Electronic Supplementary Information for

Photoinduced polyelectrolyte complexation for the formation of stable films with reversible crosslinking

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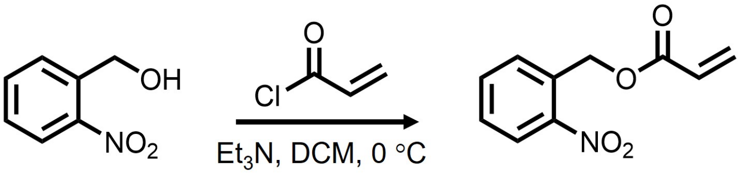
Materials

All chemicals were used as received unless otherwise noted. *N*-Hydroxyethyl acrylamide (HEAA, Sigma-Aldrich, 97%) and acrylic acid (AA, Thermo Scientific, 98%) were passed through a column of basic alumina to remove inhibitors immediately prior to use. Azobis(isobutyronitrile) (AIBN, Millipore Sigma, 98%) was recrystallized from methanol and dried *in vacuo* prior to use. 2-Nitrobenzyl alcohol (97%) was purchased from Alfa Aesar. Acryloyl chloride, 2-chloroethanol, 4-methylumbelliferone (98%), poly(*N*,*N*-diallyldimethylammonium chloride) solution (PDADMAC, average M_w < 100,000 g/mol, 35 wt% in H_2O), potassium carbonate (K_2CO_3), and triethylamine (Et_3N) were purchased from Sigma-Aldrich. Chloroform, dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethyl acetate (EtOAc), methanol, hexane, sodium bicarbonate ($NaHCO_3$), sodium chloride (NaCl), and anhydrous magnesium sulfate were purchased from Fisher Scientific. Deuterated chloroform ($CDCl_3$, 99.8%) and deuterated dimethyl sulfoxide (DMSO-d_6, 99.9%) were purchased from Cambridge Isotope Laboratories, Inc. Deionized water was used throughout the experiments.

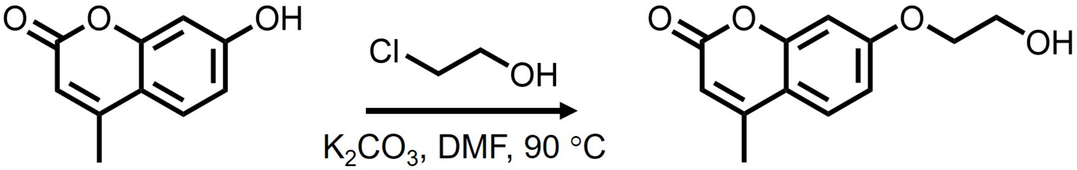
Monomer synthesis

o-Nitrobenzyl acrylate (NBA)



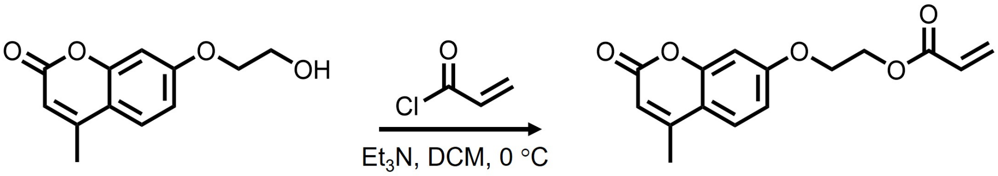
The synthesis of NBA was adapted from previous literature procedures.[1,2] *o*-Nitrobenzyl alcohol (11.4 g, 74.6 mmol) and DCM (100 mL) were added to a 500 mL round-bottom flask (RBF) along with a stir bar. Triethylamine (11.4 mL, 82.1 mmol) was added dropwise to the RBF on ice under an argon atmosphere. Following the addition of triethylamine, acryloyl chloride (6.63 mL, 82.1 mmol) was added dropwise to the RBF on ice and allowed to react for 15 h. The reaction was allowed to warm to room temperature with stirring. The reaction solution was washed sequentially with cold deionized water (200 mL × 4), cold saturated sodium bicarbonate solution (200 mL × 2), and cold sodium chloride solution (200 mL × 2). The organic phase was dried over anhydrous magnesium sulfate before removing the solvent under reduced pressure. The crude product was purified by column chromatography on silica gel with a mixture of hexane/ethyl acetate (4:1) to provide 10.6 g (68.6% yield) of pure product as a clear off-white liquid.

7-(2-Hydroxyethoxy)-4-methylcoumarin



The synthesis of 7-(2-hydroxyethoxy)-4-methylcoumarin was adapted from previous literature procedures.[3,4] 4-Methylumbelliferone (4.00 g, 22.7 mmol) and DMF (40 mL) were added to a 250 mL RBF along with a stir bar. To the RBF, potassium carbonate (6.27 g, 45.4 mmol) was added. Following the addition of potassium carbonate, 2-chloroethanol (2.74 mL, 34.1 mmol) was added to the RBF under an argon atmosphere and stirred for 18 h at 90 °C. The reaction mixture was cooled to room temperature and poured into ice-cold water (200 mL). The white precipitate was collected by vacuum filtration and dried *in vacuo*, yielding a white solid 4.50 g (90.2% yield).

7-(2-Acryloyloxyethoxy)-4-methylcoumarin (CoumAc)



The synthesis of CoumAc was adapted from previous literature procedures.[3,4] 7-(2-hydroxyethoxy)-4-methylcoumarin (4.00 g, 18.2 mmol) and DCM (80 mL) were added to a 250 mL RBF along with a stir bar. Triethylamine (7.60 mL, 54.6 mmol) was added dropwise to the RBF on ice under an argon atmosphere. Following the addition of triethylamine, acryloyl chloride (4.41 mL, 54.6 mmol) was added dropwise to the RBF on ice and allowed to react for 15 h. The reaction was allowed to warm to room temperature with stirring. The reaction solution was washed sequentially with cold deionized water (200 mL × 4), cold saturated sodium bicarbonate solution (200 mL × 2), and cold saturated sodium chloride solution (200 mL × 2). The organic phase was dried over anhydrous magnesium sulfate before removing the solvent under reduced pressure. The crude product was purified by column chromatography on silica gel with a mixture of DCM/ethyl acetate (9:1) to provide 4.40 g (88.1% yield) of pure product as a white solid.

