Rapid and precise synthesis of acrylic polymers driven by visible light

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I. Supplementary methods

A. General information

A−1. Chemicals

All chemicals and solvents were purchased commercially and used without further purification. The inhibitor in all the liquid monomers were removed by percolating over an aluminum oxide (Aldrich, activated, basic, Brockmann I) column. The chain transfer agent (CTA) used in this paper, 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA, Aldrich, 97%(HPLC)), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB, Aldrich, 88-112% (titration by NaOH)), and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CETCPA, Aldrich, 95%) were used without any further purification. Pre-prepared stock solution of the CTA was used for the higher reproducibility.

A−2. Sample measurements

■ *Size-exclusion chromatography (SEC)*

Synthesized polymers were characterized by ^{1}H NMR and two size-exclusion chromatography (SEC) system. The first system, the SEC (Waters system; Waters 1515 isocratic pump, Waters 2707 autosampler) coupled with a refractive index (RI) detector (Waters 2414 RI detector), UV/Vis detector (Waters 2489 UV/Vis detector), MALLS (Wyatt DAWN 8) and three different columns (Agilent Polypore 300 × 7.5 mm, Jordi mixed bed 300 × 8.0 mm, Waters Styragel HR4 300 × 7.8 mm) was used to determine the molecular weights (MWs) and dispersity ($Đ$) of hydrophobic polymers synthesized. Tetrahydrofuran (THF, Samchun Chemicals, HPLC grade, stabilized, > 99.9%) was used as the eluent at 35 °C with a flow rate of 0.7 mL/min. Poly(methyl methacrylate) (PMMA) standards were used for calibration of RI signal.

The second system, the SEC (Waters system; Waters 1515 isocratic pump, Waters 2707 autosampler) coupled with a refractive index (RI) detector (Waters 2414 RI detector), UV/Vis detector (Waters 2489 UV/Vis detector), MALLS (Wyatt DAWN 8) and three different columns (Waters Ultrahydrogel 120 300 × 7.8 mm, Waters Ultrahydrogel 250 300 × 7.8 mm, Waters Ultrahydrogel 2000 300 × 7.8 mm) was used to determine the molecular weights (MWs) and dispersity ($Đ$) of hydrophilic polymers synthesized. Different aqueous solvents were used as eluents at 35 °C with a flow rate of 0.7 mL/min (neutral: water (added 0.1 M $NaNO_3$); zwitterionic: water (added 0.1 M $NaNO_3$). Poly(ethylene glycol) (PEG) standards were used for calibration of RI signal.

■ *Nuclear magnetic resonance (NMR)*

The polymer composition and conversion were determined using a ^{1}H NMR spectrometer (JEOL, JNM-ECX400 (400 MHz)) with $CDCl_3$, acetone-d_6 or D_2O as the solvent.

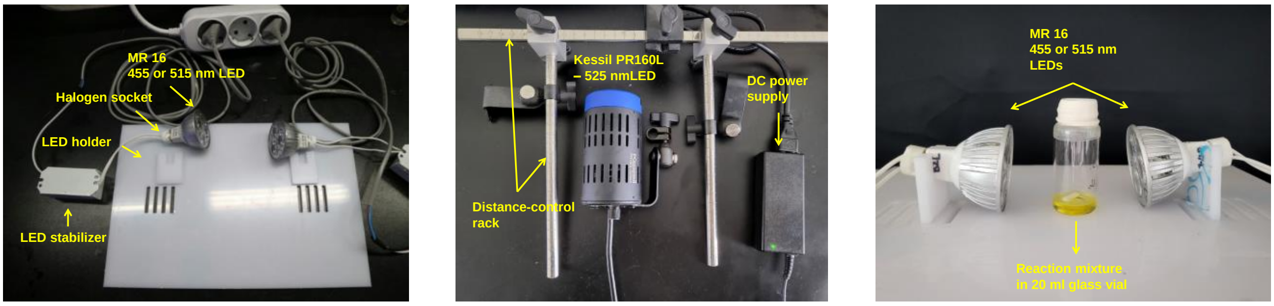
■ *Ultraviolet-visible-near infrared spectroscopy (UV-vis-NIR)*

UV/Vis absorbance measurements were done with a UV-Vis-NIR spectrometer (JASCO, V-770). The spectrum of CTA and polymers were measured in DMSO (200 μM).

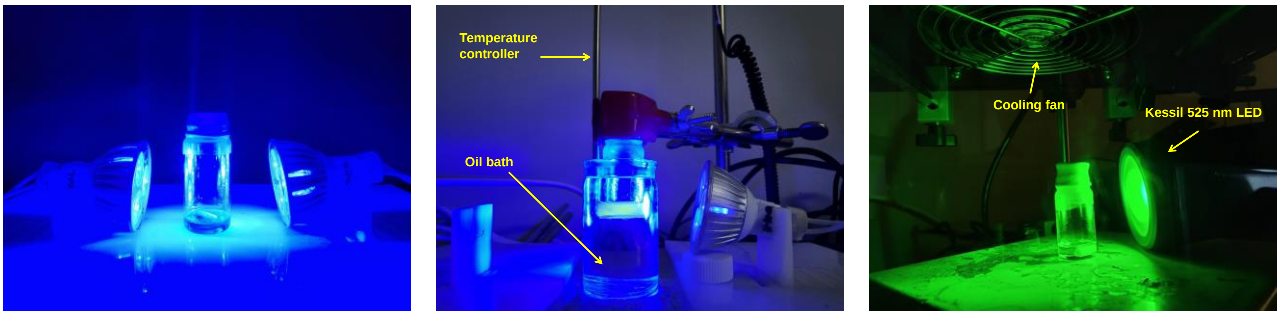
B. Procedures of photoiniferter polymerizations

B−1. Experimental setups for photoiniferter polymerization

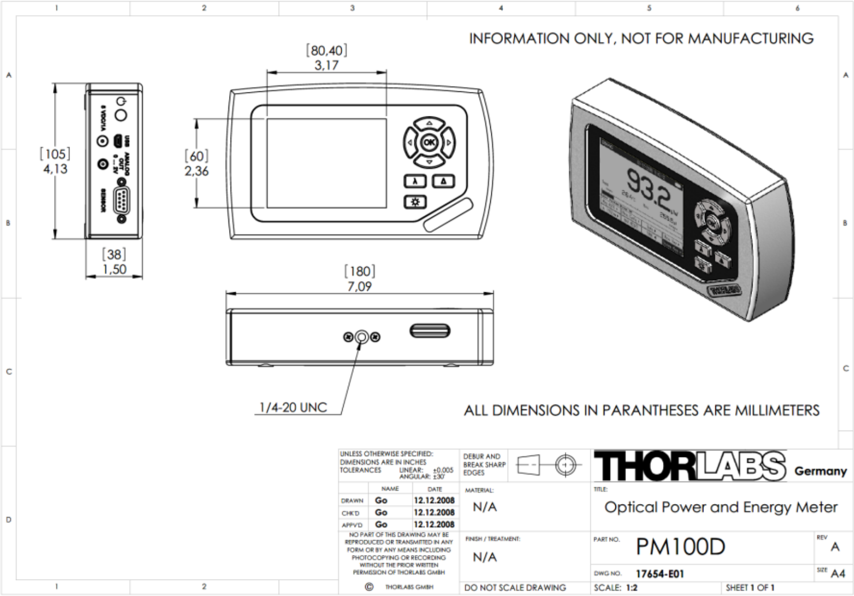
a) LED set-up



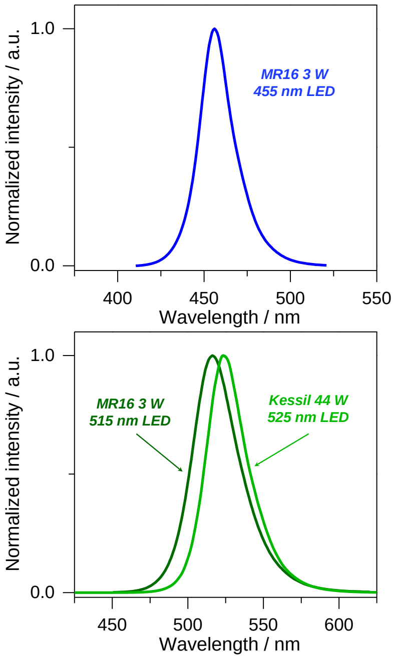
b) Set-up for typical photoiniferter polymerization



c) Optical power and energy meter (Thorlabs, PM100D)



d) LED emission spectrum



The photoiniferter polymerization was carried out in a 20 ml glass vial, and the volume the reaction mixture was fixed at 2 mL. As a light source, one, two or four LEDs (MR16, wavelength: 455 or 515 nm, watt: 3 W or Kessil PR 160L, wavelength: 525 nm, watt: 44 W) were used. The light intensity of one bulb was about 50 mW/cm^2 at 3 cm distance from 455 nm LED and 25 mW/cm^2 at 3 cm distance from 515 nm LED. In the temperature control experiment, oil bath in 70 mL glass vial was used for uniform heat transfer to the reaction mixture. Light intensity (mW/cm^2) was measured using an energy meter (PM100D, Thorlabs, USA) equipped by S175C microscope slide thermal power sensor as a detector. The active detector area was adjusted 18 mm square and total light intensity was evaluated.

B−2. Procedures of negative control experiments

A procedure for the standard reaction conditions [Monomer]:[CDTPA] = [100]:[0] to verify the self-initiation of monomers was carried out as follows. The inhibitor in monomers was removed by percolating over an aluminum oxide column. A 20 mL glass vial equipped with a stirring bar was charged with MMA (1.0 mL, 9.29 mmol) or MA (1.0 mL, 10.9 mmol), and anhydrous DMSO (1 mL; Aldrich, anhydrous, 99.9%) as the solvent. Afterwards, the vial was capped with a rubber septum and sealed with parafilm, and bubbled with nitrogen (99.999%) for 30 min. Subsequently, the polymerization was carried out under a 6 W 455 nm LED (*ca.* 100 mW/cm^2) irradiation at room temperature.

After 24 h, 0.2 mL aliquot of the reaction mixture was removed via syringe and dissolved 0.1 mL of aliquot in $CDCl_3$ and 0.1 mL aliquot in THF. Without storing, the aliquot was then immediately analyzed by ^{1}H NMR for conversion and end-group, and SEC for MW and *Đ* analysis.

B−3. General procedures of photoiniferter polymerizations

B−3−1. Photoiniferter polymerization of MMA

A typical photoiniferter procedure for the reaction conditions [MMA]:[CDTPA] = [100]:[1] was carried out as follows. The inhibitor in MMA was removed by percolating over an aluminum oxide column. The stock solution of CDTPA was made (100 mg/ml (0.247 mol/L), in anhydrous DMSO). A 20 mL glass vial equipped with a stirring bar was charged with MMA (1.0 mL, 9.29 mmol), CDTPA solution (0.386 mL, 9.29 x 10^{-2} mmol) and additional anhydrous DMSO (0.614 mL) as the solvent. Afterwards, the vial was capped with a rubber septum and sealed with parafilm, and bubbled with nitrogen (99.999%) for 30 min. Subsequently, the polymerization was carried out under 1 W 515 nm LED (*ca.* 10 mW/cm^2) irradiation at room temperature.

After 16 h, 0.2 mL aliquot of the reaction mixture was removed via syringe and dissolved 0.1 mL of aliquot in $CDCl_3$ and 0.1 mL aliquot in THF. Without storing, the aliquot was then immediately analyzed by ^{1}H NMR for conversion and end-group analysis, SEC for MW and *Đ* analysis. If purification is necessary, remaining polymer solution was dissolved in THF (2 mL) first and precipitated in methanol (75 mL). Additional THF (1 mL) was used to gather remaining polymer completely and precipitated in the same mixture. The precipitated polymer was filtered and dried under reduced pressure for overnight.

B−3−2. Photoiniferter polymerization of MA

A typical photoiniferter procedure for the reaction conditions [MA]:[CDTPA] = [100]:[1] was carried out as follows. The inhibitor in MA was removed by percolating over an aluminum oxide column. The stock solution of CDTPA was made (100 mg/ml (0.247 mol/L), in anhydrous DMSO). A 20 mL glass vial equipped with a stirring bar was charged with MA (1.0 mL, 10.9 mmol), CDTPA solution (0.455 mL, 1.09 x 10^{-1} mmol) and additional anhydrous DMSO (0.545 mL) as the solvent. Afterwards, the vial was capped with a rubber septum and sealed with parafilm, and bubbled with nitrogen (99.999%) for 30 min. Subsequently, the polymerization was carried out under 455 nm or 515 nm LEDs at various temperature (r.t. – 80 °C).

After polymerization, 0.2 mL aliquot of the reaction mixture was removed via syringe and dissolved 0.1 mL of aliquot in $CDCl_3$ and 0.1 mL aliquot in THF. Without storing, the aliquot was then immediately analyzed by ^{1}H NMR for conversion and end-group analysis, SEC for MW and *Đ* analysis.

B−3−3. Photoiniferter polymerization of other hydrophobic acrylate monomers

A typical photoiniferter procedure for the reaction conditions [monomer]:[CDTPA] = [100]:[1] was carried out as follows. The inhibitor in hydrophobic acrylate monomers was removed by percolating over an aluminum oxide column. The stock solution of CDTPA was made (100 mg/ml (0.247 mol/L), in anhydrous anisole). A 20 mL glass vial equipped with a stirring bar was charged with monomer (1.0 mL), CDTPA solution (1/100 mol compared to monomer) and additional anhydrous anisole (to make total volume as 2 mL) as the solvent. Afterwards, the vial was capped with a rubber septum and sealed with parafilm, and bubbled with nitrogen (99.999%) for 30 min. Subsequently, the polymerization was carried out under 6 W 455 nm LEDs (*ca.* 100 mW/cm^2) irradiation at room temperature.

After 16 h, 0.2 mL aliquot of the reaction mixture was removed via syringe and dissolved 0.1 mL of aliquot in $CDCl_3$ (acetone-d_6 for only 1,1,1,3,3,3-hexafluoroisopropyl acrylate monomer) and 0.1 mL aliquot in THF. Without storing, the aliquot was then immediately analyzed by ^{1}H NMR for conversion and end-group analysis, SEC for MW and *Đ* analysis.

B−3−4. Photoiniferter polymerization of hydrophilic acrylate monomers

A typical photoiniferter procedure for the reaction conditions [monomer]:[CETCPA] = [100]:[1] was carried out as follows. The inhibitor in hydrophilic acrylate monomers was removed by percolating over an aluminum oxide column. Unlike CDTPA, CETCPA used for photoiniferter polymerization of hydrophilic acrylate monomers in water does not dissolve well in water and cannot make a stock solution. However, when monomer was added, it became a completely clear solution. In the case of solid type monomers such as zwitterionic, it is not possible to charge by volume ratio, so it was calculated to have a concentration of 3.5 M based on a total 2 mL solution for N_2 atmosphere experiment. A 20 mL glass vial equipped with a stirring bar was charged with monomer (1.0 mL), CETCPA (1/100 mol compared to monomer) and additional DI water (to make total volume as 2 mL) as the solvent. Afterwards, the vial was capped with a rubber septum and sealed with parafilm, and bubbled with nitrogen (99.999%) for 30 min. Subsequently, the polymerization was carried out under 3 W 455 nm LEDs (*ca.* 50 mW/cm^2) irradiation at room temperature. After 16 h, 0.2 mL aliquot of the reaction mixture was removed via syringe and dissolved 0.1 mL of aliquot in D_2O and 0.1 mL aliquot in 0.1 M $NaNO_3$ aqueous solution. Without storing, the aliquot was then immediately analyzed by ^{1}H NMR for conversion and end-group analysis, SEC for MW and *Đ* analysis.

B−3−5. Photoiniferter polymerization of random copolymer

A typical photoiniferter random copolymerization procedure for the reaction conditions [M_1]:[M_2]:[M_3]:[CDTPA] = 50:50:50:1 was carried out as follows. The inhibitor in *iso*-butyl acylate (*i*BA), lauryl acrylate (LA), and cyclohexyl acrylate (CHA) was removed by percolating over an aluminum oxide column. The stock solution of CDTPA was made (100 mg/ml (0.247 mol/L), in anhydrous anisole). A 20 mL glass vial equipped with a stirring bar was charged with *t*BA (0.280 mL, 2.54 mmol), LA (0.378 mL, 2.54 mmol), CHA (0.361 mL, 2.54 mmol), CDTPA solution (0.211 mL, 5.08 x 10^{-2} mmol), and additional anhydrous anisole (0.789 mL) as the solvent. Afterwards, the vial was capped with a rubber septum and sealed with parafilm, and bubbled with nitrogen (99.999%) for 30 min. Subsequently, the polymerization was carried out under 6 W 455 nm LEDs (*ca.* 100 mW/cm^2) irradiation at room temperature. After 16 h, 0.2 mL aliquot of the reaction mixture was removed via syringe and dissolved 0.1 mL of aliquot in $CDCl_3$ and 0.1 mL aliquot in THF. Without storing, the aliquot was then immediately analyzed by ^{1}H NMR for conversion and end-group analysis, SEC for MW and *Đ* analysis.

