Supplementary Material: Fluorescent Polyolefins by Ring-Opening Metathesis Polymerization of 3-substituted cyclooctenes

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NMR SPECTRA OF MONOMERS

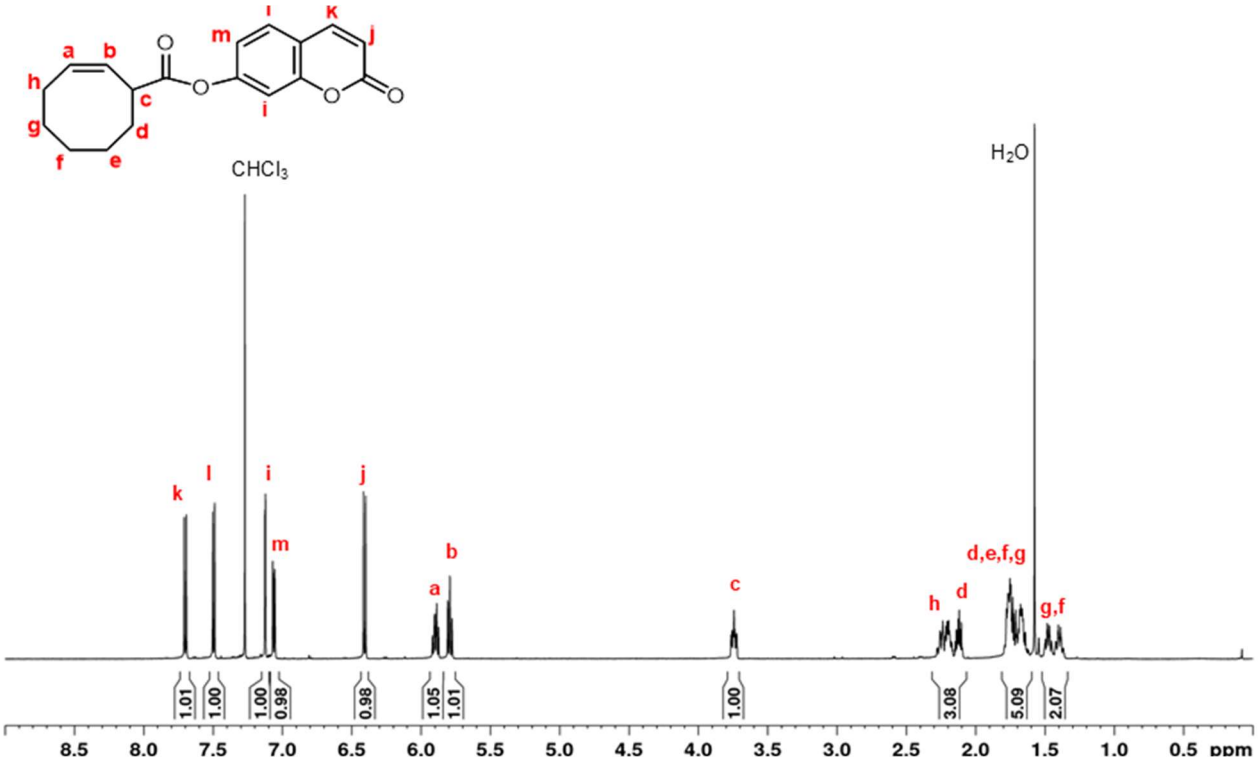

Figure S1. ^{1}H NMR spectrum of **M1** ($CDCl_3$, 600 MHz).

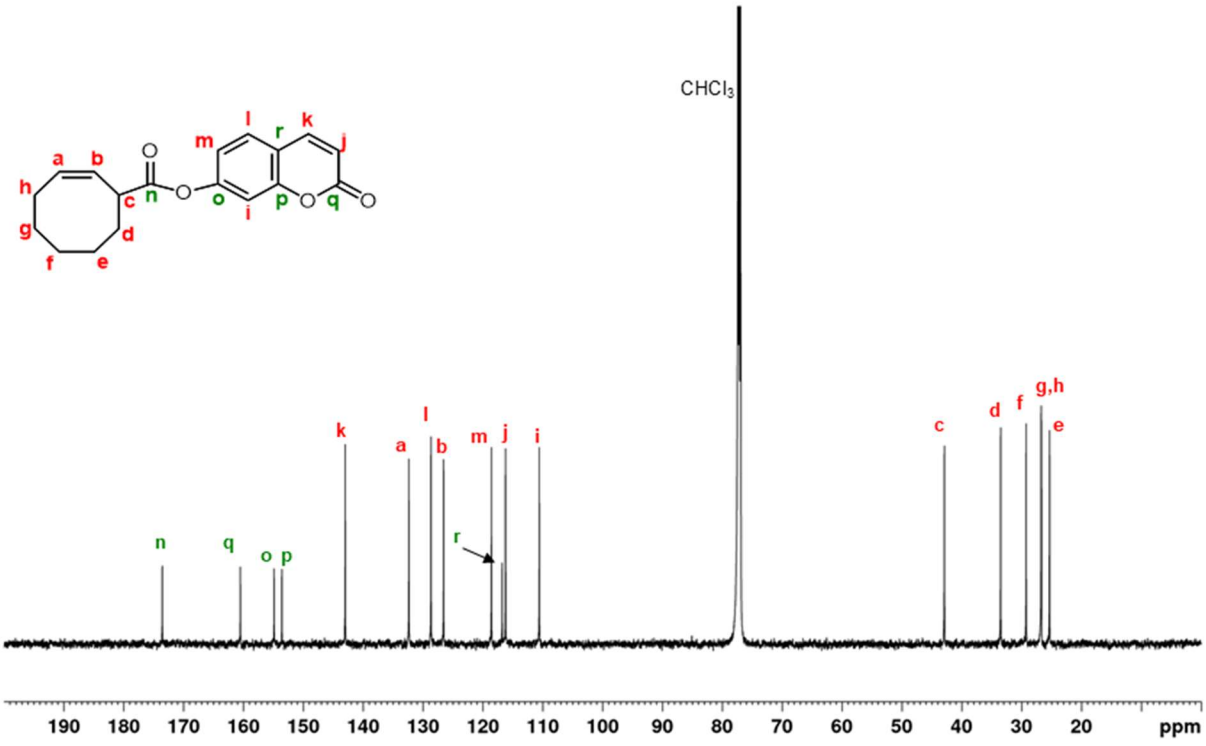

Figure S2. ^{13}C NMR spectrum of **M1** ($CDCl_3$, 150 MHz).

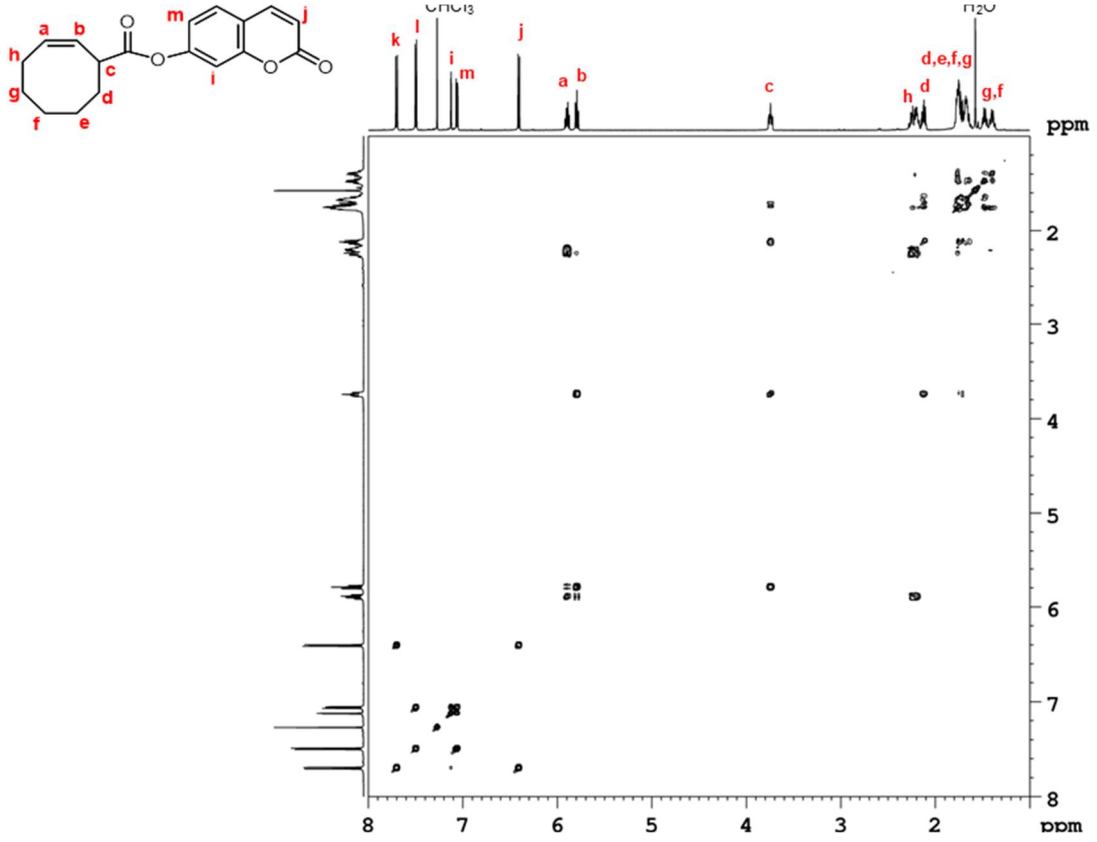

Figure S3. ^{1}H-^{1}H COSY spectrum of **M1** ($CDCl_3$, 600 MHz).

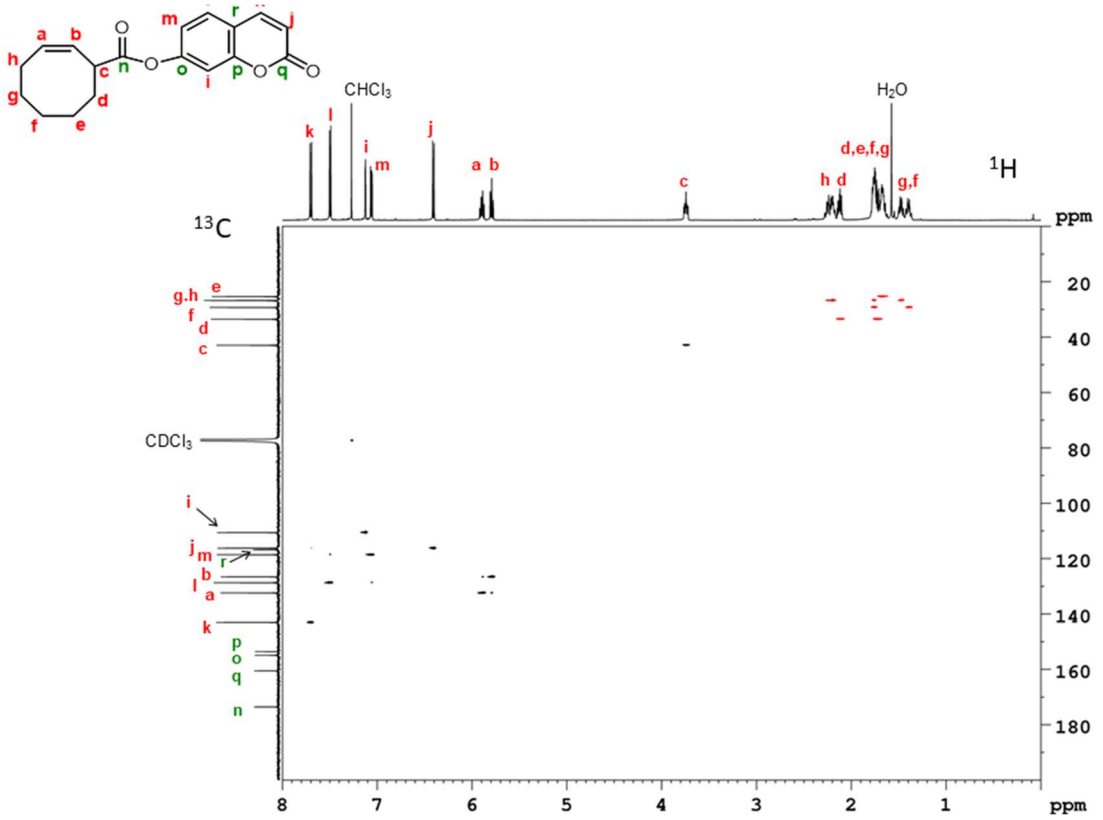

Figure S4. ^{1}H-^{13}C HSQC spectrum of **M1** ($CDCl_3$, 600 MHz for ^{1}H, 150 MHz for 13C).

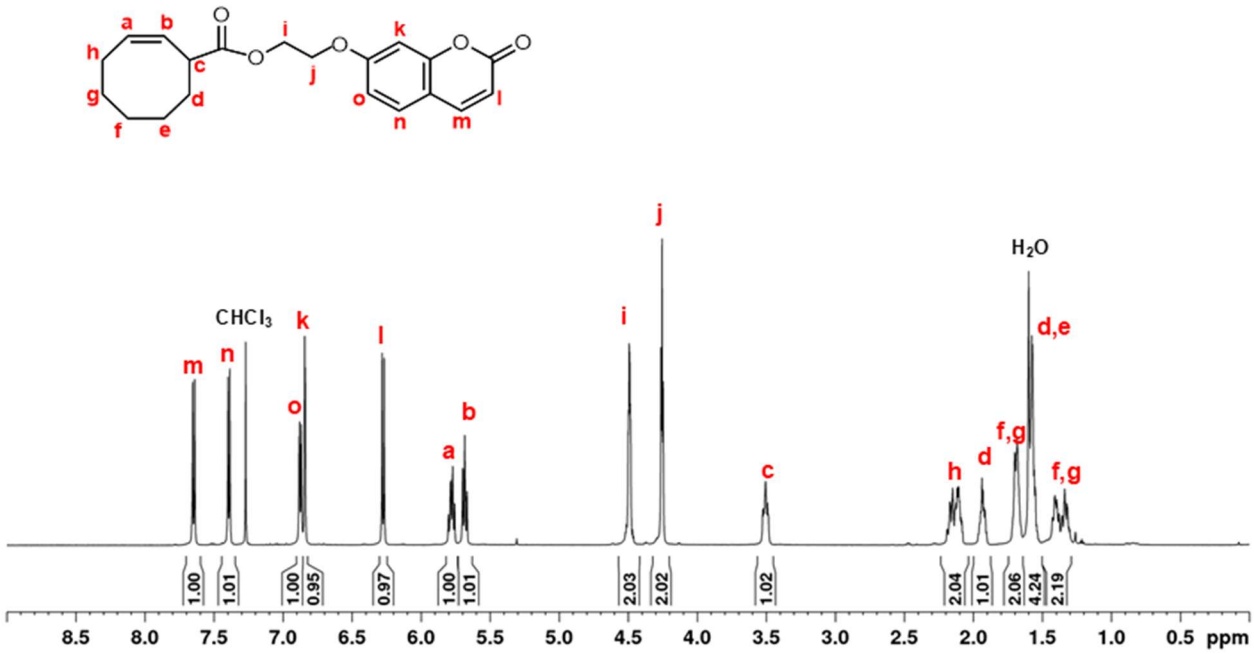

Figure S5. ^{1}H NMR of **M2** ($CDCl_3$, 600 MHz).

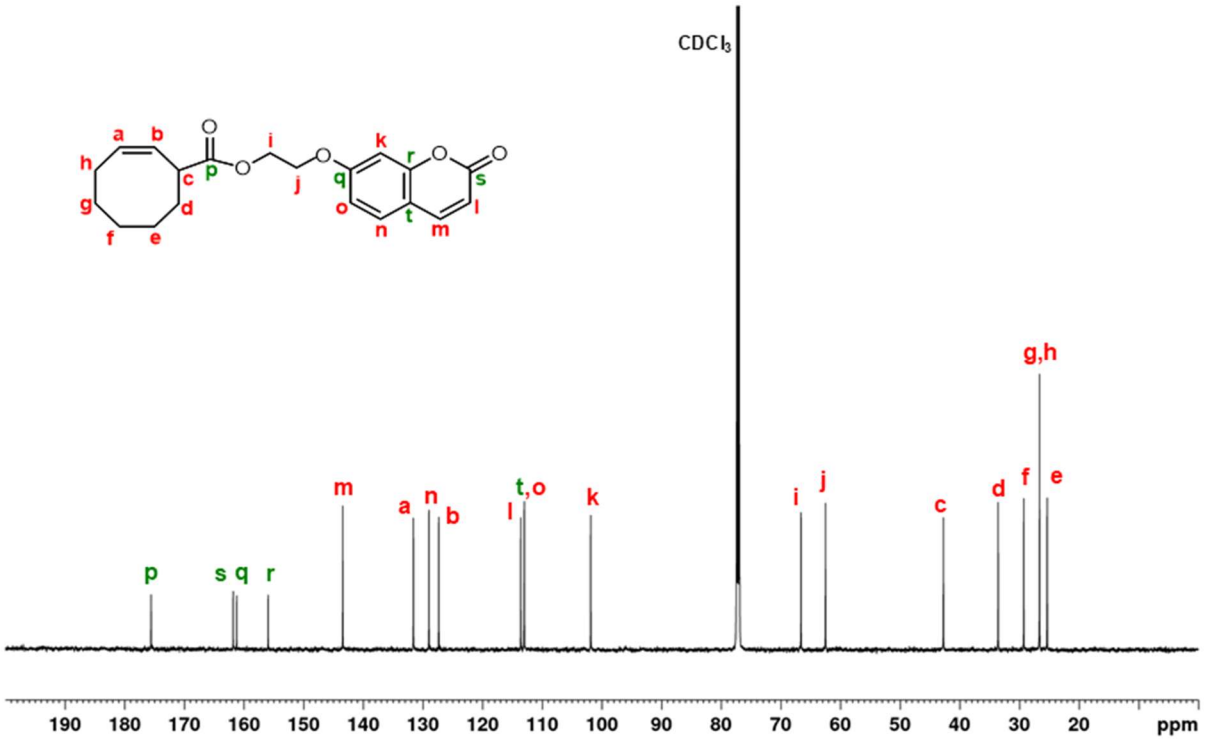

Figure S6. ^{13}C NMR of **M2** ($CDCl_3$, 150 MHz).

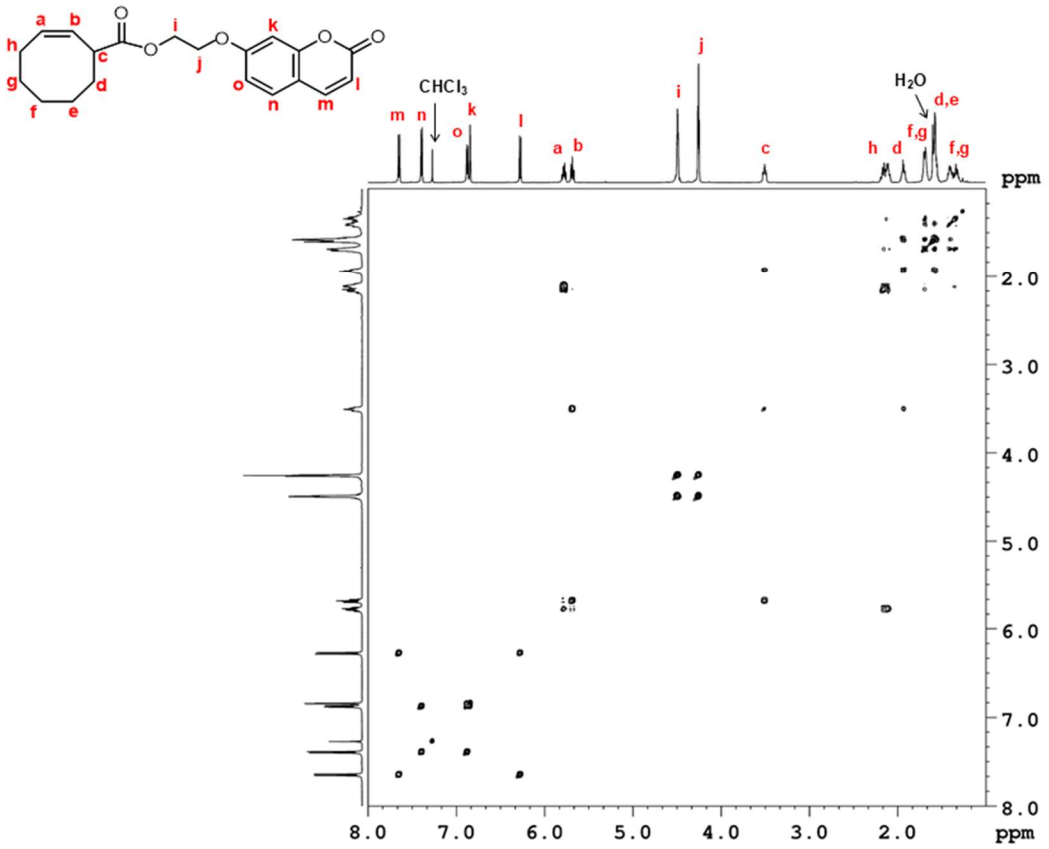

Figure S7. ^{1}H-^{1}H COSY spectrum of **M2** ($CDCl_3$, 600 MHz).

