Supplementary Information (SI) for Polymer Chemistry.

Electronic Supporting Information

Troponoid-Mediated Radical Polymerization in Aqueous Medium

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1. Materials

Dichloromethane was refluxed at least 24 hours CaH_2 to remove water and purchased from ACROS. *N*-vinylpyrrolidone (*N*VP, Acros, 99%) was distilled under reduced pressure and degassed by three freeze–pump–thaw cycles. 2-Hydroxyethyl acrylate (HEA, Acros, 97%) was dissolved in water (25% by volume), and the solution was extracted 10 times with hexane to remove diacrylates. *N, N*-Dimethylacrylamide (DMA, TCI, 99%) was passed through the basic Al_2O_3 to remove the inhibitor before use. Hydrochloric acid (SHOWA), diethyl ether (Echo Chemical Co., Ltd, 99%), n-hexane (Seed chem, 95%), diethylamine (Alfa Aesar, 99%), tropone (**TP**, Alfa Aesar, 97%), tropolone (**TP-OH**, TCI, 98%), 2-methoxytropone (**TP-OMe**, TCI, 98%), 2-chlorotropone (**TP-Cl**, Aldrich, > 98%), 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, TCI, 98%), 4,4’-Azobis(4-cyanovaleric acid) (V-501, Alfa Aesar, 98%), 2,2'-azobisisobutyronitrile(AIBN, Otsuka chemical, 99%) and deuterated solvents (Aldrich) were used as received without any purification. The water used in all the experiments was purified by a Milli-Q system (Merck) with a resistivity of 18 MΩ cm.

2. Characterization

NMR spectroscopy was used to characterize the structures of all chemicals and monomer conversion. The spectrum was recorded by Bruker Avance III HD 400 MHz, 500 MHz, and 800 MHz spectrometers at 298 K. The chemical shifts in ^1H NMR were shown in ppm referring to residual solvent in $CDCl_3$ as δ 7.24 ppm, D_2O as δ 4.79 ppm, and DMSO-d_6 as δ 2.50 ppm. ^{13}C NMR chemical shifts are given in ppm refer to residual solvent in $CDCl_3$ as δ 77 ppm. Polymeric products of poly(*N*-vinylpyrrolidone), poly(*N*, *N*-dimethylacrylamide) and poly(2-hydroxyethyl acrylate) were characterized by Gel permeation chromatography (GPC) system equipped with Ultimate 3000 liquid chromatograph associated with a 101 refractive index (RI) detector and three Waters columns (Styragel® HR 2 DMF, Styragel® HR 4 DMF, and Styragel® HR 5 DMF) using DMF-LiBr (0.1 M) as the eluent at 80 °C with a flow rate of 1 ml/min. The calibration was based on linear poly(methyl methacrylate) (PMMA) with molecular weights 1810, 4760, 9720, 30780, 72800, 146500, 260900, and 675500 g/mol with a narrow polydispersity ($Đ$ = 1.01~1.05). The number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), and polydispersity index ($Đ$) of the polymeric products were obtained using DIONEX chromeleon software. Poly(acrylic acid) was characterized by GPC equipped with Agilent columns (PL aquagel-OH 20 and PL aquagel-OH 30) using a neutral solution containing $NaNO_3$ (0.2 M) and NaH_2PO_4 (0.01 M) as the eluent at 30 °C with a flow rate equal of 1 mL/min. The calibration was based on linear poly(acrylic acid) as standard ranging in molecular weight from 1.25×10^3 g/mol to 3.92×10^5 g/mol with a narrow polydispersity ($Đ$ = 1.01~1.05). The M_n, M_w, and polydispersity ($Đ$) of the polymeric products were calculated by DIONEX chromeleon software. UV-vis spectra were recorded by SHIMADZU UV-1800 instrument from 1100 to 190 nm with a double beam photometer and blank solution. Mass measurements were measured by Bruker Autoflex Speed and micrOTOF-Q II with an electrospray ionization (ESI) ion source.

3. General procedure for polymerization in aqueous

The mediator and VA-044 were placed in a 50 ml Schlenk flask and cycled three times with vacuum/nitrogen to remove oxygen. Deoxygenated deionized water and dried monomer were then added using a syringe under nitrogen. The mixture was stirred and heated to 40 ºC to initiate the polymerization process. A small portion of the polymerization mixture was extracted to measure the monomer conversion, molecular weight, and polydispersity using ^{1}H NMR spectroscopy and GPC system. The procedure for polymerizing 2-hydroxyethyl acrylate and *N*, *N*-Dimethylacrylamide was the same.

4. Synthesis of PVP-*b*-PVP block copolymer for chain extension

Macroinitiators of PVP-tropone were prepared by the *N*VP polymerization mediated by tropone under the conditions of $[\mathbf{TP}]_0/[\mathrm{AIBN}]_0/[N\mathrm{VP}]_0 = 1/10/200$ in bulk at 60 °C. Unreacted monomers and AIBN were extracte by deoxygenated diethyl ether. The macroinitiators were characterized using ^{1}H NMR spectrum and GPC to confirm the conversion and molecular weight. The flask containing macroinitiators was then purged with nitrogen, after which deoxygenated *N*VP monomer was added. The mixture was stirred and heated at 60 °C to start the polymerization.

5. Synthesis of PHEA-*b*-PHEA block copolymer for chain extension

Macroinitiators of PHEA-tropone were prepared by the HEA polymerization mediated by tropone under the conditions of $[\mathbf{TP}]_0/[\text{VA-044}]_0/[\mathrm{HEA}]_0 = 1/5/200$, $[\mathrm{HEA}]_0 = 1.93$ M, in deionized water at 40 °C. Unreacted monomers and water were removed under vacuum. The macroinitiators were characterized using ^{1}H NMR spectra and GPC to confirm the conversion and molecular weight. The flask containing macroinitiators was then purged with nitrogen, and then water and HEA ($[\mathrm{HEA}]_0 = 1.93$ M) solution treated with three cycles of freeze-pump-thaw process in another schlenk flask were injected into the reaction. The mixture was stirred and heated at 40 °C to start the polymerization.