B−3−6. Photoiniferter polymerization of block copolymer

A typical photoiniferter block copolymerization procedure for the reaction conditions $[M_1]:[M_2]:[M_3]:[CDTPA]$ = 50:50:50:1 was carried out as follows. The inhibitor in ethyl acrylate (EA), benzyl acrylate (BzA), and *n*-butyl acrylate (*n*BA) was removed by percolating over an aluminum oxide column. The stock solution of CDTPA was made (100 mg/ml (0.247 mol/L), in anhydrous anisole). A 20 mL glass vial equipped with a stirring bar was charged with EA (0.5 mL, 3.11 mmol), CDTPA solution (0.259 mL, 6.22×10^{-2} mmol), and additional anhydrous anisole (0.741 mL) as the solvent. Afterwards, the vial was capped with a rubber septum and sealed with parafilm, and bubbled with nitrogen (99.999%) for 30 min. Subsequently, the polymerization was carried out under 6 W 455 nm LEDs (*ca.* 100 mW/cm^2) irradiation at room temperature. After 24 h, 0.2 mL aliquot of the reaction mixture was removed via syringe and dissolved 0.1 mL of aliquot in $CDCl_3$ and 0.1 mL aliquot in THF. Without storing, the aliquot was then immediately analyzed by ^{1}H NMR for conversion and end-group analysis, SEC for MW and *Đ* analysis. For the sequential block copolymerization, second monomer (BzA) was bubbled with nitrogen for 30 min. 0.833 mL (3.11 mmol) of BzA was injected directly in the glass vial batch, then second polymerization was carried out under 6 W 455 nm LEDs (*ca.* 100 mW/cm^2) irradiation at room temperature without any purification process. After 12 h, 0.2 mL aliquot of the reaction mixture was removed via syringe and dissolved 0.1 mL of aliquot in $CDCl_3$ and 0.1 mL aliquot in THF. The last monomer *n*BA and anhydrous anisole were bubbled and injected to the glass vial batch (*n*BA; 0.444 ml, 3.11 mmol, anisole; 0.5 mL) to reduce the viscous media. Last block copolymerization was carried out under 6 W 455 nm LEDs (*ca.* 100 mW/cm^2) irradiation at room temperature without any purification process. After 8 h, 0.2 mL aliquot of the reaction mixture was removed via syringe and dissolved 0.1 mL of aliquot in $CDCl_3$ and 0.1 mL aliquot in THF.

B−4. Experimental procedures of kinetic studies

A typical photoiniferter procedure for the reaction conditions [MA]:[CDTPA] = [100]:[1] was carried out as follows. The inhibitor in MA was removed by percolating over an aluminum oxide column. The stock solution of CDTPA was made (100 mg/ml (0.247 mol/L), in anhydrous DMSO). A 20 mL glass vial equipped with a stirring bar was charged with MA (1.0 mL, 10.9 mmol), CDTPA solution (0.455 mL, 1.09×10^{-1} mmol) and additional anhydrous DMSO (0.545 mL) as the solvent. Afterwards, the vial was capped with a rubber septum and sealed with parafilm, and bubbled with nitrogen (99.999%) for 30 min. Subsequently, the polymerization was carried out under 12 W 455 nm LEDs (*ca.* 200 mW/cm^2) at elevated temperatures (40 – 80 °C). A 0.2 mL aliquot of the reaction mixture was taken via syringe at predetermined interval times and dissolved 0.1 mL of aliquot in $CDCl_3$ and 0.1 mL aliquot in THF. Without storing, the aliquot was then immediately analyzed by ^{1}H NMR for conversion and end-group analysis, SEC for MW and *Đ* analysis.

B−5. Experimental procedures of MA chain extension

A procedure for the hepta-block copolymer through chain extension of MA was carried out as follows. The inhibitor in monomers was removed by percolating over an aluminum oxide column. A 20 mL glass vial equipped with a stirring bar was charged with MA (1.0 mL, 10.9 mmol), CDTPA (1.47 g, 3.63 mmol) and anhydrous DMSO (1.0 mL) as the solvent. Afterwards, the vial was capped with a rubber septum and sealed with parafilm, and bubbled with nitrogen (99.999%) for 30 min. Subsequently, the polymerization was carried out under a 6 W 455 nm LED (*ca.* 100 mW/cm^2) irradiation at room temperature. After each extension step, N_2 bubbled MA (1.0 mL, 10.9 mmol) was added to the reaction batch without any purification. Detailed reaction time, MW and *Đ* were summarized in ***Table S6***.

B−6. Calculation of Reynolds number in photo-flow setup.

Calculation procedures of Reynolds number were referred by Boyer's work.[6] The Reynolds number (Re) is defined as:

$$Re = \frac{\rho \cdot u \cdot D}{\mu}$$

Where, ρ is the fluid density (kg/m^3), u is the fluid velocity (m/s), D is the inner diameter of tubing (m) and μ is the dynamic viscosity (kg/m/s)

Assume the dynamic viscosity for liquid mixtures can be calculated through the following equation:

$$\ln(\mu) = \sum_{i=1}^{n} \frac{1}{n} \cdot (x_i + \emptyset_{vi}) \cdot \ln(\mu_i)$$

Where, x_i is the mole fraction of component i, $\emptyset_{vi}$ is the volume fraction of component i and μ_i is the dynamic viscosity of component *i*.

For a 50/50 volume/volume ratio of MA/DMSO the dynamic viscosity is found to be 0.00465 kg/m/s. Also for a 50/50 volume/volume ratio of MA/DMSO, assume the density is a constant 1025 kg/m^3 (numerical average). For a 2.05 m length of tubing, a reaction time of 50 minutes gives a velocity, u, of 6.83×10^{-4} m/s. The following Reynolds number (Re) is calculated as ~ 0.38, resulting in laminar flow.

C. Quantum chemical calculations

C−1. Computational details

We performed (time-dependent) density functional theory (TDDFT) calculations at the M06-2X/6-31G* level of theory[1] to obtain structures and energies of CDTPA and CDTPA-(MA/MMA) conformers with Q-Chem 5.4 program.[2] The solvent effect was considered with polarizable continuum model (PCM).[3] In particular, the minimum energy conical intersection is obtained by the so-called "direct" algorithm implemented in Q-Chem 5.4 program.[4] For the computational efficiency, we replaced a long alkyl chain in CDTPA with ethyl group by assuming that local excitations at TCT moiety are dominant in photodissociation reactions (***Figure 2***). We further calculated excited states of dissociated radicals of TCT moiety (***Figure 2***) at 4SA-CASSCF(3,4)/6-31+G* level of theory using Molpro[5] to check the possibility of photodissociation along the excited state. Natural orbital analysis shows that the excitation energy for the corresponding *nπ** transition (D_3) is 3.73 eV.

C−2. Bond dissociation via triplet state (See Figure S4)

We perform TDDFT calculations at the M06-2X/6-31G* level of theory with Q-Chem 5.4 program to obtain T_1 minimum energy structures of CDTPA-MA and CDTPA-MMA, and compare the T_1 minimum energies with bond dissociation energies. The solvent effect was considered with polarizable continuum model (PCM). The obtained T_1 minimum energy structures are almost identical to the S_1 minimum energy structures i_2 for both CDTPA-MA and CDTPA-MMA. The bond dissociation energies of CDTPA-MA and CDTPA-MMA are 0.57 eV and 0.29 eV higher than the T_1 minimum energies, respectively. Therefore, the bond dissociation via triplet state is unlikely for both CDTPA-MA and CDTPA-MMA.

C−3. nπ excitation energy of TCT radical of CDTPA (See Figure 1d)*

We calculated excited states of the dissociated radical of TCT moiety at 4SA-CASSCF(3,4)/6-31+G* level of theory using Molpro to check the possibility of photodissociation along the excited state to yield i_3* [R(D$_0$)] + Z($n\pi$*)]. Natural orbital analysis shows that the excitation energy for the corresponding $n\pi$* transition (D$_3$) is 3.73 eV**.** Since the excitation is localized on the TCT moiety, we calculated the energy of i_3* [R(D$_0$)] + Z(D$_3$, $n\pi$*)] by adding 3.73 eV to the energy of i_3 [R(D$_0$)] + Z(D$_0$)] (***Figure 3***).

C−4. Reaction pathway of $i_1 \rightarrow i_2 \rightarrow i_{CI}$ on S_1 state for CDTPA-(MA/MMA) (See Figure S12)

We obtained energy profiles and structural changes along $i_1 \rightarrow i_2$ and $i_2 \rightarrow i_{CI}$. After FC excitation to i_1, both CDTPA-MA and CDTPA-MMA can be directly thermalized to i_2 with changes of dihedral angles in TCT group. Then, i_{CI} is reached by change of S=C-S(-Et) bond angle, which acts a barrier for internal conversion to S$_0$ state.

C−5. Energetics of CPADB-(MA/MMA) conformers (See Figures 2c and S5)

We performed same calculations for CPADB-(MA/MMA) as CDTPA-(MA/MMA), i.e. TDDFT calculations at M06-2X/6-31G* level of theory with PCM to obtain energies and molecular structures of relevant intermediates. Similar to the CDTPA-(MA/MMA), the energy of i_3 [R(D$_0$) + Z(D$_0$)] is lower compared to i_{CI} in CPADB-MMA, but the energy of i_3 is higher than i_{CI} in CPADB-MA.

II. Supplementary Figures and Tables

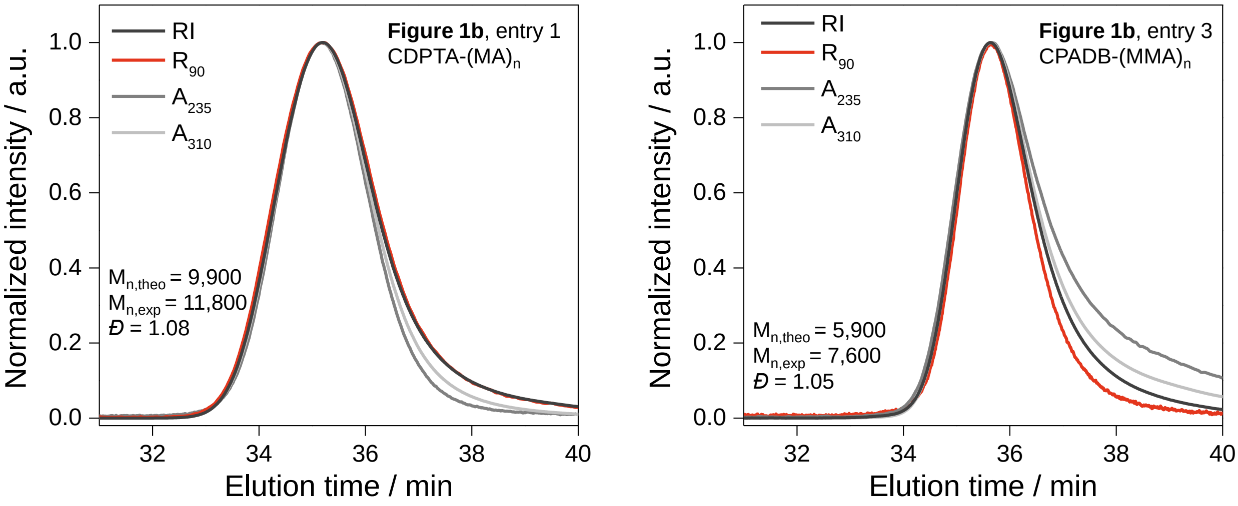


Figure S1. SEC curves of the synthesized polymers recorded by RI (black), LS (red) and UV at 235 nm (green) and 310 nm (blue) in the presence of CDTPA or CPADB (**Figure 1b**).

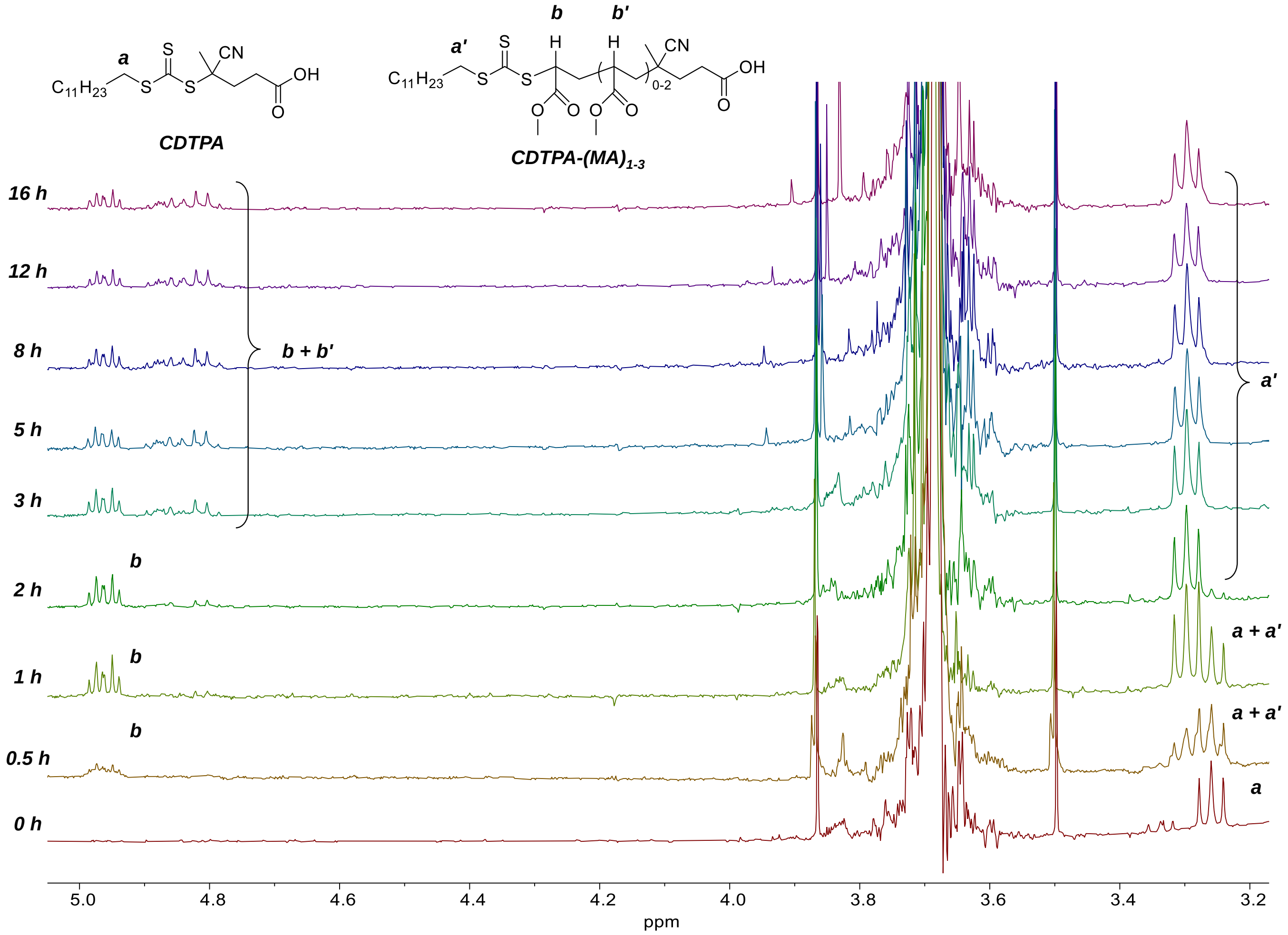


Figure S2. ^{1}H NMR spectrum change of PMA polymerization result in the presence of CDTPA under 515 nm LED (50 mW/cm^{2}) irradiation.

