Supporting Information

Functional nanostructures by NiCCo-PISA of helical poly(aryl isocyanide) copolymers

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Experimental

Materials

4-(Dimethylamino)pyridine (≥98%, DMAP), l-menthol, poly(ethylene glycol) methyl ether (M_n ~ 550 g·mol^{-1}, mPEG$_{12}$-OH), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), pentafluorophenol, 4-chloropyridine, 2-(methylamino)ethanol, triethylamine (NEt$_3$), nickel(II) chloride hexahydrate, 1,2-(diphenylphosphino)ethane, *o*-tolylmagnesium chloride (1.0 M in THF), palladium on carbon loading 10 wt% (Pd/C 10%), ethanolamine and dimethyl sulfoxide (DMSO) anhydrous (≥99%) were purchased from Sigma-Aldrich. DMSO was dried over molecular sieves overnight before use. Ethyl formate, dichloromethane (CH_2Cl_2), sodium hydroxide (NaOH) and molecular sieves (4 Å) were purchased from Fisher Scientific. Tetrahydrofuran (HPLC grade, THF) and methanol (MeOH) were purchased from VWR Chemicals. THF was purified *via* passage through a column of basic alumina prior to use. 4-nitrobenzoyl chloride, 2,2,2-trifluoroethylamine (98%) and trifluoroacetic acid (TFA) were purchased from Alfa Aesar. Phosphorus (V) oxychloride ($POCl_3$) was obtained from Acros Organics.

Characterisation techniques

NMR Spectroscopy. ^{1}H NMR and ^{19}F NMR spectra were recorded at 300 MHz or 400 MHz on a Bruker DPX-300 or a Bruker DPX-400 spectrometer, using chloroform-*d* ($CDCl_3$) as the solvent. Chemical shifts of protons are reported as δ in parts per million (ppm) and are relative to $CHCl_3$ at $\delta = 7.26$ ppm.

Size Exclusion Chromatography. Size exclusion chromatography (SEC) analysis was performed on a system composed of an Agilent 1260 Infinity II LC system equipped with an Agilent guard column (PLGel 5 μM, 50 × 7.5 mm) and two Agilent Mixed-C columns (PLGel 5 μM, 300 × 7.5 mm). The mobile phase used was THF (HPLC grade) containing 2% v/v NEt$_3$ at 40 °C at flow rate of 1.0 mL·min^{-1} (polystyrene (PS) standards were used for calibration). Number average molecular weights (M_n), weight average molecular weights (M_w) and dispersities ($Đ_M = M_w/M_n$) were determined using the Agilent GPC/SEC software.

Dynamic Light Scattering. Hydrodynamic diameters (D_H) and size distributions (PD) of nano-objects were determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS with a 4 mW He-Ne 633 nm laser module operating at 25 °C. Measurements were carried out at an angle of 173° (back scattering), and results were analysed using Malvern DTS v7.03 software. All determinations were repeated 5 times with at least 10 measurements recorded for each run. D_H values were calculated using the Stokes-Einstein equation where particles are assumed to be spherical.

UV/Vis Spectroscopy. UV-Vis spectroscopy was performed on Evolution 350 UV-Vis spectrophotometer equipped with Xenon Flash Lamp light source and Dual Matched Silicon Photodiodes detector. Quartz cells (path length 1 cm, 170 - 2000 nm) from Hellma with two polished sides were used for examining the absorption spectral data by using Thermo INSIGHT-2 v.10.0.30319.1 software.

Infrared Spectroscopy. Infrared spectra were recorded (neat) on an Agilent Technologies Cary 630 FTIR spectrometer. 16 Scans from 600 to 4000 cm^{-1} were taken at a resolution of 4 cm^{-1}, and the spectra were corrected for background absorbance.

Circular Dichroism Spectroscopy. Circular dichroism (CD) spectra were recorded on a JASCO J810-150S spectropolarimeter using Quartz cells (path length 1 mm, 170 - 2000 nm) from Hellma. For the spectra range 650-450 nm, the following parameters were used: bandwidth 5 nm, data pitch 0.1 nm, scanning speed 100 nm·s^{-1}, D.I.T. 4 s. For the spectra range 650-200 nm, the following parameters were employed: bandwidth 5 nm, data pitch 0.2 nm, scanning speed 200 nm·s^{-1}, D.I.T. 1 s. 3 accumulations were taken.

Spectrophotometry. FL spectra were recorded on an Edinburgh Instruments FS5 spectrofluorometer equipped with Xenon lamp using 10 mm path length quartz cuvettes with four transparent polished faces (Starna Cells, type: 3-Q-10). (λ_{ex} = 540 nm, slit width ex. = 2 nm, slit width em. = 2 nm)

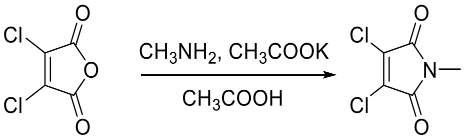
Synthetic procedures

PAIC[1], **MAIC**,[2] **FAIC**[3] and *o*-Tol(dppe)Cl[4] were synthesised according to the literature procedures.

Synthesis of maleimide dye (ACM)

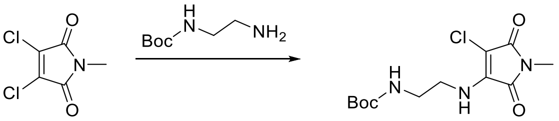
The maleimide dye was synthesised following a methodology modified from the literature.[5]

3,4-dichloro-1-methyl-1H-pyrrole-2,5-dione



In a 50 mL round-bottom flask, 3,4-dichloromaleic anhydride (1 g, 5.98 mmol, 1 eq.), methylamine hydrochloride (0.605 g, 8.97 mmol, 1.5 eq.), and potassium acetate (1.24 g, 8.97 mmol, 1.5 eq.) were added to a solution of acetic acid (10 ml). The reaction mixture was stirred for 4 h under reflux (120 °C). The solution turned yellow and was cooled to 25-30 °C before it was slowly poured into a cold sodium bicarbonate solution (1 M, 50 ml) until no effervescence was observed. The suspension was stirred for 1 h then, the solids were filtered, washed with n-hexane (2 x 30 ml) and dried *in vacuo* to obtain the product (0.732 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.12 (s, 1H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 162.8 (*C*=O), 133.51 (*C*-Cl), 25.1 (*C*H$_3$). Characterisation was consistent with that reported previously.[6]

Tert-butyl (2-((4-chloro-1-methyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)amino)ethyl)carbamate (Boc-ACM)



3,4-dichloro-1-methyl-1H-pyrrole-2,5-dione (1 eq.), sodium carbonate (2.5 eq.) and *N*-Boc-ethylenediamine (1.05 eq.) were mixed in THF (20 mL). Consumption of 2,3-chloromethylmaleimide was monitored by TLC, and was complete within 30 min. The solvent was then evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2 (150 mL). The solution was washed with water (2 × 150 mL), dried with Na_2SO_4 and purified *via* column chromatography on silica gel (petroleum ether/ethyl acetate 4:1 v/v) yielding the product as a yellow solid (47%). ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 3.66 (t, 2H, *H$_2$*C–NHC(O)O), 3.29 (t, 2H, *H$_2$*C–NHC), 2.95 (s, 3H, N–C*H$_3$*), 1.44 (s, 9H, C–(C*H$_3$*)$_3$). ^{13}C NMR (101 MHz, CD_3OD): δ (ppm) 42.6 (H$_2$*C*–NHC(O)O), 40.5 (H$_2$*C*–NHC), 27.3 (C–(*C*H$_3$)$_3$), 22.7 (N–*C*H$_3$). HRMS: m/z $[C_{12}H_{18}ClN_3O_4+Na]^+$ calc. 326.0883 g·mol^{-1}, exp. 326.0887 g·mol^{-1}.

