHPC]_0:[CTA\text{-}1]_0:[AIBN]_0=150:1:0.1$; CTA-1; 33wt% in DMF at 70℃. [b] As determined by UV-vis. [c] As determined by the equation: $Mn,th=DP*Conv.*M_{VBzTHPC}+MCTA$. [d] Aa determined by GPC (DMF containing 50mM LiBr)

Table S4. Results of RAFT polymerization in DMF (entry D)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	7	0.0701	1,590	37,350	1.06
1	14	0.1512	2,940	41,420	1.07
1.5	21	0.2363	4,300	49,400	1.08
2	32	0.3824	6,420	57,120	1.07
3	46	0.6236	9,130	65,080	1.07
4	55	0.7879	10,860	74,750	1.08
8	68	1.1255	13,380	83,060	1.09
24	76	1.4343	14,920	89,550	1.10

[a] RAFT polymerization condition: $[VBzTHPC]_0:[CTA\text{-}1]_0:[AIBN]_0=70:1:0.1$; CTA-1; 33wt% in DMF at 70℃. [b] As determined by UV-vis. [c] As determined by the equation: $Mn,th=DP*Conv.*M_{VBzTHPC}+MCTA$. [d] Aa determined by GPC (DMF containing 50mM LiBr).

Table S5. Results of RAFT polymerization in DMF (entry E)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	7	0.0737	3,140	54,870	1.09
1	26	0.3020	11,000	69,560	1.10
1.5	34	0.4136	14,310	79,430	1.11
2	43	0.5570	18,040	94,160	1.11
3	50	0.6943	20,940	111,900	1.13
4	62	0.9777	25,910	123,900	1.17
8	72	1.2727	30,050	131,100	1.18
24	79	1.5383	32,940	143,000	1.22

[a] RAFT polymerization condition: $[VBzTHPC]_0:[CTA\text{-}1]_0:[AIBN]_0=150:1:0.3$; CTA-1; 25wt% in DMF at 70℃. [b] As determined by UV-vis. [c] As determined by the equation: $Mn,th=DP*Conv.*M_{VBzTHPC}+MCTA$. [d] Aa determined by GPC (DMF containing 50mM LiBr).

Table S6. Results of RAFT polymerization in DMF (entry F)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	6	0.0638	2,720	50,340	1.09
1	19	0.2104	8,100	58,530	1.10
1.5	29	0.3420	12,240	70,940	1.12
2	37	0.4637	15,560	82,880	1.12
3	45	0.6019	18,870	104,600	1.14
4	52	0.7273	21,770	113,000	1.16
8	69	1.1649	28,800	127,000	1.15
24	74	1.3554	30,870	135,800	1.19

[a] RAFT polymerization condition: $[VBzTHPC]_0:[CTA\text{-}1]_0:[AIBN]_0=150:1:0.3$; CTA-1; 20wt% in DMF at 70℃. [b] As determined by UV-vis. [c] As determined by the equation: Mn,th=DP*Conv.*$M_{VBzTHPC}$+MCTA. [d] Aa determined by GPC (DMF containing 50mM LiBr).

Table S7. Results of RAFT polymerization in DMF (entry G)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	15	0.1636	6,460	36,420	1.04
1	24	0.2751	10,190	54,850	1.07
1.5	41	0.5199	17,230	71,530	1.07
2	49	0.6707	20,540	77,710	1.05
3	60	0.9129	25,090	107,300	1.07
4	65	1.0625	27,160	113,200	1.16
8	75	1.3765	31,300	116,800	1.27
24	80	1.6254	33,370	134,100	1.30

[a] RAFT polymerization condition: $[VBzTHPC]_0:[CTA\text{-}1]_0:[AIBN]_0=150:1:0.3$; CTA-2; 33wt% in DMF at 70℃. [b] As determined by UV-vis. [c] As determined by the equation: $M_{n,th}=DP*Conv.*M_{VBzTHPC}+M_{CTA}$. [d] Aa determined by GPC (DMF containing 50mM LiBr).