6. Synthesis of PDMA-*b*-PDMA block copolymer for chain extension

Macroinitiators of PDMA-tropone were prepared by the DMA polymerization mediated by tropone under the conditions of $[\mathbf{TP}]_0/[\text{VA-044}]_0/[\text{DMA}]_0$ = 1/5/200, $[\text{DMA}]_0$ = 2.15 M, in deionized water at 40 °C. Unreacted monomers and water were removed under vacuum. The macroinitiators were characterized using ^{1}H NMR spectrum and GPC to confirm the conversion and molecular weight. The flask containing macroinitiators was then purged with nitrogen, and then water and DMA ($[\text{DMA}]_0$ = 2.15 M) solution treated with three cycles of freeze-pump-thaw process in another schlenk flask were injected into the reaction. The mixture was stirred and heated at 40 °C to start the polymerization.

7. Synthesis of PDMA-*b*-PVP block copolymer

Macroinitiators of PDMA-tropone were prepared by the DMA polymerization mediated by tropone under the conditions of $[\mathbf{TP}]_0/[\text{VA-044}]_0/[\text{DMA}]_0$ = 1/5/200, $[\text{DMA}]_0$ = 2.15 M, in deionized water at 40 °C. Unreacted monomers and water were removed under vacuum. The macroinitiators were characterized using ^{1}H NMR spectrum and GPC to confirm the conversion and molecular weight. The flask containing macroinitiators was then purged with nitrogen, and then water and *N*VP ($[N\text{VP}]_0$ = 4.68 M) solution treated with three cycles of freeze-pump-thaw process in another schlenk flask were injected into the reaction. The mixture was stirred and heated at 40 °C to start the polymerization.

8. Synthesis of PHEA-*b*-PVP block copolymer

Macroinitiators of PHEA-tropone were prepared by the HEA polymerization mediated by tropone under the conditions of [**TP**]$_0$/[VA-044]$_0$/[HEA]$_0$ = 1/5/200, [HEA]$_0$ = 1.93 M, in deionized water at 40 °C. Unreacted monomers and water were removed under vacuum. The macroinitiators were characterized using ^{1}H NMR spectrum and GPC to confirm the conversion and molecular weight. The flask containing macroinitiators was then purged with nitrogen, and then water and *N*VP ([*N*VP]$_0$ = 4.68 M) solution treated with three cycles of freeze-pump-thaw process in another schlenk flask were injected into the reaction. The mixture was stirred and heated at 40 °C to start the polymerization.

9. The first-order kinetic plots and GPC traces for the *N*VP polymerizations mediated by TP-OH

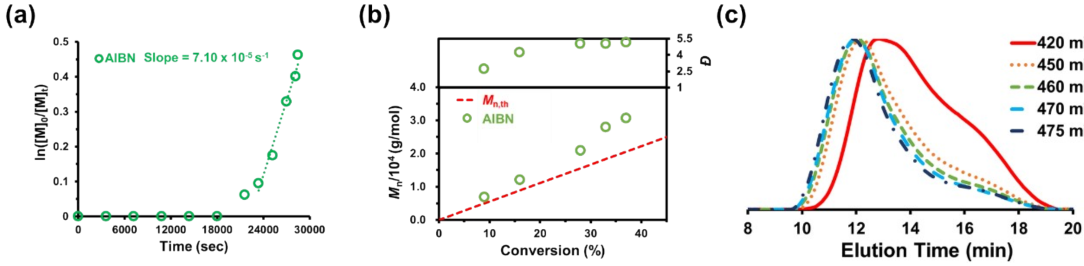

Figure S1 The *N*VP polymerizations mediated by **TP-OH** with AIBN as an initiator under the condition of [**TP-OH**]$_0$/[AIBN]$_0$/[*N*VP]$_0$ = 1/10/500, [*N*VP] = 4.68 M in DI water at 60 °C. (a) The first-order kinetic plots. (b) The plots of M_n and $Đ$ *versus* *N*VP conversion. (c) The GPC traces of *N*VP polymerization.

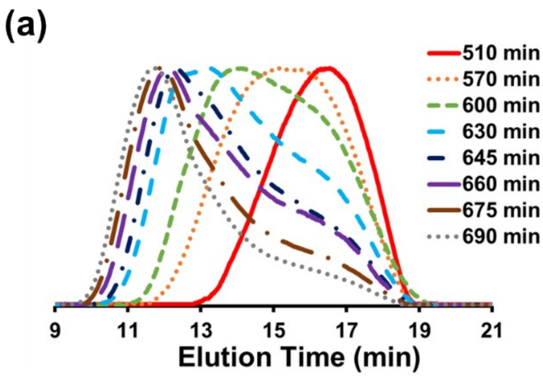

Figure S2 The GPC traces of *N*VP polymerization mediated by **TP-OH** under the condition of [**TP-OH**]$_0$/[VA-044]$_0$/[*N*VP]$_0$ = 1/x/500, [*N*VP]$_0$ = 4.68 M in DI water at 40 °C, when (a) x = 5 and (b) 20.

