Supporting Information:

Investigations into CTA-differentiation involved polymerization of fluorous monomers: exploitation of experimental variances in fine-tuning of molecular weights

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1. General information of materials and analytical methods

1.1. Materials

All the reagents or catalysts were purchased from Sigma-Aldrich, Adamas or TCI. Monomers including nonafluorohexyl methacrylate (NFHMA), dodecafluoroheptyl methacrylate (DDFHMA) and *N,N*-dimethylacrylamide (DMA) were filtered through a plug of anhydrous basic alumina to remove inhibitors before use. Solvents including dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were freshly distilled with CaH_2 to remove water before use. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was recrystallized in ethanol before use. Other reagents were used as received without further purification. The while LED bulb (13 W) was purchased from PHILIPS Lighting and used as light source.

1.2. Characterization

Nuclear magnetic resonance (NMR) was recorded on an Advance III 400 MHz Bruker spectrometer at 298 K. ^1H NMR signals were measured relative to the signal of residual chloroform (7.26 ppm) in deuterochloroform ($CDCl_3$), and were reported in δ units, parts per million (ppm). Size exclusion chromatography (SEC) measurements were performed in DMF ([LiBr] = 0.02 mol/L) at 50 °C with an elution rate of 1.0 mL/min on an Agilent 1100 instrument equipped with a G1310A pump, a G1362A refractive index detector. Three columns were employed including one 5 μm LP gel column (molecular weight range 500 ~ 2×10^4 $g\cdot mol^{-1}$) and two 5 μm LP gel mixed bed columns (molecular weight range 200 ~ 3×10^6 $g\cdot mol^{-1}$). The calibration was performed with PMMA standards. $M_{n,\ MALLS}$ was measured with a WyattDawn HELEOS-II 18-Angle Laser Light detector. Gas chromatography (GC) measurements were carried out on SHIMADZU GC-2014 instrument using chiral capillary columns. Light intensities were determined through the optical power meter of Thorlabs. Differential scanning calorimetry (DSC) measurements were carried out on a TA Q2000 thermal analysis system at a scanning rate of 10 °C·min^{-1} from -30 °C to 100 °C after eliminating the thermal history. Tensile test experiments were investigated using dumbbell-shaped samples (effective gauge length = 12 mm, width = 2 mm, thickness = 0.5 mm) using an Instron 5966 universal testing machine equipped with a 1 kN sensor. The measurements were performed at room temperature using a preload of about 0.01 N and a pulling speed of 10 mm/min until sample failure. Hydrodynamic radius (r_H) was determined with 3D LS Spectrometer of LS Instruments in DMF at 25 °C.

2. Preparations of the chain-transfer agent (CTA)

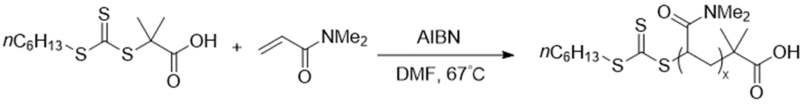

Figure S1. Synthetic route of poly(*N,N*-dimethylacrylamide) (PDMA) as CTAs.

A series of poly(*N,N*-dimethylacrylamide) (PDMA) with different chain lengths were synthesized according to a procedure in literature.[1] Taking the synthesis of PDMA$_{5000}$ (PDMA with $M_n = 5.03\times10^3$ Da) as an example: A oven-dried 100 mL Schlenk flask equipped with a stir bar was charged with DMA (4.24 mL, 40 mmol), HPMA (2-(((hexylthio)carbonothioyl)thio)-2-methylpropanoic acid, 112.2 mg, 0.40 mmol), AIBN (6.6 mg, 0.04 mmol) and DMF (20 mL) ([DMA]/[HPMA]/[AIBN] = 100/1/0.1). After the flask was sealed with a rubber septum, the solution contained in the vial was first frozen by liquid N_2 and kept under vacuum to remove oxygen. Afterwards the liquid N_2 was removed to let the solution thaw. This freeze-pump-thaw cycle was repeated for three times for effective deoxygenation. Then the mixture was heated to 67 °C and stirred (500 rpm) for reaction. During reaction, small aliquots were taken out via a micro-syringe under N_2 atmosphere to give monomer conversion at 52% as measured by GC. The mixture was subsequently quenched by exposing to air and cooling. The solution was added into cold ethyl ether to give crude polymer product, which was dissolved in acetone and precipitated with cold ethyl ether for three times and dried under vacuum at room temperature to afford PDMA$_{5000}$ as a yellow solid. For the synthesis of PDMA with other chain lengths, see Table S1.

Table S1. Synthesis of CTA with different chain lengths of PDMA.[a]

Entry	CTA	[DMA]/[HPMA]/[AIBN]	Conv.[b] (%)	$M_{n,\text{ theory}}$[c] (×10⁴ Da)	$M_{n,\text{ NMR}}$[d] (×10⁴ Da)	$M_{n,\text{ SEC}}$[e] (×10⁴ Da)	$M_{n,\text{ MALLS}}$[f] (×10⁴ Da)	$Đ$[e]
1	PDMA$_{5000}$	100/1/0.1	52	0.54	0.53	0.50	0.47	1.11

2	PDMA$_{10000}$	200/1/0.1	50	1.02	0.95	0.97	1.06	1.08
3	PDMA$_{15000}$	300/1/0.1	49	1.49	1.29	1.58	1.61	1.08
4	PDMA$_{20000}$	400/1/0.1	54	2.17	1.92	2.05	1.94	1.10

