Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for "Reversible-Deactivation Radical Polymerization of Vinyl Acetate Mediated by Tralen, An Organomediator"

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^{1}H NMR and ^{13}C NMR spectrum

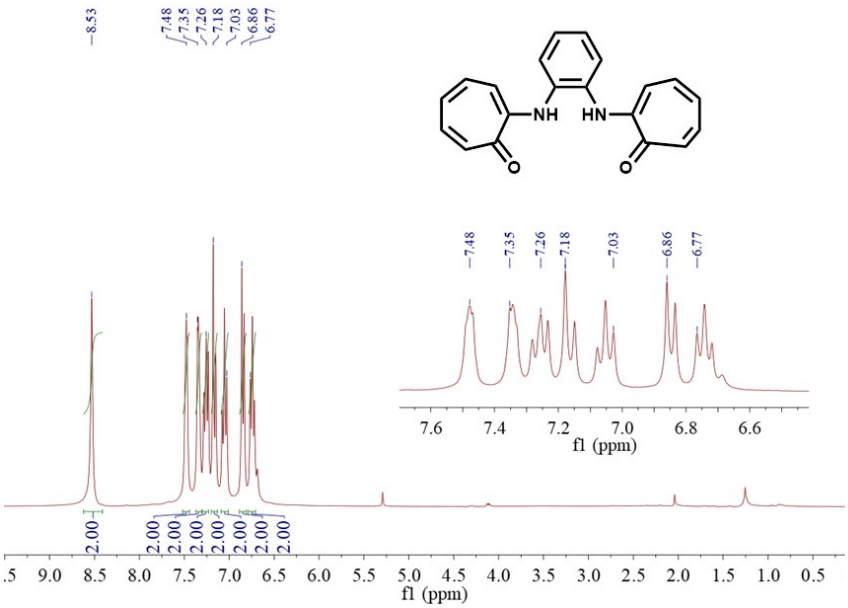


Figure S1. ^{1}H NMR spectrum of 2,2'-(1,2-phenylenebis(azan-ediyl))bis(cyclohepta-2,4,6-trien-1-one) in $CDCl_3$.

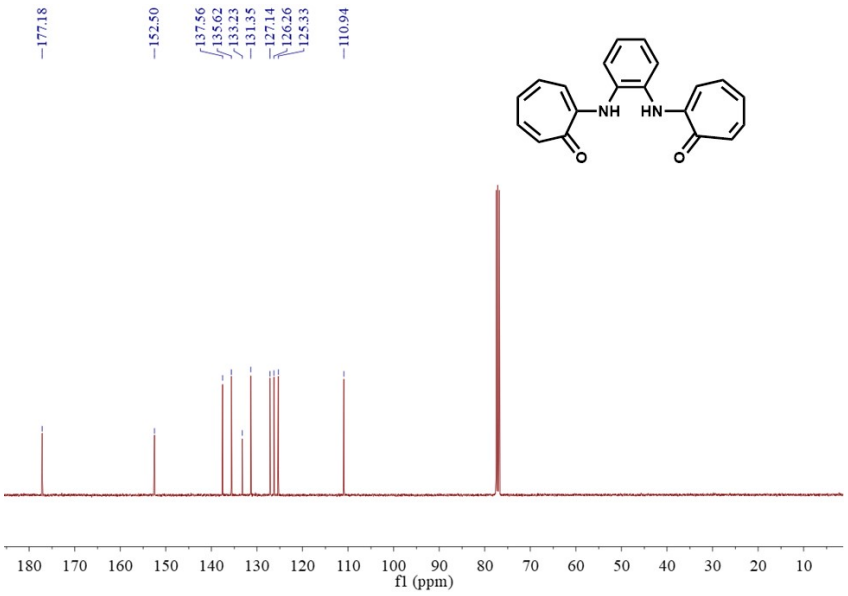


Figure S2. ^{13}C NMR spectrum of 2,2'-(1,2-phenylenebis(azan-ediyl))bis(cyclohepta-2,4,6-trien-1-one) in $CDCl_3$.

UV-Vis spectrum

The absorption wavelengths of tralen shown the dual peaks at 345 and 387 nm, respectively. Moreover, it exhibited the broad shoulder peak around 400 to 450 nm.

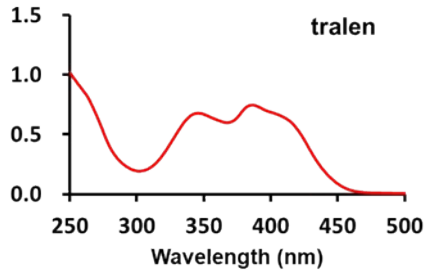


Figure S3. UV-Vis spectrum of tralen.

The metal content of tralen detected by ICP-MS

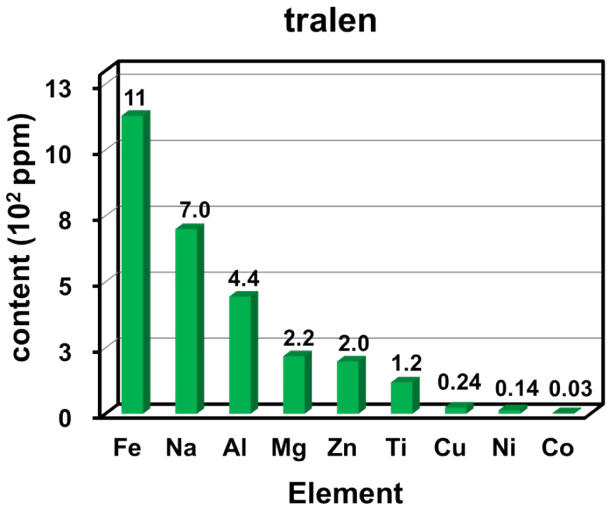


Figure S4. The content of metal in tralen organic compound.