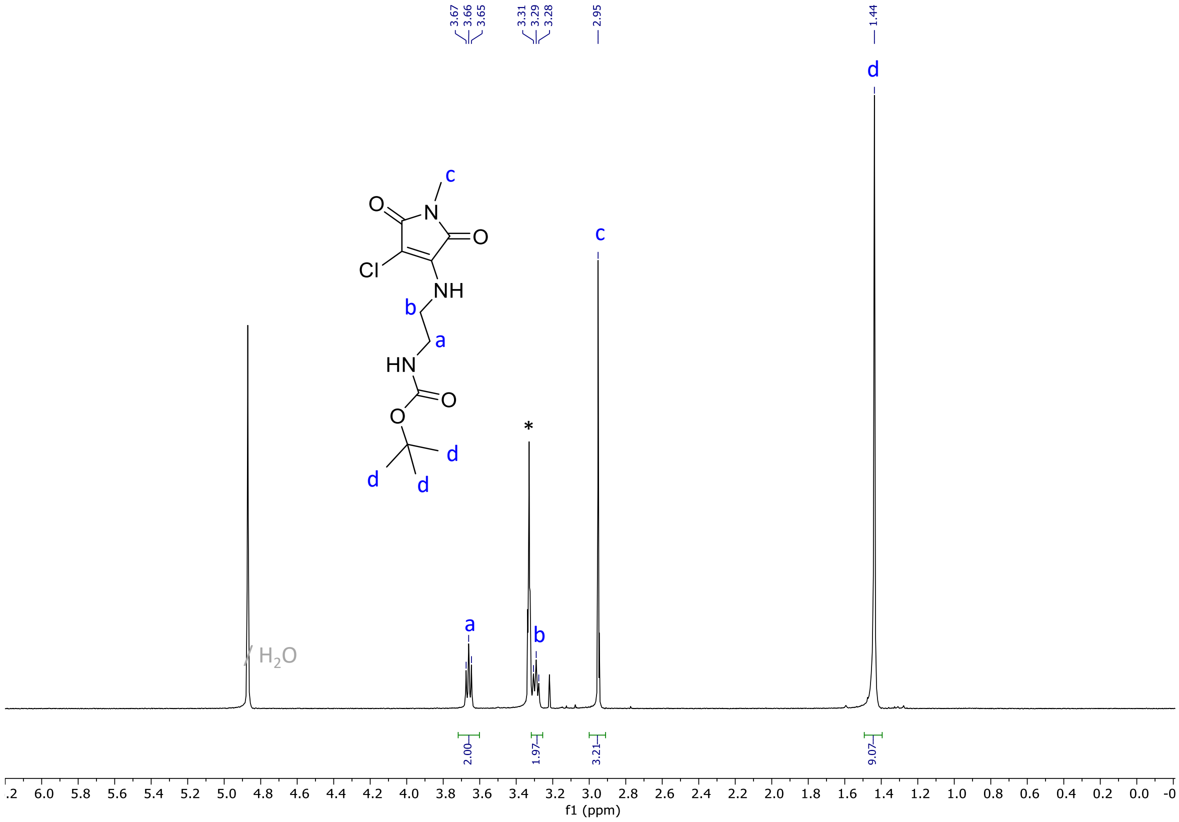


Figure S1. ^{1}H NMR of the Boc-protected maleimide dye in CD_3OD (400 MHz, 298 K)

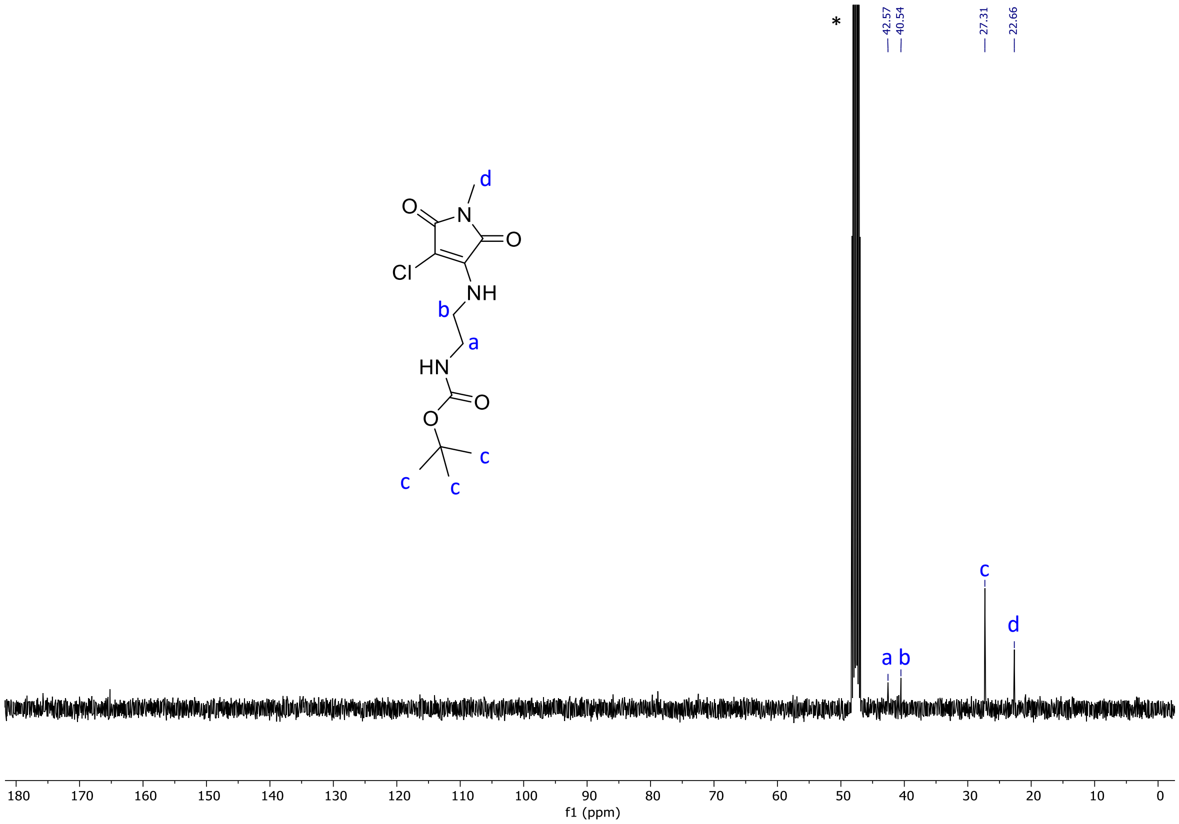
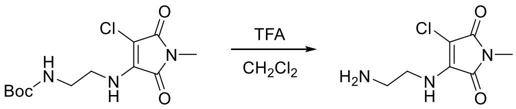


Figure S2. ^{13}C NMR of the Boc-protected maleimide dye in CD_3OD (101 MHz, 298 K)

3-((2-aminoethyl)amino)-4-chloro-1-methyl-1H-pyrrole-2,5-dione (ACM)



The Boc-ACM was reacted for 2 h in a DCM/ TFA (10:1 v/v) solution at room temperature before the rection mixture was dried *in vacuo*. The crude product was purified *via* column chromatography on silica gel (petroleum ether/ethyl acetate 1:2 v/v) yielding the product as a yellow solid (86%). ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 3.90 (t, 2H, H_2N–CH_2), 3.21 (t, 2H, HN–CH_2), 2.97 (s, 3H, N–CH_3). ^{13}C NMR (101 MHz, CD_3OD): δ (ppm) 167.9 (ClC–*C*=O), 165.1 (HNC–*C*=O), 141.4 (*C*–NH), 118.3 (*C*–Cl), 39.8 (H_2N–CH_2), 39.7 (HN–CH_2), 22.7 (N–CH_3). HRMS: m/z $[C_7H_{10}ClN_3O_2+H]^+$ calc. 204.0540 g·mol^{-1}, exp. 7204.0535 g·mol^{-1}.