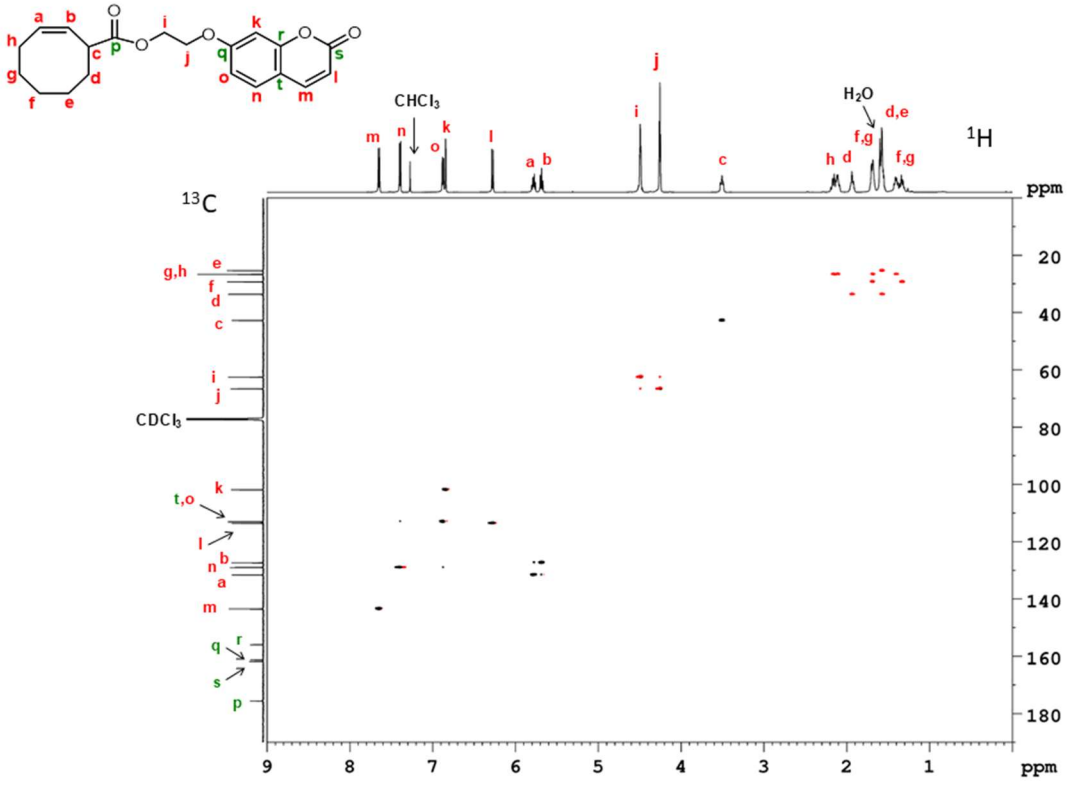

Figure S8. ^{1}H-^{13}C HSQC spectrum of **M2** ($CDCl_3$, 600 MHz for ^{1}H, 150 MHz for 13C).

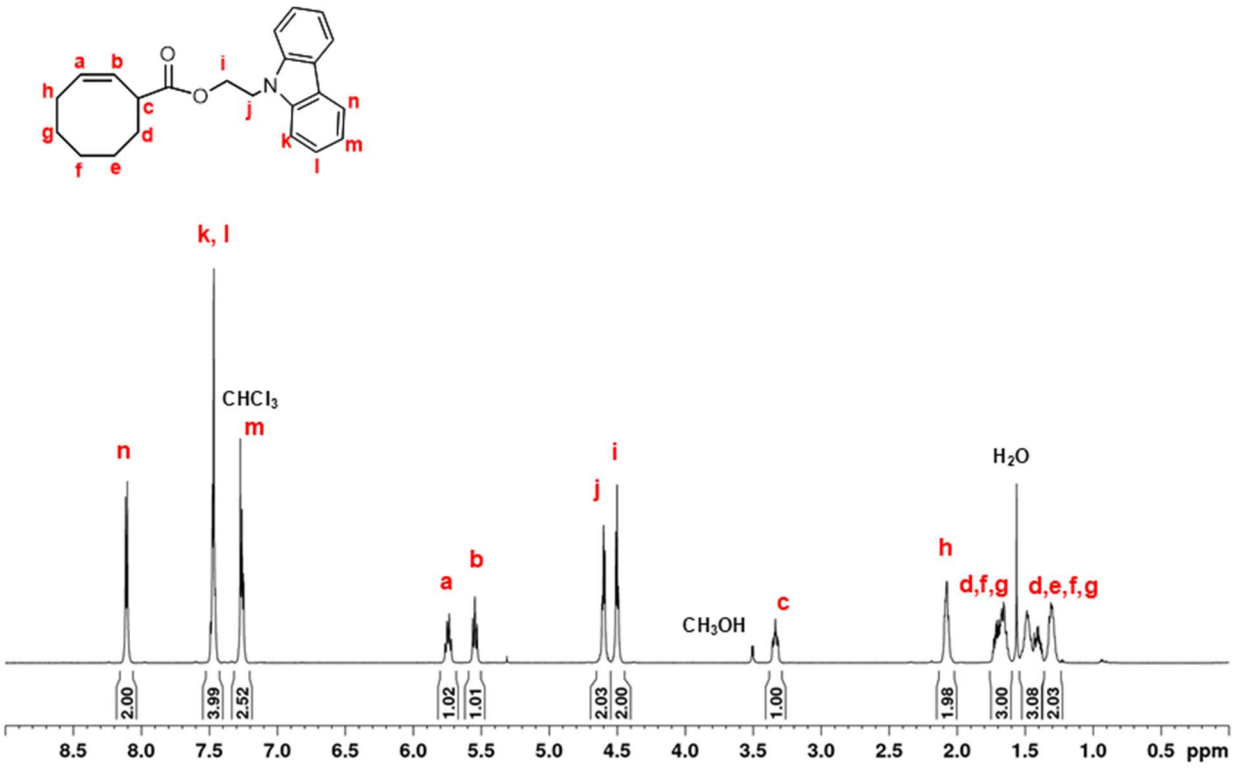

Figure S9. ^{1}H NMR of **M3** ($CDCl_3$, 400 MHz).

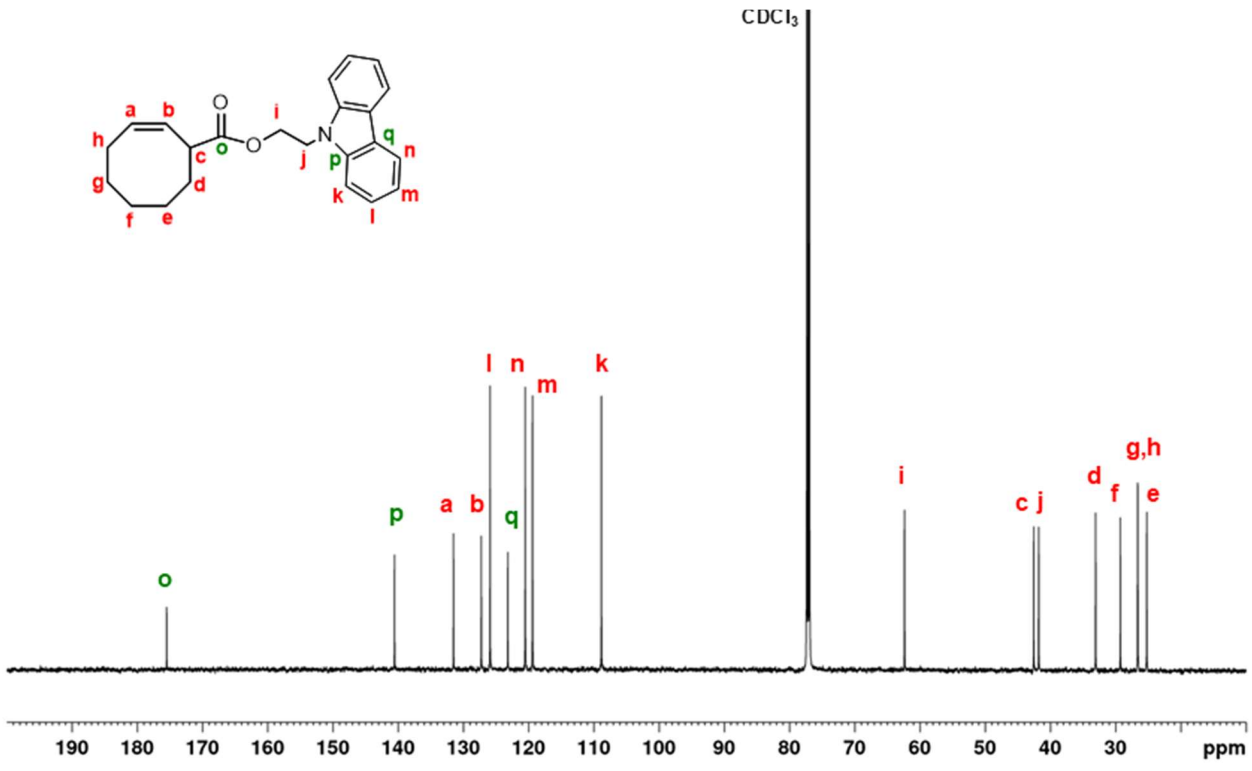

Figure S10. ^{13}C NMR of **M3** ($CDCl_3$, 100 MHz).

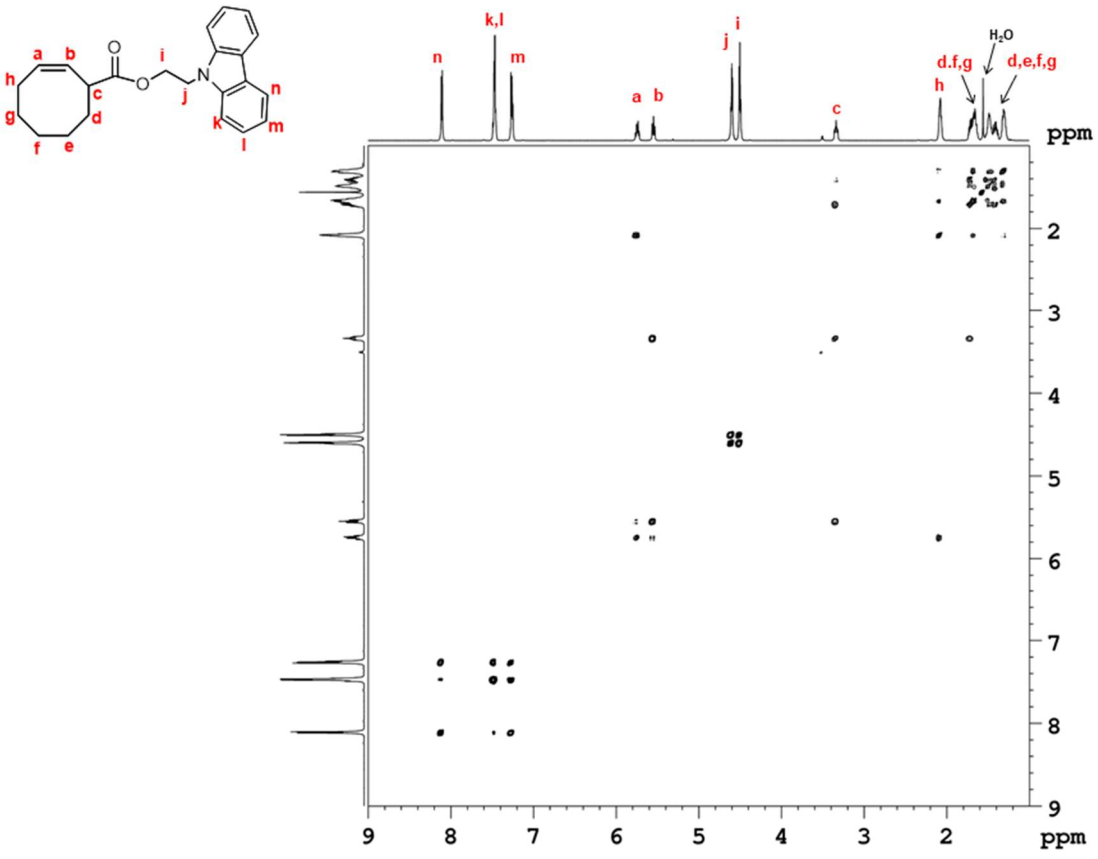

Figure S11. ^{1}H-^{1}H COSY spectrum of **M3** ($CDCl_3$, 600 MHz).

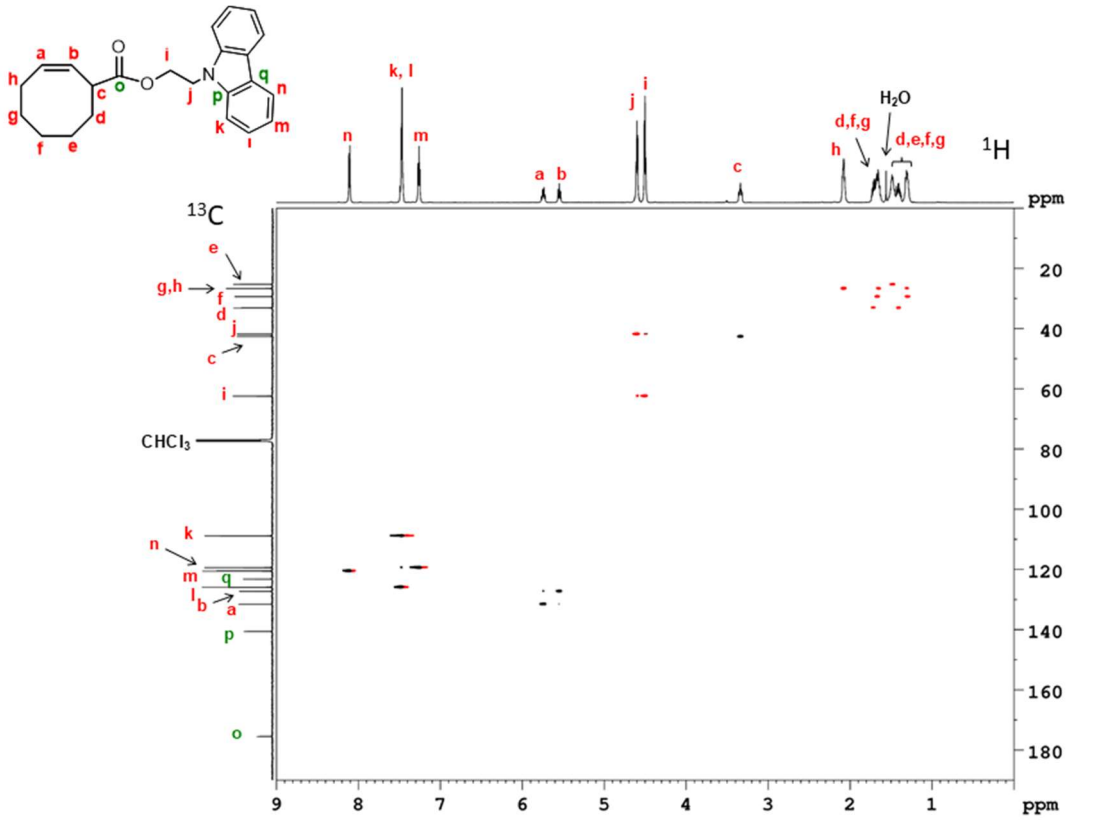

Figure S12. ^{1}H-^{13}C HSQC spectrum of **M3** ($CDCl_3$, 600 MHz for ^{1}H, 150 MHz for 13C).

UV visible absorption spectra of monomers

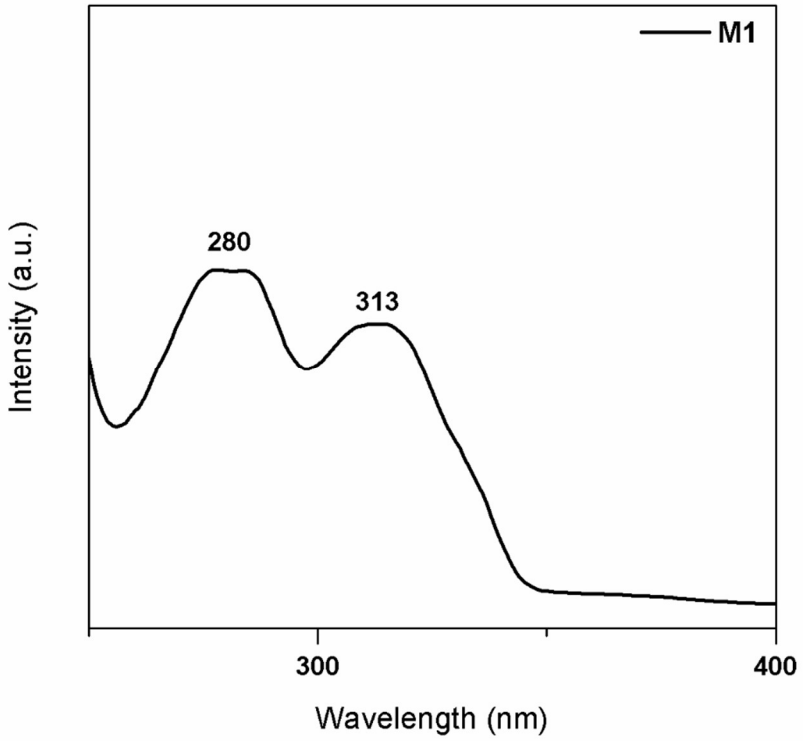

Figure S13. UV-vis absorption spectrum of **M1** ($CHCl_3$ solution, 1 mg/mL).

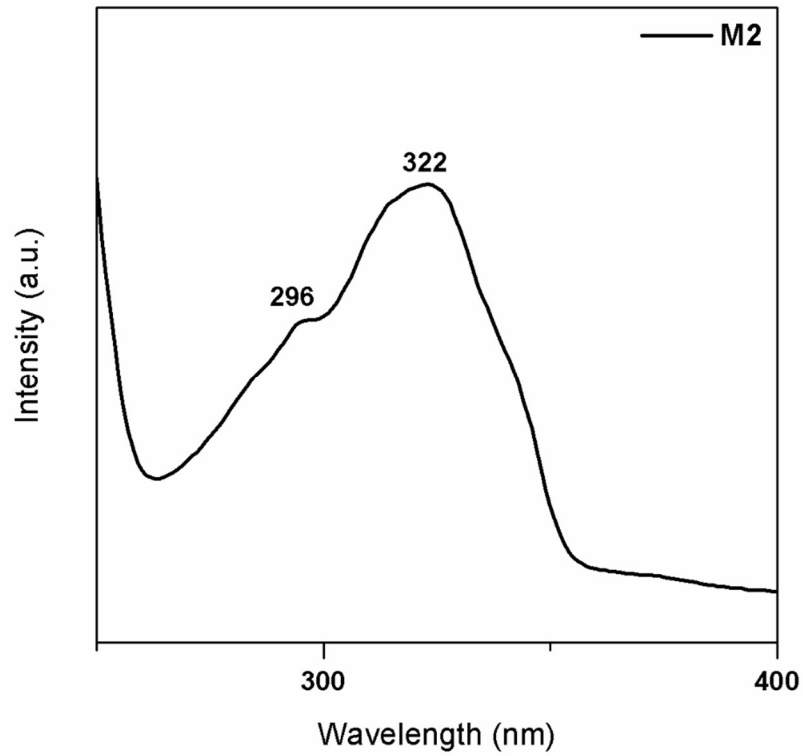

Figure S14. UV-vis absorption spectrum of **M2 (**$CHCl_3$ solution, 1 mg/1 mL).

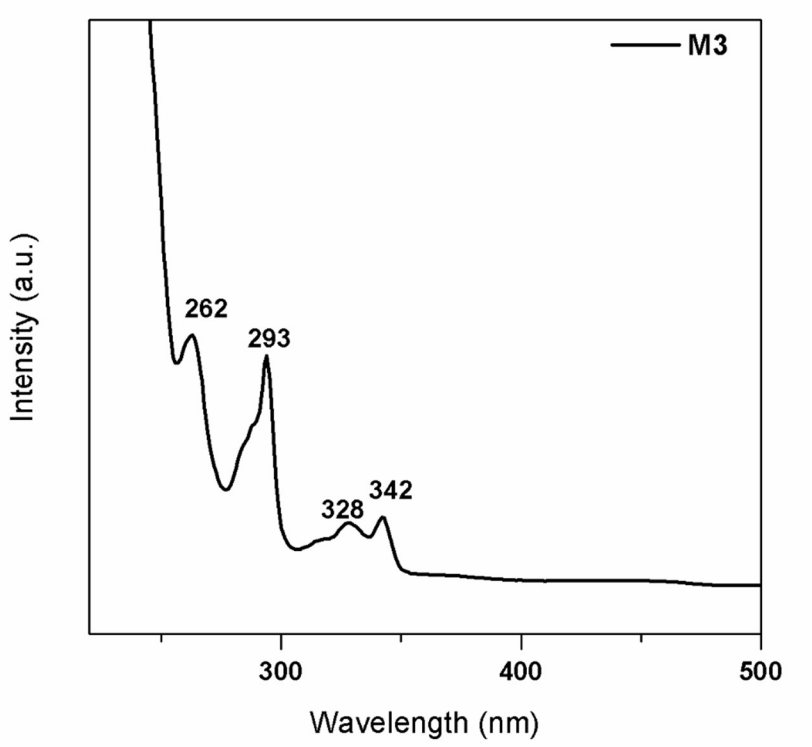

Figure S15. UV-vis absorption spectrum of **M3** ($CHCl_3$ solution, 1 mg/1 mL).

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Fluorescence spectra of monomers

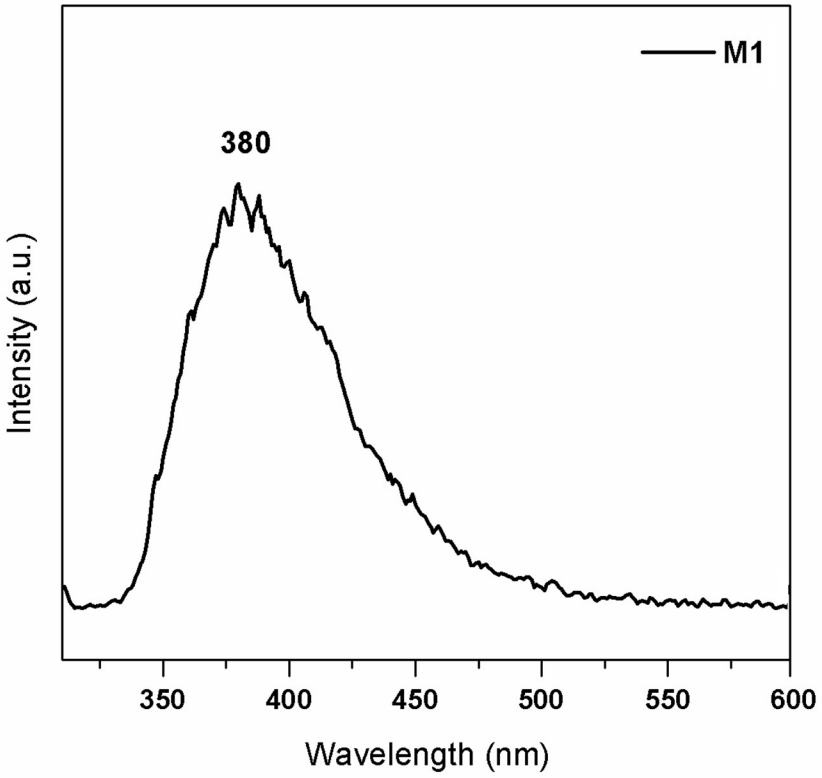

Figure S16: Emission spectrum of **M1** ($CHCl_3$ solution, 1 mg/1 mL).