The polymerization of VAc was performed with tralen (17.2 mg, 0.05 mmol) and AIBN (44.5 mg, 0.27 mmol) in the bulk solution of VAc (5 ml, 54 mmol). The reaction was heated to 60 °C to start the polymerization. Accordingly, we can calculate the molar concentration (M) of metal ions in the polymerization from the contents (ppm) of metal ions measured by ICP-MS:

Fe = 1100 (g) / 10^6 g x 17.2 x10^{-3} (g) / 55.845 (g mol^{-1}) / 5 x 10^{-3} (L) = 6.78 x 10^{-5} (M)

Na = 700/10^6 x 17.2 x10^{-3}/22.990/5 x 10^{-3} = 1.05 x 10^{-4} (M)

Al = 440/10^6 x 17.2 x10^{-3}/26.982/5 x 10^{-3} = 5.61 x 10^{-5} (M)

Mg = 220/10^6 x 17.2 x10^{-3}/24.305/5 x 10^{-3} = 3.11 x 10^{-5} (M)

Zn = 200/10^6 x 17.2 x10^{-3}/65.38/5 x 10^{-3} = 1.05 x 10^{-5} (M)

Ti = 120/10^6 x 17.2 x10^{-3}/47.867/5 x 10^{-3} = 8.62 x 10^{-6} (M)

Cu = 24/10^6 x 17.2 x10^{-3}/63.546/5 x 10^{-3} = 1.30 x 10^{-6} (M)

Ni = $14/10^6$ x 17.2 x10^{-3}/58.693/5 x 10^{-3} = 8.21 x 10^{-7} (M) Co = $3/10^6$ x 17.2 x10^{-3}/58.933/5 x 10^{-3} = 1.75 x 10^{-7} (M)

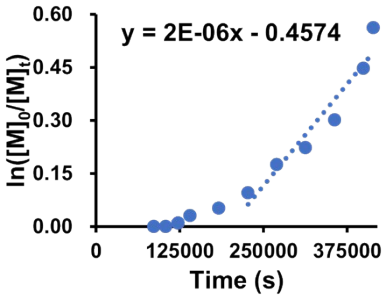
Experimental data of each polymerization

Table S1 Polymerization of VAc mediated by tralen compound with AIBN as initiator at 60 °C in bulk under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/5/1000

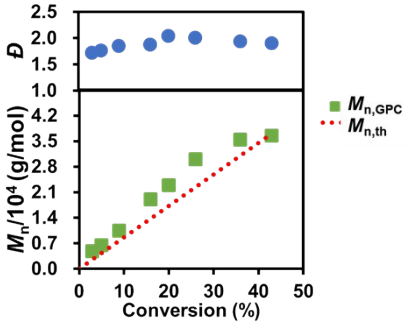
Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
24.0	0	-	-	-
29.0	0	-	-	-
34.0	1	4100	900	1.59
39.0	3	4700	2600	1.72
51.0	5	6400	4300	1.76
63.0	9	10400	7700	1.85
75.0	16	19000	13800	1.87
87.0	20	22900	17200	2.04
99.0	26	30000	23400	2.00
111.0	36	35300	31000	1.93
115.0	43	36500	37000	1.90

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th}$ = ($[VAc]_0/[tralen]_0$) × (M.W. of VAc) × Conv.

(a)



(b)



(c)

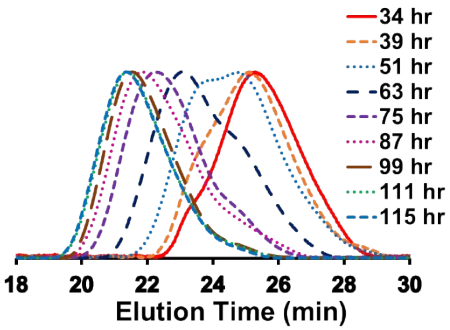


Figure S5. (a) First-order kinetics plots. (b) The plots of M_n and $Đ$ versus conversion. (c) The GPC traces for the polymerization of VAc mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/5/1000, at 60 °C in bulk.

Table S2 Polymerization of VAc mediated by tralen compound with AIBN as initiator at 60 °C in bulk under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/10/1000

Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
13.0	1	3700	900	1.99
17.0	3	5500	2600	1.92
21.0	10	10400	8600	2.41
23.0	15	15900	12900	2.49
25.0	22	23200	18900	2.44
27.0	26	30400	22400	2.33
29.0	32	39100	27500	2.14
31.0	34	43900	29300	2.08
33.0	43	50100	37000	2.05

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th}$ = ($[VAc]_0/[tralen]_0$) × (M.W. of VAc) × Conv.

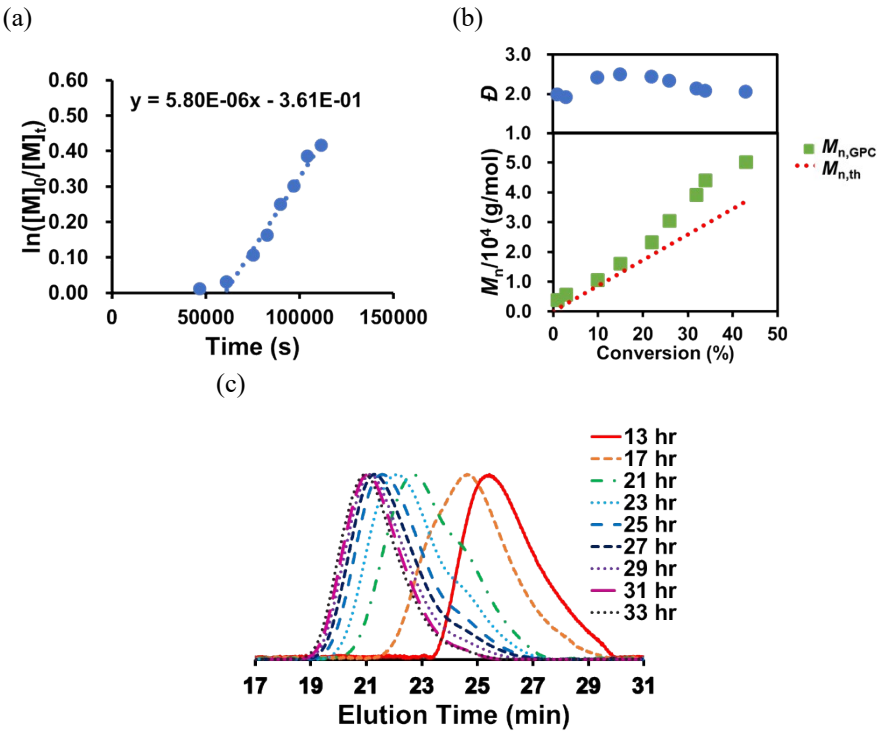


Figure S6. (a) First-order kinetics plots. (b) The plots of M_n and $Đ$ versus conversion. (c) The GPC traces for the polymerization of VAc mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/10/1000, at 60 °C in bulk.