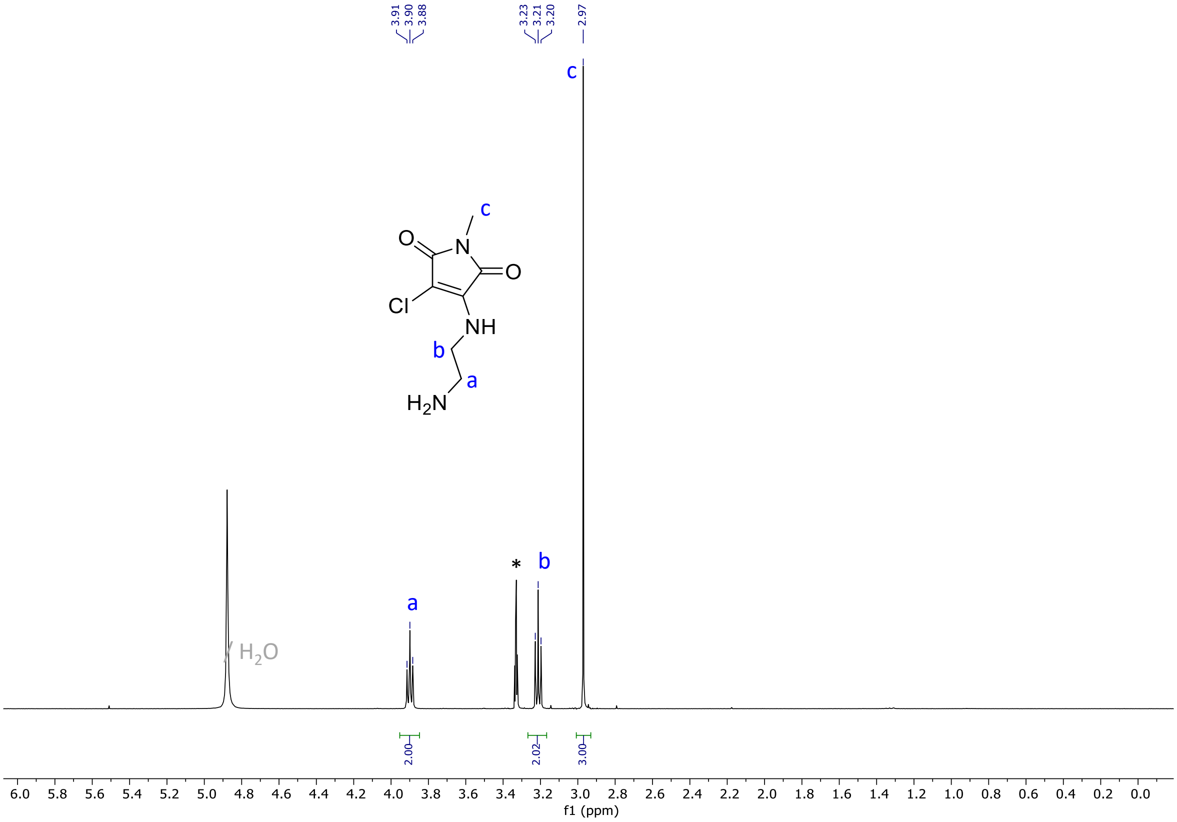


Figure S3. ^{1}H NMR of the maleimide dye in CD_3OD (400 MHz, 298 K)

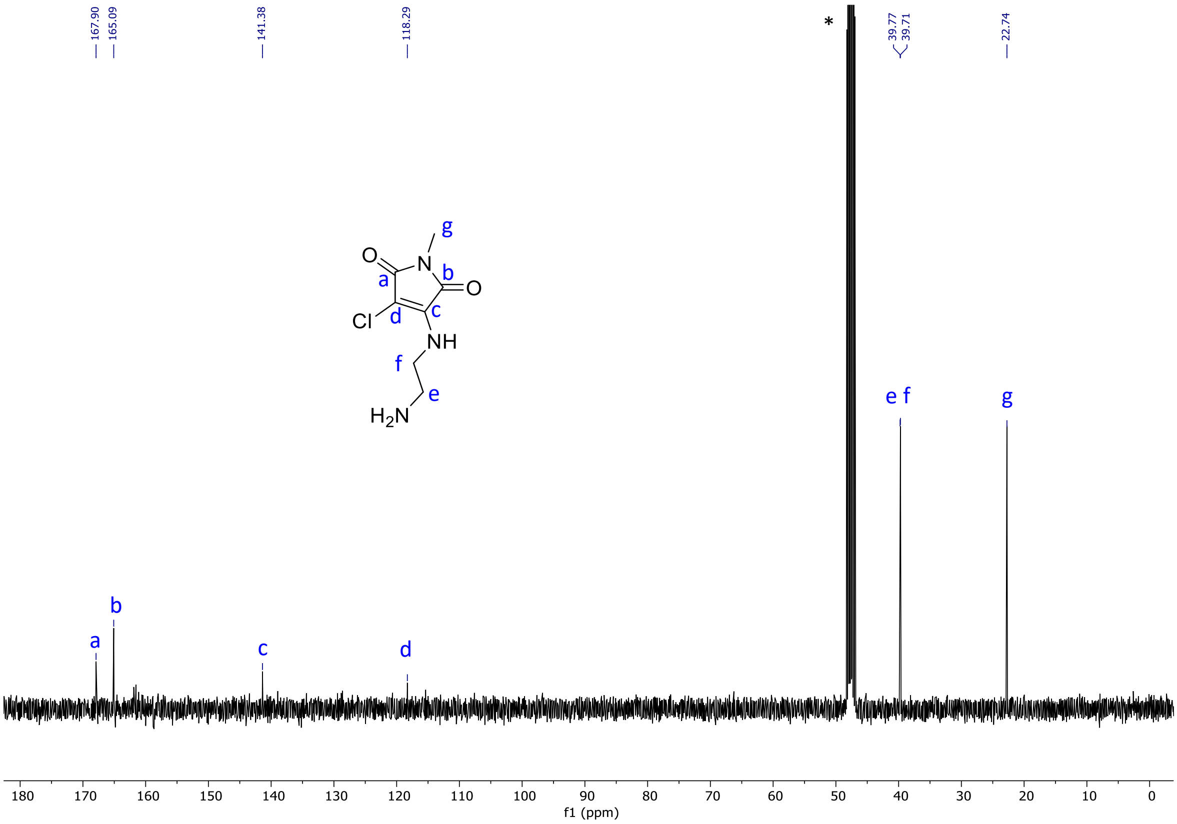


Figure S4. ^{13}C NMR of the maleimide dye in CD_3OD (101 MHz, 298 K)

General procedure for NiCCo-PISA

In a 7 mL vial, under inert atmosphere, the PAIC monomer in DMSO (0.5 mL) was added to the *o*-Tol(dppe)NiCl initiator (121 μL, 17.5 mg·mL^{-1} in DMSO) and stirred for 2 min. A solution of the MAIC and FAIC monomers in DMSO was then added and the reaction mixture was stirred for an additional 2 min before opening to atmosphere. The reaction's solids weight content was 50 mg·mL^{-1}.