Table S8. Results of RAFT polymerization in DMF (entry H)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	2	0.0154	1,070	41,140	1.05
1	9	0.0931	3,960	47,410	1.07
1.5	17	0.1849	7,280	52,470	1.09
2	24	0.2740	10,170	63,180	1.09
3	38	0.4776	15,970	77,830	1.09
4	46	0.6164	19,280	94,470	1.09
8	66	1.0680	27,560	126,600	1.13
24	86	1.9355	35,840	140,700	1.18

[a] RAFT polymerization condition: $[VBzTHPC]_0:[CTA\text{-}1]_0:[AIBN]_0=150:1:0.3$; CTA-1; 33wt% in DMF at 60℃. [b] As determined by UV-vis. [c] As determined by the equation: $Mn,th=DP*Conv.*M_{VBzTHPC}+MCTA$. [d] Aa determined by GPC (DMF containing 50mM LiBr).

Table S9. Results of RAFT polymerization in DMF (entry I)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	27	0.2275	11,420	53,720	1.09
1	39	0.4170	16,380	79,420	1.10
1.5	49	0.4669	20,520	95,890	1.18
2	60	0.5559	25,080	113,100	1.12
3	69	0.6583	28,800	122,000	1.15
4	73	0.7077	30,460	127,700	1.16
8	79	0.7759	32,940	135,300	1.14
24	81	0.7952	33,770	136,200	1.17

[a] RAFT polymerization condition: $[VBzTHPC]_0$:$[CTA\text{-}1]_0$:$[AIVN]_0$=150:1:0.3; CTA-1; 33wt% in DMF at 60℃. [b] As determined by UV-vis. [c] As determined by the equation: Mn,th=DP*Conv.*$M_{VBzTHPC}$+MCTA. [d] Aa determined by GPC (DMF containing 50mM LiBr).

Table S10. Results of RAFT polymerization in DMF (entry J)[a].

Time (h)	*Conv.* (%)[b]	$ln([M]_0/[M])$	$M_{n,th}$ (g/mol)[c]	$M_{n,GPC}$ (g/mol)[d]	M_w/M_n[d]
0.5	23	0.2581	9,780	58,200	1.09
1	42	0.5396	17,640	92,620	1.11
1.5	47	0.6291	19,710	110,300	1.12
2	56	0.8116	23,440	113,400	1.14
3	66	1.0737	27,580	128,100	1.17
4	71	1.2300	29,650	133,700	1.18
8	76	1.4958	31,720	140,200	1.20
24	80	1.5855	33,370	143,400	1.22

[a] RAFT polymerization condition: $[VBzTHPC]_0:[CTA\text{-}1]_0:[AIVN]_0=150:1:0.3$; CTA-2; 33wt% in DMF at 60℃. [b] As determined by UV-vis. [c] As determined by the equation: $Mn,th=DP*Conv.*M_{VBzTHPC}+MCTA$. [d] Aa determined by GPC (DMF containing 50mM LiBr).