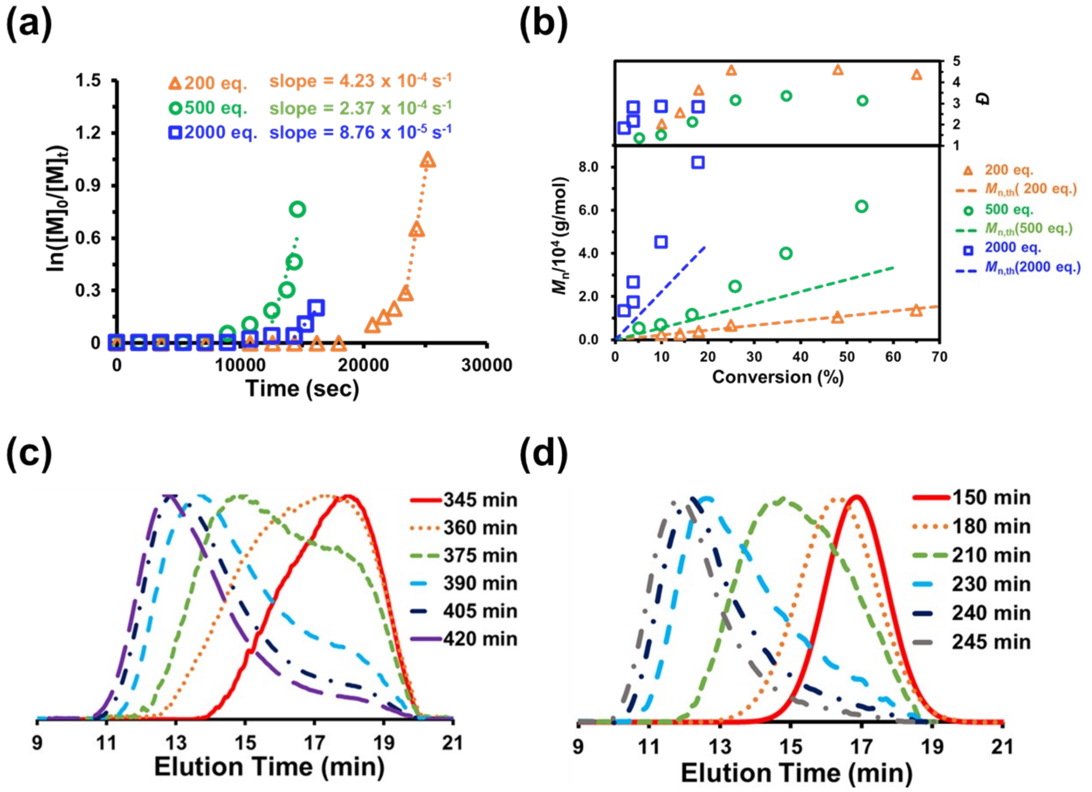

Figure S3 The *N*VP polymerization mediated by **TP-OH** under the condition of [**TP-OH**]$_0$/[VA-044]$_0$/[*N*VP]$_0$ = 1/10/x, x = 200, 500, or 2000, [*N*VP]$_0$ = 4.68 M in DI water at 40 °C. (a) The first-order kinetic plots. (b) The plots of M_n and polydispersity *versus* *N*VP conversion. The GPC traces of *N*VP polymerization when (c) x = 200 and (d) 2000.

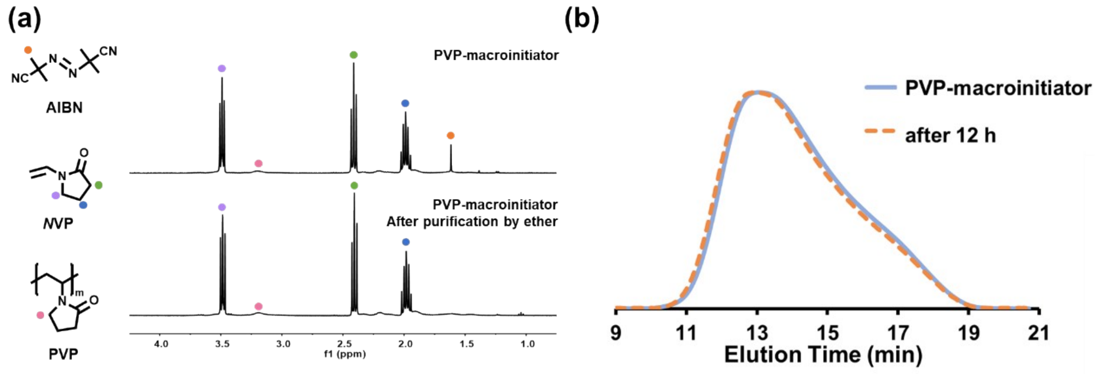

Figure S4 (a) ^{1}H NMR spectra of PVP-macroinitiator before purification (upper one) and after purification (lower one). (b) The GPC traces of chain extension from PVP-macroinitiator (conditions: [**TP-OH**]$_0$/[AIBN]$_0$/[*N*VP]$_0$ = 1/10/500, [*N*VP]$_0$ = 4.68 M in DI water at 60 °C, with conversion = 16% in 4 h, M_n = 11200 g/mol, $Đ$ = 4.27) to *N*VP without AIBN for 12 h (conversion = 0%, M_n = 11900 g/mol, $Đ$ = 4.27) under the conditions of [PVP-macroinitiator]$_0$/[*N*VP]$_0$ = 1//1000, [*N*VP]$_0$ = 4.68 M in DI water at 60 °C.