[a] All reactions were performed in 20 mL DMF. [b] The Conv. (%) were determined through GC measurements. [c] The $M_{\mathrm{n,\ theory}}$ values were calculated according to [DMA]/[HPMA] × Conv. × M_n(DMA) + M_n(HPMA), where M_n(DMA) and M_n(HPMA) represent the molecular weight of DMA and HPMA, respectively. [d] The $M_{\mathrm{n,\ NMR}}$ values were calculated according to Equation S1 based on ^{1}H NMR results. [e] $M_{\mathrm{n,\ SEC}}$ and $Đ$ values were determined through SEC measurements in DMF at 50 °C. The difference of hydrodynamic volumes between PMMA standards and PDMA was corrected using Mark-Houwink constants of PMMA and PDMA ($K = 7.5\times10^3$ ml/g and $\alpha = 0.72$ for PMMA; $K = 17.5\times10^3$ ml/g and $\alpha = 0.68$ for PDMA, as reported in reference[2]). [f] $M_{\mathrm{n,\ MALLS}}$ were determined through SEC measurements using a MALLS detector in DMF at 50 °C.

The $M_{\mathrm{n,\ NMR}}$ values of PDMA were calculated according to Equation S1:

$$M_{\mathrm{n,\ NMR}}=\frac{S_\mathrm{b}}{2S_\mathrm{a}}\times M_\mathrm{n}(\mathrm{DMA})+M_\mathrm{n}(\mathrm{HPMA}) \qquad \text{(Equation S1)}$$

where S_a and S_b represent the integral areas of protons in -N(CH$_3$)$_2$ (H$_\mathrm{a}$) and -CH$_3$ (H$_\mathrm{b}$), as shown in Figure S2.

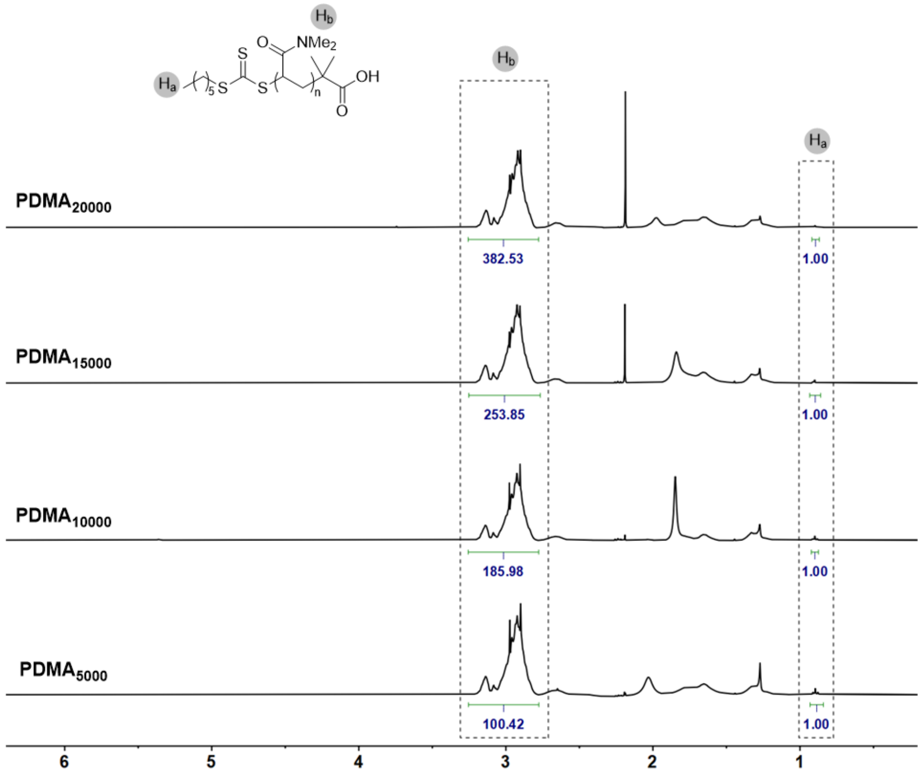

Figure S2. ^{1}H NMR spectrum of CTA with different chain lengths of PDMA (400 MHz, $CDCl_3$).

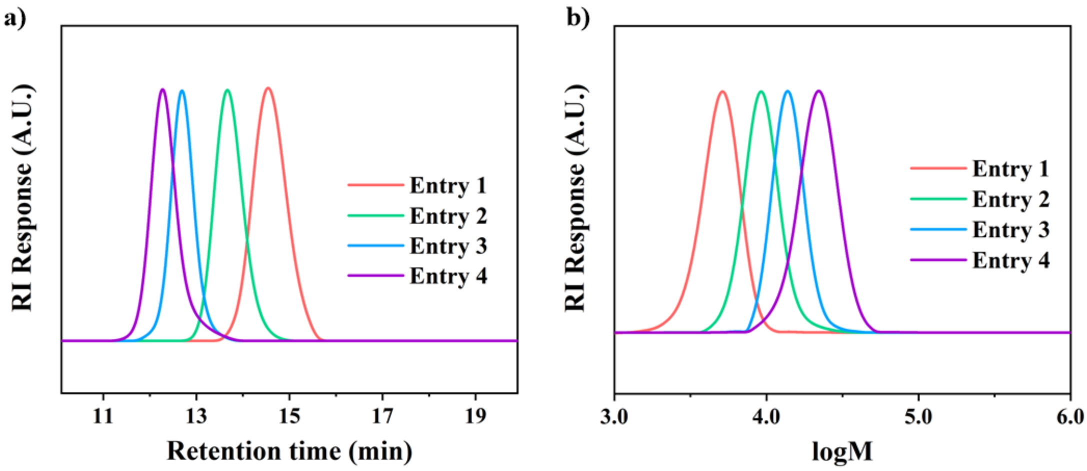

Figure S3. SEC curves of entries 1-4 in Table S1 with (a) retention time and (b) molar mass as axis.