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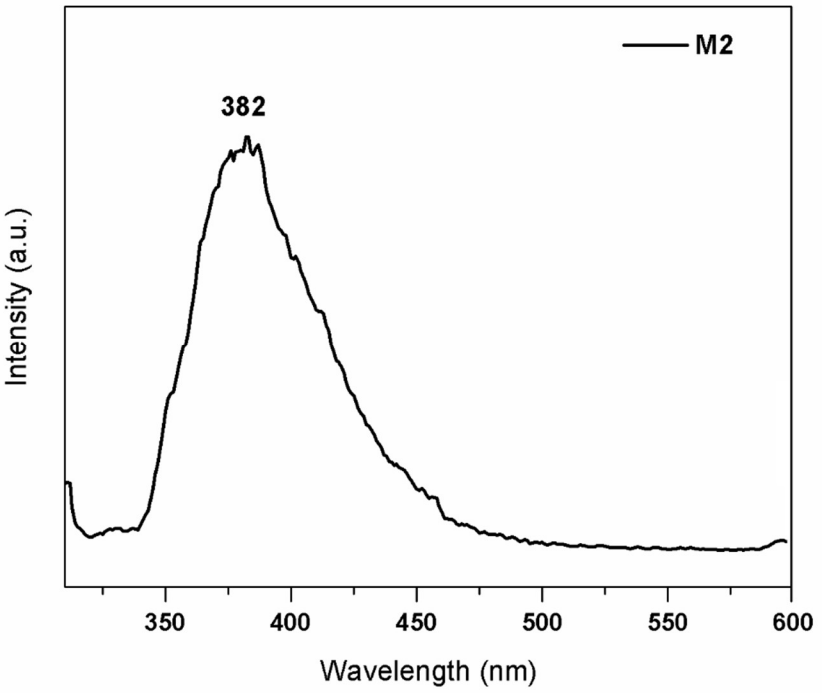

Figure S17. Emission spectrum of **M2** ($CHCl_3$ solution, 1 mg/1 mL).

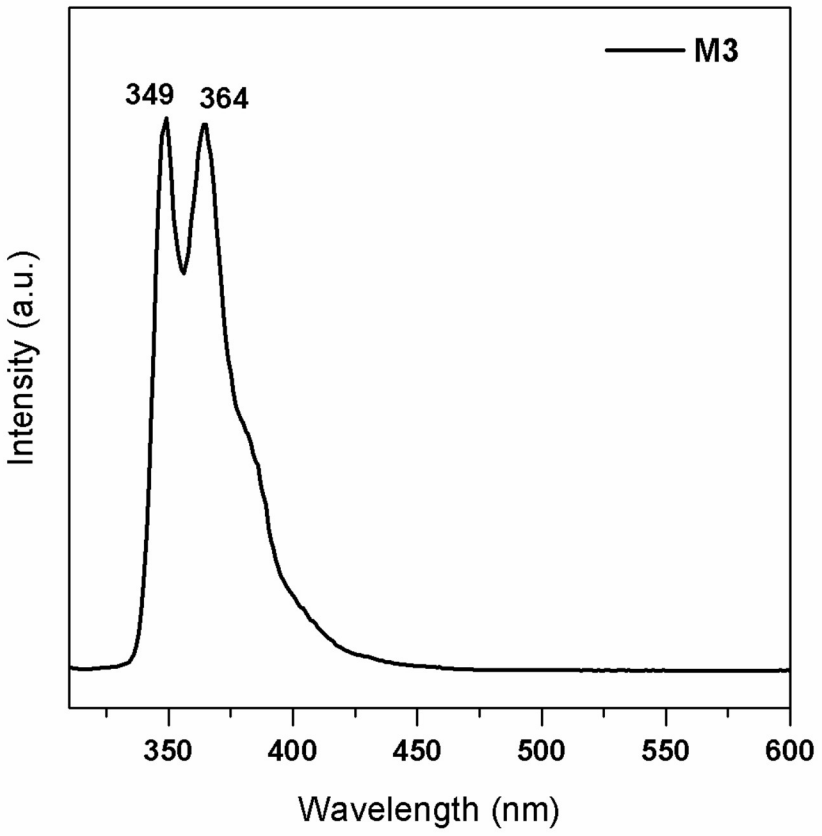

Figure S18. Emission spectrum of **M3** ($CHCl_3$ solution, 1 mg/1 mL).

Crystal structure determination and refinement for M3

Data indexing was performed using APEX3.[1] Data integration and reduction were performed using SAINT.[2] Absorption correction was performed by multi-scan method in SADABS.[3] The structure was solved using SHELXT[4] and refined by means of full matrix least-squares based on F^2 using the program SHELXL[5] using OLEX2[6] as GUI. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were positioned geometrically and included in structure factors calculations but not refined. The atoms C21A and C22A belonging to the cyclooctene unit are disordered over two positions. The disordered atoms were modelled as two parts with refined occupancy factors of 0.742(14) and 0.258(14). ORTEP was drawn using OLEX2 (Figure S19). Relevant crystallographic data are reported in Table S1.

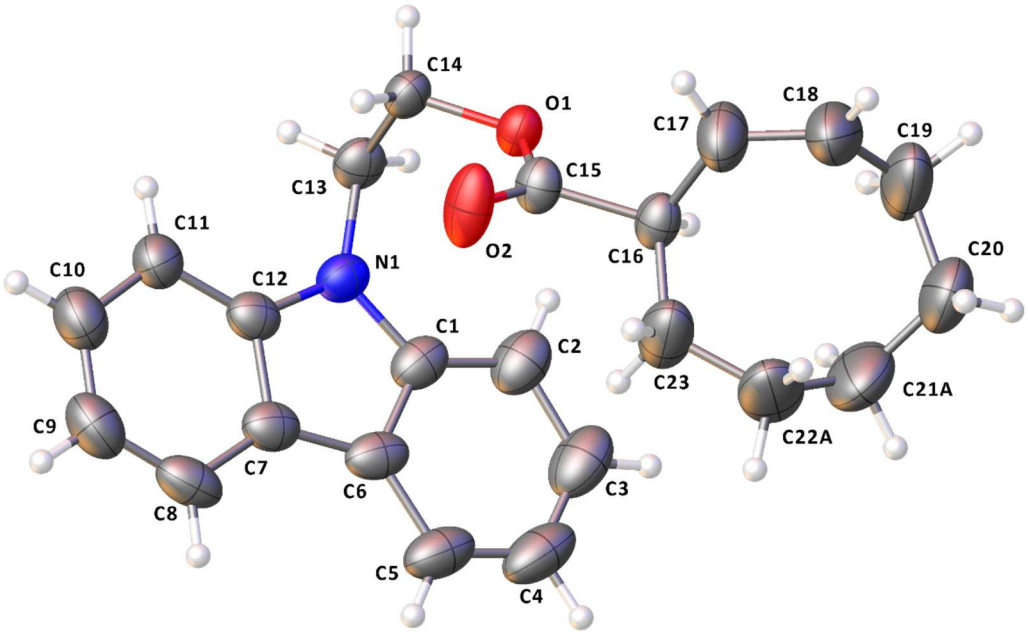

Figure S19. X-ray molecular structure (ORTEP) of **M3**. Thermal ellipsoids are drawn at the 30% probability level. For clarity, only the atoms with the highest occupancy factor are shown. Atom types: C grey, H white, O red, N blue.

Table S1. Relevant crystallographic data and refinement details.

	M3
Temperature (K)	296
Formula	$C_{23}H_{25}NO_2$
Formula weight	347.44
Colour	colourless
Shape	prism-shaped
Crystal size (mm^3)	0.58×0.22×0.09
Crystal system	monoclinic
Space group	$P2_1/n$
***a* (Å)**	11.636(6)
***b* (Å)**	6.080(3)
***c* (Å)**	27.807(12)
α (°)	90
β (°)	98.860(10)
γ (°)	90
***V* ($Å^3$)**	1943.9(15)
Z	4
***Dx* (g cm^{-3})**	1.187
μ (mm^{-1})	0.590
F000	744
λ (Å)	1.54178
Θ_{min} (°)	3.933
Θ_{max} (°)	70.039
Measured Refl's.	26290
Indep't Refl's	3663
Refl's I≥2σ(I)	2970
R_{int}	0.0672
R_1 (I > 2σI)	0.0727(2970)
wR_2	0.2244(3663)
GooF	1.035
Parameters	255
Restraints	/
ρ_{min}, ρ_{max} (e$Å^{-3}$)	-0.21, 0.27

1. APEX3, version 2015.5-2; Bruker AXS Inc., **2016**, Madison, Wisconsin, USA.
2. SAINT, version 8.34A; Bruker AXS Inc., **2013**, Madison, Wisconsin, USA.
3. SADABS, version 2014/5; Bruker AXS Inc., **2014**, Madison, Wisconsin, USA.
4. Sheldrick, G.M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Cryst.* **2014**, A71, 3–8.
5. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71, 3–8.
6. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, **2009**, 42, 339–341.

NMR spectra of polymers

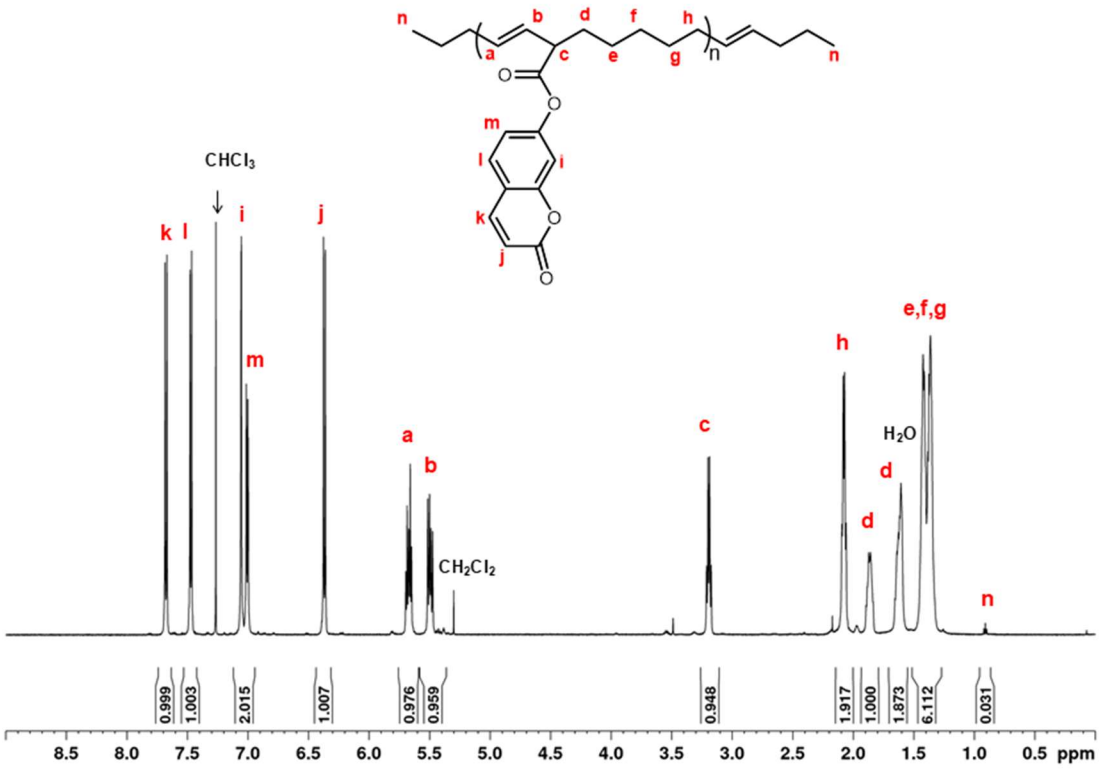

Figure S20. ^{1}H NMR of poly-**M1** ($CDCl_3$, 600 MHz).

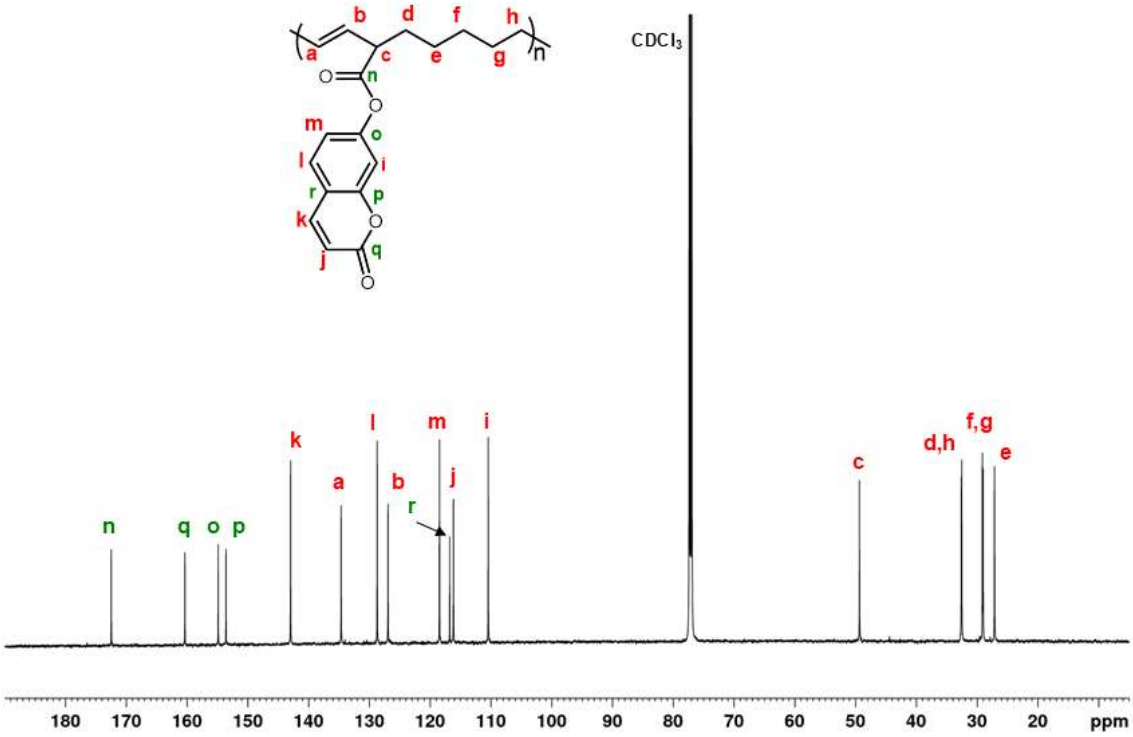

Figure S21. ^{13}C NMR of poly-**M1** ($CDCl_3$, 150 MHz).

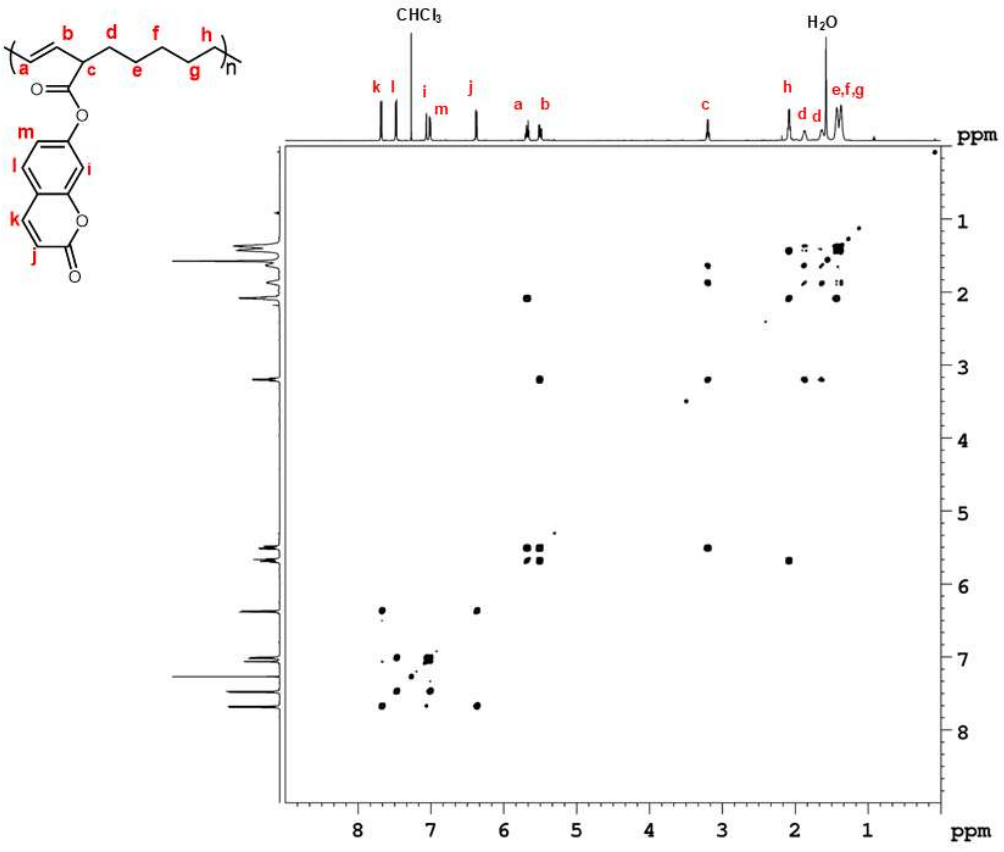

Figure S22. ^{1}H-^{1}H COSY spectrum of poly-**M1** ($CDCl_3$, 600 MHz).

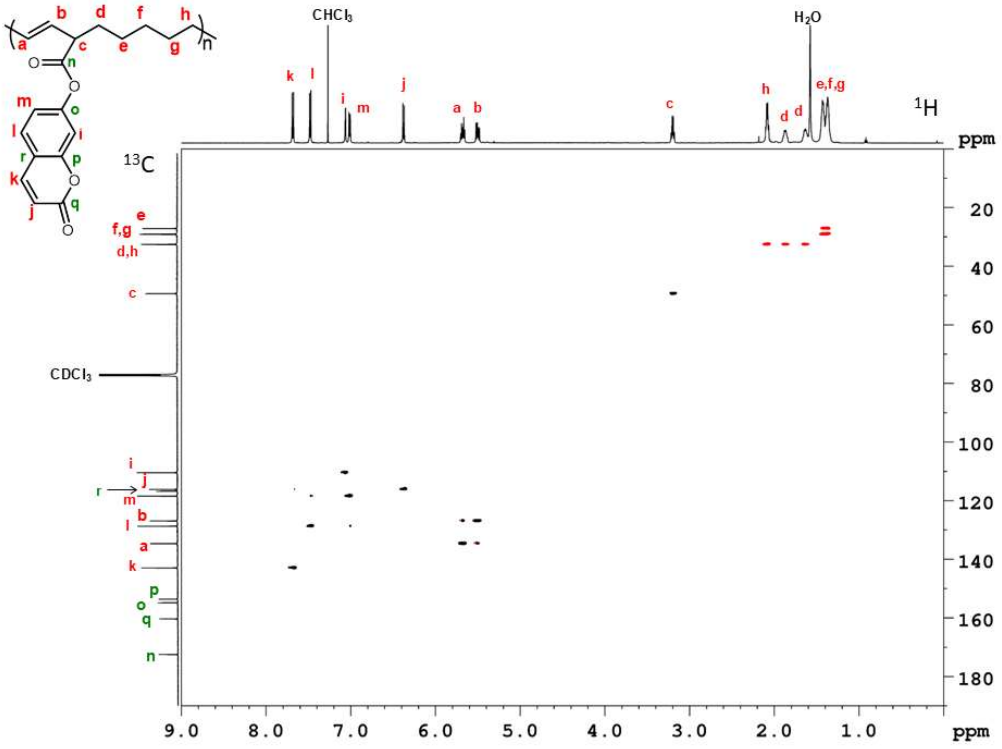

Figure S23. ^{1}H-^{13}C HSQC spectrum of poly-**M1** ($CDCl_3$, 600 MHz for ^{1}H, 150 MHz for ^{13}C).