10. The control study for the *N*VP polymerization

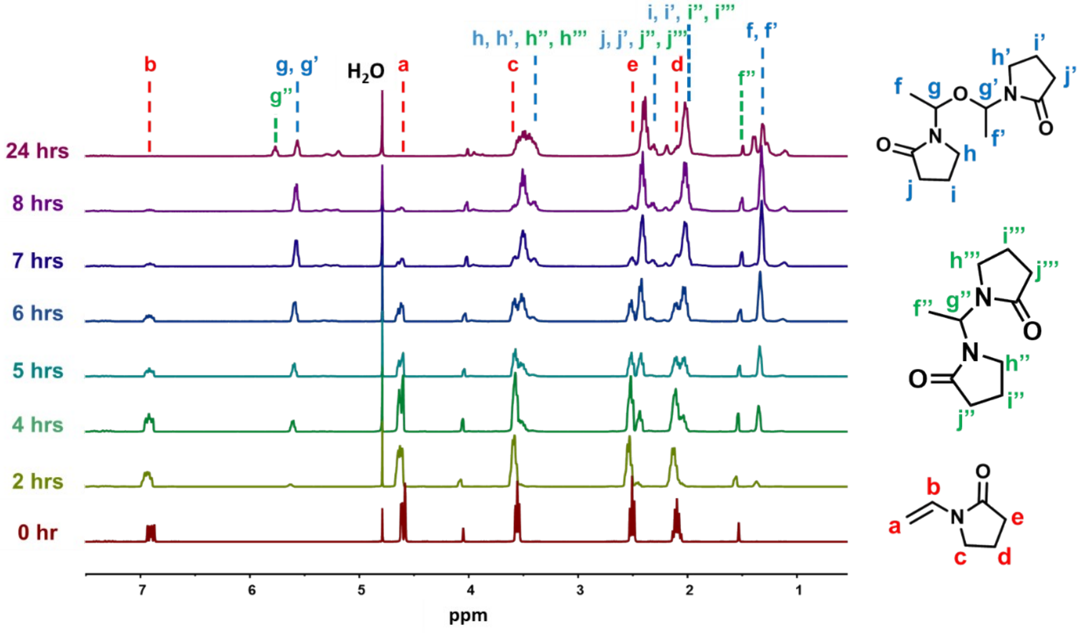

Figure S5 Time-dependent ^{1}H NMR spectra of reaction product for the *N*VP polymerization mediated by **TP-OH** with V-501 as an initiator under the condition of [**TP-OH**]$_0$/[V-501]$_0$/[*N*VP]$_0$ = 1/1/60, [*N*VP]$_0$ = 2.34 M in D_2O at 60 °C.

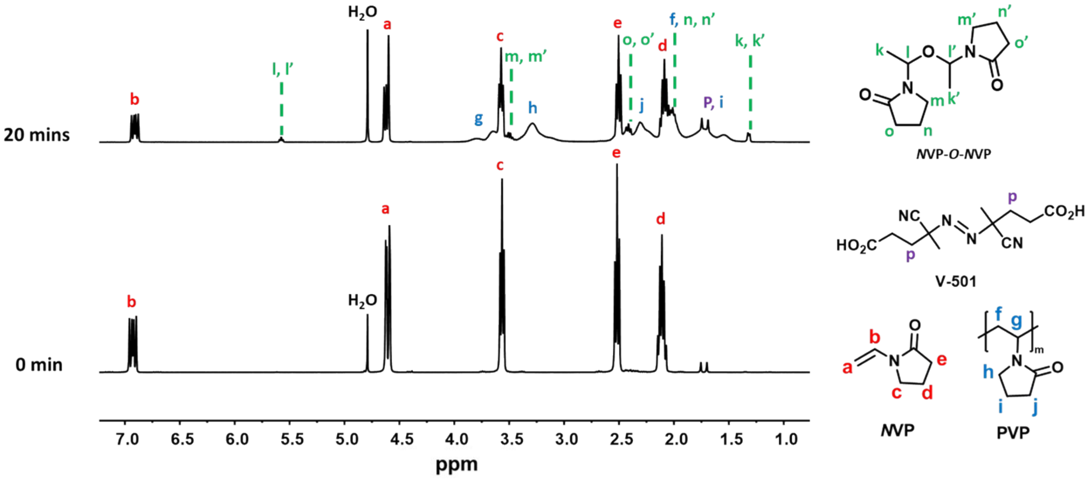

Figure S6 Time-dependent ^{1}H NMR spectra of reaction for the *N*VP polymerization with V-501 as an initiator under the condition of [V-501]$_0$/[*N*VP]$_0$ = 1/60, [*N*VP]$_0$ = 2.34 M in D_2O at 60 °C.

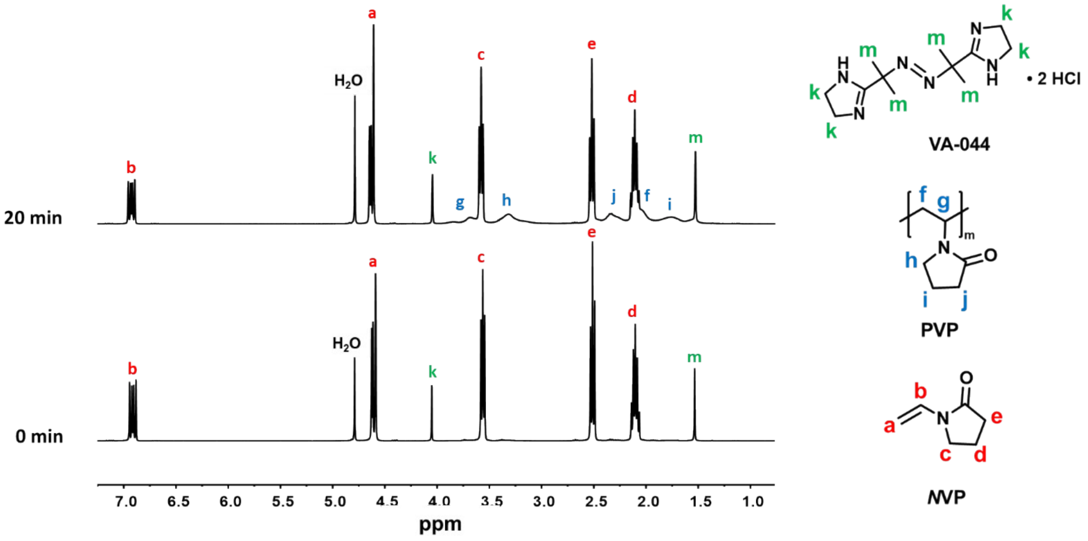

Figure S7 Time-dependent ^{1}H NMR spectra of reaction for the *N*VP polymerization with VA-044 as an initiator under the condition of [VA-044]$_0$/[*N*VP]$_0$ = 1/50, [*N*VP]$_0$ = 2.34 M in D_2O at 60 °C.