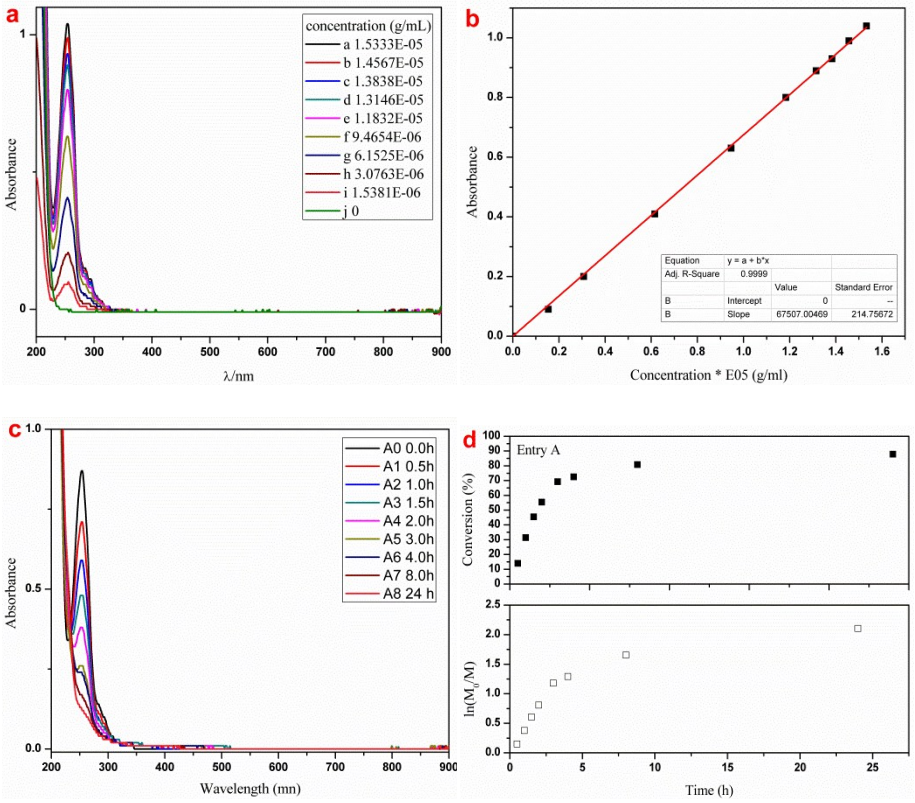

Figure S1. The calculation of monomer conversion by UV-vis spectrum measurements (Taking entry A as example, a)UV-vis spectra of monomer with known monomer concentration; b)the standard curve of monomer conversion versus absorbance at λ_{max}=254nm; c)UV-vis spectra during the RAFT polymerization; d)The relationship between monomer conversion or $\ln(M_0/M)$ and polymerization time.

Notes: The monomer conversion was calculated via UV-vis spectrum measurements. Firstly, we found that the maximum absorption of vinyl group in monomer located at 254nm without any interference. The linear relationship has been figured out between the monomer concentration and absorbance at 254nm in the UV-vis spectra. So the monomer conversion can be obtained from the absorbance of the polymerization mixture.

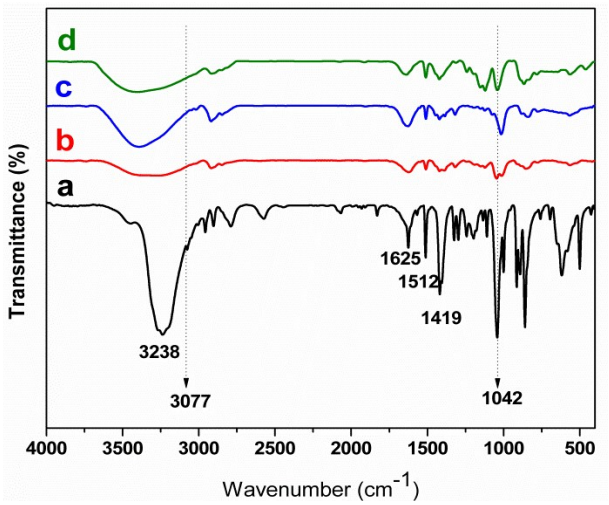

Figure S2. FT-IR spectra of VBzTHPC(a), PVBzTHPC(b), PVBzBHAPO(c) and PVBzBHPO(d).

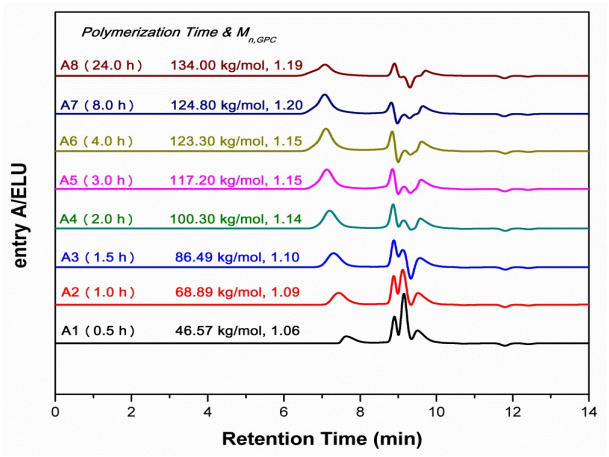

Figure S3. GPC elution curves of polymers synthesized by RAFT polymerization (entry A).