Table S1. Quantities used for the copolymerisation of **D0%**, **D20%**, **D50%** and **D100%**.

Copolymer	PAIC (mg)	MAIC (mg)	FAIC (mg)	DMSO (mL)
D0%	59.0	30.5	-	1.83
D20%	59.0	24.4	6.8	1.84
D50%	59.0	15.2	17.1	1.87
D100%	59.0	-	34.2	1.85

General procedure for the PPM of NiCCo-PISA micelles

In a 7 mL vial, the crude NiCCo-PISA solution (0.5 mL, 50 mg·mL^{-1}) was diluted with DMSO (2 mL) to 10 mg·mL^{-1} and the neat nucleophile was added (5 equiv.). The reaction mixture was stirred for 24 hours before analysis by DLS. An aliquot of the resulting solution was diluted in DMSO and dialysed against water (6-8 kDa MWCO) for 3 days. The purified suspension was freeze-dried, precipitated from THF to hexane, and dried under vacuum. The purified copolymer was analysed by FT-IR then dissolved in THF or $CDCl_3$ for CD and NMR spectroscopy, respectively.

Characterisations

P(MAIC)-*co*-P(FAIC) copolymer characterisation

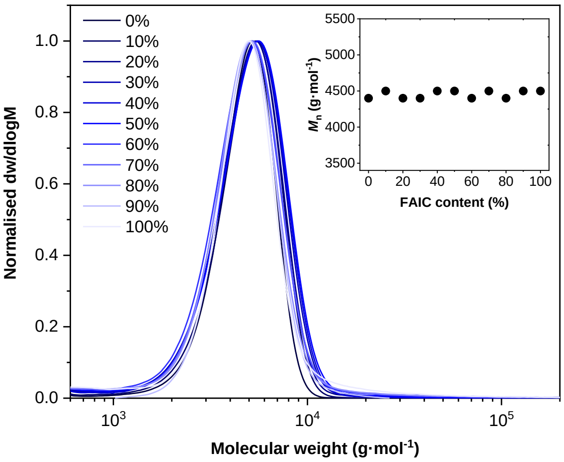


Figure S5. Normalised SEC molecular weight distributions (THF + 2% v/v NEt_3, 40 °C, PS standards) of P(**MAIC**)$_x$-*co*-P(**FAIC**)$_y$ copolymers (total DP = 30) with **FAIC** content ranging from 0 to 100 mol %.

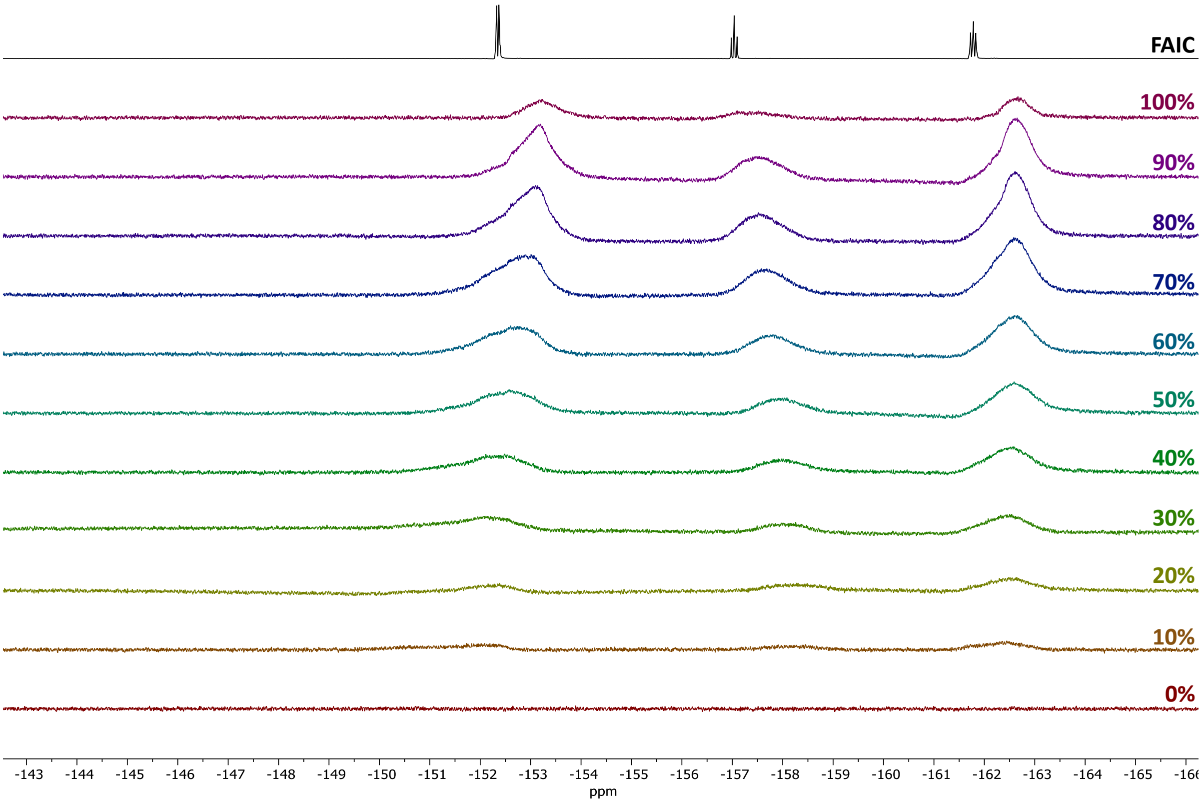


Figure S6. ^{19}F NMR spectra of **P(MAIC)$_x$-*co*-P(FAIC)$_y$** (total DP = 30) with **FAIC** content from 0% to 100%, compared to molecular **FAIC**, in $CDCl_3$ (377 MHz, 298 K).

EOA- and TFEA-substituted copolymer characterisations

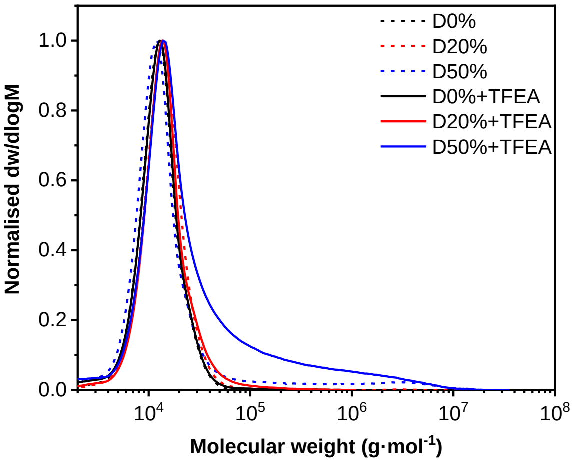


Figure S7. Normalised SEC molecular weight distributions (THF + 2% v/v NEt_3, 40 °C, PS standards) of **D0%**, **D0%+TFEA D20%**, **D20%+TFEA**, **D50%** and **D50%+TFEA**.