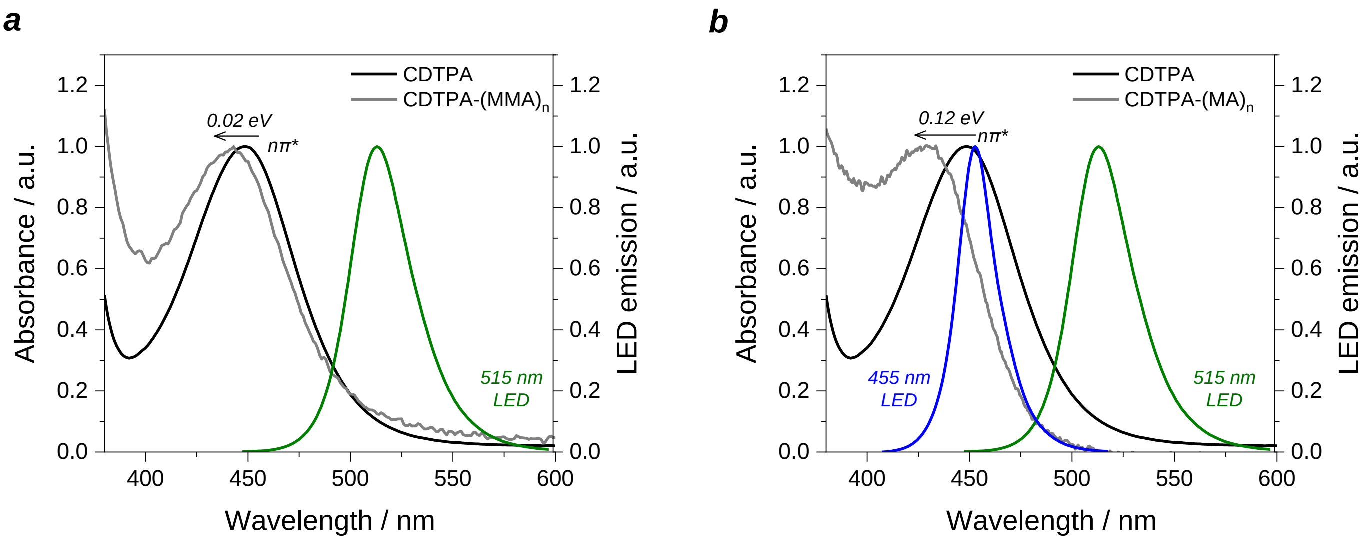
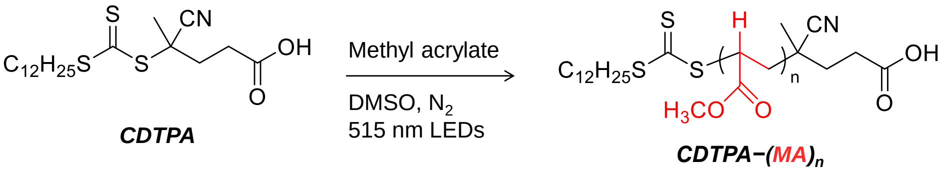


Figure S3. (a) UV-Vis graph of 200 μM CDTPA and CDTPA-$(MMA)_n$ solution in DMSO overlapped with 515 nm LED emission spectrum. (b) UV-Vis graph of 200 μM CDTPA and CDTPA-$(MA)_n$ solution in DMSO overlapped with 455 and 515 nm LED emission spectrum

Table S1. Results of photoiniferter polymerizations of methyl acrylate (MA) in the presence of CDTPA under different temperatures and luminous intensities.



Entry	Light source	Temp (°C)	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	*Đ*
1	515 nm, *250 mW/cm^2*	r.t.	16	100:1	62	5,600	6,400	1.01
2	515 nm, *50 mW/cm^2*	60	16	100:1	30	3,000	2,400	1.03

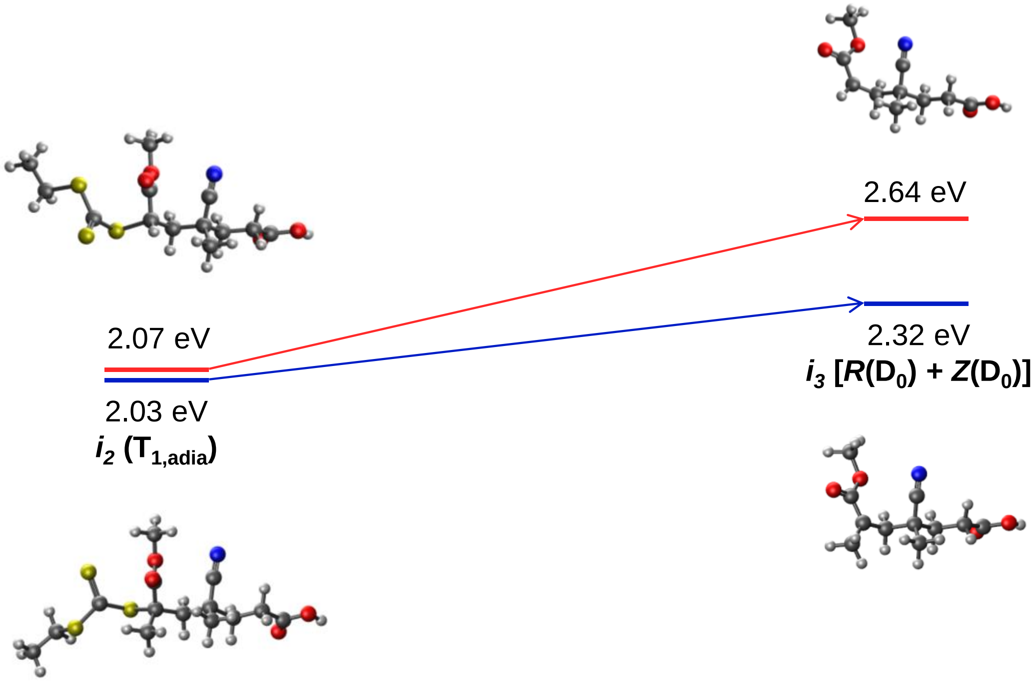


Figure S4. Energies of i_2 ($T_{1,adia}$) and i_3 of CDTPA-MA (red) and CDTPA-MMA (blue) compared to i_0 (S_0) with corresponding molecular structures.

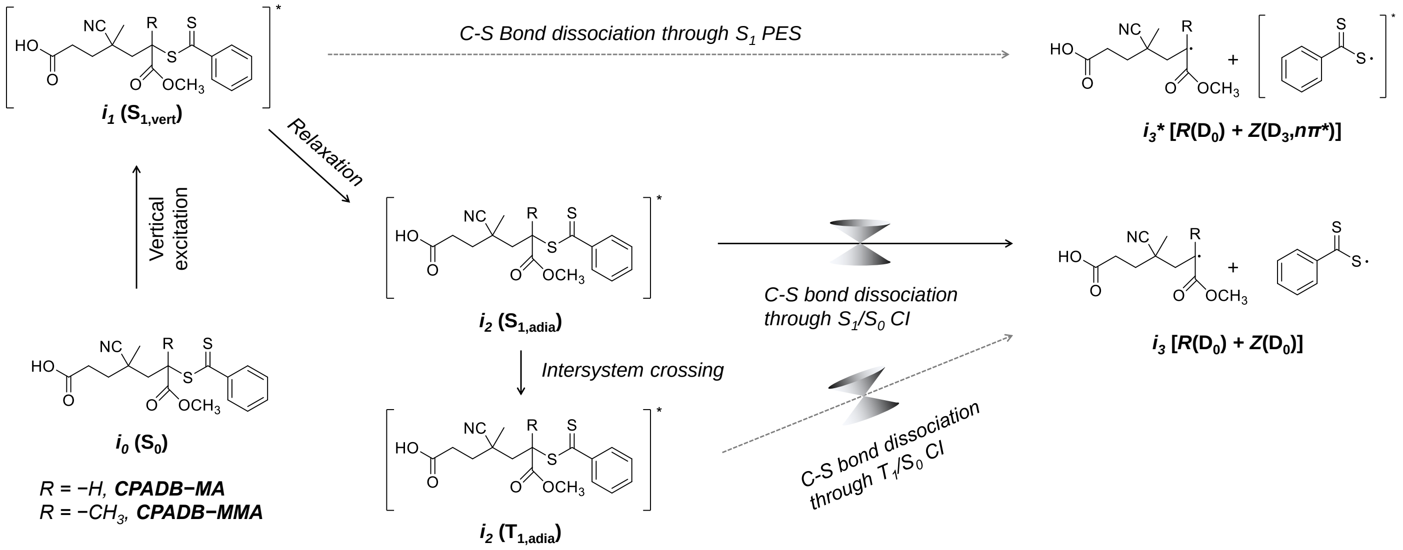


Figure S5. Plausible reaction pathway for CPADB-MA and CPADB-MMA.

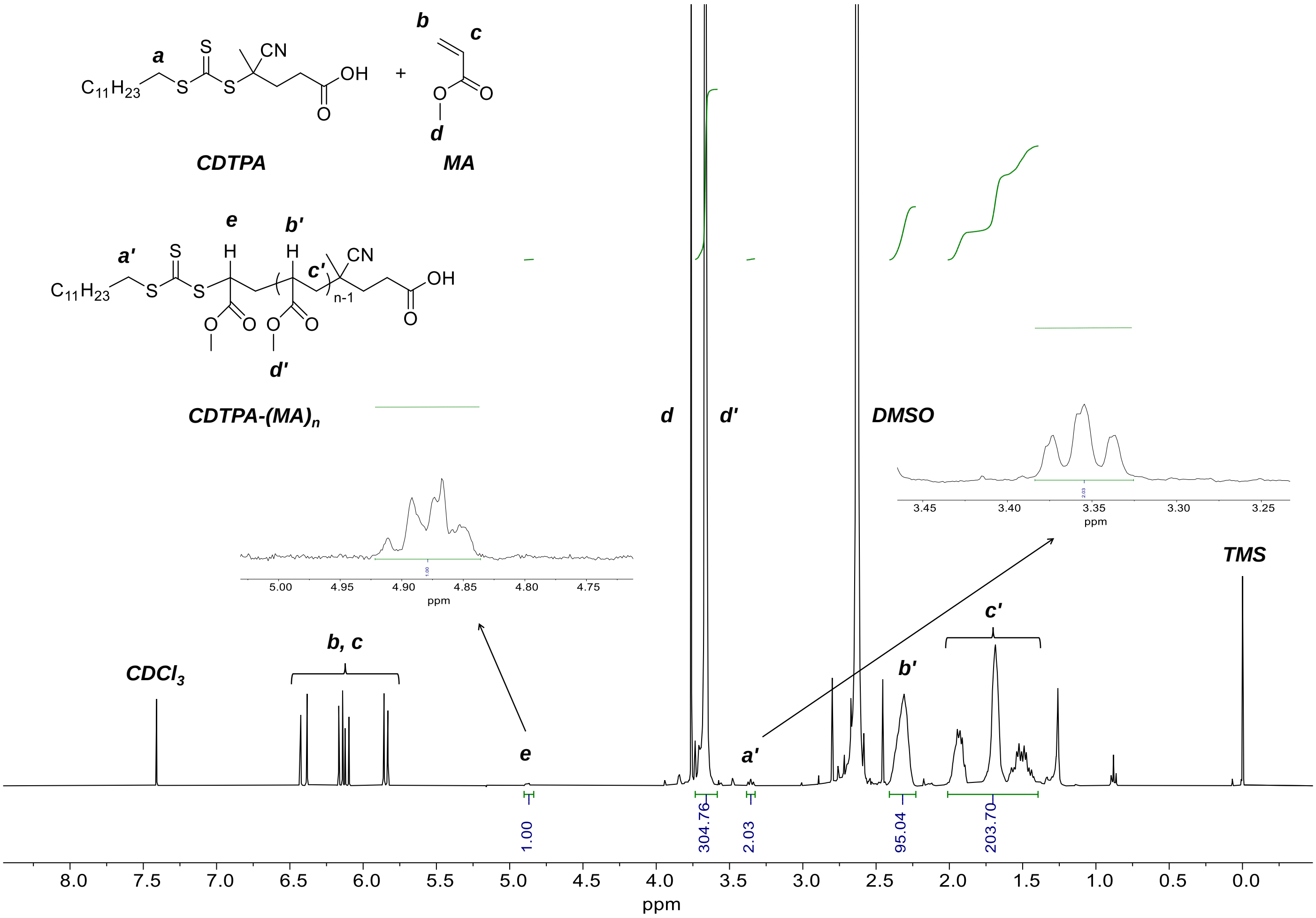


Figure S6. ^{1}H NMR spectrum of PMA polymerization result in the presence of CDTPA under 455 nm LED (100 mW/cm^2) irradiation.

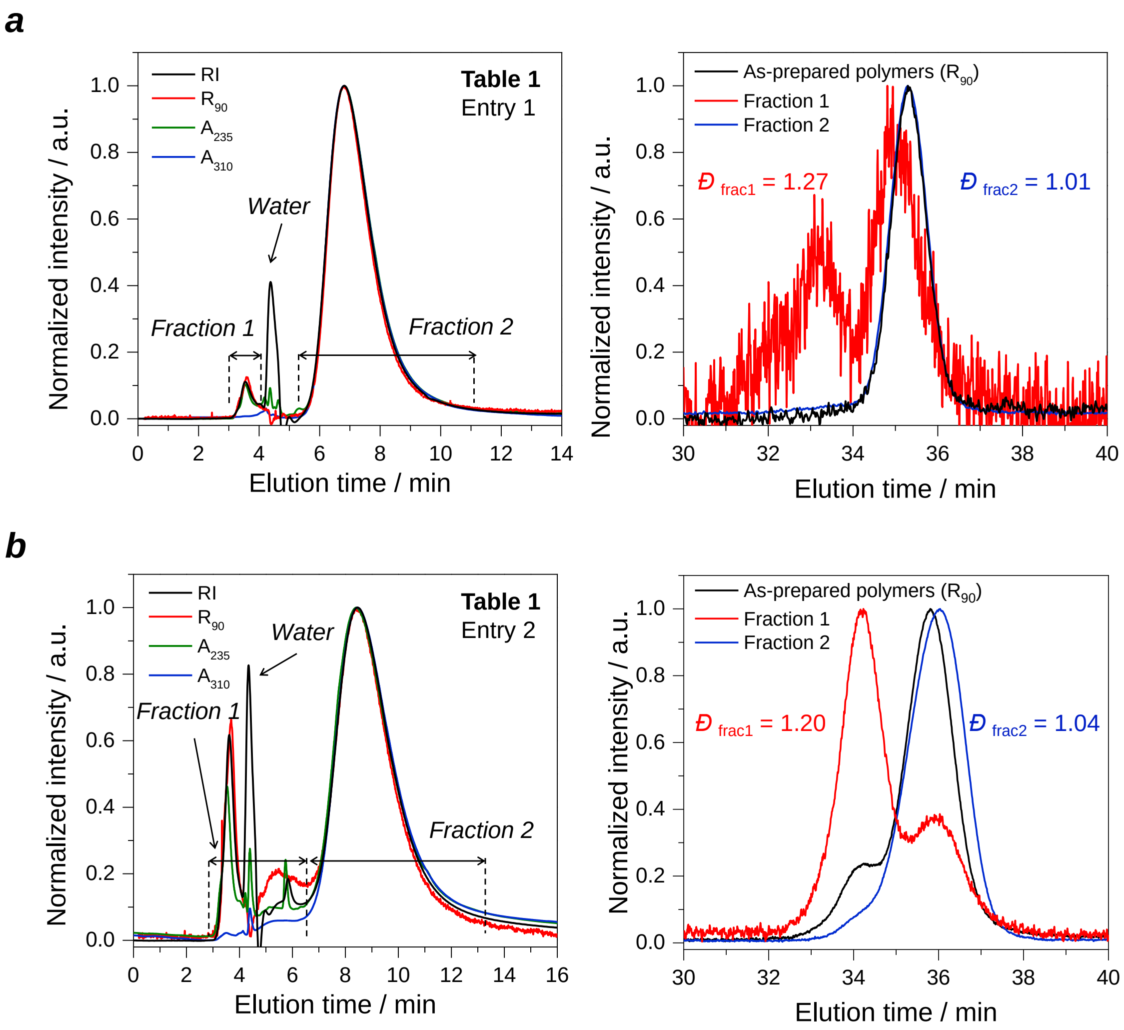


Figure S7. (a) HPLC profiles of the as-prepared PMA (left) and SEC profiles of the fractionized PMA by HPLC (right) synthesized by photoiniferter. (b) HPLC profiles of the as-prepared PMA (left) and SEC profiles of the fractionized PMA by HPLC (right) synthesized by conventional RAFT.