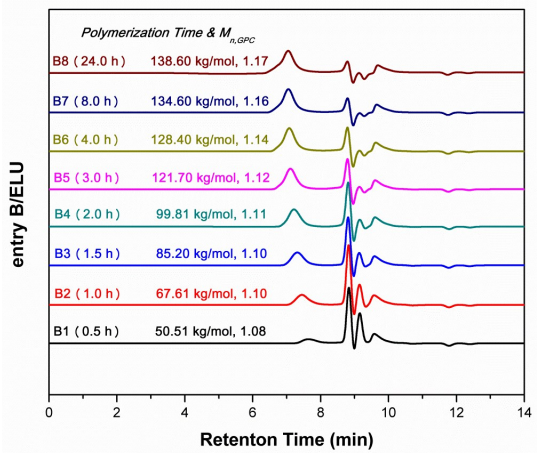

Figure S4. GPC elution curves of polymers synthesized by RAFT polymerization (entry B).

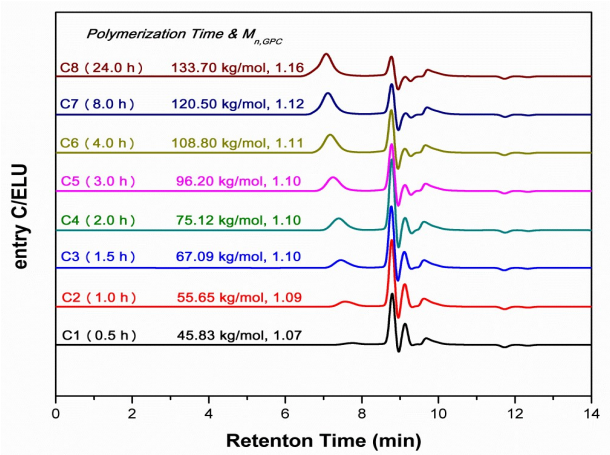

Figure S5. GPC elution curves of polymers synthesized by RAFT polymerization (entry C).

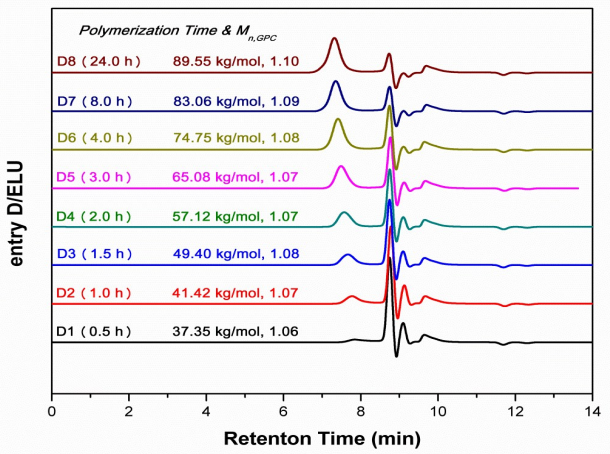

Figure S6. GPC elution curves of polymers synthesized by RAFT polymerization (entry D).

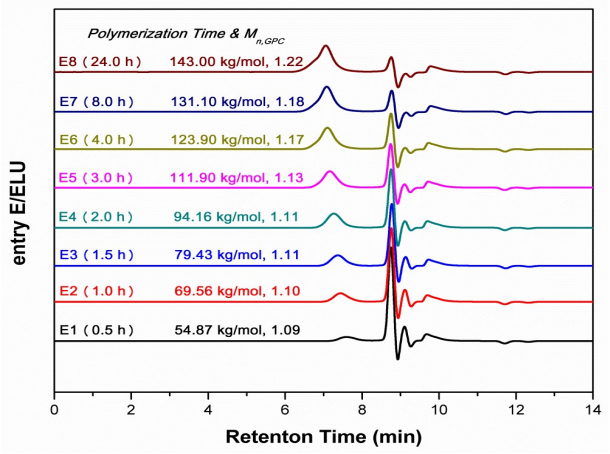

Figure S7. GPC elution curves of polymers synthesized by RAFT polymerization (entry E).

