

Modulation of Flexo-Rigid Balance in Photoresponsive Thymine Grafted Copolymers towards Designing Smart Healable Coating

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1. Materials & methods:

Solvents used in synthesis were of reagent grades. Acetone, chloroform, THF and 1,4 dioxane used were dried as per the literature protocol.^{S1} The reagents ethyl bromoacetate, 1,4-dioxane, tetra-*n*-butylammonium fluoride (TBAF), and triethylamine were purchased from Alfa-Aeser and glacial acetic acid was purchased from SD fine and were used without further purification. The chemicals thymine, pentamethyl diethyl tetraamine (PMDETA), methyl 2-bromo propionate, ethyl bromo isobutyrate (EtBrIB), Cu(I)Br, *N,N'*-diisopropylcarbodiimide (DIPC) (99%) were purchased from TCI and were used without further purification. 4-(Dimethylamino)pyridinium4-toluenesulfonate (DPTS) was prepared according to a reported procedure.^{S2} 2-Hydroxy ethyl acrylate (HEA), butyl acrylate (*n*-BA) were purchased from TCI and were passed through basic alumina (to remove inhibitor MEHQ) before using them for ATRP.^{S3}

¹H-NMR spectra were acquired on a 400 MHz Bruker. The chemical shifts are reported in ppm and appear downfield to that of tetramethylsilane using the resonance of the deuterated solvent as an internal standard. Splitting patterns are designated as singlet (s), doublet (d), triplet (t), and multiplet (m).

The sample for the GPC measurement was prepared by filtering solutions through a 0.2 μm PTFE-filter into a 2 mL GPC glass vial. GPC measurements were done using Malvern Omnisec instrument having RI, right-angle light scattering (RALS) detectors after passing through T6000M-T3000 columns in series with THF as eluent (flow rate of 1 mL/min at a temperature of 35 °C) and polystyrene as standard for all the samples. The results were analysed by using Omnisec software. The sample peaks were analysed for M_n , M_w , and PDI by means of the conventional and triple detector universal calibration method.

Dynamic light scattering measurements were performed on a Malvern Zetasizer Nano ZS ZEN3600 equipped with a Helium–Neon laser (wavelength, $\lambda = 633$ nm with backscattering angle of 173°). Samples were prepared by filtering solutions through 0.2 μm PTFE-filter into a glass cuvette.

UV crosslinking was performed using an UV chamber equipped with 1* 8W UV_B lamp ($\lambda_{\text{max}} = 320$ nm, Intensity at 15 cm = 790 $\mu\text{W}/\text{cm}^2$) and 1*8W UV_C lamp ($\lambda_{\text{max}} = 254$ nm, Intensity at 15 cm = 820 $\mu\text{W}/\text{cm}^2$) and the sample in liquid state or solid film was kept at a distance of 15 cm for irradiation. The luminous intensity of irradiation at time t was determined in J/cm^2 by the formula $[(\mu\text{W}/\text{cm}^2)/10^6]*t$ (s). UV spectra were recorded using Shimadzu UV 6000 UV-vis spectrophotometer at a wavelength range of 800 to 200 nm.

The samples were drop-casted on a silicon wafer and analysed using Atomic Force Microscopy (AFM) was done on tapping mode analysis on a Bruker Multimode 8 scanning probe microscope.

The sample was drop cast on a 300 mesh carbon-coated copper grid and TEM images were recorded using JEOL JEM 2100 with a Tungsten filament at an accelerating voltage of 200 kV.

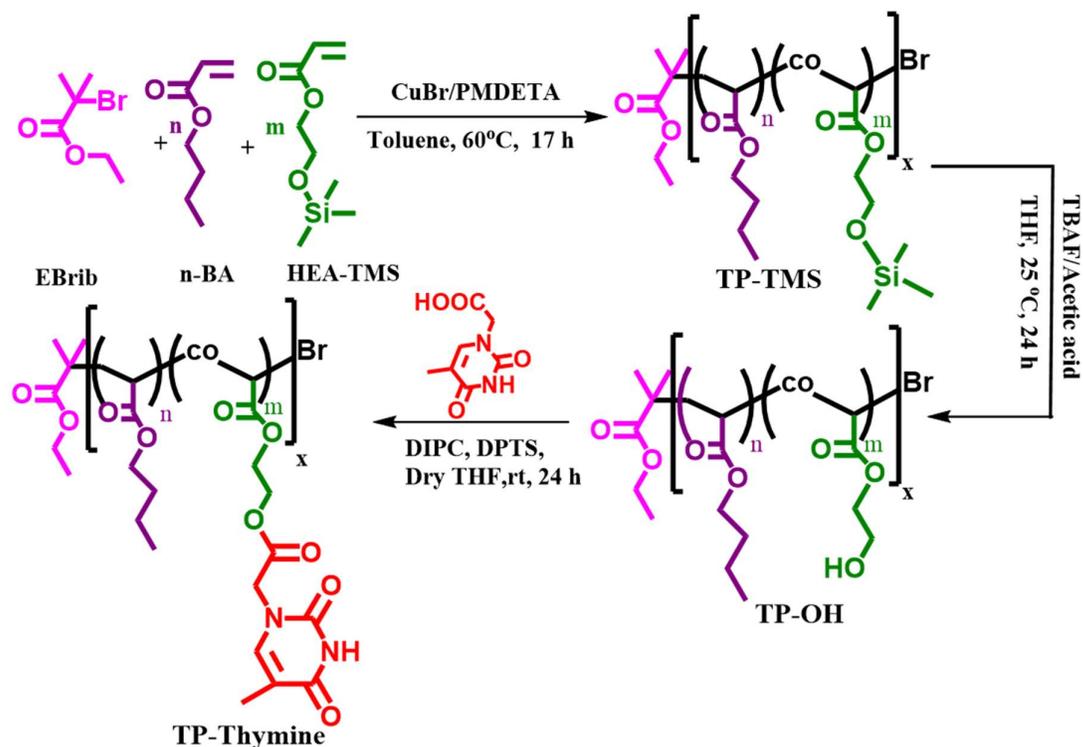
Thermal studies were performed on Perkin Elmer Differential Scanning Calorimeter DSC 8000 model and the samples were heated from -80 to 150 °C at a heating rate of 10 °C/min.

Thickness measurement of the polymer sample was done by drop-casting the polymeric sample on glass film followed by preparing the thin film of the polymers using spin coater Apex Instruments Co. Pvt. Ltd. The thickness of polymeric film on the glass slide was measured using a spectroscopic Ellipsometer (Angstrom Sun Technology Inc. USA) and thickness was calculated using the best fit in the Cauchy equation.^{S4}

Optical microscopy images of the self-healing polymer films were recorded on an Olympus BX53 model upright fluorescent microscope equipped with sCCD camera.

The hydrophobicity of the polymeric films were measured using a drop shape analyser of model DSA25 from KRUSS GmbH, Germany to calculate the contact angles.

2. Synthesis and characterization of the polymers:



Scheme S1: General scheme for synthesis of thymine functionalized polymers (TP1-TP4).

General procedure for random copolymerization of HEA-TMS with butyl acrylate by ATRP method followed by deprotection of the TMS and post-functionalization of polymer with thymine moieties.

Random copolymerization by ATRP:

Cu(I)Br, *n*-BA, HEA-TMS, initiator (EtBriB), and toluene were placed in a schlenk tube and the N₂ environment is maintained using freeze-thaw-pump cycles (three times). PMDETA was then added to the mixture and the solution was degassed again. The whole reaction mixture was stirred in an oil bath at 70 °C for 17 hours. Then it was cooled to room temperature and the reaction mixture was diluted with THF. The diluted solution of the reaction mixture was then pass through neutral alumina to separate the copper catalyst. The unreacted monomers and solvents are removed in vacuo to yield the TMS protected copolymer.