Polymer synthesis

P(HEAA$_{0.90}$-*co*-NBA$_{0.10}$)

To a 50 mL round-bottom flask, NBA (0.52 g, 2.50 mmol), HEAA (2.59 g, 22.5 mmol), AIBN (0.08 g, 0.50 mmol), and DMSO (10.2 mL, $[M]_0 = 2$ M) were added along with a magnetic stir bar. The reaction solution was sparged with argon for 30 min prior to heating the reaction at 70 °C until high conversion was reached. After polymerization, the reaction mixtures were cooled to room temperature and purified by dialysis against water for 72 h (Spectra/Por Dialysis Membrane, RC Tubing with 10 kDa molecular weight cut-off) before lyophilizing for 48 h until dry. The purified polymer was analyzed by ^{1}H NMR spectroscopy and SEC.

P(CoumAc$_{0.01}$-*co*-HEAA$_{0.89}$-*co*-NBA$_{0.10}$)

To a 50 mL round-bottom flask, CoumAc (0.04 g, 0.15 mmol), NBA (0.31 g, 1.50 mmol), HEAA (1.54 g, 13.4 mmol), AIBN (0.05 g, 0.30 mmol), and DMSO (6.12 mL, $[M]_0 = 2$ M) were added along with a stir bar. The reaction solution was sparged with argon for 30 min prior to heating the reaction at 70 °C until high conversion was reached. After polymerization, the reaction mixtures were cooled to room temperature and purified by dialysis against water for 72 h (Spectra/Por Dialysis Membrane, RC Tubing with 10 kDa molecular weight cut-off) before lyophilizing for 48 h until dry. The purified polymer was analyzed by ^{1}H NMR spectroscopy and SEC.

P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$)

To a 50 mL round-bottom flask, CoumAc (0.12 g, 0.45 mmol), NBA (0.31 g, 1.50 mmol), HEAA (1.50 g, 13.1 mmol), AIBN (0.05 g, 0.30 mmol), and DMSO (6.15 mL, $[M]_0 = 2$ M) were added along with a stir bar. The reaction solution was sparged with argon for 30 min prior to heating the reaction at 70 °C until high conversion was reached. After polymerization, the reaction mixtures were cooled to room temperature and purified by dialysis against water for 72 h (Spectra/Por Dialysis Membrane, RC Tubing with 10 kDa molecular weight cut-off) before lyophilizing for 48 h until dry. The purified polymer was analyzed by ^{1}H NMR spectroscopy and SEC.

P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-AA$_{0.10}$)

To a 50 mL round-bottom flask, CoumAc (0.12 g, 0.45 mmol), AA (0.11 g, 1.50 mmol), HEAA (1.50 g, 13.1 mmol), AIBN (0.05 g, 0.30 mmol), and DMSO (13.6 mL, $[M]_0 = 1$ M) were added along with a stir bar. The reaction solution was sparged with argon for 30 min prior to heating the reaction at 70 °C until high conversion was reached. After polymerization, the reaction mixtures were cooled to room temperature and purified by dialysis against water for 72 h (Spectra/Por Dialysis Membrane, RC Tubing with 10 kDa molecular weight cut-off) before lyophilizing for 48 h until dry. The purified polymer was analyzed by ^{1}H NMR spectroscopy.

Methods

Release of photolabile group from copolymers. Polymer (5 mg) was dissolved in DMSO-*d*$_6$ in NMR tubes. The solutions were exposed to long-wave UV irradiation (365 nm) for different time intervals, up to 5 h. The release kinetics of the *o*-nitrobenzyl group were monitored by ^{1}H NMR spectroscopy as a function of irradiation time.

UV-vis study of reversibly crosslinked reaction. For the photodimerization study, an aqueous solution of P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-AA$_{0.10}$) copolymer (0.1 wt%) was exposed to long-wave UV irradiation (365 nm) for different time intervals, up to 5 h. For the photocleavage study, an aqueous solution of P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-AA$_{0.10}$) copolymer (0.1 wt%) that had been exposed to long-wave UV for 4 h was used for these measurements. The solution was exposed to short-wave UV irradiation (254 nm) for different time intervals, up to 4 min. The photodimerization and photocleavage reactions were monitored by UV-Vis spectroscopy as a function of irradiation time. Long-wave UV irradiation was performed in nail dryer (Sol 1 UV nail lamp, melodysusie) equipped with four 365 nm light bulbs (8 W each). Short-wave UV irradiation was performed using a commercial 254 nm UV lamp (CTUV-25, Coospider) with an intensity of 25 mW/cm^{2} in a Stratagene Stratalinker UV 1800 Crosslinker.

Polyelectrolyte complex formation. Polyelectrolyte complexes (PECs) were prepared under charge-balanced conditions, where the repeating units of polyanions and polycations were mixed at a 1:1 molar ratio. The total polymer concentrations during the complexation were 1, 5, and 10 wt%. To a 1.5 mL Eppendorf tube, stock solutions of polyanions and polycations were added after deionized water and immediately vortexed to ensure homogeneous mixing (Table S2 and S3). The mixture solutions were then irradiated with UV light at 365 nm for 4 h.

Preparation of polymer coating. Glass microscope slides (Fisherbrand) were cut into 1.0 cm × 3.0 cm × 0.1 cm and cleaned with deionized water and ethanol in an ultrasound bath for 10 min, followed by air drying. 50 μL of a mixture containing photolabile anionic polymer, cationic polymer, and deionized water was drop-cast onto the dried glass substrates. The total polyelectrolyte concentration was kept at 5 wt% (Table S2). The coated substrates were irradiated with UV light at 365 nm for 4 h, followed by drying at room temperature (25 °C) for 24 h.

Preparation of free-standing film. 200 μL of a mixture containing photolabile anionic polymer, cationic polymer, and deionized water was drop-cast on PTFE fabric sheet. The total polyelectrolyte concentration was kept at 5 wt% (Table S2). The samples were then irradiated with UV light at 365 nm for 4 h, followed by drying at room temperature (25 °C) for 24 h.

Stability test in deionized water. The coated glass substrates were immersed in 10 mL of deionized water within individual scintillation vials. The coatings were dried using a hot air gun before measuring mass. The change in mass of the coated substrates was characterized as a function of immersion time to determine the coating’s resistance to degradation or dissolution in DI water.

Stability test in a 1 M NaCl aqueous solution. The free-standing films were immersed in an aqueous NaCl solution (5 mL,1 M) within individual scintillation vials. Images of the films were captured as a function of immersion time to determine the film’s resistance to degradation or dissolution in the salt solution.

Instrumentation

NMR spectroscopy. ^{1}H NMR spectra were acquired on a Bruker 400 MHz spectrometer. Deuterated chloroform ($CDCl_3$) and deuterated dimethyl sulfoxide (DMSO-d_6) were used as solvents.

