Supplementary Information (SI) for Polymer Chemistry.
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UV-degradable poly(phenyl vinyl ketone) particles produced by polymerisation-induced self-assembly in ethanol or water

– Supplementary Information

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General information:

Reagents and solvents:

Styrene (99%, Aldrich), 4,4′-azobis(4-cyanovaleric acid) (ACVA, 98%, Aldrich), 2-methyl-1-propanethiol (92%, Aldrich), tripotassium phosphate (K_3PO_4, ≥ 98%, Sigma-Aldrich), carbon disulfide (99.9%, Acros Organics), 2-bromoisobutyric acid (98%, Thermo Scientific Chemicals), polyethylene glycol 5000 monomethyl ether (MPEG-5000, Fluka), DCC (99%, Sigma-Aldrich), and DMAP (99% Acros Organics) were used for the synthesis. Ethanol (99%) was purchased from Sigma Aldrich and acetone-d6 (99.8%) was purchased from Eurisotop. All chemicals were used as received unless stated otherwise. Phenyl vinyl ketone (PVK) was prepared in house as reported previously.[1] PEG functionalised RAFT agents, PEG2K-TTC and PEG5K-TTC**,** were synthesised in house adapting an already existing procedure.[2] MPEG-5000 was dried by azeotropic distillation with dry toluene prior to the synthesis of the macro-RAFT agent.

NMR: ^{1}H spectra were recorded on a Bruker 300 MHz spectrometer in 5 mm diameter tubes. Chemical shifts were noted on the δ scale in parts per million (ppm). ^{1}H NMR spectra were deuterated acetone using the residual signal 2.05 ppm.

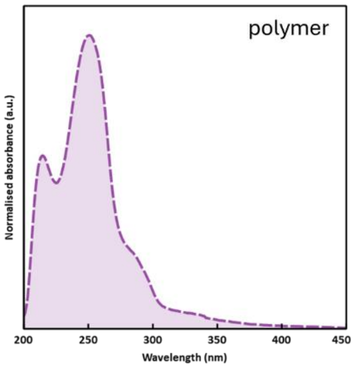
SEC: Polymer samples (2 – 10 mg) were dissolved in SEC grade THF (1 mL) and filtered using a 0.45 µm PTFE syringe filter. SEC analyses of the filtered polymer samples were carried out in SEC grade THF at a flow rate of 1 mL min^{-1} at 40 °C. Size exclusion chromatography (SEC) measurements were carried out on three PL Gel Mixed C 5µm columns (7.5 x 300 mm; separation limits: 0.2 to 2000 kg mol^{-1}) maintained at 40 °C coupled with a solvent and sample delivery module Viscotek GPCmax and 2 modular detectors: a differential refractive index (RI) detector Viscoteck 3580 and a Diode Array UV Detector Shimadzu SPD20-AV. Molar masses (M_n, the number-average molar mass, M_w, the weight-average molar mass) and dispersity ($Đ = M_w/M_n$) were derived from a calibration curve based on polystyrene (PS) from Polymer Standards Service. The OmniSEC 5.12 software was used for data acquisition and data analysis.

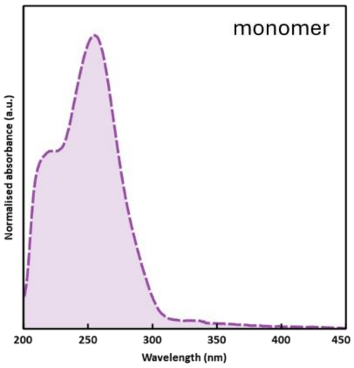
DLS: Measurements were performed using a Malvern Zetasizer Nano ZS instrument equipped with a 4 mW He–Ne 633 nm laser and an avalanche photodiode detector. Back-scattered light was detected at an angle of 173° and data were recorded at a copolymer concentration of 0.2 % w/w at 25 °C. Malvern Zetasizer Software v7.11 was used to calculate z-average hydrodynamic diameters (D_z) via the Stokes-Einstein equation, which assumes perfectly monodisperse, non-interacting spherical particles. Data were averaged over at least three consecutive runs with at least ten measurements being recorded for each run.

SAXS: Small Angle X-rays Scattering experiments were performed on a Nano-inXider SW system (Xenocs) in transmission mode using Cu Kα radiation ($\lambda = 1.54$ Å, 8 keV) from an X-ray microsource (GeniX3D) operating at 50 kV-0.6 mA (30 W). Scattering patterns were collected using an in vacuum 2D Pilatus3 Hybrid pixel detector (83.8 x 33.5 mm^2, pixel size: 172 x 172 µm^2) (Dectris), localized at a distance of 938 mm. The collimation was chosen to maximize the intensity while adjusting the q range to the studied samples. The q range is between 0.003 Å^{-1} and 0.2 Å^{-1}. The reduction of 2D datasets from the Pilatus3 detector to 1D was achieved by radially averaging the raw data detector counts using Xsact data reduction software. Then, SAXS spectra were normalized by the acquisition time and by the number of transmitted photons. The measurements were performed at a concentration of 1% w/w. Standard correction procedures were applied for X-ray beam transmission, detector efficiency, and signal subtraction of the 1 mm capillary filled with the solvent. The data were fitted using the Sasfit software (http://www.sasfit.org/). The data were fitted with a block copolymer spherical micelle form factor.[3]

TEM: Samples were prepared on carbon-coated copper grids. A 5 µL droplet of the freshly-prepared 0.2% w/w copolymer dispersion was placed on the grid for 30 seconds, blotted to remove excess sample and then stained with phosphotungstic acid solution (0.05% w/w; 5 µL) for a further 30 seconds. Excess stain was removed by blotting and each grid was carefully dried with a vacuumThe transmission electron microscope (TEM) images were acquired using a JEOL JEM-1011 microscope (W filament, operating at 100 kV), equipped with a Gatan Orius CCD camera. The particle sizes were determined using Fiji (ImageJ) software.

UV-Vis absorption spectroscopy: The absorbance spectra at 25 °C were recorded with a Jasco V-670 spectrometer. Analyses were performed on dilute ethanol solutions in 10 x 10 mm quartz cuvettes at a scan rate of 400 nm/min, from 800 to 200 nm. The baseline (recorded with the pure solvent) was removed from the absorbance values obtained. UV-vis absorption spectra of polymer 4 (left) and the PVK monomer (right) are shown below.





Polymer synthesis and degradation

Synthesis of the RAFT agent

The RAFT agent was obtained by adapting a procedure from previous work[4]:

2-Methyl-1-propanethiol (3.78 mL g, 32 mmol), K_3PO_4 (6.94 g, 32 mmol) and 50 mL of acetone were added to a 250 mL round-bottomed flask equipped with a magnetic stir bar. This mixture was stirred and degassed for 30 min. Carbon disulfide (3.5 mL, 58 mmol) was added dropwise resulting in a yellow mixture which was further stirred for 20 min. A solution of 2-bromoisobutyric acid (5.63 g, 33 mmol) was prepared in 10 mL of acetone. The main mixture was placed in an ice bath and the 2-bromoisobutyric acid solution added dropwise. The reaction proceeded for 20h and gave a thick yellow mixture. The mixture was filtered and the filtrate was acidified by the addition of HCl 1M (70 mL). Acetone was evaporated and the product extracted with DCM (150 mL). The organic phase was washed with water (2 x 150 mL) and dried with $MgSO_4$. The solvent was evaporated to afford a dark orange oil. This oil crystallized in the refrigerator. The crystals were washed with cold pentane to remove a side product (4-hydroxy-4-methylpentan-2-one) and dried under vacuum for over 3h at room temperature. The product (1.52 g, 18 % yield) was characterized by ^1H NMR in $CDCl_3$.

^1H-NMR ($CDCl_3$, δ ppm): 1.00 (d, 6H, $-CH_2CH\mathbf{(C\underline{H}_3)_2}$), 1.73 (s, 6H, $-C\mathbf{(C\underline{H}_3)_2}-SC(S)S-$), 1.98 (m, 1H, $-CH_2\mathbf{C\underline{H}}(CH_3)_2$), 3.20 (d, 2H, $-\mathbf{C\underline{H}_2}CH(CH_3)_2$).