Table S3 Polymerization of VAc mediated by tralen compound with AIBN as initiator at 60 °C in bulk under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/20/1000

Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
3	0	-	-	-
4	2	3200	1700	1.58
5	4	4300	3400	1.69
6	6	5500	5200	1.99
7	12	8600	10300	2.28
8	19	12900	16300	2.72
9	29	19400	24900	2.65
10	40	24700	34400	2.60
11	43	29300	37000	2.53

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th}$ = ($[VAc]_0/[tralen]_0$) × (M.W. of VAc) × Conv.

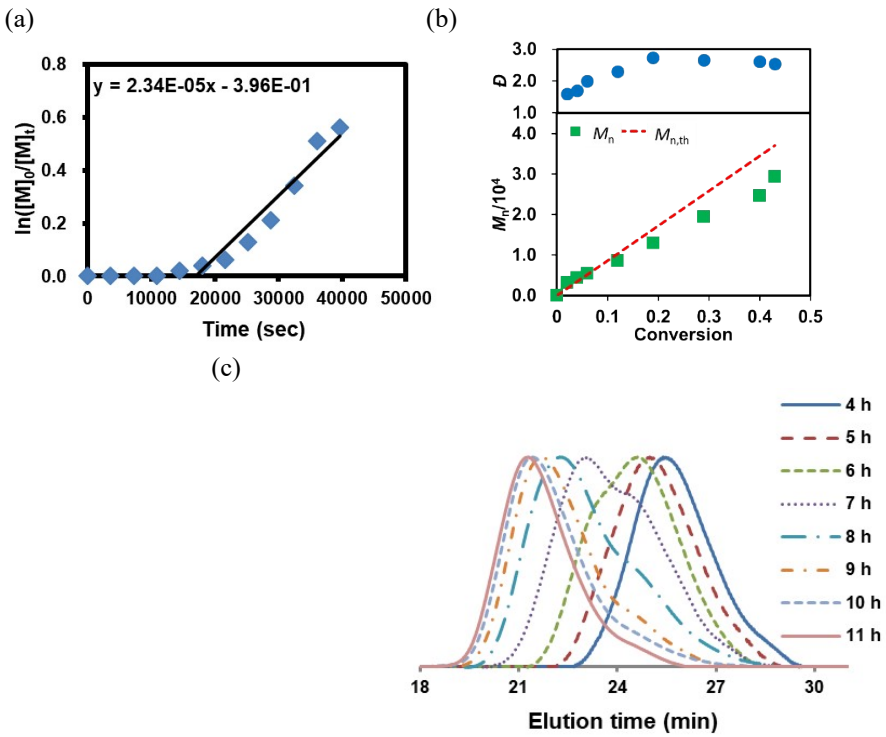


Figure S7. (a) First-order kinetics plots. (b) The plots of M_n and $Đ$ versus conversion. (c) The GPC traces for the polymerization of VAc mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/20/1000, at 60 °C in bulk.

Table S4 Polymerization of VAc mediated by tralen compound with AIBN as initiator at 60 °C in bulk under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/20/500

Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
3.0	0	-	-	-
4.0	3	2000	1300	1.37
5.0	8	2700	3400	1.66
6.0	12	4800	5200	2.08
7.0	23	6200	9900	2.60
9.0	43	14800	18500	2.11
10.5	69	27600	29700	2.18

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th}$ = $([VAc]_0/[tralen]_0)$ × (M.W. of VAc) × Conv.

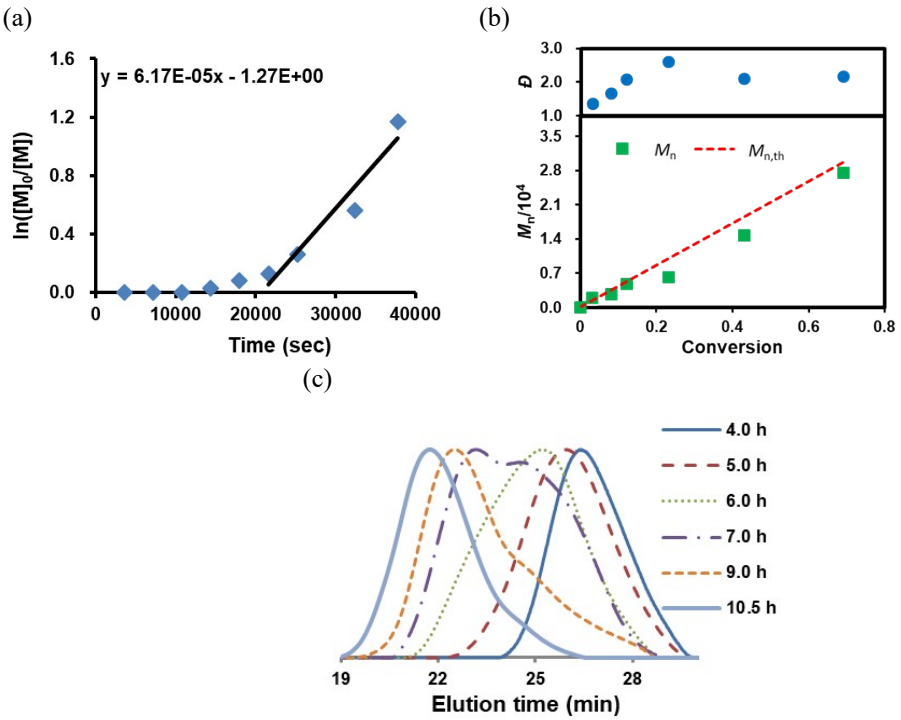


Figure S8. (a) First-order kinetics plots. (b) The plots of M_n and $Đ$ versus conversion. (c) The GPC traces for the polymerization of VAc mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/20/500, at 60 °C in bulk.

