Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Photoresponsive Chain Collapse in Flexo-rigid Functional Copolymer to Modulate Self-healing Behavior

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1. Materials & methods:

Solvents used in the syntheses were reagent grade. Acetone, chloroform, THF, 1,4-dioxane were dried as per literature protocol.[S1] The reagents, ethyl bromoacetate, tetra-*n*-butylammonium fluoride (TBAF), triethyl amine were purchased from Alfa-aeser and used without further purification. Glacial acetic acid was purchased from SD fine. The chemicals 7-hydroxy coumarin, pentamethyl diethyl tetraamine (PMDETA), Cu(I)Br were purchased from Sigma. The reagents ethyl bromo isobutyrate (EtBriB), N,N'-diisopropylcarbodiimide (DIPC) (99%) were purchased from TCI and were used without further purification. 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was prepared according to a reported procedure.[S2] The monomers, 2-hydroxy ethyl acrylate (HEA), butyl acrylate (n-BA) was purchased from TCI and were passed through basic alumina (to remove inhibitor MEHQ) before using them for ATRP. 2(Trimethylsilyloxy)ethyl acrylate (TMS-HEA) was prepared according to a literature procedure.[S3]

NMR spectra were acquired on a 400 MHz Bruker machine. The chemical shifts were reported in ppm with downfield of tetramethylsilane using the resonance of the deuterated solvent as internal standard. Splitting patterns were designated as singlet (s), doublet (d), triplet (t) and multiplet (m). % of functionality was calculated using the formula, %Functionality = $\{(I_p)/(I_p+I_e)\}$x100 where, I_p is integral per proton of corresponding functional group, I_e is integral proton of end group (e. g. methyl group of butyl acrylate chain). Size exclusion chromatography (SEC) was performed on a Malvern Viscotek instrument having RI, right angle light scattering (RALS), viscometer detector using T_{6000M}-T_{3000} columns in series with THF as eluent at 35 °C with a flow rate of 1 mL/min. The results were analysed by using Omnisec software. The sample peaks were analysed for M_n, M_w PDI, intrinsic viscosity (IV) as well as R_H by means of conventional and triple detector universal calibration method obtained using polystyrene standards. Samples were prepared by filtering solutions through a 0.2 μm PTFE-filter into a 2 mL GPC glass vial. Dynamic light scattering measurements were done on Malvern Zetasizer Nano ZS ZEN3600 equipped with a Helium−Neon laser (wavelength, λ= 633 nm with backscattering angle of 173°. Samples were prepared by filtering solutions through a 0.2 μm PTFE-filter into a glass cuvette. UV crosslinking was performed using an UV chamber equipped with 2* 8W UV_B lamp (λ_{max} = 320 nm, Intensity at 15 cm = 790 $\mu W/cm^2$) and 1*8W UV_C lamp (λ_{max} = 254 nm, Intensity at 15 cm = 820 $\mu W/cm^2$) and the sample in liquid state or solid film was kept at a distance of 15 cm for irradiation. Luminous intensity of irradiation at time *t* was determined in J/cm^2 by the formula **$[(\mu W/cm^2)/10^6]*t$ (s)**. UV spectra was recorded using Shimadzu UV 6000 UV-vis spectrophotometer in a wavelength range of 800 to 200 nm. The samples were drop-casted on silicon wafer and AFM height images were recorded using tapping mode on a Bruker multimode 8 scanning probe microscope with silicon cantilever. Thermal studies of 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/min. Optical microscopy images of the self-healing polymer films were recorded on Olympus BX53 model upright fluorescent microscope equipped with sCCD camera.

2. Synthesis and characterization of the polymers:

General procedure for random copolymerization of 2(Trimethylsilyloxy)ethyl acrylate (HEA-TMS) with n-butyl acrylate (n-BA) by ATRP method followed by deprotection of the TMS and post-functionalization of polymer with coumarin moieties.

ATRP polymerization was performed with *n*-BA and HEA-TMS as co-monomers followed by deprotection of TMS group (Scheme 1). Coumarin carboxylic acid was then tethered to the resulting copolymers using esterification. The detailed synthetic procedures of **P1-P5** are described as follows.

Random copolymerization by ATRP:

Cu(I)Br, n-BA, HEA-TMS, initiator (EtBriB), and toluene were placed in a schlenk tube capped with a rubber septum followed by degassing using freeze-thaw-pump cycles (three times). PMDETA was then added to the mixture and was degassed again. The reaction mixture was placed in an oil bath for stirring at 70 °C for around 17 hours. Then it was cooled to room temperature and diluted with THF. The solution was filtered through neutral alumina to trap the copper catalyst with subsequent removal of unreacted monomers and solvents in vacuum at 50 °C to yield the TMS protected copolymer. NMR and GPC analysis confirmed the polymer with the percentage of comonomers and M_w, M_n, PDI.

P-TMS-1. Random copolymer of butyl acrylate and 2(Trimethylsilyloxy)ethyl acrylate (intended % functionality = 15%, DP = 25): Cu(I)Br (0.32 mmol), BA (3.4 mmol), HEA-TMS (0.6 mmol), initiator (EtBriB) (0.16 mmol), and toluene (1 ml) were placed in a schlenk tube capped with a rubber septum followed by degassing using freeze-thaw-pump cycles (three times). PMDETA (0.32 mmol) was then added to the mixture and was again degassed. The reaction mixture was placed in an oil bath for stirring at 70 °C for around 17 hours. Then it was cooled to room temperature and diluted with THF. The solution was filtered through neutral alumina to trap the copper catalyst with subsequent removal of unreacted monomers and solvents in vacuum at 50 °C to yield the TMS protected copolymer. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.06– 3.99 (m, 5H, $OC\boldsymbol{H_2}$), 3.83-3.70 (m,1H, $O\boldsymbol{CH_2}C\boldsymbol{H_2}O$), 2.41–2.23 (m, 3H, $C\boldsymbol{H_2}$), 1.98-1.90 (m, 1H, $C\boldsymbol{H_2}$), 1.66-1.55 (m, 12H, $C\boldsymbol{H_2}$), 1.43-1.38 (m, 9H, $OCH_2C\boldsymbol{H_2CH_2}CH_3$), 0.95–0.92 (t, 8H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$), 0.13-0.05 (m, 2H, Si $(C\boldsymbol{H_3})_3$). %Functionality = 10%, SEC analysis (THF, polystyrene standards): M_n = 3000 g/mol; M_w/M_n = 1.11.

P-TMS-2. Random copolymer of butyl acrylate and 2(Trimethylsilyloxy)ethyl acrylate (intended % functionality = 15%, DP = 50): Cu(I)Br (0.16 mmol), BA (3.4 mmol), HEA-TMS (0.6 mmol), initiator (EtBriB) (0.08 mmol), and toluene (1 ml) were placed in a schlenk tube capped with a rubber septum followed by degassing using freeze-thaw-pump cycles (three times). PMDETA (0.16 mmol) was then added to the mixture and was again degassed. The reaction mixture was placed in an oil bath for stirring at 70 °C for around 17 hours. Then it was cooled to room temperature and diluted with THF. The solution was filtered through neutral alumina to trap the copper catalyst with subsequent removal of unreacted monomers and solvents in vacuum at 50 °C to yield the TMS protected copolymer. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.31– 4.27 (m, 6H, $OC\boldsymbol{H_2}CH_2O$, 3.98-3.90 (m, 20H, $OC\boldsymbol{H_2}$), 3.68-3.72 (m, 5H,), 2.46–2.40 (m, 7H, $C\boldsymbol{H_2}$), 2.24-2.18 (m, 15H, $C\boldsymbol{H_2}$), 1.86-1.83(m, 11H, $C\boldsymbol{H_2}$),1.58-1.53 (m, 30H, $OCH_2C\boldsymbol{H_2}CH_2CH_3$), 1.34-1.29 (m, 20H, $OCH_2CH_2C\boldsymbol{H_2}CH_3$), 0.89–0.85 (t, 29H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$), 0.15–0.09 (m, 10 H, Si $(C\boldsymbol{H_3})_3$). %Functionality = 12%. SEC analysis (THF, polystyrene standards): M_n = 5437 g/mol; M_w/M_n = 1.23.

P-TMS-3. Random copolymer of butyl acrylate and 2(Trimethylsilyloxy)ethyl acrylate (intended % functionality = 40%, DP = 50): Cu(I)Br (0.16 mmol), BA (2.4 mmol), HEA-TMS (1.6 mmol), initiator (EBrib) (0.08 mmol), and toluene (1 ml) were placed in a schlenk tube capped with a rubber septum followed by degassing using freeze-thaw-pump cycles (three times). PMDETA (0.16 mmol) was then added to the mixture and was again degassed. The reaction mixture was placed in an oil bath for stirring at 70 °C for around 17 hours. Then it was cooled to room temperature and diluted with THF. The solution was filtered through neutral alumina to trap the copper catalyst with subsequent removal of unreacted monomers and solvents in vacuum at 50 °C to yield the TMS protected copolymer. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.25– 4.04 (m, 10H, $OC\boldsymbol{H_2}CH_2O$, 3.78-3.74 (m, 4H, $OCH_2C\boldsymbol{H_2}O$ & $OC\boldsymbol{H_2}$), 2.4–2.19 (m, 6H, $C\boldsymbol{H_2}$), 2.02–1.90 (m, 3H, $C\boldsymbol{H_2}$), 1.79–1.54 (m, 15H, $C\boldsymbol{H_2}$), 1.22-1.43 (m, 6H, $OCH_2C\boldsymbol{H_2}C\boldsymbol{H_2}CH_3$), 0.98–0.89 (t, 11H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$), 0.16–0.07 (m, 9H, Si $(C\boldsymbol{H_3})_3$). %Functionality = 29%. SEC analysis (THF, polystyrene standards): M_n = 6000 g/mol; M_w/M_n = 1.26.

P-TMS-4. Random copolymer of butyl acrylate and 2(Trimethylsilyloxy)ethyl acrylate (intended % functionality = 15%, DP = 150): Cu(I)Br (0.16 mmol), BA (10.2 mmol), HEA-TMS (1.8 mmol), initiator (EtBriB) (0.08 mmol), and toluene (1 ml) were placed in a schlenk tube capped with a rubber septum followed by degassing using freeze-thaw-pump cycles (three times). PMDETA (0.16 mmol) was then added to the mixture and was again degassed. The reaction mixture was placed in an oil bath for stirring at 70 °C for around 17 hours. Then it was cooled to room temperature and diluted with THF. The solution was filtered through neutral alumina to trap the copper catalyst with subsequent removal of unreacted monomers and solvents in vacuum at 50 °C to yield the TMS protected copolymer. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.05– 3.98 (m, 5H, $OC\boldsymbol{H_2}$), 3.83-3.70 (m,1H, $O\boldsymbol{CH_2}C\boldsymbol{H_2}O$), 2.41–2.23 (m, 3H, $C\boldsymbol{H_2}$), 1.98-1.90 (m, 2H, $C\boldsymbol{H_2}$), 1.66-1.55 (m, 9H, $C\boldsymbol{H_2}$), 1.43-1.38 (m, 5H, $OCH_2C\boldsymbol{H_2CH_2}CH_3$), 0.95–0.92 (t, 6H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$), 0.13-0.05 (m, 2H, Si $(C\boldsymbol{H_3})_3$). %Functionality = 18%. SEC analysis (THF, polystyrene standards): M_n = 19718 g/mol; M_w/M_n = 1.12.

P-TMS-5. Random copolymer of butyl acrylate and 2(Trimethylsilyloxy)ethyl acrylate (intended % functionality = 15%, DP = 300): Cu(I)Br (0.16 mmol), BA (20.4 mmol), HEA-TMS (3.6 mmol), initiator (EtBriB) (0.08 mmol), and toluene (1 ml) were placed in a schlenk tube capped with a rubber septum followed by degassing using freeze-thaw-pump cycles (three times). PMDETA (0.16 mmol) was then added to the mixture and was again degassed. The reaction mixture was placed in an oil bath for stirring at 70 °C for around 17 hours. Then it was cooled to room temperature and diluted with THF. The solution was filtered through neutral alumina to trap the copper catalyst with subsequent removal of unreacted monomers and solvents in vacuum at 50 °C to yield the TMS protected copolymer. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.06– 3.99 (m, 5H, $OC\boldsymbol{H_2}$), 3.83-3.70 (m,1H, $O\boldsymbol{CH_2}C\boldsymbol{H_2}O$), 2.41–2.23 (m, 3H, $C\boldsymbol{H_2}$), 1.98-1.90 (m, 1H, $C\boldsymbol{H_2}$), 1.66-1.55 (m, 10H, $C\boldsymbol{H_2}$), 1.43-1.38 (m, 6H, $OCH_2C\boldsymbol{H_2CH_2}CH_3$), 0.95–0.92 (t, 7H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$), 0.13-0.05 (m, 2H, Si $(C\boldsymbol{H_3})_3$). %Functionality = 12%. SEC analysis (THF, polystyrene standards): M_n = 33640 g/mol; M_w/M_n = 1.13.

Deprotection of TMS group:

The TMS groups in copolymers were deprotected with TBAF and acetic acid in THF solvent by stirring at room temperature for 24 h. Then the solvent was evaporated off and precipitation from methanol-water (9:1) mixture followed by drying under P_2O_5 in vacuum furnished the deprotected polymer.

P-OH-1. Random copolymer of butyl acrylate and hydroxy ethyl acrylate (intended %functionality = 15%, DP = 25): The deprotection of TMS was achieved by stirring the polymer **P-TMS-1** (0.027 mmol) with 0.54 mmol of TBAF and 3.3 mmol of acetic acid in THF at room temperature for 24 hours. Solvent was evaporated off and precipitation from methanol-water (9:1) followed by drying under P_2O_5 in vacuum furnished the polymer **P-OH-1.** ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.35– 4.25 (m, 5H, $OC\boldsymbol{H_2}$), 3.75-3.69 (m, 1H, $O\boldsymbol{CH_2}C\boldsymbol{H_2}O$), 3.15 (s, 1H, OH), 2.37–2.20 (m, 3H, $C\boldsymbol{H_2}$), 1.90-1.89 (m, 1H, $C\boldsymbol{H_2}$), 1.65-1.53 (m, 12H, $C\boldsymbol{H_2}$), 1.46-1.35 (m, 8H, $OCH_2C\boldsymbol{H_2}\boldsymbol{CH_2}CH_3$), 0.98–0.94 (t, 8H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$).%Functionality = 10%. SEC analysis (THF, polystyrene standards): M_n = 2730 g/mol; M_w/M_n = 1.27.