Synthesis of the macro-RAFT agent

PEG2K-TTC and PEG5K-TTC were synthesized following a procedure similar to previous work[2]. The main differences are that dry DCM was used instead of anhydrous THF and that pentane was used for the precipitation of the polymer, instead of diethyl ether. Details for a typical synthesis :

A flask containing 11.8 g of dried MPEG-5000 (2.4×10^{-3} mol) in 25 mL of dry DCM was prepared under argon atmosphere. The content of the flask was heated up to 65°C to get a homogeneous mixture. A solution of 1.24 g of RAFT agent (4.72×10^{-3} mol), 0.99 g DCC (4.73×10^{-3} mol) and 0.06 g DMAP (4.6×10^{-4} mol) in 35 mL of dry DCM was then prepared. This solution was introduced dropwise in the flask containing the MPEG, with an ice bath. The esterification reaction proceeded under stirring at room temperature for 144 h. The reaction mixture was then stored in the freezer, before filtration with recovery of a yellow liquid. This liquid was concentrated under vacuum until an orange oil was obtained. The polymer was recovered by precipitating the mixture in cold pentane twice. After filtration, it was further washed with cold toluene. After filtration, the product was dried under vacuum at 40°C for over 24h and stored at around 5°C. The product (8.57 g, M_n = 5326 g/mol, 68 % yield) was characterized by ^1H and ^{13}C NMR in $CDCl_3$

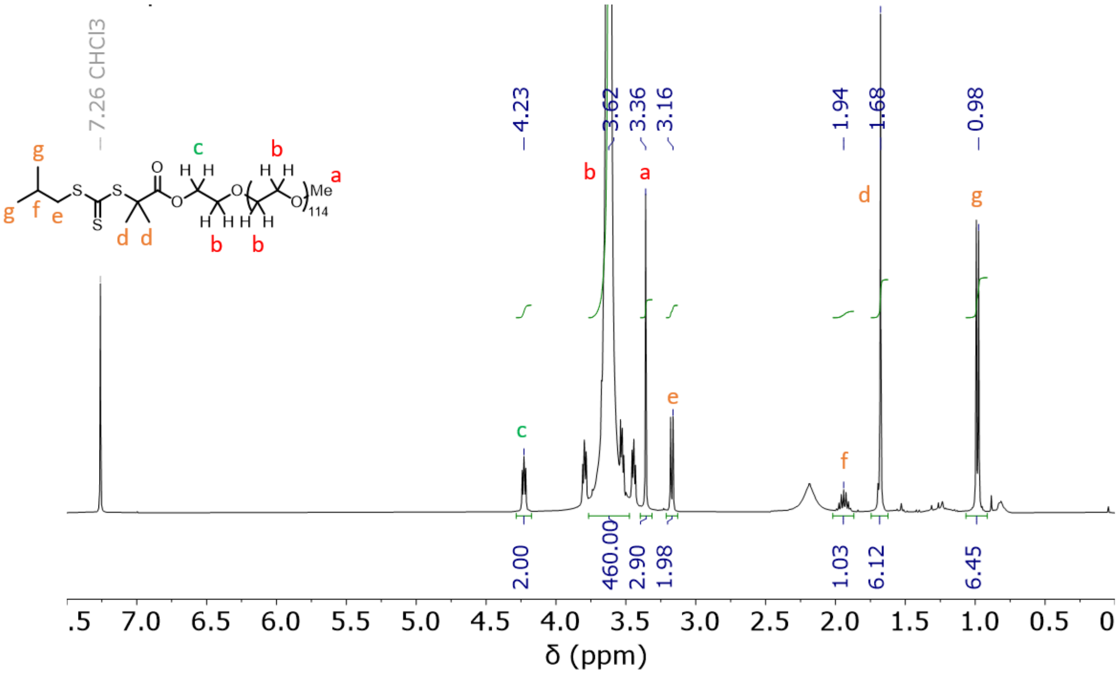
End-functionality was close to quantitative as determined by ^1H-NMR.

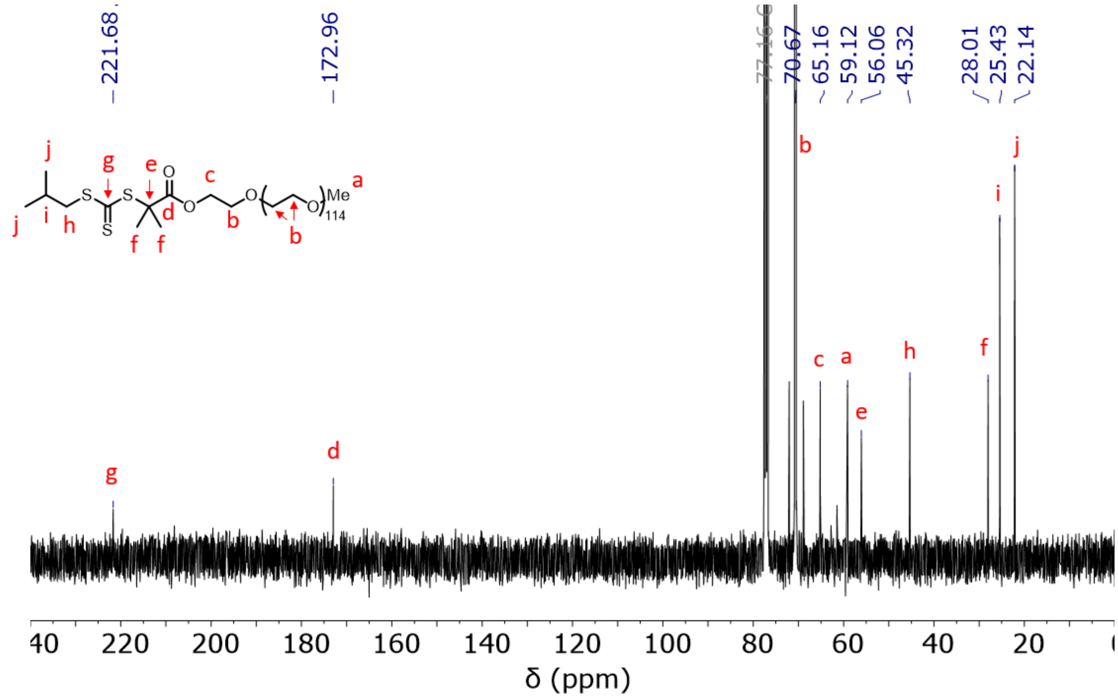
^1H-NMR ($CDCl_3$, δ ppm): 0.98 (d, 6H, $-CH_2CH\mathbf{(C\underline{H}_3)_2}$), 1.68 (s, 6H, $-C\mathbf{(C\underline{H}_3)_2}-SC(S)S-$), 1.94 (m, 1H, $-CH_2\mathbf{C\underline{H}}(CH_3)_2$), 3.16 (d, 2H, $-\mathbf{C\underline{H}_2}CH(CH_3)_2$), 3.36 (s, 3H, $\mathbf{C\underline{H}_3}OCH_2-$ of the PEG moiety), 3.62 (M, $CH_3O-(\mathbf{C\underline{H}_2C\underline{H}_2}O)_{n-1}-\mathbf{C\underline{H}_2}CH_2-OC(O)C(CH_3)_2-$of the PEG moiety), 4.23 (t, 2H, $-CH_2\mathbf{C\underline{H}_2}-OC(O)C(CH_3)_2-$ of the PEG moiety).