Table S5 Polymerization of VAc mediated by tralen compound with AIBN as initiator at 60 °C in bulk under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/20/4000

Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
4.0	0	-	-	-
5.0	2	9400	6900	2.05
6.0	3	13700	10300	1.77
7.5	7	18400	24100	2.40
9.0	13	37900	44700	2.04
10.5	18	48200	61900	2.13
12.0	21	62100	72300	1.95
13.0	28	82300	96400	2.00

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th}$ = ($[VAc]_0/[tralen]_0$) × (M.W. of VAc) × Conv.

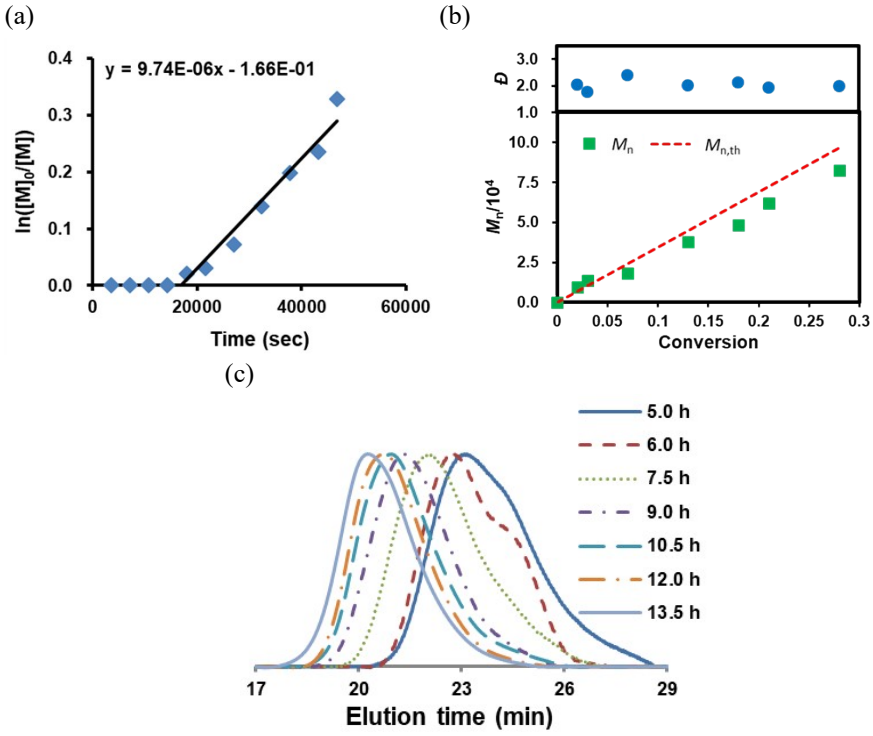


Figure S9. (a) First-order kinetics plots. (b) The plots of M_n and $Đ$ versus conversion. (c) The GPC traces for the polymerization of VAc mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/20/4000, at 60 °C in bulk.

Table S6 Polymerization of VAc mediated by tralen compound with AIBN as initiator at 60 °C in bulk under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/10/4000

Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
12.0	0	-	-	-
16.0	2	15000	6900	1.67
20.0	4	25700	13800	1.78
24.0	10	45900	34400	1.95
26.0	13	56700	44800	2.04
28.0	19	76300	65400	2.08
30.0	24	97500	82600	2.06
32.0	30	104300	103300	2.38

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th}$ = ($[VAc]_0/[tralen]_0$) × (M.W. of VAc) × Conv.

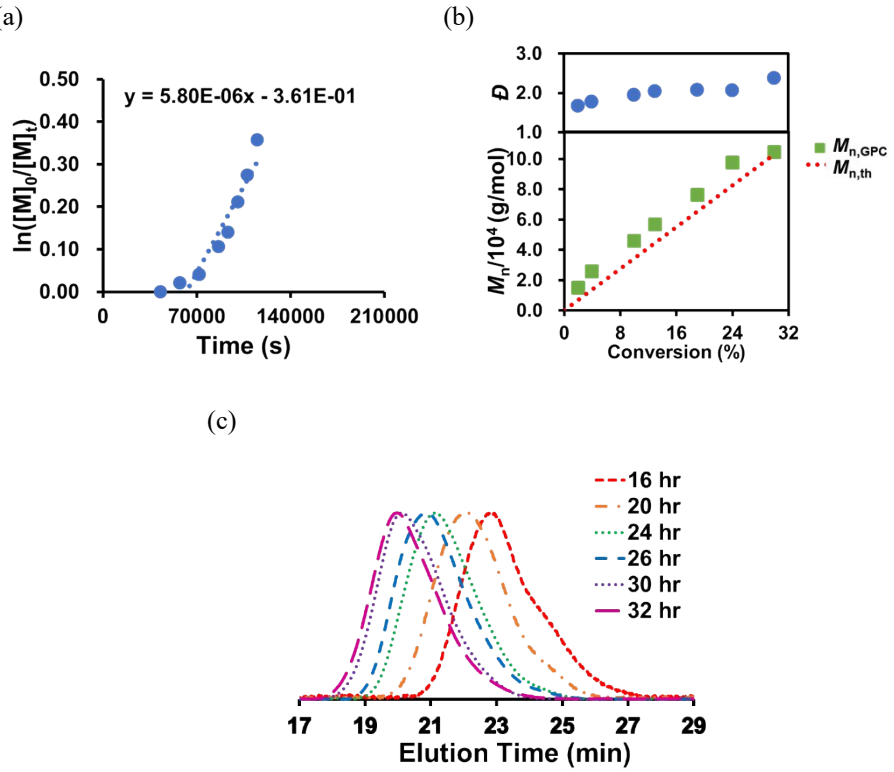


Figure S10. (a) First-order kinetics plots. (b) The plots of M_n and $Đ$ versus conversion. (c) The GPC traces for the polymerization of VAc mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/10/4000, at 60 °C in bulk.