Deprotection of TMS group:

The deprotection of TMS from the polymers was achieved by treating the polymer with 20 eqv. of TBAF (tetra butyl ammonium fluoride) and 123 eqv. of acetic acid by stirring at room temperature for 24 hours. Then the polymer was obtained by evaporation of the solvents and precipitating the remaining solution two times into MeOH: H₂O (9:1) mixture and dried under P₂O₅ in vacuo. The detailed synthesis of TMS de-protected random copolymers, NMR, and GPC analysis of the polymers are reported in the literature.^{S5}

Grafting of photo responsive thymine carboxylic acid:

Post functionalization of the polymer was performed according to the literature procedure.^{S5} The polymer solution was added to a stirred solution of thymine carboxylic acid with DPTS and DIPC under the N₂ environment and stirred at 25 °C for 24 hours. Then the polymers were obtained by precipitating the solution two times into MeOH: H₂O (9:1) mixture and dried under P₂O₅ in vacuum.

Synthesis of Polymer TP1: Thymine carboxylic acid (1.46 mmol) with DPTS (0.36 mmol) and DIPC (2.16 mmol) was kept for stirring in THF under N₂ environment for 20 min. To this solution, polymer TP-OH-1 (0.036 mmol) in THF was added slowly and was stirred under N₂ environment at 25 °C for 48 hours. The resulting polymer was precipitated using MeOH: H₂O (9:1) mixture and dried under P₂O₅ to obtain polymer TP1. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.20-7.02(m,1H,-N-CH=C(CH₃), 4.55-4.38 (m,2H, O-COCH₂), 4.37-4.12 (m, 6H, OCH₂CH₂O) 4.07-3.85 (m, 14H, OCH₂), 2.33-2.15 (m,7H, CH₂), 1.92-1.78(m,8H,N-CH=C(CH₃)),1.71-1.47 (m, 22H, CHCH₂), 1.35-1.13 (m, 32H, OCH₂CH₂CH₂CH₃), 0.88-0.85 (t, 22H, OCH₂CH₂CH₂CH₃). %Functionality (NMR) = 12%. SEC analysis (THF, polystyrene standards): M_n = 4729 g/mol, M_w/M_n = 1.22.

Synthesis of Polymer TP2: Thymine carboxylic acid (0.55 mmol) with DPTS (0.14 mmol) and DIPC (0.4 mmol) is kept for stirring in THF under the N₂ environment for 20 min. To this solution, polymer TP-OH-2 (0.0204 mmol) in THF was added slowly and was stirred under N₂ environment at 25 °C for 48 hours. The resulting polymer was precipitated using MeOH: H₂O (9:1) mixture and dried under P₂O₅ to obtain polymer TP2. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.22-7.08(m,1H,-N-CH=C(CH₃-) 4.47-4.63(m,2H, O-COCH₂), 4.47-4.19 (m, 4H, OCH₂CH₂O) 4.14-3.94 (m, 13H, OCH₂), 2.46-2.19 (m,7H, CH₂), 1.92-1.78(m,6H,N-CH=C(CH₃)),1.77-1.50 (m, 28H, CHCH₂), 1.50-1.18 (m, 21H, OCH₂CH₂CH₂CH₃), 0.98-0.78 (t, 20H, OCH₂CH₂CH₂CH₃). %Functionality (NMR) = 11.7%. SEC analysis (THF, polystyrene standards): M_n = 6759 g/mol, M_w/M_n = 1.12.

Synthesis of Polymer TP3: Thymine carboxylic acid (0.88 mmol) with DPTS (0.219 mmol) and DIPC (1.29 mmol) is kept for stirring in THF under the N₂ environment for 20 min. To this solution, polymer TP-OH-3 (0.0219 mmol) in THF was added slowly and was stirred under N₂ environment at 25 °C for 48 hours. The resulting polymer was precipitated using MeOH: H₂O (9:1) mixture and dried under P₂O₅ to obtain polymer TP3. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.20-7.08(m,1H,-N-CH=C(CH₃-) 4.64-4.46 (m,4H, O-COCH₂), 4.4-4.2 (m, 6H, OCH₂CH₂O) 4.13-3.95 (m, 6H, OCH₂), 2.4-2.2 (m,7H, CH₂), 2.02-1.8(m,10H,N-CH=C(CH₃)),1.74-1.54 (m, 13H, CHCH₂), 1.41-1.15 (m, 17H, OCH₂CH₂CH₂CH₃), 1-0.81 (t, 13H, OCH₂CH₂CH₂CH₃). %Functionality (NMR) = 27%. SEC analysis (THF, polystyrene standards): M_n = 11624 g/mol, M_w/M_n = 1.09.

Synthesis of Polymer TP4: Thymine carboxylic acid (0.16 mmol) with DPTS (0.04 mmol) and DIPC (0.24 mmol) is kept for stirring in THF under the N₂ environment for 20 min. To this solution, polymer TP-OH-3 (0.0264 mmol) in THF was added slowly and was stirred under N₂ environment at 25 °C for 48 hours. The resulting polymer was precipitated using MeOH: H₂O (9:1) mixture and dried under P₂O₅ to obtain polymer TP4. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.22-7.15 (m,1H,-N-CH=C(CH₃-) 4.48-4.38 (m,2H, O-COCH₂), 4.4-4.22 (m, 5H, OCH₂CH₂O) 4.10-3.95 (m, 15H, OCH₂), 2.43-2.23 (m,12H, CH₂), 2.0-1.84(m,8H,N-CH=C(CH₃)),1.78-1.54 (m, 30H, CHCH₂), 1.42-1.20 (m, 64H, OCH₂CH₂CH₂CH₃), 1-0.9 (t, 30H, OCH₂CH₂CH₂CH₃). %Functionality (NMR) = 8.5%. SEC analysis (THF, polystyrene standards): M_n = 33075 g/mol; M_w/M_n = 1.08

3. Determination of % functionality of thymine by UV spectroscopy:

Firstly, a calibration curve was generated by recording the absorbance of thymine acid in DMF at different concentrations. Next, the absorbance of the polymer samples (TP1-TP4) were recorded at $c = 0.005$ mM. Considering the degree of polymerization and concentration of the polymers, the absorbance values were extrapolated to the calibration curve to find out the % functionality of thymine in the random copolymers.

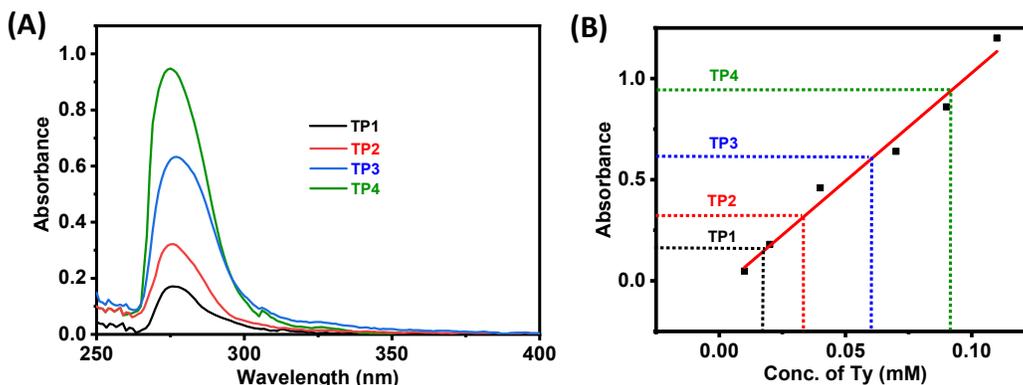


Fig. S1: Monitoring % functionality of thymine with the help of UV spectroscopy. (A) Graph showing the corresponding adsorption values for polymer TP1-TP4. (B) Calibration curve of the thymine acid in DMF into which corresponding absorbance values of the polymer TP1-TP4 were extrapolated ($c = 0.005$ mM in DMF)

Calculation of % functionality for TP2 Polymer:

The absorbance for TP2 ($c = 0.005$ mM) was 0.32 (Fig. S1A, red trace). The extrapolated concentration of thymine for TP2 from the calibration curve was 0.033 mM (Fig. S1B).