^{13}C-NMR (CDCl3, δ ppm): 221.68 ($-S\mathbf{C}(S)S-$), 172.96 ($-CH_2CH_2-O\mathbf{\underline{C}}(O)C(CH_3)_2-$), 70.67 ($CH_3O-(\mathbf{\underline{C}H_2\underline{C}H_2}O)_{n-1}-\mathbf{\underline{C}H_2}CH_2-OC(O)C(CH_3)_2-$of the PEG moiety), 65.16 ($-CH_2\mathbf{\underline{C}H_2}-OC(O)C(CH_3)_2$ of the PEG moiety), 59.12

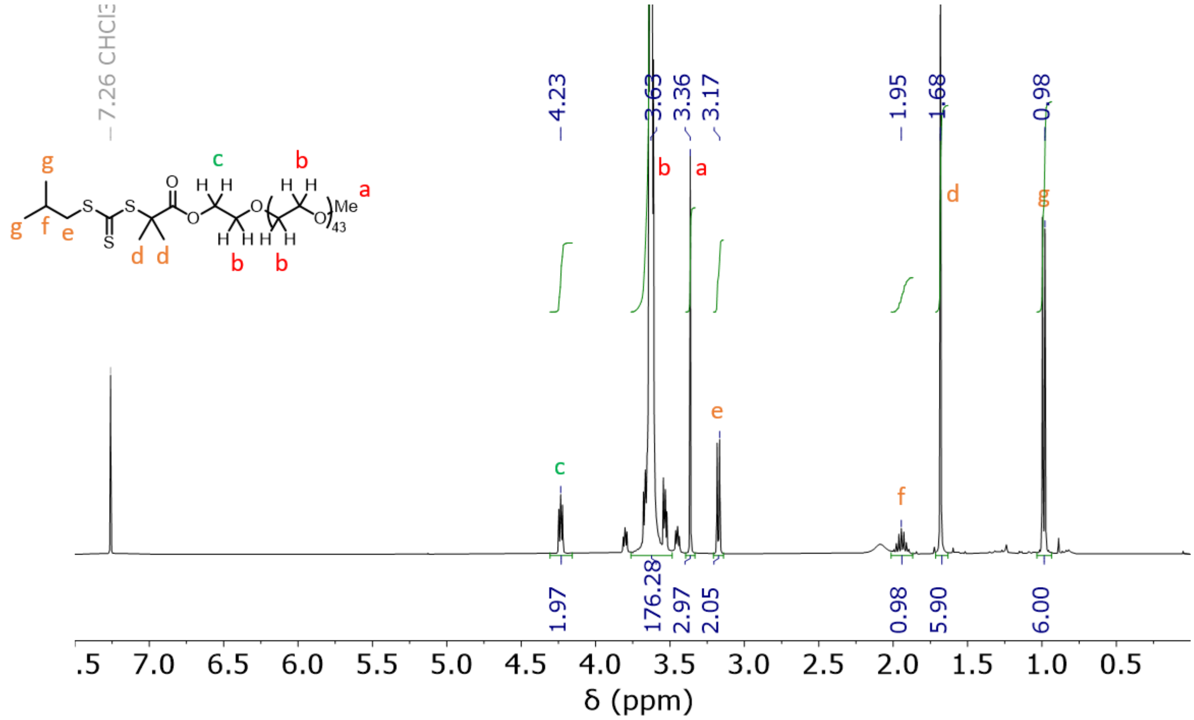
(**$\underline{C}H_3$**OCH$_2$- of the PEG), 56.06 (-**$\underline{C}$**(CH$_3$)$_2$-SC(S)S-), 45.32 (-**$\underline{C}H_2$**CH(CH$_3$)$_2$), 28.01 (-C(**$\underline{C}H_3$**)$_2$-SC(S)S-), 25.43 (-CH$_2$**$\underline{C}H$**(CH$_3$)$_2$), 22.14 (-CH$_2$CH(**$\underline{C}H_3$**)$_2$).

PEG5K-TTC :





PEG2K-TTC :



Synthesis of PEG-*b*-PPVK in solution

In a typical procedure (sample **10**, Table S1) using the PEG5K-TTC and targeting a DP_{PVK} of 50, PEG-TTC (56 mg, 11 µmol) and PVK (70 mg, 0.53 mmol) were added to a 10 mL vial and dissolved in DMF (0.44 mL). AIBN (0.35 mg, 2 µmol) was added from a 3.5 mg/mL stock solution (0.1 mL). The reaction was sealed and degassed by bubbling argon through the solution for 20 min. The flask was then placed in an oil bath at 72 °C and left to react for 5 h. The polymerisation was terminated by exposure to air and cooling to ambient temperature.

Synthesis of PEG-*b*-PPVK ethanol dispersions by thermal-RAFT PISA

In a typical procedure (sample **1**, Table 1) using the PEG5K-TTC and targeting a DP_{PVK} of 50, PEG-TTC (56 mg, 11 µmol) and PVK (70 mg, 0.53 mmol) were added to a 10 mL vial and dissolved in ethanol (0.54 mL). ACVA (0.6 mg, 2 µmol) was added from a 6 mg/mL stock solution (0.1 mL). The reaction was sealed and degassed by bubbling argon through the solution for 20 min. The flask was then placed in an oil bath at 72 °C and left to react for 16 h. The polymerisation was terminated by exposure to air and cooling to ambient temperature.

Synthesis of PEG-*b*-PPVK ethanol dispersions by photo-RAFT PISA

In a typical procedure (sample **2**, Table 1) using the PEG5K-TTC and targeting a DP_{PVK} of 50, PEG-TTC (64 mg, 12 µmol) and PVK (80 mg, 0.61 mmol) were added to a 10 mL vial and dissolved in ethanol (0.73 mL). The reaction was sealed and degassed by bubbling argon through the solution for 20 min. The flask was then placed in a beaker coated with blue LEDs and left to react for 2 h. The polymerisation was terminated by exposure to air and removing from the light source.

Synthesis of PEG-*b*-PPVK aqueous emulsions by photo-RAFT PISA (sample **6**, Table 1)

PEG5K-TTC (26 mg, 5 µmol) was added to a 10 mL vial and dissolved in deionized water (0.5 mL). PVK (100 mg, 0.76 mmol) was then added to the solution. The reaction was sealed and degassed by bubbling argon through the solution for 20 min. The flask was then placed in a beaker coated with blue LEDs and left to react for 3 h. The polymerisation was terminated by exposure to air and removing from the light source.

Synthesis of PEG-*b*-PPVK aqueous emulsion by thermal-RAFT PISA (sample **7**, Table 1)

PEG5K-TTC (13 mg, 3 µmol) was added to a 10 mL vial and dissolved in deionized water (0.47 mL). PVK (50 mg, 0.39 mmol) was then added to the solution. ACVA (0.14 mg, 1 µmol) was added from a 1.4 mg/mL stock solution (0.1 mL). The reaction was sealed and degassed by bubbling argon through the solution for 20 min. The flask was then placed in an oil bath at 82 °C and left to react for 16 h. The polymerisation was terminated by exposure to air and cooling to ambient temperature.

Synthesis of PEG-*b*-(PSt-*co*-PPVK) aqueous emulsion by thermal-RAFT PISA (sample **8**, Table 1)

PEG5K-TTC (54 mg, 10 µmol) was added to a 10 mL vial and dissolved in deionized water (1.9 mL). PVK (50 mg, 0.39 mmol) and St (120 mg, 1.15 mmol) was then added to the solution. ACVA (0.57 mg, 1 µmol) was added from a 5.7 mg/mL stock solution (0.1 mL). The reaction medium was sealed and degassed by bubbling argon through the solution for 20 min. The flask was then placed in an oil bath at 82 °C and left to react for 3 h. The polymerisation was terminated by exposure to air and cooling to ambient temperature.

Synthesis of PVK homopolymer in the absence of RAFT agent (sample **9**, Table S1)

PVK (100 mg, 0.76 mmol) were added to a 10 mL vial and dissolved in DMF (0.44 mL). The reaction was sealed and degassed by bubbling argon through the solution for 20 min. The flask was then placed in a beaker coated in blue LEDs and left to react for 2 h. The polymerisation was terminated by exposure to air and removing from the light source.

Degradation via irradiation with UV light

In a typical procedure, a 0.2% w/w or 1% w/w PEG-PVK nanoparticle dispersion was placed in a sealed vial and irradiated with a Dymax 2000-PC modular UV lamp light-curing flood (maximal emission between 315 and 400 nm, 75 mW.cm^{-2}) at a distance of 24 cm from the source. The samples were irradiated for various amounts of time and subsequently analysed by SEC, DLS and SAXS.

Additional Tables

Table S1. Polymerisation conditions used and results assessed by ^{1}H NMR spectroscopy, SEC, and DLS, respectively.