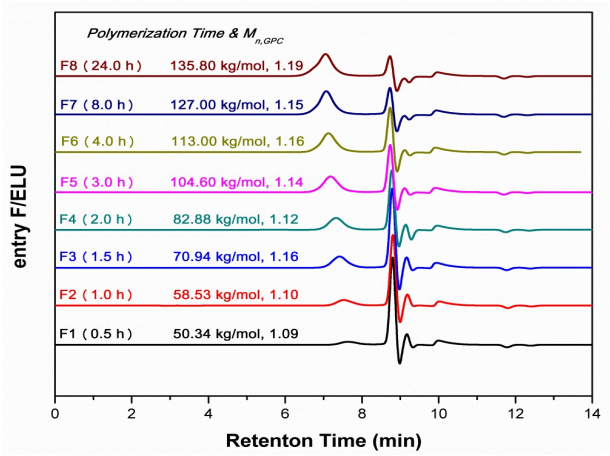

Figure S8. GPC elution curves of polymers synthesized by RAFT polymerization (entry F).

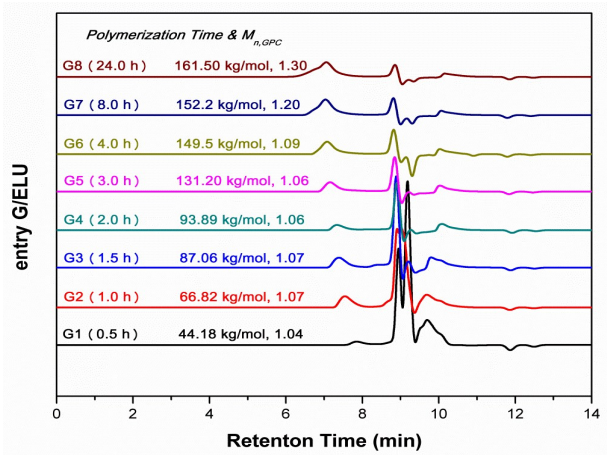

Figure S9. GPC elution curves of polymers synthesized by RAFT polymerization (entry G).

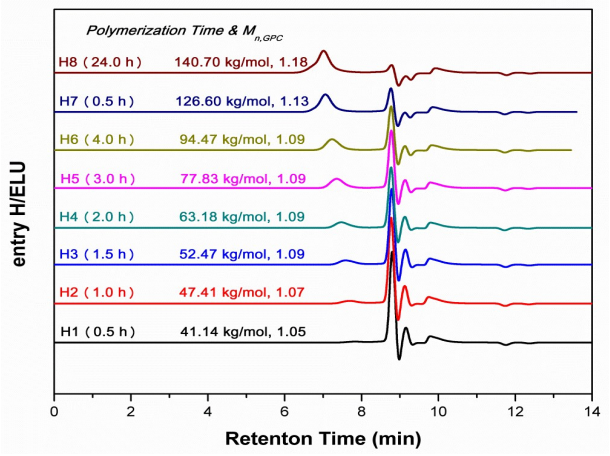

Figure S10. GPC elution curves of polymers synthesized by RAFT polymerization (entry H).

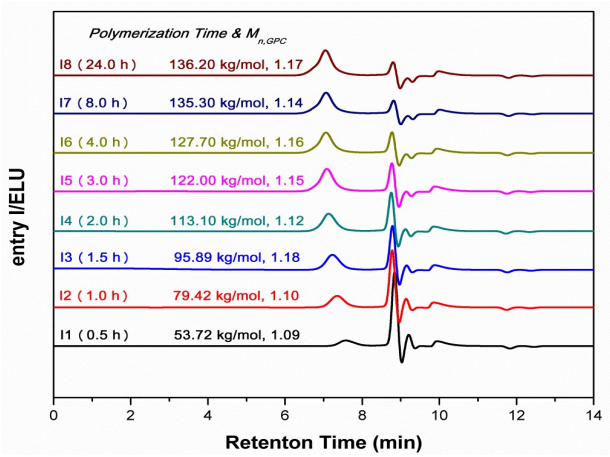

Figure S11. GPC elution curves of polymers synthesized by RAFT polymerization (entry I).