Size exclusion chromatography (SEC). SEC was performed in *N,N*-dimethylacetamide (DMAc) with 50 mM LiCl at 50 °C at a flow rate of 1.0 mL/min (Agilent isocratic pump, degasser, and autosampler; columns: Viscogel I-series 5 µm guard + two ViscoGel I-series G3078 mixed bed columns, molecular weight range 0−20,000 g/mol and 0−1,000,000 g/mol). Detection consisted of a Wyatt Optilab T-rEX refractive index detector operating at 658 nm and a Wyatt miniDAWN Treos light scattering detector operating at 690 nm. Absolute molecular weights and molecular weight distributions were calculated using the Wyatt ASTRA software, and d*n*/dc values were obtained from 100% mass-recovery methods. Samples were dissolved in DMAc at a concentration of 3 mg/mL and then the sample solutions were filtrated through a polytetrafluoroethylene membrane filter (0.45 mm pore size).

UV-vis spectroscopy. UV-vis absorbance spectra were recorded on the Molecular Devices SpectraMax M2 multimode microplate reader. Samples (2 mL) were prepared in a quartz cuvette.

UV irradiation. Long-wave UV irradiation was performed in nail dryer (Sol 1 UV nail lamp, melodysusie) equipped with four 365 nm light bulbs (8 W each). Short-wave UV irradiation was performed using a commercial 254 nm UV lamp (CTUV-25, Coospider) with an intensity of 25 mW/cm^2 in a Stratagene Stratalinker UV 1800 Crosslinker. The light intensity was monitored by a digital UV AB light meter (General UV513AB Digital UV AB Light Meter).

Differential scanning calorimetry (DSC). DSC experiments were conducted on a TA Q2500 DSC (TA Instruments, New Castle, DE) equipped with an autosampler and refrigerated cooling system using aluminum hermetic sealed pans. Ramp experiments were performed by heating under nitrogen (25 mL/min) at 10 °C/min from 0 to 100 °C and cooling from 100 to 0 °C with 5 min isotherms at each extreme. All DSC experiments were recorded using the Thermal Advantage for Q Series software from TA. The glass transition temperature (T_g) of the polymers was obtained from the inflection point of DSC thermograms of the second heating curve.

Optical microcopy. To visualize PECs, complexes were prepared as previously described. 50 µL of the solutions was dropped to a microscope glass slide. The complexes were then imaged using a Zeiss/SteREO Discovery V12 via the AxioVision software.

Profilometry. The thickness of the coatings was measured using the profilometer (DektakXT, Bruker) with a 200 µm/s measurement speed and an applied weight of 8 mg. The scan length of the samples is 4 mm.

Supplementary figures

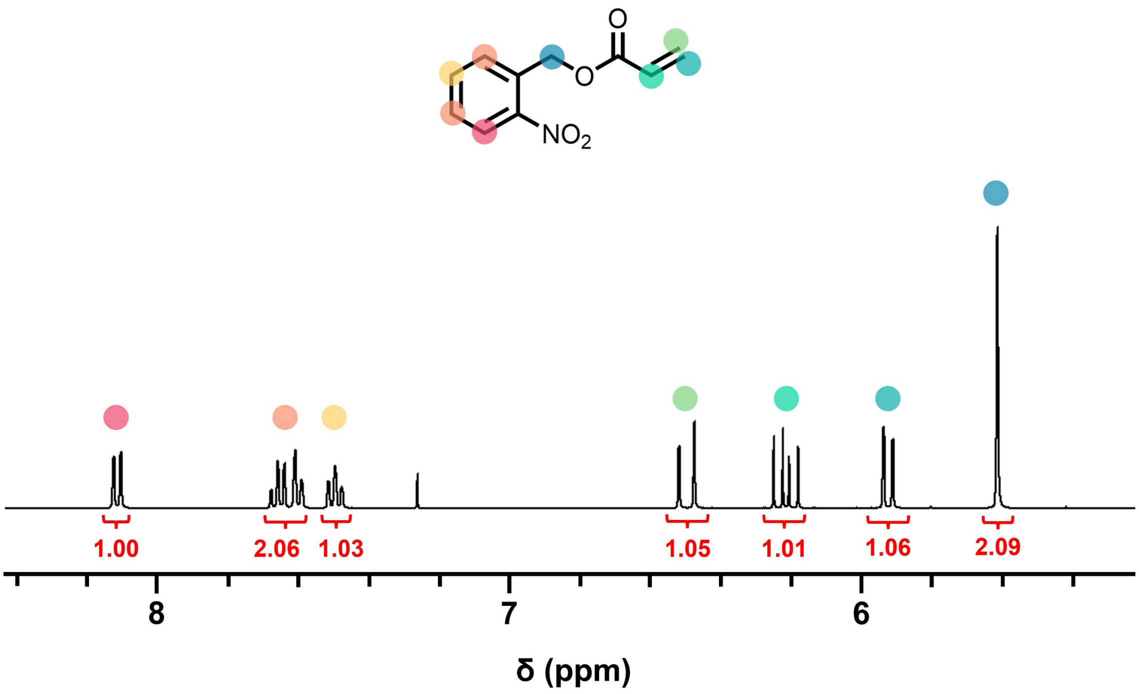


Fig. S1 ^{1}H NMR spectrum of *o*-nitrobenzyl acrylate (NBA) in CDCl$_3$.

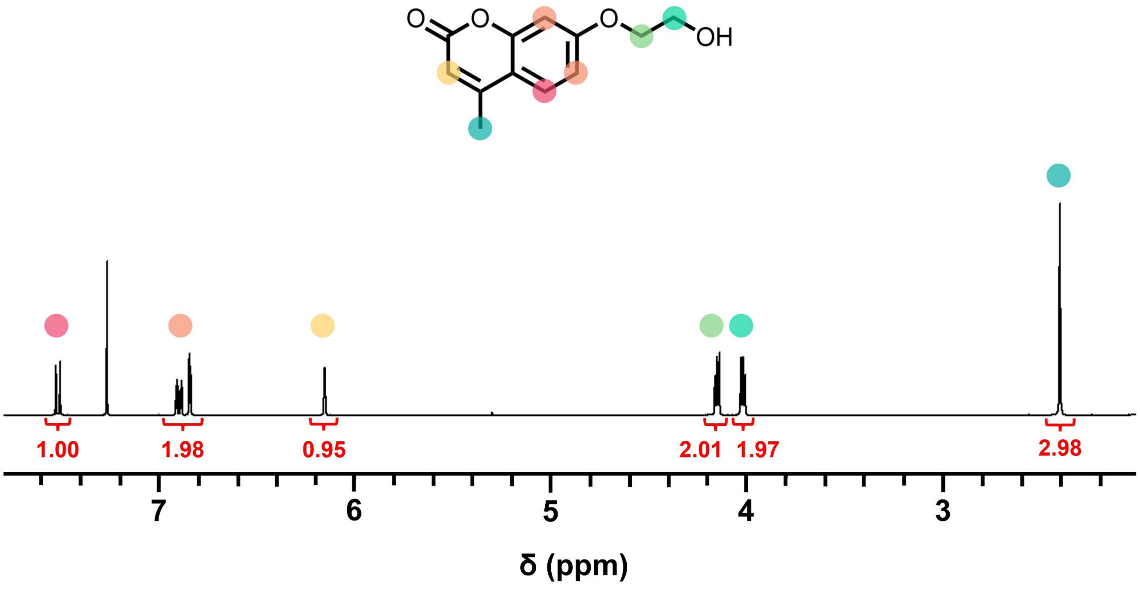


Fig. S2 ^{1}H NMR spectrum of 7-(2-hydroxyethoxy)-4-methylcoumarin in CDCl$_3$.