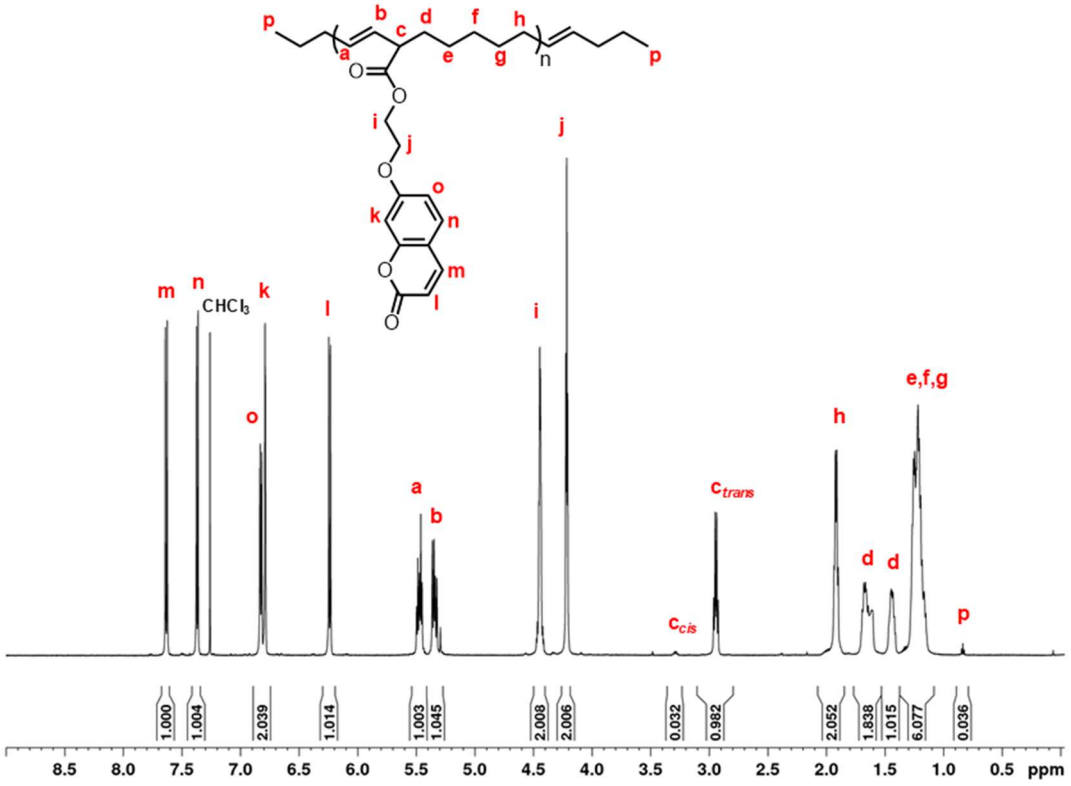

Figure S24. ^{1}H NMR of poly-**M2** ($CDCl_3$, 600 MHz).

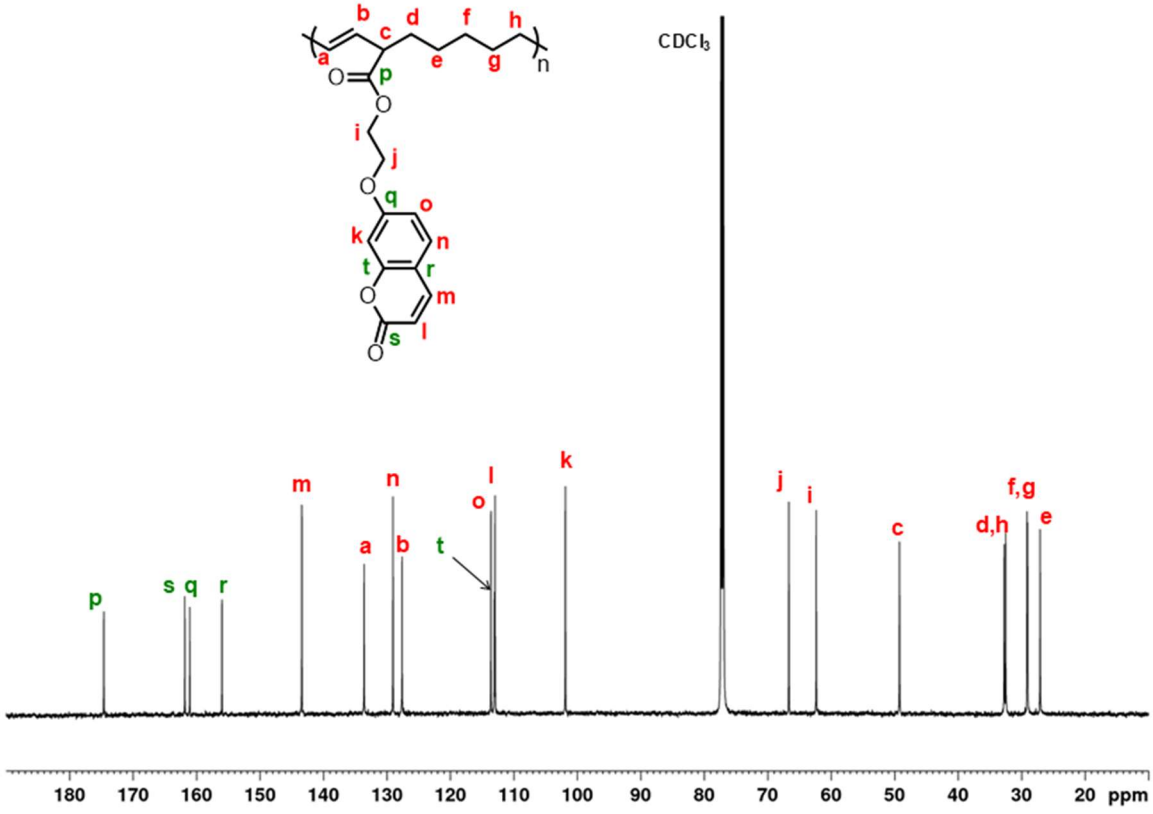

Figure S25. ^{13}C NMR of poly-**M2** ($CDCl_3$, 600 MHz).

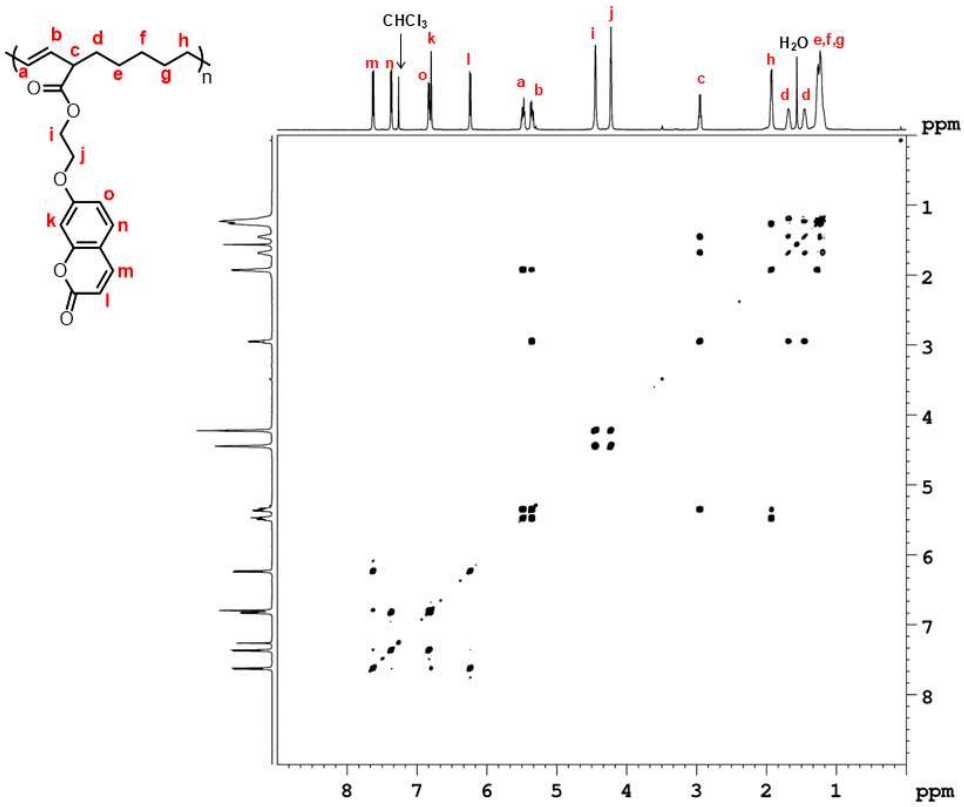

Figure S26. ^{1}H-^{1}H COSY spectrum of poly-**M2** ($CDCl_3$, 600 MHz).

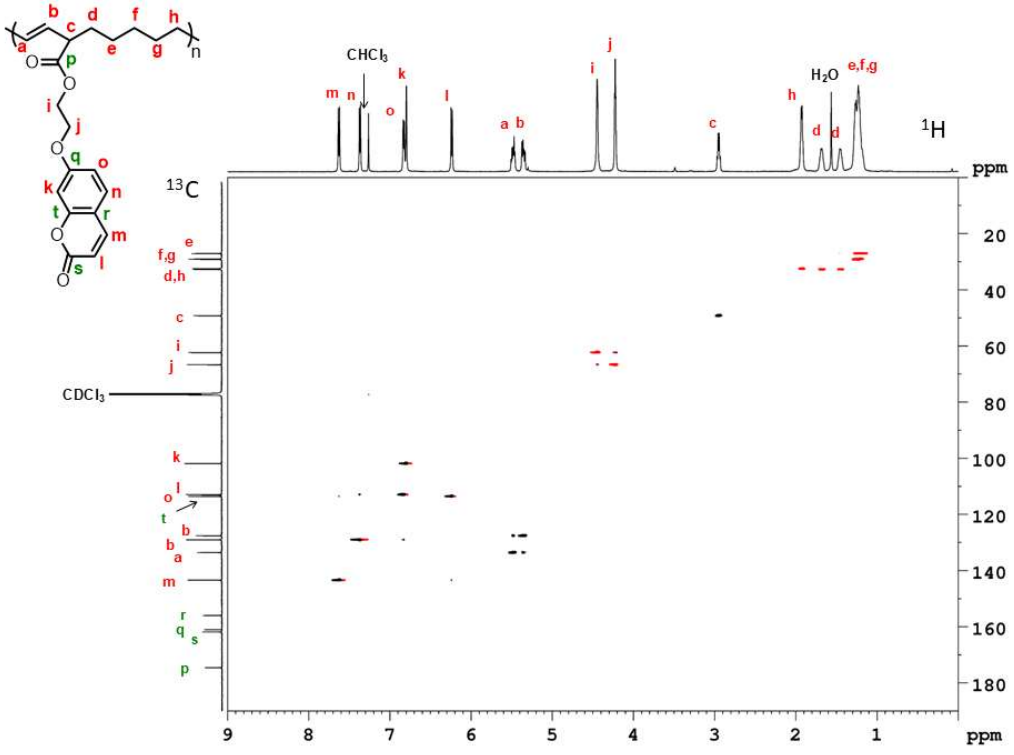

Figure S27. ^{1}H-^{13}C HSQC spectrum of poly-**M1** ($CDCl_3$, 600 MHz for ^{1}H, 150 MHz for ^{13}C).

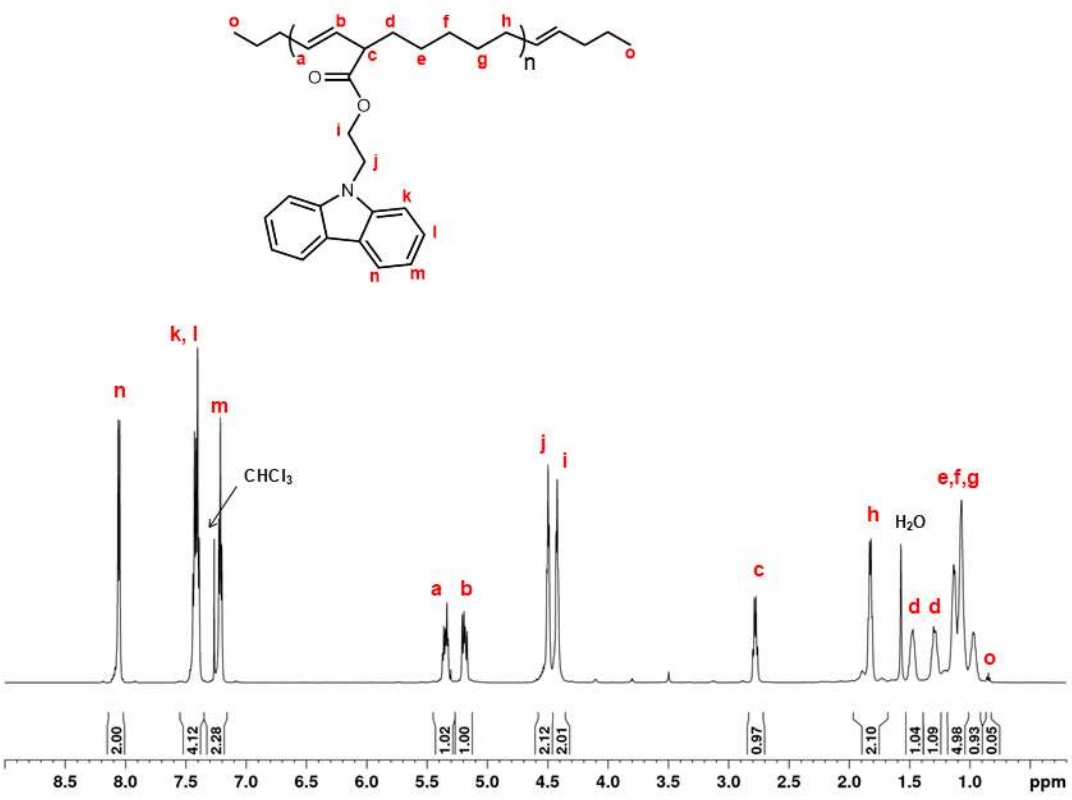

Figure S28. ^{1}H NMR of poly-**M3** ($CDCl_3$, 600 MHz).

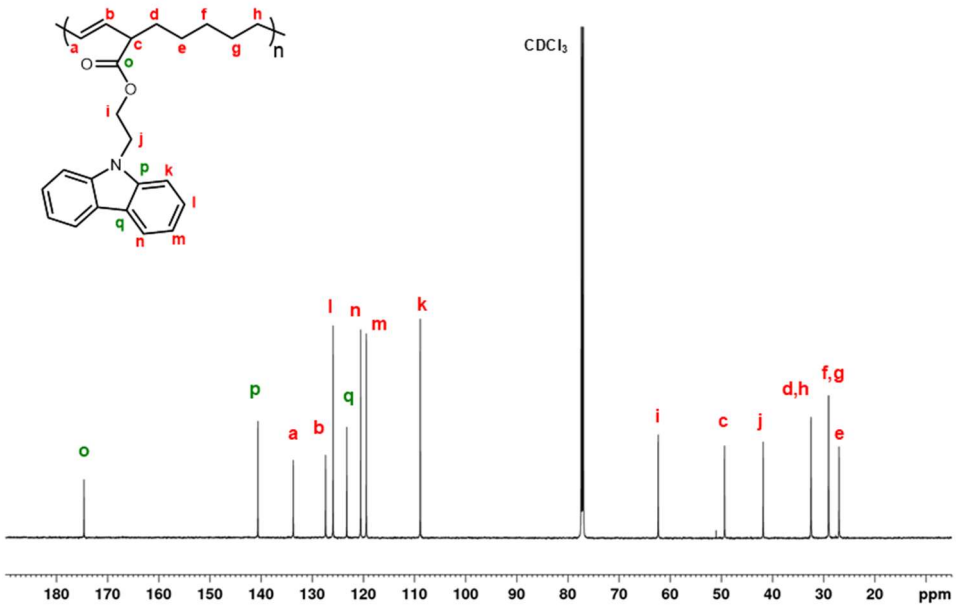

Figure S29. ^{13}C NMR of poly-**M3** ($CDCl_3$, 150 MHz).

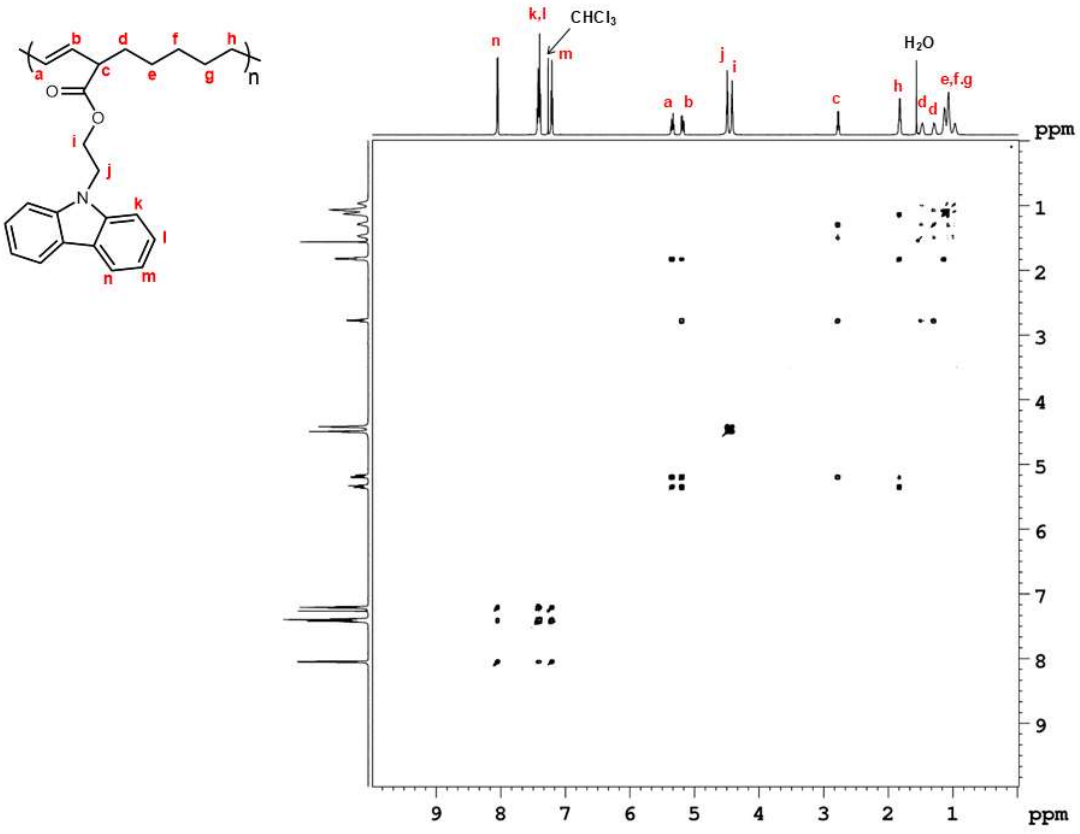

Figure S30. ^{1}H-^{1}H COSY spectrum of poly-**M3** ($CDCl_3$, 600 MHz).

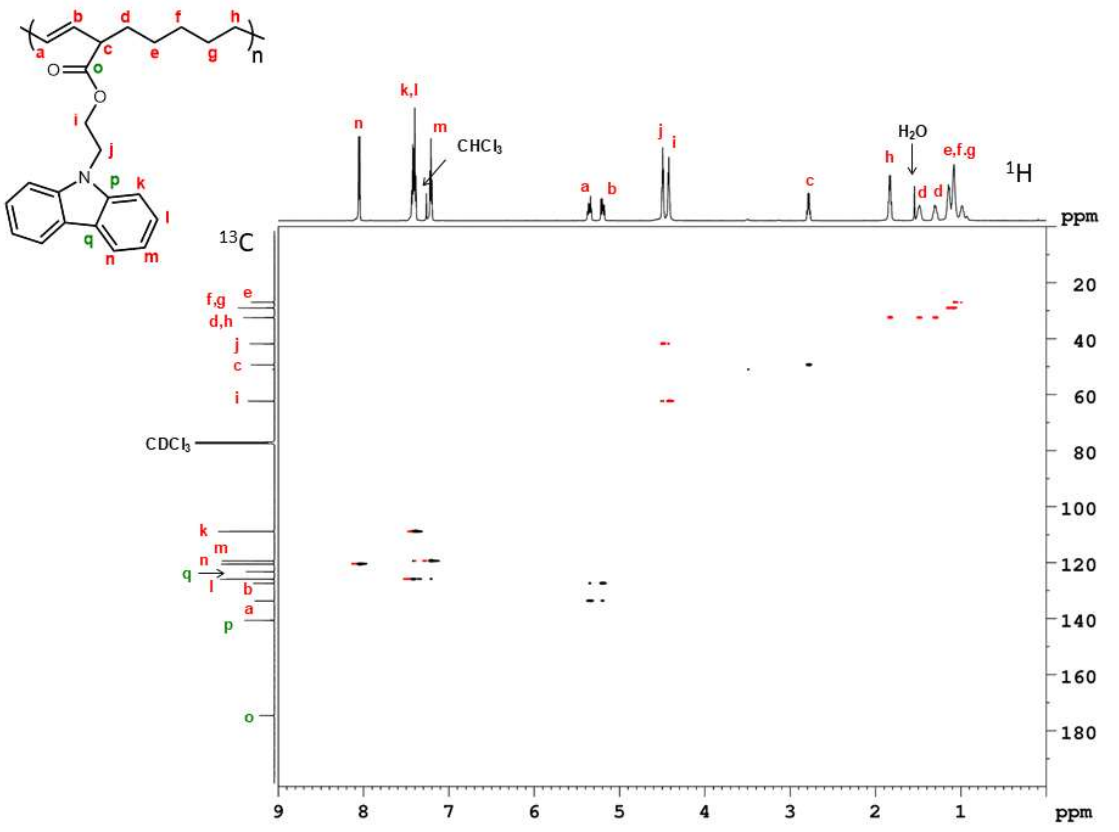

Figure S31. ^{1}H-^{13}C HSQC spectrum of poly-**M3** ($CDCl_3$, 600 MHz for ^{1}H, 150 MHz for ^{13}C).