Degree of Polymerization of TP2 is 50, out of which number of equivalent of butyl acrylate = 42.5. Therefore, concentration of butyl acrylate in 0.005 mM TP2 polymer was $(0.005 \times 42.5) = 0.2125$ mM
 Number of equivalent of hydroxy ethyl acrylate = 7.5. Therefore, concentration of hydroxy ethyl acrylate unit in 0.005 mM TP2 polymer was $(0.005 \times 7.5) = 0.0375$ mM

Therefore, the % thymine in TP2 polymer =

$$\frac{\text{Conc. of thymine obtained from UV spectroscopy}}{\text{molar feed of buthyl acrylate} + \text{molar feed of hydroxy ethyl acrylate}} * 100$$

$$= \frac{0.033}{0.2125 + 0.0375} * 100 = 13.2 \%$$

Table S1: Determination of % Functionality of TP1-TP4 by UV spectroscopy					
Polymer	Molar feed ratio of BA	Molar feed ratio of HEA	Abs. value from UV	Amount of thymine grafted on the polymers (Absolute)	% of Thy functionalization
TP1	21.25	3.75	0.17	0.017	13.6
TP2	42.5	7.5	0.32	0.033	13.2
TP3	30	20	0.63	0.06	24
TP4	255	45	0.95	0.092	6.1

4. Copolymer composition calculation by elemental analysis:

The percentage of C and H were calculated using the molecular formula of the copolymers. The number of C and H atoms in a BA unit are 7 and 12 respectively. Similarly, for thymine functionalized hydroxyethyl acrylate the number of C and H atoms are 12 and 15 respectively.

% composition is calculated according to equations

$$(7x + 12y)M_C = C\% \times 100 \text{----(1)}$$

$$(12x + 15y)M_H = H\% \times 100 \text{----(2)}$$

Where M_C and M_H molar mass of carbon, and hydrogen. C% and H% weight percentage of carbon and hydrogen in the copolymer respectively that is obtained from elemental analysis experimental data. x and y are the mole number of BA and Ty-HEA in 100 g of the copolymer, respectively.

Equations (1) and (2) can be employed as a system of two equations in the two variables x and y

$$(7x + 12y)M_C = C\% \times 100 \text{----(3)}$$

$$(12x + 15y)M_H = H\% \times 100 \text{----(4)}$$

$$39y = 12 \times C\% / M_C - 7 \times H\% / M_H \text{----(5)}$$

$$y = [12 \times C\% / M_C - 7 \times H\% / M_H] / 39 \text{----(6)}$$

$$x = [12 \times C\% / M_C - 104y] / 84 \text{----(7)}$$

Thus, Ty-HEA mol percent in the copolymer can be calculated by Equation (8) ;

$$\% \text{ functionality} = \frac{y}{(y + x)} \times 100 \text{----(8)}$$

Polymers	C%	H %	% Ty-HEA
TP1	51.40	7.02	10.8
TP2	67.15	9.08	12
TP3	106.80	14.38	21
TP4	68.91	9.52	8.3

5. Calculation of hydrodynamic radii (R_H) from weight average molecular weights (M_w):

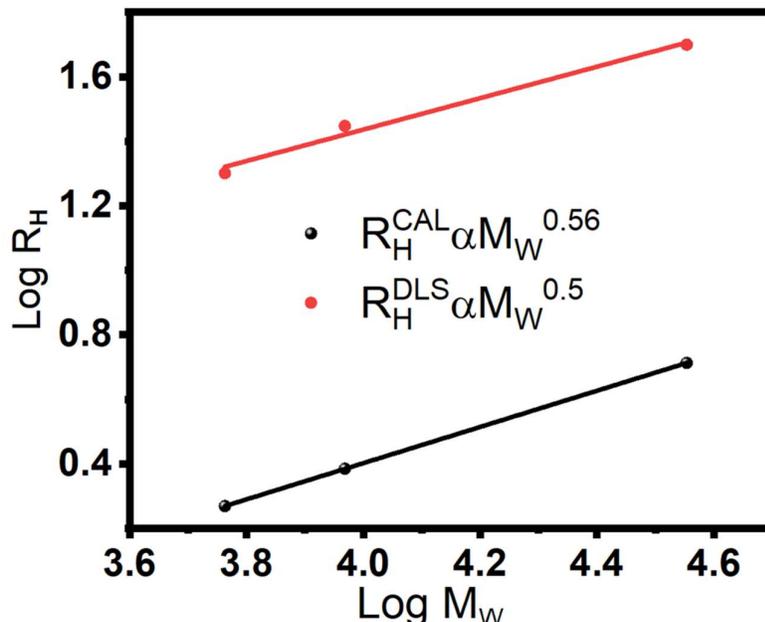


Fig. S2: Illustration of the $R_H = KM_w^v$ scaling law for polymers **TP1**, **TP2**, **TP4** based on hydrodynamic radii (R_H) and weight average molecular weights (M_w). Black colour solid circle represent calculated hydrodynamic radii (R_H^{CAL}) of the precursor polymers according to the formula $R_H^{\text{CAL}}(\text{nm}) = 1.44 \times 10^{-2} M_w^{0.561}$. The red colour solid circle represents hydrodynamic radii from the DLS result.

6. Monitoring photodimerization by UV spectroscopy:

The polymers **TP1-TP4** were dissolved in DMF, CHCl_3 , and the 0.4 v/v% DMF-THF solvents and were irradiated with UV_B light ($\lambda_{\text{max}} = 320 \text{ nm}$) that showed a gradual decrease in the characteristic absorption of the thymine peaks within 90 min. the percentage degree of photodimerization was calculated according to formula $\%PD = (A_0 - A_t)/A_0 * 100$ where A_t is the absorbance at time t and A_0 is initial absorbance.

To check the kinetics of the photodimerization the obtain value of % photodimerization was used in equations of First (9) and Second-order rate law (10).

$$\ln(1/(1-PD)) = k_1 t \dots \dots \dots (9)$$

$$1/(1-PD) = c k_2 t + 1 \dots \dots \dots (10)$$

where c the initial concentration (0.01 mM) of thymine groups, k_1 and k_2 rate constant of the first and second order kinetics of photodimerization. The polymers **TP1-TP4** exhibits greater regression coefficients for the second-order plots than those of the first-order ones confirming second order kinetics for photodimerization. The value of the rate constants calculated from the second-order kinetics is listed in Table S1.

Table S1: Second order rate constants and the corresponding regression coefficients

Polymers	Rate constant, $k_2 \times 10^2 \text{ (mM}^{-1}\text{min}^{-1})$	Regression coefficients
TP1	3.3	0.8651
TP2	3.0	0.9678
TP3	3.2	0.9853
TP4	2.5	0.9844