Table S7 Polymerization of MA mediated by tralen compound with AIBN as initiator at 60 °C in chloroform under the condition of $[tralen]_0/[AIBN]_0/[MA]_0 = 1/10/1000$, $[MA]_0 = 3.68$ M

Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
1.0	6	20500	5100	2.05
2.0	14	21600	12100	2.00
3.0	22	24200	18900	2.05
4.0	30	24300	25800	2.07
5.0	36	24000	31000	2.11
6.0	40	25200	34400	2.03
7.5	48	26700	41400	2.00
9.0	53	29500	45700	1.92
10.5	62	32200	53400	1.83
12.0	69	34100	59400	1.81
14.0	76	35500	65400	1.81

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th} = ([MA]_0/[tralen]_0) \times (\text{M.W. of MA}) \times \text{Conv.}$

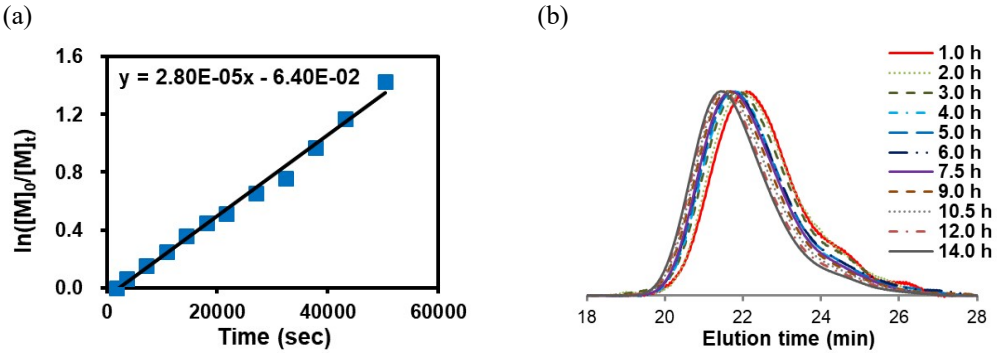


Figure S11. (a) First-order kinetics plots. (b) The GPC traces for the polymerization of MA mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[MA]_0 = 1/10/1000$, $[MA]_0 = 3.68$ M at 60 °C in chloroform.

Table S8 Polymerization of MMA mediated by tralen compound with AIBN as initiator at 60 °C in chloroform under the condition of $[tralen]_0/[AIBN]_0/[MMA]_0 = 1/10/1000$, $[MMA]_0 = 3.13$ M.

Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
0.5	8	68700	8000	1.64
1.0	19	57900	19000	1.80
2.0	42	54300	42100	1.67
3.0	52	53100	52100	1.68
4.0	64	43200	64100	1.88
5.0	73	38100	73100	2.00
6.5	80	38200	80100	1.95

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by gel permeation chromatography (GPC) with polystyrene as standard. [c] $M_{n,th} = ([MMA]_0/[tralen]_0) \times (M.W. \text{ of MMA}) \times Conv.$

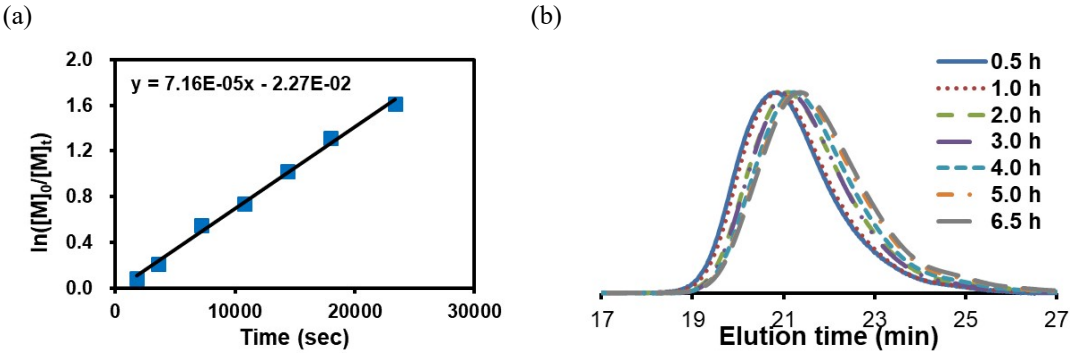


Figure S12. (a) First-order kinetics plots (b) The GPC traces for the polymerization of MMA mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[MMA]_0 = 1/10/1000$, $[MMA]_0 = 3.13$ M at 60 °C in chloroform.

Table S9 Polymerization of Sty mediated by tralen compound with AIBN as initiator at 90 °C in acetonitrile under the condition of $[tralen]_0/[AIBN]_0/[Sty]_0$ = 1/10/1000, $[Sty]_0$ = 2.90 M

Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
0.5	7	8500	7300	1.69
1.5	22	8800	22900	1.82
3.0	35	9600	36500	1.90
5.5	57	7900	59400	2.11
7.0	63	8300	65600	2.18

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th}$ = ($[Sty]_0/[tralen]_0$) × (M.W. of Sty) × Conv.

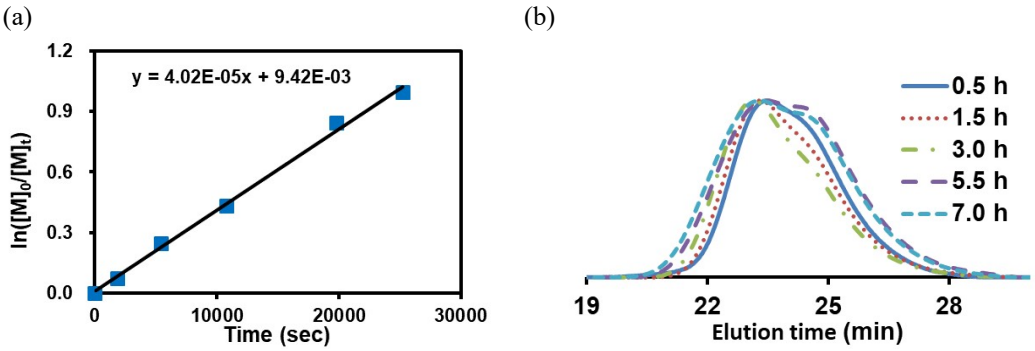


Figure S13. (a) First-order kinetics plots. (b) The GPC traces for the polymerization of Sty mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[Sty]_0$ = 1/10/1000, $[Sty]_0$ = 2.90 M at 90 °C in acetonitrile.