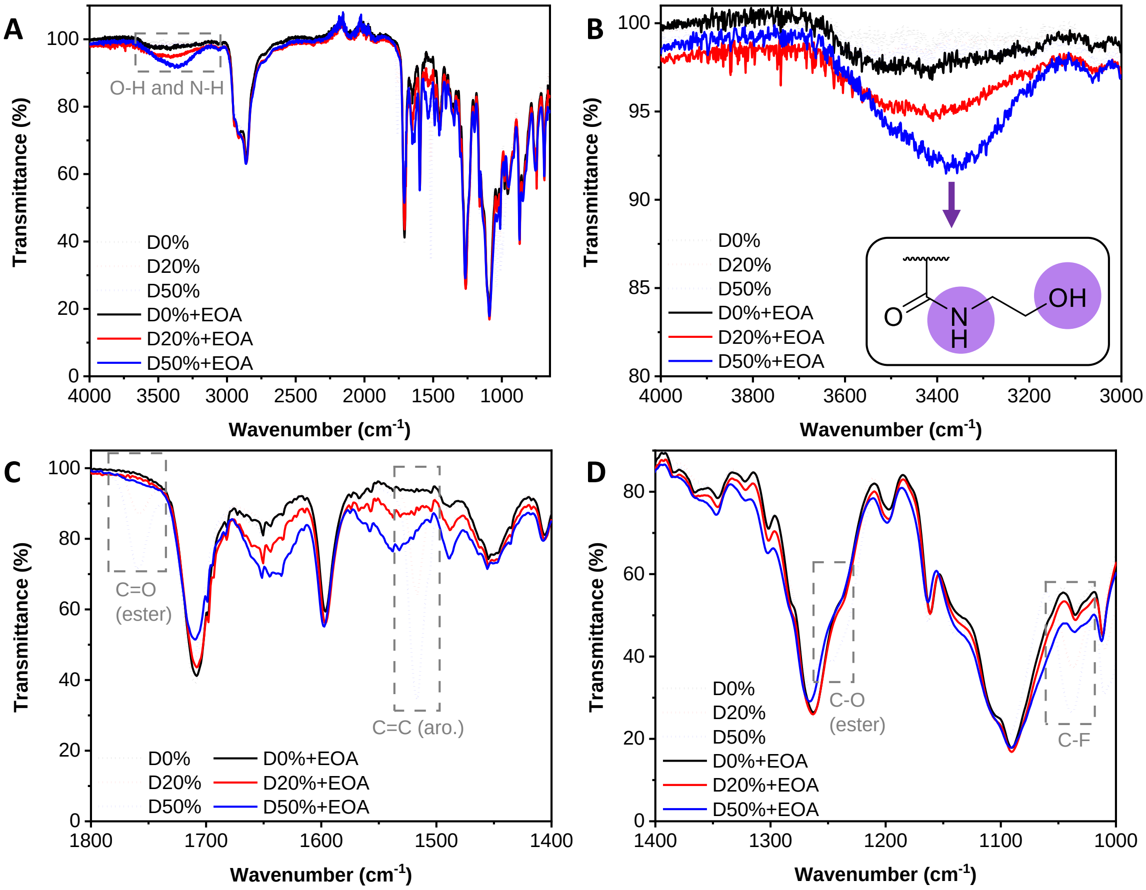


Figure S8. FT-IR spectra of the **D0%** (black)**, D20%** (red) **and D50%** (blue) copolymers before (dotted line) and after reaction with **EOA** (solid line). (A) Full spectrum. (B) Zoom in the 4000-3000 cm^{-1} region. (C) Zoom in the 1800-1400 cm^{-1} region. (D) Zoom in the 1400-1000 cm^{-1} region.

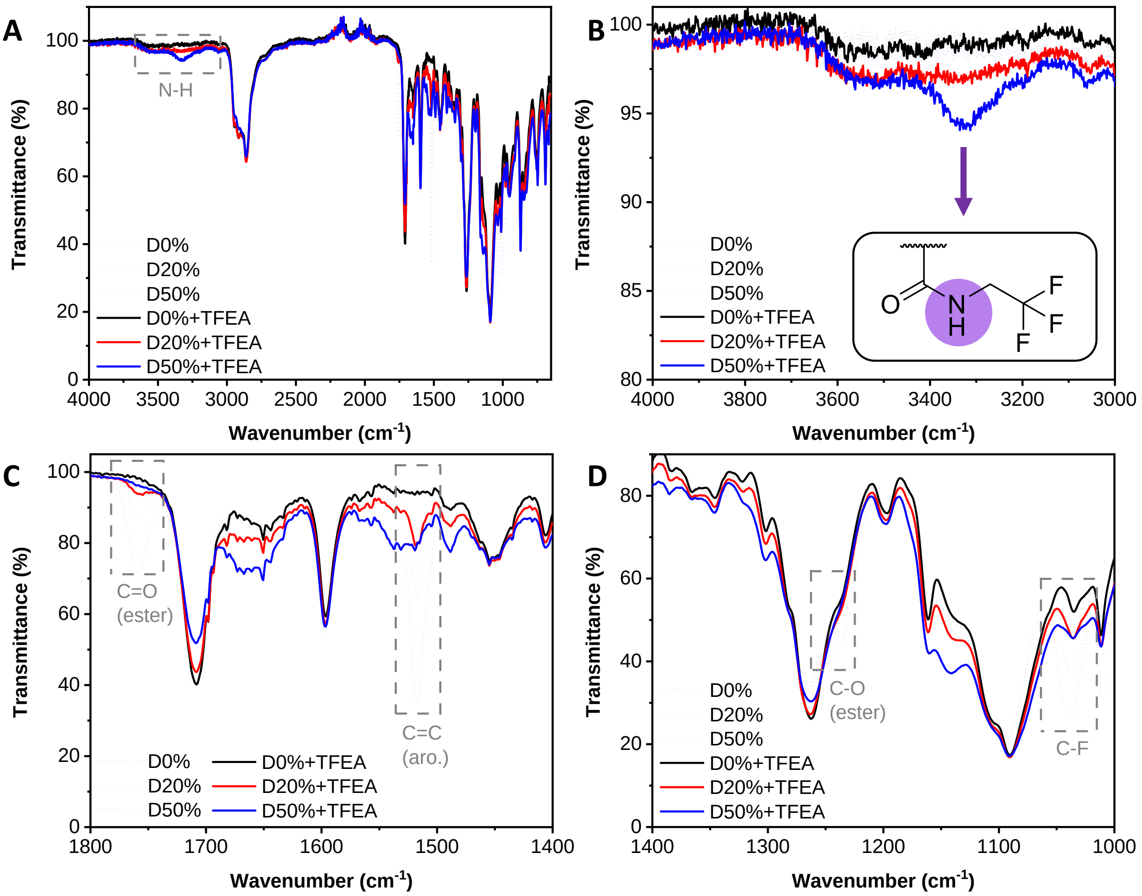


Figure S9. FT-IR spectra of the **D0%** (black)**, D20%** (red) **and D50%** (blue) copolymers before (dotted line) and after reaction with **TFEA** (solid line). (A) Full spectrum. (B) Zoom in the 4000-3000 cm^{-1} region. (C) Zoom in the 1800-1400 cm^{-1} region. (D) Zoom in the 1400-1000 cm^{-1} region.