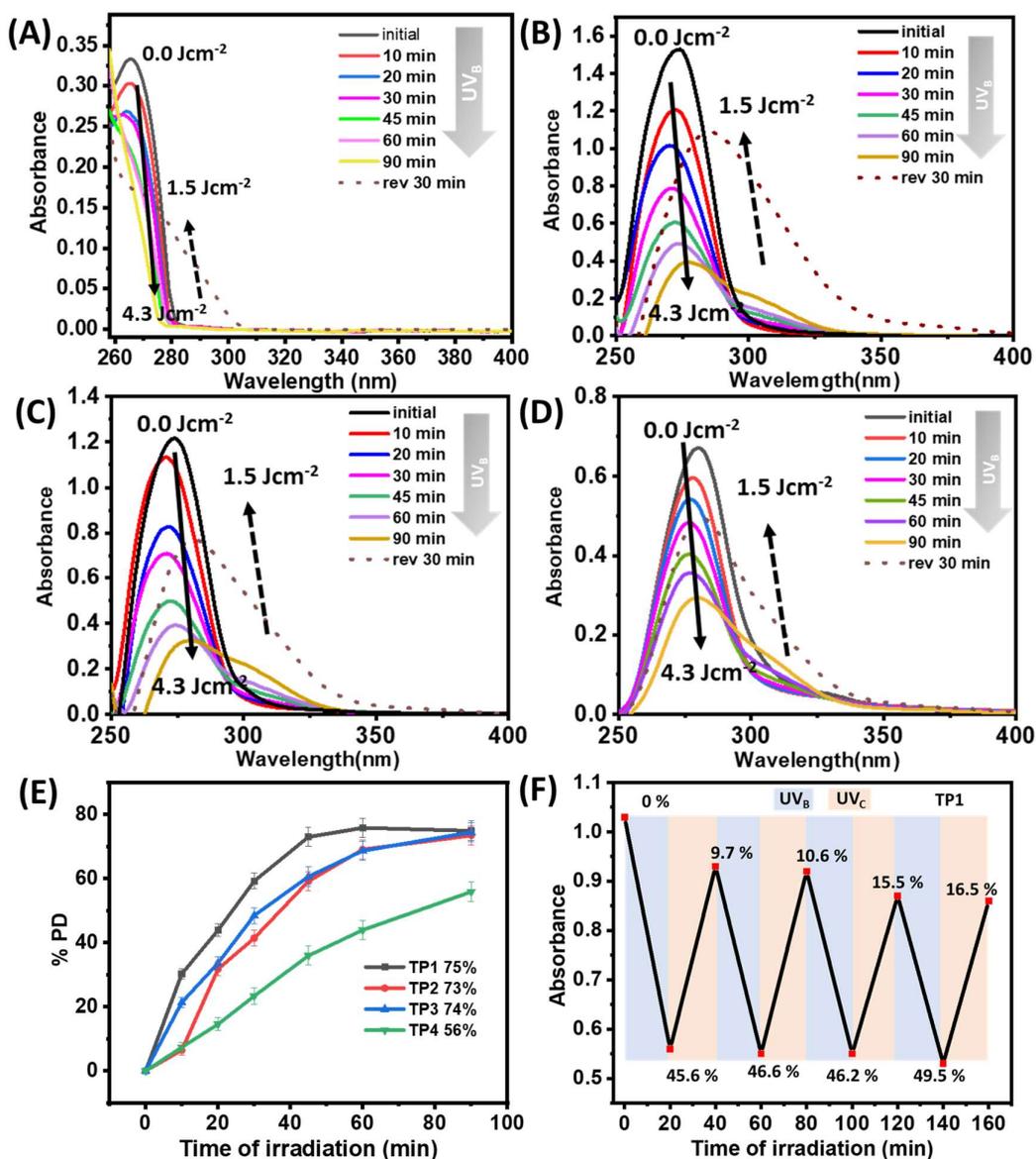


Fig. S3: UV spectroscopy data showing photodimerization of the thymine moieties in the polymers upon irradiation with UV_B light ($\lambda_{\text{max}} = 320 \text{ nm}$). (A) **TP1** in DMF, (B) **TP2**, (C) **TP3** and (D) **TP4** in 0.4 v/v% DMF-THF. (E) Graph showing photodimerization degrees (PD) of different polymers in THF after UV_B irradiation at 1.5 h. (UV_B lamp 1*8W). (F) Study of the photo reversible nature of **TP1** upon consecutive irradiations with UV_B and UV_C to observe the change in %PD values.

7. Monitoring photodimerization by ¹H NMR:

The polymer **TP1** was dissolved in CHCl₃ at the concentration of 1 mM and ¹H-NMR spectra were recorded after different times of irradiation with UV_B light. %Photodimerization degree (%PD) was calculated according to the formula $\%PD = \{(I_o - I_t)/I_o\} \times 100$, $I_t = I(i)/I(BA)$, where I_t and I_{BA} is the integral area of i and BA protons, It is the ratio of the integral area of i with BA protons at a specific time of

irradiation (t). I_0 is the ratio of the integral area of l with BA protons for the native polymers. %PD for the reversibility was calculated according to the formula $\%PD = \{(I_t - I_0)/I_0\} \times 100$, $I_t = I(t)/I_{(BA)}$

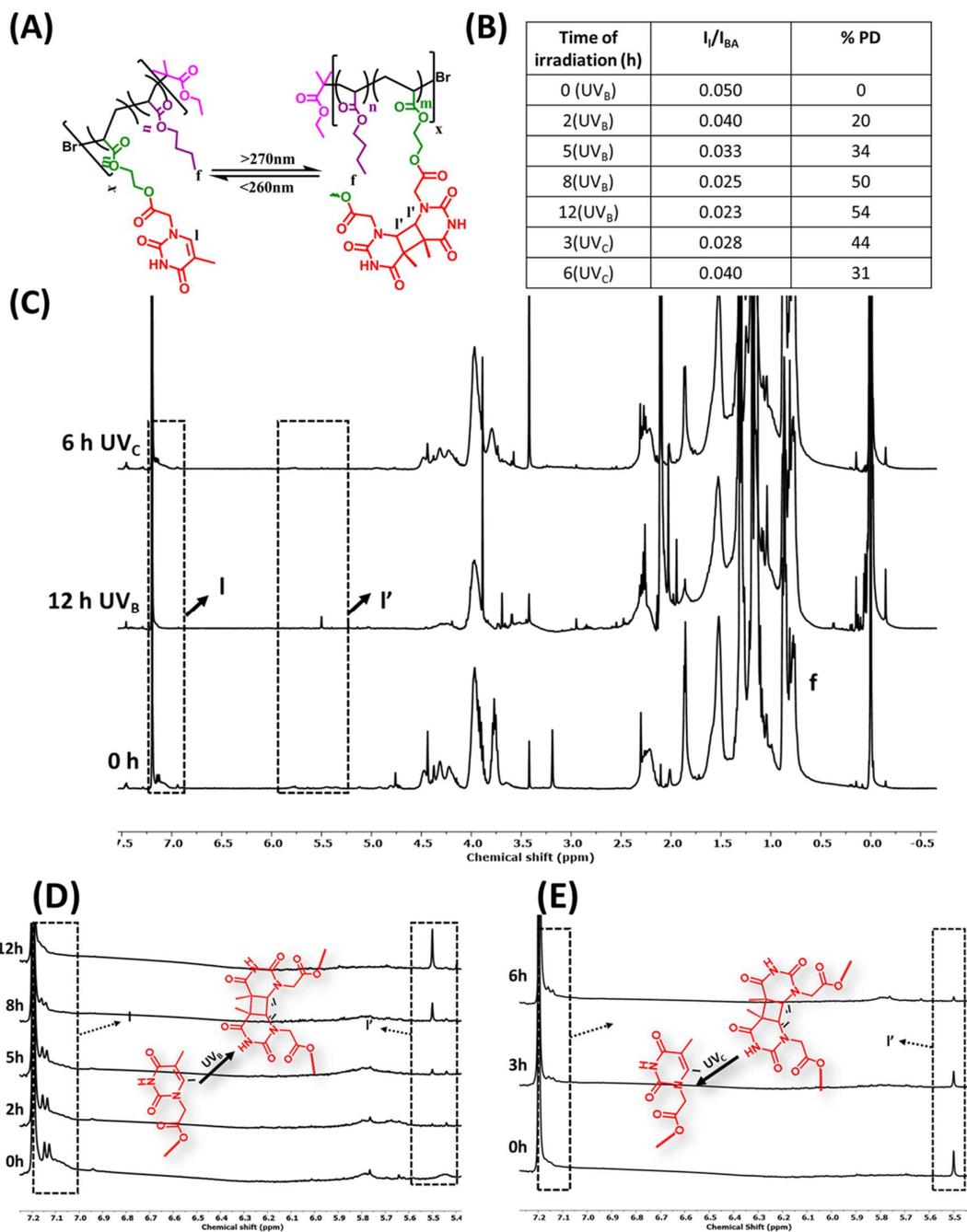


Fig. S4: Monitoring photodimerization by ^1H NMR spectroscopy. (A) Structural changes as a result of $[2\pi + 2\pi]$ photodimerization of thymine moiety in polymer to form cyclobutane adduct. (B) Integral ratio $I_t = I_t/I_{BA}$, $\%PD = \{(I_t - I_0)/I_0\} \times 100$ for UV_A and $\%PD = \{(I_t - I_0)/I_0\} \times 100$ for UV_B as calculated from ^1H -NMR spectra. (C) ^1H -NMR spectra showing the effect of photo-crosslinking and decrosslinking of thymine moieties. (D) Zoomed ^1H -NMR region of 5.5-7.2 ppm showing the increase in the intensity of peak with time of irradiation as a result of photodimerization of thymine moieties. (E) Zoomed ^1H -NMR region of 5.5-7.2 ppm showing the decrease in the intensity of peak with time of irradiation as a result of reversal of photodimerization of thymine moieties.