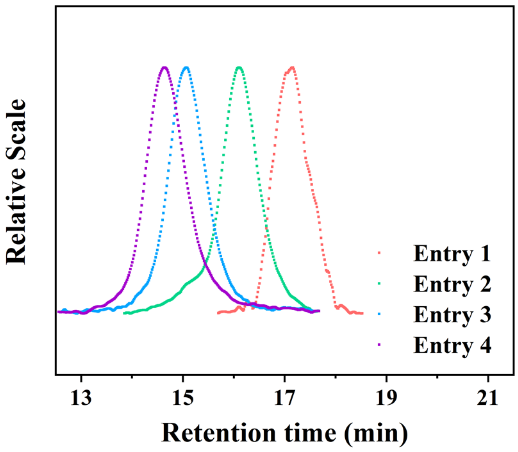

Figure S4. SEC-MALLS curves of entries 1-4 in Table S1.

3. General procedures of CTA-differentiation involved polymerization

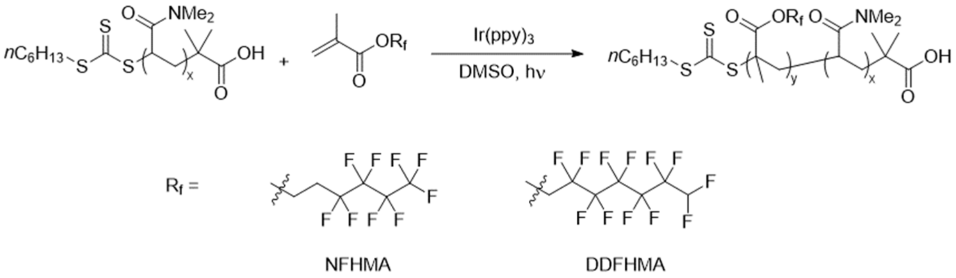

Figure S5. General process of the CTA-differentiation involved polymerization.

Taking the polymerization of entry 1, Table 1 as an example: An oven-dried 4 mL vial equipped with a stir bar was charged with NFHMA (59 μL, 0.25 mmol), CTA ($PDMA_{5000}$, 25.2 mg, 5×10^{-3} mmol), photoredox catalyst (PC) (tris(2-phenylpyridine)iridium, $Ir(ppy)_3$, 0.3 mg, 5×10^{-4} mmol) ([M]/[CTA]/[PC] = 50/1/0.1) and DMSO (1 mL). After the vial was sealed with a rubber septum, the solution contained in the vial was first frozen by liquid N_2 and kept under vacuum to remove oxygen. Afterwards the liquid N_2 was removed to let the solution thaw. This freeze-pump-thaw cycle was repeated for three times for effective deoxygenation. Then, the mixture was stirred (500 rpm) in front of a 13 W white LED light bulb (0.5 cm of distance, light intensity = 33 mW/cm^2) for irradiation while cooling with compressed air to maintain room temperature. After 3 h of reaction, internal standard (ethyl benzoate, with equivalent amounts as the monomer) was added into solution while stirring, then the mixture was sampled and analyzed using ^{1}H NMR and SEC instruments to measure the monomer conversion, molecular weight (M_n) and molecular weight distribution ($Đ$). All the polymerizations in this work followed the same procedure, while the [M], [M]/[CTA]/[PC] ratio, chain length of CTA and light intensity were varied for individual experiments.

4. General procedures of the kinetics experiments of CTA-differentiation involved polymerization.

Taking the kinetic experiments of Figures 3c and 3d as an example: An oven-dried 10 mL vial equipped with a stir bar was charged with NFHMA (236 μL, 1.00 mmol), CTA ($PDMA_{5000}$, 25.2 mg, 5×10^{-3} mmol), PC ($Ir(ppy)_3$, 0.7 mg, 1×10^{-3} mmol) ([M]/[CTA]/[PC] = 200/1/0.2) and DMSO (2 mL). After the vial was sealed with a rubber septum, the solution contained in the vial was first frozen by liquid N_2 and kept under vacuum to remove oxygen. Afterwards the liquid N_2 was removed to let the solution thaw. This freeze-pump-thaw cycle was repeated for three times for effective deoxygenation. Then, the mixture was stirred (500 rpm) in front of a 13 W white LED light bulb (0.5 cm or 4 cm of distance, light intensity = 33 or 0.52 mW/cm^2) for irradiation while cooling with compressed air to maintain room temperature. During reactions, small aliquots were taken out via a micro-syringe under N_2 atmosphere at corresponding intervals, and diluted before characterization with ^{1}H NMR and SEC instruments to give monomer conversions, M_n and $Đ$.

5. Calculation of the percentage of differentiation (POD).

Derivation process of Equation 1 is displayed in Equations S2 to S7, according to literature:[3]

The definition of POD is the percentage of propagating group (PG) in the initial amount of CTA, which is shown as Equation S2:

$$\mathrm{POD} = \frac{[\mathrm{PG}]}{[\mathrm{CTA}]_0} \times 100\% \qquad \text{(Equation S2)}$$

where [PG] and $[\mathrm{CTA}]_0$ represent the molar quantity of the propagating group and the initial CTA, respectively.