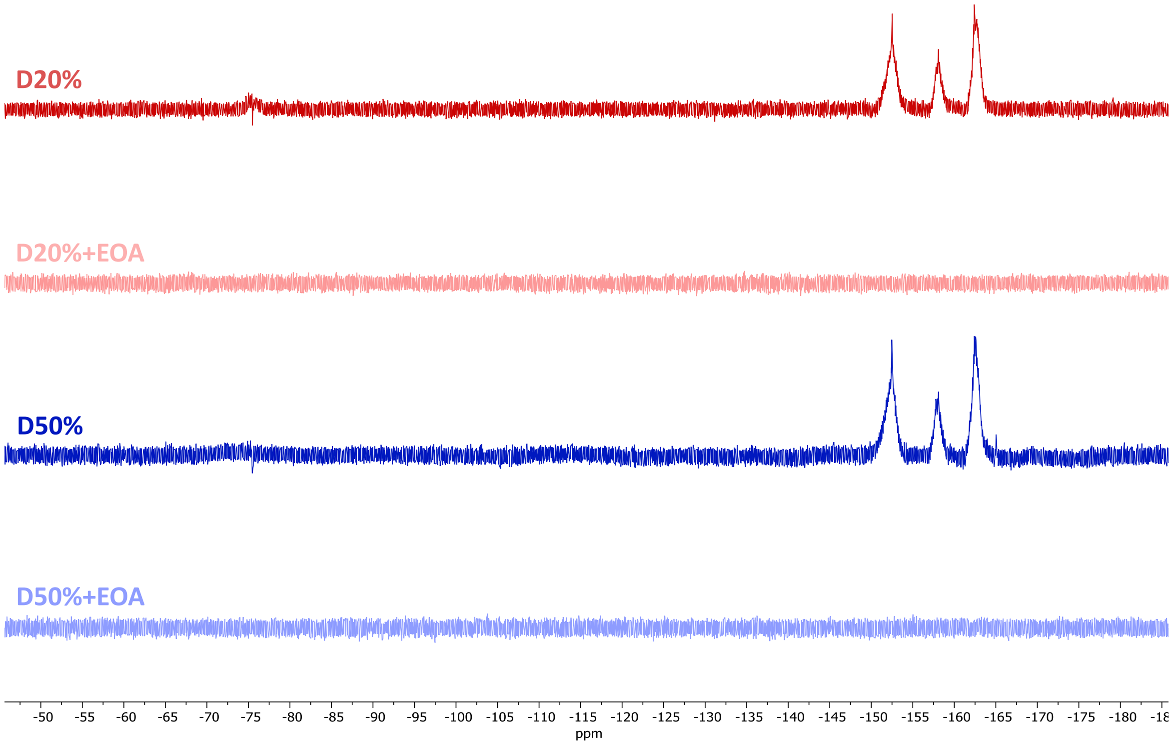


Figure S10. ^{19}F NMR spectra of **D20%**, **D20%+EOA**, **D50%** and **D50%+EOA** in $CDCl_3$ (377 MHz, 298 K).

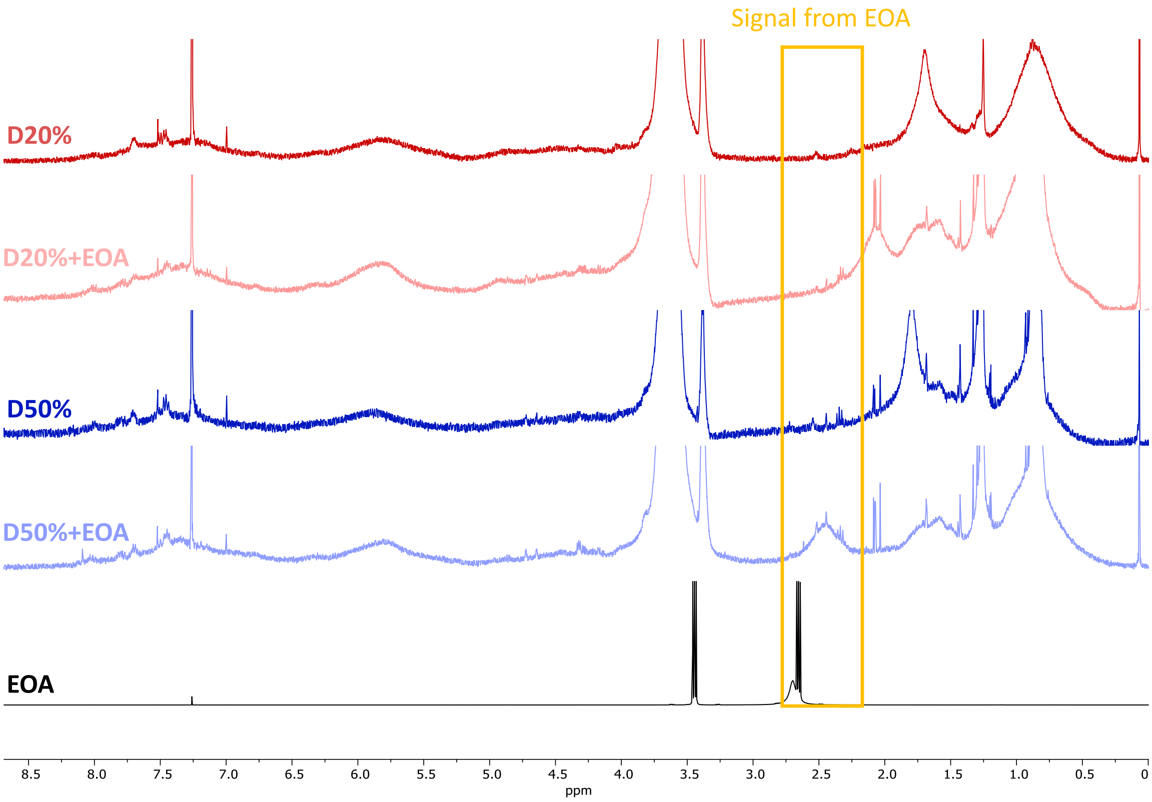


Figure S11. ^{1}H NMR spectra of **D20%**, **D20%+EOA**, **D50%**, **D50%+EOA** and EOA in $CDCl_3$ (400 MHz, 298 K).