8. Monitoring chain collapse by DLS:

DLS measurements were performed on Malvern Zetasizer Nano ZS ZEN3600 equipped with a Helium-Neon laser ($\lambda = 633$ nm with backscattering angle of 173°). 6 mg/mL solution of **TP1-TP4** in 0.4 v/v% DMF: THF (2 mL) was filtered through 0.2 μm PTFE-filter in a glass cuvette with a path length of 1 cm. The samples were irradiated with UV_B light for 1.5 h and were analysed by DLS.

Table S2: DLS data for native Polymer and irradiated polymer **TP1-TP4**

Polymer	R_H^{oDLS} (nm) ^a	R_H^{DLS} (nm) ^b	% Compaction
TP1	20	7	65
TP2	28	11	61
TP3	22	8	64
TP4	50	24	52

^aHydrodynamic radii of the native polymer solution in 0.4 v/v% DMF:THF (6 mg/mL) as seen in DLS
^bHydrodynamic radii of the polymer solution in 0.4 v/v% DMF:THF (6 mg/mL) after irradiated with UV_B light (1x8W) for 1.5 h

9. Visualisation of nanostructures by Atomic Force Microscopy:

The nanostructure formation as a result of the polymer folding upon irradiation was investigated by atomic force microscopy. The AFM images show the formation of uniform globular nanoparticles in the shape of nanoellipsoidal of short height ranges (Fig. S4A-H). The size distributions of the nanoparticles were analysed using image-J software, from the U.S. National Institutes of Health. 50 random nanoparticles were selected from different areas of the images and a histogram was generated by choosing bin and frequency in Microsoft Excel. The number average radius (R_n), weight average radius (R_w), and PDI were estimated by using the equation. 1-3, where N_i is the number of nanoparticles of radius R_i and n is the number of nanoparticles examined in each sample.

$$R_w = \frac{\sum_{i=1}^n N_i R_i^2}{\sum_{i=1}^n N_i R_i} \quad \text{----(11)}$$

$$R_n = \frac{\sum_{i=1}^n N_i R_i}{\sum_{i=1}^n N_i} \quad \text{----(12)}$$

$$PDI = \frac{R_w}{R_n} \quad \text{----(13)}$$

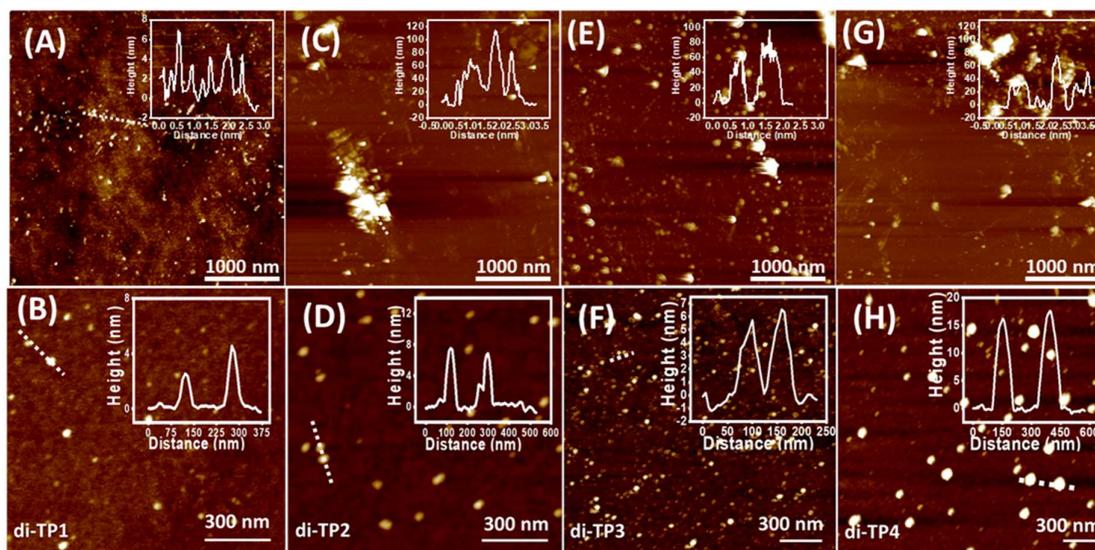


Fig S5: AFM height images of the polymers before and after UV_B irradiation in 0.4 v/v% DMF-THF. (A) **TP1**, (B) **di-TP1**, (C) **TP2**, (D) **di-TP2**, (E) **TP3**, (F) **di-TP3**, (G) **TP4**, (H) **di-TP4** (Insets have corresponding height profiles of the nanoparticles). Irradiation of all the samples was conducted at a dilute concentration of 10^{-3} mg/mL using 1 x 8w UV_B lamp for 3 h.

10. Thermal studies by differential scanning calorimetry

Thermal studies of the polymer samples were performed on Perkin Elmer Differential Scanning Calorimeter DSC 8000 model and the samples were heated from -80 to 150 °C at a heating rate of 10 °C. Thermal studies of the dried polymer films were analysed for the glass transition temperature (T_g) that corresponds to the chain mobility of the polymer. Dried polymer film on a glass substrate was exposed to UV irradiation at 320 nm (1 * 8 Watt lamp) for 5 h.

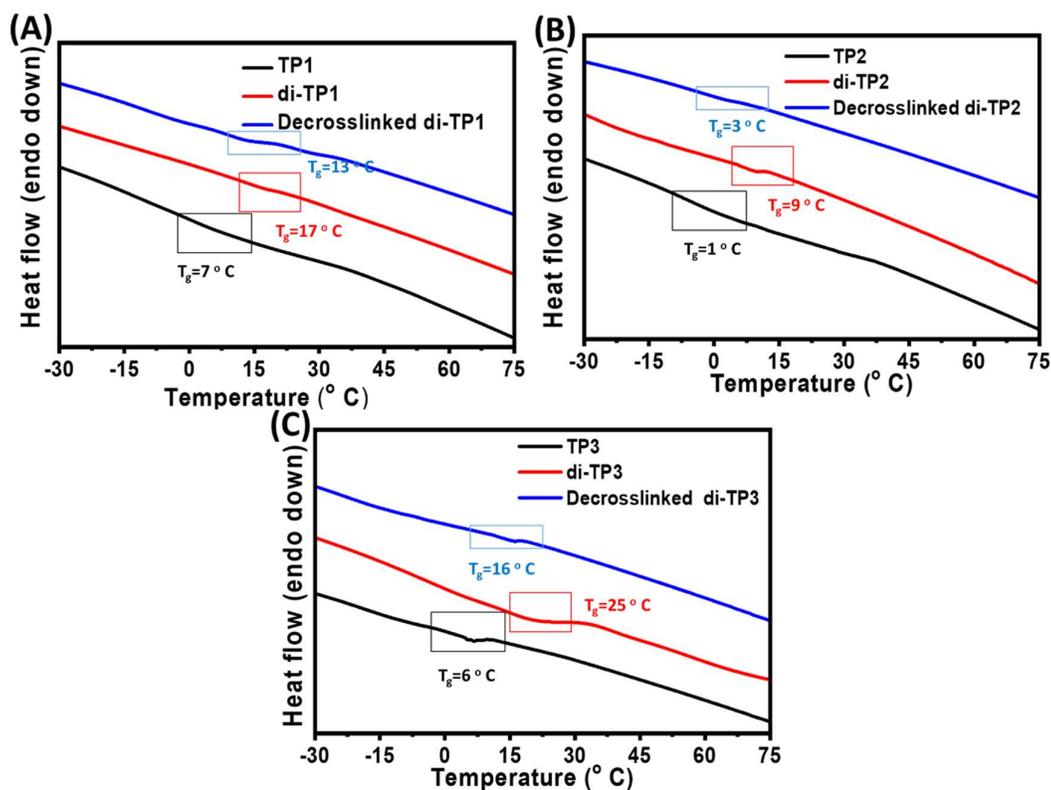


Fig. S6: DSC traces of different polymers showing glass transition temperature (T_g) values before and after crosslinking (on exposure to UV_B irradiation) and after decrosslinking (on exposure to UV_C irradiation) for (A) TP1, (B) TP2 and (C) TP3.