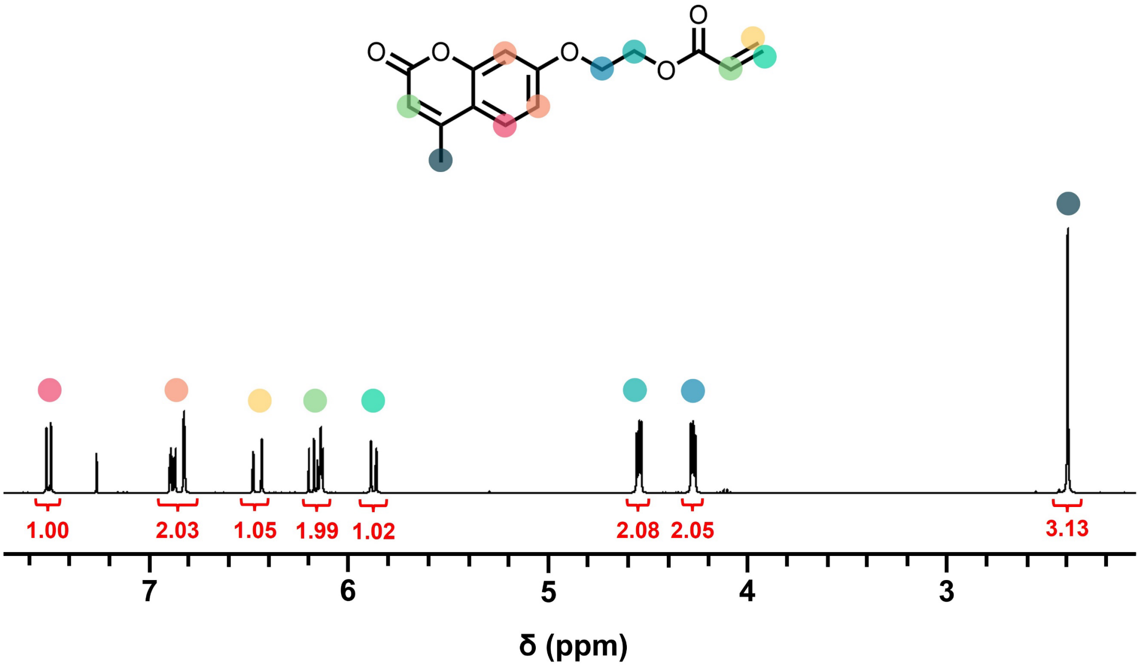


Fig. S3 ^{1}H NMR spectrum of 7-(2-acryloyloxyethoxy)-4-methylcoumarin (CoumAc) in $CDCl_3$.

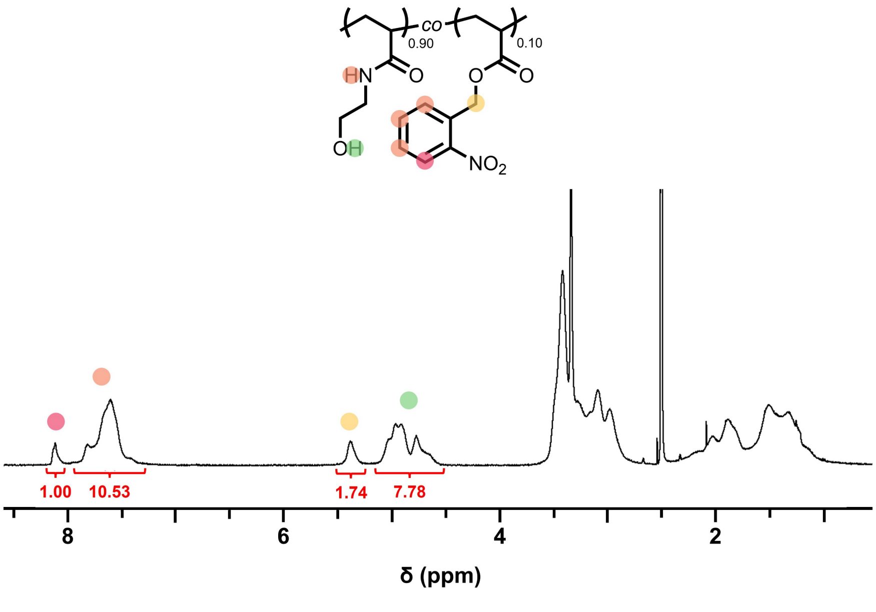


Fig. S4 ^{1}H NMR spectrum of P($HEAA_{0.90}$-*co*-$NBA_{0.10}$) in DMSO-*d*$_6$.