Table S10 Polymerization of AN mediated by tralen compound with AIBN as initiator at 60 °C in DMF under the condition of $[tralen]_0/[AIBN]_0/[AN]_0 = 1/10/1000$, $[AN]_0 = 5.08$ M

Time (hours)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
2	7	7200	3700	1.77
3	12	9600	6400	1.65
5	18	11600	9600	1.53
7	24	12100	12700	1.56
9	27	12300	14300	1.58
11	31	13000	16500	1.53
13	38	14100	20200	1.58

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with PEG as standard. [c] $M_{n,th} = ([AN]_0/[tralen]_0) \times$ (M.W. of AN) × Conv.

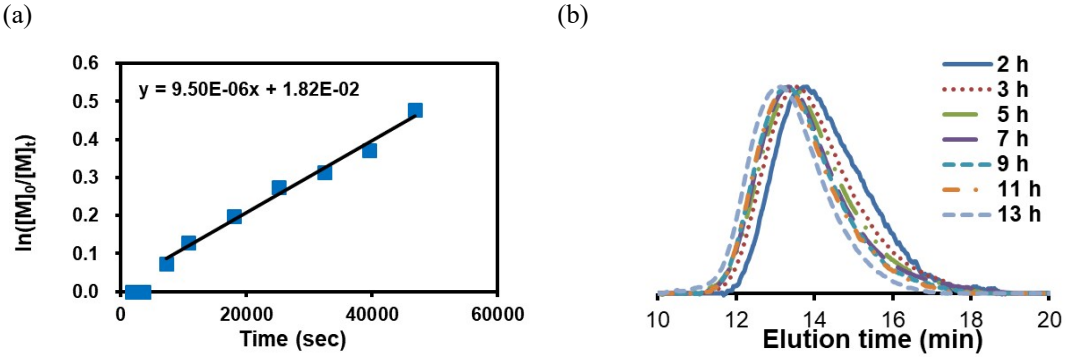


Figure S14. (a) First-order kinetics plots. (b) The GPC traces for the polymerization of AN mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[AN]_0 = 1/10/1000$, $[AN]_0 = 5.08$ M at 60 °C in DMF.

Table S11 Polymerization of *N*VP mediated by tralen compound with AIBN as initiator at 60 °C in bulk under the condition of $[tralen]_0/[AIBN]_0/[NVP]_0 = 1/10/1000$, $[NVP]_0 = 9.36$ M

Time (mins)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
345	0	-	-	-
360	9	10900	10000	3.54
375	11	14200	12200	3.45
390	15	19000	16700	3.04
405	21	20800	23300	3.06
420	28	26500	31100	2.85

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with PEG as standard. [c] $M_{n,th} = ([NVP]_0/[tralen]_0) \times$ (M.W. of *N*VP) × Conv.

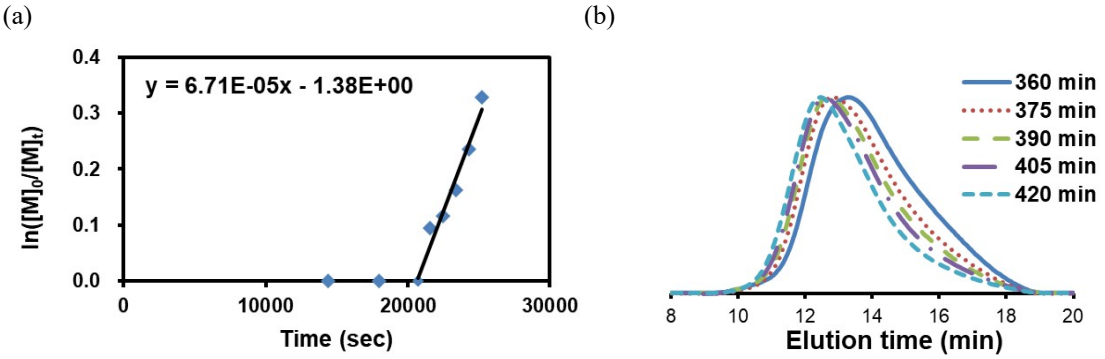


Figure S15. (a) First-order kinetics plots. (b) The GPC traces for the polymerization of *N*VP mediated by tralen under the condition of $[tralen]_0/[AIBN]_0/[NVP]_0 = 1/10/1000$, $[NVP]_0 = 9.36$ M at 60 °C in bulk.

Table S12 Polymerization of *N*VP mediated by PVAc-tralen macroinitiator without (240-1440 min) and with AIBN (1470-1560min) as initiator at 60 °C in DMF under the condition of $[PVAc\text{-}tralen]_0/[AIBN]_0/[NVP]_0 = 1/0/1000$ and 1/5/2000.

Time (mins)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
240	0	17200	8200	1.73
480	1	18200	18300	1.80
720	2	21200	19400	1.85
1440	3	25500	20500	2.08
1470	6	32600	30500	2.17
1500	14	42600	48300	2.09
1530	21	49800	63900	2.03
1560	30	50800	83900	2.08

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with PEG as standard. [c] $M_{n,th} = ([NVP]_0/[tralen]_0) \times$ (M.W. of *N*VP) × Conv.