#	Solvent	Initiation system	[PVK] / [PEG-TTC]	Solids content (%)	Time (h)	Conv. PVK (%)	M_n (kg.mol^{-1})^a	$Đ^a$
PEG5K-TTC	-		-	-	-	-	7.2	1.04
9[b]	DMF	Light	-	20	2	60	32.0	1.70
10[c]	DMF	AIBN, 72°C	50	20	5	95	11.0	1.12

[a] Molar mass measured by THF SEC against polystyrene standards. [b] Polymerisation performed in the absence of RAFT agent. [c] Solution polymerisation of PVK using PEG5K-TTC agent.

Table S2. Polymerisation conditions used and monomer conversion, molar masses, and particle sizes obtained for each polymerisation, assessed by ^{1}H NMR spectroscopy, SEC, and DLS, respectively.

#	Polymerisation Solvent	[PVK] / [PEG-RAFT]	Solids content (%)	Time (h)	Conv. PVK (%)	M_n (kg.mol^{-1})^a	$Đ^a$	D_z (nm)	*PDI*
PEG2K-TTC	-	-	-	-	-	2.8	1.04	-	-
11	EtOH	100	20	2	90	8.9	1.16	Precipitate[b]	
12	EtOH	50	10	2	99	6.3	1.15	2284	0.20
13	EtOH	70	10	2	87	7.4	1.13	3775	0.35
14	EtOH	80	10	2	86	8.4	1.12	806	0.09
15	EtOH	100	10	2	81	9.4	1.15	Precipitate[b]	

[a] Molar mass measured by THF SEC against polystyrene standards. [b] Precipitated upon dilution with ethanol.

Additional figures

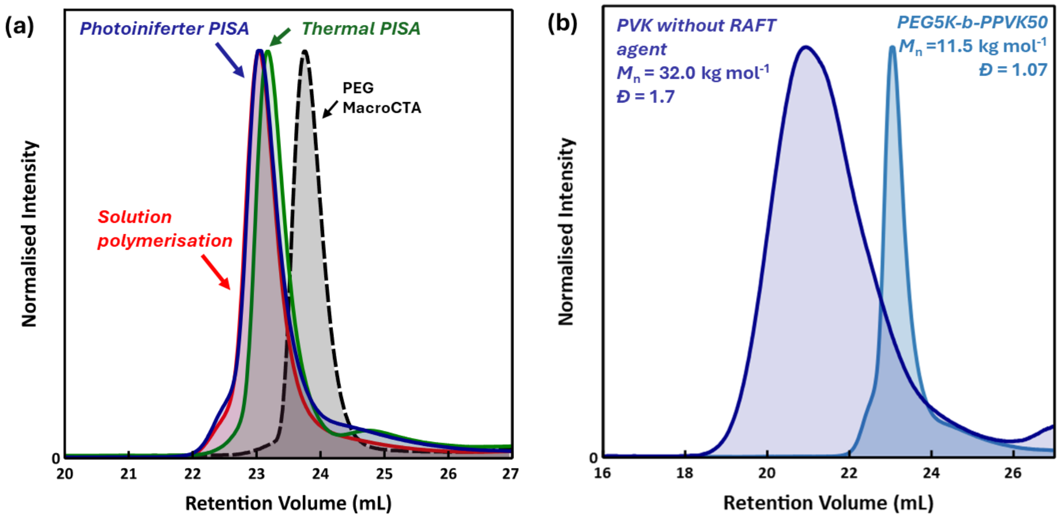


Figure S1. (a) SEC chromatograms of PEG5K-*b*-PPVK50 copolymers made using dispersion photo-RAFT PISA (polymer **2**, Table 1), dispersion thermal-RAFT (polymer **1**, Table 1), and solution thermal-RAFT polymerisation (polymer **10**, Table S1). (b) SEC chromatograms of uncontrolled solution photo-polymerisation of PVK (polymer **9**, Table S1) and PEG5K-*b*-PPVK50 synthesised using dispersion photo-RAFT PISA (polymer **2**, Table 1) as a reference.

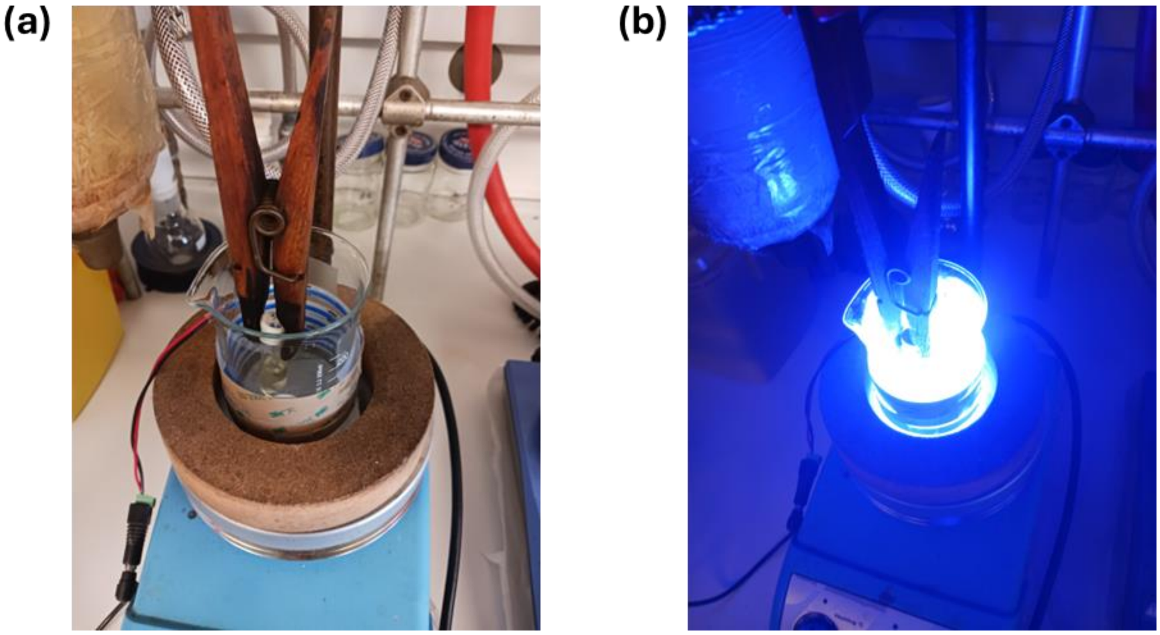


Figure S2. Digital photographs of photo-RAFT polymerization experimental setup.