P-OH-2. Random copolymer of butyl acrylate and hydroxy ethyl acrylate (intended %functionality = 15%, DP = 50): The deprotection of TMS was achieved by stirring the polymer **P-TMS-2** (0.014 mmol) with 0.28 mmol of TBAF and 1.7 mmol of acetic acid in THF at room temperature for 24 hours. Solvent was evaporated off and precipitation from methanol-water (9:1) followed by drying under P_2O_5 in vacuum furnished the polymer **P-OH-2.** ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.37– 4.19 (m, 24H, $OC\boldsymbol{H_2}$), 3.95-3.79 (m, 4H, $O\boldsymbol{CH_2}C\boldsymbol{H_2}O$), 3.30(s, 2H, OH), 2.15–1.92 (m, 13H, $C\boldsymbol{H_2}$), 1.61-1.58 (m, 39H, $C\boldsymbol{H_2}$), 1.38-1.25 (m, 23H, $OCH_2C\boldsymbol{H_2}\boldsymbol{CH_2}CH_3$), 0.95–0.88 (t, 37H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$). %Functionality = 12%. SEC analysis (THF, polystyrene standards): M_n = 4888 g/mol; M_w/M_n = 1.21.

P-OH-3. . Random copolymer of butyl acrylate and hydroxy ethyl acrylate (intended %functionality = 40%, DP = 50): The deprotection of TMS was achieved by stirring the polymer **P-TMS-3** (0.013 mmol) with 0.26 mmol of TBAF and 2.5 mmol of acetic acid in THF at room temperature for 24 hours. Solvent was evaporated off and precipitation from methanol-water (9:1) followed by drying under P_2O_5 in vacuum furnished the polymer **P-OH-3.** ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) δ (ppm) 4.32– 4.15 (m, 8H, $OC\boldsymbol{H}_2$), 3.84-3.74 (m, 4H, $OC\boldsymbol{H}_2C\boldsymbol{H}_2O$), 2.37–2.23 (m, 5H, $C\boldsymbol{H}_2$), 1.99-1.93 (m, 3H, $C\boldsymbol{H}_2$), 1.68-1.60 (m, 20H, $C\boldsymbol{H}_2$), 1.42-1.35 (m, 11H, $OC\boldsymbol{H}_2C\boldsymbol{H}_2C\boldsymbol{H}_2CH_3$), 0.96–0.92 (t,10H, $OCH_2CH_2CH_2C\boldsymbol{H}_3$). %Functionality = 29%. SEC analysis (THF, polystyrene standards): M_n = 4552 g/mol; M_w/M_n = 1.31.

P-OH-4. Random copolymer of butyl acrylate and hydroxy ethyl acrylate (intended %functionality = 15%, DP = 150): The deprotection of TMS was achieved by stirring the polymer **P-TMS-4** (0.048 mmol) with 2.88 mmol of TBAF and 18 mmol of acetic acid in THF at room temperature for 24 hours. Solvent was evaporated off and precipitation from methanol-water (9:1) followed by drying under P_2O_5 in vacuum furnished the polymer **P-OH-4.** ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.32– 4.15 (m, 26H, $OC\boldsymbol{H_2}$), 3.84-3.74 (m, 11H, $O\boldsymbol{CH_2}C\boldsymbol{H_2}O$), 3.35(s, 1H, OH), 2.37–2.23 (m, 14H, $C\boldsymbol{H_2}$), 1.99-1.93 (m, 5H, $C\boldsymbol{H_2}$), 1.68-1.60 (m, 47H, $C\boldsymbol{H_2}$), 1.42-1.35 (m, 35H, $OCH_2C\boldsymbol{H_2}\boldsymbol{CH_2}CH_3$), 0.96–0.92 (t, 24H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$). %Functionality = 18%. SEC analysis (THF, polystyrene standards): M_n = 18076 g/mol; M_w/M_n = 1.27.

P-OH-5. Random copolymer of butyl acrylate and hydroxy ethyl acrylate (intended %functionality = 15%, DP = 300): The deprotection of TMS was achieved by stirring the polymer **P-TMS-5** (0.048 mmol) with 2.88 mmol of TBAF and 18 mmol of acetic acid in THF at room temperature for 24 hours. Solvent was evaporated off and precipitation from methanol-water (9:1) followed by drying under P_2O_5 in vacuum furnished the polymer **P-OH-5.** ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) δ (ppm) 4.32– 4.15 (m, 27H, $OC\boldsymbol{H_2}$), 3.84-3.74 (m, 10H, $O\boldsymbol{CH_2}C\boldsymbol{H_2}O$), 3.35(s, 1H, OH), 2.37–2.23 (m, 13H, $C\boldsymbol{H_2}$), 1.99-1.93 (m, 5H, $C\boldsymbol{H_2}$), 1.68-1.60 (m, 46H, $C\boldsymbol{H_2}$), 1.42-1.35 (m, 34H, $OCH_2C\boldsymbol{H_2}\boldsymbol{CH_2}CH_3$), 0.96–0.92 (t, 25H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$). %Functionality = 12%. SEC analysis (THF, polystyrene standards): M_n = 30640 g/mol; M_w/M_n = 1.35.

Grafting of photoresponsive moieties on the polymers:

The synthesis of coumarin carboxylic acid was performed according to literature procedure.[S4] The polymer solution was added to a stirred solution of coumarin carboxylic acid with DPTS and DIPC. The solution was stirred under N_2 environment at 25 °C for 48 hours. Then the solvent was evaporated and the solid was precipitated from methanol-water (20 mL, 9:1 v/v) three times to purify the desired polymer.[S5] The resultant polymer subsequently dried under P_2O_5 in vacuum furnished the polymer **P1-5**.

Polymer P1: The solution of polymer **P-OH-1** in THF (14.2 µmol) was added to a stirred solution of coumarin carboxylic acid (568 µmol) with DPTS (142 µmol) and DIPC (837.8 µmol) under N_2 environment. The solution was stirred under N_2 environment at 25 °C for 48 hours. Precipitaion from methanol-water (9:1) and subsequent drying under P_2O_5 in vacuum furnished the polymer **P1.** ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.57 (m, 1H, >C=$\boldsymbol{CH}$-),7.36-7.32 (m, 1H, >C=$\boldsymbol{CH}$-), 6.89-6.77 (m, 2H, , =CH-$\boldsymbol{CH}$=C-$\boldsymbol{CH}$=), 6.22-6.17 (m, 1H, =$\boldsymbol{CH}$-CO-O-), 4.75-4.62 (m, 1.23H, O$\boldsymbol{CH_2}$CO-O), 4.36-4.06 (m, 4H, O$\boldsymbol{CH_2CH_2}$O) 3.95-3.66 (m, 19H, OC$\boldsymbol{H_2}$), 2.37-2.12 (m, 12H, $\boldsymbol{CH_2}$), 1.85-1.79 (m,11H, C$\boldsymbol{H_2}$), 1.46-1.31 (m, 41H, C$\boldsymbol{H_2}$), 1.24-1.13 (m, 23H, $0CH_2C\boldsymbol{H_2}C\boldsymbol{H_2}CH_3$), 0.88-0.85 (t, 30H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$). %Functionality = 9.6%. SEC analysis (THF, polystyrene standards): M_n = 6299 g/mol; M_w/M_n = 1.40.

Polymer P2: The solution of polymer **P-OH-2** in THF (7.1 µmol) was added to a stirred solution of coumarin carboxylic acid (CA) (192 µmol) with DPTS (48 µmol) and DIPC (292 µmol) under N_2 environment. The solution was stirred under N_2 environment at 25 °C for 48 hours. Precipitaion from methanol-water (9:1) and subsequent drying under P_2O_5 in vacuum furnished the polymer **P2.**. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.55 (m, 1H, >C=$\boldsymbol{CH}$-),7.35-7.33 (m, 1H, >C=$\boldsymbol{CH}$-), 6.85-6.80 (m, 2H, , =CH-$\boldsymbol{CH}$=C-$\boldsymbol{CH}$=), 6.20-6.15 (m, 1H, =$\boldsymbol{CH}$-CO-O-), 4.75-4.70(m, 2H, O$\boldsymbol{CH_2}$CO-O), 4.35-4.24 (m, 4H, O$\boldsymbol{CH_2CH_2}$O) 3.98-3.90 (m, 15H, OC$\boldsymbol{H_2}$), 2.24-2.20 (m, 8H, $\boldsymbol{CH_2}$), 1.98-1.84 (m, 4H, C$\boldsymbol{H_2}$), 1.53-1.50 (m, 26H, C$\boldsymbol{H_2}$), 1.38-1.36 (m, 16H, $0CH_2C\boldsymbol{H_2}C\boldsymbol{H_2}CH_3$), 0.88-0.85 (t, 21H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$). %Functionality = 12%. SEC analysis (THF, polystyrene standards): M_n = 9597 g/mol; M_w/M_n = 1.16.

Polymer P3: The solution of polymer **P-OH-3** in THF (5.7 µmol) was added to a stirred solution of coumarin carboxylic acid (CA) (228 µmol) with DPTS (57 µmol) and DIPC (336 µmol) under N_2 environment. The solution was stirred under N_2 environment at 25 °C for 48 hours. Precipitaion from methanol-water (9:1) and subsequent drying under P_2O_5 in vacuum furnished the polymer **P3**. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.57 (m, 1H, >C=$\boldsymbol{CH}$-),7.35-7.33 (m, 1H, >C=$\boldsymbol{CH}$-), 6.85-6.80 (m, 2H, =CH-$\boldsymbol{CH}$=C-$\boldsymbol{CH}$=), 6.28-6.20 (m, 1H, =$\boldsymbol{CH}$-CO-O-), 5.01-4.75 (m, 2H, O$\boldsymbol{CH_2}$CO-O), 4.41-4.19 (m, 4H, OC$\boldsymbol{H_2}$) 3.80-3.65 (m, 6H, O$\boldsymbol{CH_2CH_2}$O), 2.30-2.21 (m, 4H, $\boldsymbol{CH_2}$), 2.10-1.93 (m, 3H, C$\boldsymbol{H_2}$), 1.70-1.50 (m, 12H, C$\boldsymbol{H_2}$), 1.43-1.24 (m, 8H, $0CH_2C\boldsymbol{H_2}C\boldsymbol{H_2}CH_3$), 0.92-0.90 (t, 8H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$). %Functionality = 28%. SEC analysis (THF, polystyrene standards): M_n = 11009 g/mol; M_w/M_n = 1.23.

Polymer P4: The solution of polymer **P-OH-4** in THF (5.1 µmol) was added to a stirred solution of coumarin carboxylic acid (CA) (316 µmol) with DPTS (75 µmol) and DIPC (450 µmol) under N_2 environment. The solution was stirred under N_2 environment at 25 °C for 48 hours. Precipitaion from methanol-water (9:1) and subsequent drying under P_2O_5 in vacuum furnished the polymer **P4**. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.55 (m, 1H, >C=$\boldsymbol{CH}$-),7.35-7.33 (m, 1H, >C=$\boldsymbol{CH}$-), 6.85-6.80 (m, 2H, , =CH-$\boldsymbol{CH}$=C-$\boldsymbol{CH}$=), 6.20-6.15 (m, 1H, =$\boldsymbol{CH}$-CO-O-), 4.75-4.70(m, 2H, O$\boldsymbol{CH_2}$CO-O), 4.35-4.24 (m, 4H, O$\boldsymbol{CH_2CH_2}$O) 3.98-3.90 (m, 9H, OC$\boldsymbol{H_2}$), 2.24-2.20 (m, 7H, $\boldsymbol{CH_2}$), 1.98-1.84 (m, 4H, C$\boldsymbol{H_2}$), 1.53-1.50 (m, 15H, C$\boldsymbol{H_2}$), 1.38-1.36 (m, 8H, $0CH_2C\boldsymbol{H_2}C\boldsymbol{H_2}CH_3$), 0.88-0.85 (t, 16H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$). %Functionality = 14%. SEC analysis (THF, polystyrene standards): M_n = 22586 g/mol; M_w/M_n = 1.44.

Polymer P5: The solution of polymer **P-OH-5** in THF (1.3 µmol) was added to a stirred solution of coumarin carboxylic acid (CA) (79 µmol) with DPTS (20 µmol) and DIPC (120 µmol) under N_2 environment. The solution was stirred under N_2 environment at 25 °C for 48 hours. Precipitaion from methanol-water (9:1) and subsequent drying under P_2O_5 in vacuum furnished the polymer **P4**. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.55 (m, 1H, >C=$\boldsymbol{CH}$-),7.35-7.33 (m, 1H, >C=$\boldsymbol{CH}$-), 6.85-6.80 (m, 2H, , =CH-$\boldsymbol{CH}$=C-$\boldsymbol{CH}$=), 6.20-6.15 (m, 1H, =$\boldsymbol{CH}$-CO-O-), 4.75-4.70(m, 5H, O$\boldsymbol{CH_2}$CO-O), 4.35-4.24 (m, 7H, O$\boldsymbol{CH_2CH_2}$O) 3.98-3.90 (m, 53H, OC$\boldsymbol{H_2}$), 2.24-2.20 (m, 16H, $\boldsymbol{CH_2}$), 1.98-1.84 (m, 41H, C$\boldsymbol{H_2}$), 1.53-1.50 (m, 92H, C$\boldsymbol{H_2}$), 1.38-1.36 (m, 33H, $0CH_2C\boldsymbol{H_2}C\boldsymbol{H_2}CH_3$), 0.88-0.85 (t, 69H, $OCH_2CH_2CH_2C\boldsymbol{H_3}$). %Functionality = 4%. SEC analysis (THF, polystyrene standards): M_n = 32453 g/mol; M_w/M_n = 1.47.