11. Self-healing studies by optical microscopy:

The polymer solutions of TP1-TP4 (20 mg/mL in THF) were drop-cast on a glass substrate and dried overnight to get a stable polymeric film. Then a cut of micron level was made onto the coated sample using a surgical knife and self-healing behaviour was investigated with the help of a bright field microscope. Interestingly, the cut on polymer TP4 film exhibited autonomic self-healing behaviour to heal itself within 3 min. However, the TP4 polymer films was exposed to UV_B irradiation to result in crosslinked di-TP4 polymer film that showed a delayed and incomplete healing of the cut owing to the photocrosslinked rigidification. Further, self-healing process was switched on with the help of UV_C light that promoted the decrosslinking of the [2+2] photoadducts. Also, the polymers with a shorter chain length (TP1-TP3) and higher percentage of rigid copolymer (thymine anchored HEA) exhibited a partial and incomplete self-healing. 1x8W UV_B Lamps and 1x8W UV_C Lamps were used for crosslinking and decrosslinking the polymer. The width of the cut was determined using image-J from

the U.S. National Institutes of Health. different areas of the cut in the images. The average width (W_n), percentage healing efficiency ($\%H$) were calculated using equations 14-15.

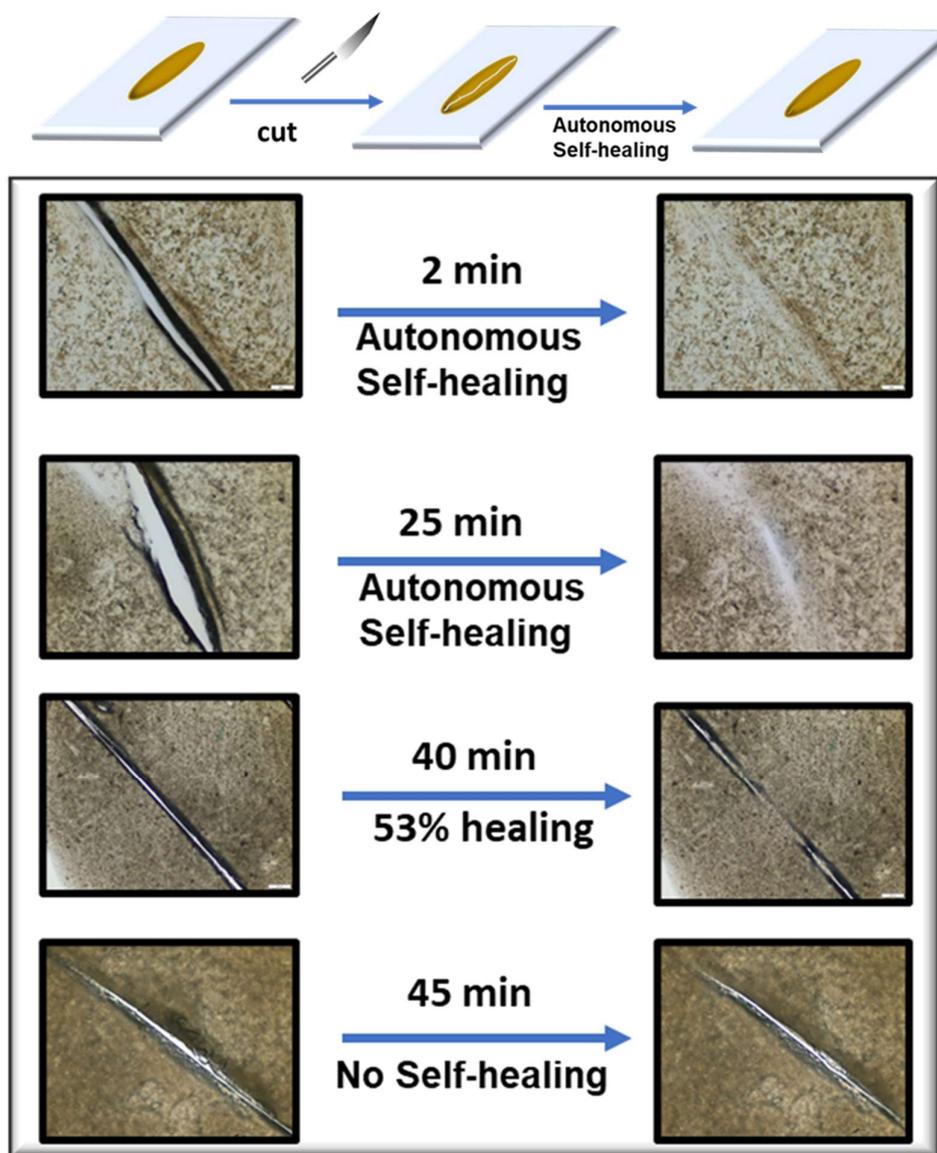


Fig. S7. Self-healing pathway with corresponding optical microscopic images depicting the autonomous self-healing of the film of native polymer **TP1** to show complete autonomous healing of a cut of average width 141 μm within 25 min and **TP2** with the cut of average width 22 μm show 20% self-healing in 40 min whereas **TP3** shows no sign of self-healing even at 45 min.



Fig. S8. Self-healing pathway with corresponding optical microscopic images depicting the autonomous self-healing of the film of decrosslinked polymer **TP4** to show complete autonomous healing within 3 min.

$$W_n = \frac{\sum_{i=1}^n (NiWi)}{\sum_{i=1}^n Ni} \quad (14)$$

$$\%H = \frac{W_{initial} - W_{healed}}{W_{initial}} \quad (15)$$

12. Thickness measurement by Ellipsometry:

The thickness of the polymeric film was measured using a spectroscopic Ellipsometer. Cauchy equation (16) provides an excellent model to calculate the thickness of the film by adjusting fit parameters. The thickness parameters for different films of TP4 were depicted in Table S3.

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4 \text{ -----(16)}$$

$$k = 0$$

A , B , and C are the dispersion parameters to be fitted and λ represents the wavelength of light.

Table S3: Parameters of polymer film of TP4 of upon fitting in Cauchy equation					
Polymer	Thickness (nm)	Goodness of fit	Fit parameter		
			A	B (nm ²)	C (nm ⁴)
TP4	50 ± 0.84	0.9910	3.2 ± 0.05	-0.39 ± 0.02	0.016 ± 0.001
	115 ± 4.74	0.9613	1.0 ± 0.01	2.8x10 ⁻³ ± 2.5x10 ⁻⁴	-0.04 ± 0.003
	184 ± 5.3	0.9645	3.1 ± 0.08	-0.34 ± 0.01	0.015 ± 0.001