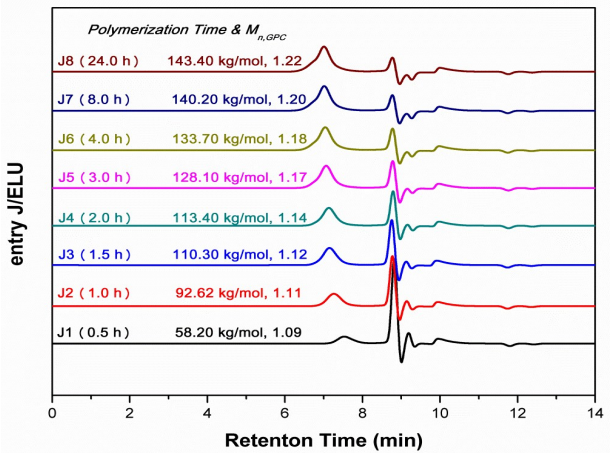

Figure S12. GPC elution curves of polymers synthesized by RAFT polymerization (entry J).

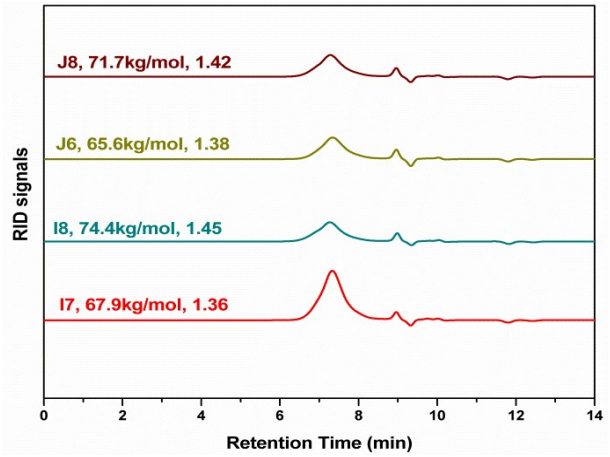

Figure S13. GPC elution curves of polymers synthesized by RAFT polymerization after post-modified by benzyl bromide.

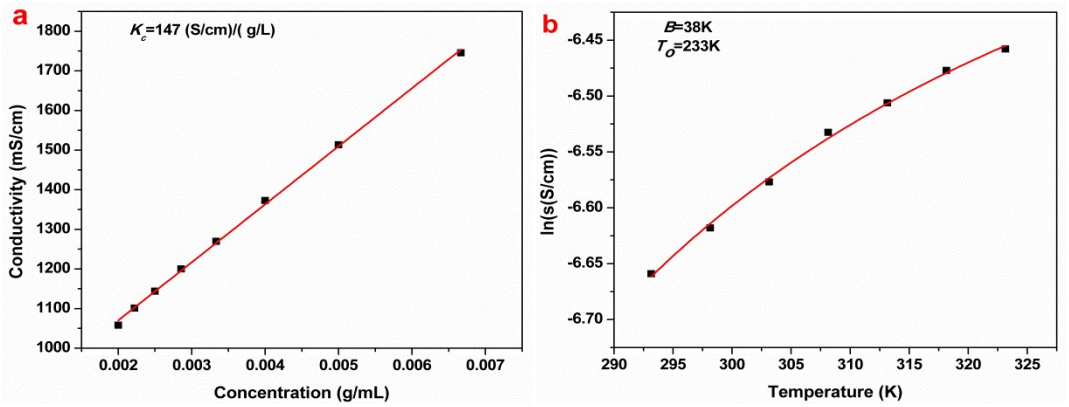

Figure S14. Conductivity of PVBzTHPC (P5) in water at different conditions: temperature (a) or concentration (b).