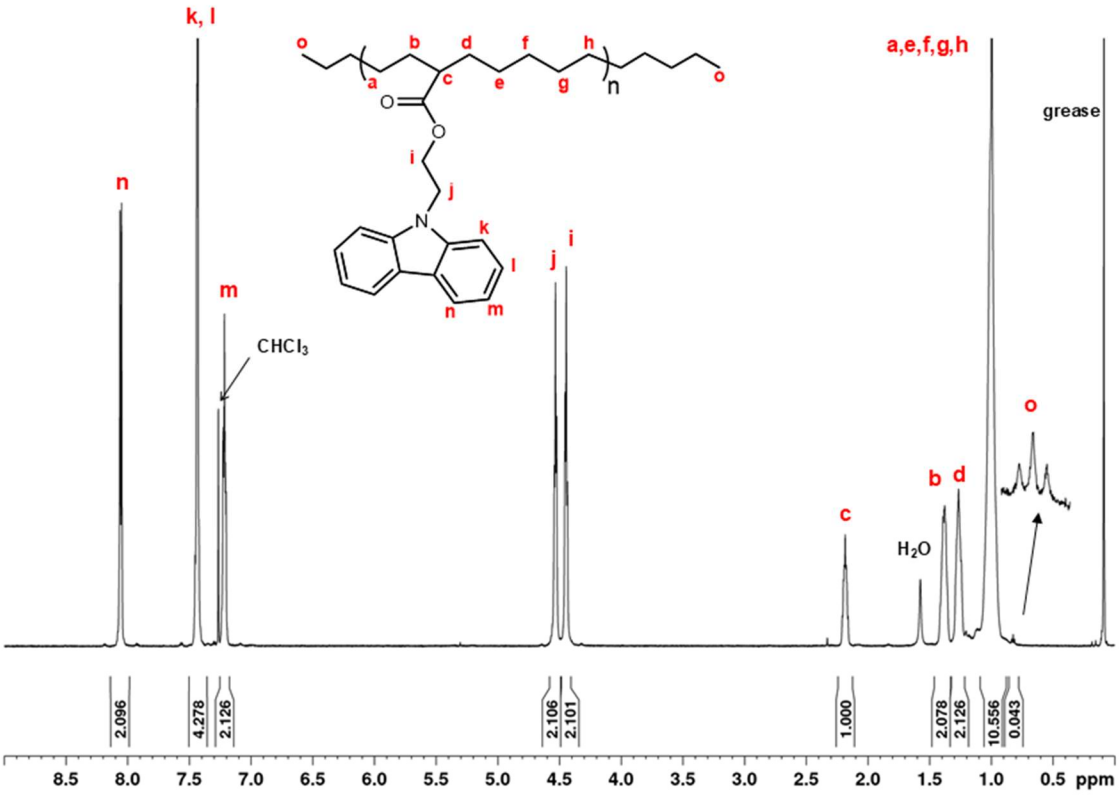

Figure S32. ^{1}H spectrum of poly-**M3H** ($CDCl_3$, 600 MHz)

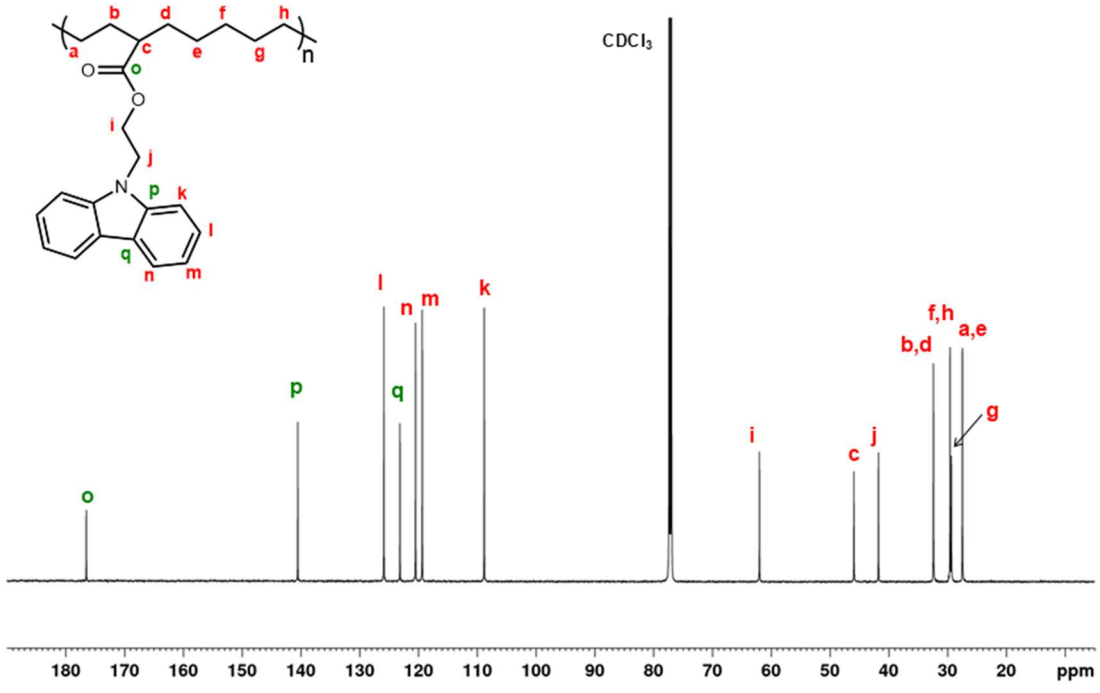

Figure S33. ^{13}C spectrum of poly-**M3H** ($CDCl_3$, 150 MHz).

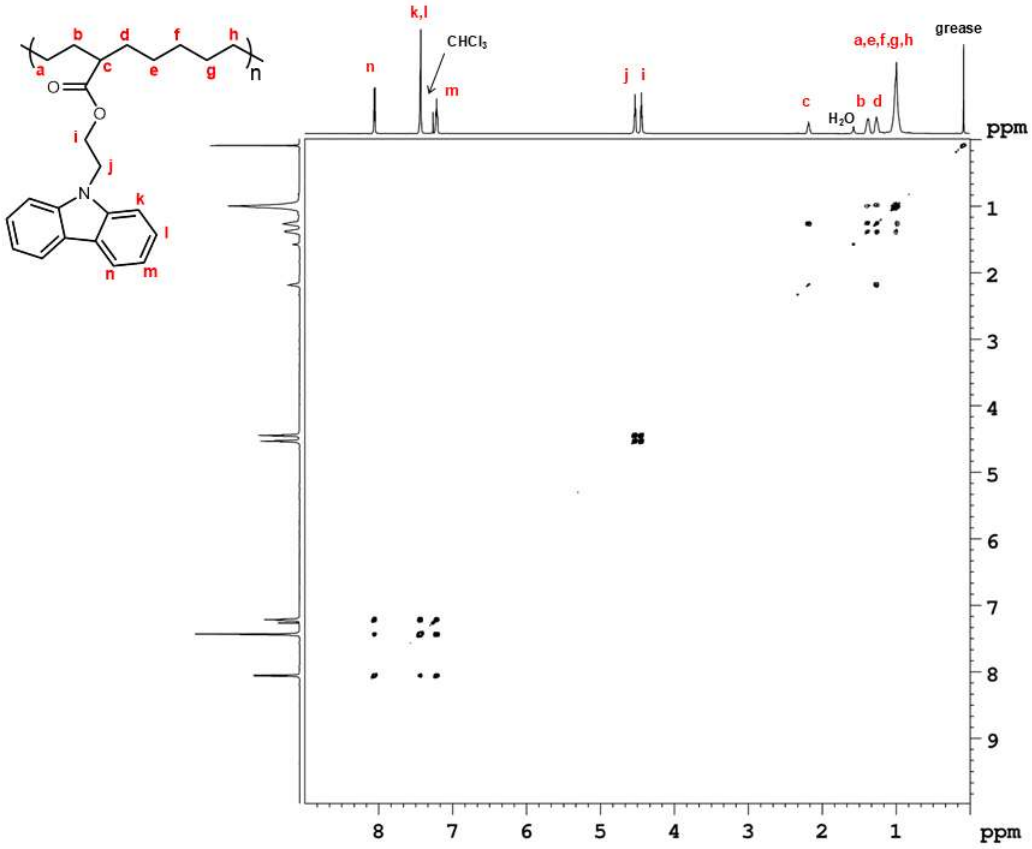

Figure S34. ^{1}H-^{1}H COSY spectrum of poly-**M3H** ($CDCl_3$, 600 MHz).

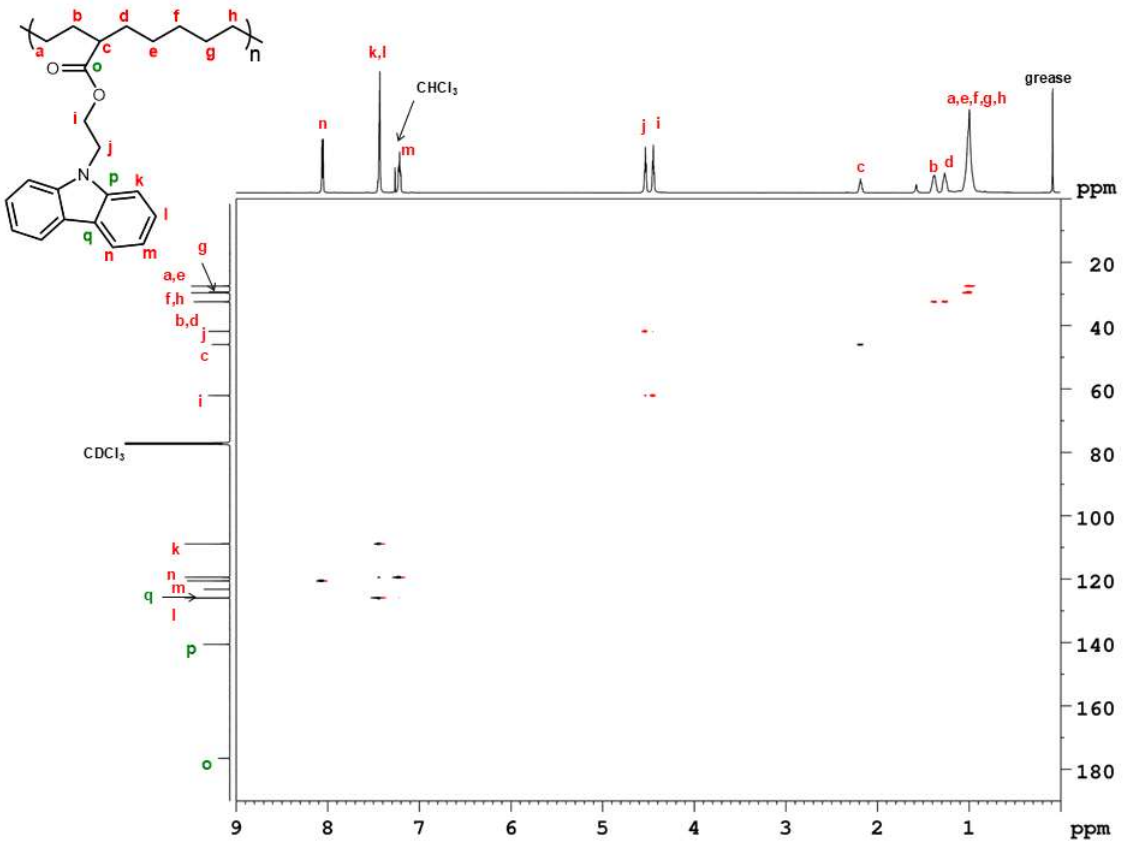

Figure S35. ^{1}H-^{13}C HSQC spectrum of poly-**M3H** ($CDCl_3$, 600 MHz for ^{1}H, 150 MHz for ^{13}C).

TGA curves of polymers

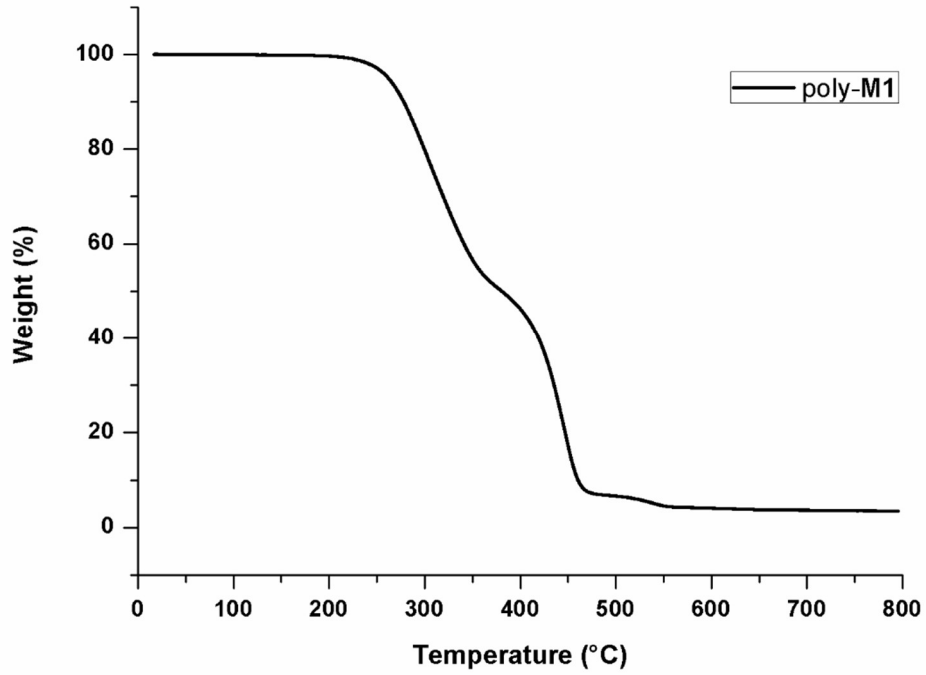

Figure S36. TGA curve for poly-**M1** (entry 1, Table 1).

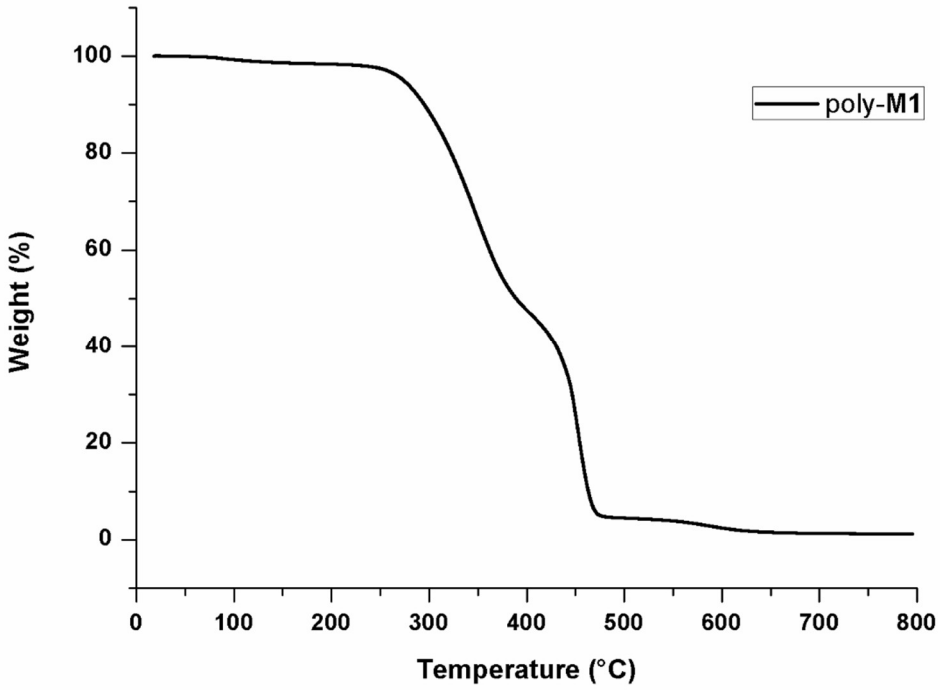

Figure S37. TGA curve for poly-**M1** (entry 2, Table 1).

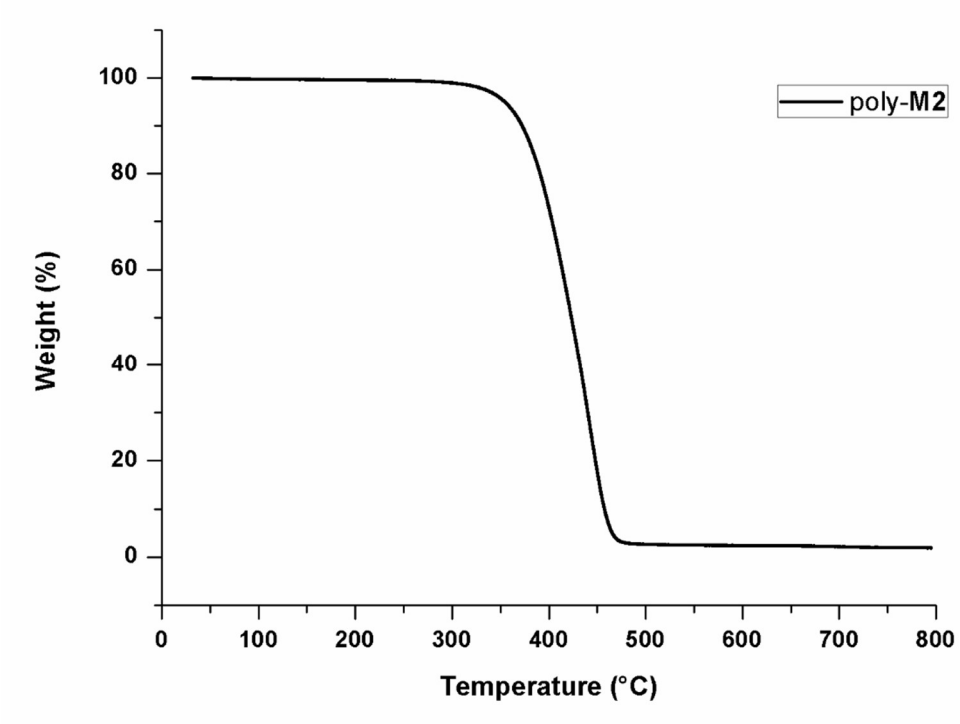

Figure S38. TGA curve for poly-**M2** (entry 3, Table 1).

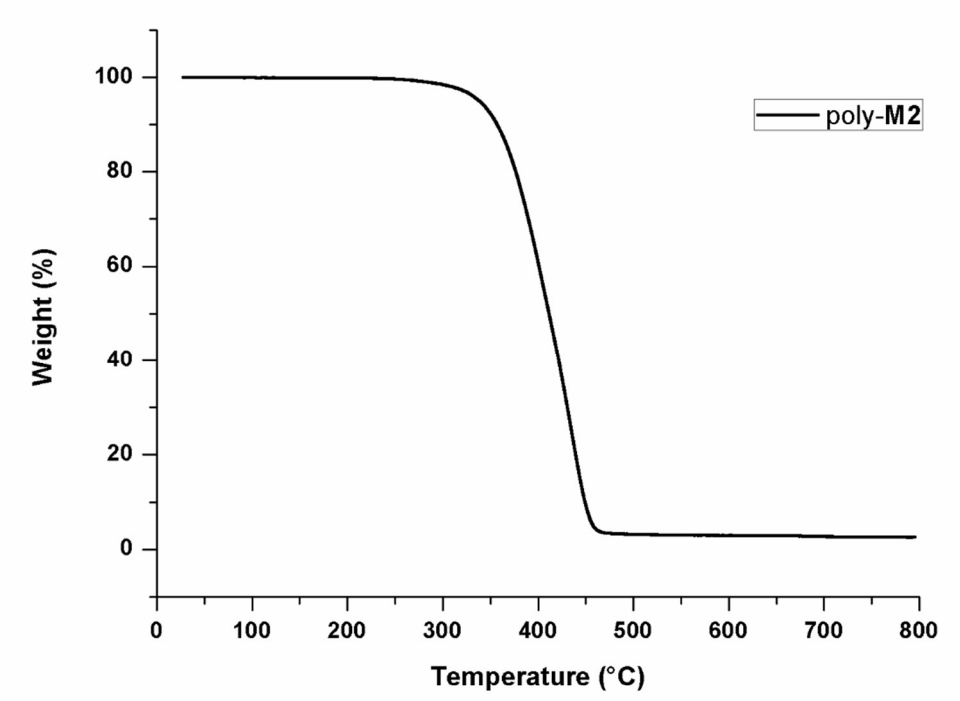

Figure S39. TGA curve for poly-**M2** (entry 4, Table 1).

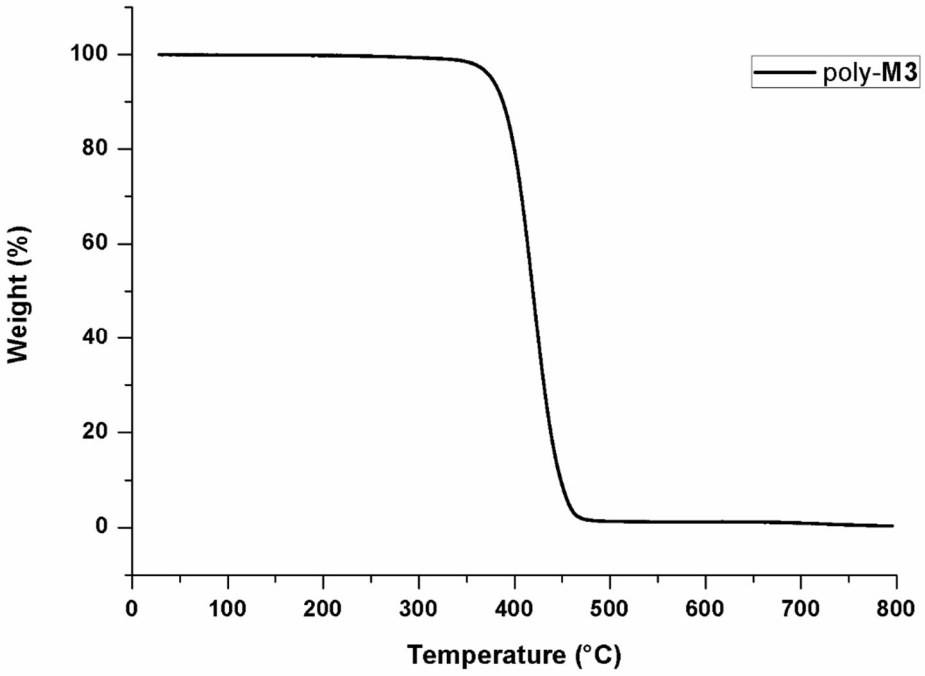

Figure S40. TGA curve for poly-**M3** (entry 5, Table 1).