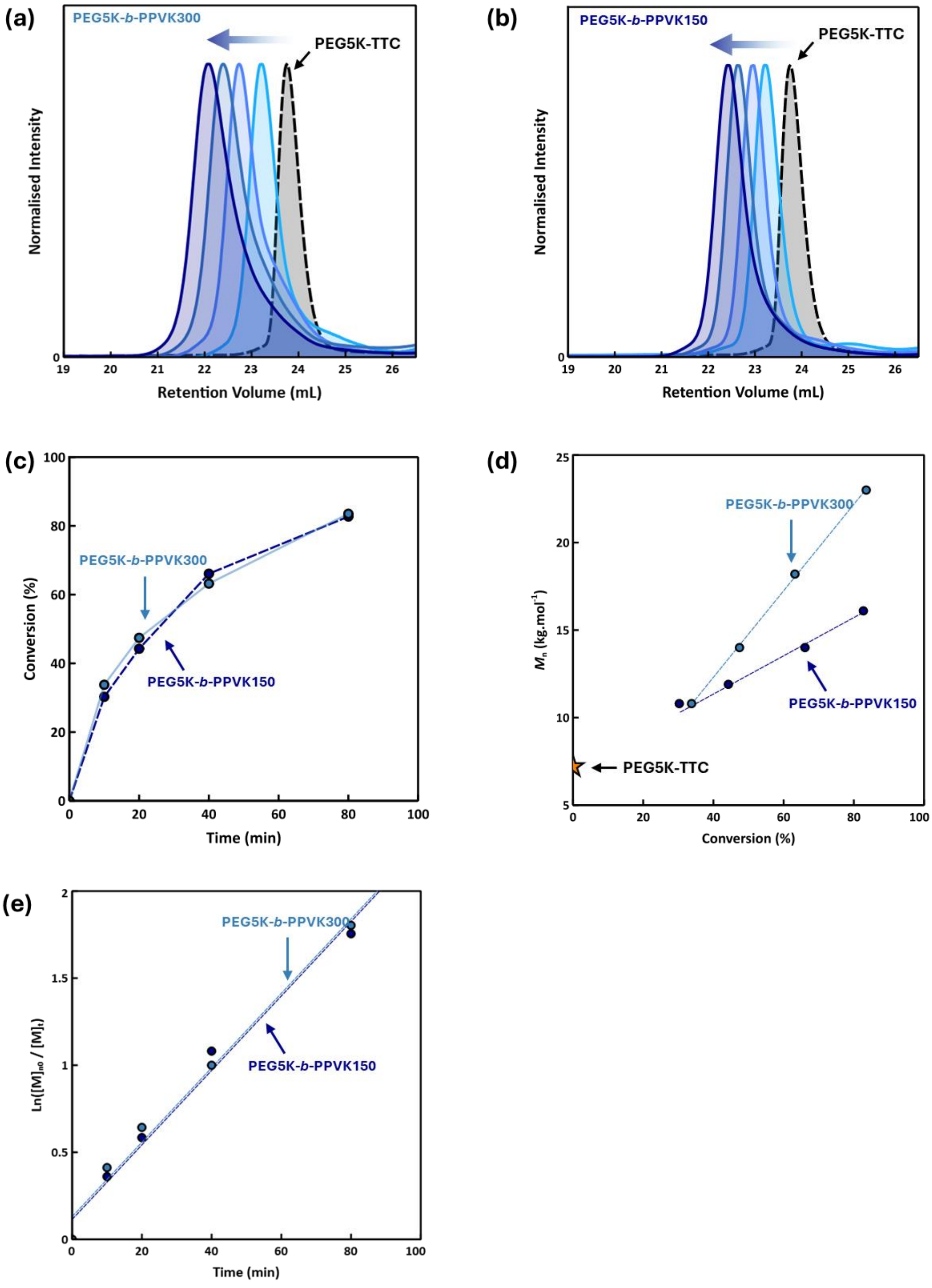


Figure S3. Kinetic data for the dispersion photo-RAFT PISA polymerisation of PVK (PEG5K-*b*-PPVK300 [light blue, sample 4] and PEG5K-*b*-PPVK150 [dark blue, sample 3]) where (a) & (b) are respective the SEC chromatograms showing the evolution of molar mass during the polymerisation, (c) is plot of monomer conversion vs polymerisation time, (d) is a plot of M_n vs monomer conversion, and (e) is the 1st order kinetic plot.

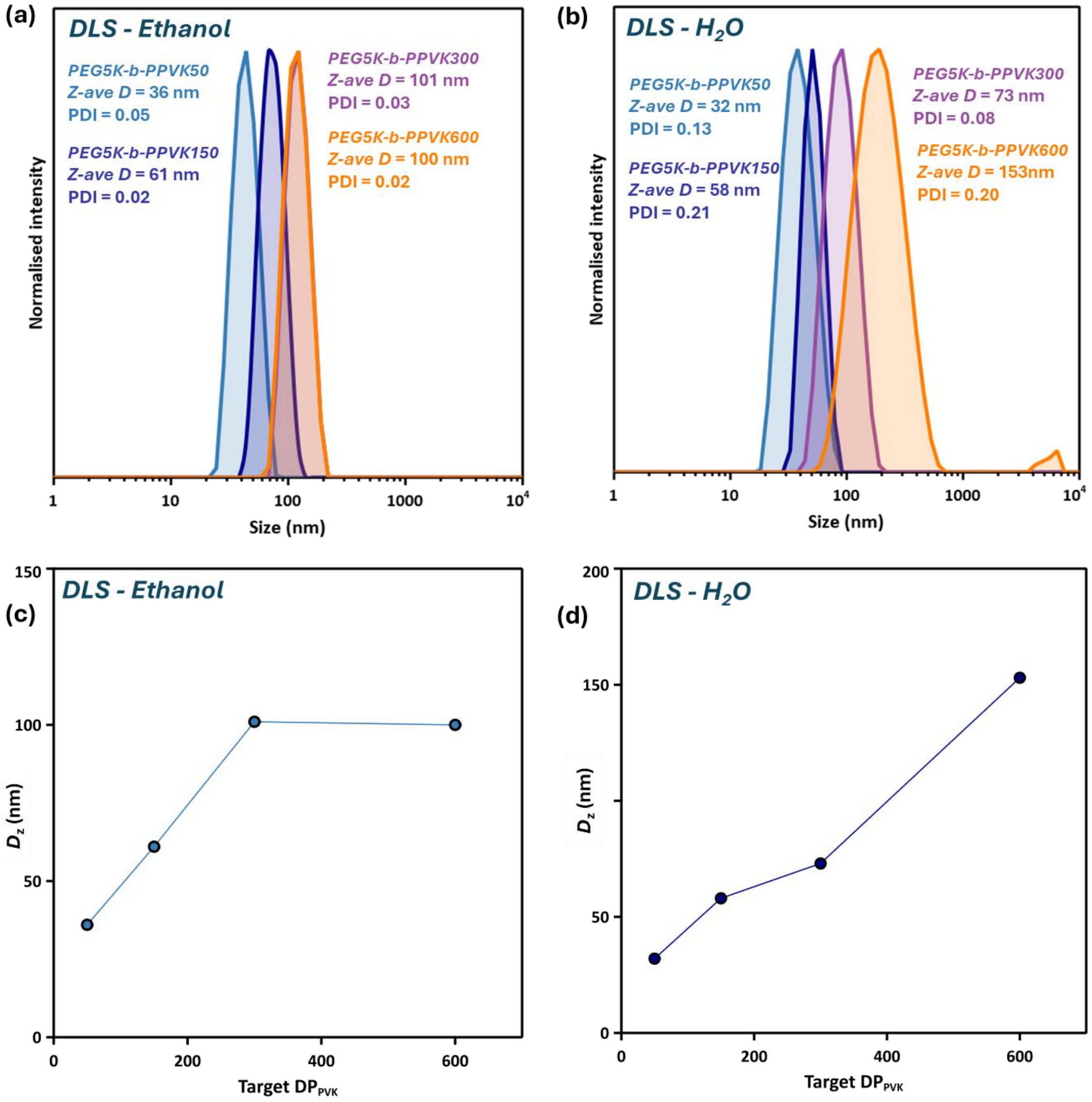


Figure S4. Normalized DLS intensity-average particle size distributions recorded at 25 °C for 0.2 % w/w (a) alcoholic dispersions (samples **2- 5**, Table 1) and (b) aqueous dispersions of PEG5K-*b*-PPVK nanoparticles. Plots of z-average diameter, D_z, against target DP_{PVK} for (c) alcoholic dispersions and (d) aqueous dispersions of PEG5K-*b*-PPVK nanoparticles

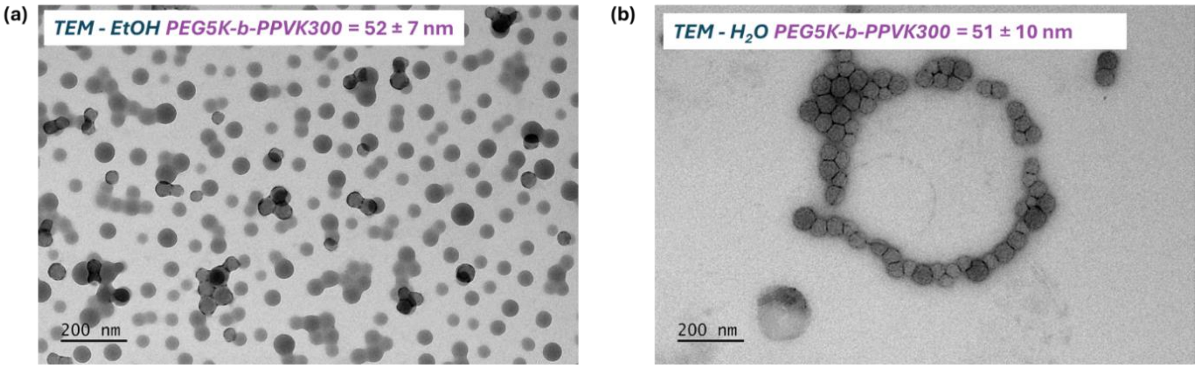


Figure S5. TEM images recorded after drying of a 0.2% w/w (a) PEG5K-*b*-PPVK300 alcoholic dispersion (sample **4**, Table 1) and (b) PEG5K-*b*-PPVK300 aqueous dispersion.