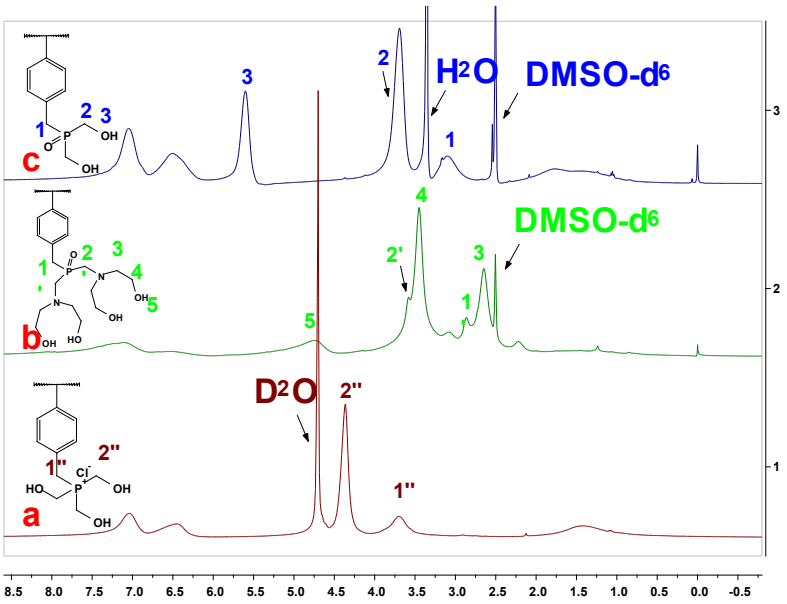

Figure S15. ^{1}H spectra of PVBzTHPC (a) in D_2O, PVBzBHAPO (b) and PVBzBHPO (c) in DMSO-d_6.

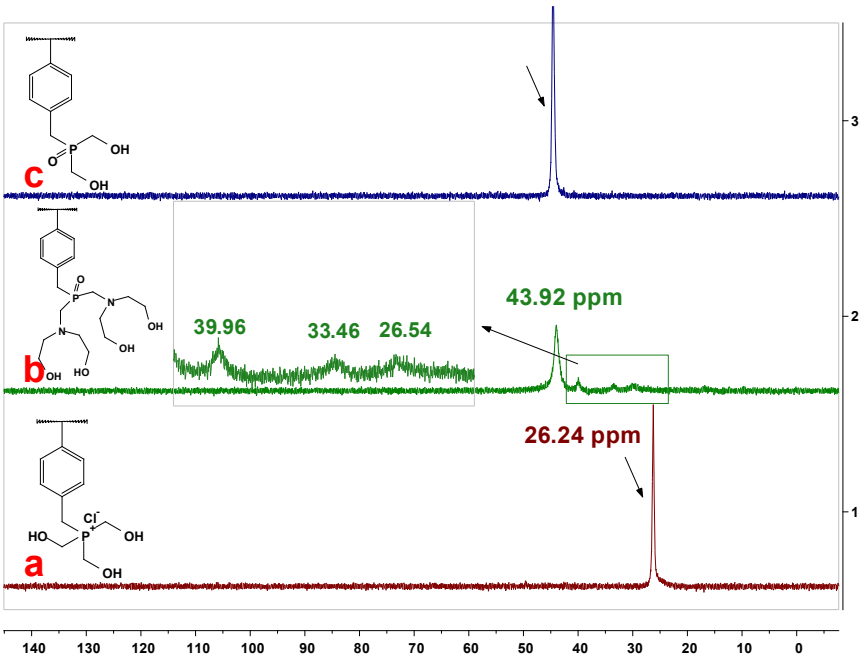

Figure S16. ^{31}P spectra of PVBzTHPC (a) in D_2O, PVBzBHAPO (b) and PVBzBHPO (c) in DMSO-d_6.

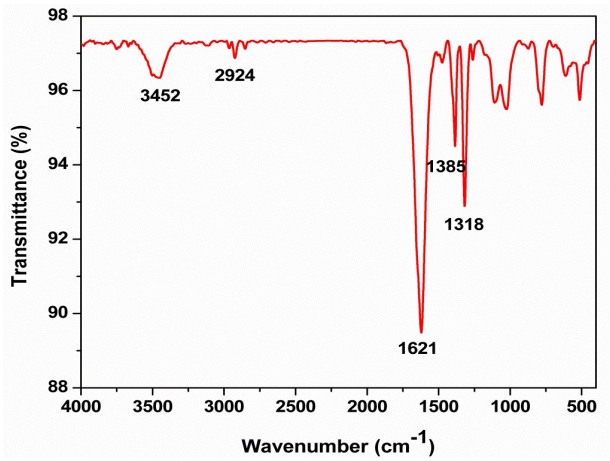

Figure S17. FT-IR spectra of silver particles after dispersion and centrifugation with water for five times.