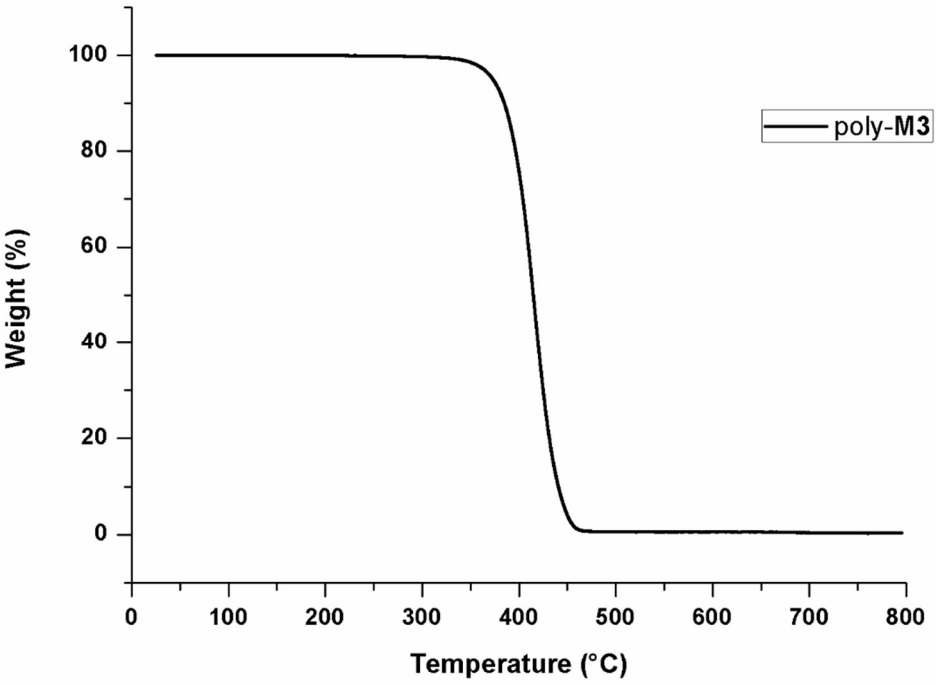

Figure S41. TGA curve for poly-**M3** (entry 6, Table 1).

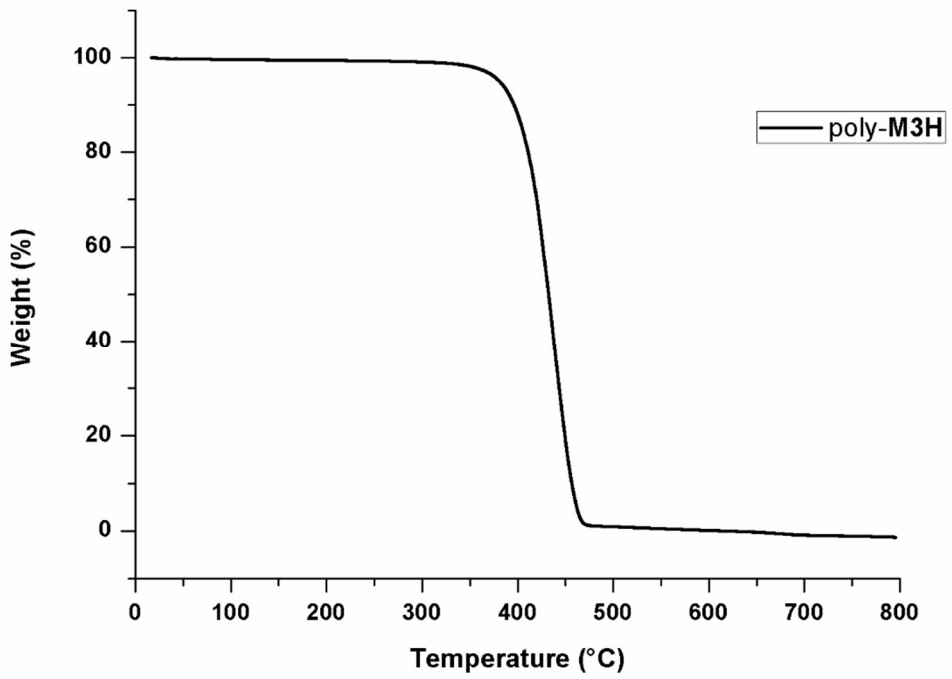

Figure S42. TGA curve for poly-**M3H**.

DSC thermograms of polymers

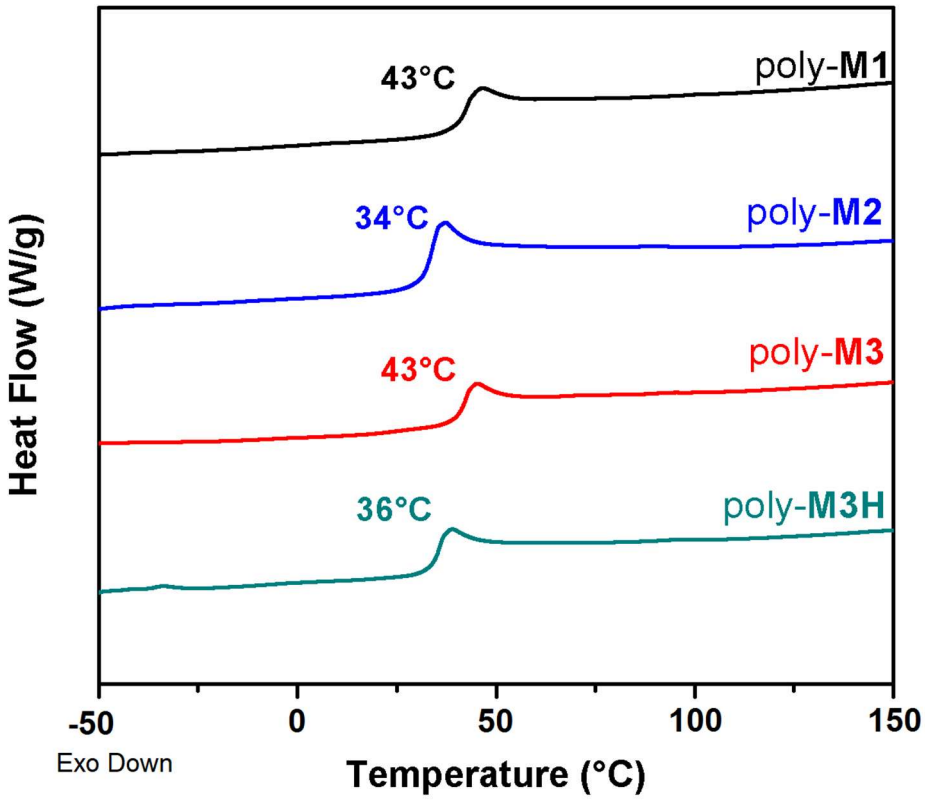

Figure S43. DSC thermograms (second heating run) of poly-**M1**, poly-**M2**, poly-**M3** obtained in the presence of **G2** and poly-**M3H**. Individual thermograms shifted vertically for clarity.

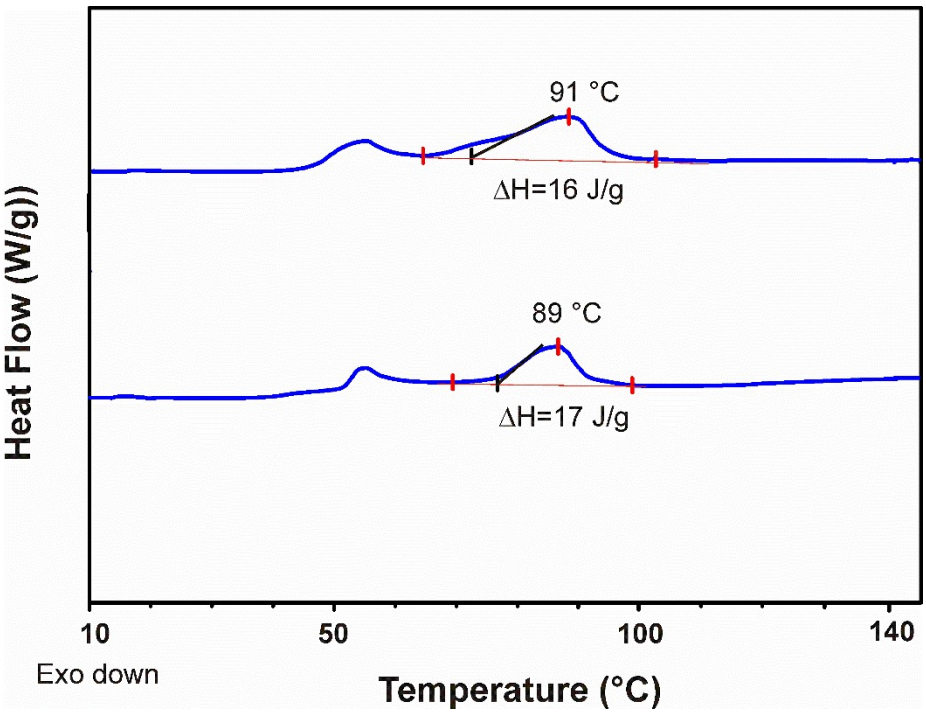

Figure S44. DSC thermograms (first heating run) of poly-**M1** obtained in the presence of **G2** (top) and **G3** (down). Individual thermograms shifted vertically for clarity.

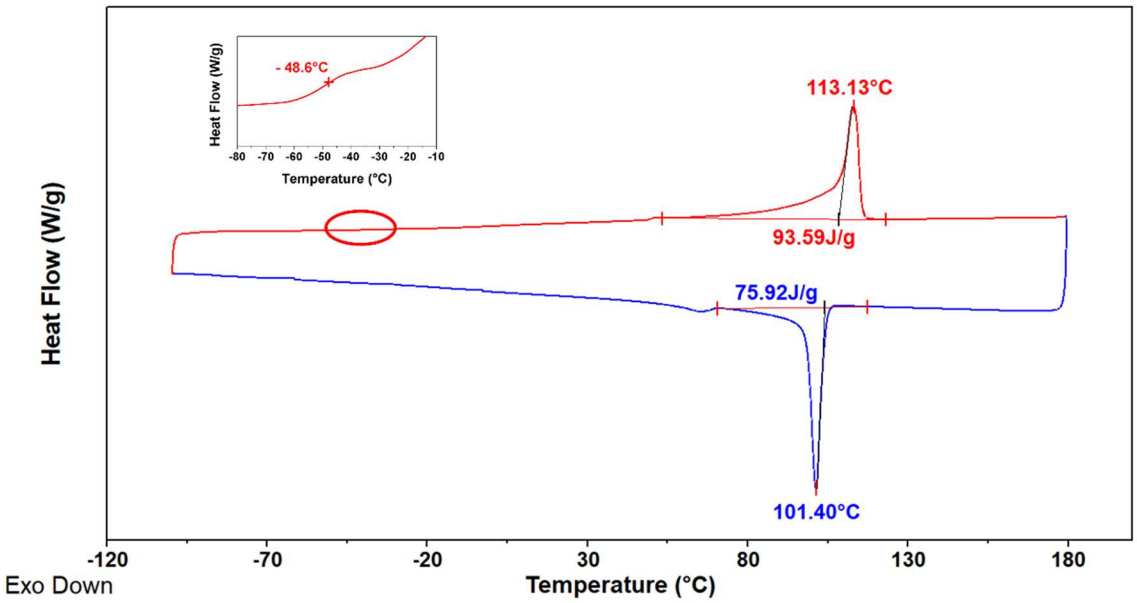

Figure S45. DSC thermogram of poly-(**M3-***s*-COE)**H**.

X-ray diffraction spectra of polymers

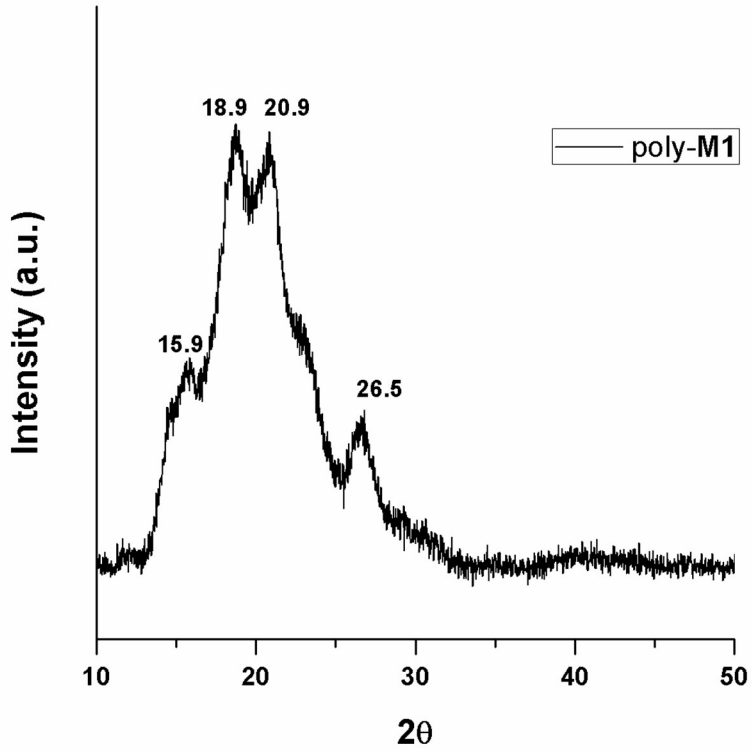

Figure S46. X-ray spectrum of poly-**M1** (entry 1, Table1).

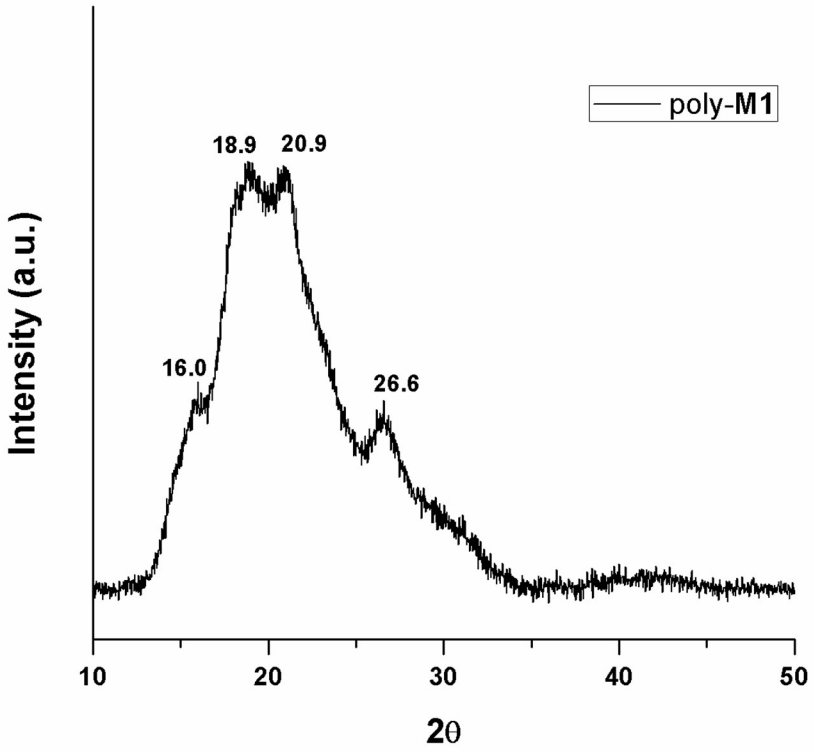

Figure S47. X-ray spectrum of poly-**M1** (entry 2, Table1).

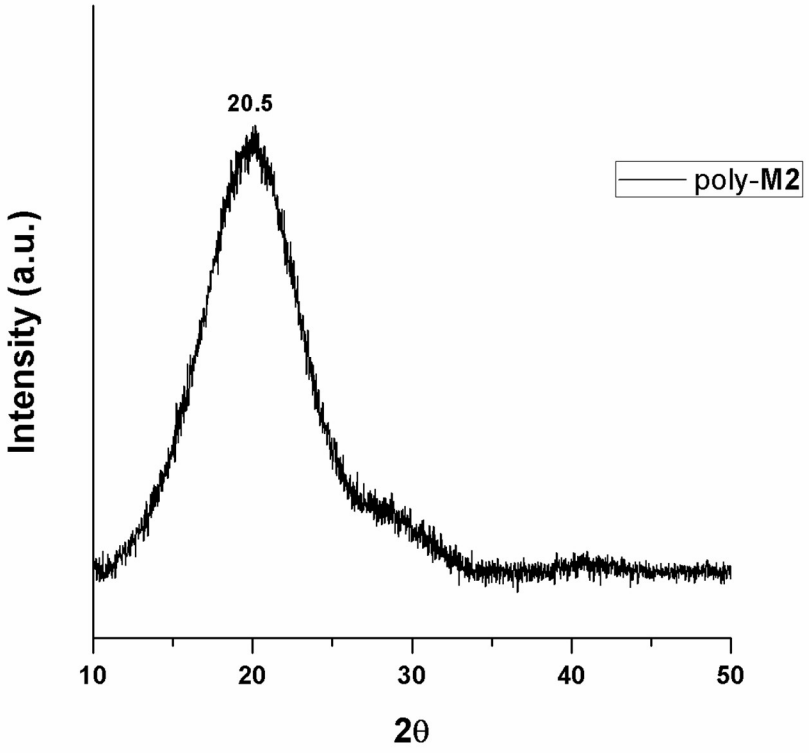

Figure S48. X-ray spectrum of poly-**M2** (entry 3, Table1).

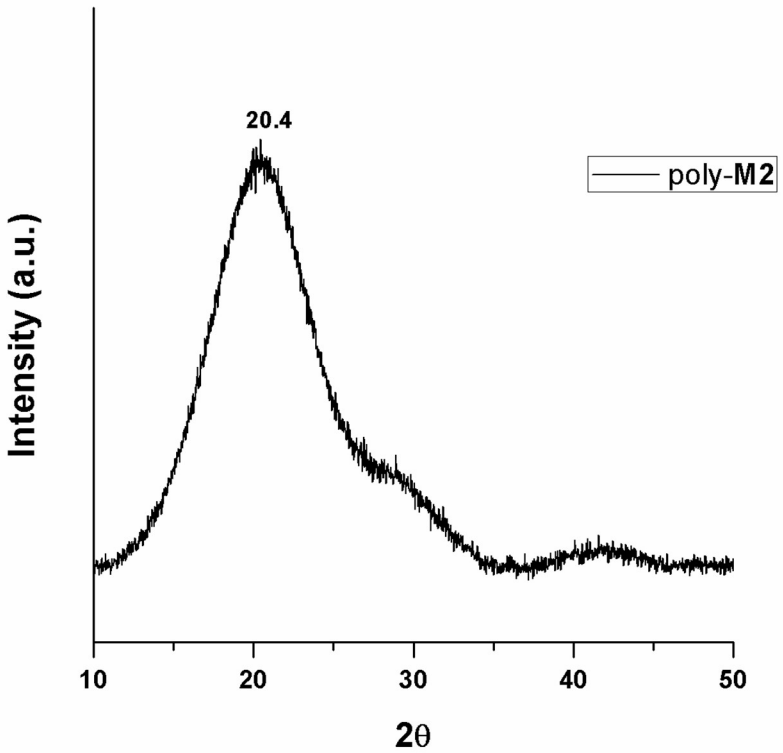

Figure S49. X-ray spectrum of poly-**M2** (entry 4, Table1).

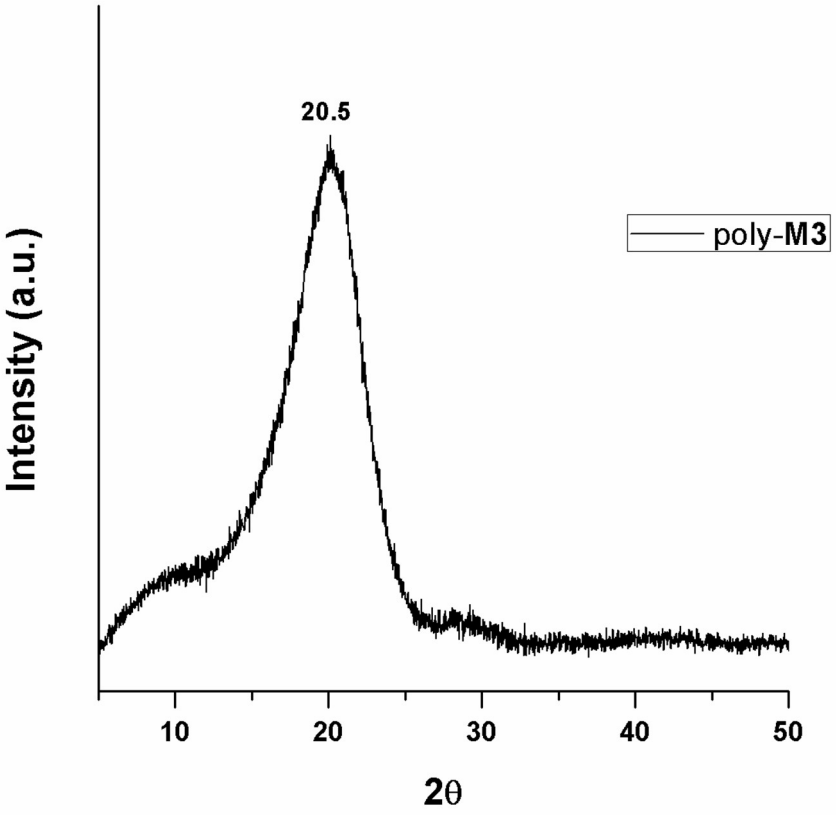

Figure S50. X-ray spectrum of poly-**M3** (entry 5, Table1).