13. Hydrophobicity of the polymer films:

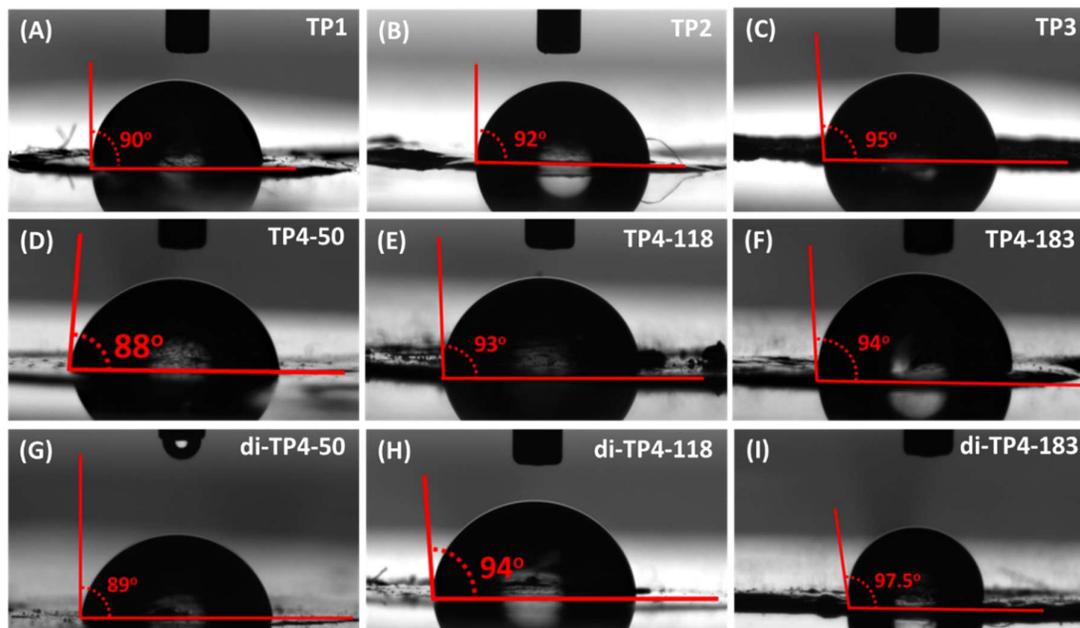
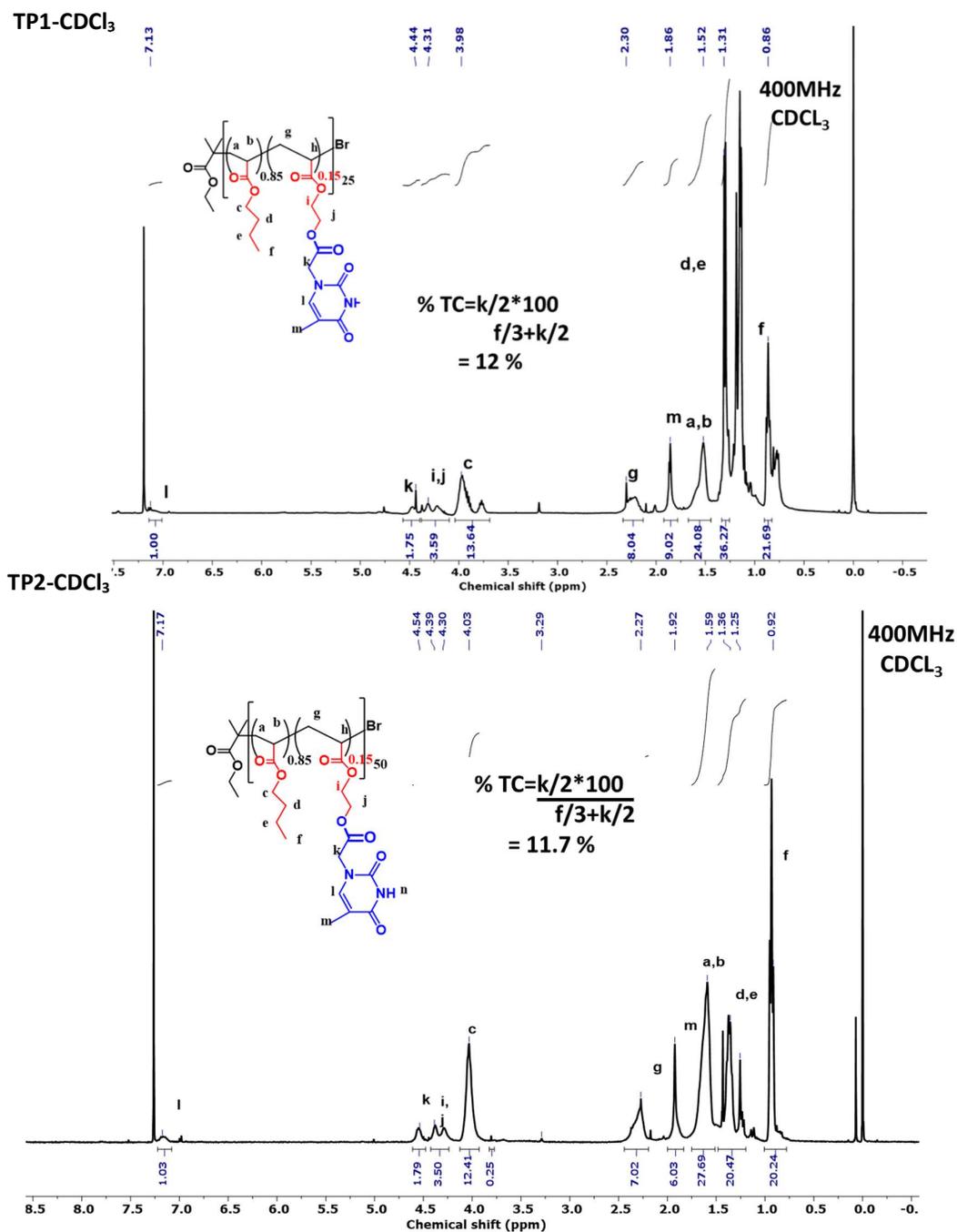


Fig. S9. Static contact angles of (A) TP1, (B) TP2, (C) TP3. The static contact angles of native polymer of TP4 of different thickness (D) 50 nm, (E) 118 nm and (F) 183 nm. The static contact angles of photo-crosslinked sample of (G) di-TP4-50 (H) di-TP4-118 (I) di-TP4-183.

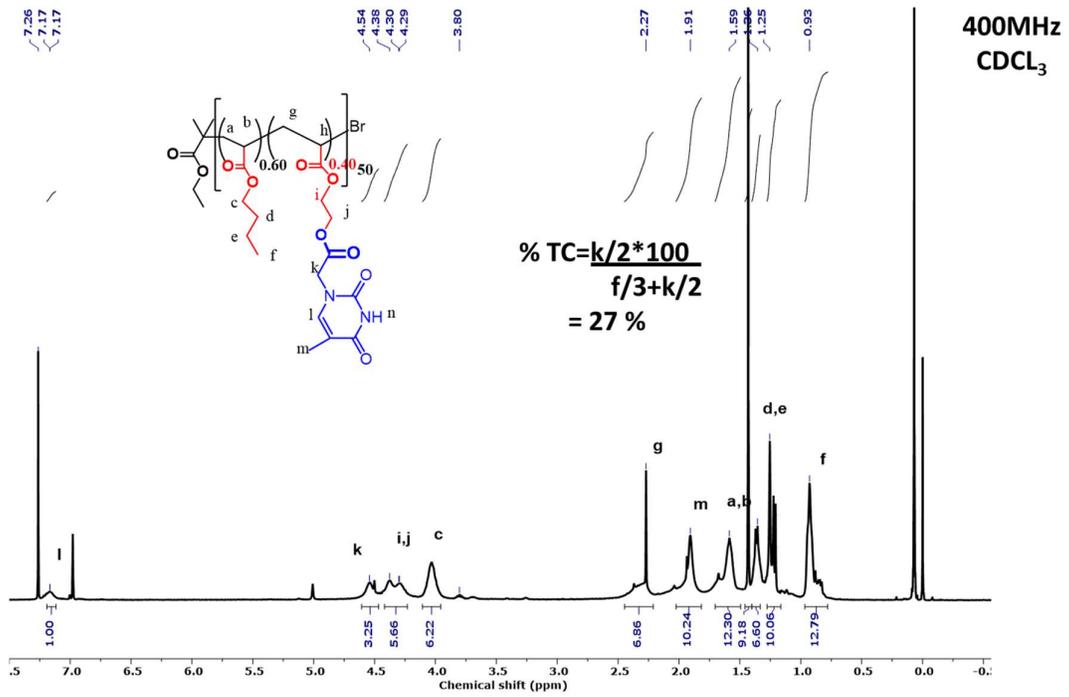
14. References

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 [S3] H. Gao, Y. Tang, Z. Hu, Q. Guan, X. Shi, F. Zhu, Q. Wu, *Polym. Chem.*, **2013**, 4, 1107-1114.
 [S4] L. Cauchy, *Bull. Des. Sc. Math.*, **1830**, 14, 9.
 [S5] J. P. Joseph, C. Miglani, A. Singh, D. Gupta, A. Pal, *Soft Matter* **2020**, 16, 2506-2515.