Diffusion-ordered NMR spectroscopy (DOSY-NMR) of PVAc-*b*-P*N*VP block copolymer

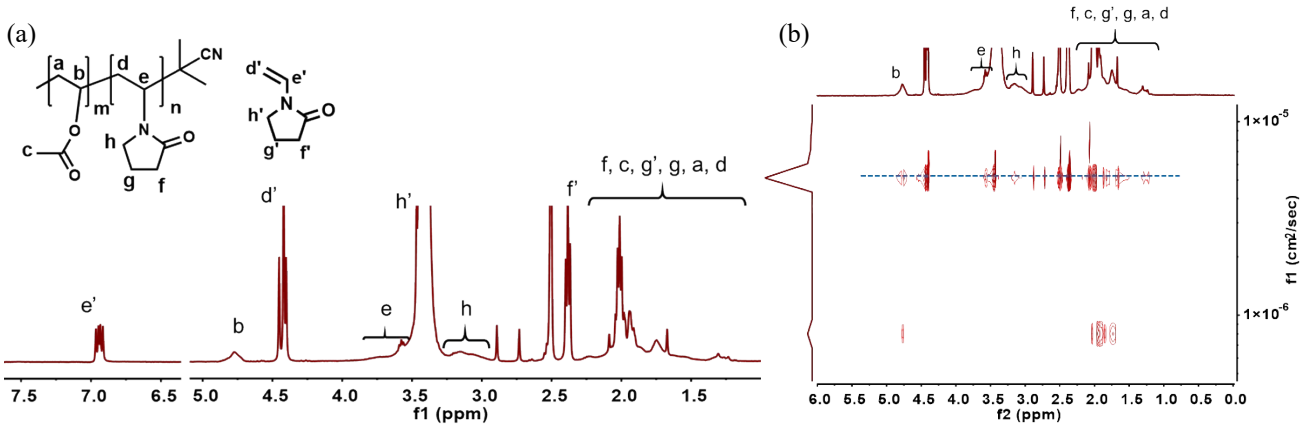
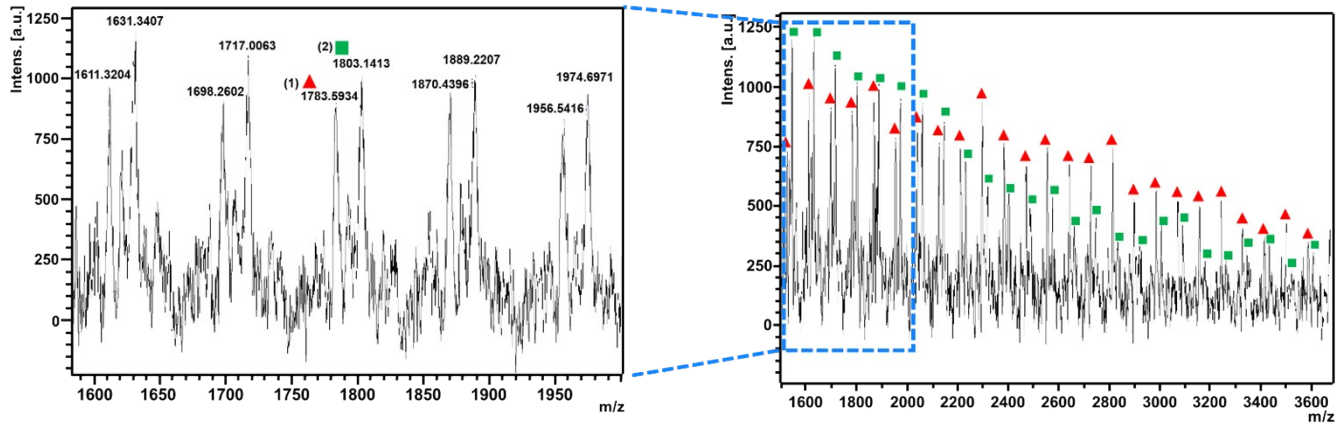


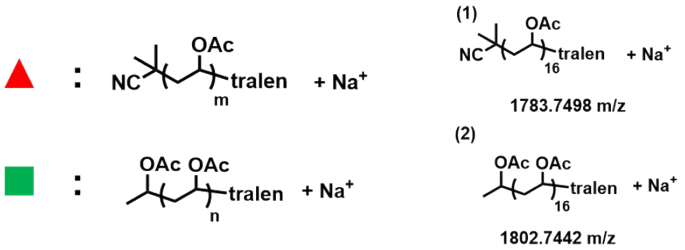
Figure S16. (a) ^{1}H NMR spectrum of PVAc-*b*-P*N*VP block copolymer in DMSO-d_6. (b) DOSY-NMR spectrum of PVAc-*b*-P*N*VP block copolymer in DMSO-d_6.

MALDI TOF spectrum

(a)



(b)



(1) 1783.7498 m/z

(2) 1802.7442 m/z

Figure S17. (a) MALDI-TOF spectra for the macro-initiator of PVAc-tralen obtained from the polymerization under the condition of $[tralen]_0/[AIBN]_0/[VAc]_0$ = 1/20/500 in bulk at 60 °C. The polymerization was stopped in 370 minutes with the conversion = 5% and M_n = 1900 g mol^{-1}. (b) Possible molecular formula and their theoretical molecular weight.

Model reaction for mechanism study

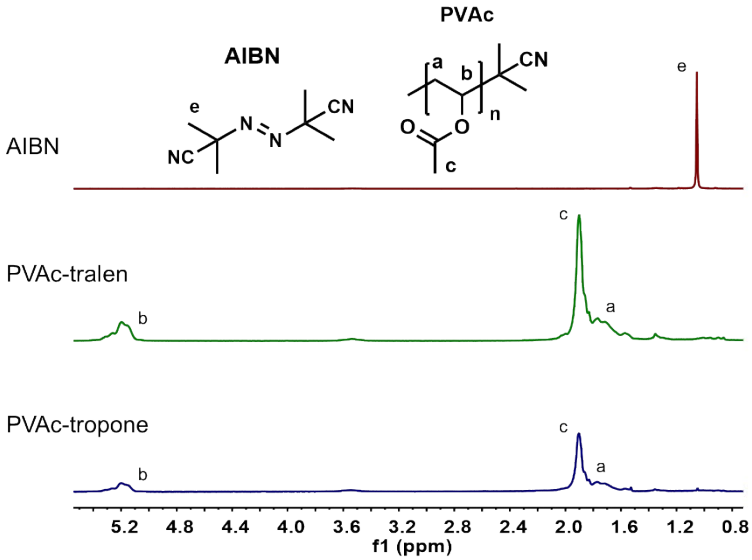


Figure S18. The ^{1}H NMR spectrum of PVAc-tralen, PVAc-tropone, were purified by dry ether, and AIBN in benzene-d_6.