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

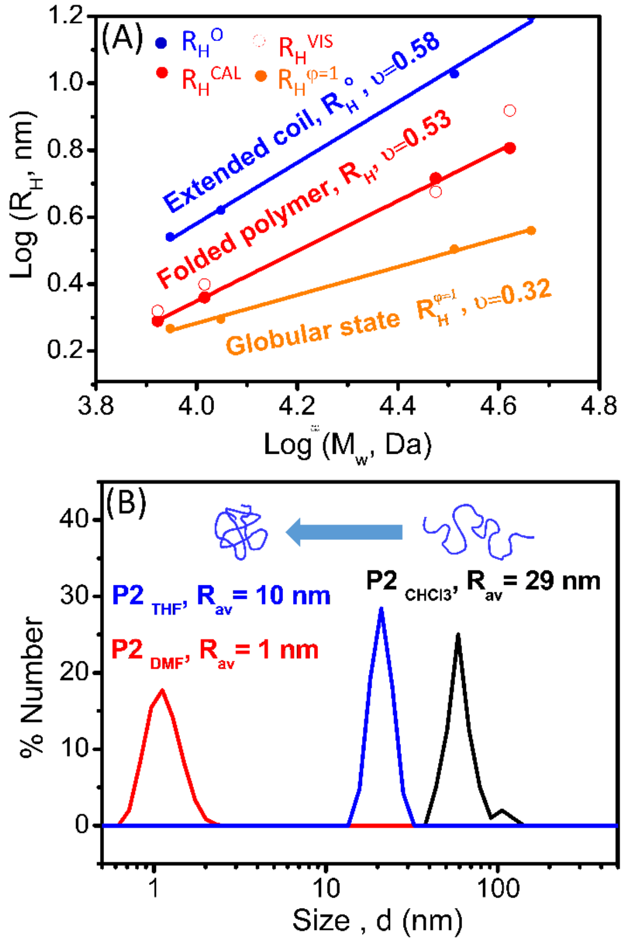


Fig. S1: Illustration of the $R_H = KM_w^{v}$ scaling law for polymers **P1, P2, P4, P5** based on hydrodynamic radii (R_H) and weight average molecular weights (M_w). Closed blue circles represent calculated hydrodynamic radii (R_H^{o}) of the precursor polymers according to the formula R_H^{oCAL}(nm) = $1.44\times10^{-2}*M_w^{0.561}$. The blue line is a fit of calculated hydrodynamic radii (R_H^{oCAL}) of precursor polymers giving exponent value of υ = 0.58 denoting extended coil state of polymer. Closed red circles represent calculated hydrodynamic radii (R_H^{CAL}) of photodimerized polymer according to the formula R_H^{CAL} (nm) = R_H^{oCAL} $(1-f)^{0.6}$. A linear fit (red line) of calculated hydrodynamic radii (R_H^{CAL}) of photodimerized polymer gives exponent value of υ = 0.53 denoting folded state of polymer. Open red circles represent R_H values (R_H^{VIS}) as determined from viscometer signal in SEC measurements, that also shows similar folding states. Closed orange circles represent calculated hydrodynamic radii of compact globular conformation of the polymer calculated according to the formula: $R_H^{\varphi=1} = [3M_w/(4\pi\,\varphi\rho N_A)]^{1/3}$ with $\varphi = 1$ and $\rho = 1.05$ g/cm^3. The orange solid lines shows linear fit of calculated hydrodynamic radii (R_H^{φ}) of complete ($R_H^{\varphi=1}$) globular state of polymers with exponent value of υ = 0.32. (B) Dynamic light scattering studies of the polymer **P2** showing hydrodynamic radii in THF, chloroform and DMF.

4. Monitoring photodimerization by UV spectroscopy:

The polymers were dissolved in THF, $CHCl_3$ and DMF and monitored for decrease in absorbance at 300 to 350 nm with increase in exposure to UV irradiation at 320 nm with different time of exposure. Photodimerization Degree, PD= $(A_o-A_t)/A_o$, %PD= $(A_o-A_t)/A_o$ *100 where A_t is absorbance at time t and A_o is initial absorbance.

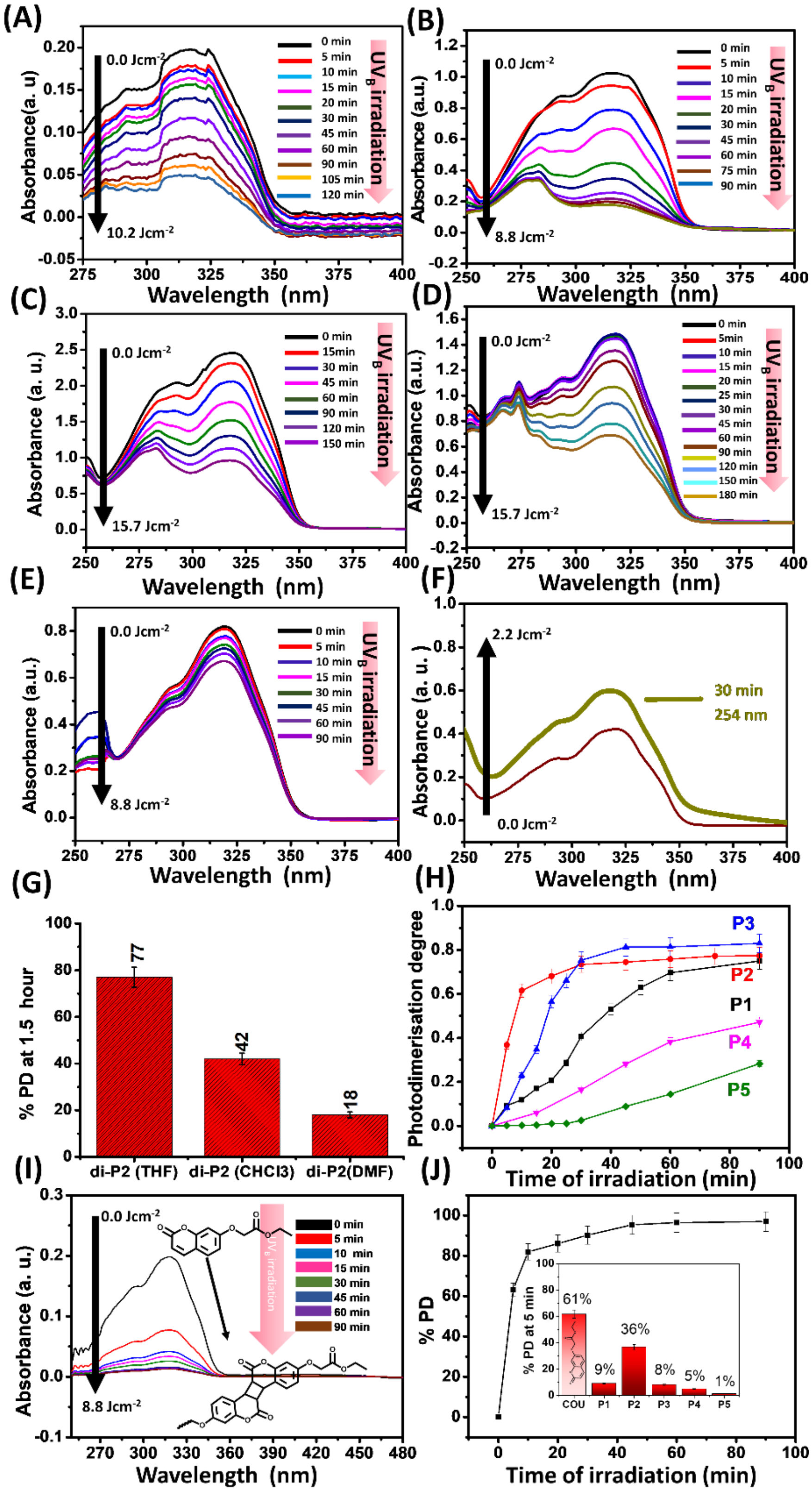


Fig. S2: UV spectroscopy data showing photodimerization of the polymers **P1**-**P5** upon irradiation with UV$_B$ light (λ_{max} = 320 nm). (A) **P1** (B) **P3** (C) **P4** (D) **P5** in THF and (E) **P2** in DMF solvent (concentration 0.01 mM). (F) Retrieval of absorbance for **P2** in the range of 300-350 nm after UV$_C$ irradiation (λ_{max} = 254 nm) for 30 min. (G) Bar diagram showing photodimerisation degree (%PD) of **di-P2** polymer in different solvents *e.g.* THF, CHCl$_3$ and DMF after UV irradiation for 1.5 h. (H) Graph showing photodimerization degree (PD) of different polymers in THF at different time intervals of UV$_B$ irradiation. (UV$_B$ lamp 2x8W). (I) UV spectroscopy data showing photodimerization of the coumarin ethyl acetate ester (Small molecule analouge) upon irradiation with UV$_B$ light (λ_{max} = 320 nm) showing faster kinetics as compared to the polymers. (J) Graph showing percentage photodimerization degree (% PD) of coumarin ethyl acetate ester in THF at different time intervals of UV$_B$ irradiation. (Inset showing comparison of % PD of the polymers after UV irradiation for 1.5 h).

Photodimerization degree (PD) values obtained from UV studies were used in Eq 1 and 2 to obtain the first- and second-order kinetics of photodimerizaton respectively:

$$\ln[1/(1-PD)] = k_1 t \qquad (1)$$

$$[1/(1-PD)] = ck_2 t + 1 \qquad (2)$$

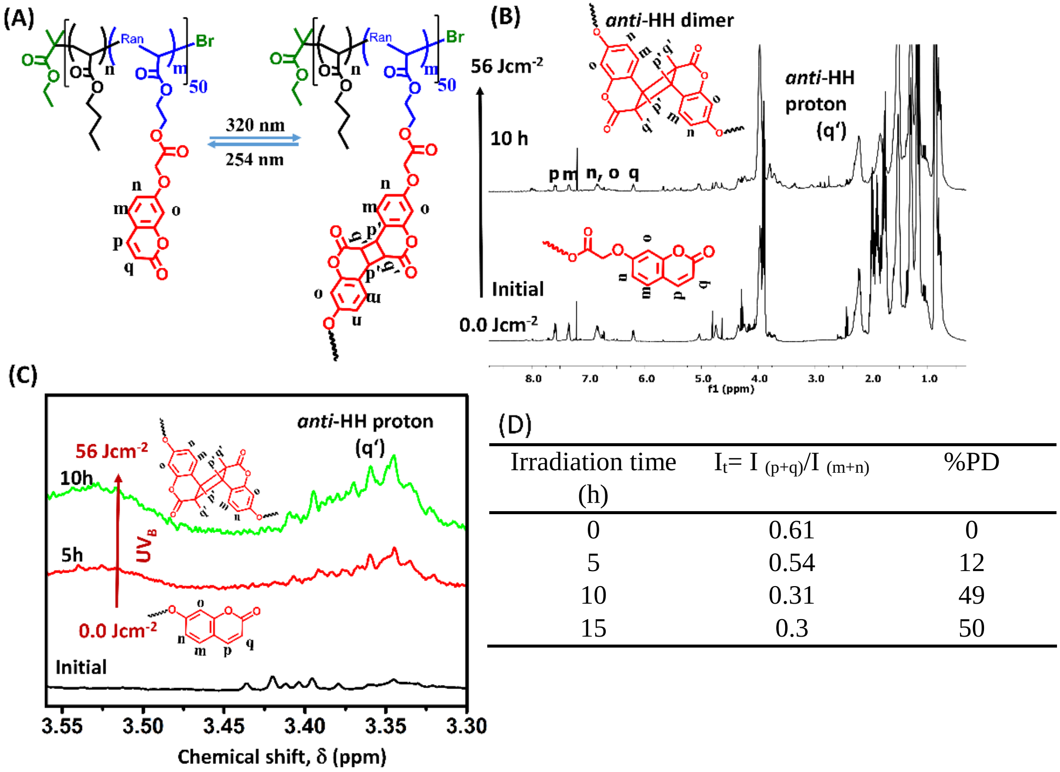
where c the initial concentration of coumarin groups i. e. 0.01 mM, k_1 and k_2 rate constant of the first- and second-order kinetics of photodimerizaton. The polymers **P1-P5** and the small molecular analougue of coumarin exhibits greater regression coefficients for the second-order plots than those of the first-order ones confirming second order kinetics for photodimerization. Hence, the rate constants calculated from the second-order kinetics are listed in Table S1. In general, the rate constants depends on the polymer chain length and % of coumarin functionality

Table S1: Rate constant for second order kinetics of photodimerization in THF

	Rate constant, $K_2 \times 10^2$ ($mM^{-1}min^{-1}$)	**R^2**
P1	3.2	0.98528
P2	4.9	0.93634
P3	6.7	0.95813
P4	1	0.99803
P5	0.3	0.99716
Coumarin ester	39	0.98032

5. Monitoring photodimerization by ^{1}H NMR:

^{1}H NMR spectra for 1 mM solution of the polymer (**P2**) in $CDCl_3$ was recorded. Further, the solution was exposed to UV_B irradiation in the NMR tube and spectra was recorded at different time intervals (5h, 10, 15h). The photodimerization degree (PD) was calculated according to the formula %PD= $\{(I_o-I_t)/I_o\}$x100, $I_t = I_{(p+q)}/I_{(m+n)}$, where I_{p+q} and I_{m+n} is integration area of p, q, m, n protons, I_t is the ratio of integral area of p+q with m+n protons at a specific time of irradiation (t). I_o is the ratio of integral area of p+q with m, n protons for the native polymers.



Irradiation time (h)	$I_t = I_{(p+q)}/I_{(m+n)}$	%PD
0	0.61	0
5	0.54	12
10	0.31	49
15	0.3	50

Fig. S3: Monitoring photodimerization by ^{1}H-NMR spectroscopy. (A) Stuctural changes as a result of [2π + 2π] photodimerization of coumarin moiety in polymer to form cyclobutane adduct with table showing integral ratio $I_t = I_{(p+q)}/I_{(m+n)}$, %PD= $\{(I_o-I_t)/I_o\}$x100 as calculated from ^{1}H-NMR spectra. (B) Full and (C) Expanded region of ^{1}H NMR spectra showing increase in anti-HH dimer proton signal at δ 3.30-3.6 ppm. (^{1}H-NMR studies in $CDCl_3$, UV irradiation at 1 mM concentration in THF (2x8W UV_B lamp, λ_{max} = 320 nm) (D) Table showing change in integral ratio as well as % PD along with time of irradiation

6. Monitoring photodimerization by SEC:

100 µL of 6 mg/ml solution of **P2** in THF was injected and run at a flow rate of 1 mL/min using THF as eluent at 35 °C. The same sample was irradiated with UV_B light (2x8W) and was analysed by SEC after different time of irradiation (2, 4, 6, 8h). The SEC traces (normalised RALS signals) showed an increase in retention time corresponding to compaction of size of the polymer structure which directly corresponds to chain collapse due to photodimerization.