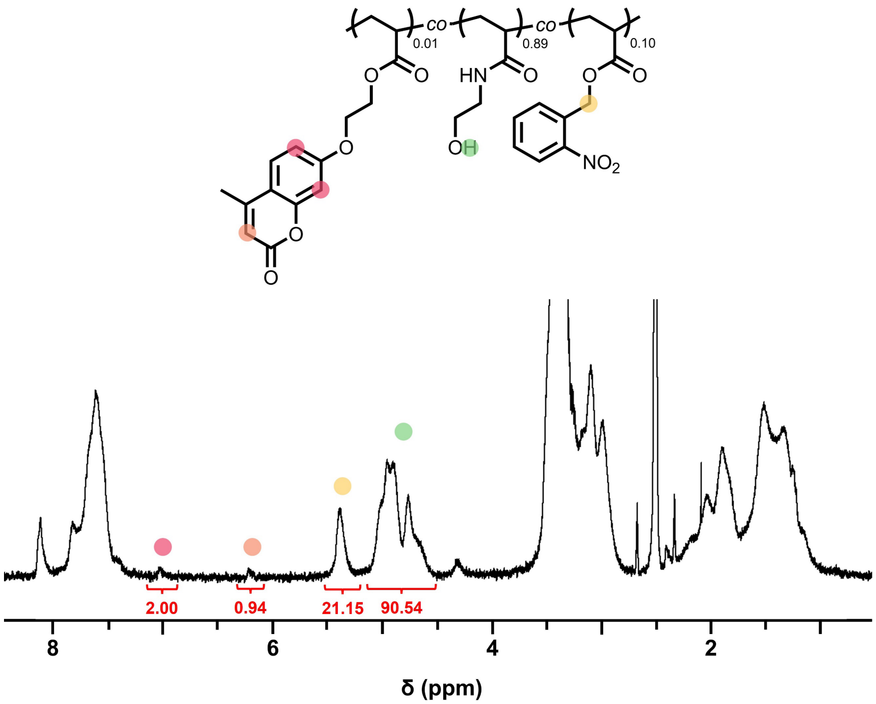


Fig. S5 ^{1}H NMR spectrum of P(CoumAc$_{0.01}$-*co*-HEAA$_{0.89}$-*co*-NBA$_{0.10}$) in DMSO-d_6.

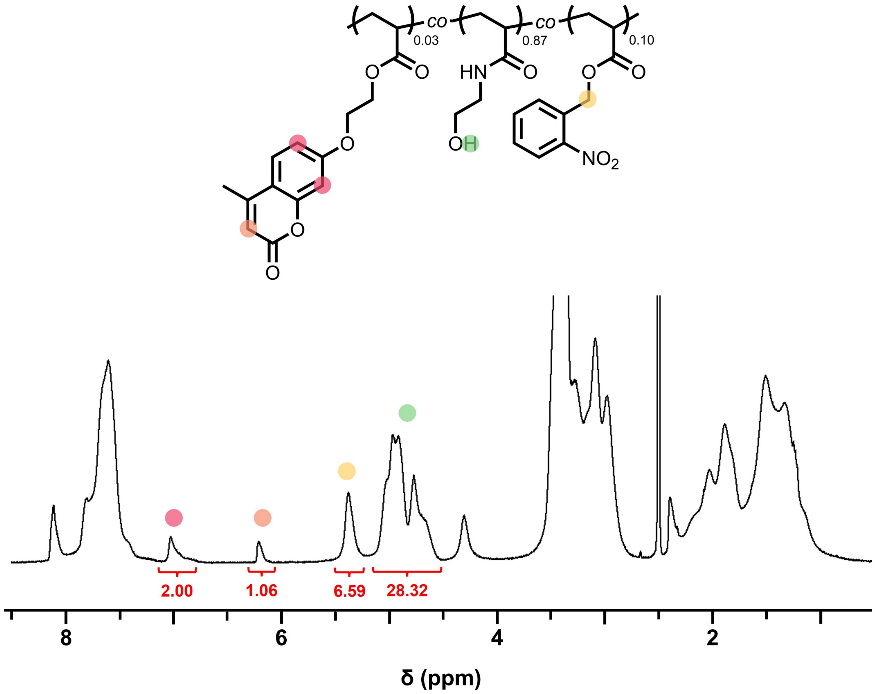


Fig. S6 ^{1}H NMR spectrum of P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$) in DMSO-d_6.

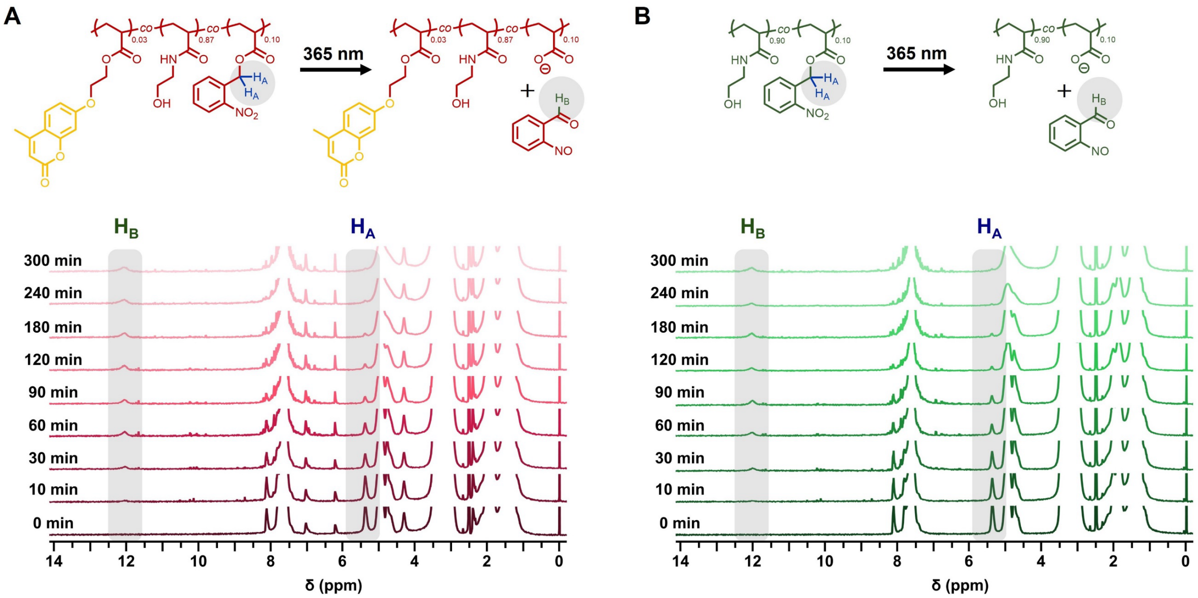


Fig. S7 Temporal evolution of ^{1}H NMR spectra of (A) P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$) and (B) P(HEAA$_{0.90}$-*co*-AA$_{0.10}$) in DMSO-*d*$_6$.

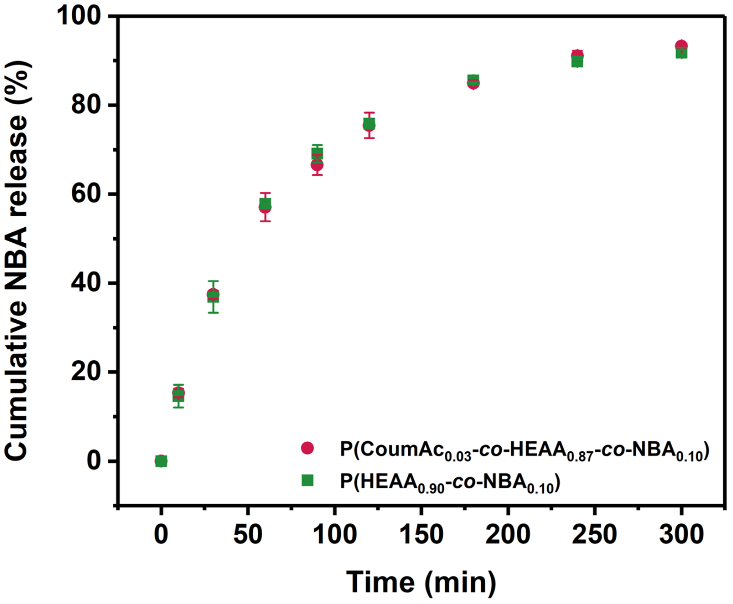


Fig. S8 Release profiles of *o*-nitrobenzyl group from copolymers in DMSO-*d*$_6$.