The theoretical molecular weight ($M_{\mathrm{n,theory}}$) and the actual molecular weight (M_{n}) can be calculated based on the molar ratio of monomer to the growing chain, as Equations S3 and S4:

$$M_{\mathrm{n,theory}} = \frac{[\mathrm{M}]}{[\mathrm{CTA}]_0} \times M_{\mathrm{n}}(\mathrm{monomer}) + M_{\mathrm{n}}(\mathrm{CTA}) \qquad \text{(Equation S3)}$$

$$M_{\mathrm{n}} = \frac{[\mathrm{M}]}{[\mathrm{PG}]} \times M_{\mathrm{n}}(\mathrm{monomer}) + M_{\mathrm{n}}(\mathrm{CTA}) \qquad \text{(Equation S4)}$$

where M_{n}(monomer) and M_{n}(CTA) represent the molecular weight of the monomer and CTA, respectively. According to Equations S3 and S4, the [PG] and $[\mathrm{CTA}]_0$ can be derived as Equations S5 and S6:

$$[\mathrm{CTA}]_0 = \frac{M_{\mathrm{n.theory}} - M_{\mathrm{n}}(\mathrm{CTA})}{[\mathrm{M}]M_{\mathrm{n}}(\mathrm{monomer})} \qquad \text{(Equation S5)}$$

$$[\mathrm{PG}] = \frac{M_{\mathrm{n}} - M_{\mathrm{n}}(\mathrm{CTA})}{[\mathrm{M}]M_{\mathrm{n}}(\mathrm{monomer})} \qquad \text{(Equation S6)}$$

Using Equations S5 and S6, the Equation S2 can be transformed into Equation S7:

$$\mathrm{POD} = \frac{M_{\mathrm{n,theory}} - M_{\mathrm{n}}(\mathrm{CTA})}{M_{\mathrm{n}} - M_{\mathrm{n}}(\mathrm{CTA})} \times 100\% \qquad \text{(Equation S7)}$$

which is Equation 1 in the manuscript.

6. Supporting information of Figure 1.

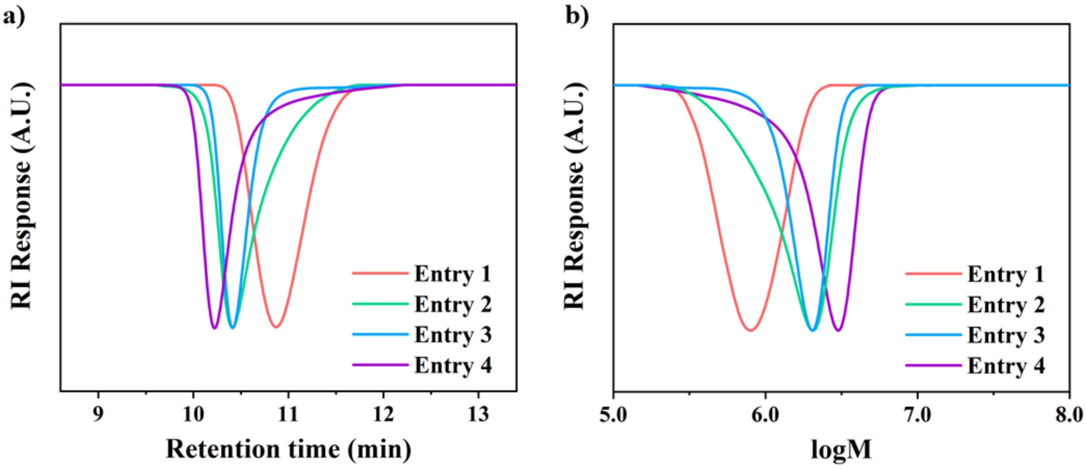

Figure S6. SEC curves of entries 1-4 in Table 1 with (a) retention time and (b) molar mass as axis.

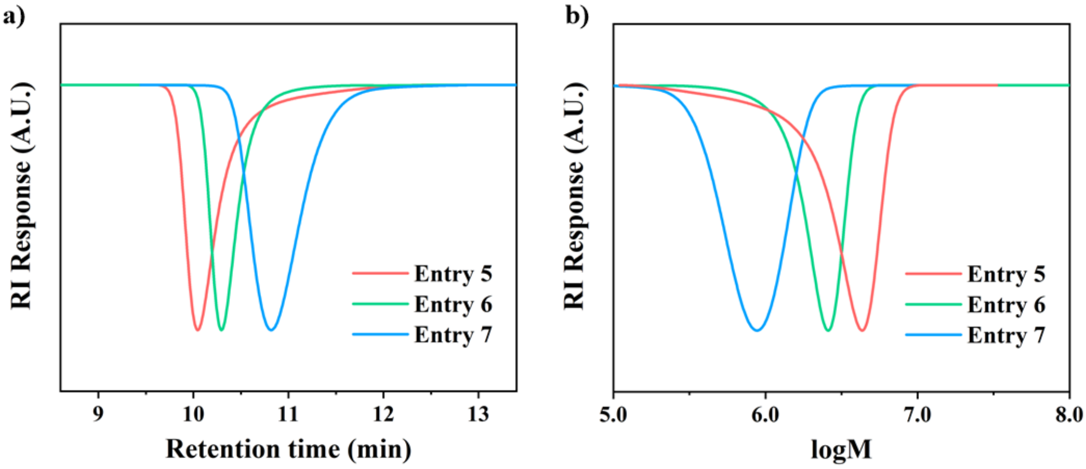

Figure S7. SEC curves of entries 5-7 in Table 1 with (a) retention time and (b) molar mass as axis.