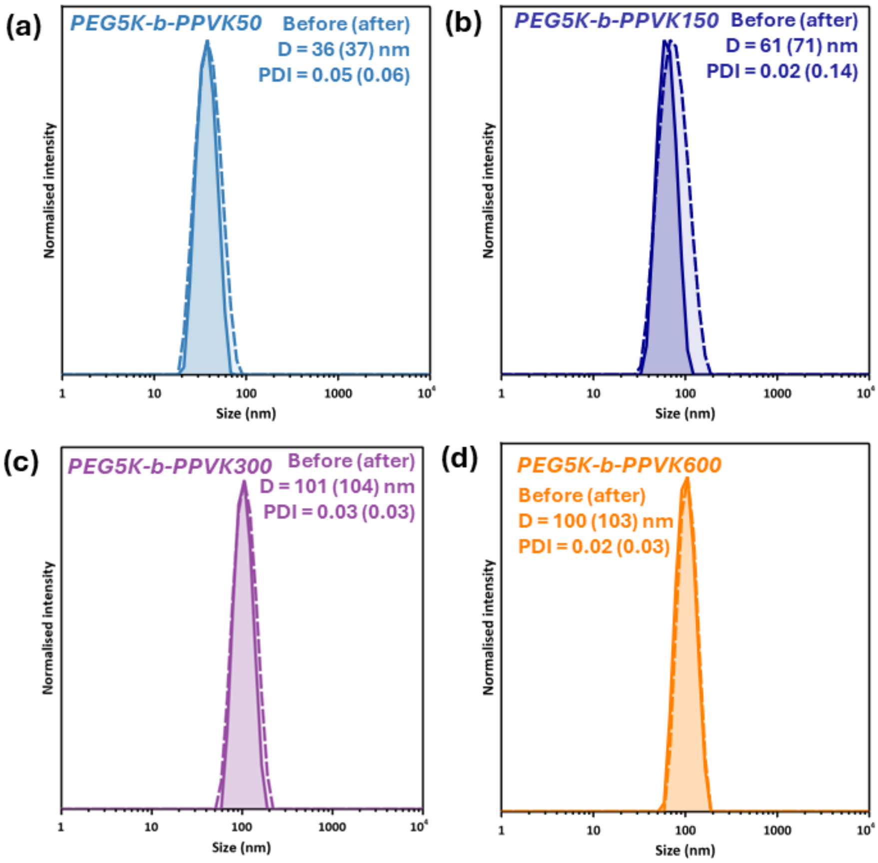


Figure S6. Normalized DLS intensity-average particle size distributions recorded at 25 °C for 0.2 % w/w alcoholic dispersion (samples **2 – 5**, Table 1) of (a) PEG5K-*b*-PPVK50, (b) PEG5K-*b*-PPVK150, (c) PEG5K-*b*-PPVK300, and (d) PEG5K-*b*-PPVK600 nanoparticles, where the original data is shown as a solid line and data collected after 5 months of storage is shown as a dashed line.

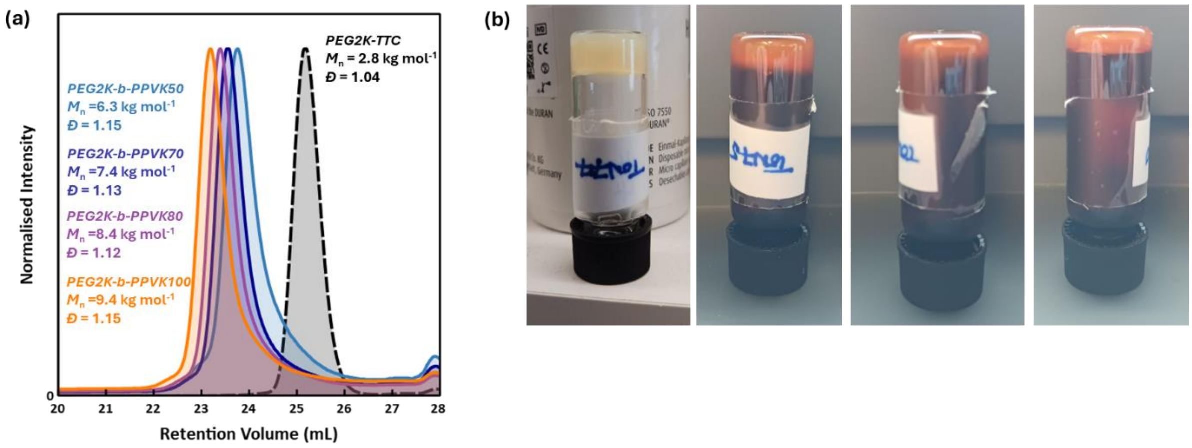


Figure S7. (a) SEC chromatograms of PEG2K-*b*-PPVK block copolymers (**12 – 15**, Table S1) synthesised via alcoholic dispersion photo-RAFT PISA. The SEC chromatograms of PEG2K-TTC is shown for reference (black dashed line). (b) Digital photographs of PEG2K-*b*-PPVK alcoholic dispersions at 10% w/w (from left to right: sample 12, 13, 14 and 15).

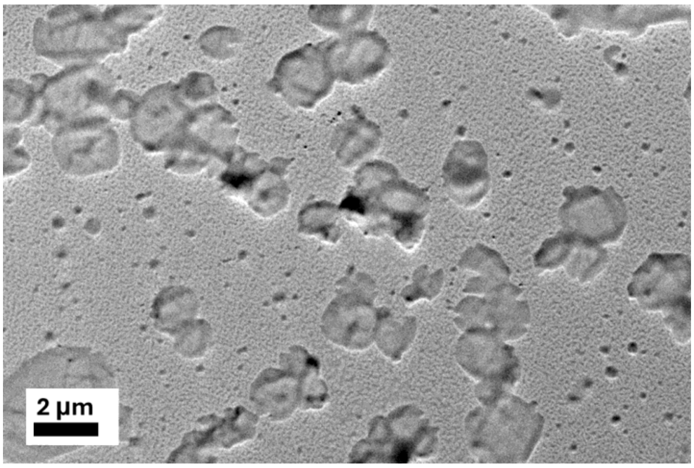


Figure S8. TEM image recorded after drying of a 0.2% w/w of PEG2K-*b*-PVK50 (sample **12**) alcoholic dispersion.

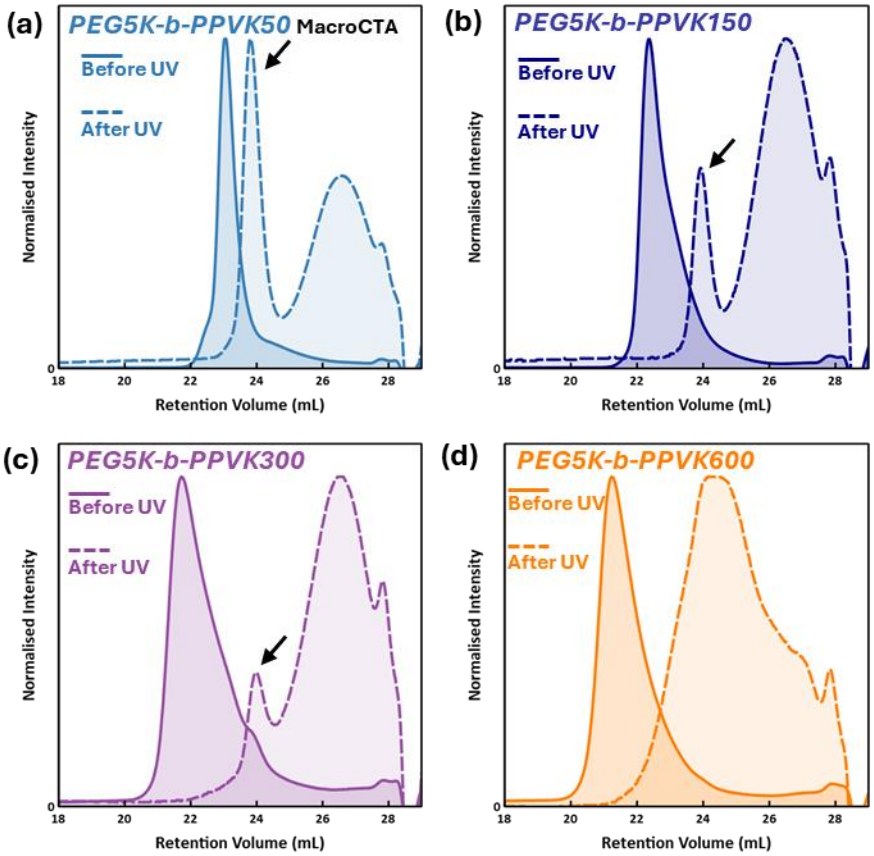


Figure S9. Evolution of the SEC chromatograms of PEG5K-*b*-PPVK copolymer alcoholic dispersions (samples **2 - 5**, Table 1) before (solid line) and after degradation under UV-light (dashed line), where (a) is PEG5K-*b*-PPVK50, (b) is PEG5K-*b*-PPVK150, (c) is PEG5K-*b*-PPVK300, and (d) is PEG5K-*b*-PPVK600.