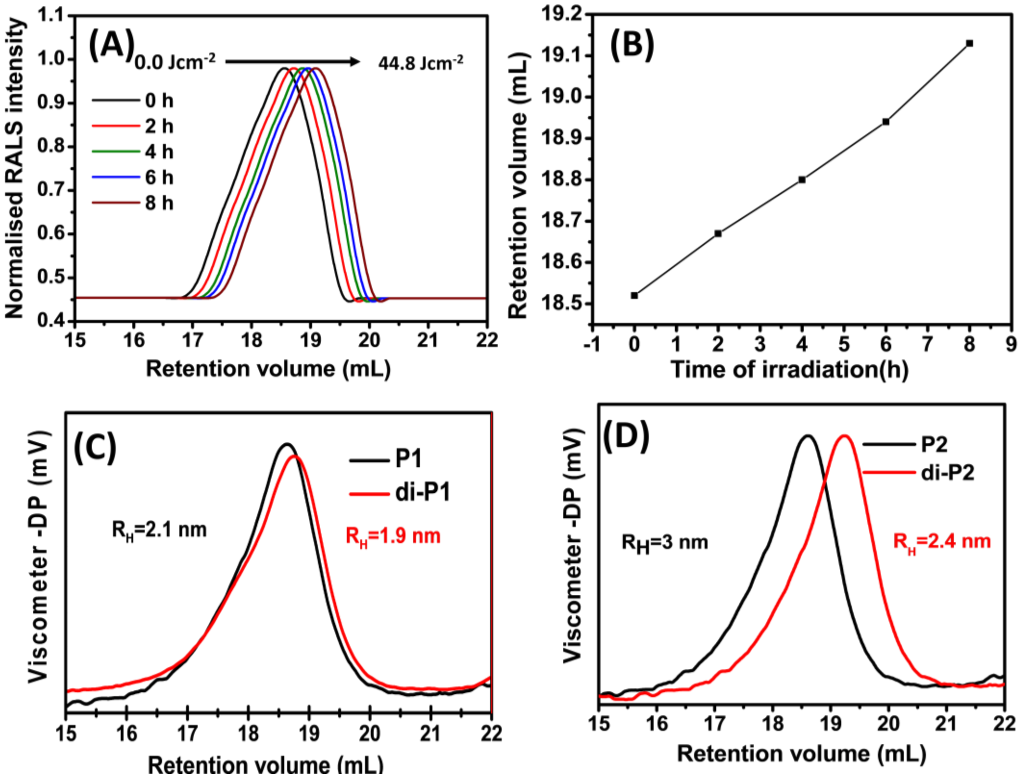


Fig. S4: Monitoring photodimerization using SEC traces of **P2** with time of irradiation. (A) Normalised RALS signal showing increase in retention volume that corresponds to compaction of polymer chain coil. (B) Graph showing gradual change in retention time of the peak against the time of irradiation. SEC analyses showing delay in retention volume upon UV irradiation of polymer sample (C) **P1** (D) **P2** (Irradiation of sample solution (c = 6 mg/mL) in THF with 2x8W UV_B lamp, 4h)

7. Monitoring chain collapse by DLS:

Dynamic light scattering measurements were done on Malvern Zetasizer Nano ZS ZEN3600 equipped with a Helium-Neon laser (wavelength, λ= 633 nm with backscattering angle of 173°. 6 mg/mL solution of **P1-P5** in THF (2 mL) and was filtered through a 0.2 µm PTFE-filter in a glass cuvette with a path length of 1 cm. The same samples were irradiated with UV_B light (2x8W) and was analysed by DLS after 4 h of irradiation.

Table S2: DLS data for native and irradiated polymer of **P1-P5**

Polymer	**R_H^{oDLS} (nm)^a**	**R_H^{DLS} (nm)$_b$**	**% Compaction**
P1	9	5	0.44
P2	20	10	0.5
P3	12	5	0.58
P4	60	43	0.28
P5	104	83	0.2

[a] Hydrodynamic radii of native polymer solution in THF (6 mg/mL) as seen in DLS [b] Hydrodynamic radii of polymer solution in THF (6 mg/mL) after irradiated with UV_B light (2x8W) for 4 h

8. Visualisation of nanostructures by Atomic Force Microscopy:

A. AFM Scanning and Histogram analysis: AFM images of polymer samples showed a clear distinct differences in structural signatures from highly diverse nanostructures of considerably variable long height (20 nm) to nearly uniform nanoellipsoidal structures of short height (Fig S5A-F). The size distributions of the nanoparticles were analyzed 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 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.

$$R_w = \frac{\sum_{i=1}^{n} N_i R_i^2}{\sum_{i=1}^{n} N_i R_i} \quad (1), \quad R_n = \frac{\sum_{i=1}^{n} N_i R_i}{\sum_{i=1}^{n} N_i} \quad (2),$$

$$PDI = \frac{R_w}{R_n} \quad (3)$$

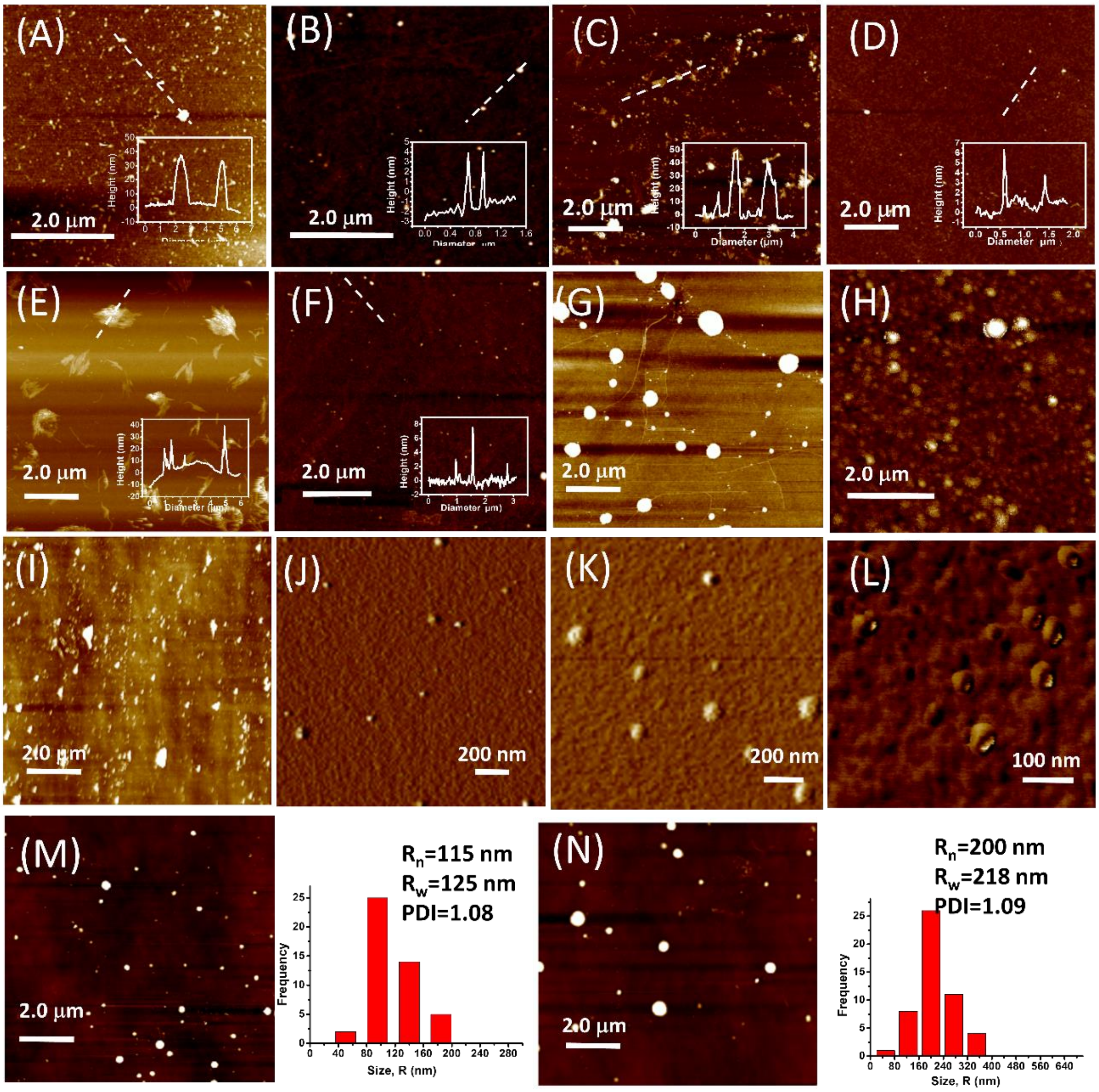


Fig S5: AFM Height images of polymer **P1** (A) before and (B) after, polymer **P2** (C) before and (D) after, polymer **P3** (E) before and (F) after UV_B irradiation in THF (Inset has corresponding height profiles of corresponding nanostructures) AFM Height images of polymer **P2** (G) before and (H) after 3h of UV_B irradiation in $CHCl_3$. (I) AFM Height images of native polymer **P2** (c = 10^{-3} mg/mL) in DMF solvent. AFM phase images of selected zoomed area of (J) **di-P1** in THF, (K) **di-P2** in THF, (L) **di-P3** in THF. AFM Height images of irradiated polymer samples and their corresponding histograms (M) **di-P4** in THF, (N) **di-P5** in THF. Iradiation of all the samples were conducted at a concentration of 10^{-3} mg/mL using 2 UV_B lamps for 3h.

B. Spherical diameter from the hemi-ellipsoidal particle adsorbed on silicon surface

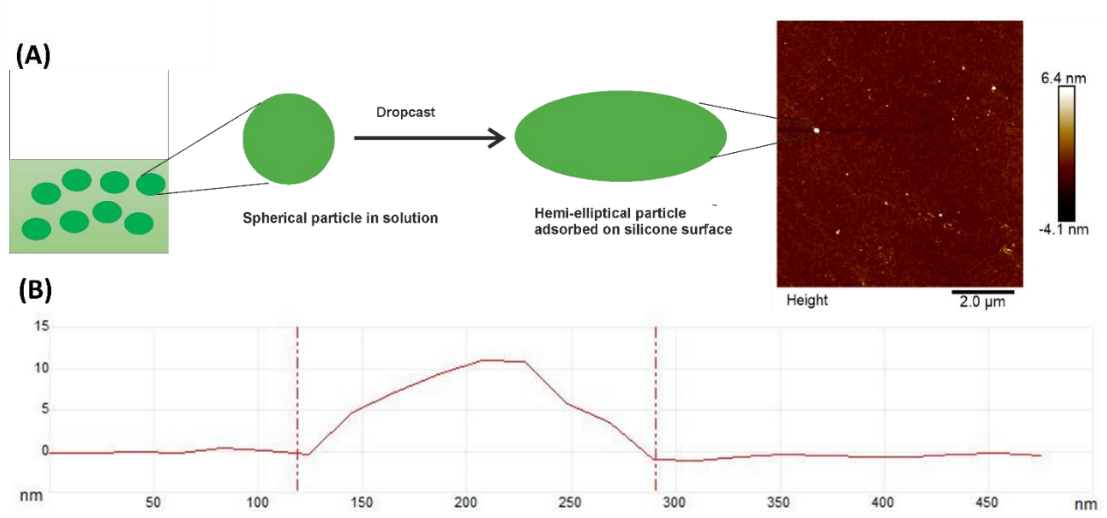


Fig. S6: Determination of spherical radii from half ellipsoid particle adsorbed on silicon wafer surface (A) Schematic representation of spherical nanoparticles drop-casted on silicon wafer forming half ellipsoid shape due to surface adsorption and a representative AFM image showing nanoparticles from **P2** polymer. (B) Height profile of a selected nanoparticle from the same AFM image.

Example: Calculation of spherical diameter from half volume of ellipsoidal particle adsorbed on silicone surface[S6]

$$V = 1/2 \text{ x } 4/3 \text{ x } \pi \text{ x } R_{he}^2 \text{ x } h$$

Where R_{he} = radii of the hemiellipsoid from the AFM, h = height from AFM (in nm)

R_{he} = 49 nm, h = 9 nm

$$V = 0.5 \text{ x } 4/3\text{x } \pi \text{ x } (49^2) \text{ x } 9$$

$$V = 10804 \text{ nm}^3$$

$$\text{Volume of a sphere} = 4/3 \text{ x } \pi \text{ x } R_{sph}^3$$

$$4/3 \text{ x } \pi \text{ x } R^3 = 10804 \text{ nm}^3$$

$$R_{sph} = 22.5 \text{ nm}$$

C. Concentration dependant nanostructure formation

The polymer samples **P1-P5** in different concentrations of 10^{-3} mg/mL (lower), 10^{-1} mg/mL (intermediate), 1 mg/mL (higher) in THF, DMF, chloroform were irradiated by UV_B light.

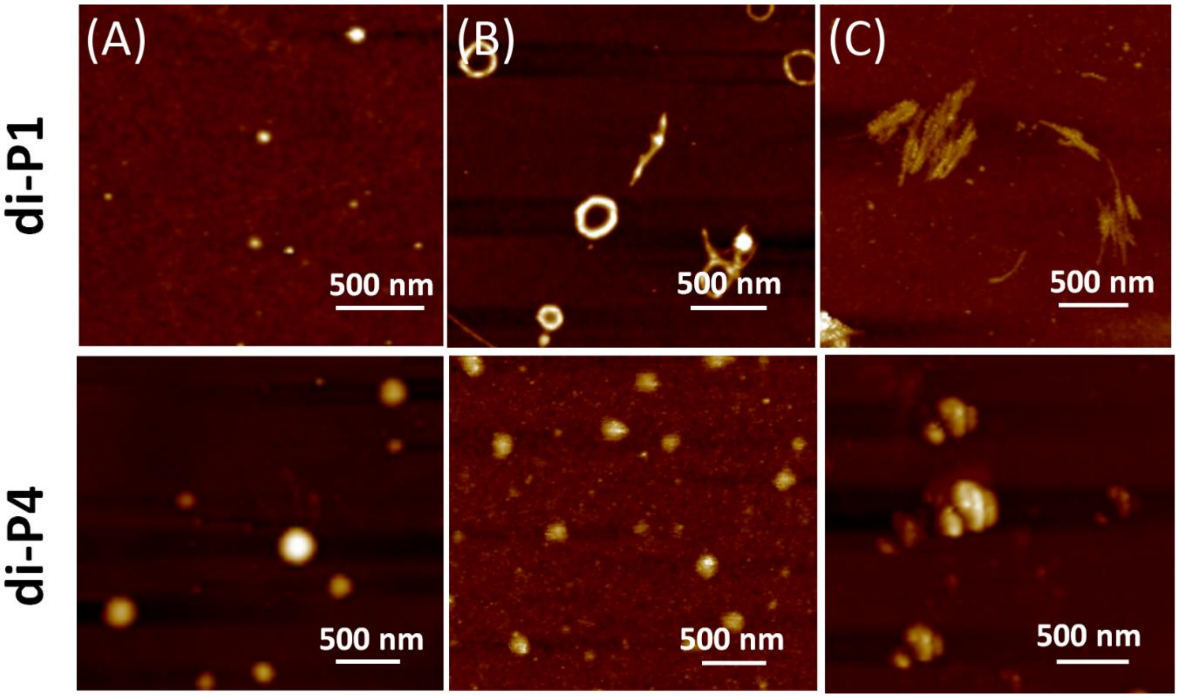


Fig. S7: Scheme depicting concentration dependent nanostructures formation as a result of crowding of polymer chains. Diverse nanostructures as observed from AFM images of the polymers **di-P1** and **di-P4** with different concentration A, B, C at 0.001 mg/mL, 0.1 mg/mL, at 1 mg/mL in THF respectively. (Irradiation with 2x8W UV_B lamp, 3 h).

9. Thermal studies by differential scanning calorimetry

Thermal studies of polymer samples were performed on Perkin Elmer Differential Scanning Calorimeter DSC 8000 model and the samples were heated from -80 to 150 ºC at a heating rate of 10 ºC. Thermal studies of the dried polymer films were analyzed for the glass transition temperature (T_g) that corresponds to the chain mobility of the polymer. Dried polymer film which casted on a glass substrate was crosslinked by exposure to UV_B irradiation at (λ_{max} = 320 nm, UV_B lamp) for 15h (84 J cm^{-2}). Further the crosslinked sample was exposed to UV_C irradiation (λ_{max} = 254 nm, UV_c lamp) for 5 h (15 J cm^{-2}) for decrosslinking.