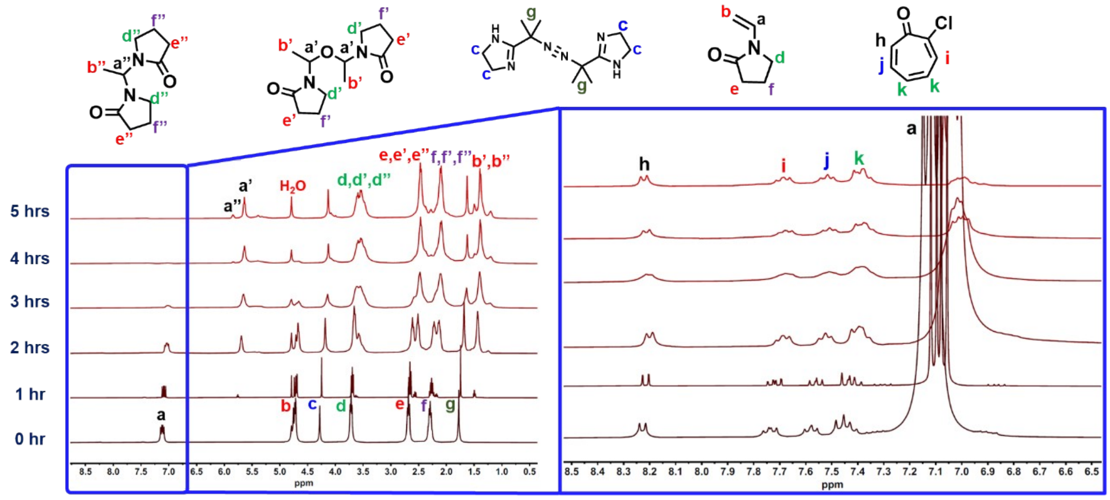

Figure S8 Time-dependent ^{1}H NMR spectra of reaction product for the *N*VP polymerization mediated by **TP-Cl** under the condition of [**TP-Cl**]$_0$/[VA-044]$_0$/[*N*VP]$_0$ = 1/5/50, [*N*VP]$_0$ = 4.68 M in D_2O at 40 °C.

11. First-order kinetic plots for the monomer scopes in the TP mediated radical aqueous polymerization

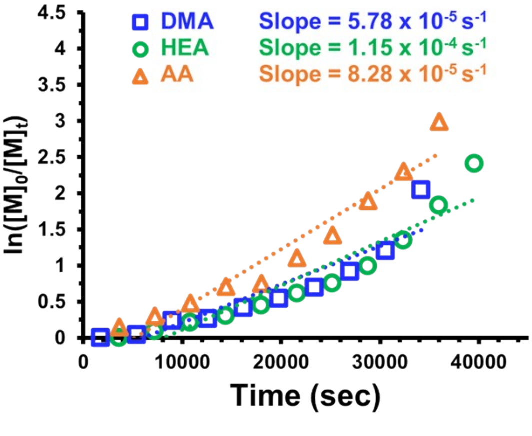

Figure S9 The first-order kinetic plots of DMA, HEA, and AA polymerizations mediated by **TP** under the condition of [**TP**]$_0$/[VA-044]$_0$/[monomer]$_0$ = 1/5/500 in DI water at 40 °C.

12. GPC traces for the chain extension of DMA and HEA polymerization mediated by TP

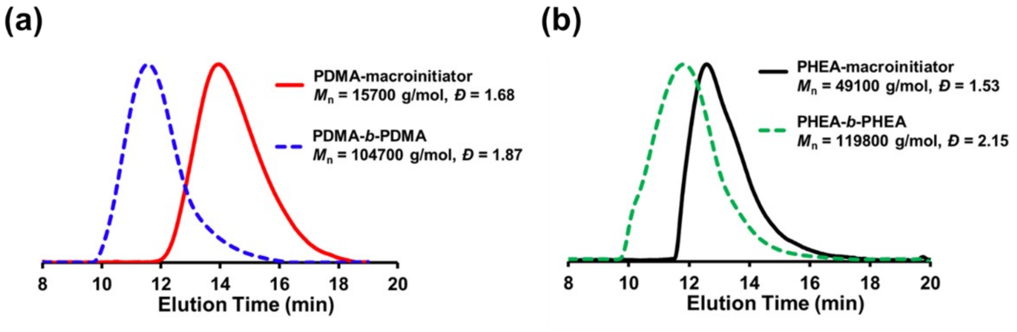

Figure S10 The GPC traces of chain extension initiated by the PDMA-macroinitiator (conditions: [**TP**]$_0$/[VA-044]$_0$/[DMA]$_0$ = 1/5/200, [DMA]$_0$ = 2.15 M in DI water at 40 °C, with conversion = 13%) or PHEA-macroinitiator (conditions: [**TP**]$_0$/[VA-044]$_0$/[HEA]$_0$ = 1/5/200, [HEA]$_0$ = 1.93 M in DI water at 40 °C, with conversion = 12%) under the condition of [macroinitiator]$_0$/[monomer]$_0$ = 1/1000, in DI water at 40 °C, with either (a) DMA or (b) HEA as the monomer.

13. Model reaction for the mechanism study

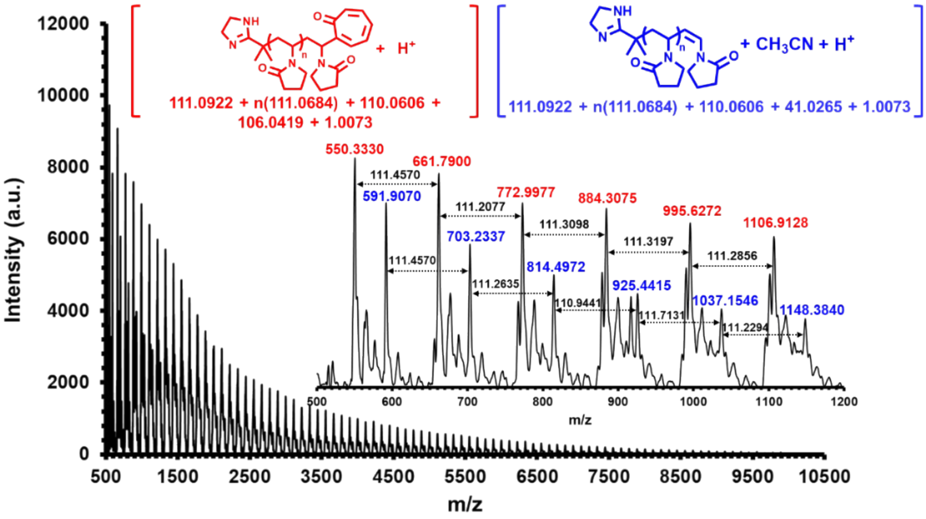

Figure S11 MALDI-TOF MS spectra for the PVP polymer obtained from the polymerization under the condition of [**TP**]$_0$/[VA-044]$_0$/[*N*VP]$_0$ = 1/5/500, [*N*VP]$_0$ = 4.68 M in DI water at 40 °C. The polymerization was stopped in 615 mins with the conversion = 27% and M_n = 50500 g/mol.