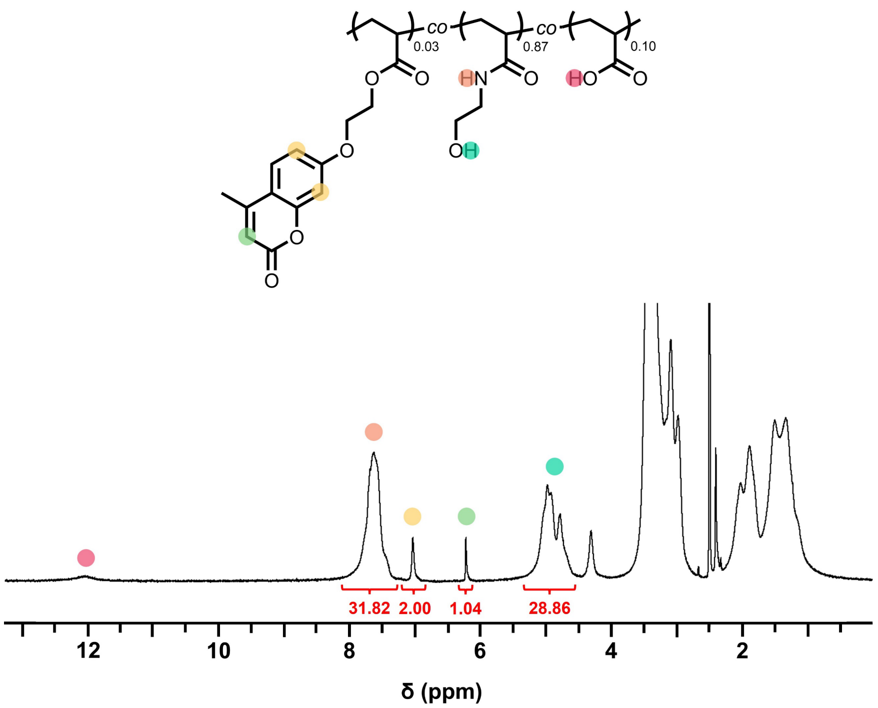


Fig. S9 ^{1}H NMR spectrum of P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-AA$_{0.10}$) in DMSO-d_6.

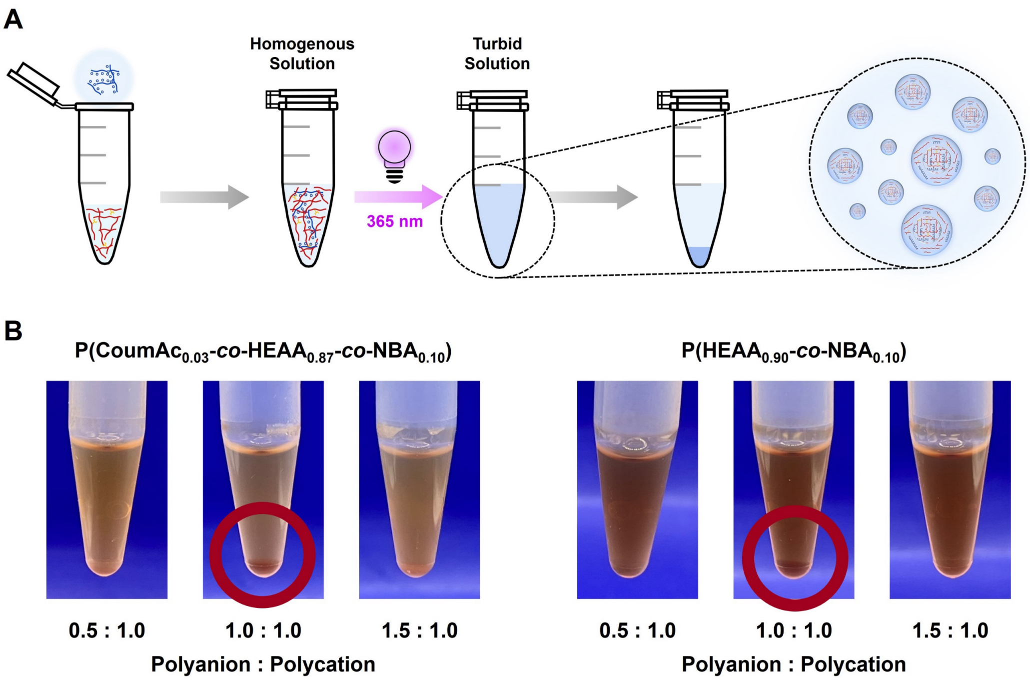
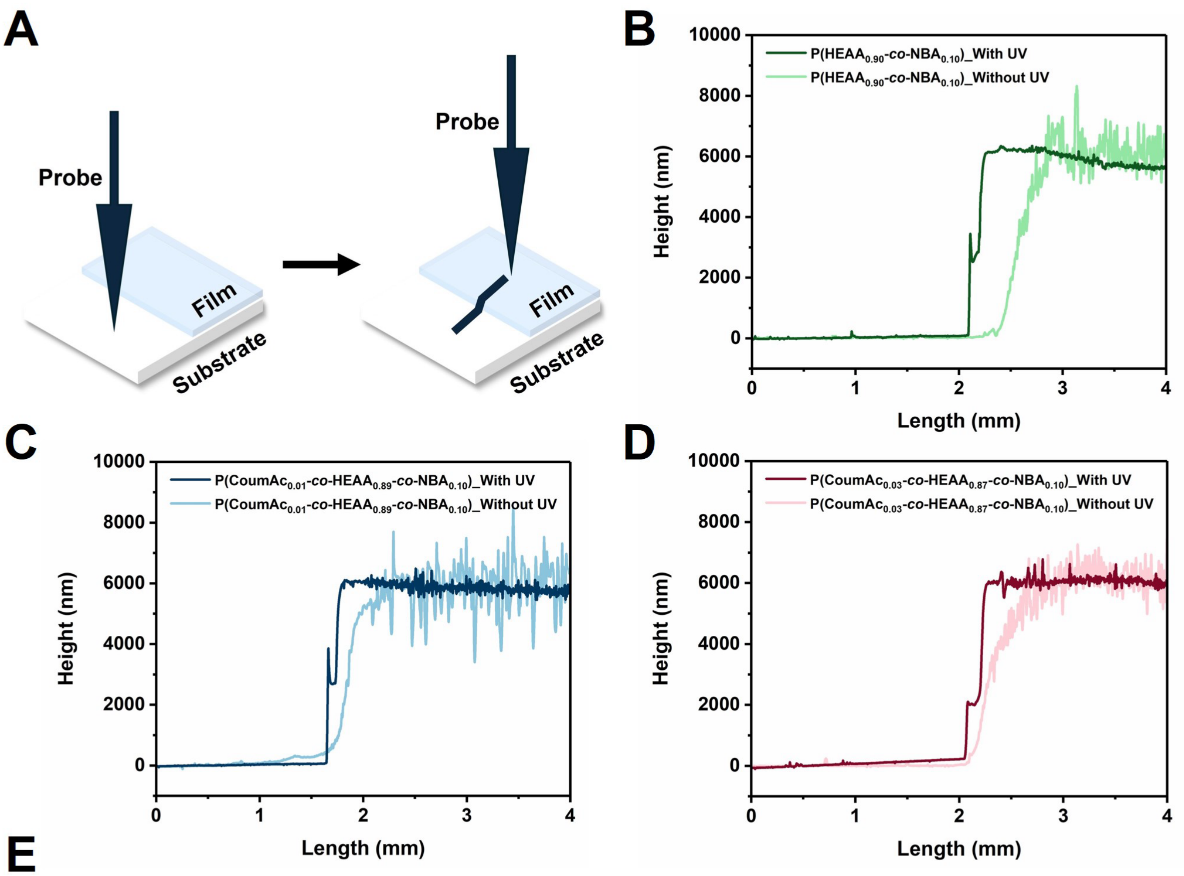