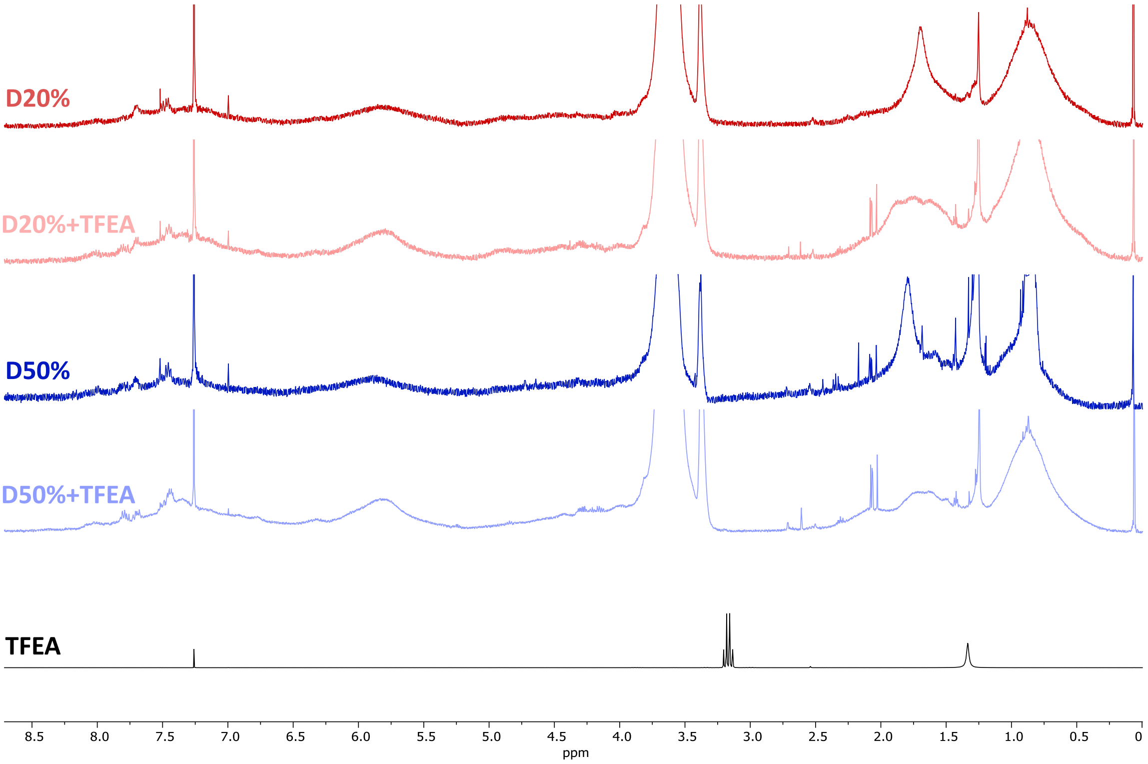


Figure S12. ^{1}H NMR spectra of **D20%**, **D20%+TFEA**, **D50%**, **D50%+TFEA** and TFEA in $CDCl_3$ (400 MHz, 298 K).

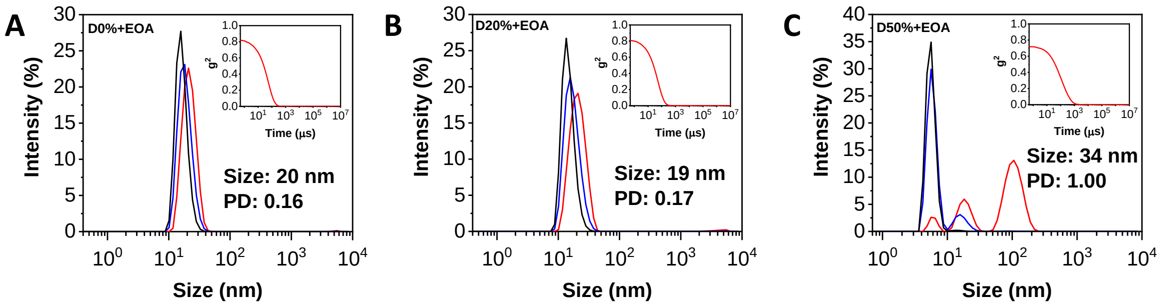


Figure S13. Size distributions of (A) **D0%+EOA**, (B) **D20%+EOA**, and (C) **D50%+EOA** in DMSO obtained by DLS. The intensity (red line), volume (blue line) and number (black line) distributions are displayed. The insets show the correlograms.

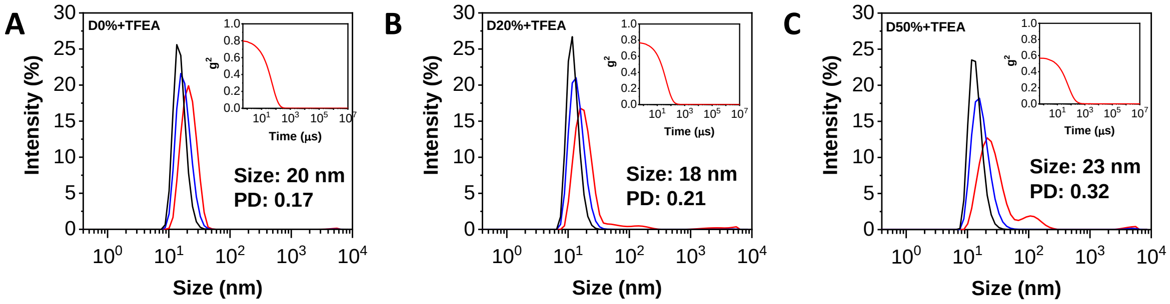


Figure S14. Size distributions of (A) **D0%+TFEA**, (B) **D20%+TFEA**, and (C) **D50%+TFEA** in DMSO obtained by DLS. The intensity (red line), volume (blue line) and number (black line) distributions are displayed. The insets show the correlograms.

ACM-substituted copolymers characterisation

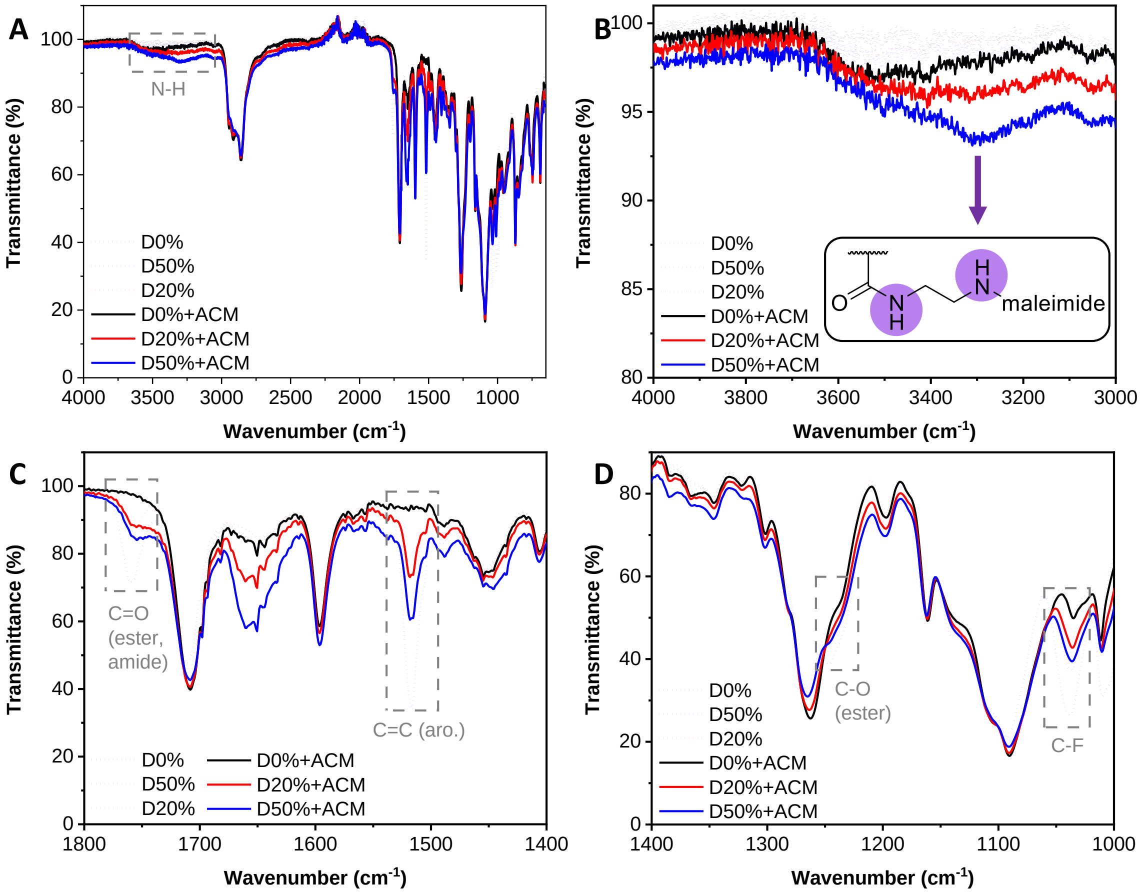


Figure S15. FT-IR spectra of the **D0%** (black), **D20%** (red) **and D50%** (blue) copolymers before (dotted line) and after reaction with ACM (solid line). (A) Full spectrum. (B) Zoom in the 4000-3000 cm^{-1} region. (C) Zoom in the 1800-1400 cm^{-1} region. (D) Zoom in the 1400-1000 cm^{-1} region