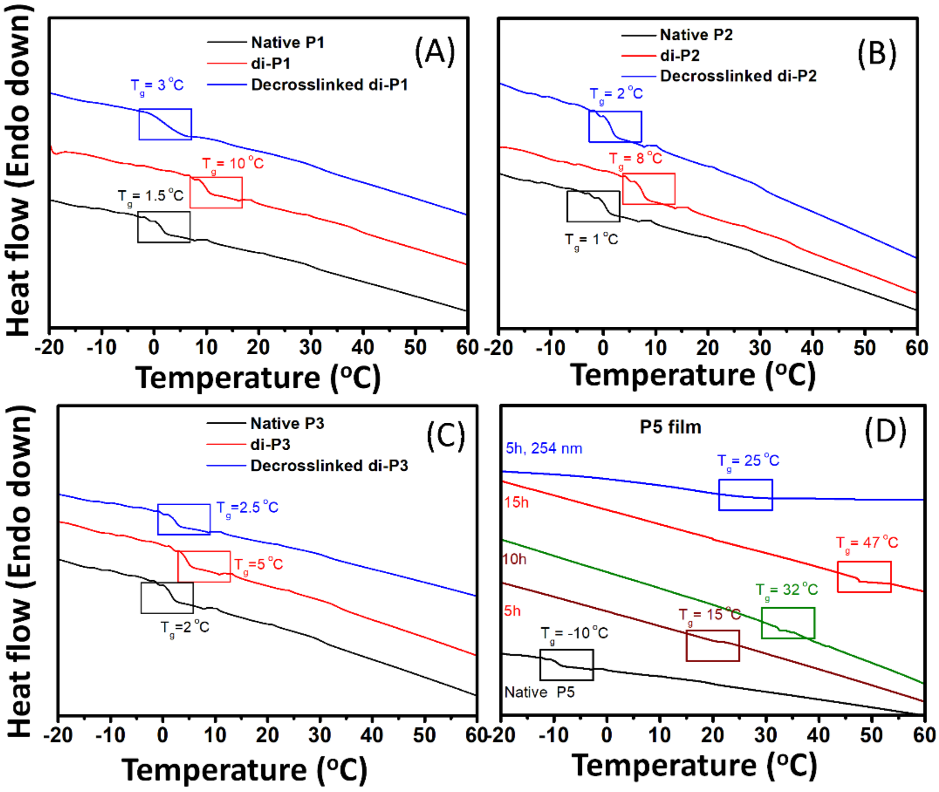


Fig. S8: Differential Scanning Calorimetry traces of different samples from polymer film showing glass transition temperature (T_g) for native (black line), crosslinked (red line), decrosslinked (blue line) polymers of (A) **P1** (B) **P2** (C) **P3.** (D) DSC traces of **P5** polymer film at different time period of irradiation and (E) table showing summary of T_g values for different polymer samples at native, crosslinked and decrosslinked conditions.

Table S3: DSC data of different polymers of P1-P5

Polymer	$T_{g\ Native}$ (ºC)	$T_{g\ crosslinked}$ (ºC)	$T_{g\ decrosslinked}$ (ºC)
P1	1.5	10	3
P2	1	8	2
P3	2	5	2.5
P4	-3	15	1
P5	-10	47	25

10. UV studies on polymer film

Samples from the polymer **P5** film used for DSC which was irradiated at different time point of irradiation was used for solid UV studies. The polymer film was crosslinked by UV$_B$ irradiation for 15 h and analysed at different time point of irradiation at 0h, 5h, 10h, 15h taking a common weight of 1mg. Additionally the crosslinked polymer sample was irradiated with UV$_C$ irradiation for 5h (decrosslinking). Degree of photodimerization, PD= $(A_o-A_t)/A_o$, %PD= $(A_o-A_t)/A_o$ x 100, where A_t is absorbance at time t and A_o is initial absorbance.

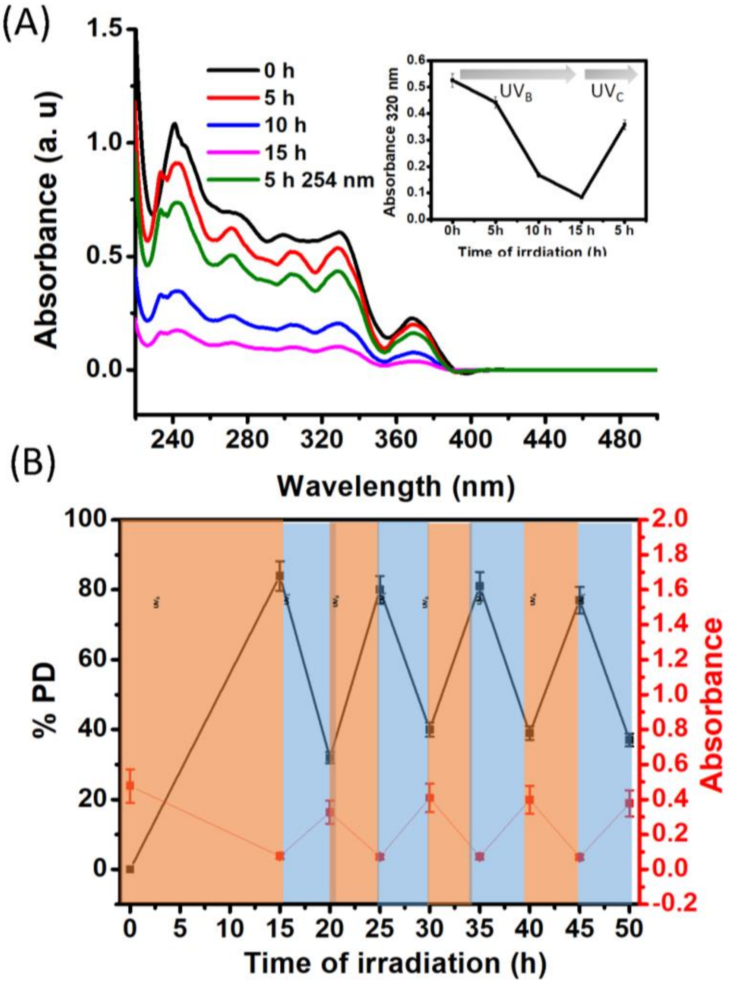


Fig. S9: (A) UV studies of polymer **P5** film showing absorbance of coumarin moiety on irradiation with UV$_{\mathbf{B}}$ (crosslinking) and UVc light (decrosslinking) at different time intervals of irradiation. Inset showing change in absorbance at 320 nm with different time intervals of irradiation. (B) Reversible photodimerization of the coumarin moieties as exhibited by % PD and absorbance values at 320 nm in **P5** polymer film renders consecutive crosslinking/decrosslinking performed for four cycles. After initial irradiation with UV$_B$ for 15 h to prepare the cross-linked network, the film was irradiated with consecutive UV$_C$ (λ_{max} = 254 nm) for 5 h and UV$_B$ (λ_{max} = 320 nm) for 5h upto 4 cycles.

11. Self-healing studies by optical microscopy

Polymer solution (20 mg/mL in DCM) was drop-casted on a glass substrate and dried overnight. Scratches made at a micron level with a surgical knife and investigated for the self-healing with the aid of a bright field optical microscope. The scratches exhibited autonomic self healing within a few minutes. Further, the polymer films were exposed to UV_B irradiation and crosslinked which showed delayed and incomplete healing of the scratches. Thus, while native polymer **P5** showed complete healing within 3 min, a photocrosslinking of **P5** polymer for 5 h, 10, 15 h rigidify the polymers and delay the healing with reduced % of self-healing efficacy. Interestingly, UV_C irradiation upon the crosslinked polymer film photo-trigger the switch on the self healing behavior of the scraches mediated by [2+2] decycloaddition of the coumarin moieties. 2x8W UV_B Lamps and 1x8W UV_c Lamps were used for crosslinking and decrosslinking the polymer. The width of the scratches were determined using image-J software, from the U.S. National Institutes of Health. 10 random width areas were selected from different areas of the scratches in the images.The average width W_n, percentage healing efficency (%H) was calculated using equation 1-2 given in experimental section in main text, where N_i is the number of width W_i and N is the number of width areas examined in each sample.

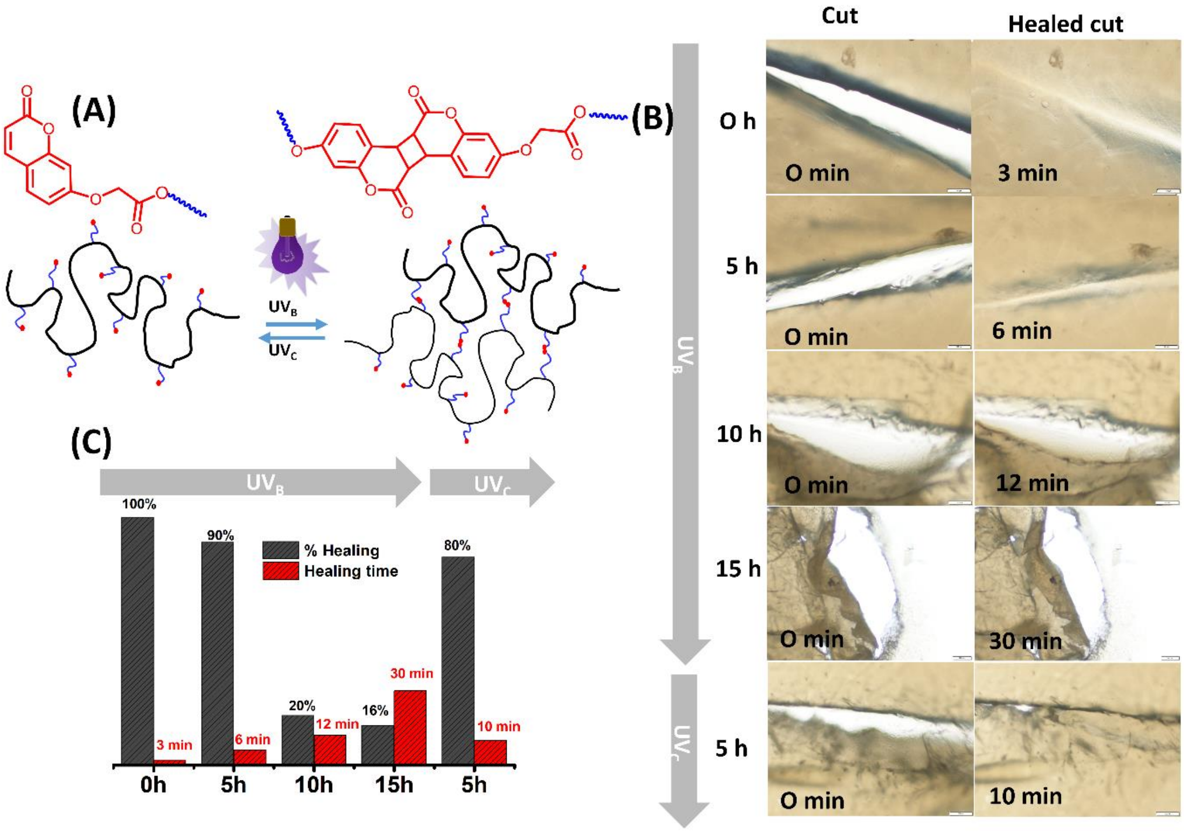


Fig. S10: (A) Schematic representation depicting [2π + 2π] cycloaddition of coumarin moieties mediated reversible crosslinking/decrosslinking of the polymer chain by exposure of UV_B and UV_c light. (B) Self-healing studies of the **P5** polymer films (irradiated with UV_B for increasing time of exposure, top to bottom) as observed bright field microscopic images showing healing of the scratches. (C) Bar graph representing the changes in % healing and healing time along with time of irradiation for polymer **P5**.

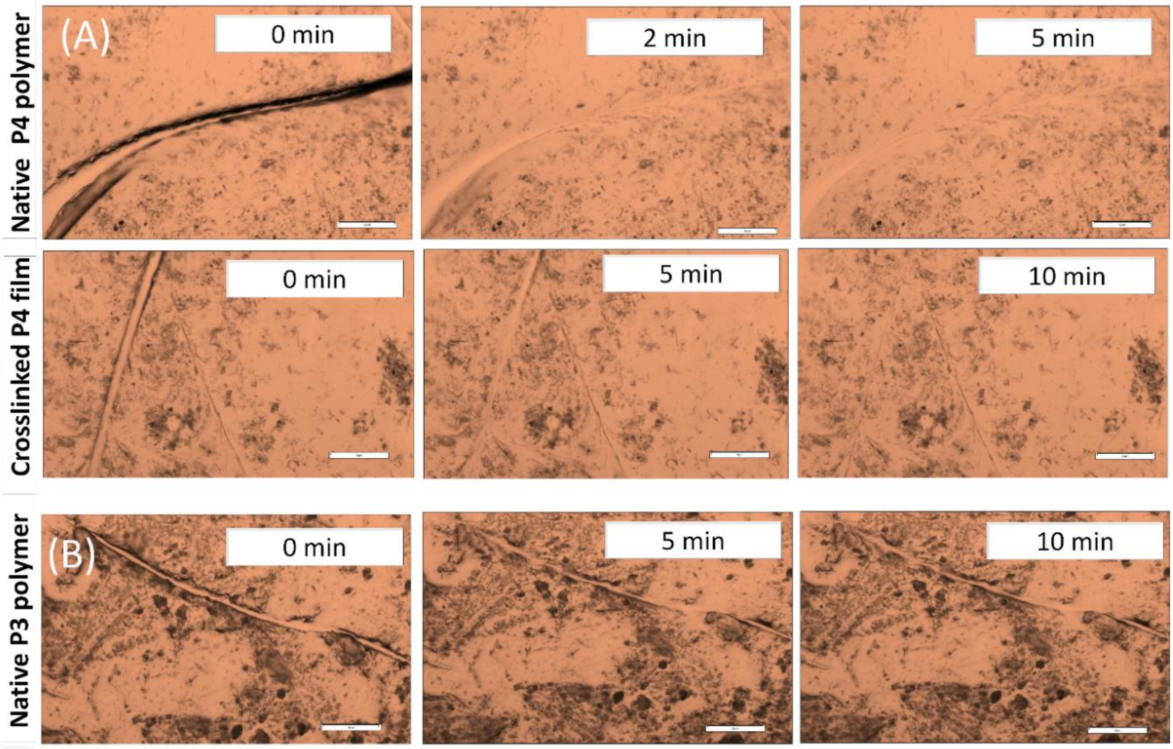


Fig. S11: (A) Self-healing of the scratch made on the films of native **P4** (size ~ 60 µm in width) (upper panel) and irradiated **di-P4** polymer (size ~ 20 µm in width) (lower). Native **P4** showed 80% healing of the scratch after 4 min and **di-P4** polymer showed 55% healing after 10 min (B) Self-healing studies of the films made from native **P3** polymer showed only 60% healing of the scratch (size ~ 8 µm in width) for native **P3** film (concentration = 20 mg/mL) even after 10 min.