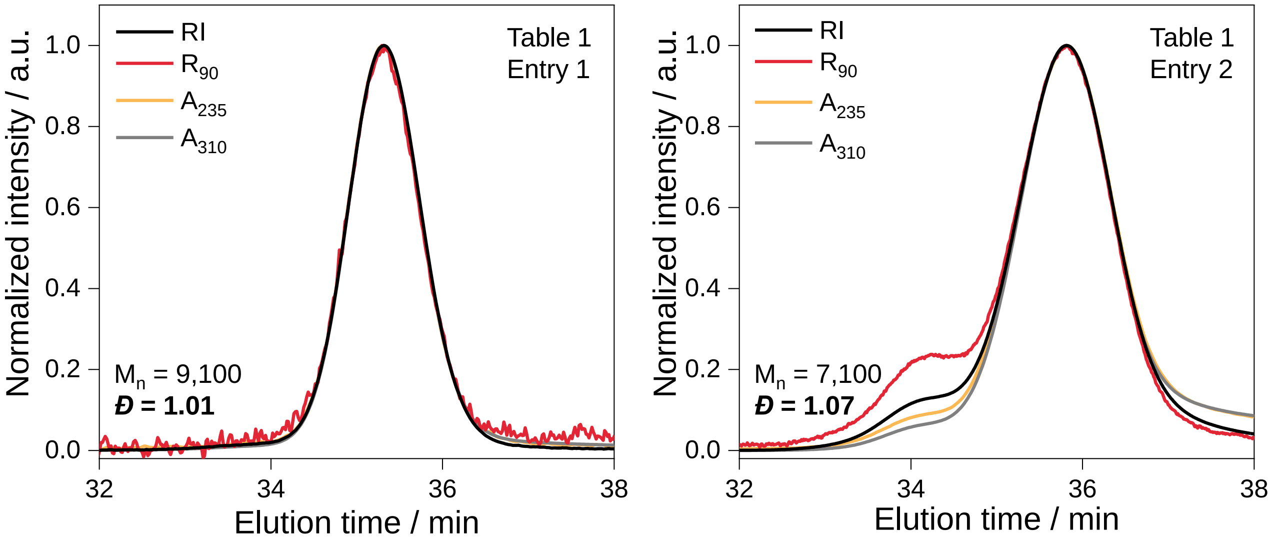
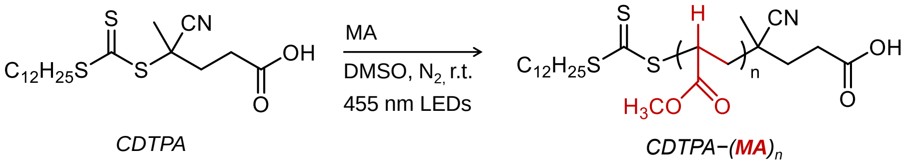


Figure S8. SEC profiles of the as-synthesized poly(methyl acrylate) (PMA) prepared by photoiniferter RAFT (left) and conventional RAFT polymerization (right).

Table S2. Results of MA photoiniferter RAFT polymerization results under higher intensities of 455nm LEDs irradiation in the presence of CDTPA.



Entry	Light source	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	Đ
1	455 nm *300 mW/cm²*	4	100:1	93	8,200	10,200	1.02
2	455 nm *400 mW/cm²*	4	100:1	94	8,300	10,100	1.02

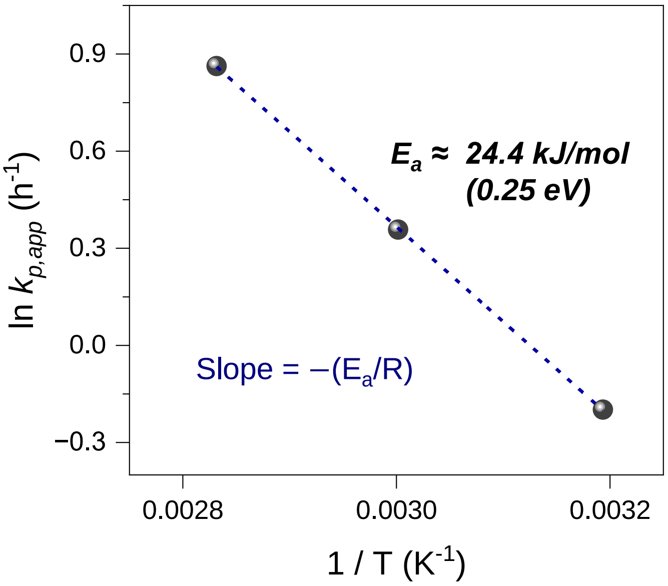


Figure S9. Arrhenius plot for calculating activation energy at different temperatures (***Table 1***).

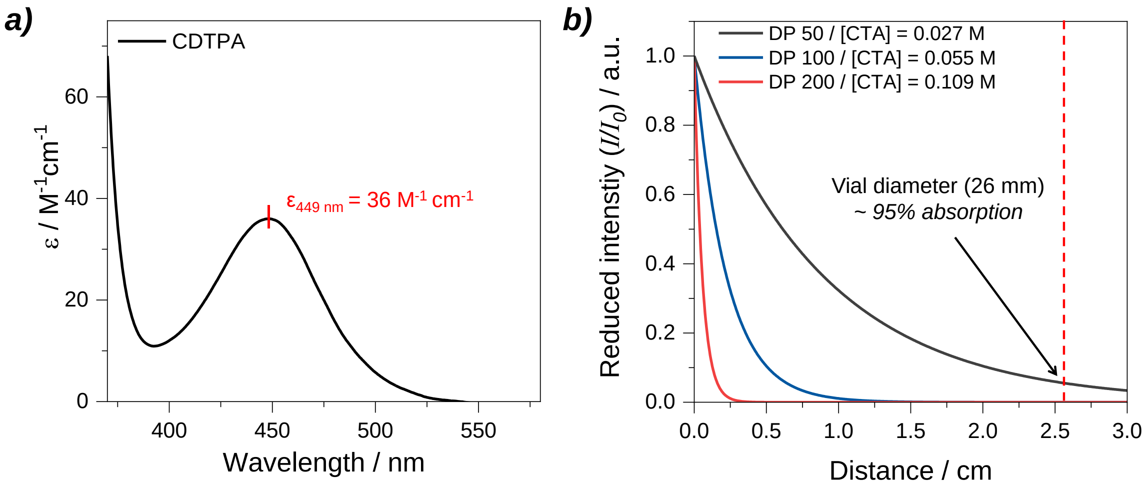
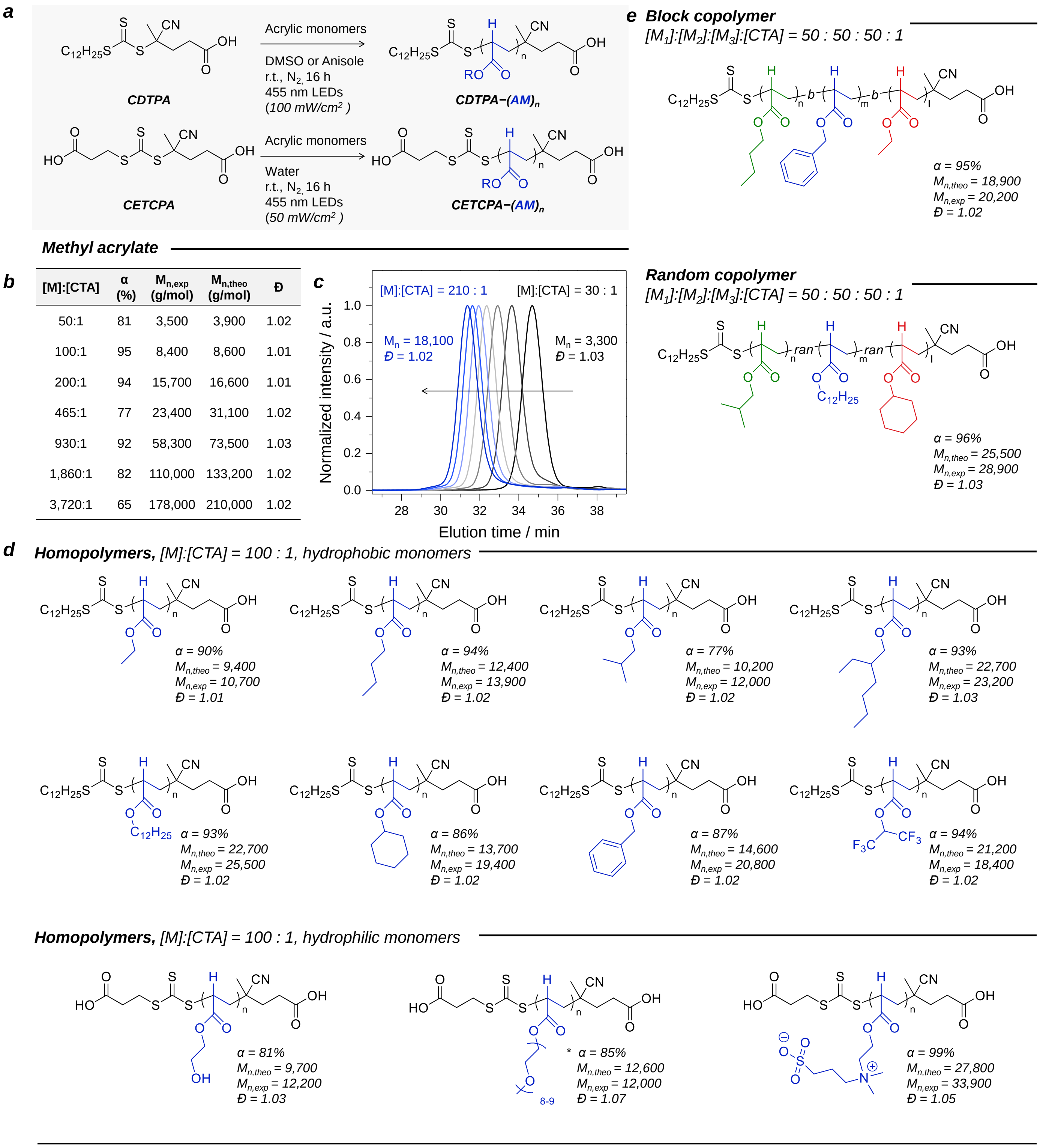


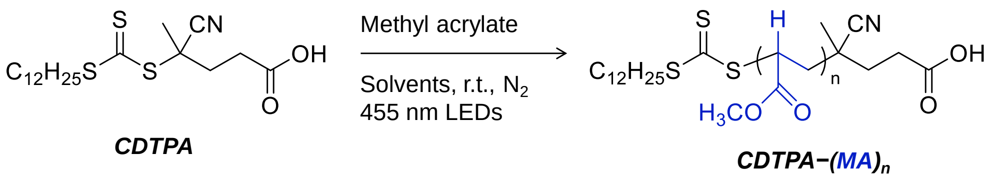
Figure S10. a) UV–vis graph of 200 µM CDTPA solution in DMSO. b) Light penetration curve under 455 nm light irradiation under different concentrations of CTA.



[M]:[CTA]	α (%)	$M_{n,exp}$ (g/mol)	$M_{n,theo}$ (g/mol)	Đ
50:1	81	3,500	3,900	1.02
100:1	95	8,400	8,600	1.01
200:1	94	15,700	16,600	1.01
465:1	77	23,400	31,100	1.02
930:1	92	58,300	73,500	1.03
1,860:1	82	110,000	133,200	1.02
3,720:1	65	178,000	210,000	1.02

Figure S11. (a) Polymerization conditions and various acrylic homopolymer synthesis results for (a) hydrophobic monomers in the presence of CDTPA and (b) hydrophilic monomers in the presence of CETCPA. (c) block and random copolymer results in the presence of CDTPA. *Targeted degree of polymerization is 30.

Table S3. Polymerization results of PMA in the presence of CDTPA under 455nm LEDs irradiation at various solvents.



Entry	Light source	Solvents	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	*Đ*
1	455 nm, *100 mW/cm²*	DMF	16	100:1	74	6,800	7,700	1.01
2		Toluene			76	6,900	7,300	1.01
3		Anisole			95	8,600	9,100	1.01
4		Dioxane			86	7,800	6,100	1.01
5		Acetone			54	5,000	3,900	1.02
6		THF			83	7,500	7,200	1.02
7		Ethyl acetate			6	900	1,500	1.03
8		Chloroform			13	1,500	2,100	1.03

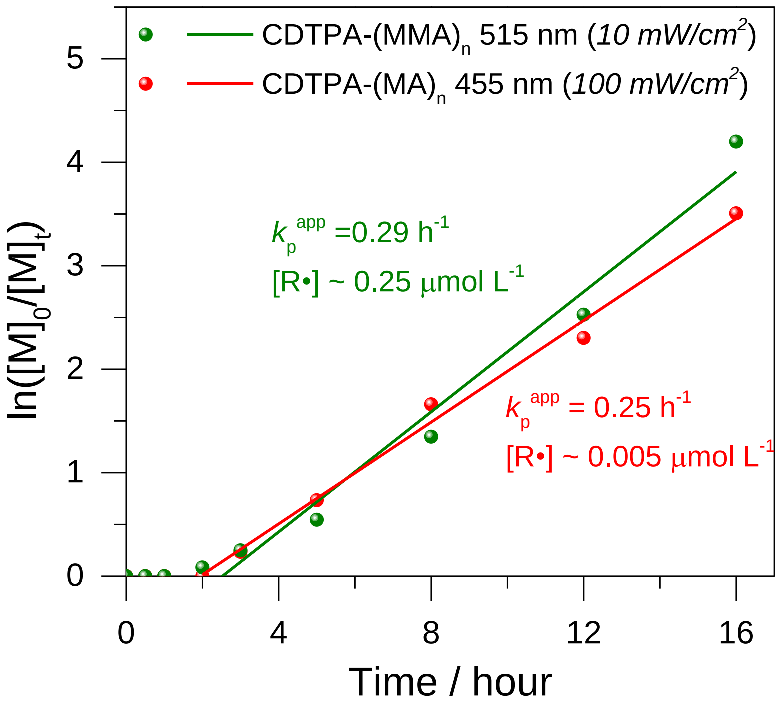
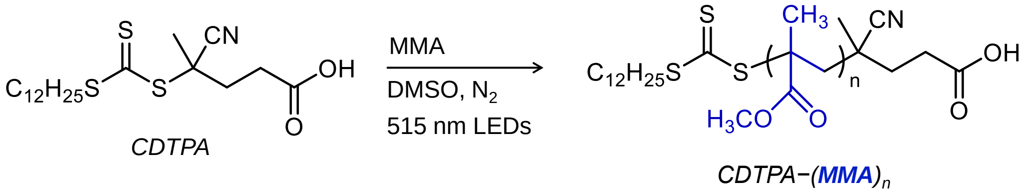


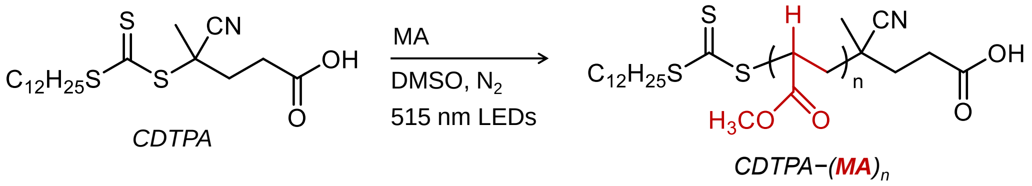
Figure S12. Kinetic plots for the photoiniferter polymerization of MA and MMA with CDTPA under 515 & 455 nm LED irradiation.

Table S4. Summary of photoiniferter RAFT polymerization results under various light source and intensities at different temperatures in this study to show the overview trend of polymerization behavior.