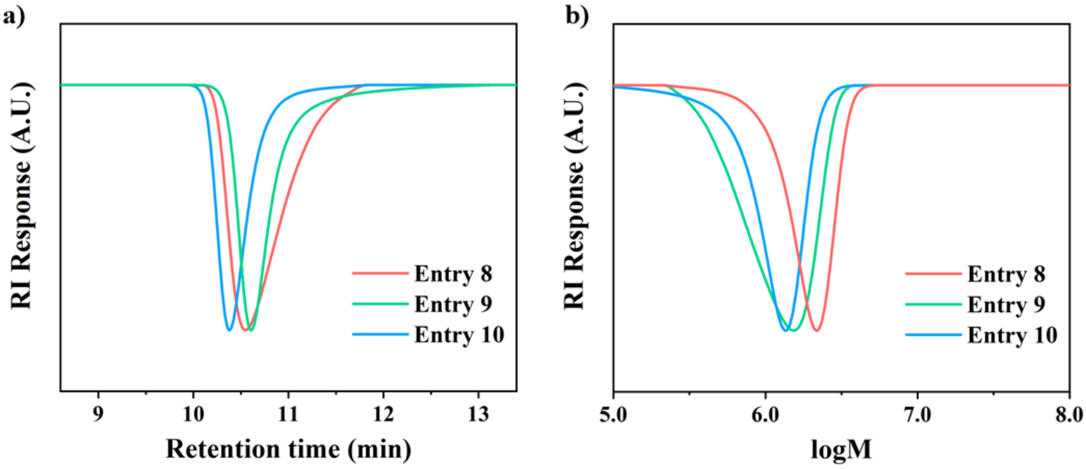

Figure S8. SEC curves of entries 8-10 in Table 1 with (a) retention time and (b) molar mass as axis.

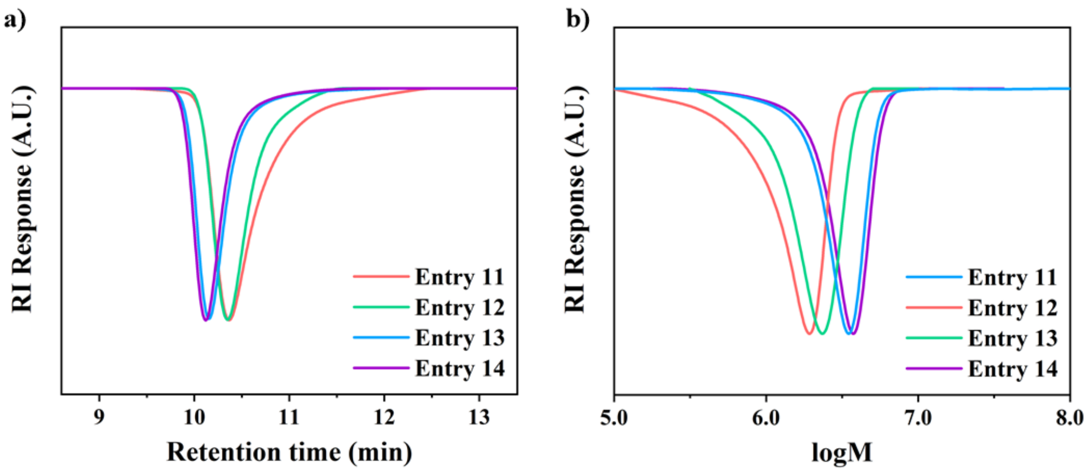

Figure S9. SEC curves of entries 11-14 in Table 1 with (a) retention time and (b) molar mass as axis.

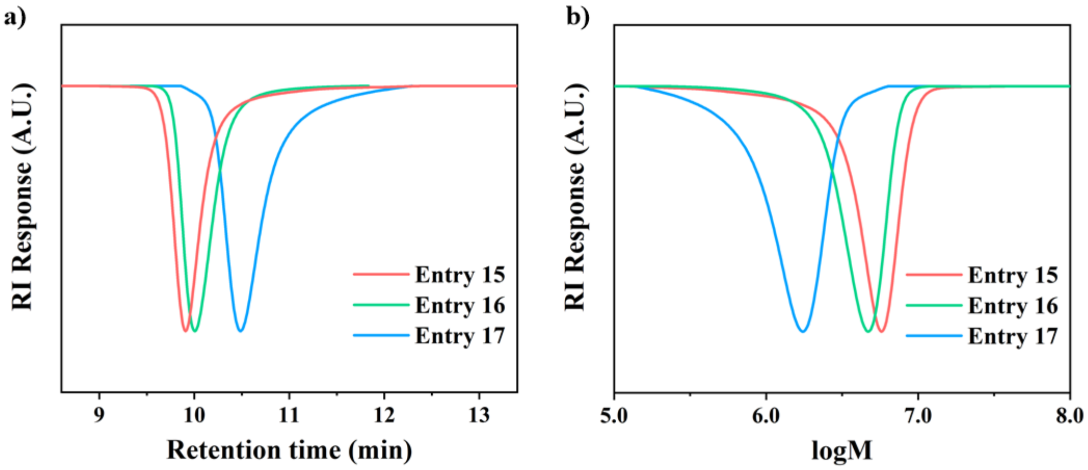

Figure S10. SEC curves of entries 15-17 in Table 1 with (a) retention time and (b) molar mass as axis.