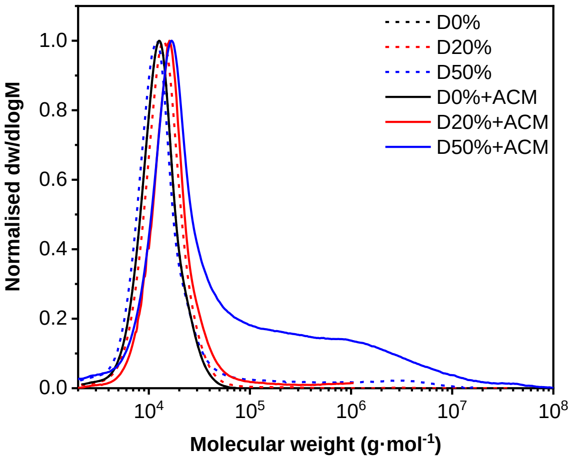


Figure S16. Normalised SEC molecular weight distributions (THF + 2% v/v NEt_3, 40 °C, PS standards) of **D0%**, **D0%+AMC D20%**, **D20%+AMC**, **D50%** and **D50%+AMC**.

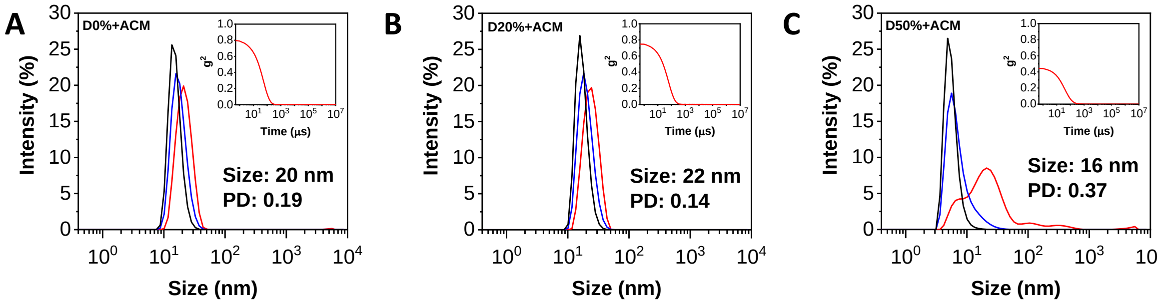


Figure S17. Size distributions of (A) **D0%+AMC**, (B) **D20%+AMC**, and (C) **D50%+AMC** in DMSO obtained by DLS. The intensity (red line), volume (blue line) and number (black line) distributions are displayed. The insets show the correlograms.

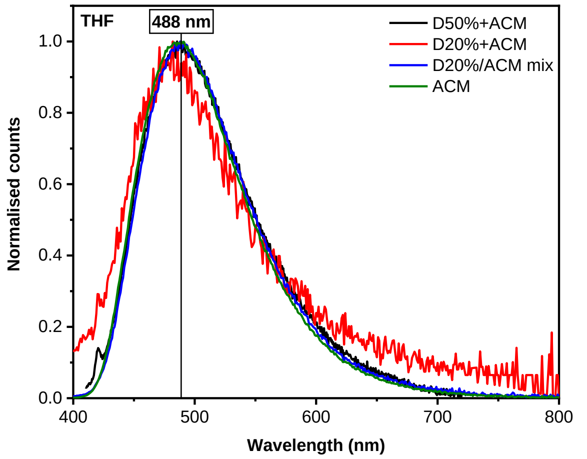


Figure S18. Fluorescence spectra for the different copolymers substituted by ACM along with the free ACM in THF.

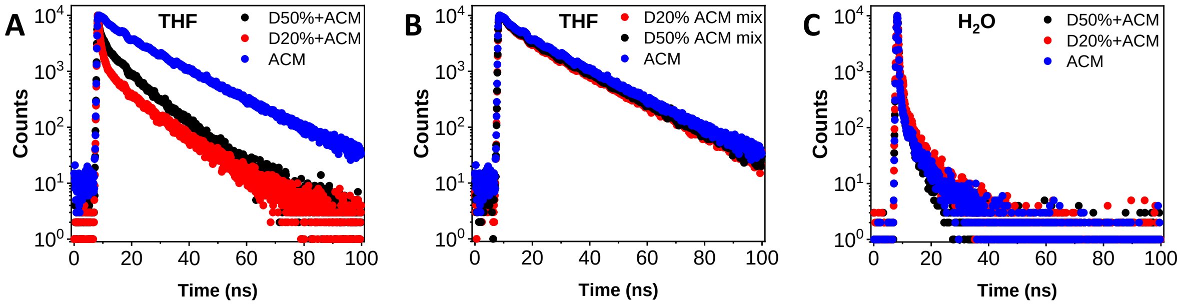


Figure S19. Fluorescence lifetime spectra of: (A) Comparison between **D20%+ACM**, **D50%+ACM** and the free ACM in THF, and the free ACM in water. (B) Copolymers mixed with ACM and ACM alone in THF. (C) Copolymers mixed with ACM and ACM alone in water.

Table S2. Lifetime measurements of the different assembled copolymers and free ACM in water and THF.

Sample	$\tau_{Av,a}$ (ns)	$\tau_{Av,I}$ (ns)
D20%+ACM (THF)[a]	6.5 ± 0.2	11.1 ± 0.3
D20%+ACM (water)[b]	1.1 ± 0.1	4.2 ± 0.1
D20%/ACM (mix, THF)[c]	13.8 ± 0.1	15.4 ± 0.1
D50%+ACM (THF)[a]	7.7 ± 0.2	9.9 ± 0.3
D50%+ACM (water)[b]	0.7 ± 0.1	3.2 ± 0.1
D50%/ACM (mix, THF)[c]	14.2 ± 0.1	15.5 ± 0.1
ACM (THF)	14.8 ± 0.1	15.7 ± 0.1
ACM (water)	0.8 ± 0.1	5.1 ± 0.2

[a] Functionalised copolymer after solution in THF (disassembled). [b] Functionalised copolymer in water (assembled). [c] Mixture of non-functionalised copolymer and AMC in THF (disassembled)

Table S3. Characterisation of **D0%**, **D20%** and **D50%** before and after treatment with EOA, TFEA or ACM.

Polymer	D_{DLS} (nm)[a]	$M_{n,SEC}$ (kDa)[b]	$Đ_M$ [b]	CD_{360} (mdeg)[c]
D0%	20 (0.18)	11.2	1.24	14
D0%+EAO	20 (0.16)	11.4	1.22	-
D0%+TFEA	20 (0.17)	11.4	1.25	-
D0%+ACM	20 (0.19)	11.2	1.24	-
D20%	21 (0.14)	12.4	1.24	13
D20%+EOA	19 (0.17)	13.5	1.38	13
D20%+TFEA	18 (0.21)	13.0	1.20	13
D20%+ACM	22 (0.14)	14.5	1.28	16
D50%	20 (0.25)	10.5	1.34	9
D50%+EOA	34 (1.00)	-[d]	-[d]	8
D50%+TFEA	23 (0.32)	-[d]	-[d]	8
D50%+ACM	16 (0.37)	-[d]	-[d]	10

[a] Particle size measured by DLS with PDI in parenthesis. [b] Determined by SEC (THF + 2% v/v NEt_3) using PS standards. [c] CD (THF, 0.5 mg·mL^{-1}) signal at λ = 360 nm. [d] Molecular weight distribution is outside the calibration range

References

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