1) CDTPA – 515 nm irradiation

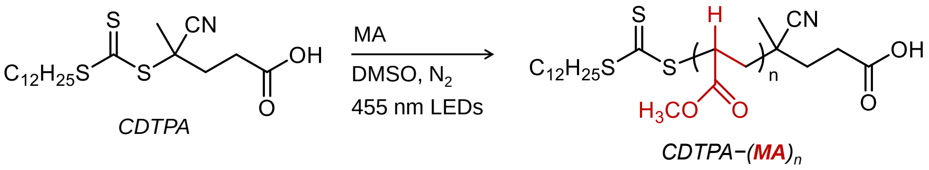


Entry	Monomer	Light source	Temp. (°C)	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	Đ
1	MMA	515 nm ***10 mW/cm^2***	**r.t.**	16	100:1	95	9,900	11,800	1.08



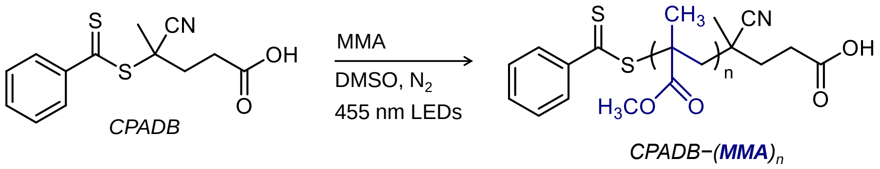
Entry	Monomer	Light source	Temp. (°C)	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	Đ
1	MA	515 nm ***50 mW/cm^2***	**r.t.**	16	100:1	<1	-	-	-
2		515 nm ***250 mW/cm^2***	**r.t.**	16	100:1	62	5,600	6,400	1.01
3		515 nm ***50 mW/cm^2***	**60**	16	100:1	30	3,000	2,400	1.03

2) CDTPA – 455 nm irradiation

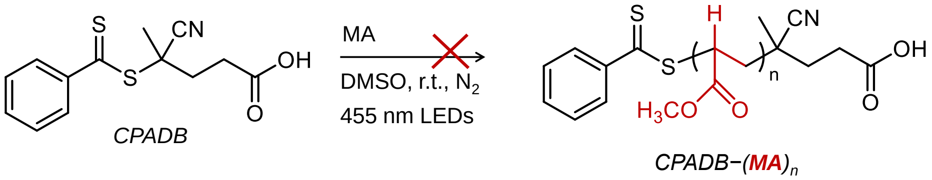


Entry	Monomer	Light source	Temp. (ºC)	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	Đ
1	MA	455 nm ***100 mW/cm^2***	**r.t.**	16	100:1	95	8,600	9,100	1.01
2		455 nm ***200 mW/cm^2***	**r.t.**	12	100:1	94	8,500	8,800	1.01
3		455 nm ***100 mW/cm^2***	**60**	3	100:1	93	8,400	8,000	1.01
4		455 nm ***200 mW/cm^2***	**60**	2	100:1	97	8,800	10,300	1.02
5		455 nm ***100 mW/cm^2***	**80**	2	100:1	91	8,200	7,200	1.02
6		455 nm ***200 mW/cm^2***	**80**	1.5	100:1	95	8,600	8,400	1.03
7		455 nm ***30 mW/cm^2***	**80**	5	100:1	90	8,100	7,200	1.02

3) CPADB – 455 nm irradiation

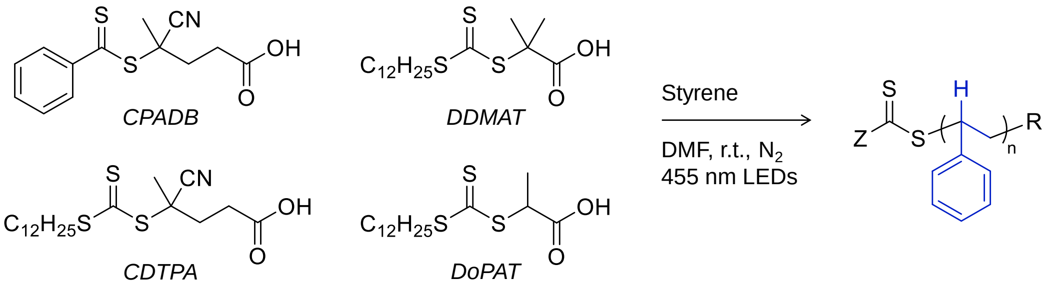


Entry	Monomer	Light source	Temp. (ºC)	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	Đ
1	MMA	455 nm ***100 mW/cm^2***	**r.t.**	16	100:1	56	5,900	7,600	1.05
2		455 nm ***200 mW/cm^2***	**r.t.**	12	100:1	90	9,300	10,500	1.06
3		455 nm ***100 mW/cm^2***	**60**	3	100:1	80	8,300	8,800	1.04
4		455 nm ***200 mW/cm^2***	**60**	2	100:1	90	9,300	10,400	1.03



Entry	Monomer	Light source	Temp. (ºC)	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	Đ
1	MA	515 nm ***100 mW/cm^2***	**r.t.**	16	100:1	<1	-	-	-
2		515 nm ***250 mW/cm^2***	**r.t.**	16	100:1	<1	-	-	-
3		515 nm ***100 mW/cm^2***	**60**	16	100:1	<1	-	-	-

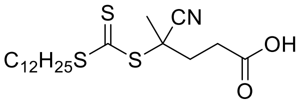
Table S5. Photoiniferter RAFT polymerization results of styrene under 455nm LEDs irradiation in the presence of various CTAs.



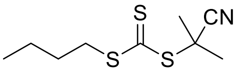
Entry	**Light source**	**CTA**	**Time (h)**	**[M]:[CTA]**	**α (%)**	**$M_{n,theo}$ (g/mol)**	**$M_{n,exp}$ (g/mol)**	***Đ***
1	*455 nm* *100 mW/cm^2*	CPADB	72	100:1	~1	-	-	-
2	*455 nm* *100 mW/cm^2*	CDTPA	72	100:1	48	5,300	6,700	1.27
3	*455 nm* *100 mW/cm^2*	DDMAT	72	100:1	65	7,100	6,900	1.19
4	*455 nm* *100 mW/cm^2*	DoPAT	72	100:1	57	6,200	6,000	1.27

Table S6. Summary of photoiniferter RAFT polymerization results with acrylic monomers under flow system.

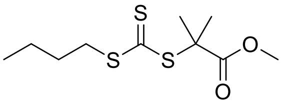
CTA structures



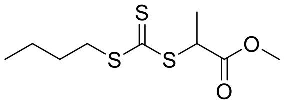
CDTPA



BCN-TTC



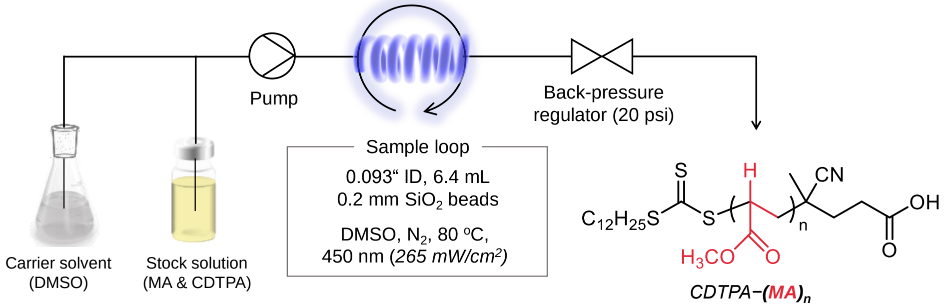
BDMMT



PMBTC

Entry	Monomer	CTA	Temp. (℃)	Light source	Monomer conc.	[M]: [CTA]	Time (min)	α (%)	$M_{n,exp}$ (g/mol)	*Đ*	***Ref***
1	MA	CDTPA	80	450 nm *265 mW/cm*^{2}	5.5 M in DMSO	100:1	20	89	9,300	1.02	This work
2	MMA	CDTPA	90	450 nm *14.4 W*	3.7 M in DMSO	25:1	60	> 90	~2,900	< 1.3	56
3						50:1			~5,900		
4						75:1			~6,800		
5						100:1			~9,800		
6	MA	BCN-TTC	70	460 nm *15 mW/cm*^{2}	3.0 M in DMSO	50:1	30	47	2,300	1.13	49
7	MA	BDMMT						62	3,500	1.11	
8	MA	PMBTC						57	3,200	1.16	
9	MMA	BCN-TTC	70	460 nm *15 mW/cm*^{2}	3.0 M in DMSO	50:1	30	60	4,600	1.48	49
10	MMA	BDMMT						52	6,500	1.74	
11	MMA	PMBTC						19	71,000	1.71	

Table S7. Photoiniferter RAFT polymerization results of MA under flow reactor packed with 0.2 mm size of SiO_2 beads varying the monomer concentration and targeted DP in the presence of CDTPA at 80 °C.



Entry	SiO_2 bead size (mm)	Time (min)	Monomer concentration	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	*Đ*
1	0.2	20	7.3 mol/L (MA:DMSO (v/v) =2:1)	100:1	92	8,100	10,200	1.02
2	0.2	15	8.7 mol/L (MA:DMSO (v/v) = 4:1)	100:1	92	8,100	8,300	1.03
3	0.2	25	5.5 mol/L (MA:DMSO (v/v) = 1:1)	200:1	90	15,700	18,200	1.04
4	0.2	30	5.5 mol/L (MA:DMSO (v/v) = 1:1)	400:1	86	29,800	33,400	1.05

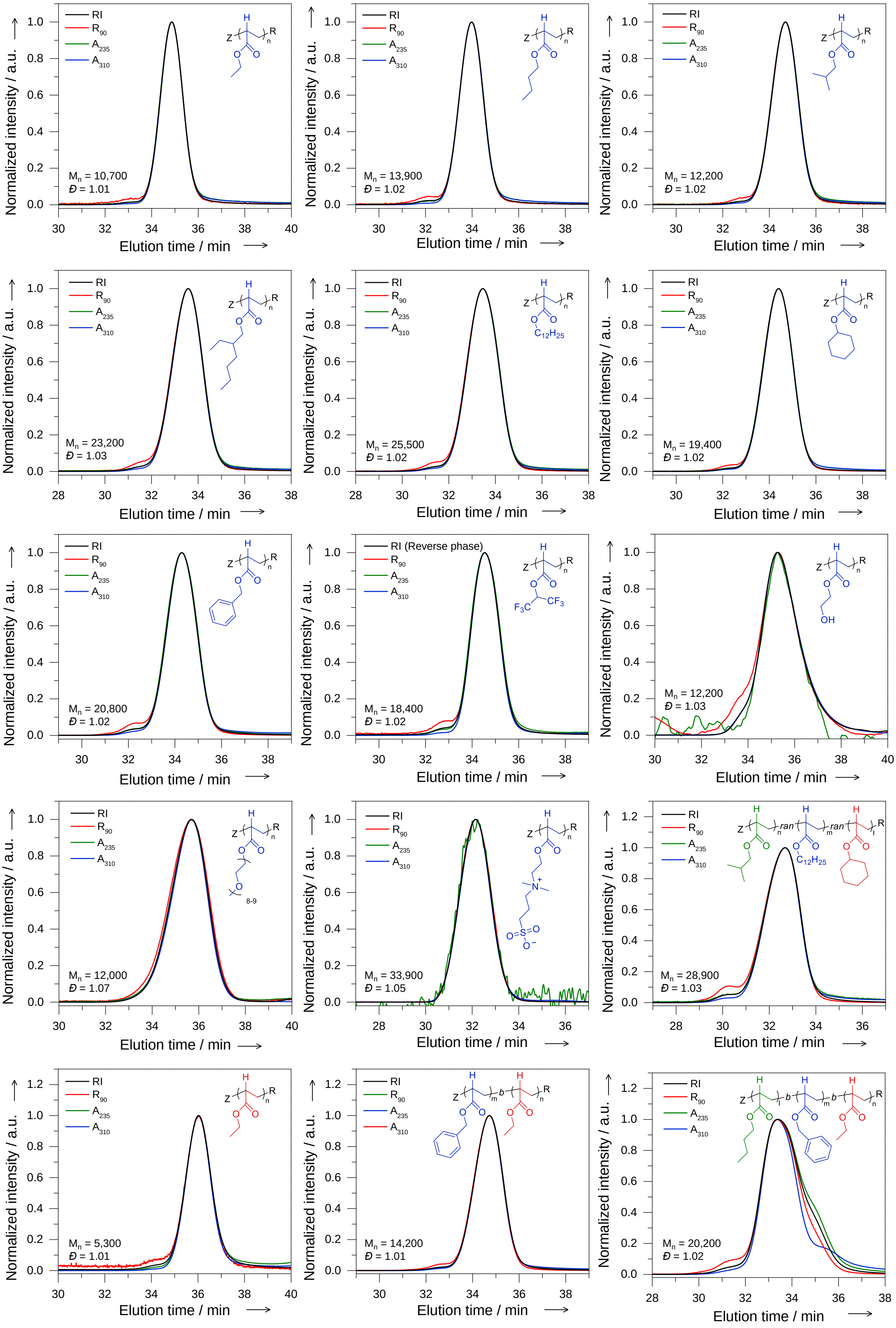


Figure S13. SEC curves of the synthesized polyacrylates under 455 nm irradiation recorded by RI (black), LS (red) and UV at 235 nm (green) and 310 nm (blue) (***Figure S11***).

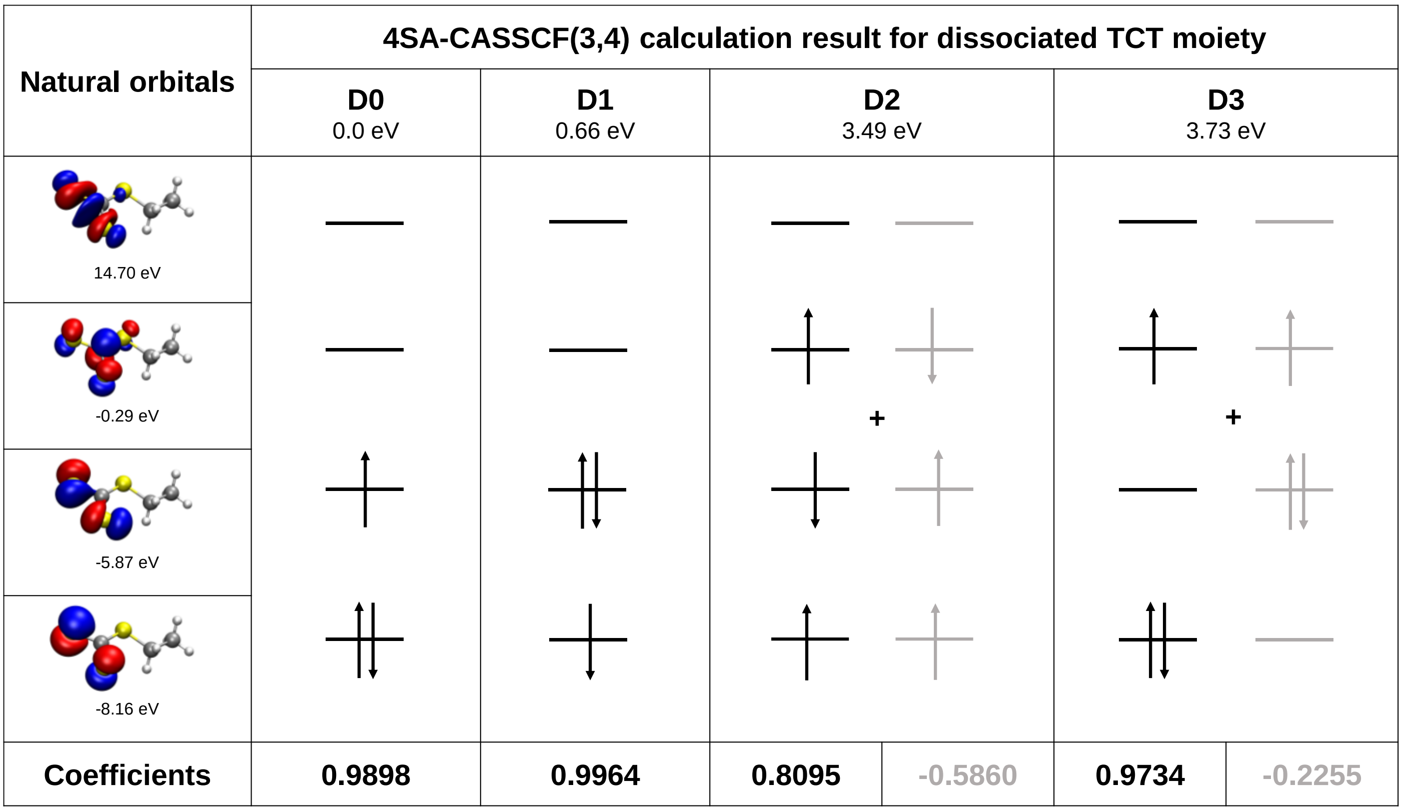


Figure S14. 4SA-CASSCF(3,4)/6-31+G* calculation result for dissociated thiocarbonylthio radical of CDTPA. The relative state energies to D_0 state and their most dominant configurations based on natural orbitals are given with corresponding coefficients. The natural orbitals are shown with their energies.