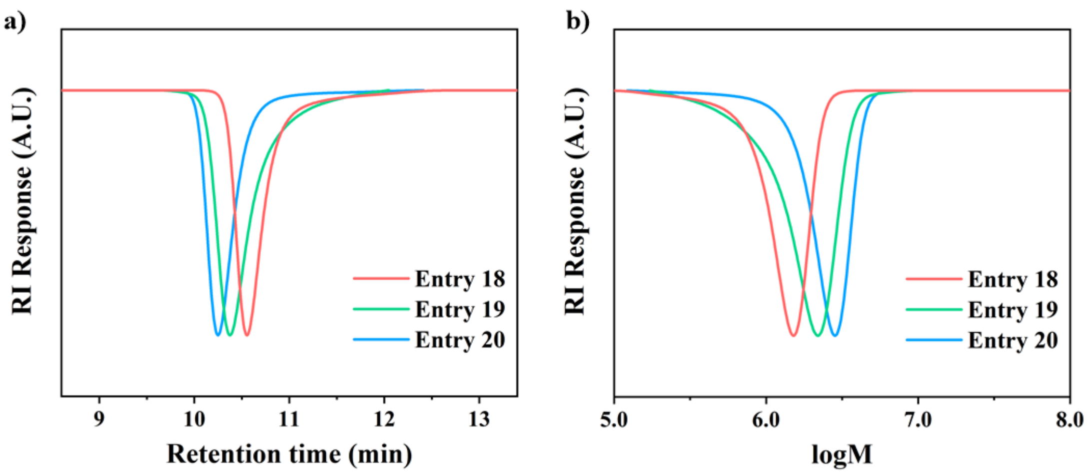

Figure S11. SEC curves of entries 18-20 in Table 1 with (a) retention time and (b) molar mass as axis.

7. Supporting information of Figure 3.

Table S2. Polymerizations with different light intensites.[a]

Entry	Monomer	Distance[b] (cm)	Light intensity[c] (mW/cm^2)	M_n[d] (Da)	$Đ$[d]	POD (%)
1	NFHMA	0.5	33	1.18×10^6	1.25	2.83
2	NFHMA	1.0	8.25	1.88×10^6	1.12	1.77
3	NFHMA	2.0	2.06	2.60×10^6	1.15	1.28
4	NFHMA	4.0	0.52	3.20×10^6	1.09	1.04
5	DDFHMA	0.5	33	1.70×10^6	1.09	2.36
6	DDFHMA	1.0	8.25	2.52×10^6	1.14	1.59
7	DDFHMA	2.0	2.06	3.16×10^6	1.13	1.27
8	DDFHMA	4.0	0.52	3.52×10^6	1.21	1.14

[a] All reactions were performed in 1.0 mL DMSO, PC = Ir(ppy)$_3$, [M] = 0.5 mol·L^{-1}, [M]/[CTA]/[PC] = 100/1/0.1. A 13 W white LED bulb (light intensity = 33 mW/cm^2) was used as a light source. Irradiation times was controlled to reach full monomer conversion (0.5 - 4 h). [b] Distance between the reaction mixture and the light bulb. [c] Light intensities were determined through the optical power meter of Thorlabs. [d] M_n and $Đ$ were determined by SEC measurements in DMF at 50 °C.

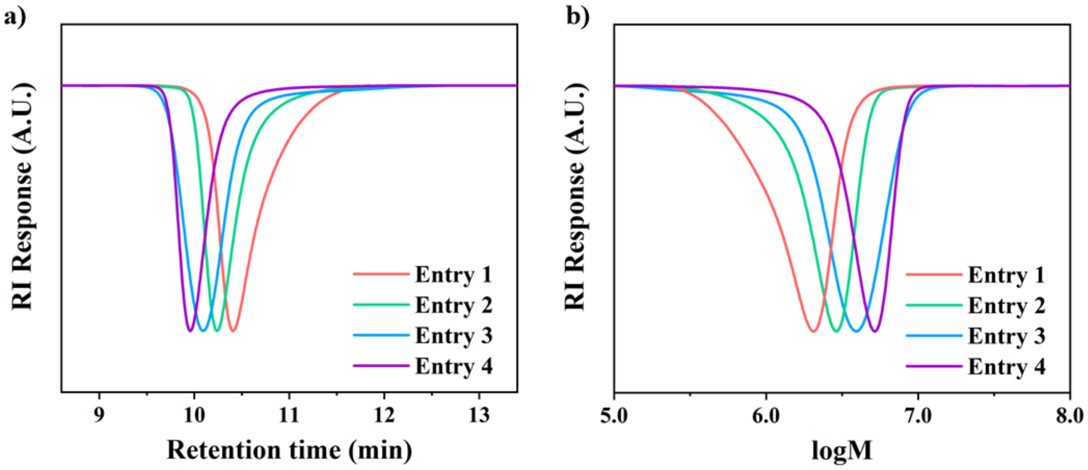

Figure S12. SEC curves of entries 1-4 in Table S2 with (a) retention time and (b) molar mass as axis.

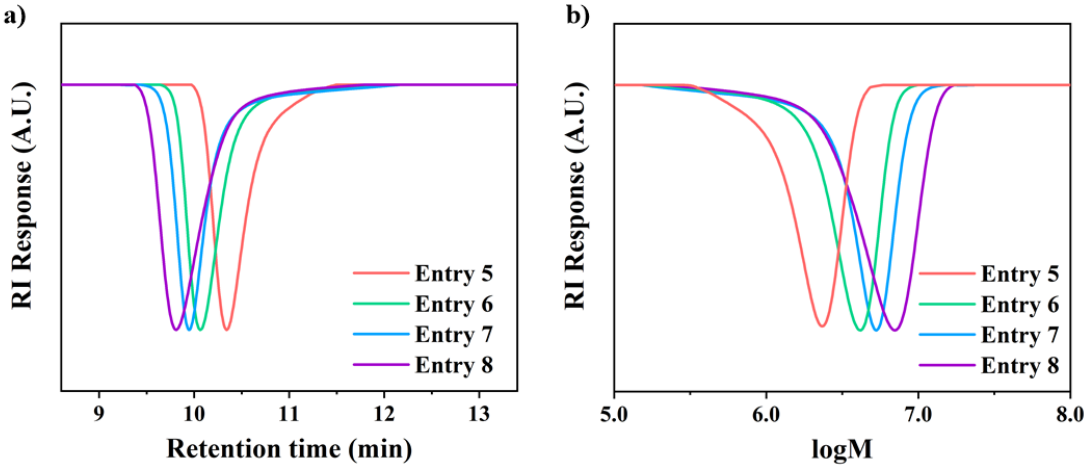

Figure S13. SEC curves of entries 5-8 in Table S2 with (a) retention time and (b) molar mass as axis.