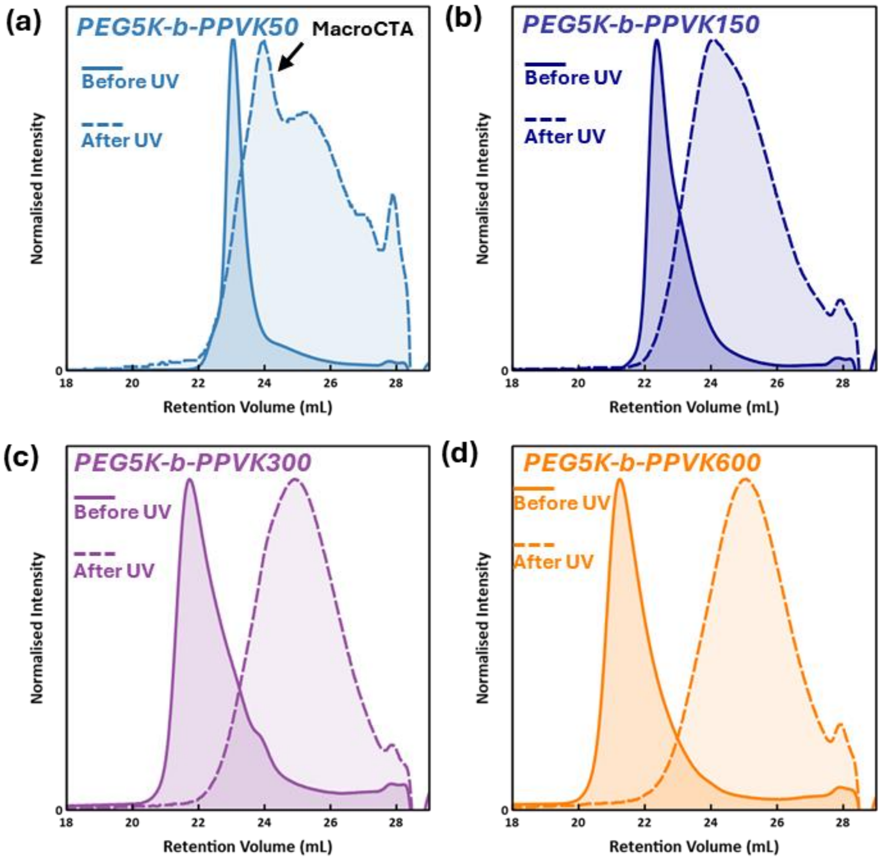


Figure S10. Evolution of the SEC chromatograms of PEG5K-*b*-PPVK copolymer aqueous dispersions (samples **2 – 5**, Table 1) before (solid line) and after degradation under UV-light (dashed line), where (a) is PEG5K-*b*-PPVK50, (b) is PEG5K-*b*-PPVK150, (c) is PEG5K-*b*-PPVK300, and (d) is PEG5K-*b*-PPVK600.

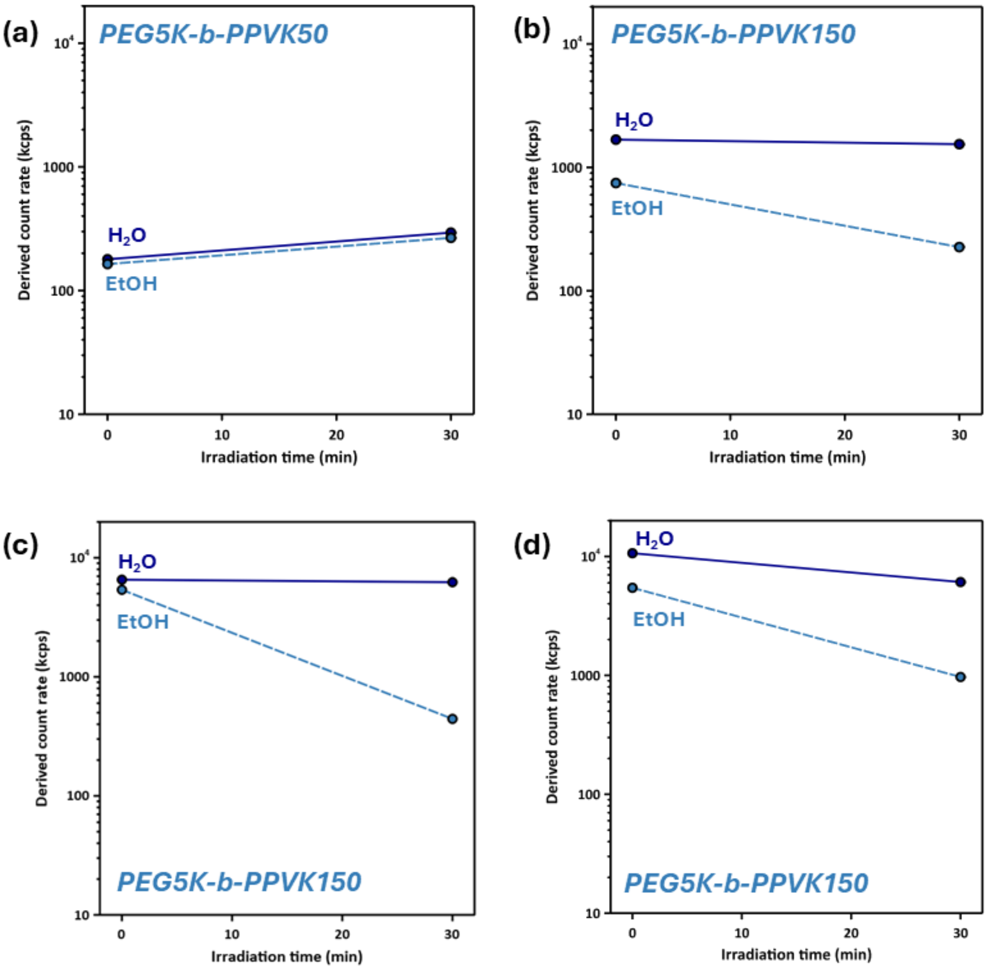


Figure S11. Plots of the derived count rate against UV-light irradiation time for 0.2 % w/w alcoholic dispersions (samples **2 – 5**, Table 1) of (a) PEG5K-*b*-PPVK50, (b) PEG5K-*b*-PPVK150, (c) PEG5K-*b*-PPVK300, and (d) PEG5K-*b*-PPVK600.