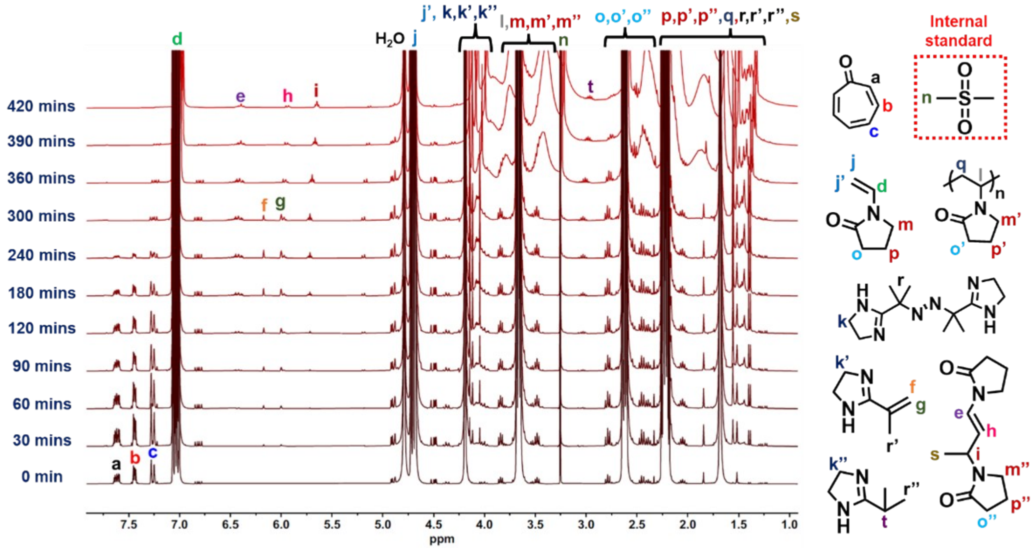

Figure S12 Time-dependent ^{1}H NMR spectra of reaction product for the NVP polymerization mediated by TP with dimethyl sulfone as the internal standard under the condition of [**TP**]$_0$/[VA-044]$_0$/[NVP]$_0$ = 1/5/50, [dimethyl sulfone]$_0$ = 0.0331 M, [NVP]$_0$ = 3.10 M in D_2O at 40 °C.

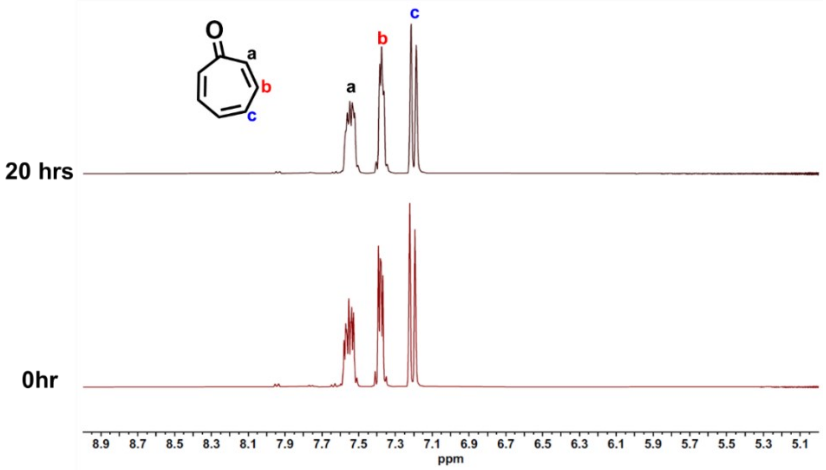

Figure S13 Time-dependent ^{1}H NMR spectra of TP and HCl solution, [**TP**]$_0$ = 0.1835 M and [HCl]$_0$ = 0.0059 M in D_2O at 40 °C.

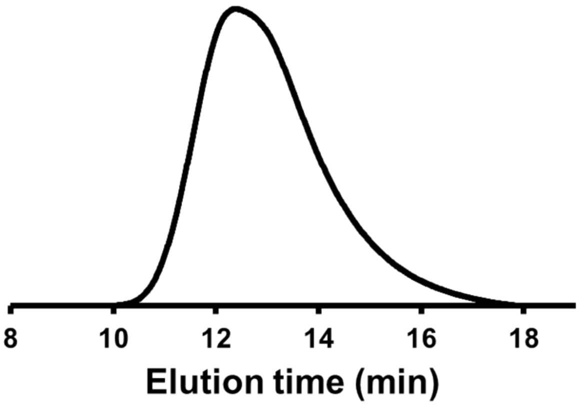

Figure S14 The GPC traces of PVP obtained from the model reaction under the conditions of [**TP**]$_0$/[VA-044]$_0$ = 1/2 ([**TP**]$_0$ = 0.093 M) in D_2O at 40 °C for 24 hours. Subsequently, 100 eq. of *N*VP ([*N*VP]$_0$ = 4.66 M) were added into the reaction mixture and the reaction was continued at 40 °C.

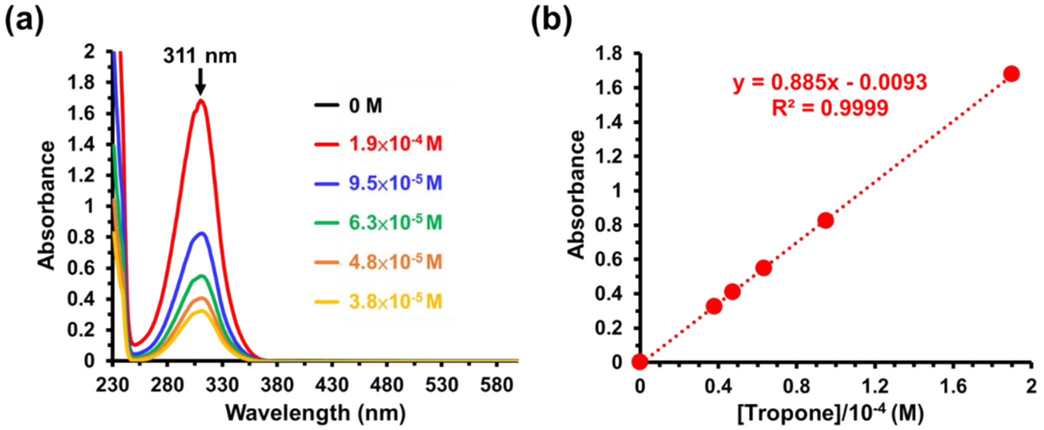

Figure S15 (a) UV/vis spectrum of **TP**. (b) The calibration curve of UV/vis spectrum of **TP** in aqueous.