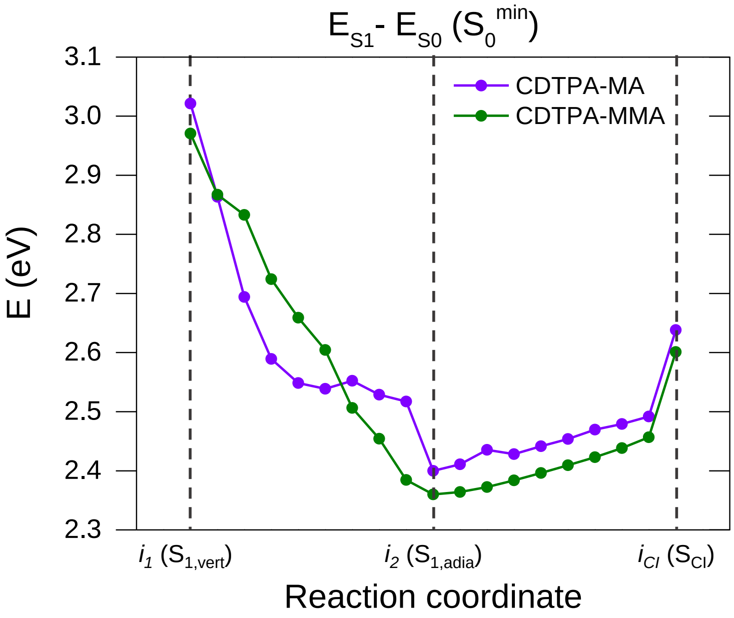


Figure S15. Reaction pathway (relative to i_0) of $i_1 \rightarrow i_2 \rightarrow i_{CI}$ for CDTPA-MA (purple) and CDTPA-MMA (green) on S_1 state.

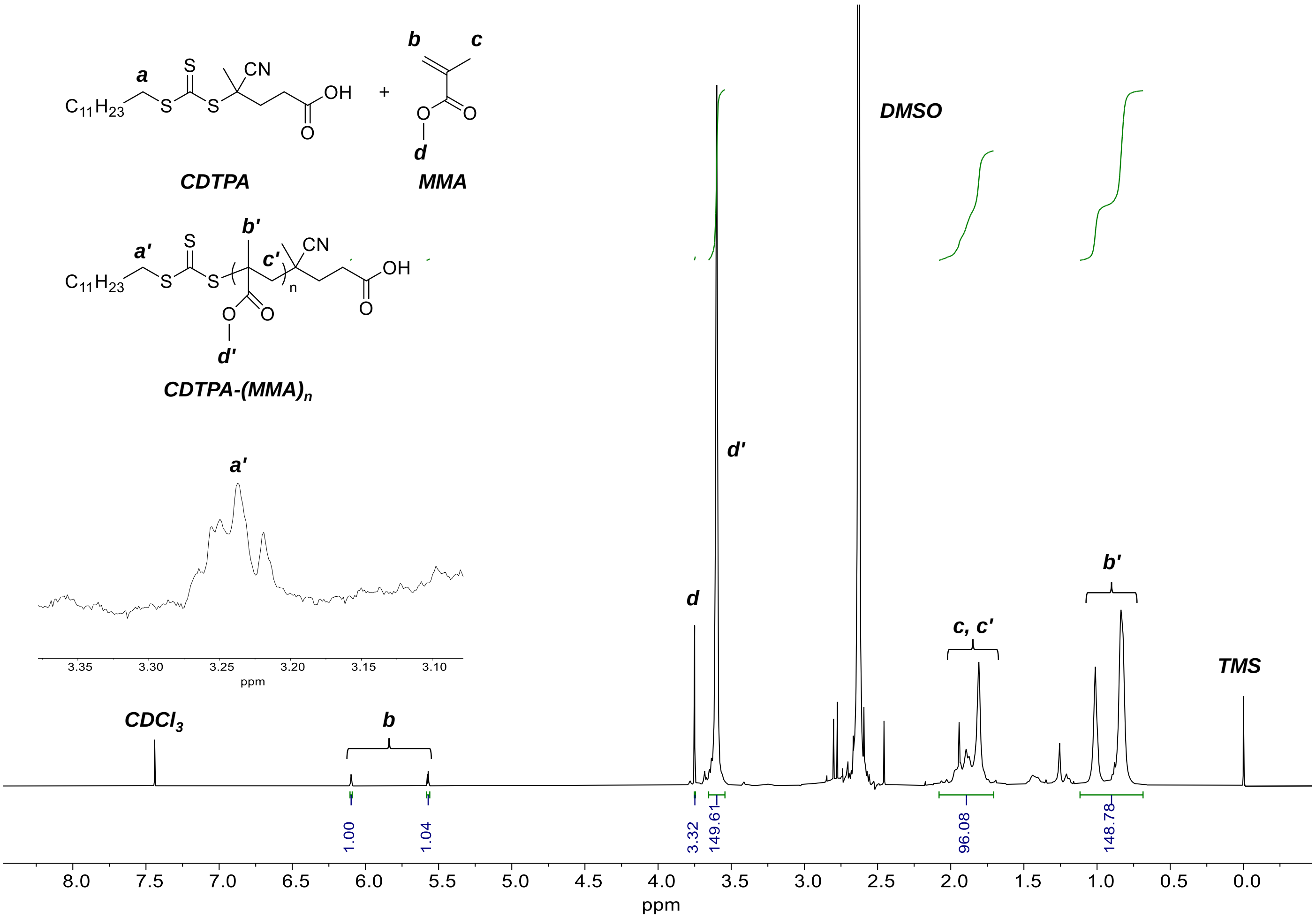


Figure S16. ^{1}H NMR spectrum of PMMA polymerization result in the presence of CDTPA under 515 nm LED (10 mW/cm^2) irradiation.

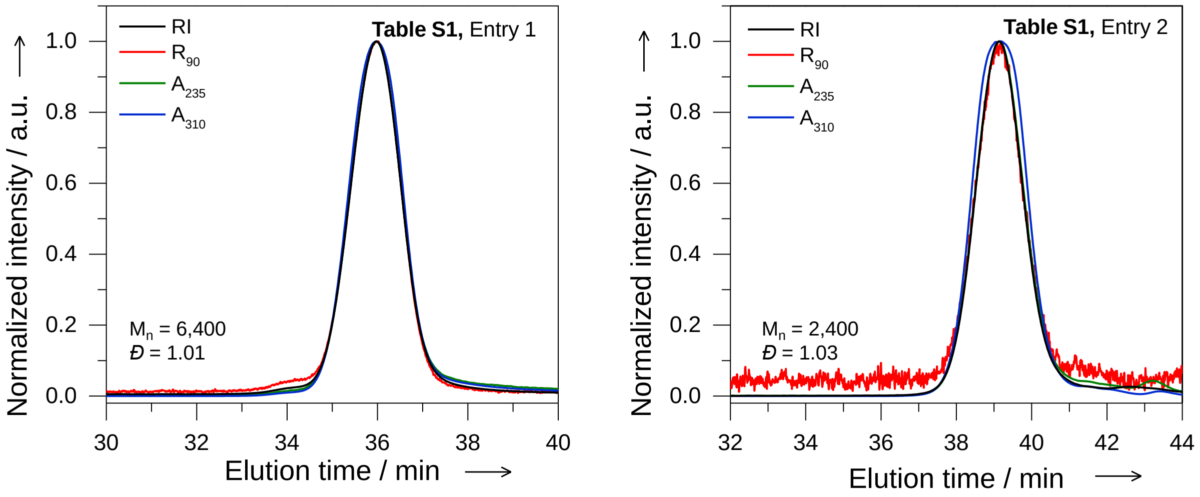


Figure S17. SEC curves of the synthesized PMA recorded by RI (black), LS (red) and UV at 235 nm (green) and 310 nm (blue) (***Table S1***).

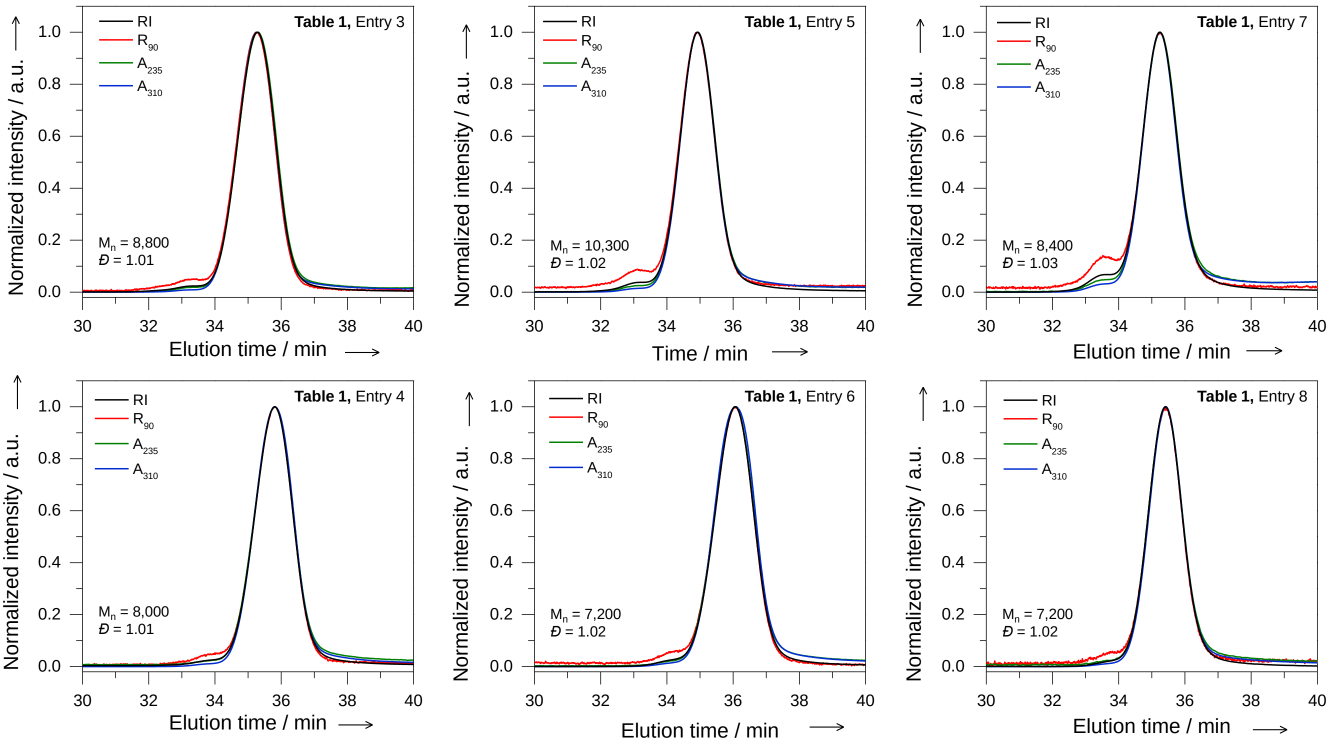
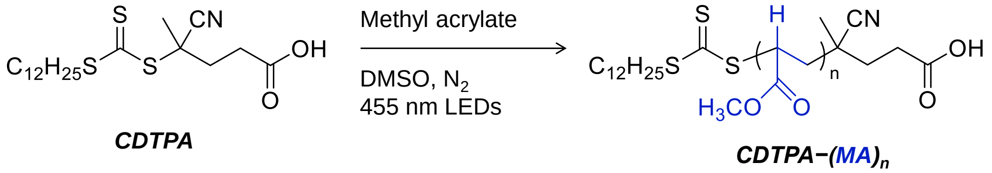


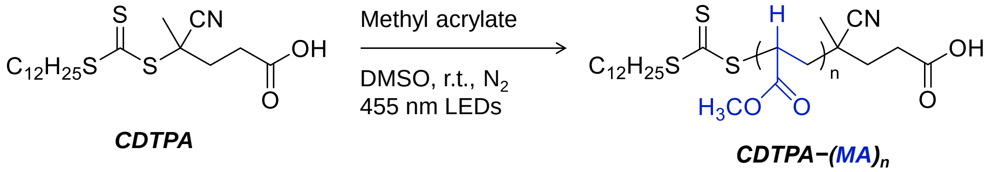
Figure S18. SEC curves of the synthesized PMA recorded by RI (black), LS (red) and UV at 235 nm (green) and 310 nm (blue) (***Table 1,*** *entries 3–8*).

Table S8. Polymerization kinetics results of PMA in the presence of CDTPA under 455nm LEDs irradiation (***Table 1***).



Entry	Light source	Temp (ºC)	Time (min)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	*Đ*
1	455 nm, *200 mW/cm²*	60	5	100:1	<1	-	-	-
2			10		<1	-	-	-
3			20		24	-	-	-
4			30		49	4,600	4,000	1.01
5			50		68	6,300	5,900	1.01
6			70		81	7,400	6,500	1.01
7			100		88	8,000	8,400	1.02
8	455 nm, *200 mW/cm²*	80	5	100:1	<1	-	-	-
9			10		24	-	-	-
10			20		58	5,400	5,300	1.02
11			30		73	6,700	6,100	1.01
12			50		84	7,600	7,200	1.01
13			70		93	8,400	8,300	1.02

Table S9. Polymerization kinetics results of PMA in the presence of CDTPA under 455nm LEDs irradiation (***Table 1***).



Entry	Light source	Temp (ºC)	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	*Đ*
1	455 nm, *200 mW/cm^2*	r.t.	0.5	50:1	<1	-	-	-
2			1		<1	-	-	-
3			2		<1	-	-	-
4			3		9	-	-	-
5			5		35	-	-	-
6			8		75	3,600	3,500	1.02
7			12		86	4,100	4,000	1.02
8			16		94	4,400	4,300	1.02
9	455 nm, *200 mW/cm^2*	r.t.	0.5	200:1	<1	-	-	-
10			1		19	-	-	-
11			2		59	10,600	9,900	1.01
12			3		74	13,100	12,300	1.01
13			5		89	15,700	15,200	1.01
14			8		94	16,600	16,700	1.01
15			12		98	17,300	16,900	1.01

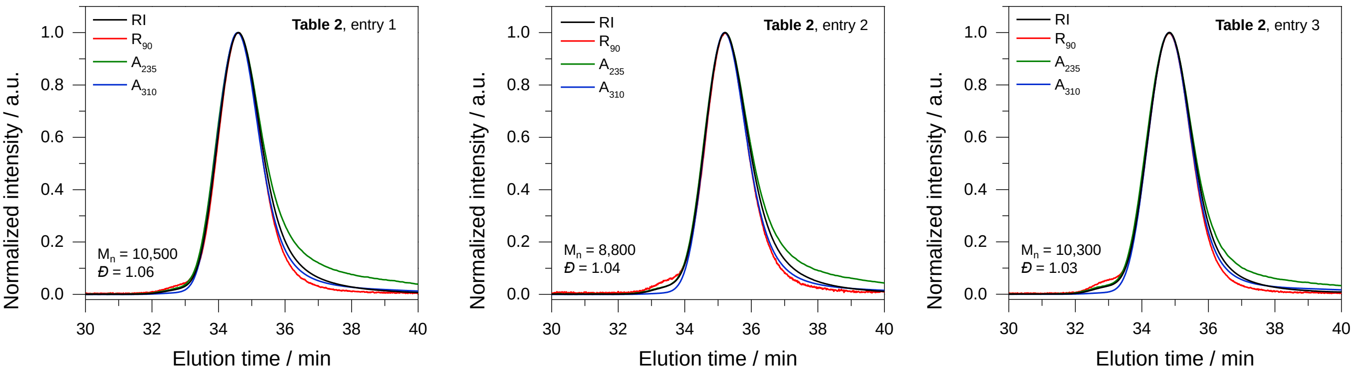


Figure S19. SEC curves of the synthesized PMMA recorded by RI (black), LS (red) and UV at 235 nm (green) and 310 nm (blue) (***Table 2,*** *entries 1–3*).

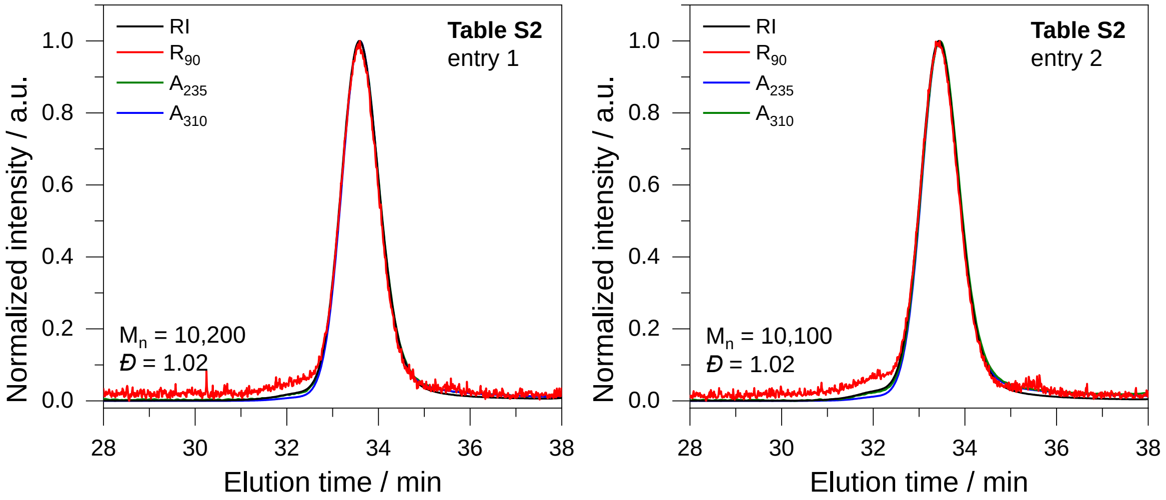


Figure S20. SEC traces of MA photoiniferter RAFT polymerization under higher intensities of 455nm LEDs irradiation in the presence of CDTPA (***Table S2***).