11. References

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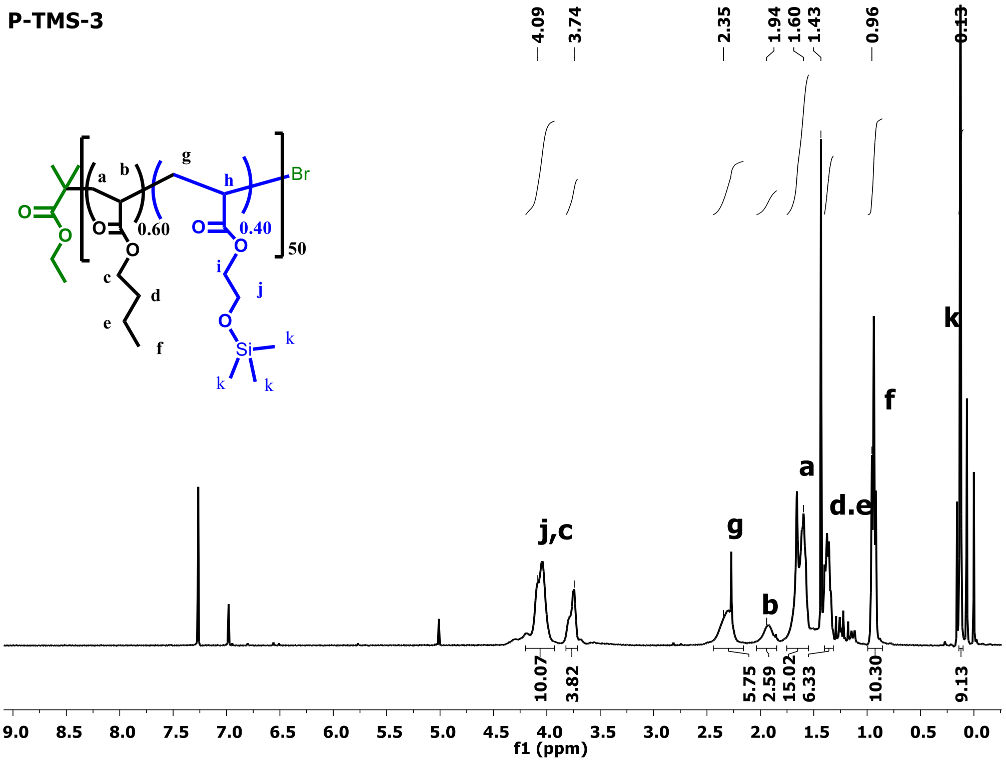
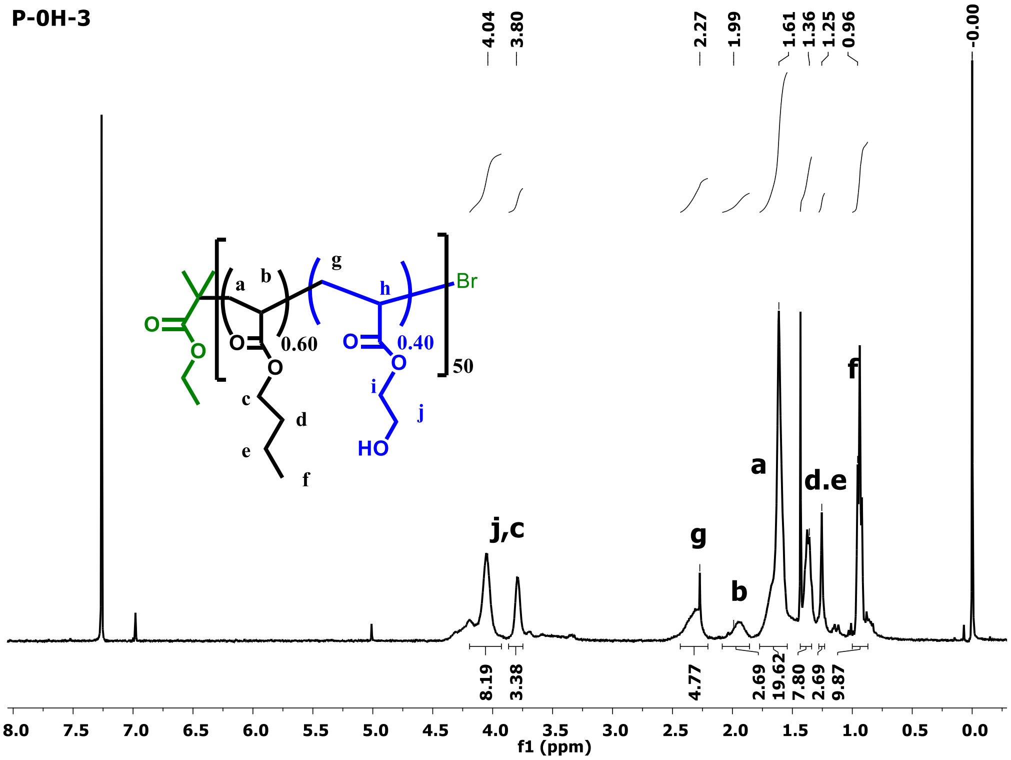
12. ^{1}H NMR characterization of polymers (CDCl$_3$, 400MHz)