Table S1 The data of the **TP** calibration curve for UV/vis spectrum.

[Tropone] (M)	Absorbance
0	0
1.9×10^{-4}	1.678
9.5×10^{-5}	0.824
6.3×10^{-5}	0.549
4.8×10^{-5}	0.408
3.8×10^{-5}	0.325

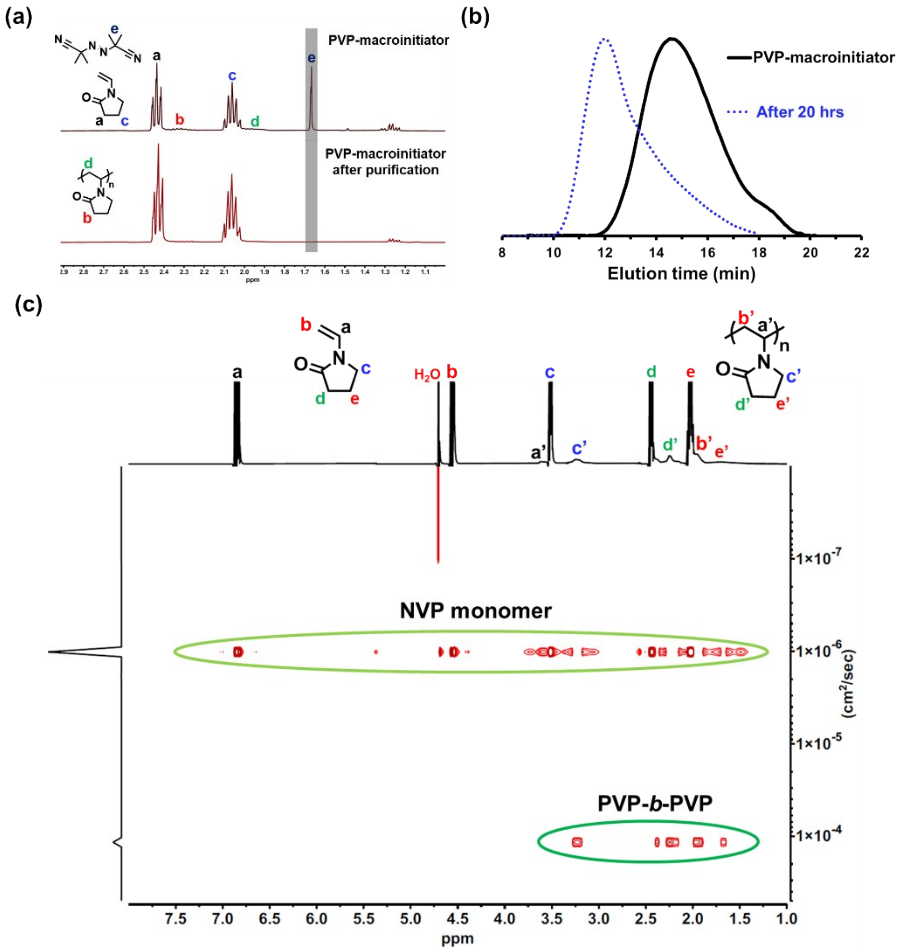

Figure S16 (a) ^{1}H NMR spectrum of PVP-macroinitiator before purification (upper one) and after purification (lower one). (b) The GPC traces of chain extension from PVP-macroinitiator (conditions: $[\mathbf{TP}]_0/[\mathrm{AIBN}]_0/[N\mathrm{VP}]_0$ = 1/10/200 in bulk at 60 °C, with conversion = 17% in 210 mins, M_n = 8600 g/mol, $Đ$ = 2.57) to *N*VP without AIBN for 20 hours (conversion = 8%, M_n = 50500 g/mol, $Đ$ = 2.75) under the conditions of $[\text{PVP-macroinitiator}]_0/[N\text{VP}]_0$ = 1/3000 in bulk at 60 °C. (c) The DOSY-NMR spectra of PVP-*b*-PVP block copolymer in D_2O.