Fig. S10 (A) Schematic for the preparation of polyelectrolyte complexes (PECs). (B) Photographs of PECs of P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$) or P(HEAA$_{0.90}$-*co*-NBA$_{0.10}$) with PDADMAC at different charge ratios.



E

Sample	Thickness (μm)	
	With UV	Without UV
P(HEAA$_{0.90}$-*co*-NBA$_{0.10}$)	5.88 ± 0.12	6.22 ± 0.19
P(CoumAc$_{0.01}$-*co*-HEAA$_{0.89}$-*co*-NBA$_{0.10}$)	5.72 ± 0.06	5.96 ± 0.48
P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$)	6.05 ± 0.11	6.18 ± 0.13

Fig. S11 (A) Schematic for the thickness measurement of polyelectrolyte complex films. Thickness of (B) P(HEAA$_{0.90}$-*co*-AA$_{0.10}$)/PDADMAC, (C) P(CoumAc$_{0.01}$-*co*-HEAA$_{0.89}$-*co*-NBA$_{0.10}$)/PDADMAC, and (D) P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$)/PDADMAC coated on glass substrates measured by profilometry (E).

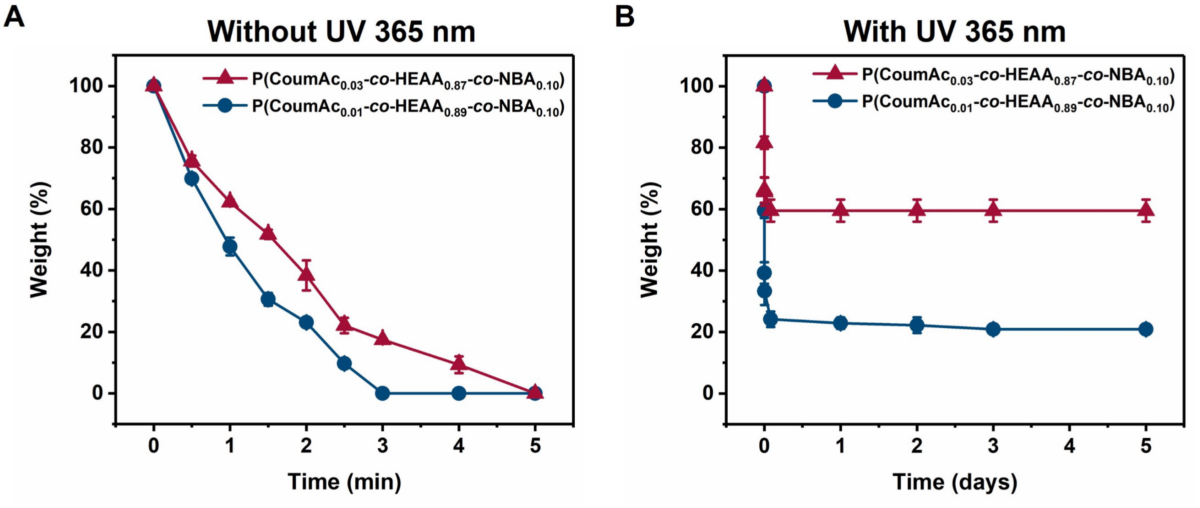


Fig. S12 Weight loss of the copolymers/PDADMAC coatings (A) without and (B) with UV irradiation at 365 nm after immersing in DI water.