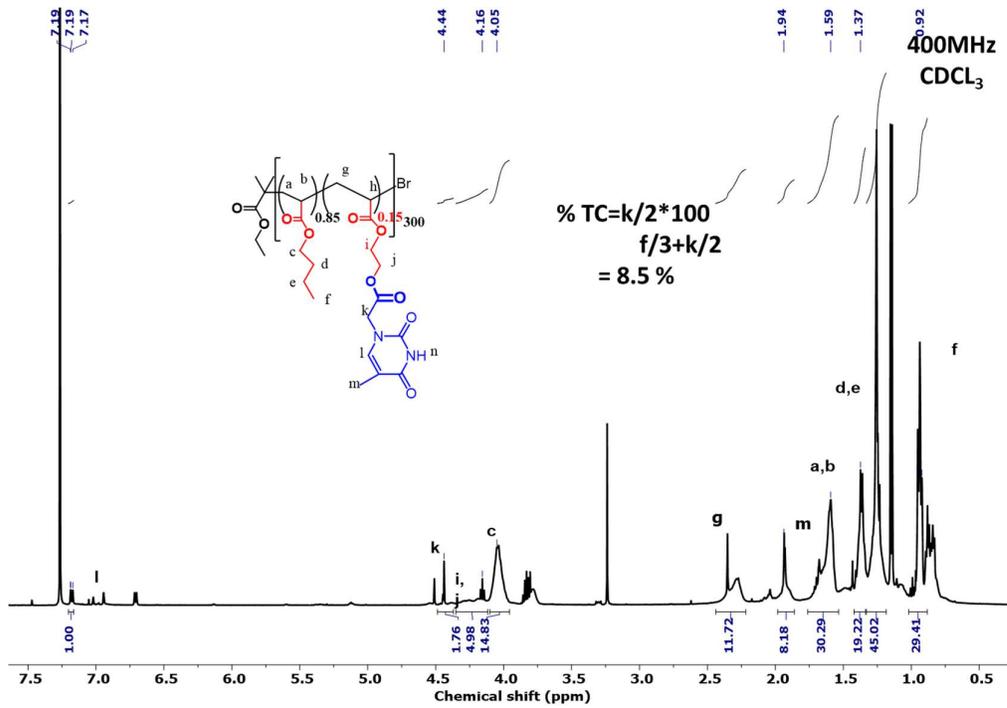
15. ¹H NMR characterization of polymers (CDCl₃, 400MHz)



TP3-CDCl₃



TP4-CDCl₃

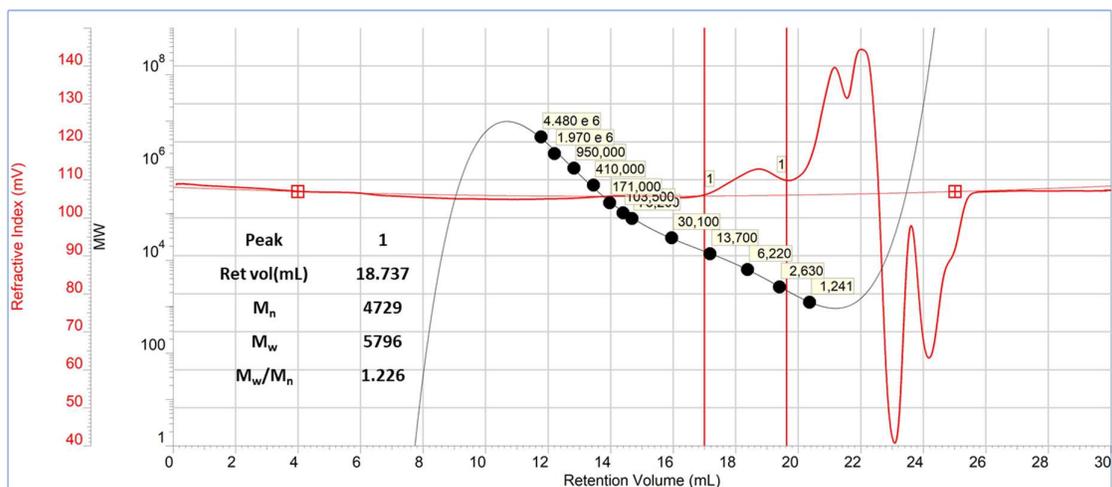


16. Size Exclusion Chromatography of the polymers

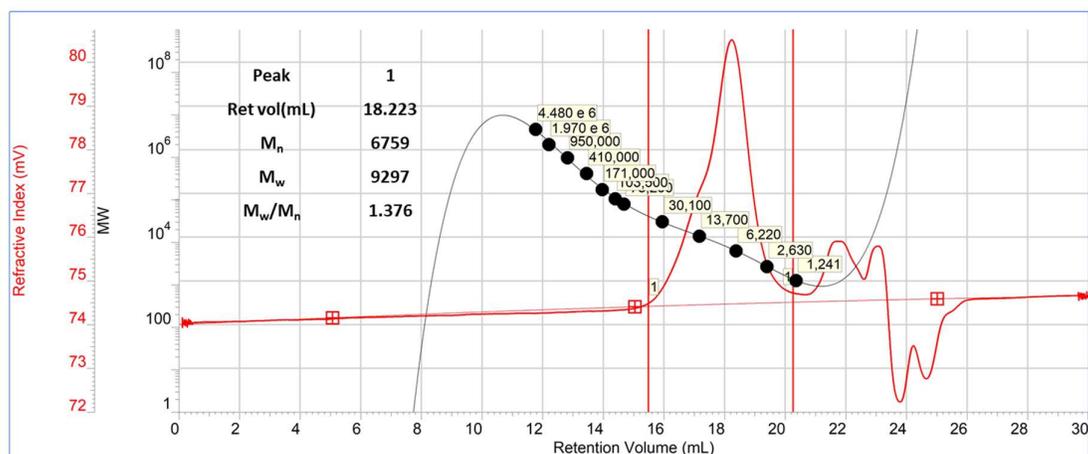
SEC measurement was performed on Malvern Viscotek instrument having RI, Right angle Light scattering (RALS), viscometer detector using T_{6000M}-T₃₀₀₀ column with THF as eluent at 35 °C at a flow rate of 1 mL/min. The results were analyzed by using Omniseq software. The sample peaks were analyzed for M_n , M_w , and PDI by means of conventional calibration as well as triple detector universal calibration using polystyrene standards.

All the polymer samples were dissolved at a concentration of 5 mg/mL in THF and were shaken for 2-3 hours in order to ensure complete solubility of the polymers. The sample solution was then filtered through PTFE syringe while adding to the vial. 100 μ L of the samples were injected and run at a flow rate of 1 mL/min for 35 min.

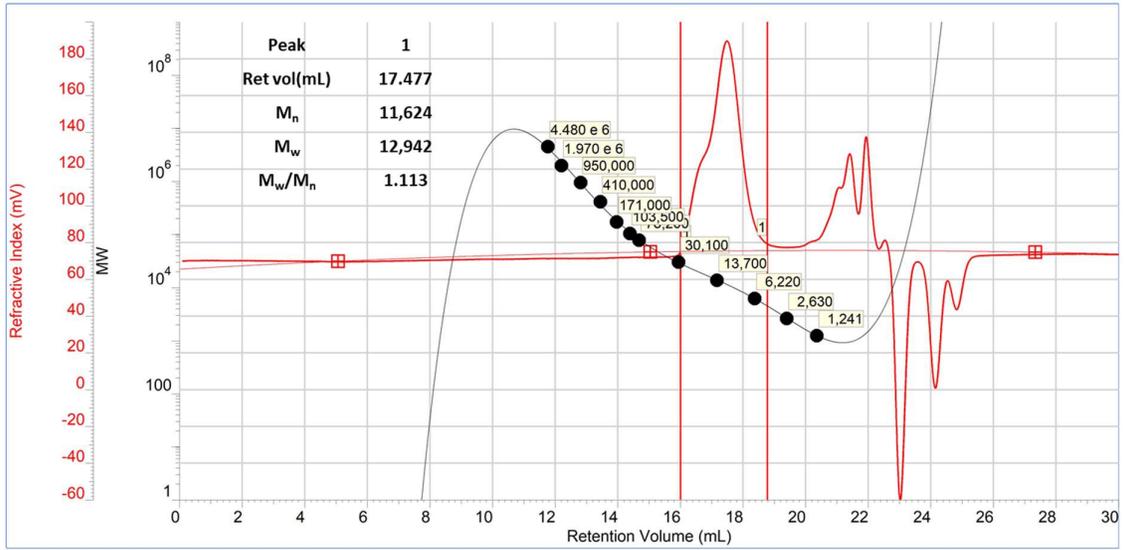
TP1



TP2



TP3



TP4