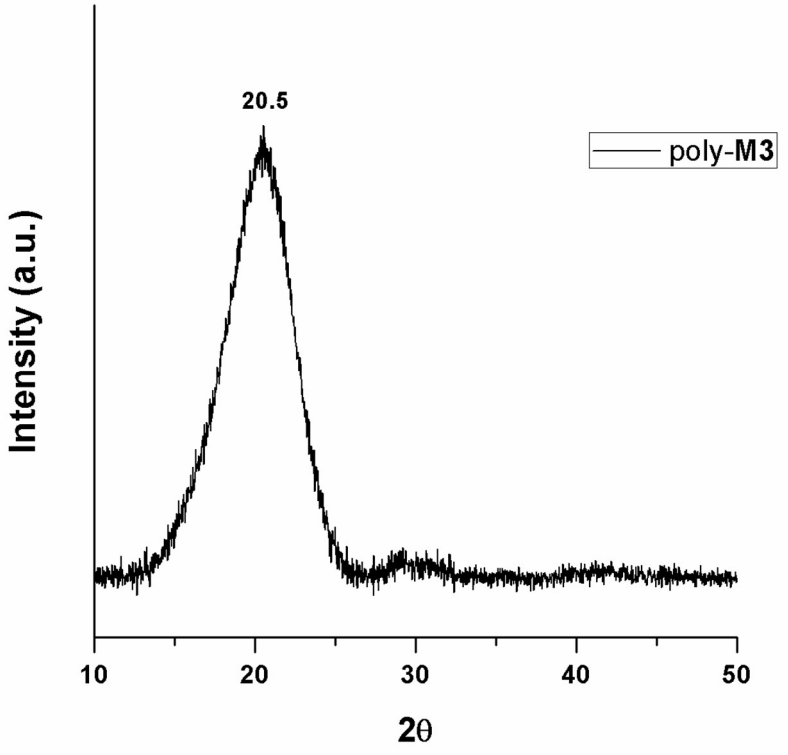

Figure S51. X-ray spectrum of poly-**M3** (entry 6, Table1).

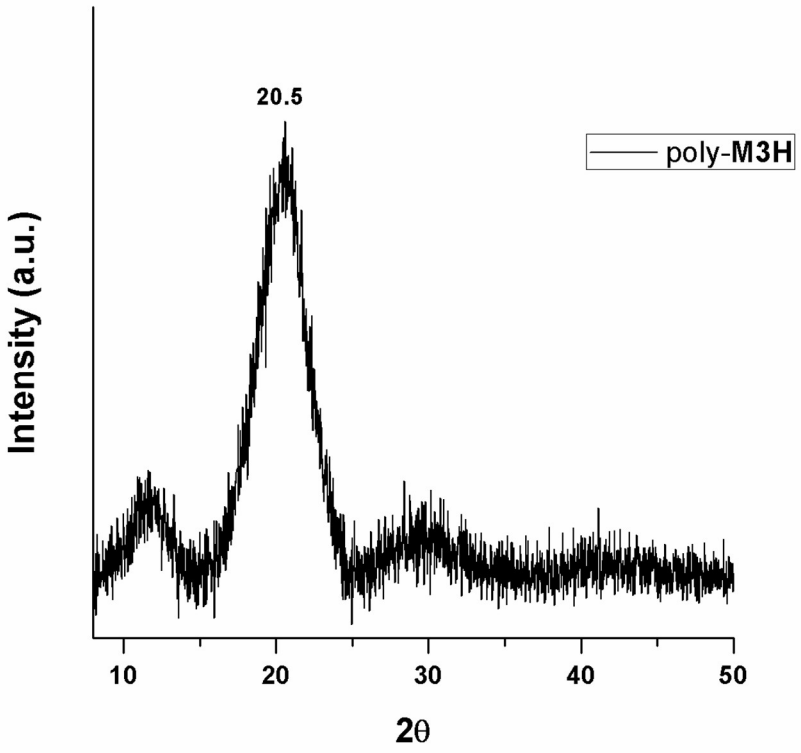

Figure S52. X-ray spectrum of poly-**M3H**.

Water contact angle measurement

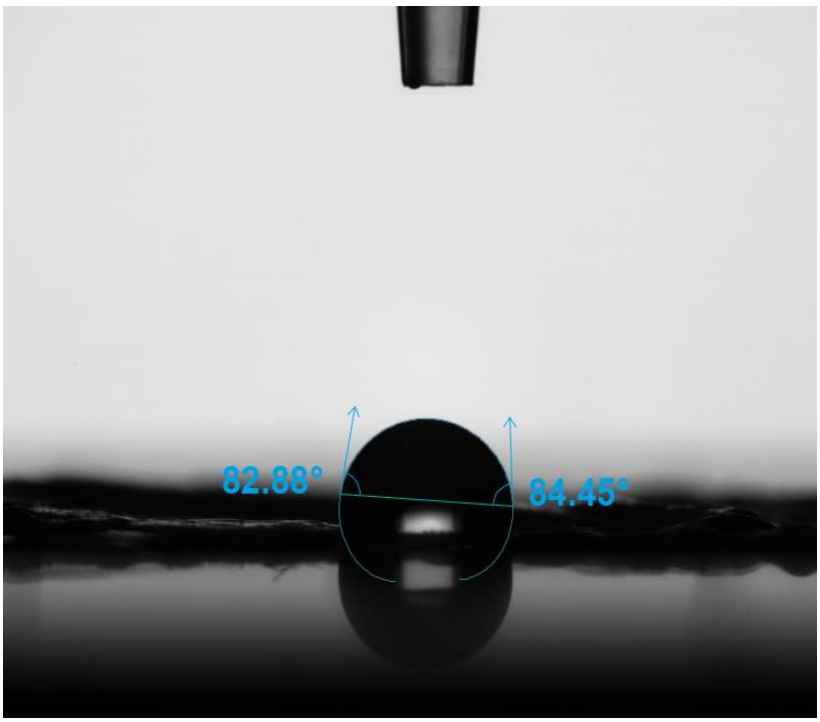

Figure S53. Water contact angle measure and shape of the drop, on poly-**M3H**, at RT.

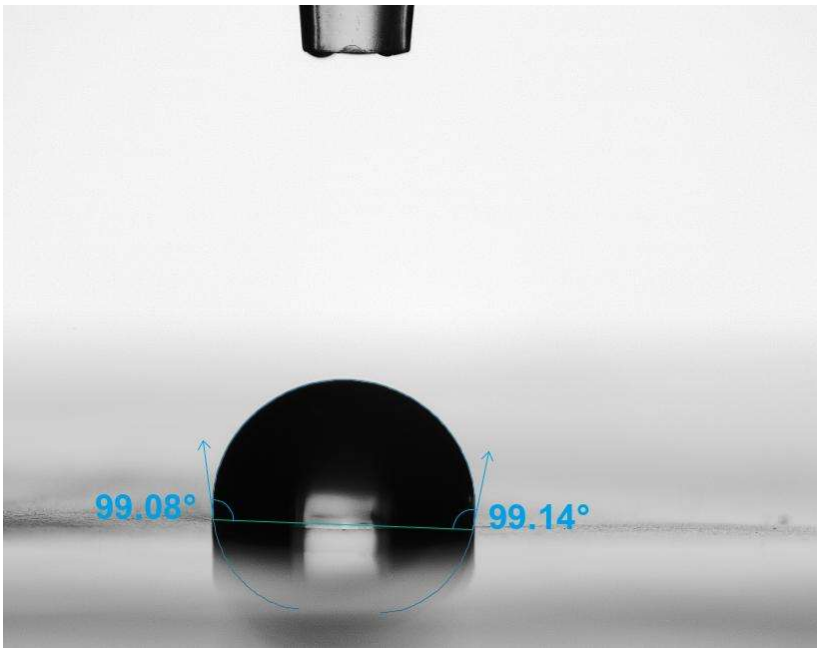

Figure S54. Water contact angle measure and shape of the drop, on commercial LDPE, at RT

Characterization of statistical copolymers

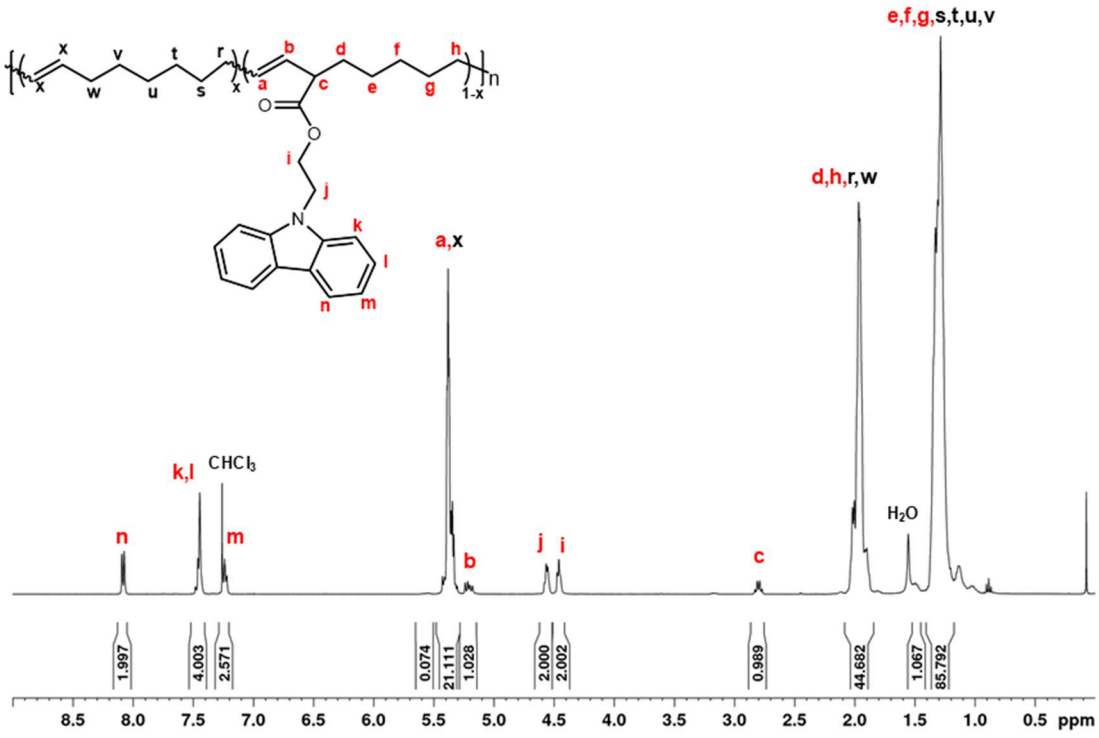

Figure S55. ^{1}H NMR spectrum of poly(**M3**-*s*-COE) (600 MHz, $CDCl_3$,). The **M3** unit content in the copolymer was evaluated considering the areas (A) of the signals of the olefinic protons of **M3** (a,b) and **COE** units (x): $\%\mathbf{M3} = \frac{A(b)}{[A(a,x-b)/2 + A(b)]} \times 100$.

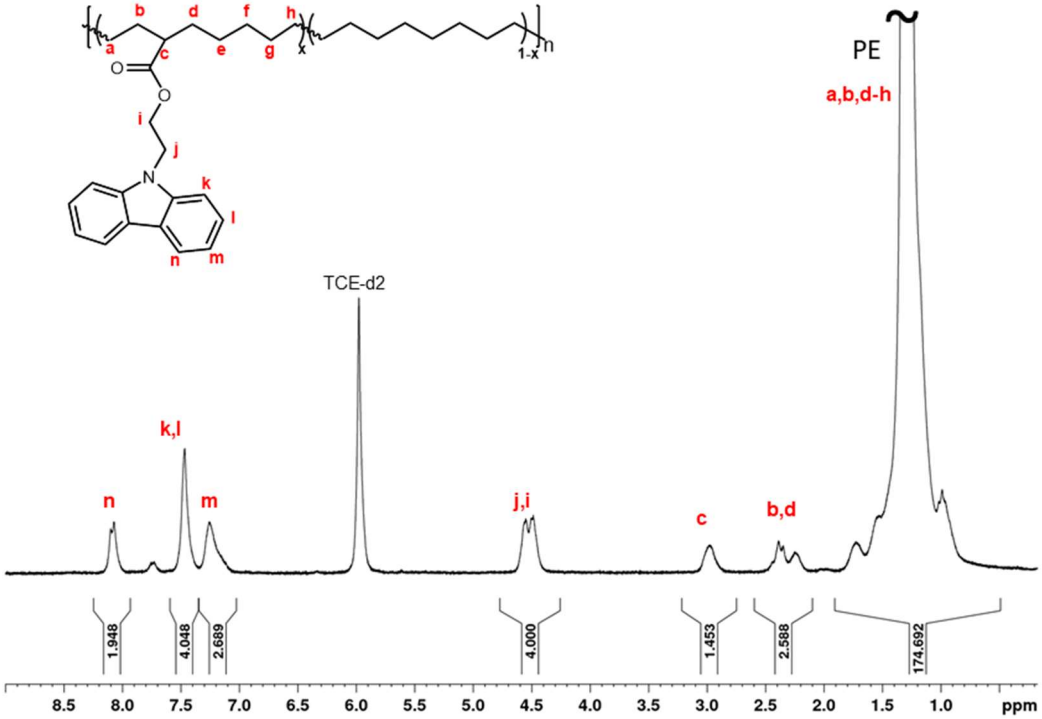

Figure S56. ^{1}H NMR spectrum of poly(**M3**-*s*-COE) measured at 80 °C ($C_2D_2Cl_4$, 250 MHz).

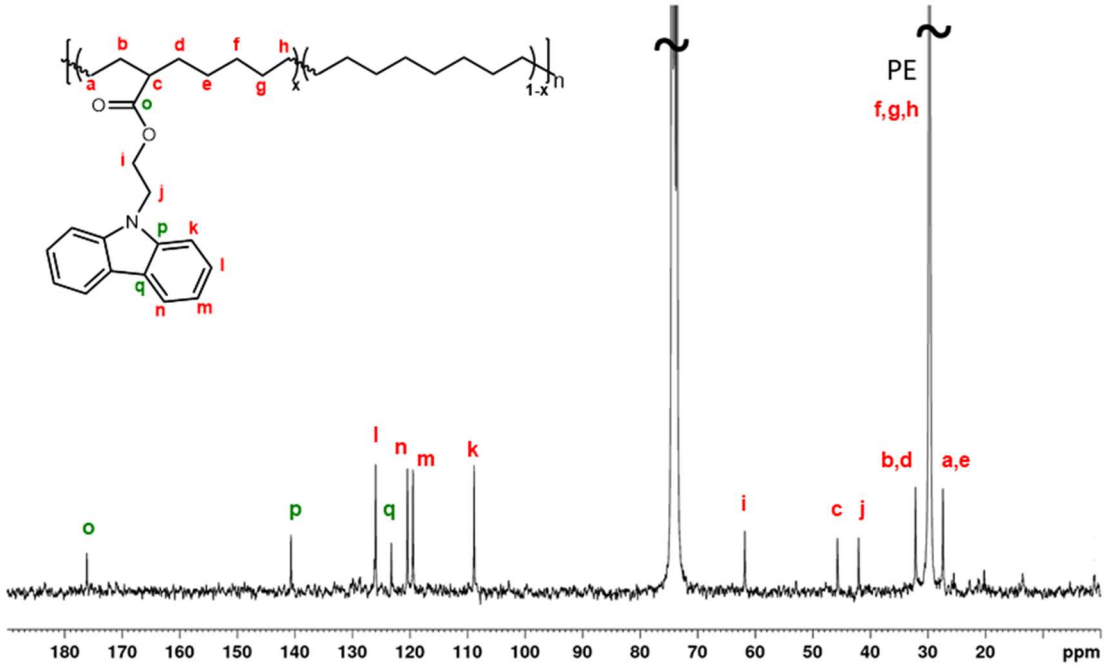

Figure S57. ^{13}C NMR spectrum of poly(**M3**-*s*-COE) measured at 80 °C ($C_2D_2Cl_4$, 62.5 MHz).

GPC traces

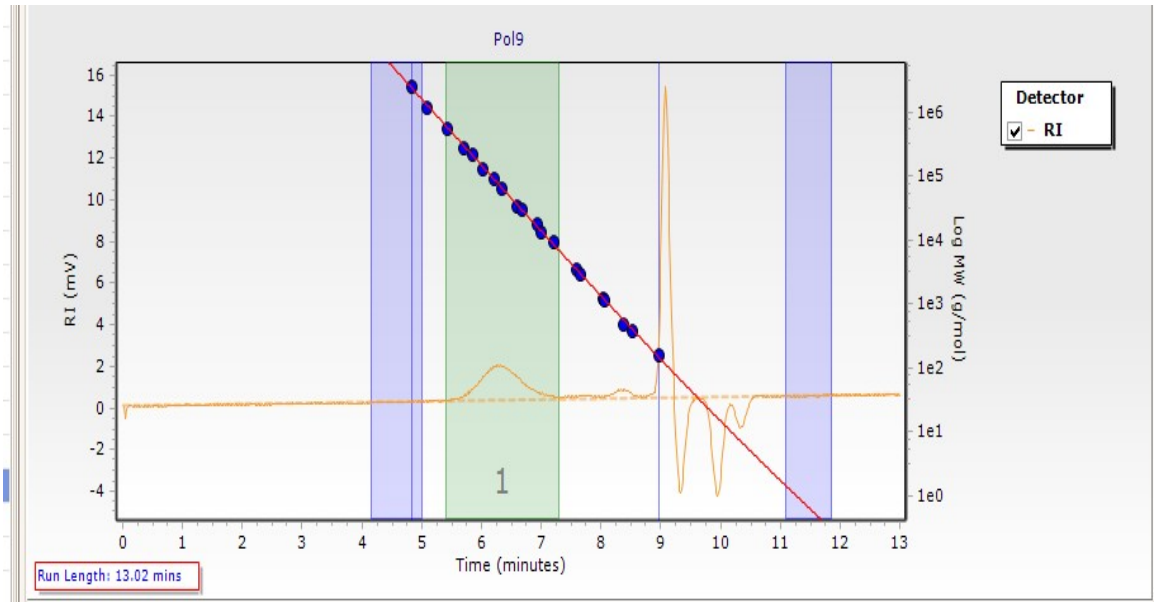

Figure S58. GPC trace of poly-**M1** (entry 1, Table 1).

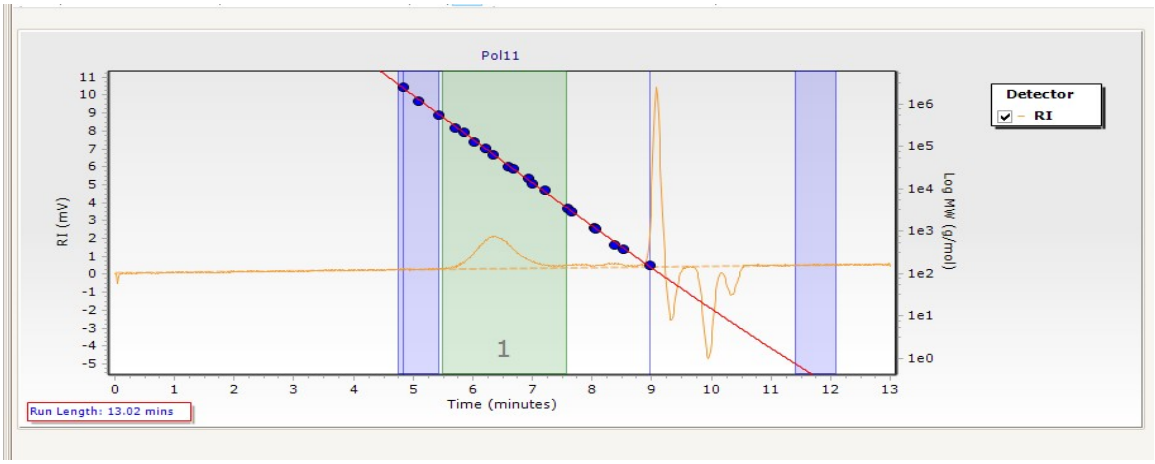

Figure S59. GPC trace of poly-**M2** (entry 3, Table 1).

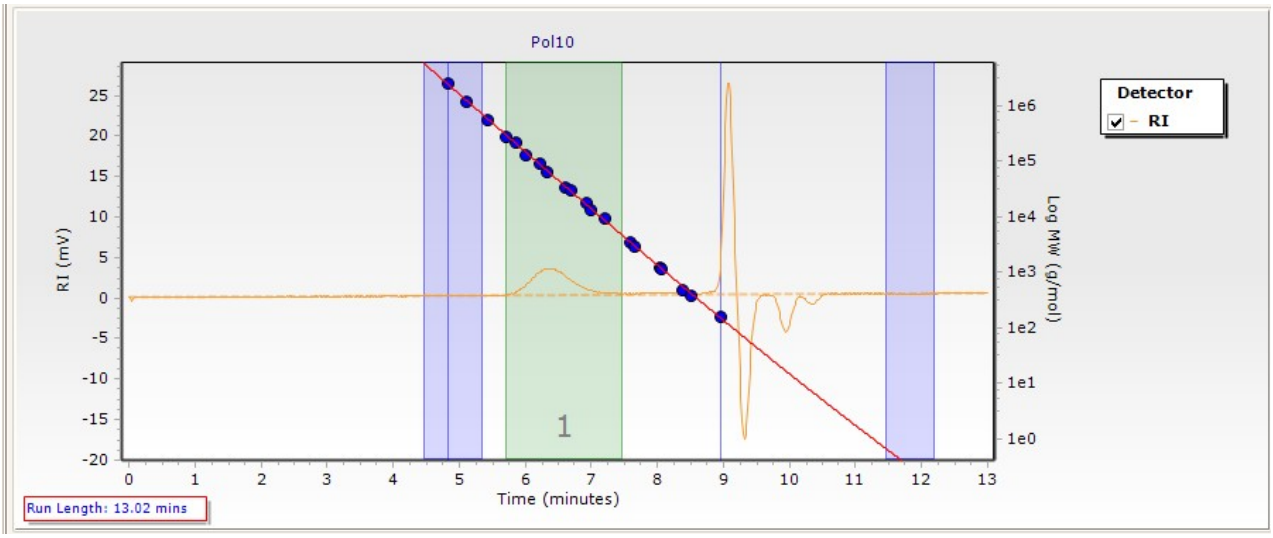

Figure S60. GPC trace of poly-**M3** (entry 5, Table 1).