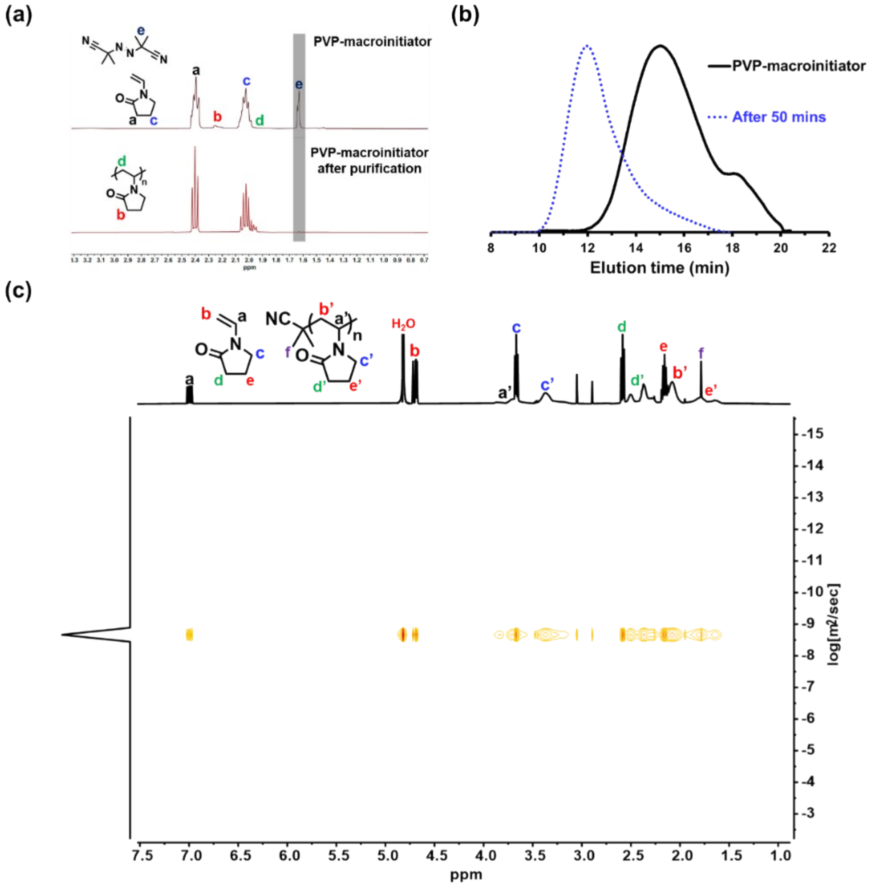

Figure S17 (a) ^{1}H NMR spectra of PVP-macroinitiator before purification (upper one) and after purification (lower one). (b) The GPC traces of chain extension from PVP-macroinitiator (conditions: $[\textbf{TP}]_0/[\text{AIBN}]_0/[N\text{VP}]_0$ = 1/10/200 in bulk at 60 °C, with conversion = 8% in 180 mins, M_n = 6600 g/mol, $Đ$ = 2.59) to *N*VP with AIBN for 50 mins (conversion = 16%, M_n = 54200 g/mol, $Đ$ = 2.86) under the conditions of $[\text{PVP-macroinitiator}]_0/[\text{AIBN}]_0/[N\text{VP}]_0$ = 1/5/1000 in bulk at 60 °C. (c) The DOSY-NMR spectra of PVP-*b*-PVP block copolymer in D_2O.

14. Kinetic simulation

We employed dynamic Monte Carlo simulations[1, 2] to model the kinetics of *N*VP polymerization mediated by **TP** in aqueous solution, aiming to determine the activation rate constant (k_{act}) and deactivation rate constant (k_{deact}). The reactions included in the simulation, along with their corresponding rate constants, are listed below.

Table S2 The reactions involved in the simulation and their respective rate constants.

	Reactions involved in the *N*VP polymerization mediated by **TP** and their rate constants
Initiation	VA-044 + *N*VP → *N*VP$^{\bullet}$
k (s^{-1})	1.93×10^{-5}
Deactivation	PVP$^{\bullet}$ + **TP** → **TP**-PVP
k ($M^{-1}s^{-1}$)[a]	1.85×10^{8} ~ 1.85×10^{9}
Activation	**TP**-PVP →PVP$^{\bullet}$ + **TP**
k (s^{-1})	1 ~ 10
Termination	Radicals + Radicals → Terminated chains
k ($M^{-1}s^{-1}$)	2×10^{9}
Propagation	$PVP_n^{\bullet}$ + *N*VP → $PVP_{n+1}^{\bullet}$
k ($M^{-1}s^{-1}$)[b]	8243

Condition: $[\mathbf{TP}]_0/[\text{VA-044}]_0/[N\text{VP}]_0$ = 1/10/500, $[N\text{VP}]_0$ = 4.68 M in DI water at 40 °C. [a]The deactivation rate constant was calculated using the equation $k_{deact} = k_{act} \times K_{eq}$, where $K_{eq} = 1.85\times10^{8}$ M^{-1}. [b]The propagation rate constant of *N*VP was obtained from reference.[3]

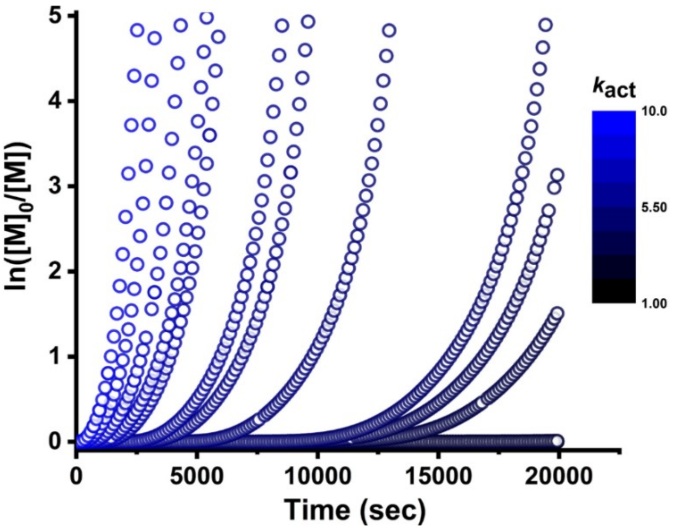

Figure S18 The first-order kinetic plots were simulated using the dynamic Monte Carlo method with the parameters listed in Table S2.

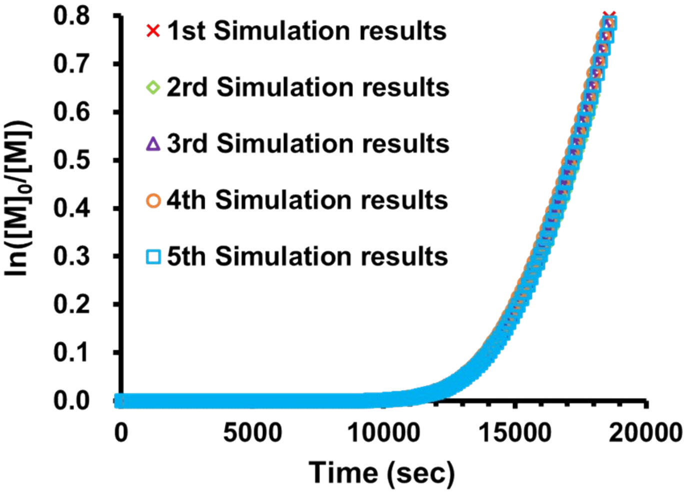

Figure S19 The first-order kinetic plot of repeating the simulation five times.

15. References

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