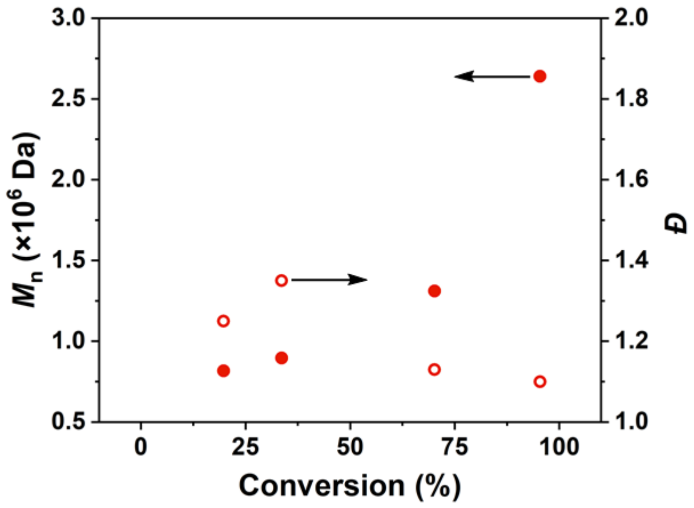

Figure S14. Plot of M_n (red solid dots) and $Đ$ (red hollow dots) as a function of monomer conversion during polymerization of NFHMA using PDMA$_{5000}$ with light intensity = 33 mW/cm^2. [M]/[CTA]/[PC]=200/1/0.2.

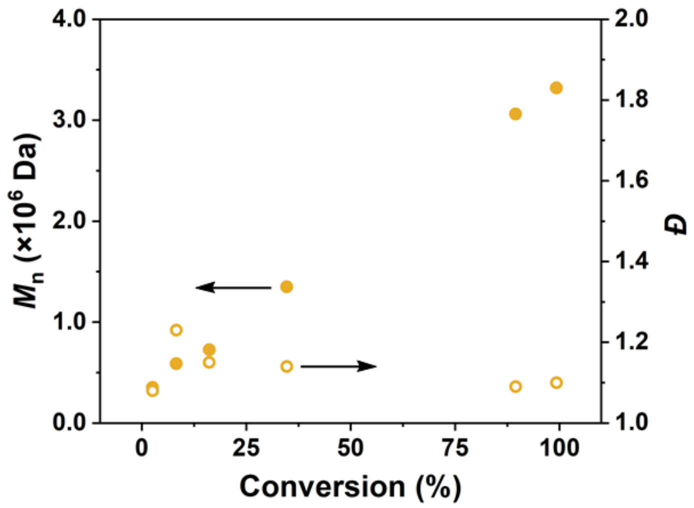

Figure S15. Plot of M_n (yellow solid dots) and $Đ$ (yellow hollow dots) as a function of monomer conversion during polymerization of NFHMA using PDMA$_{5000}$ with light intensity = 0.52 mW/cm^2. [M]/[CTA]/[PC]=200/1/0.2.

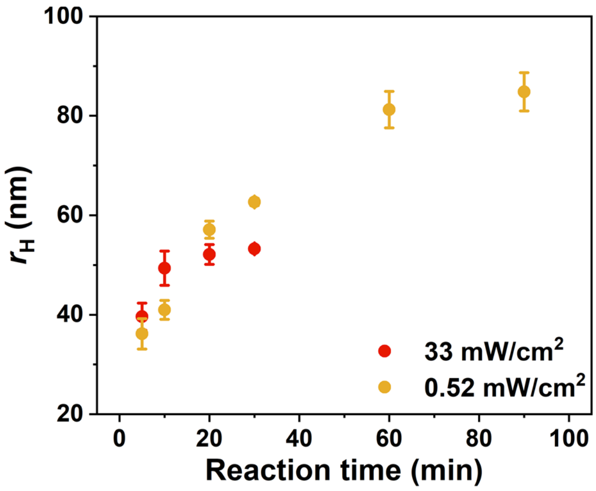

Figure S16. Hydrodynamic radius (r_H) *vs* irradiation time plots for polymerizations of NFHMA under strong and weak light irradiation with feed ratio = [M]/[CTA]/[PC]=200/1/0.2.