a. Representative precursor polymers

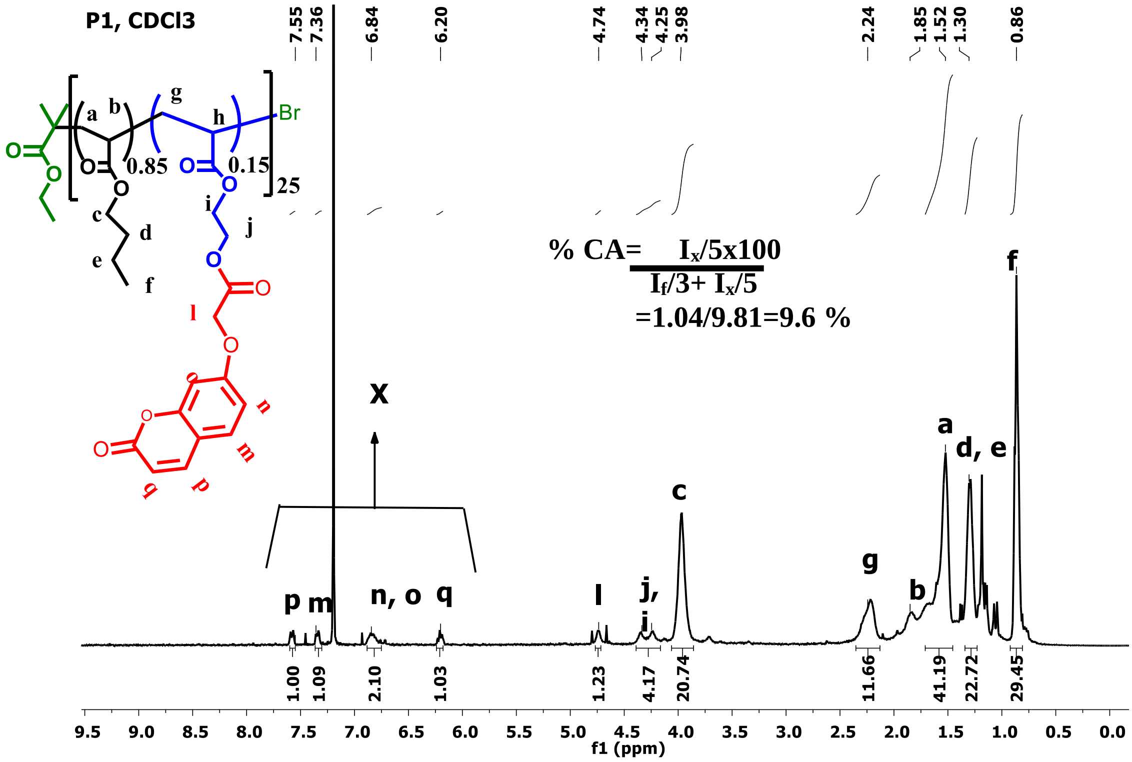
P-TMS-3

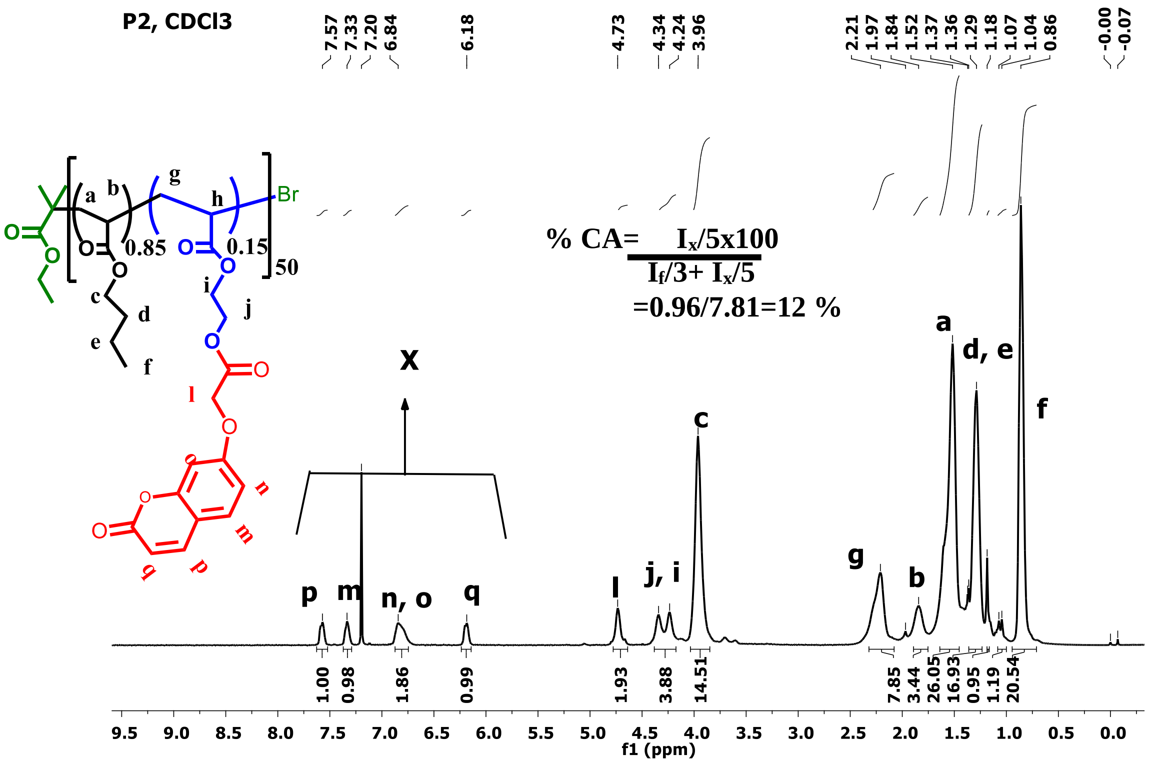


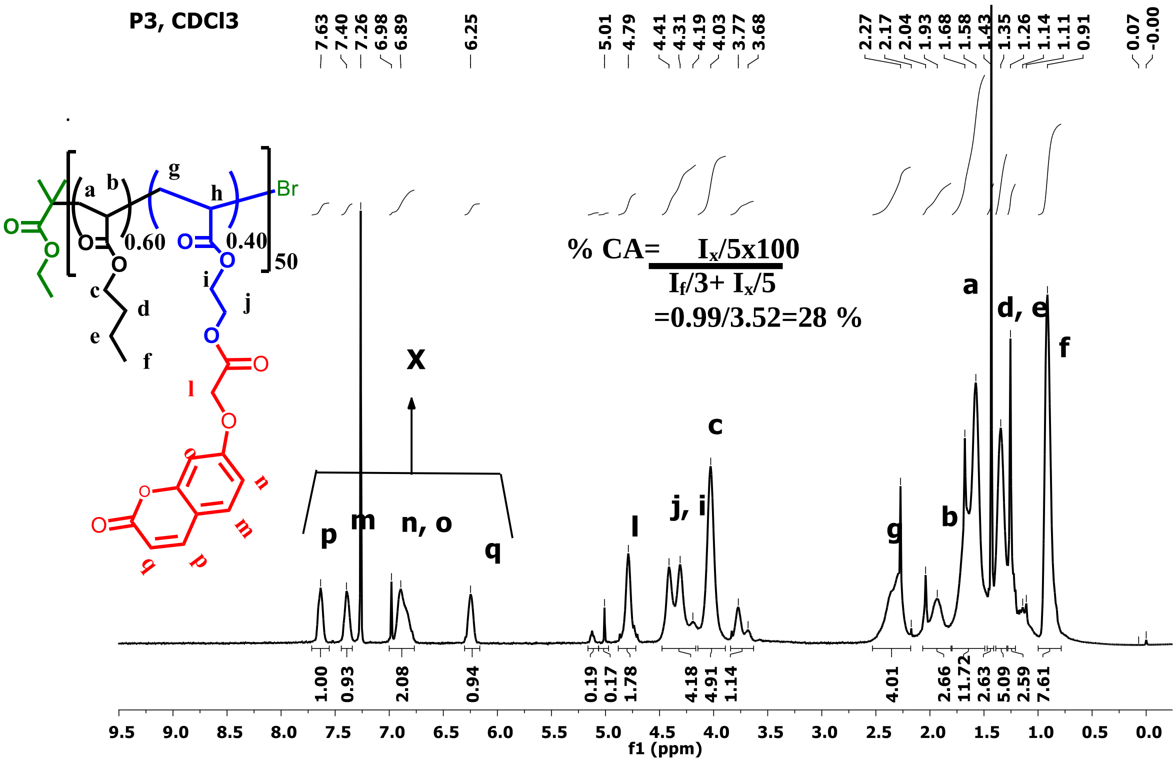
P-OH-3

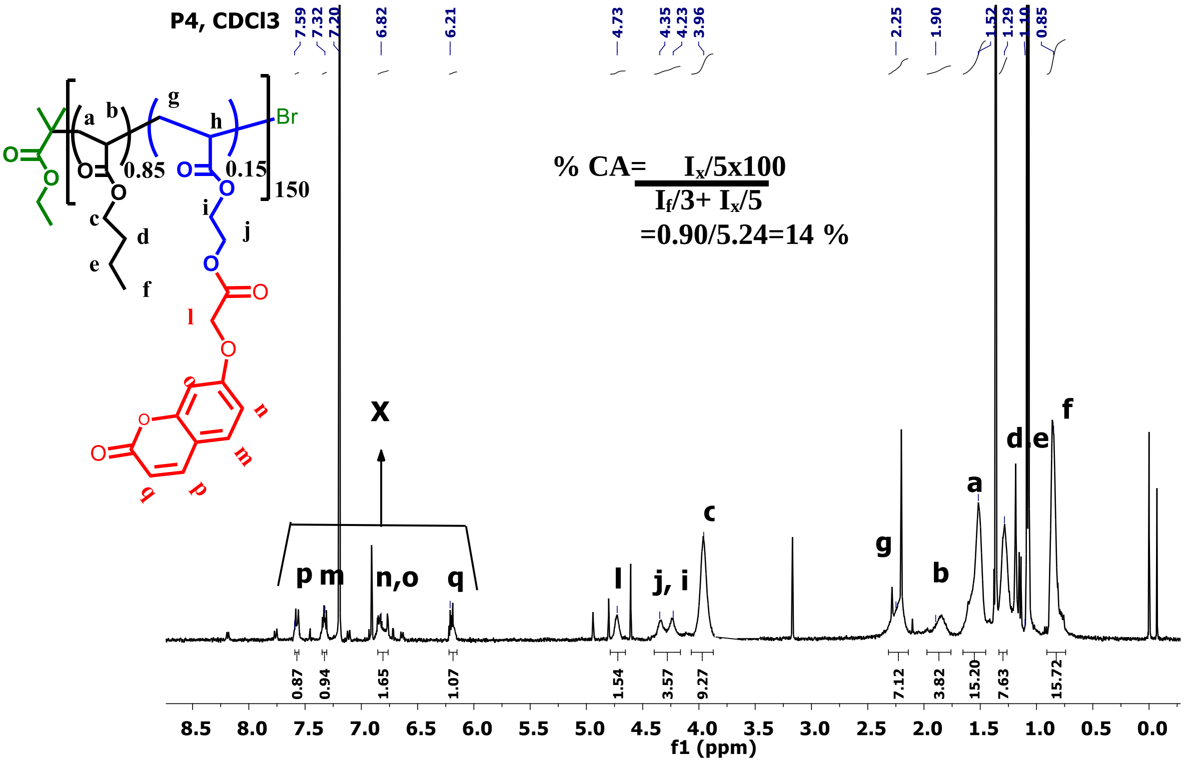


b. Final polymers






P3, CDCl3
7.63 7.40 7.26 6.98 6.89 6.25 5.01 4.79 4.41 4.31 4.19 4.03 3.77 3.68 2.27 2.17 2.04 1.93 1.68 1.58 1.43 1.35 1.26 1.14 1.11 0.91 0.07 -0.00
a b g h Br 0.60 0.40 50 c d e f i j l m n p q O
% CA= Ix/5x100 / (If/3+ Ix/5)
=0.99/3.52=28 %
X
p m n, o q l j, i c g b a d, e f
1.00 0.93 2.08 0.94 0.19 0.17 1.78 4.18 4.91 1.14 4.01 2.66 11.72 2.63 5.09 2.59 7.61
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


P4, CDCl3
7.59 7.32 7.20 6.82 6.21 4.73 4.35 4.23 3.96 2.25 1.90 1.52 1.29 1.10 0.85
a b g h Br 0.85 0.15 150 c d e f i j l m n p q O
% CA= Ix/5x100 / (If/3+ Ix/5)
=0.90/5.24=14 %
X
p m n,o q l j, i c g b a d e f
0.87 0.94 1.65 1.07 1.54 3.57 9.27 7.12 3.82 15.20 7.63 15.72
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

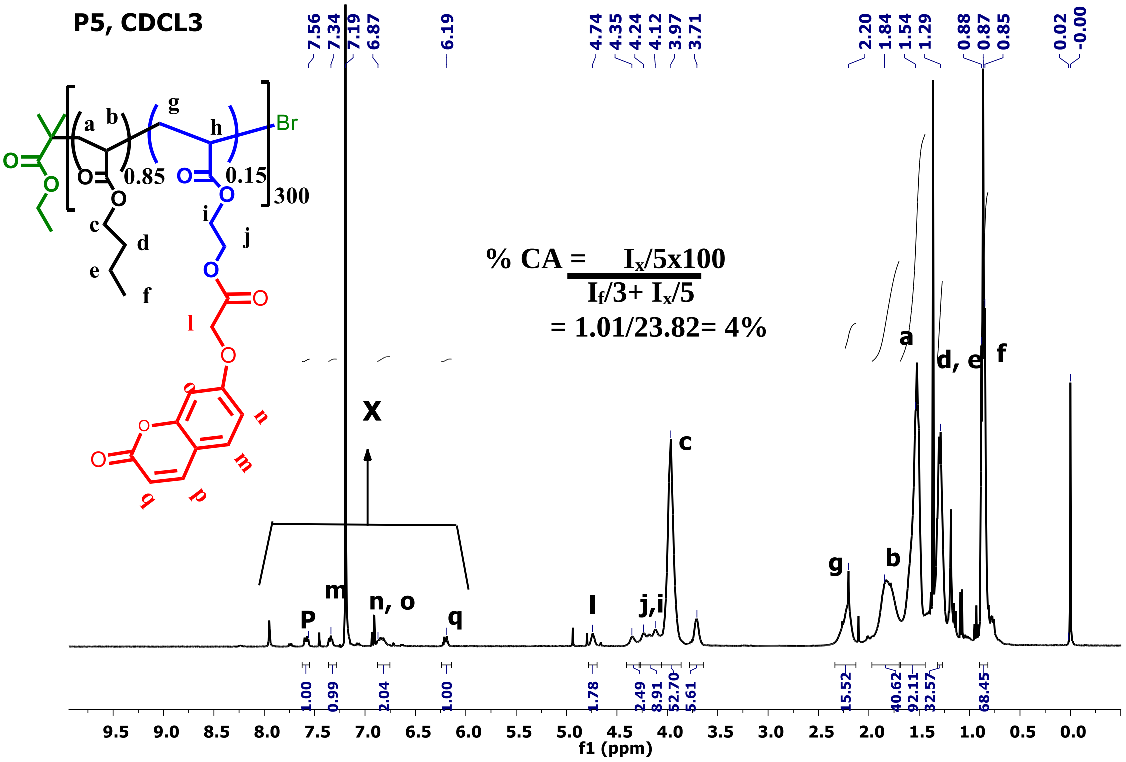


Table S1: Calculation of % functionality of polymers from integral area of ^{1}H NMR

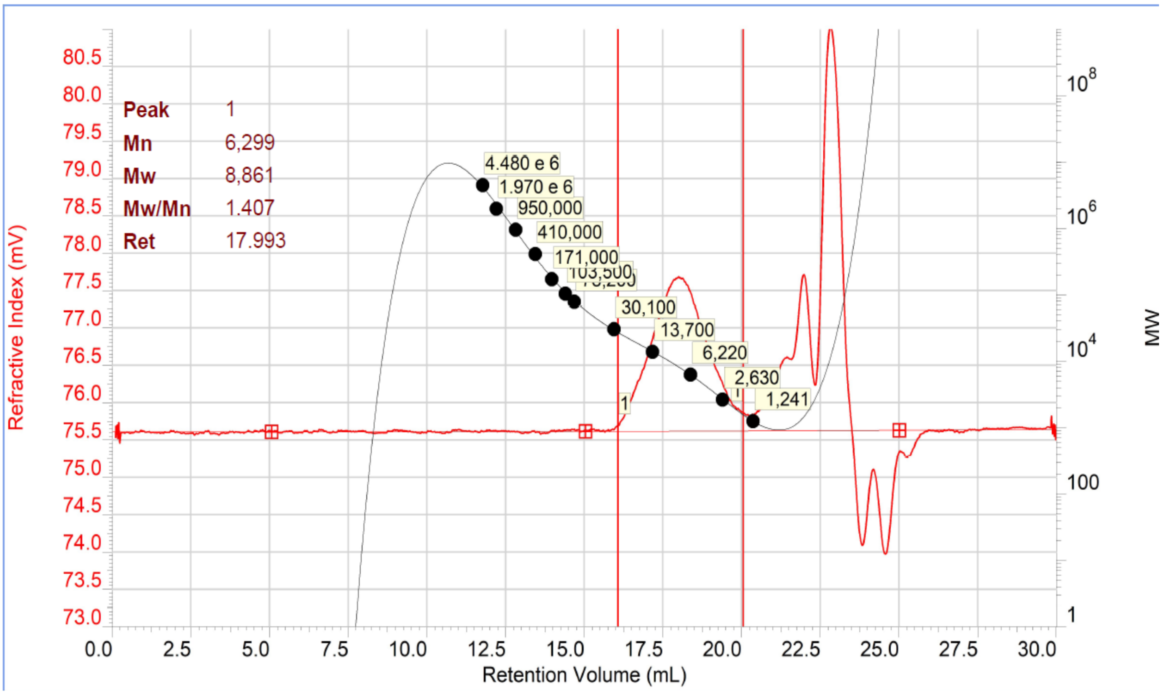
Polymer	I_x	I_f	$I_x/5$	$I_f/3$	% CA
P1	5.21	29.5	1.04	9.81	9.6
P2	5.73	20.5	0.96	7.81	12
P3	4.95	7.61	0.99	3.52	28
P4	4.53	15.7	0.90	5.24	14
P5	5.03	68.5	23.8	23.82	4

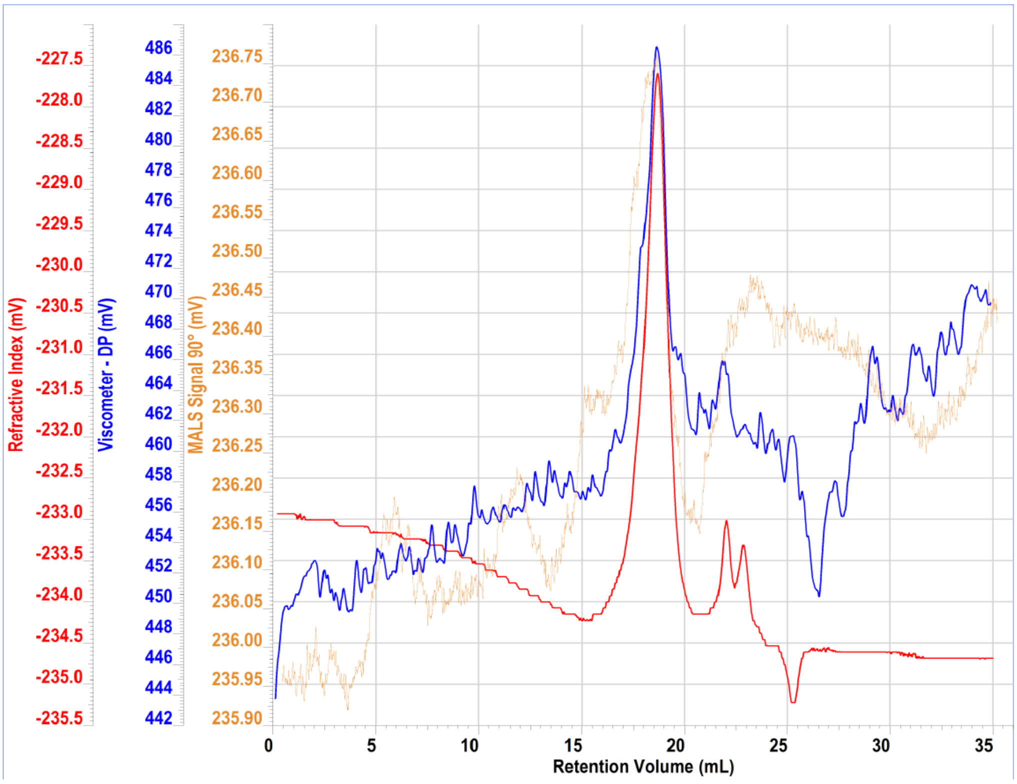
13. Size Exclusion Chromatography of the polymers

SEC measurement was perform on Malvern Viscotek instrument having RI, Right angle Light scattering (RALS), viscometer detector using T_{6000M}-T_{3000} column with THF as eluent at 35 °C at a flow rate of 1 mL/min. The results were analysed by using Omnisec software. The sample peaks were analysed for M_n, M_w PDI, IV as well as R_H by means of conventional calibration as well as triple detector universal calibration using polystyrene standards.

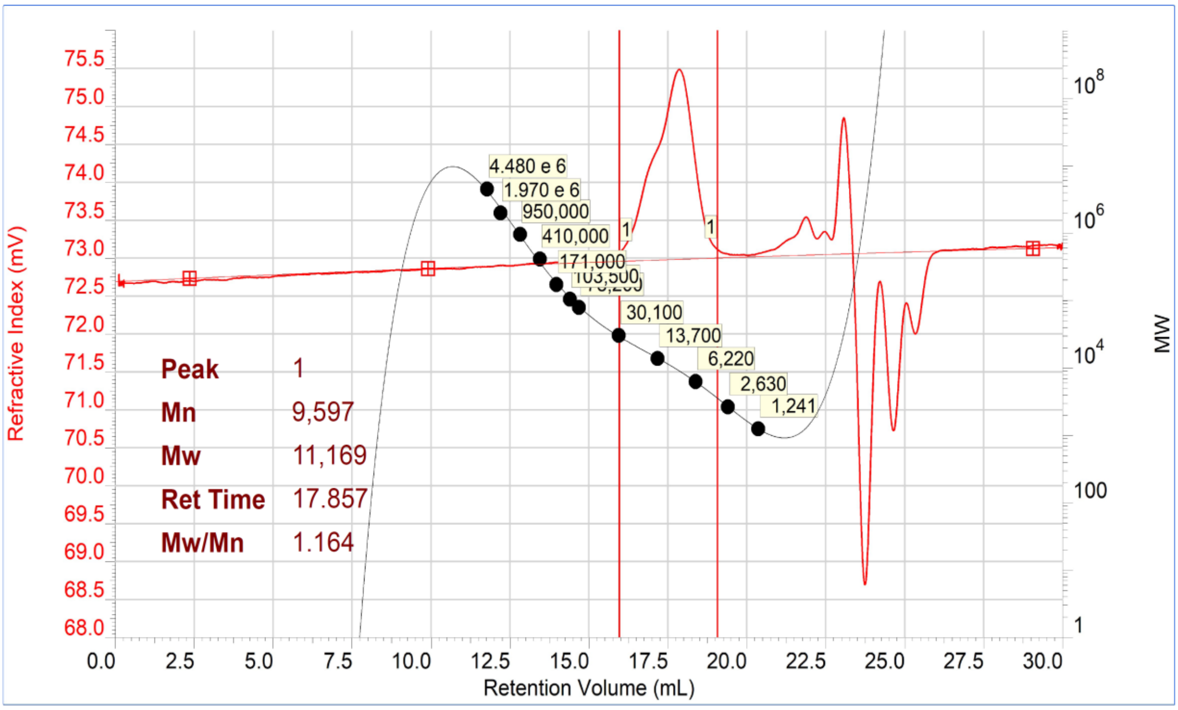
All the polymer samples were dissolved at a concentration of 5 mg/mL in THF and were shaking for 2-3 hours in order to ensure complete solubility of the polymers. Sample solution was then filtered through PTFE syringe while adding to the vial. 100 µL of the samples were injected and run at a flow rate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