Table S13 Polymerization of VAc mediated by PVAc-tralen macroinitiator without (240-1440 min) and with AIBN (1450-1470min) as initiator at 60 °C in bulk under the condition of $[PVAc\text{-}tralen]_0/[AIBN]_0/[VAc]_0$ = 1/0/1000 and 1/20/1000.

Time (mins)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
240	2	8700	9900	2.67
480	4	9400	11600	2.95
720	6	11100	13400	2.83
1440	8	12100	15100	3.26
1450	10	12200	16800	3.35
1460	19	23500	24600	2.65
1470	29	29500	33200	2.81

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th}$ = $([VAc]_0/[tralen]_0)$ × (M.W. of VAc) × Conv.

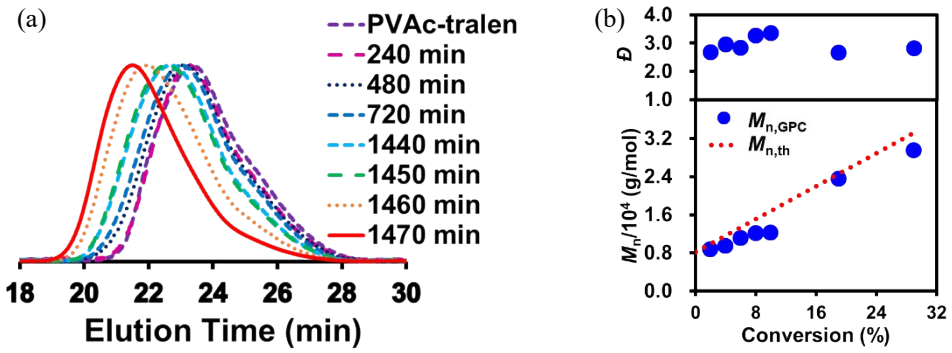


Figure S19. (a) The GPC traces of VAc polymerization mediated by PVAc-tralen under the condition of [PVAc-tralen]$_0$/[AIBN]$_0$/[VAc]$_0$ = 1/0/1000 and [PVAc-tralen]$_0$/[AIBN]$_0$/[VAc]$_0$ = 1/20/1000 in bulk at 60 °C. The macroinitiator PVAc-tralen was synthesized under the condition of [tralen]$_0$/[AIBN]$_0$/[VAc]$_0$ = 1/20/500 at 60 °C in bulk for 390 minutes with conversion equal to 27% with M_n equal to 8,200 g/mol and $Đ$ equal to 2.71. (b) the plots of M_n and $Đ$ versus conversion under the condition of [PVAc-tralen]$_0$/[AIBN]$_0$/[VAc]$_0$ = 1/0/1000 and [PVAc-tralen]$_0$/[AIBN]$_0$/[VAc]$_0$ = 1/20/1000.

Table S14 Polymerization of VAc mediated by PVAc-tropone macroinitiator at 60 °C in bulk under the condition of [PVAc-tropone]$_0$/[AIBN]$_0$/[VAc]$_0$ = 1/0/2000.

Time (mins)	Conv.[a] (%)	M_n[b] (g mol^{-1})	$M_{n,th}$[c] (g mol^{-1})	$Đ$[b]
120	2	36300	6400	1.46
180	4	51800	9900	1.44
240	7	66300	15100	1.75
360	19	97600	35700	1.99
420	29	100900	52900	2.30

[a] Conversion was detected by ^{1}H NMR. [b] M_n and $Đ$ were determined by GPC with polystyrene as standard. [c] $M_{n,th}$ = ([VAc]$_0$/[tropone]$_0$) × (M.W. of VAc) × Conv. Due to the bimodal GPC traces, the M_n and $Đ$ were the values for the single peak at high M_n region.

(a) (b)

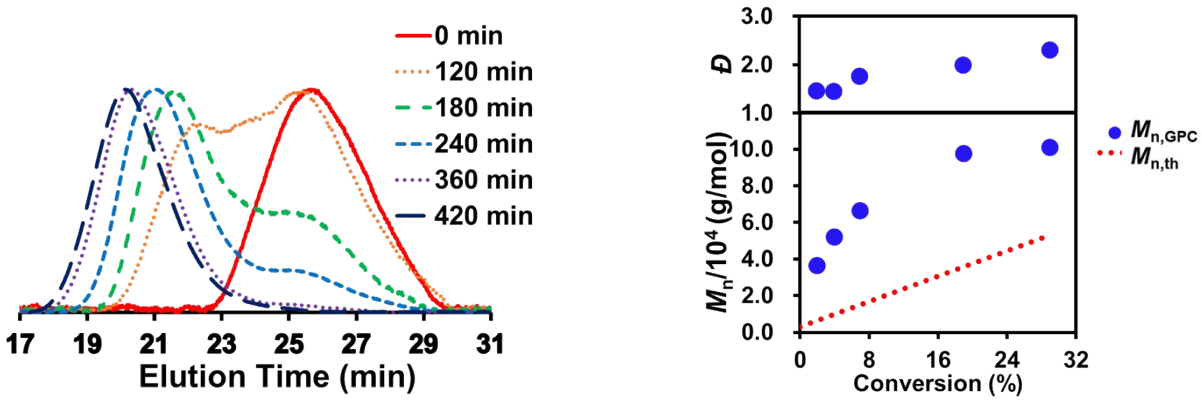


Figure S20. The GPC traces of VAc polymerization mediated by PVAc-tropone under the condition of (a) [PVAc-tropone]$_0$/[AIBN]$_0$/[VAc]$_0$ = 1/0/2000 and (b)The plots of M_n and $Đ$ versus conversion under the condition of [PVAc-tropone]$_0$/[AIBN]$_0$/[VAc]$_0$ = 1/0/2000. The macroinitiator PVAc-tropone was synthesized under the condition of [tropone]$_0$/[AIBN]$_0$/[VAc]$_0$ = 1/20/300 at 60 °C in bulk for 360 minutes with conversion equal to 2% with M_n equal to 3300 g/mol and $Đ$ equal to 1.62. Due to the bimodal GPC traces, the M_n and $Đ$ were the values for the single peak at high M_n region.

References

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