8. Supporting information of Figure 4.

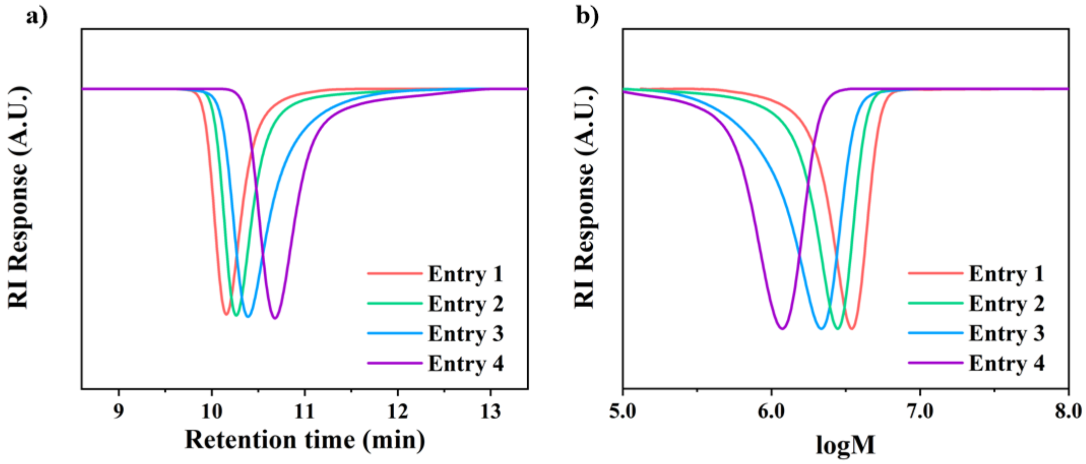

Figure S17. SEC curves of entries 1-4 in Table 4 with (a) retention time and (b) molar mass as axis.

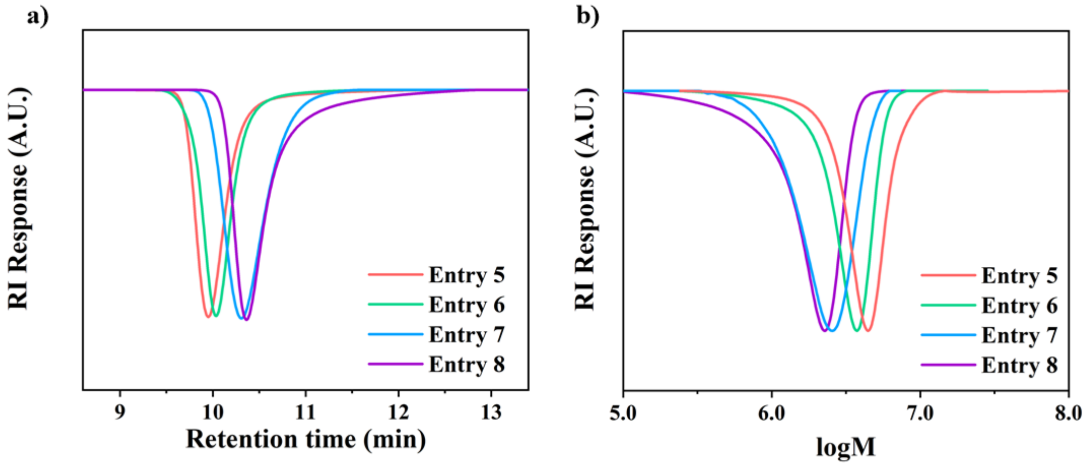

Figure S18. SEC curves of entries 5-8 in Table 4 with (a) retention time and (b) molar mass as axis.

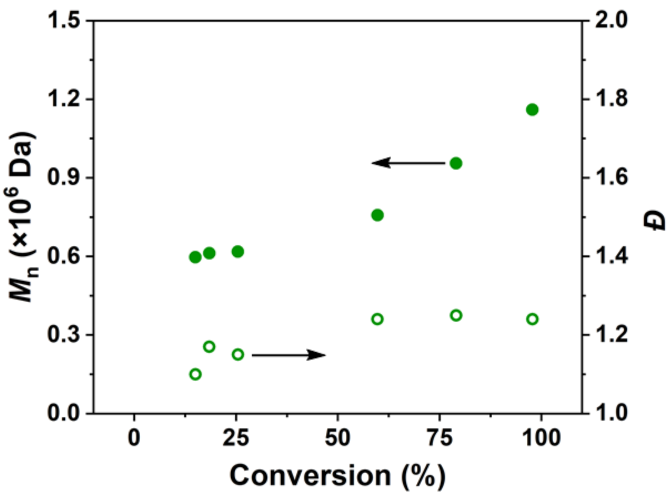

Figure S19. Plot of M_n (green solid dots) and $Đ$ (green hollow dots) as a function of monomer conversion during polymerization of NFHMA with PDMA$_{15000}$. Light intensity = 33 mW/cm^2, [M]/[CTA]/[PC]=200/1/0.2.

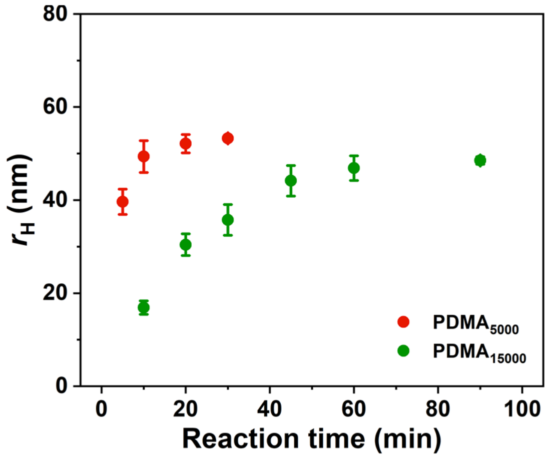

Figure S20. Hydrodynamic radius (r_H) vs irradiation time plots for polymerizations of NFHMA from PDMA with different chain lengths with feed ratio = [M]/[CTA]/[PC]=200/1/0.2.

Reference

1. H. Gong, Y. Zhao, X. Shen, J. Lin and M. Chen, *Angew. Chem. Int. Ed.*, 2018, **57**, 333-337.
2. E. H. I. J. Brandup, E. A. Grulke, *Polymer Handbook (4th Edition)*, John Wiley and Sons, New York, 1999.
3. H. Gong, Y. Gu, Y. Zhao, Q. Quan, S. Han and M. Chen, *Angew. Chem. Int. Ed.*, 2020, **59**, 919-927.