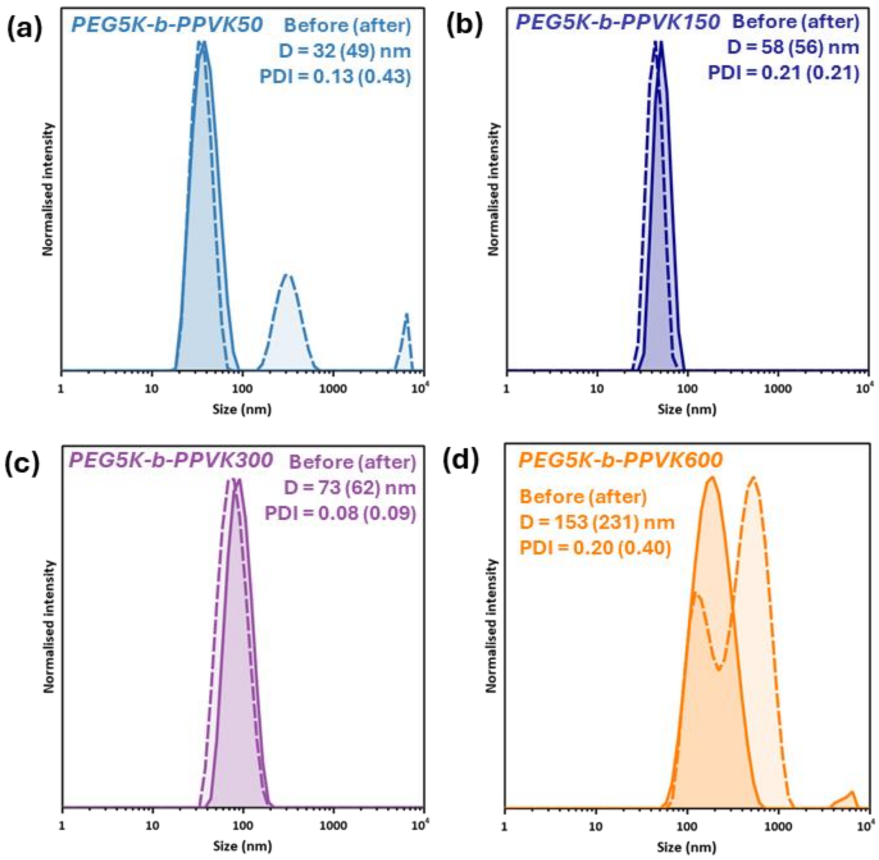


Figure S12. Normalized DLS intensity-average particle size distributions recorded at 25 °C for 0.2 % w/w aqueous dispersions of (a) PEG5K-*b*-PPVK50 (sample **2**), (b) PEG5K-*b*-PPVK150 (sample **3**), (c) PEG5K-*b*-PPVK300 (sample **4**), and (d) PEG5K-*b*-PPVK600 (sample **5**) nanoparticles, where the original data is shown as a solid line and data collected after 30 min of UV-light irradiation is shown as a dashed line.

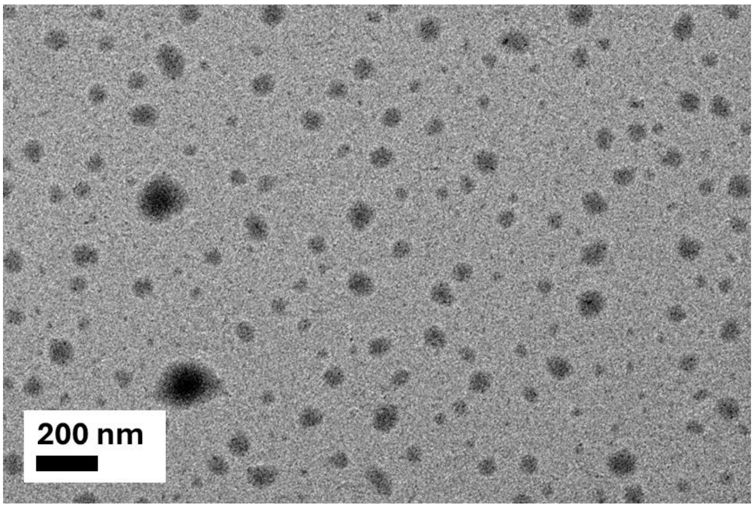


Figure S13. TEM image recorded after drying of a 0.2% w/w of PEG5K-*b*-PVK300 (sample **4**) ethanolic dispersion after 10 min of UV-light irradiation.

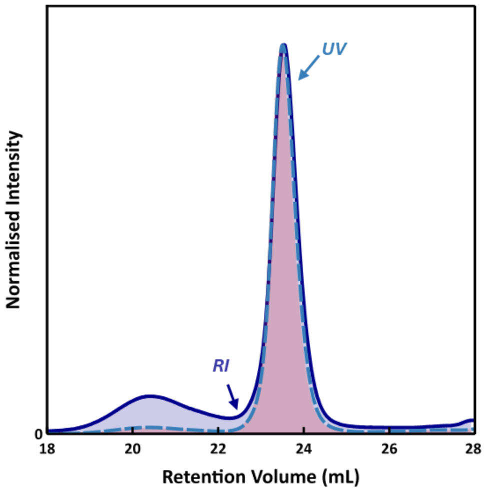


Figure S14. SEC chromatograms of PEG5K-*b*-PPVK150 block copolymer (sample **6**, Table 1) synthesised via aqueous emulsion photo-RAFT PISA, where the RI chromatogram is shown as a solid dark blue line and the UV chromatogram at 309 nm is shown as a light blue dashed line.

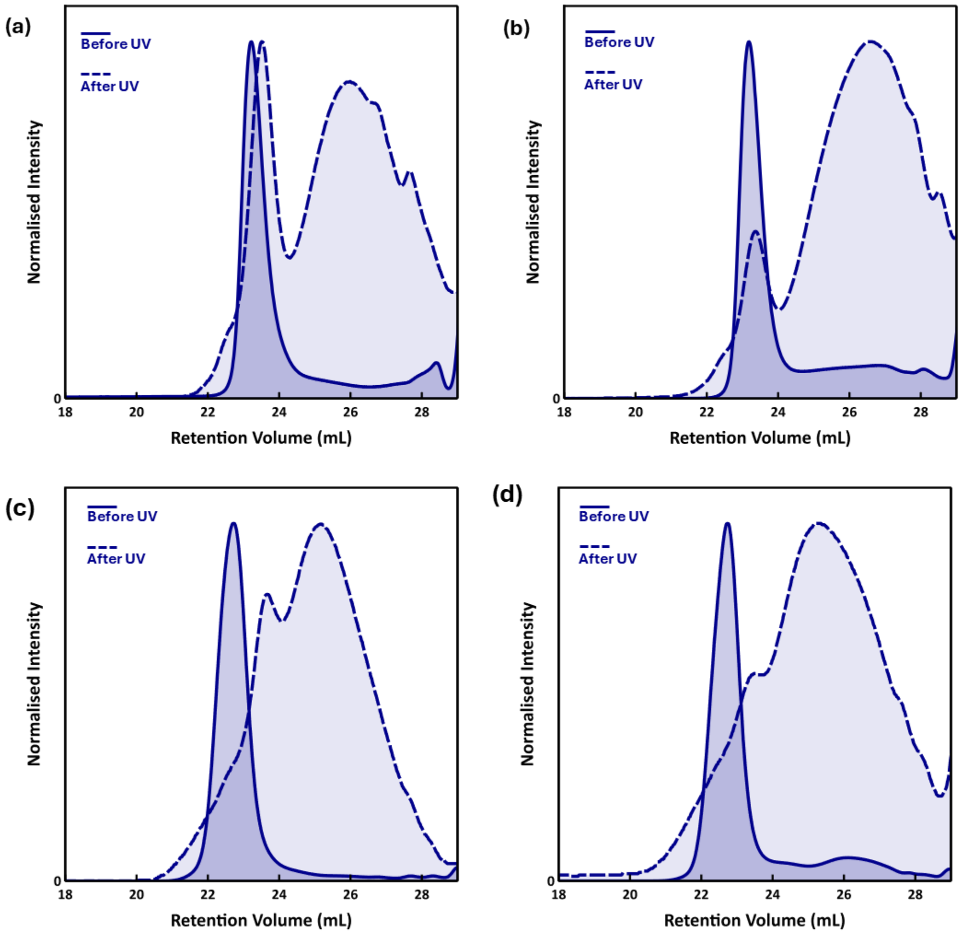


Figure S15. Evolution of the SEC chromatograms of PEG5K-*b*-PPVK150 copolymer aqueous dispersions before (solid line) and after degradation under UV-light (dashed line), where (a) is the RI chromatogram of sample **7**, (b) is the UV chromatogram of sample **7,** (c) is the RI chromatogram of sample **8**, and (d) is the UV chromatogram of sample **8**.

References

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