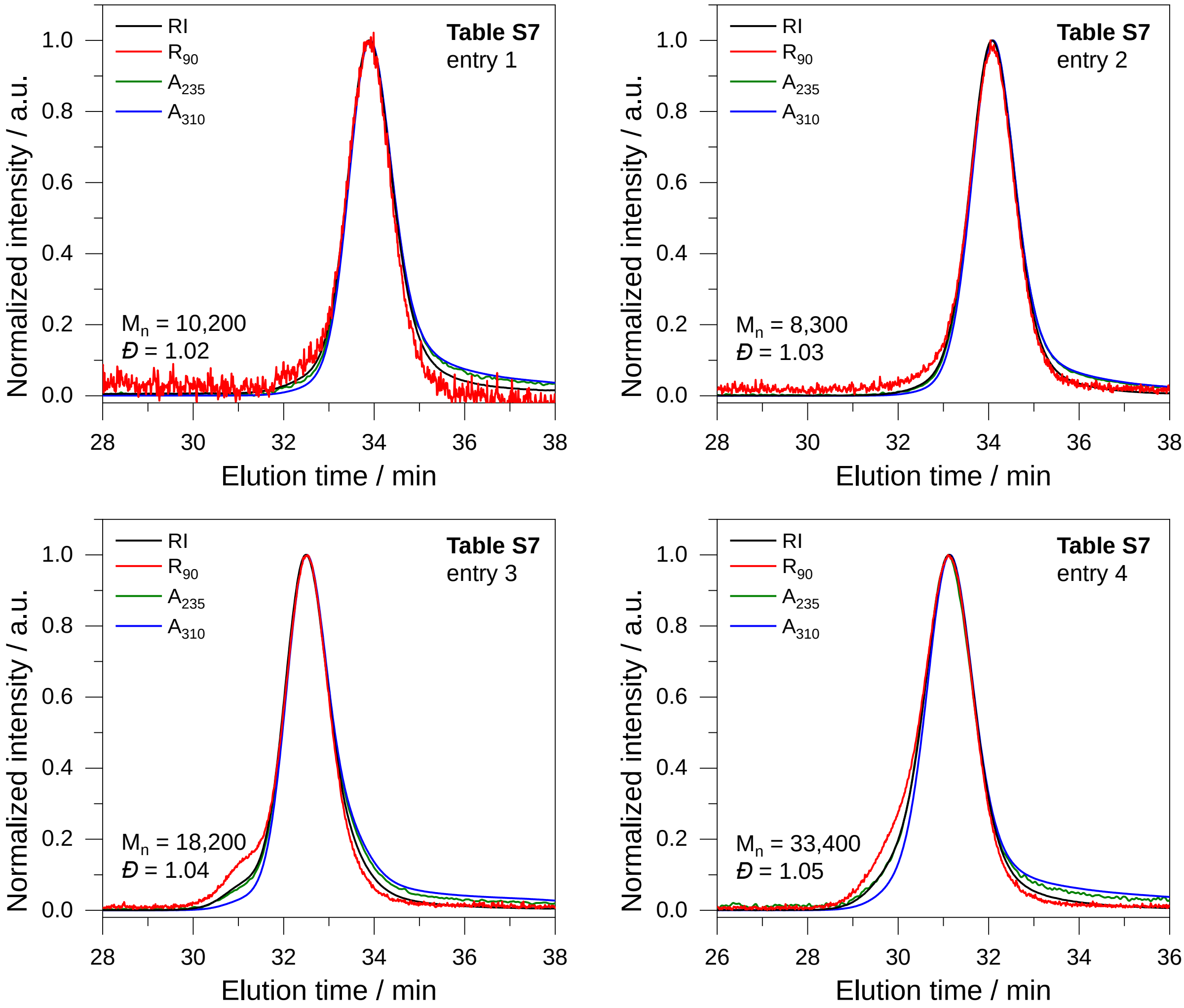
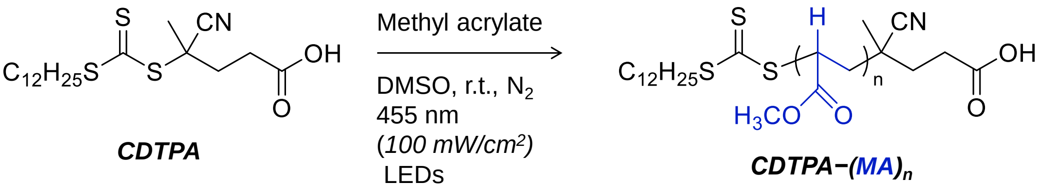
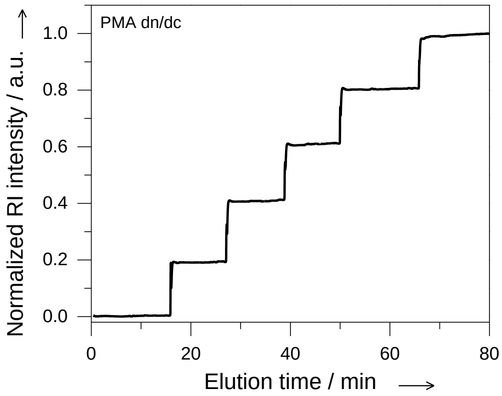


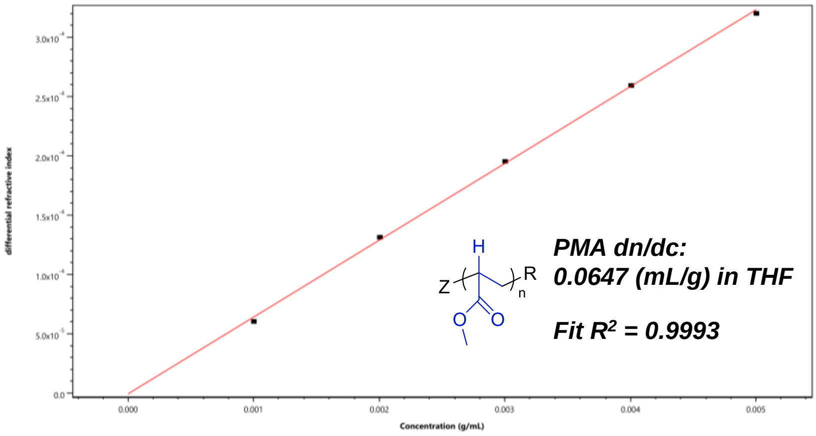
Figure S21. SEC traces of MA photoiniferter RAFT polymerization under flow reactor packed with 0.2 mm size of SiO_2 beads in the presence of CDTPA at 80 °C (***Table S7***).

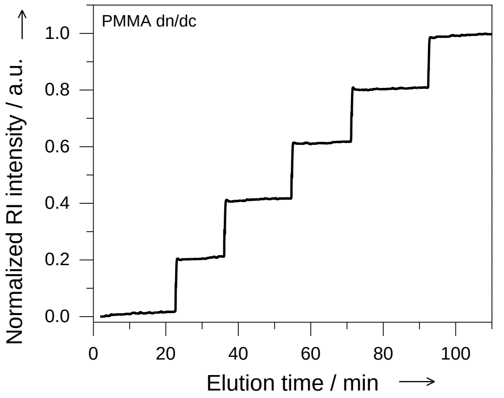
Table S10. Methyl acrylate chain extension experiment results in the presence of CDTPA under 455 nm irradiation as sequential monomer injection without further purification steps.

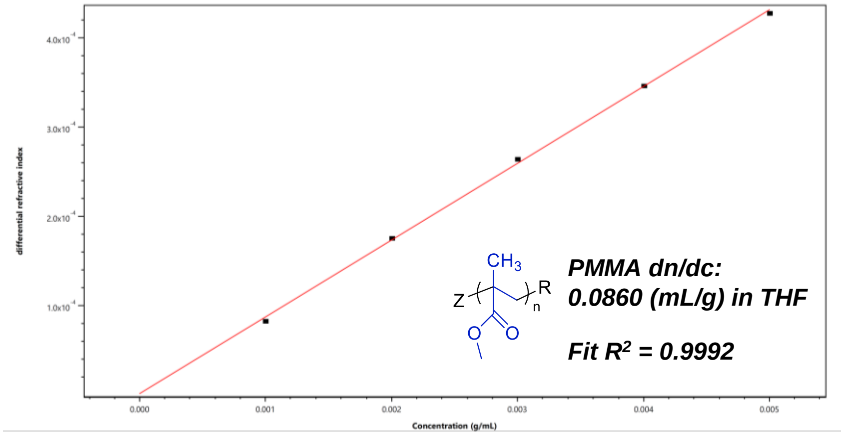


Chain extension	Light source	Time (h)	[M]:[CTA]	α (%)	$M_{n,theo}$ (g/mol)	$M_{n,exp}$ (g/mol)	*Đ*
1	455 nm, *100 mW/cm²*	24	30 : 1	86	2,600	3,300	1.03
2		18	60 : 1	92	5,200	6,100	1.02
3		12	90 : 1	89	7,300	8,900	1.01
4		12	120 : 1	90	9,700	10,700	1.01
5		6	150 : 1	85	11,300	12,900	1.02
6		3	180 : 1	86	13,700	15,200	1.02
7		3	210 : 1	82	15,200	18,100	1.02


PMA dn/dc
Normalized RI intensity / a.u.
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Elution time / min


differential refractive index
3.0x10^-4
2.5x10^-4
2.0x10^-4
1.5x10^-4
1.0x10^-4
5.0x10^-5
0.0
0.000
0.001
0.002
0.003
0.004
0.005
Concentration (g/mL)
H
Z
R
n
O
O
PMA dn/dc:
0.0647 (mL/g) in THF
Fit R² = 0.9993


PMMA dn/dc
Normalized RI intensity / a.u.
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
Elution time / min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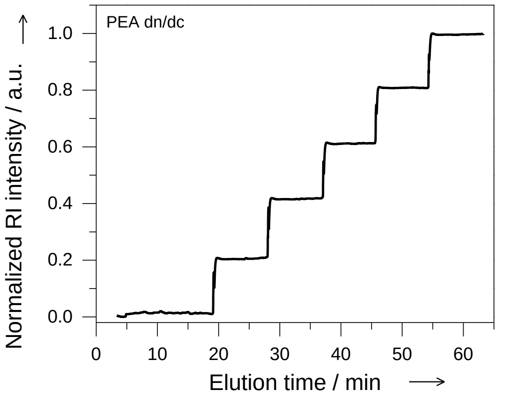
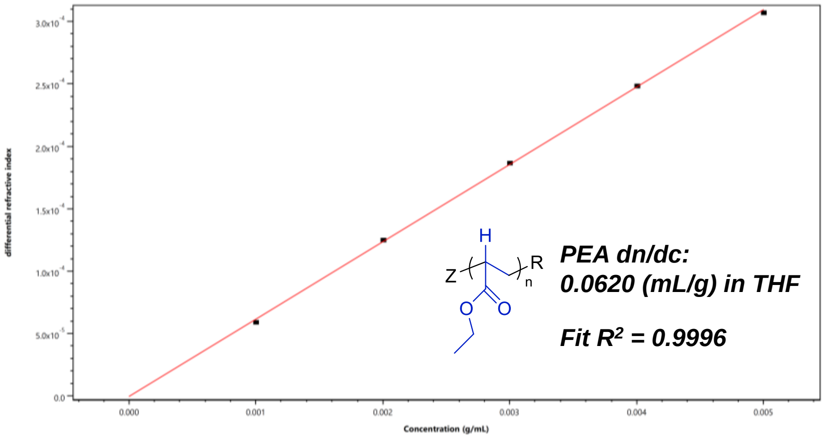
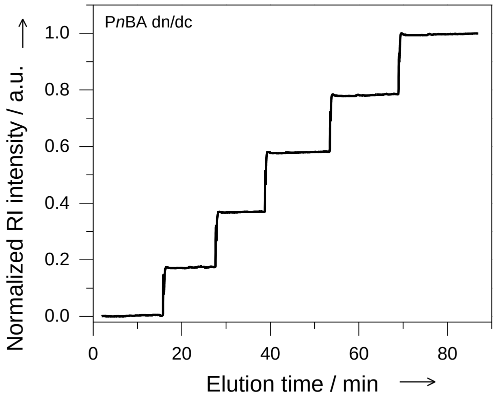
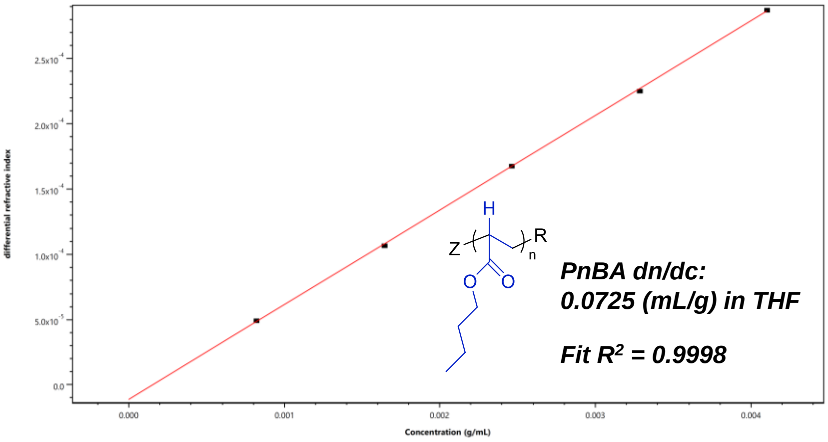
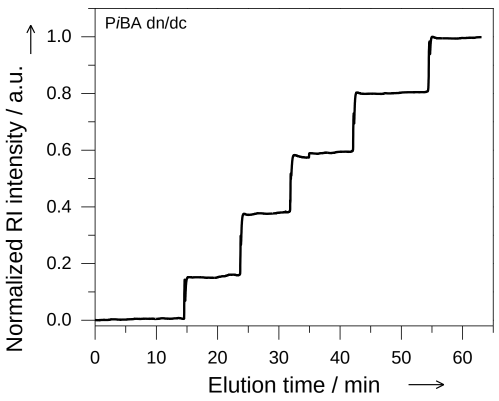
3.0x10^-4
2.0x10^-4
1.0x10^-4
0.000
0.001
0.002
0.003
0.004
0.005
Concentration (g/mL)
CH3
Z
R
n
O
O
PMMA dn/dc:
0.0860 (mL/g) in THF
Fit R² = 0.9992

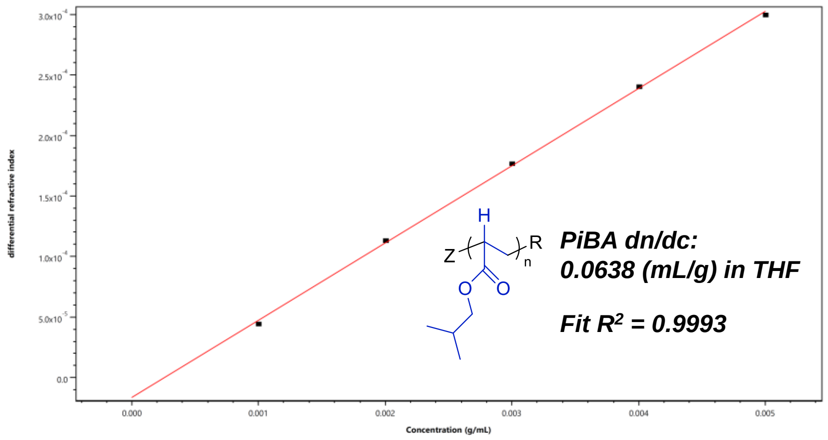

PEA dn/dc
Normalized RI intensity / a.u.
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
Elution time / min