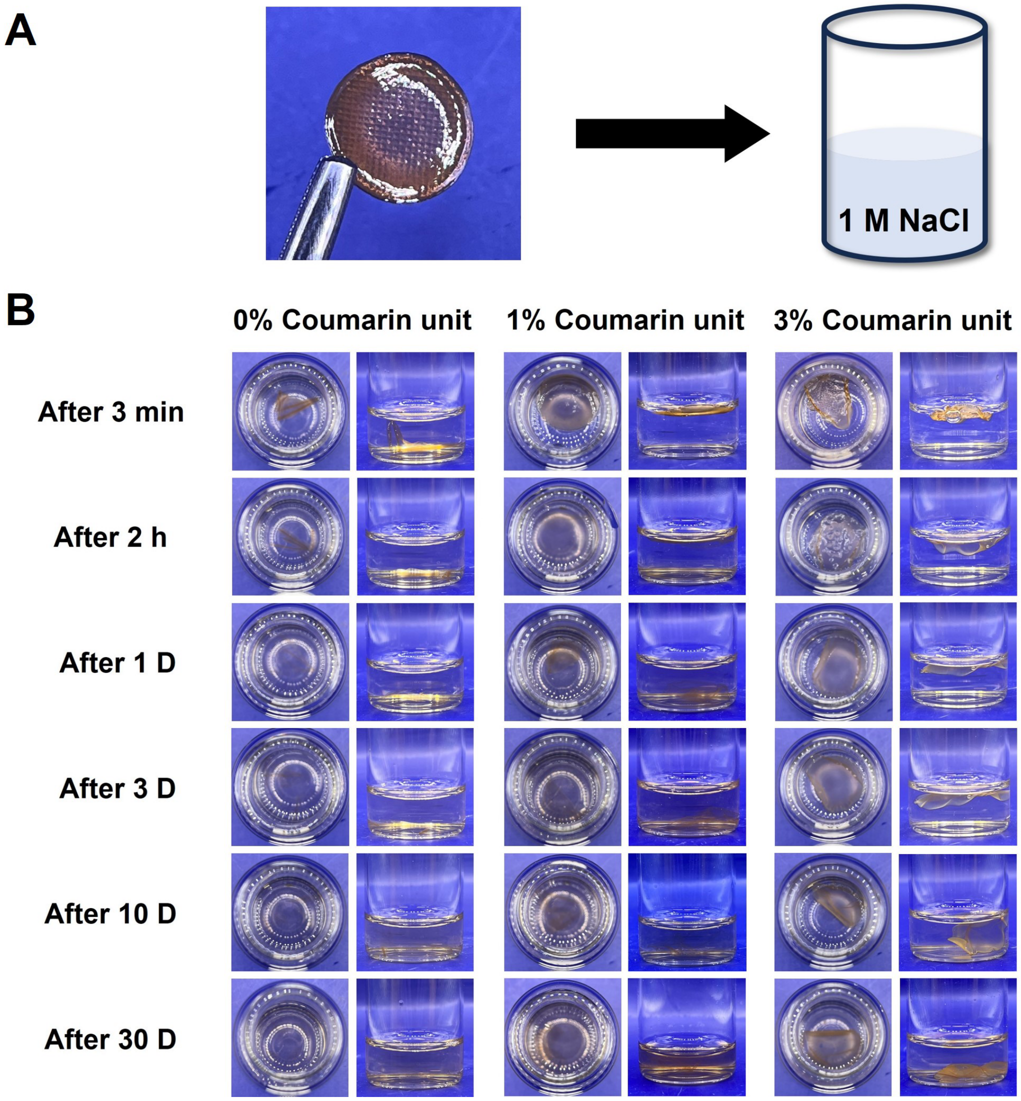


Fig. S13 Stability of P(CoumAc$_x$-*co*-HEAA$_y$-*co*-NBA$_z$)/PDADMAC films after immersing in a 1 M NaCl aqueous solution for 30 days.

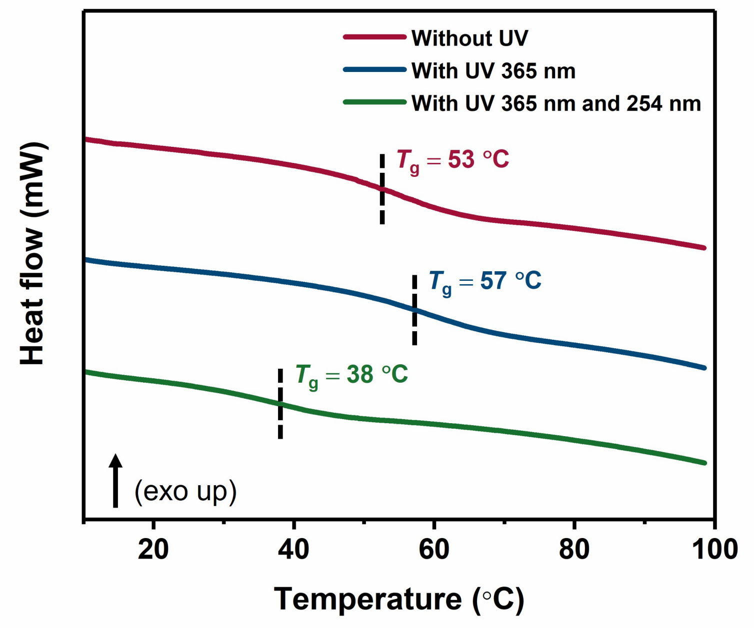


Fig. S14 DSC curves of the P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$)/PDADMAC films before irradiating with 365 nm light (red), after irradiating with 365 nm for 240 min (blue), and after irradiating with 365 nm for 240 min and 254 nm for 60 min (green).

Supplementary tables

Table S1. Composition, number-average molecular weight (M_n), and weight-average molecular weight (M_w) of photolabile anionic copolymers

Copolymer	Incorporation molar feed ratio (%)			M_n (g/mol)	M_w (g/mol)
	CoumAc	HEAA	NBA		
P(HEAA$_{0.90}$-*co*-NBA$_{0.10}$)	0	89.9	10.1	33k	59k
P(CoumAc$_{0.01}$-*co*-HEAA$_{0.89}$-*co*-NBA$_{0.10}$)	1.0	88.7	10.3	31k	70k
P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$)	3.1	86.8	10.1	30k	50k

Table S2. Composition of polyelectrolyte complexes (PECs) at different total PE concentrations

Total PE concentration (wt%)	Polyanion[a] (wt%)	Polycation[b] (wt%)	H_2O (wt%)
Polyanion with coumarin P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$)			
1	0.92	0.08	99
5	4.59	0.41	95
10	9.17	0.83	90
Polyanion without coumarin P(HEAA$_{0.90}$-*co*-NBA$_{0.10}$)			
1	0.87	0.13	99
5	4.36	0.64	95
10	8.73	1.27	90

[a]Polyanion is P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$) or P(HEAA$_{0.90}$-*co*-NBA$_{0.10}$). [b]Polycation is PDADMAC.

Table S3. Composition of polyelectrolyte complexes (PECs) at different charge ratios

Charge ratios polyanion/polycation	Polyanion[a] (wt%)	Polycation[b] (wt%)	H_2O (wt%)
Polyanion with coumarin P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$)			
0.5:1.0	4.24	0.76	95
1.0:1.0	4.59	0.41	95
1.5:1.0	4.72	0.28	95
Polyanion without coumarin P(HEAA$_{0.90}$-*co*-NBA$_{0.10}$)			
0.5:1.0	3.87	1.13	95
1.0:1.0	4.36	0.64	95
1.5:1.0	4.56	0.44	95

[a]Polyanion is P(CoumAc$_{0.03}$-*co*-HEAA$_{0.87}$-*co*-NBA$_{0.10}$) or P(HEAA$_{0.90}$-*co*-NBA$_{0.10}$). [b]Polycation is PDADMAC.

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