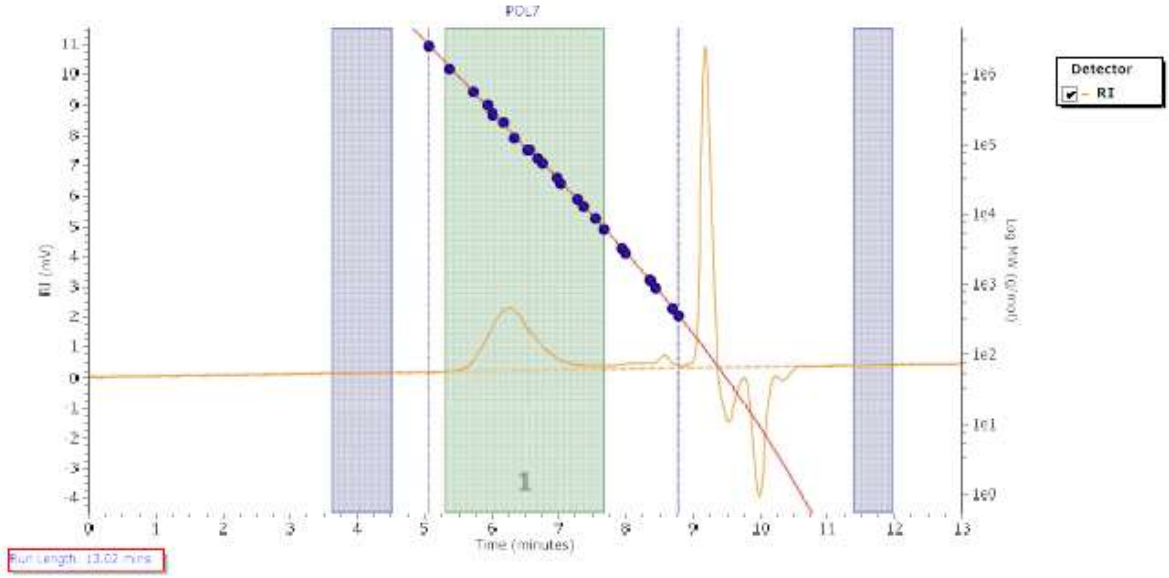

Figure S61. GPC trace of poly-**M3** (entry 6, Table 1).

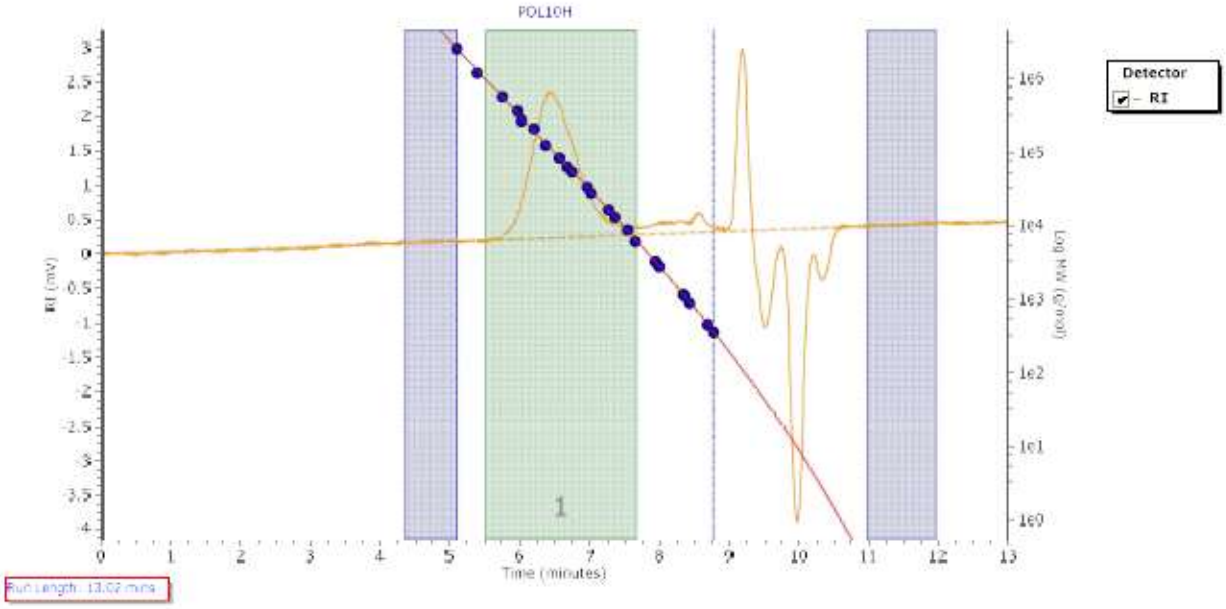

Figure S62. GPC trace of poly-**M3H**.

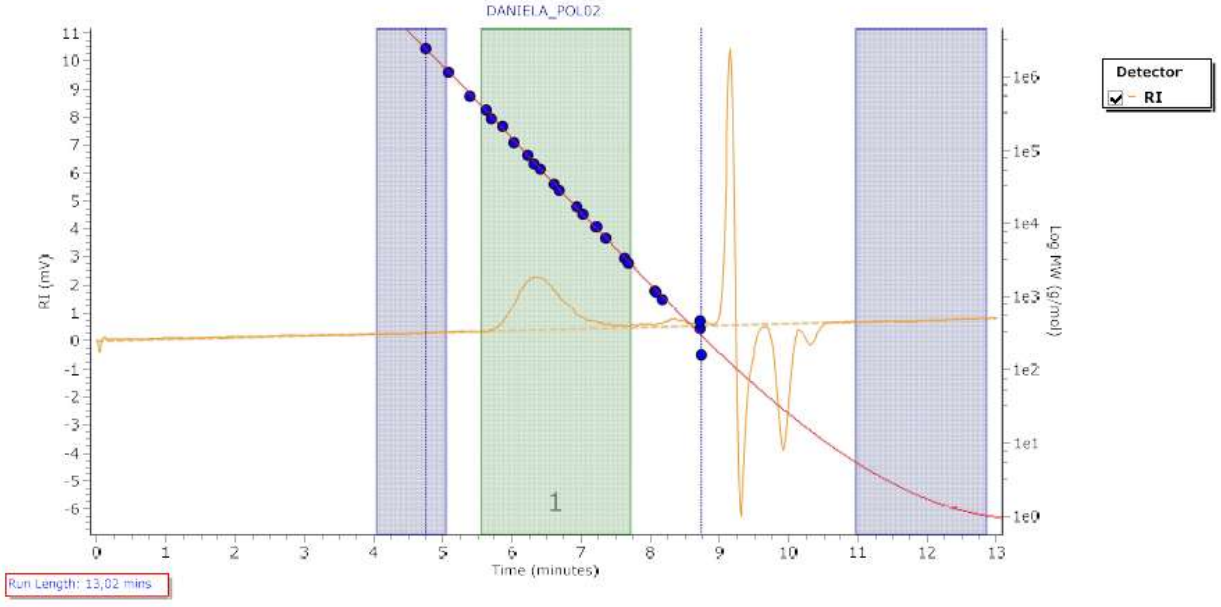

Figure S63. GPC trace of poly(**M3**-*s*-COE).

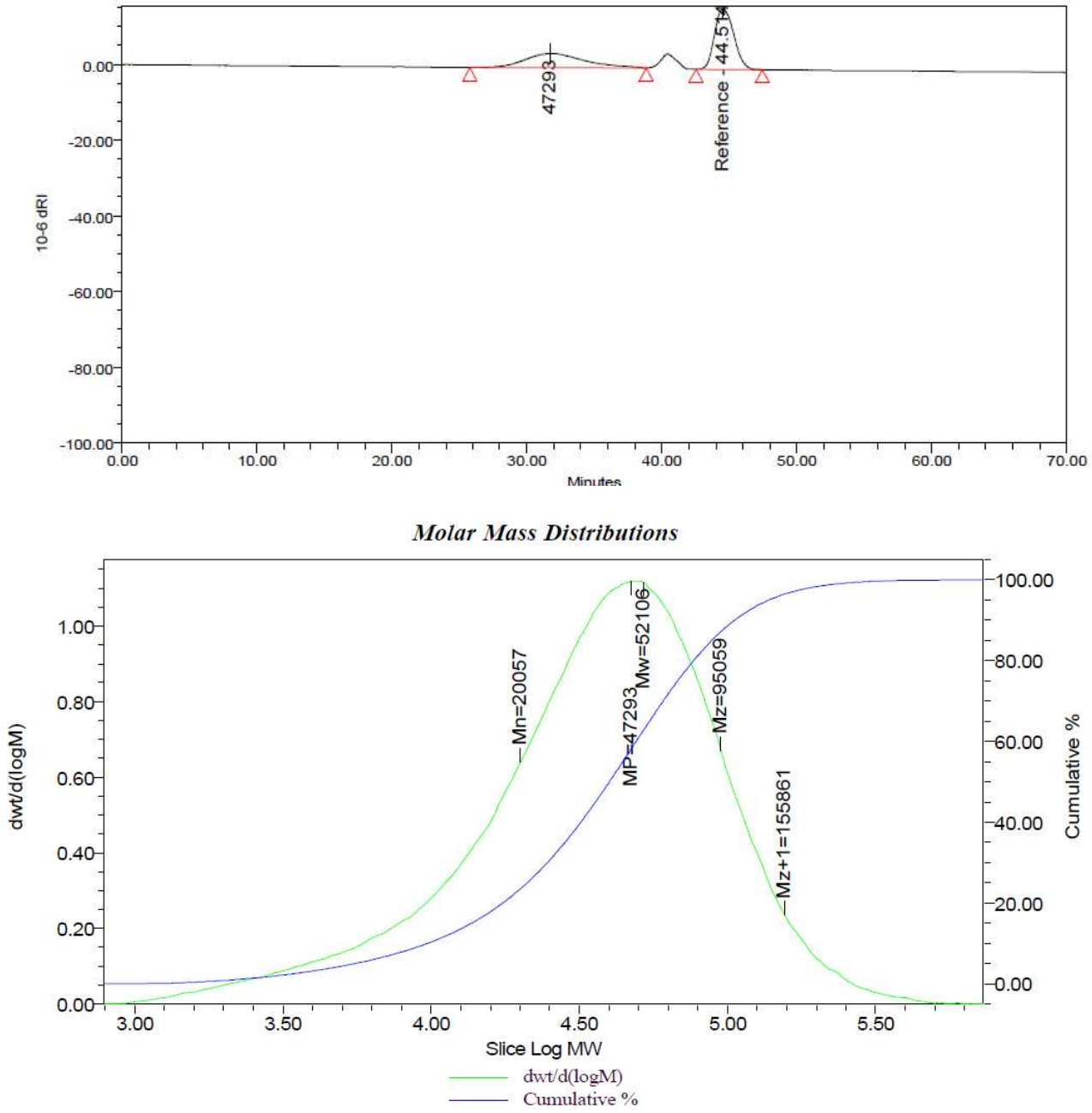

Figure S64. GPC trace of poly(**M3**-*s*-COE)**H**.

UV visible spectra of polymers

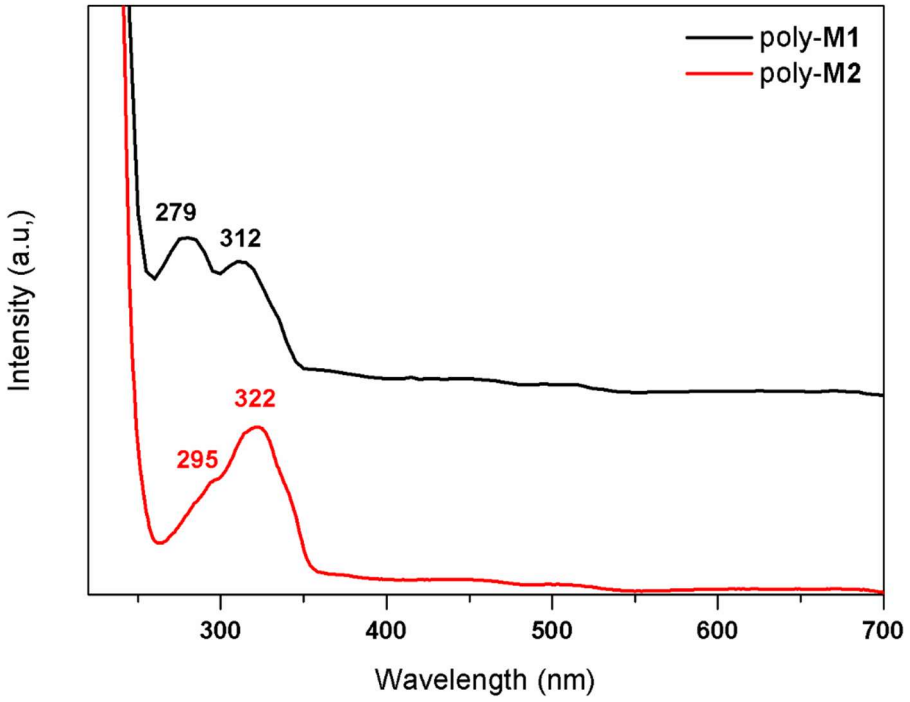

Figure S65. UV-vis absorption spectra of poly-**M1** and poly-**M2** ($CHCl_3$ solution, 1 mg/1 mL)**.**

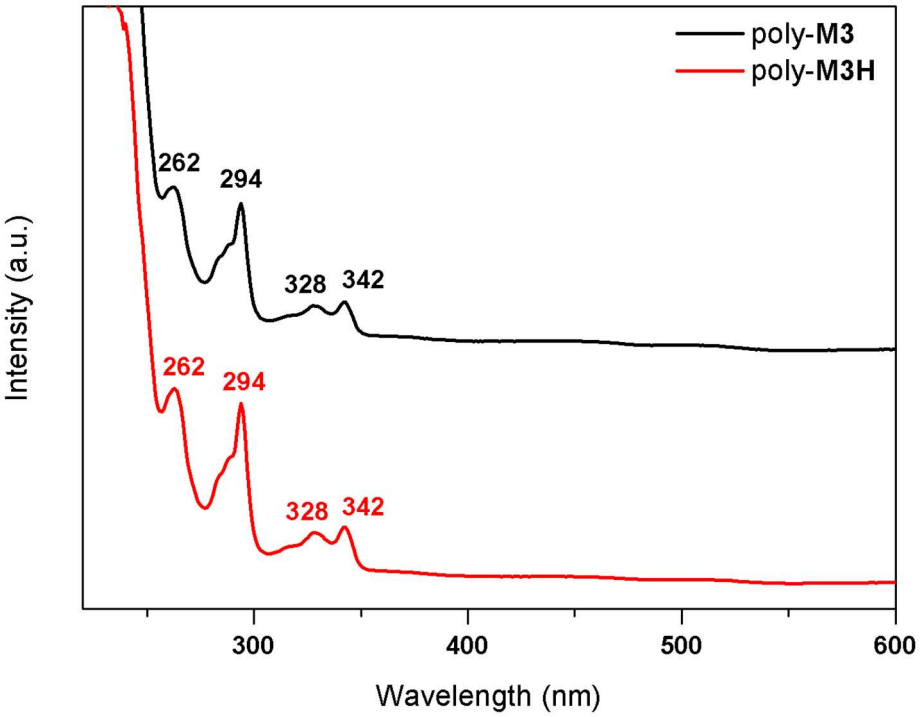

Figure S66. UV-vis absorption spectra of poly-**M3** and poly-**M3H (**$CHCl_3$ solution, 1 mg/1 mL)**.**

Fluorescence spectra of poly-M3 in THF/water mixtures

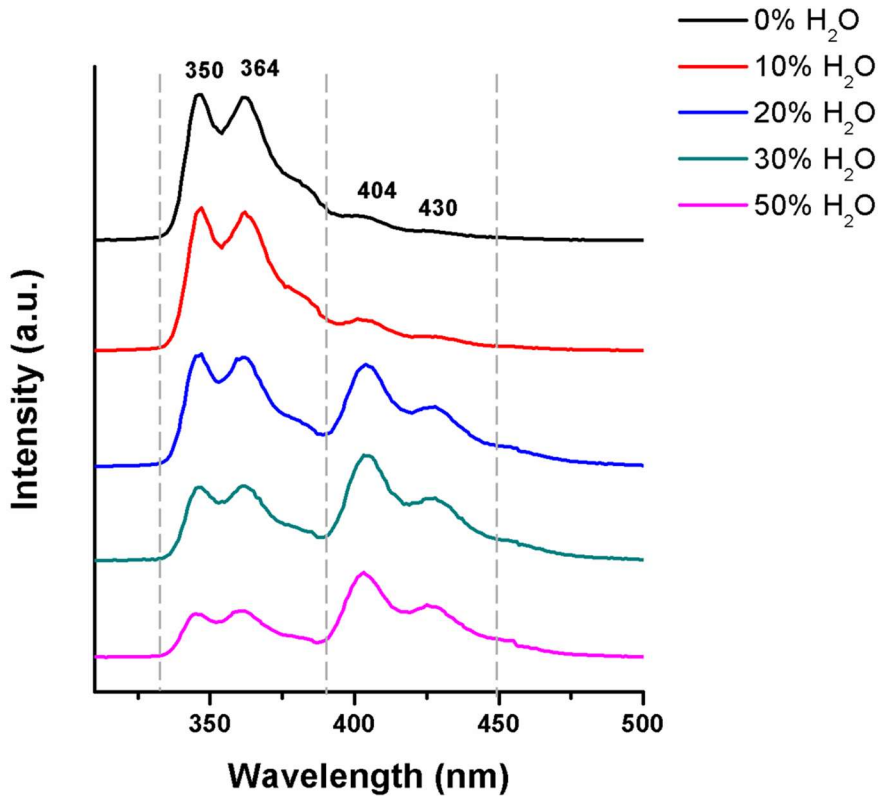

Figure S67. Emission spectra of poly-**M3** in THF (0.01mg/mL) with varied volumetric fractions of water (Λ ecc = 300 nm, 298 K). The polymer becomes insoluble when the water fraction exceeds 50%.

UV-visible and fluorescence spectra of poly(M3-*s*-COE)

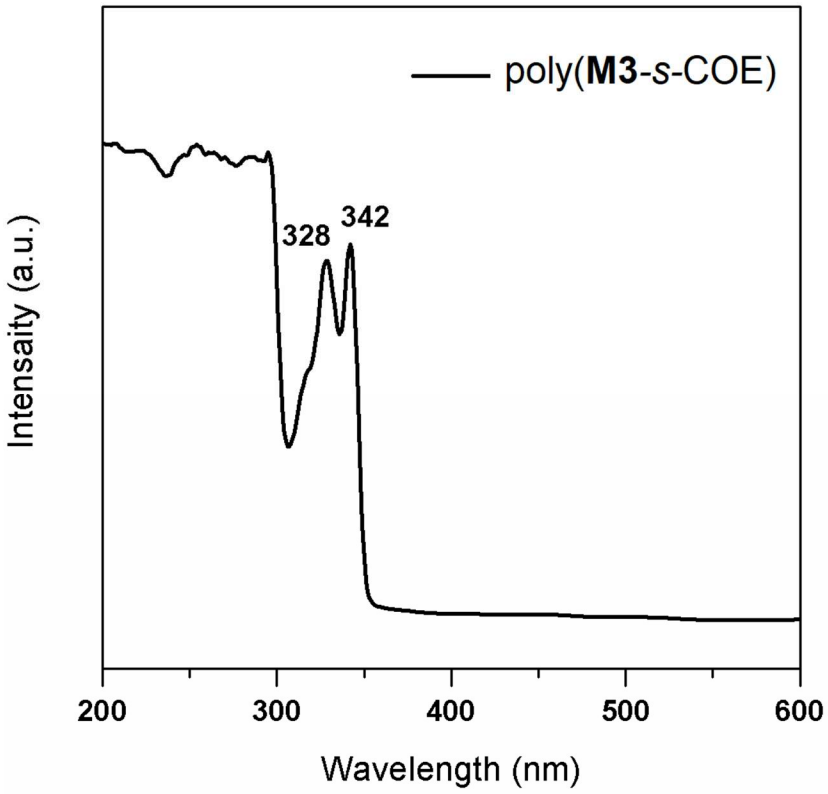

Figure S68. UV-vis absorption spectrum of poly(**M3**-*s*-COE) ($CHCl_3$ solution, 1 mg/1 mL)**.**

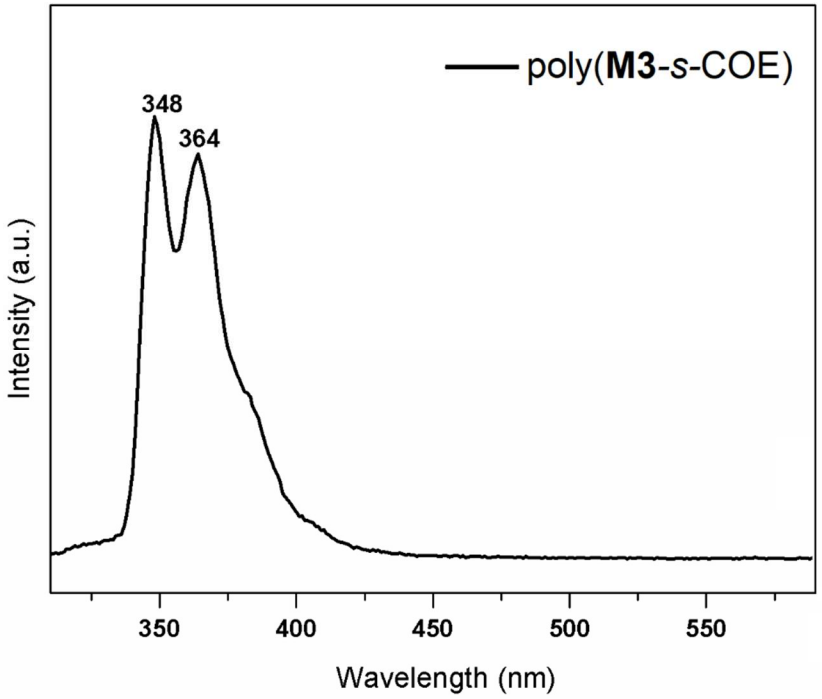

Figure S69. Emission spectrum of poly(**M3**-*s*-COE) ($CHCl_3$ solution, 1 mg/1 mL)**.**