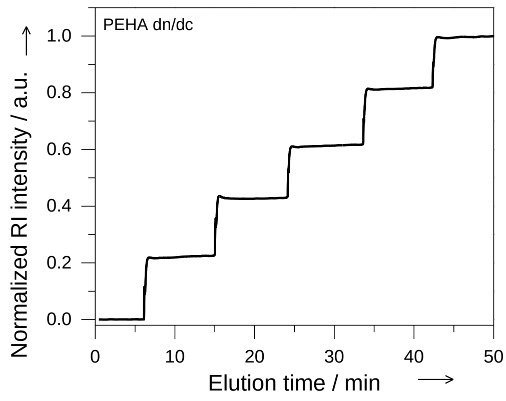

differential refractive index
3.0x10^-4
2.5x10^-4
2.0x10^-4
1.5x10^-4
1.0x10^-4
5.0x10^-5
0.0
0.000
0.001
0.002
0.003
0.004
0.005
Concentration (g/mL)
H
Z
R
n
O
O
PEA dn/dc:
0.0620 (mL/g) in THF
Fit R² = 0.9996

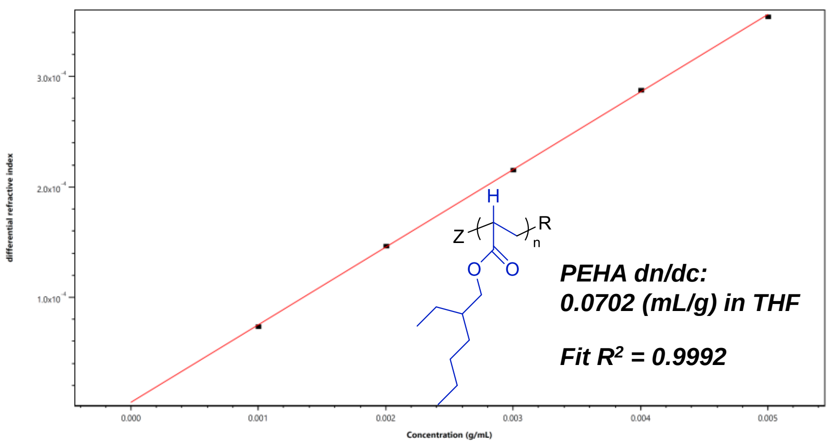

PnBA dn/dc
Normalized RI intensity / a.u.
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Elution time / min

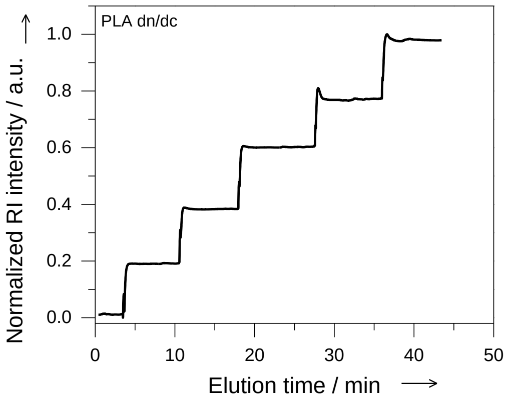

differential refractive index
2.5x10^-4
2.0x10^-4
1.5x10^-4
1.0x10^-4
5.0x10^-5
0.0
0.000
0.001
0.002
0.003
0.004
Concentration (g/mL)
H
Z
R
n
O
O
PnBA dn/dc:
0.0725 (mL/g) in THF
Fit R² = 0.9998

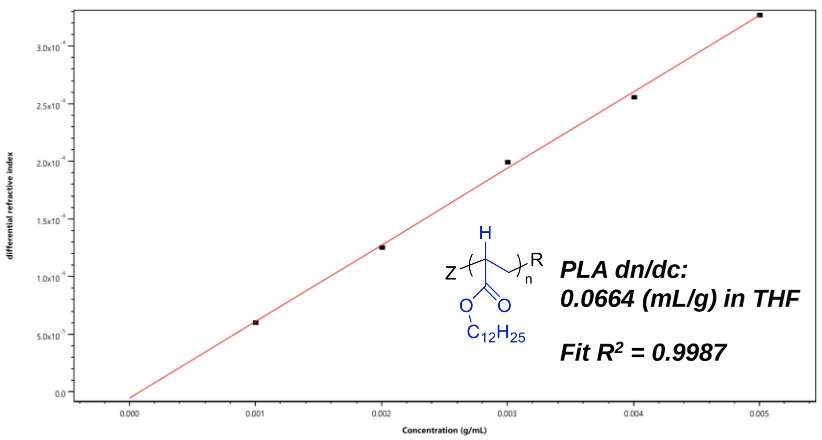

PiBA dn/dc
Normalized RI intensity / a.u.
0.0
0.2
0.4
0.6
0.8
1.0
0
10
20
30
40
50
60
Elution time / min

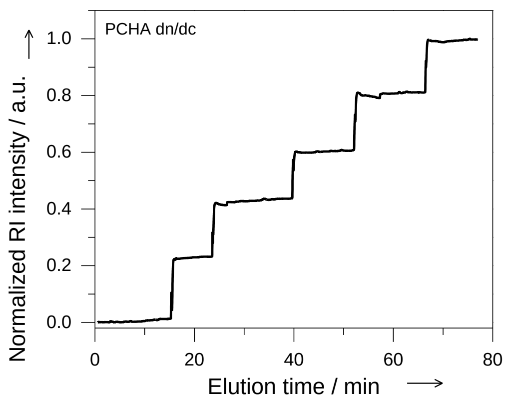

differential refractive index
0.0
5.0x10⁻⁵
1.0x10⁻⁴
1.5x10⁻⁴
2.0x10⁻⁴
2.5x10⁻⁴
3.0x10⁻⁴
0.000
0.001
0.002
0.003
0.004
0.005
Concentration (g/mL)
H
Z
R
n
O
O
PiBA dn/dc:
0.0638 (mL/g) in THF
Fit R² = 0.9993

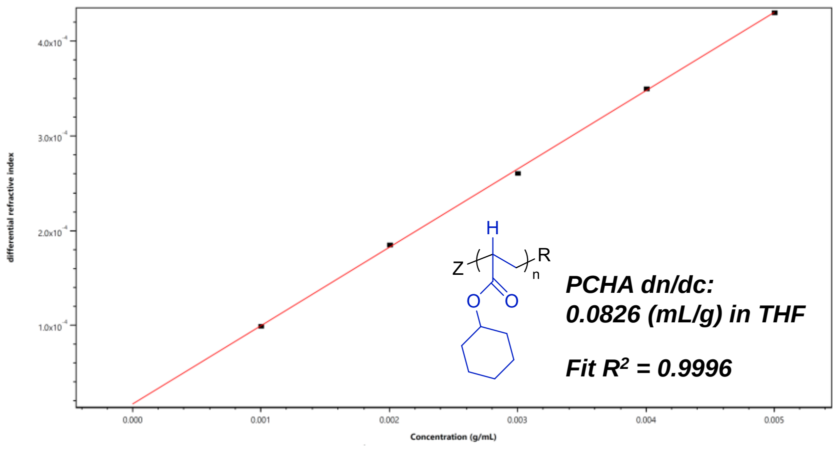

PEHA dn/dc
Normalized RI intensity / a.u.
0.0
0.2
0.4
0.6
0.8
1.0
0
10
20
30
40
50
Elution time / min

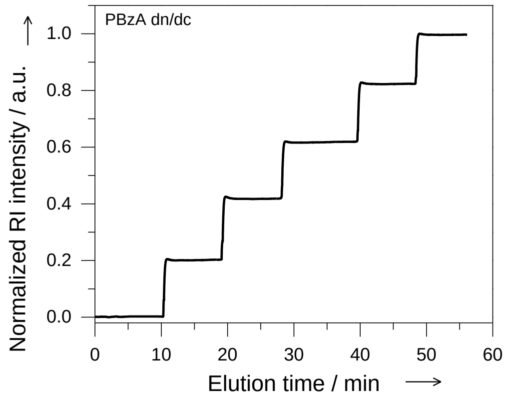

differential refractive index
1.0x10⁻⁴
2.0x10⁻⁴
3.0x10⁻⁴
0.000
0.001
0.002
0.003
0.004
0.005
Concentration (g/mL)
H
Z
R
n
O
O
PEHA dn/dc:
0.0702 (mL/g) in THF
Fit R² = 0.9992

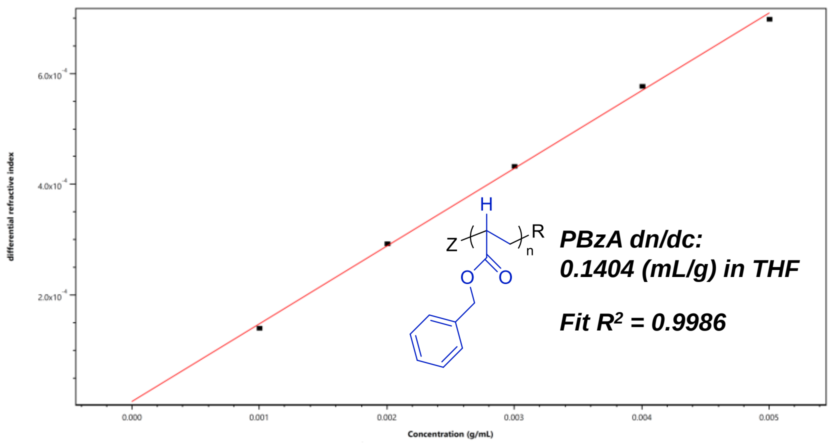

PLA dn/dc
Normalized RI intensity / a.u.
0.0
0.2
0.4
0.6
0.8
1.0
0
10
20
30
40
50
Elution time / min

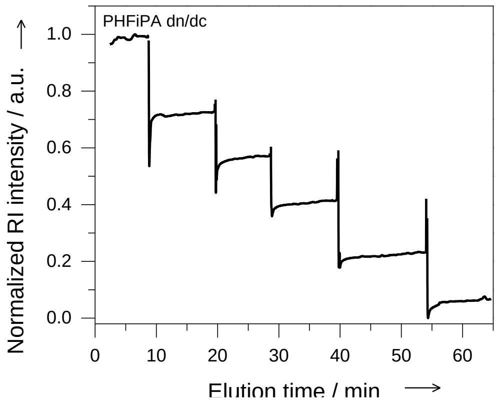

differential refractive index
0.0
5.0x10⁻⁵
1.0x10⁻⁴
1.5x10⁻⁴
2.0x10⁻⁴
2.5x10⁻⁴
3.0x10⁻⁴
0.000
0.001
0.002
0.003
0.004
0.005
Concentration (g/mL)
H
Z
R
n
O
O
C12H25
PLA dn/dc:
0.0664 (mL/g) in THF
Fit R² = 0.9987

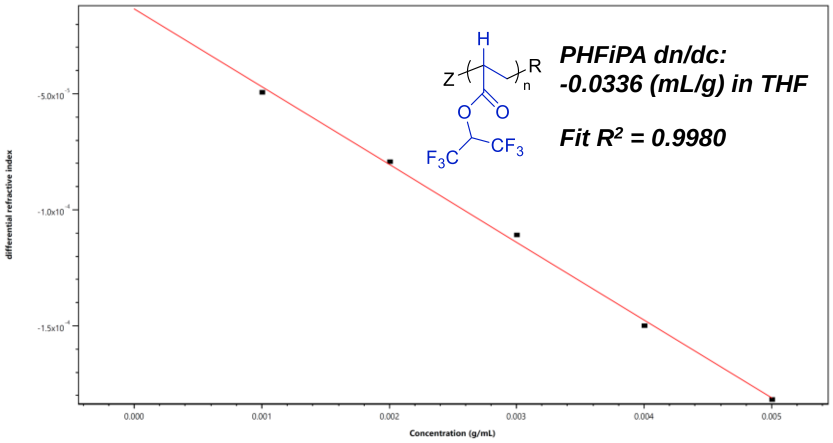

PCHA dn/dc
Normalized RI intensity / a.u.
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Elution time / min


differential refractive index
4.0x10⁻⁴
3.0x10⁻⁴
2.0x10⁻⁴
1.0x10⁻⁴
0.000
0.001
0.002
0.003
0.004
0.005
Concentration (g/mL)
H
Z
R
n
O
O
PCHA dn/dc:
0.0826 (mL/g) in THF
Fit R² = 0.9996


PBzA dn/dc
Normalized RI intensity / a.u.
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
Elution time / min


differential refractive index
6.0x10⁻⁴
4.0x10⁻⁴
2.0x10⁻⁴
0.000
0.001
0.002
0.003
0.004
0.005
Concentration (g/mL)
H
Z
R
n
O
O
PBzA dn/dc:
0.1404 (mL/g) in THF
Fit R² = 0.9986


PHFiPA dn/dc
Normalized RI intensity / a.u.
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
Elution time / min


differential refractive index
-5.0x10⁻⁵
-1.0x10⁻⁴
-1.5x10⁻⁴
0.000
0.001
0.002
0.003
0.004
0.005
Concentration (g/mL)
H
Z
R
n
O
O
F3C
CF3
PHFiPA dn/dc:
-0.0336 (mL/g) in THF
Fit R² = 0.9980

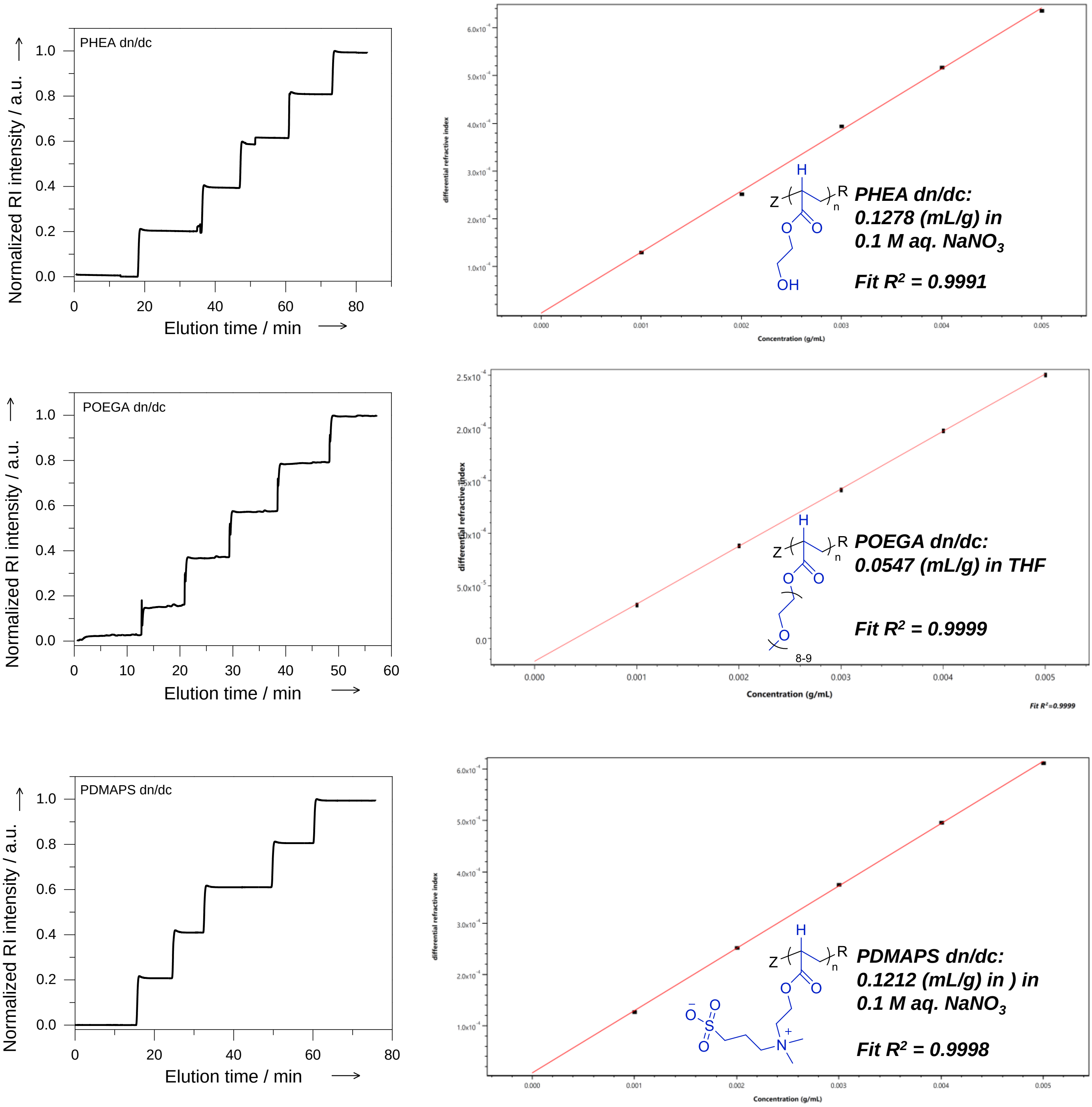


Figure S22. dn/dc measurement results of obtained polyacrylates through photoiniferter polymerization.

III. Supplementary References

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