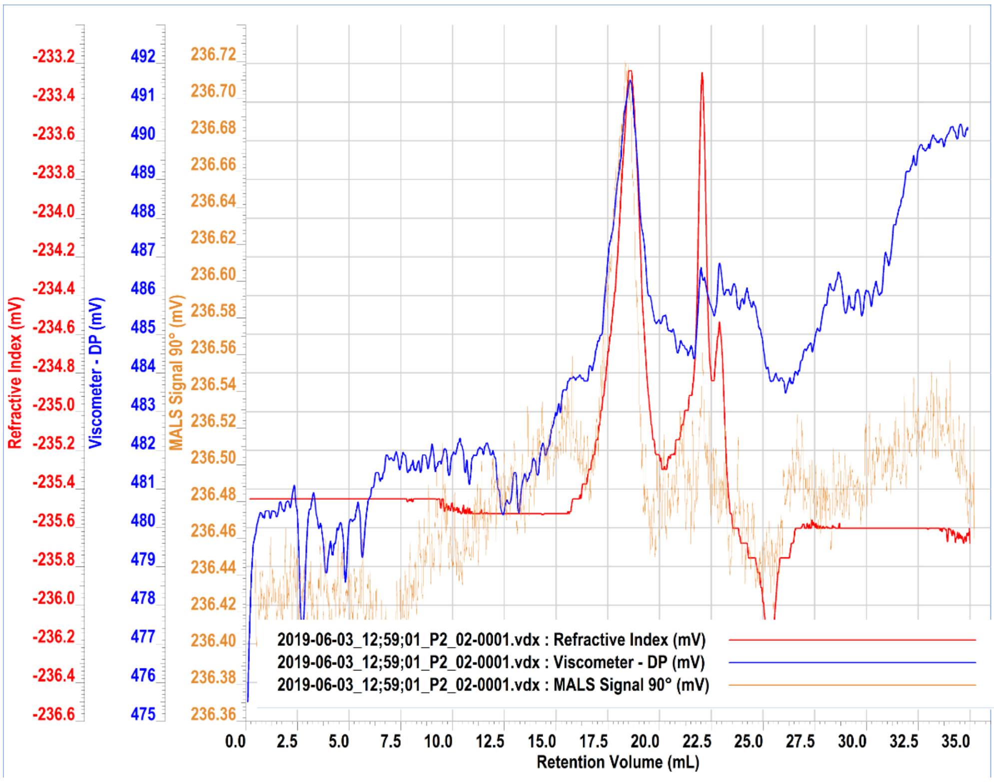
a. SEC curve of polymer P1:



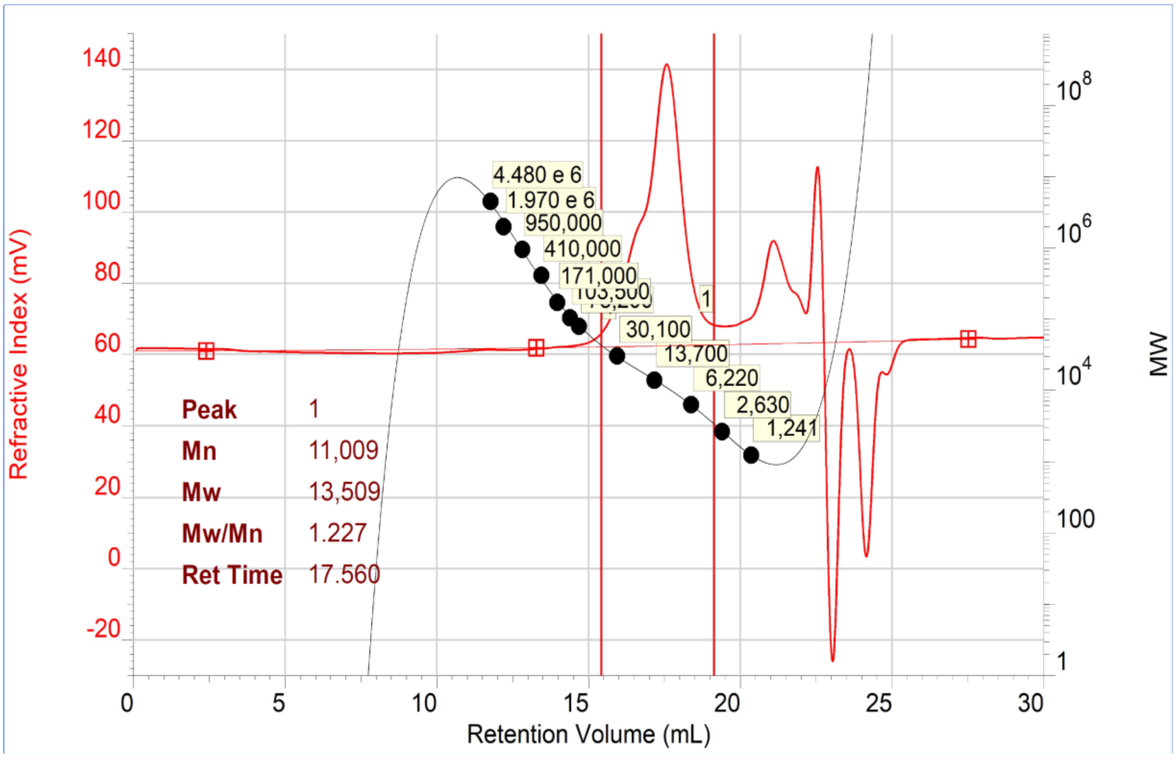


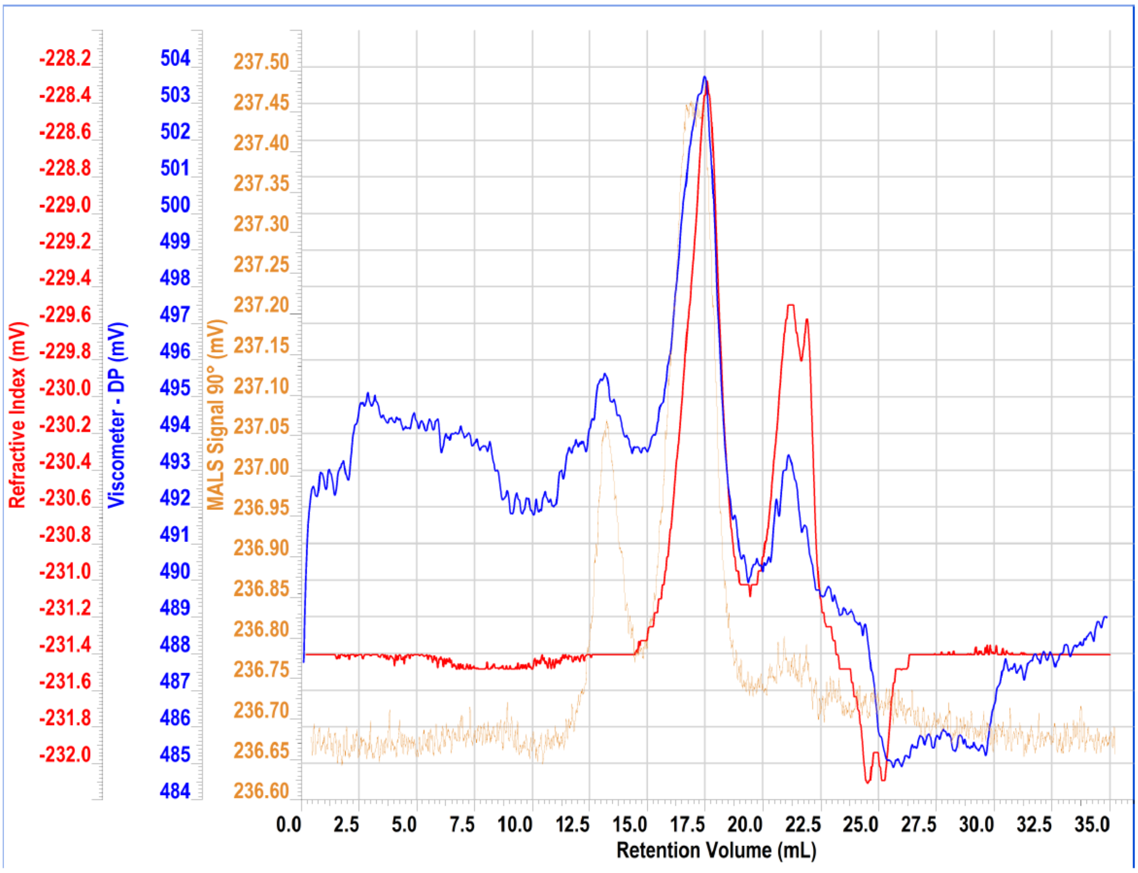
b. SEC curve of polymer P2:



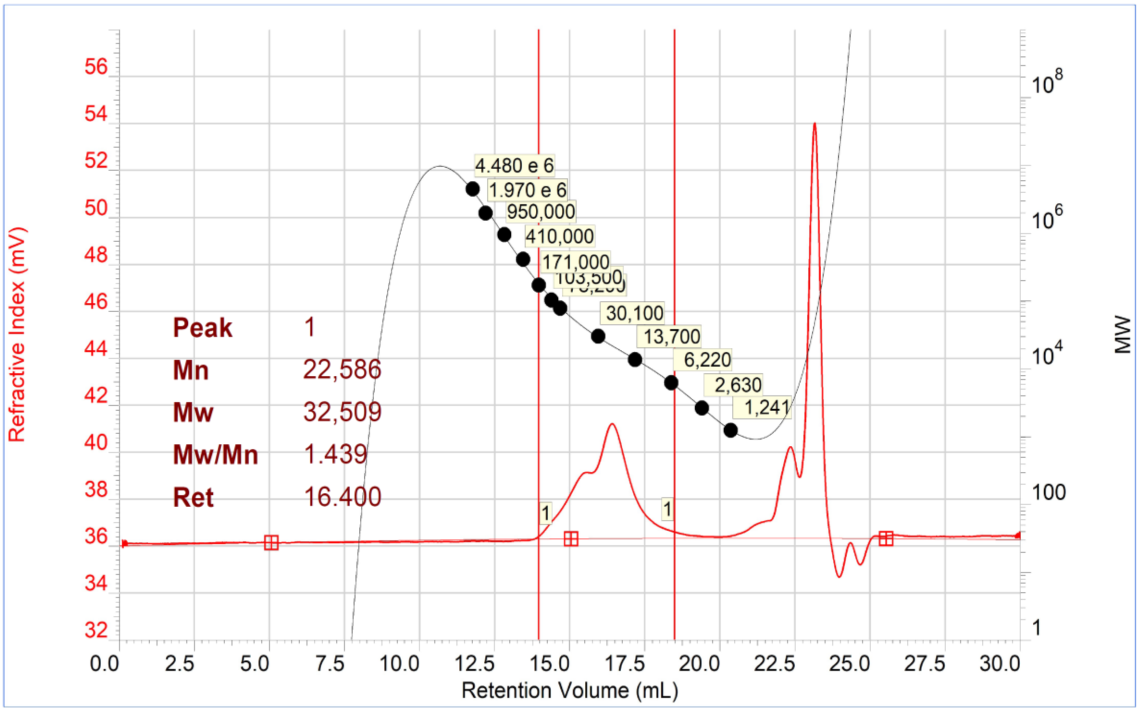


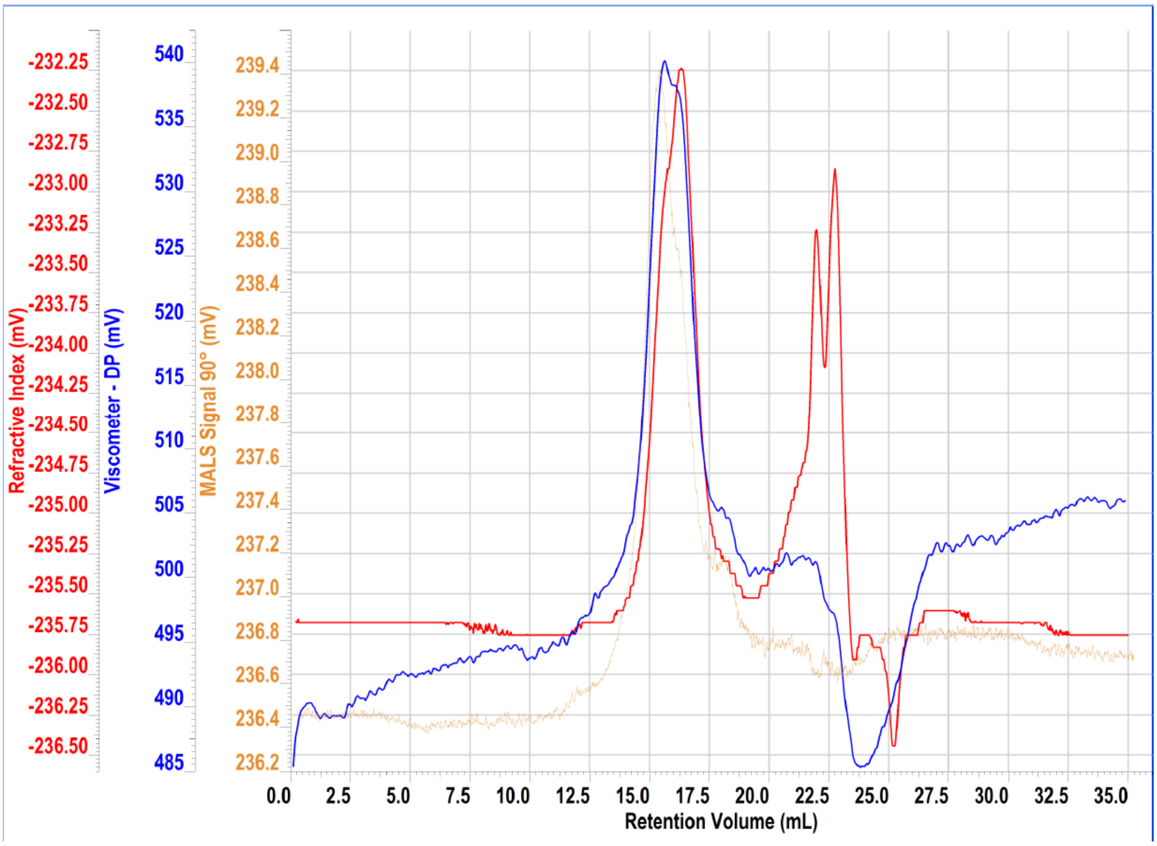
c. SEC curve of polymer P3:





d. SEC curve of polymer P4:





e. SEC curve of polymer P5: