Supporting Information For:

Tuning the Negative Photochromism of Water Soluble Spiropyran Polymers

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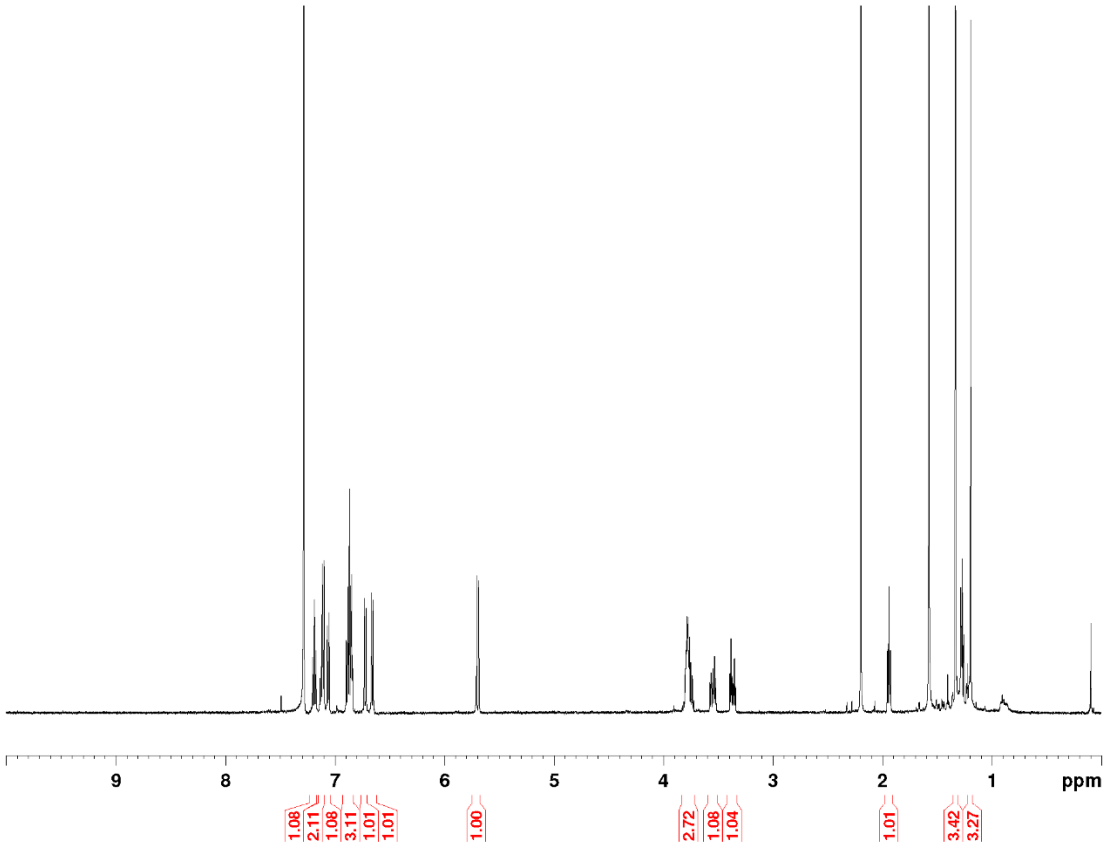
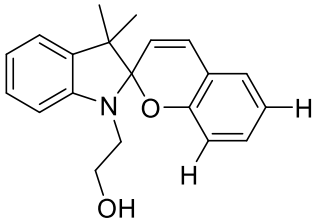
Contents:

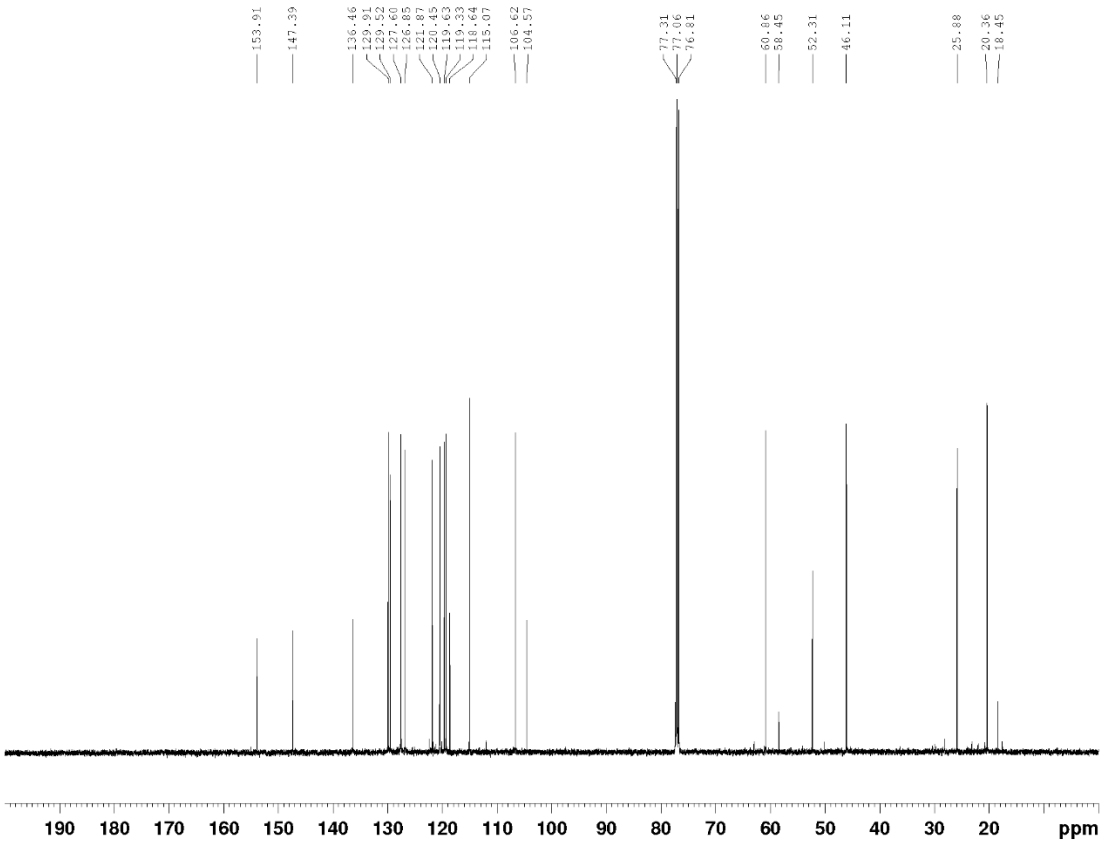
1. **NMR spectra of prepared monomers and polymers.**

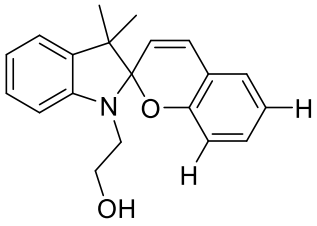




Compound 4

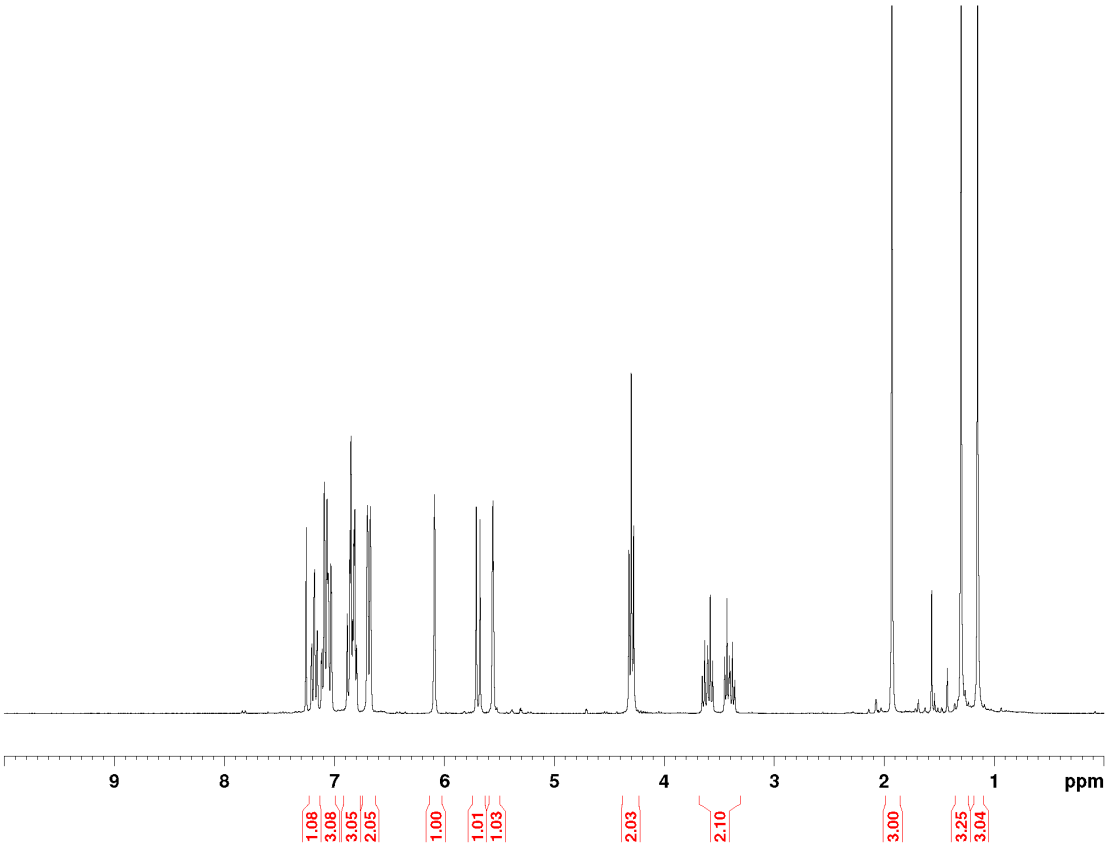
^{1}H NMR, $CHCl_3$ (500 MHz)

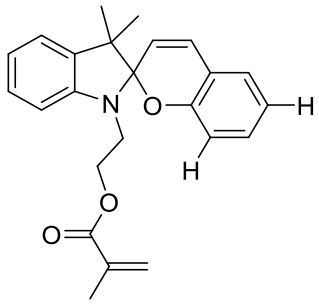




Compound 4

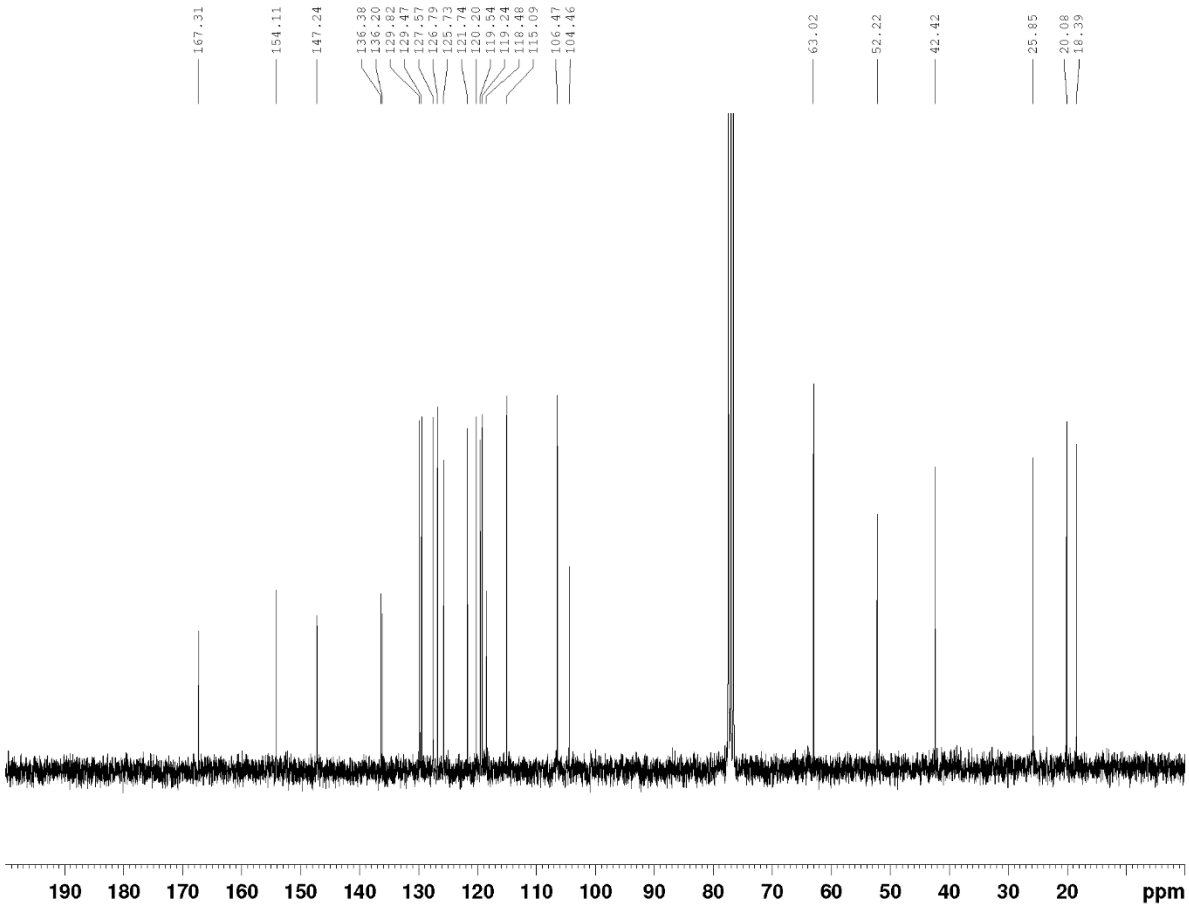
^{13}C NMR, $CHCl_3$ (125 MHz)

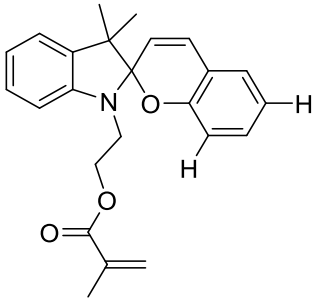




Compound 5

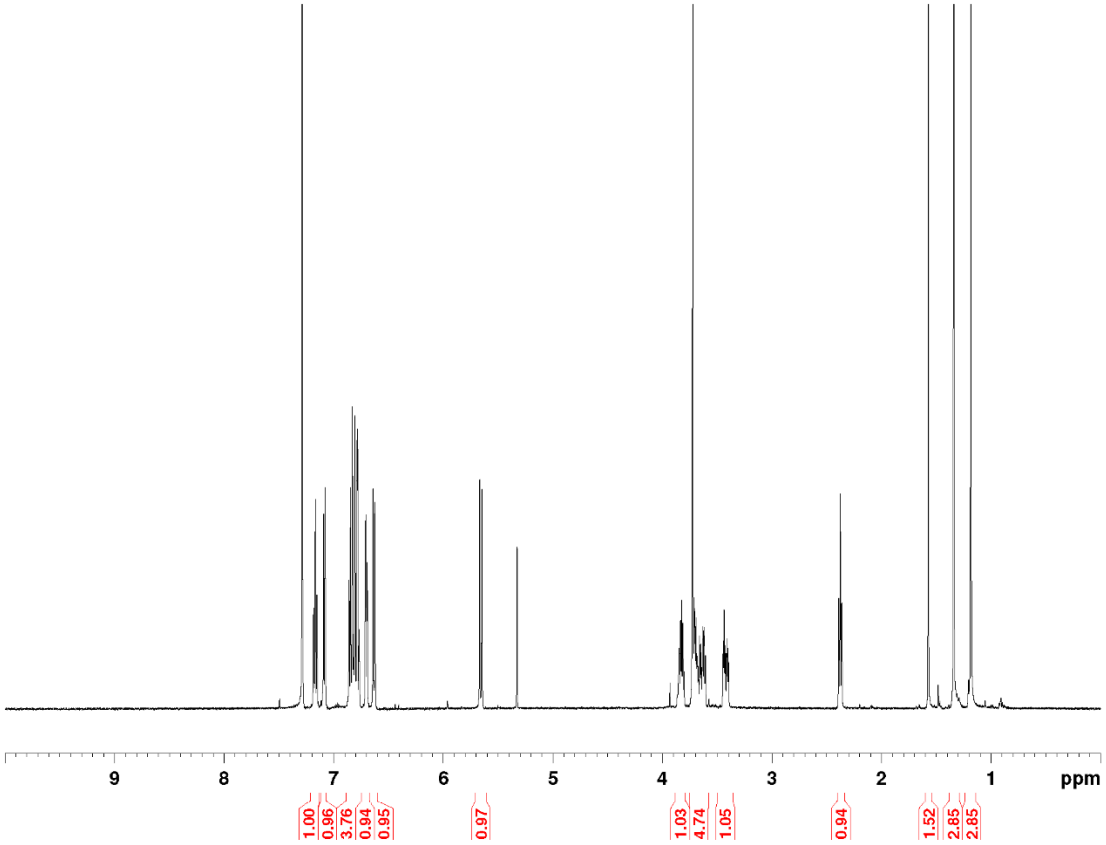
^{1}H NMR, $CHCl_3$ (300 MHz)

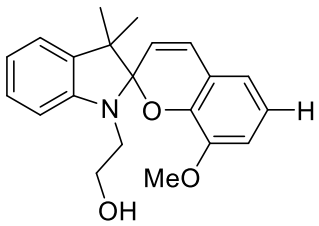




Compound 5

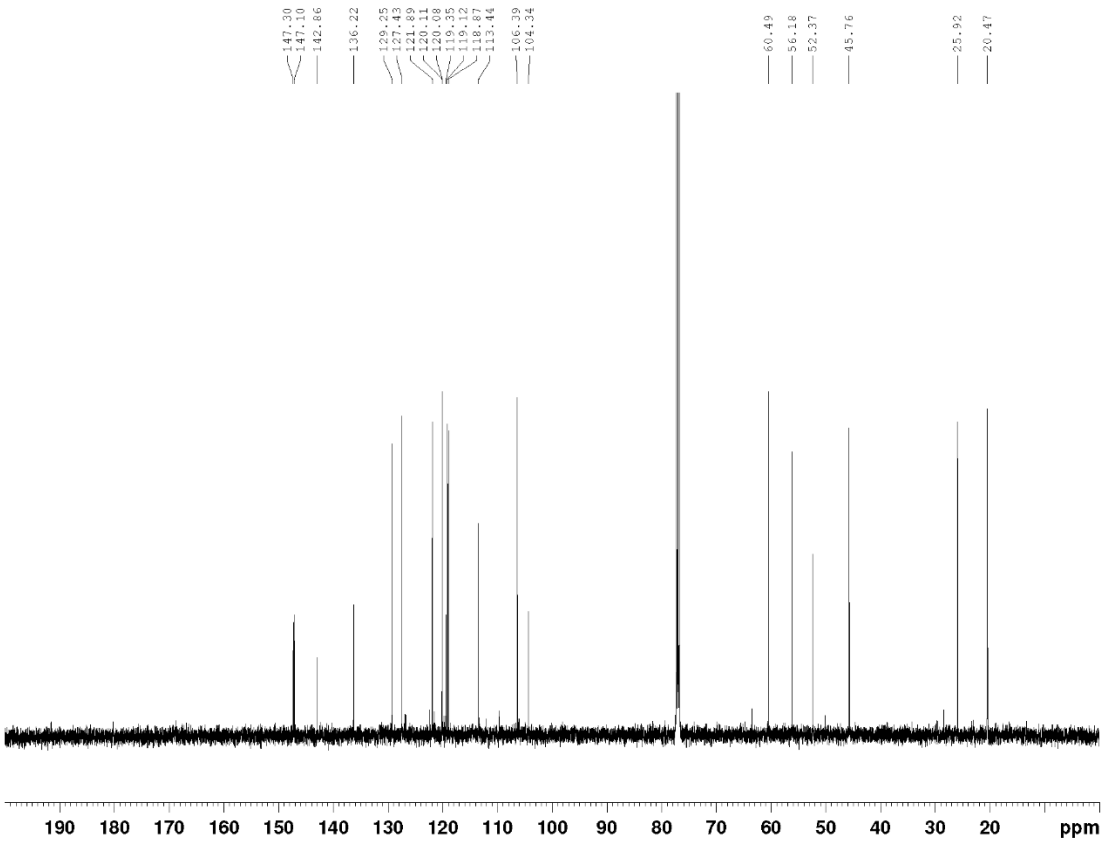
^{13}C NMR, $CHCl_3$ (75 MHz)

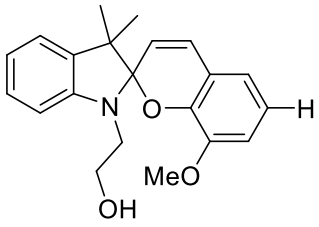




Compound 6

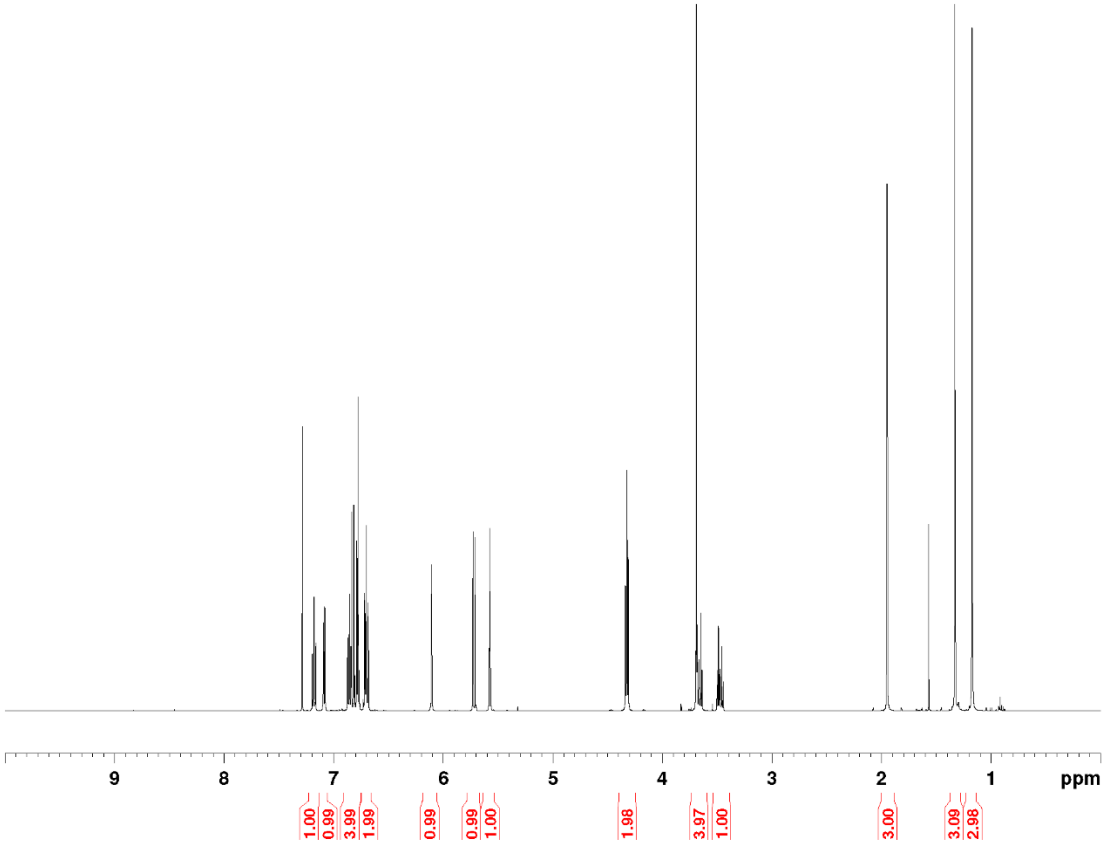
^{1}H NMR, $CHCl_3$ (500 MHz)

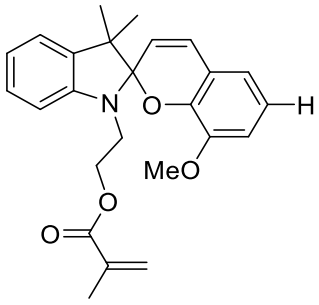




Compound 6

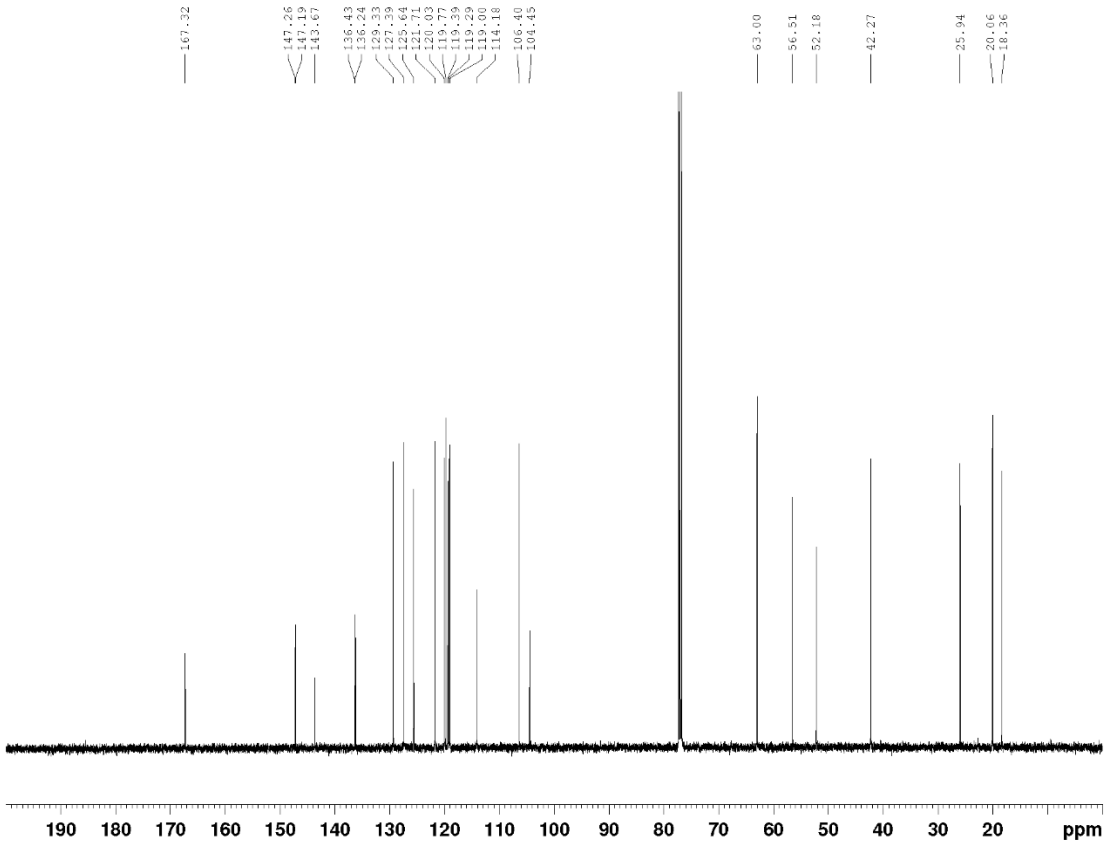
^{13}C NMR, $CHCl_3$ (125 MHz)

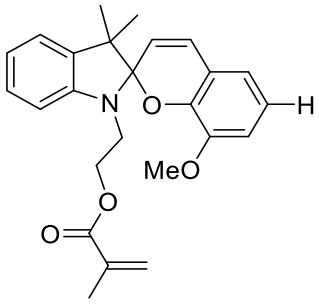




Compound 7

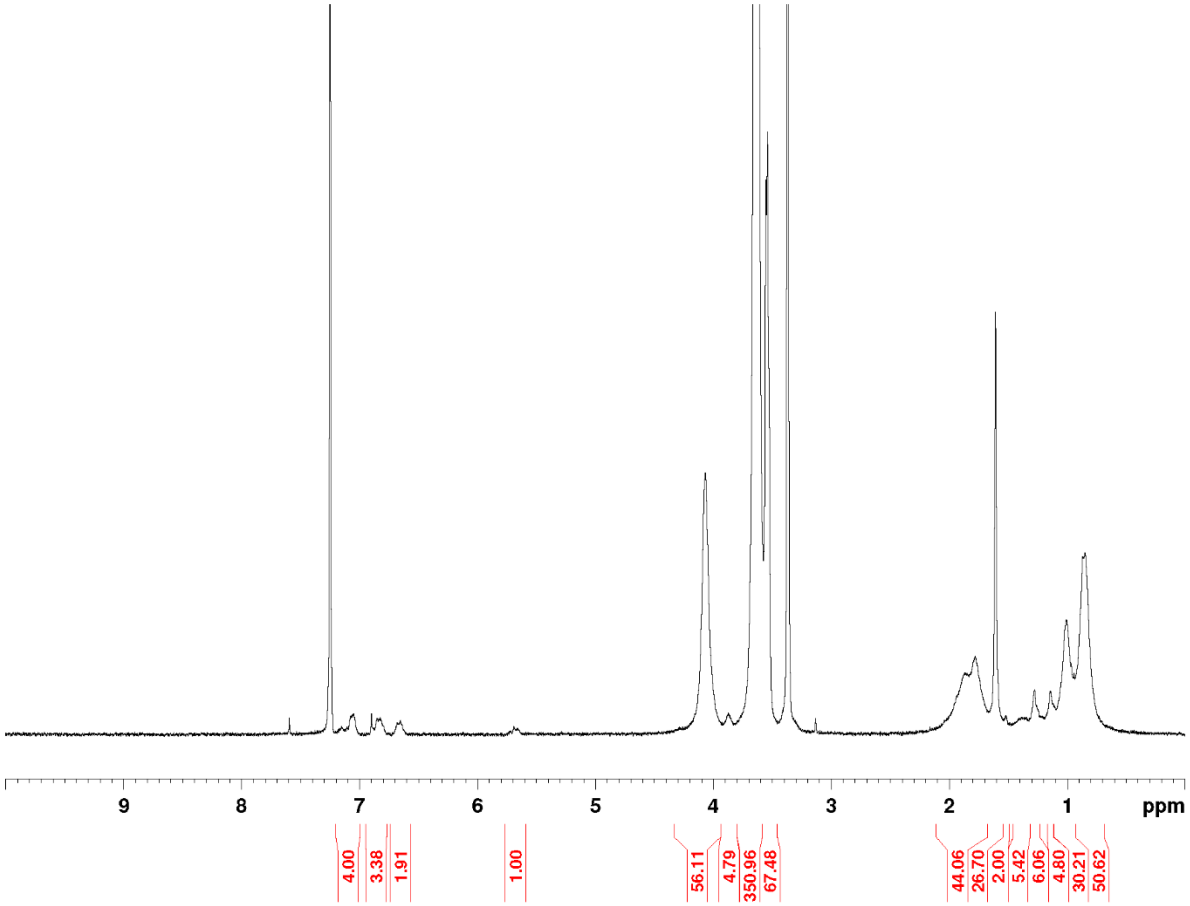
^{1}H NMR, $CHCl_3$ (500 MHz)

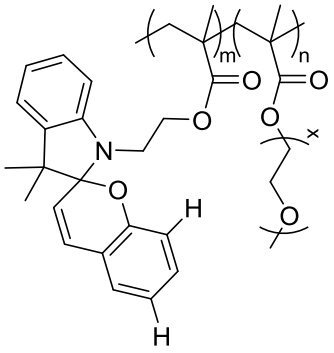




Compound 7

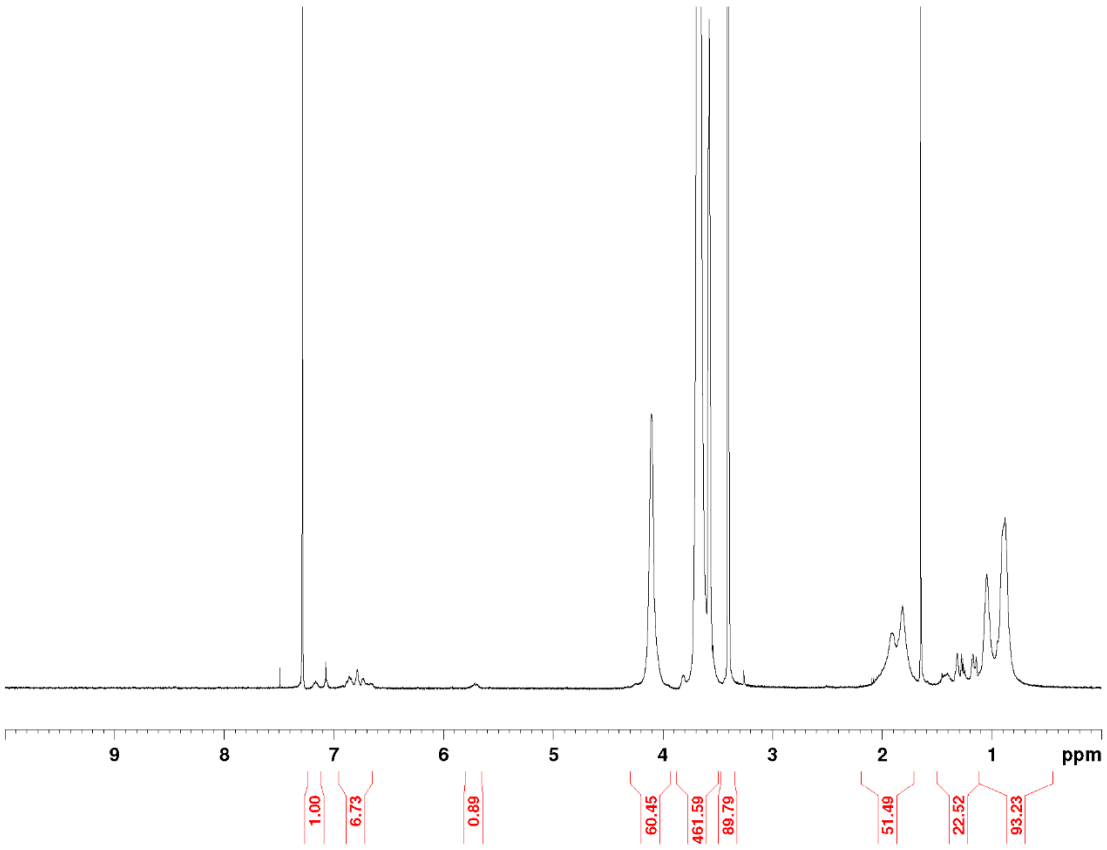
^{13}C NMR, $CHCl_3$ (125 MHz)

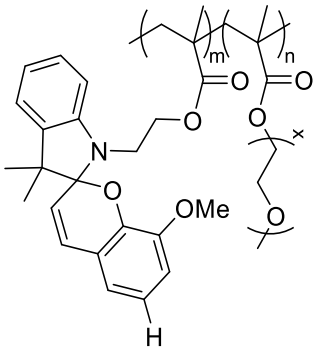




HSp-PEGMA

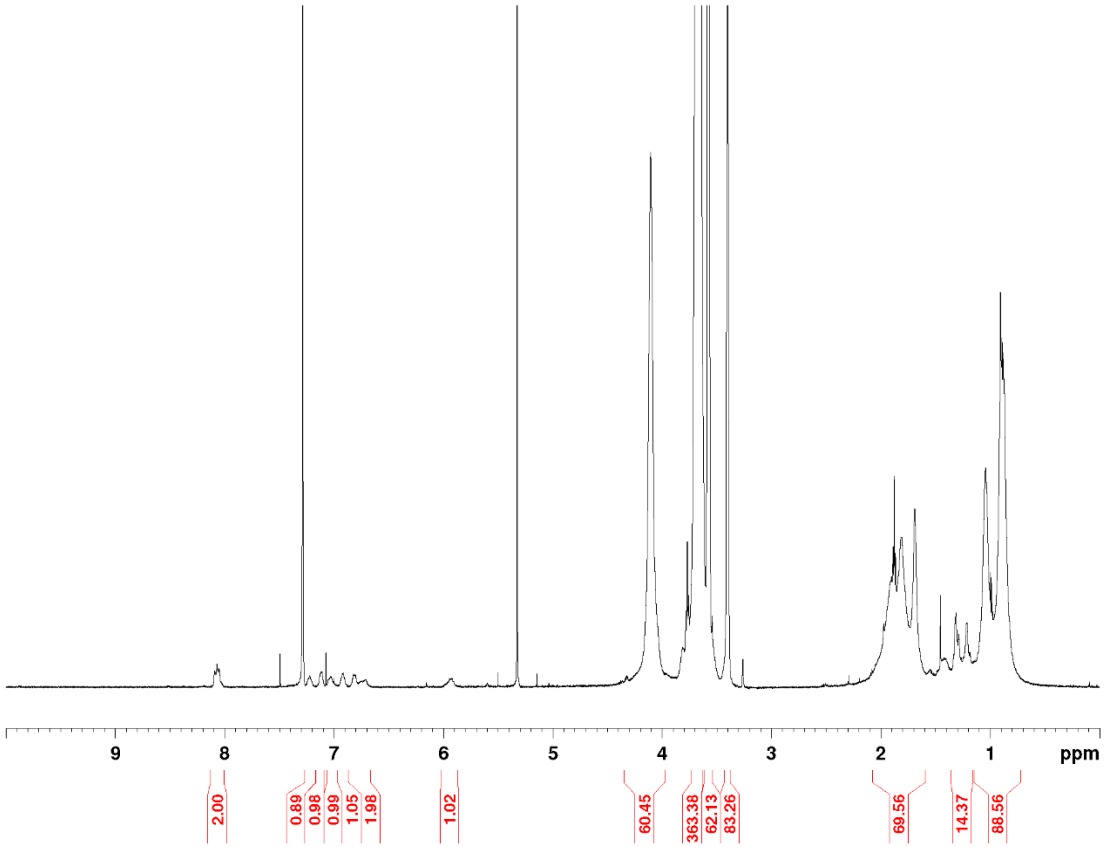
^{1}H NMR, $CHCl_3$ (300 MHz)

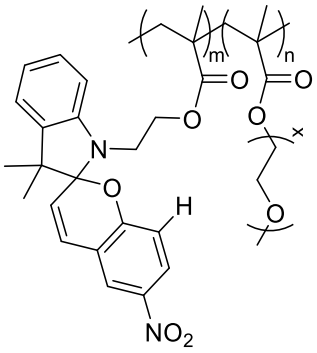




OMeSp-PEGMA

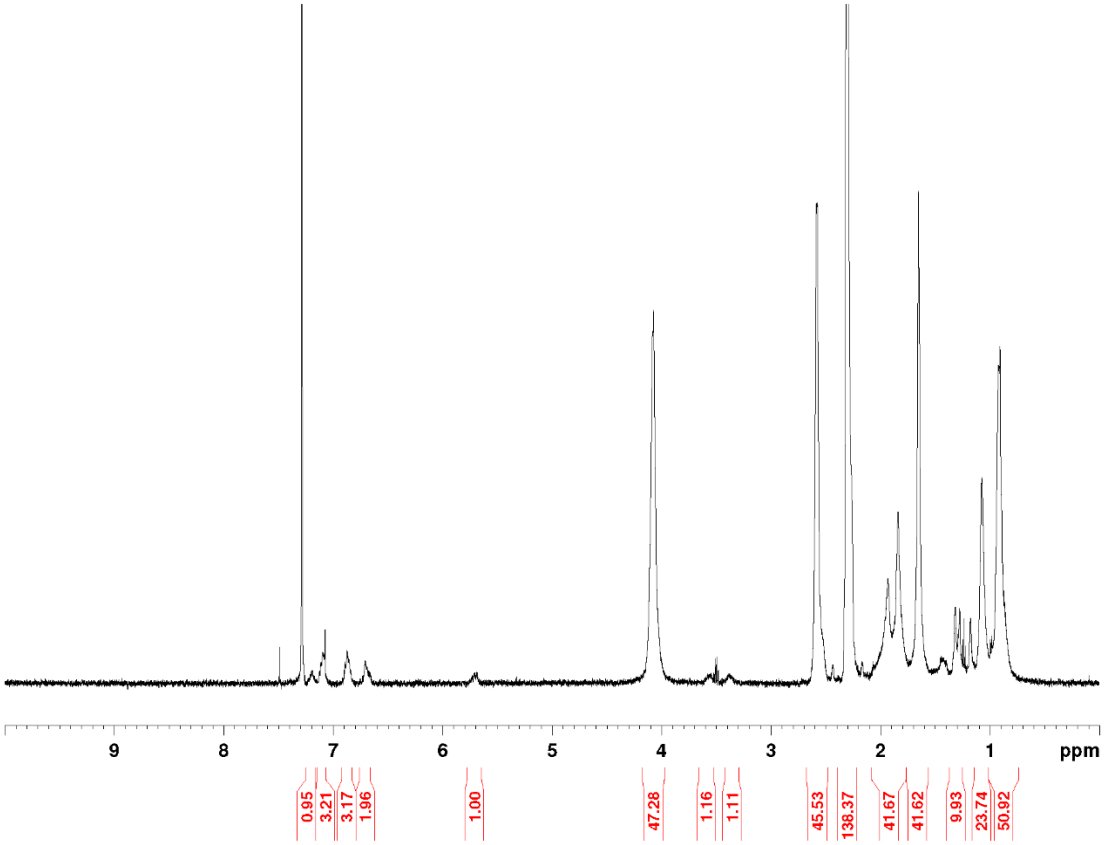
^{1}H NMR, $CHCl_3$ (500 MHz)

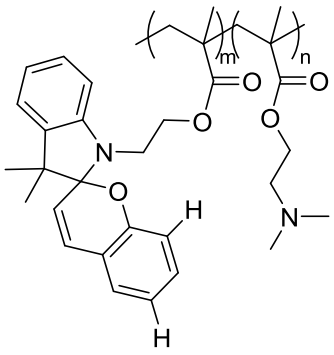




NO_2Sp-PEGMA

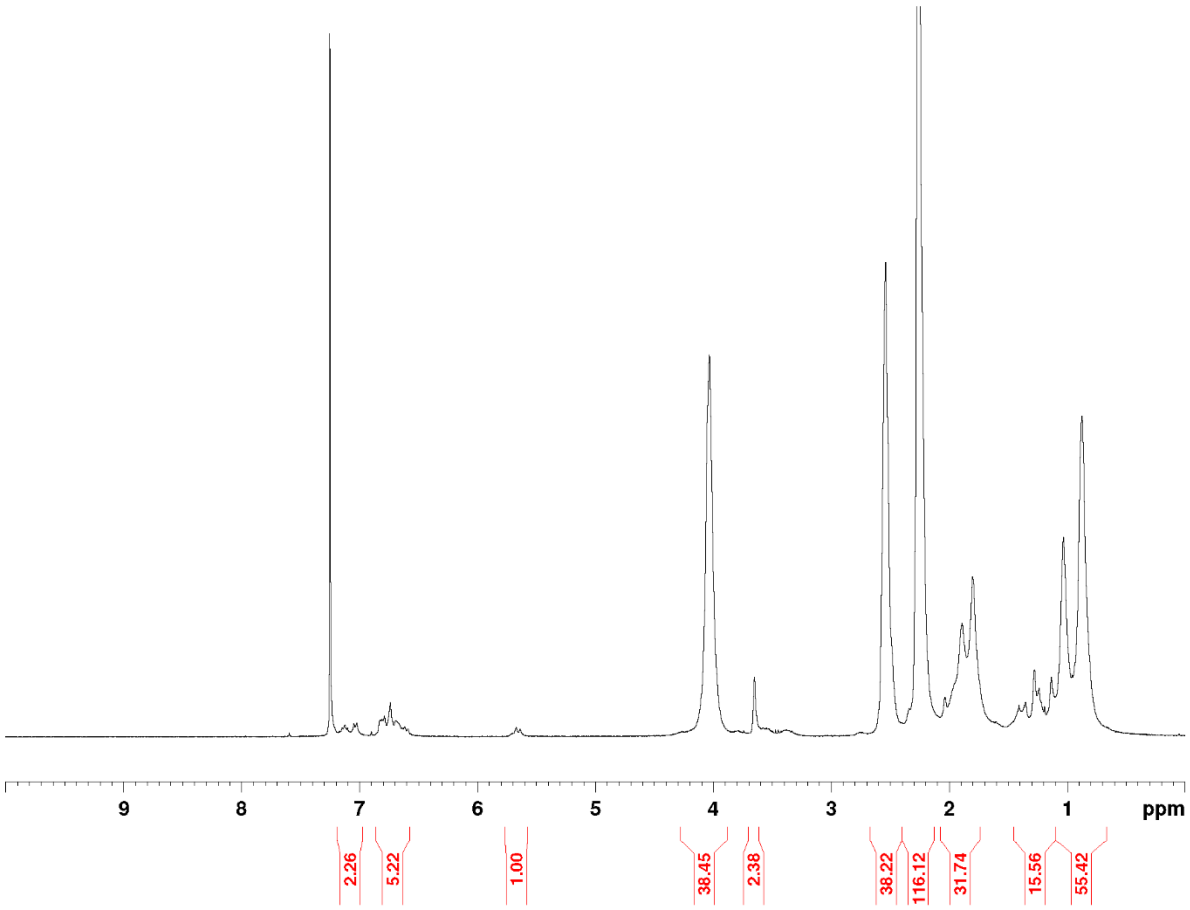
^{1}H NMR, $CHCl_3$ (500 MHz)

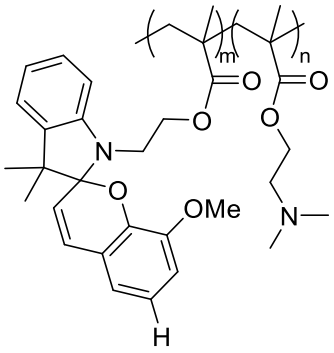




HSp-DMAEMA

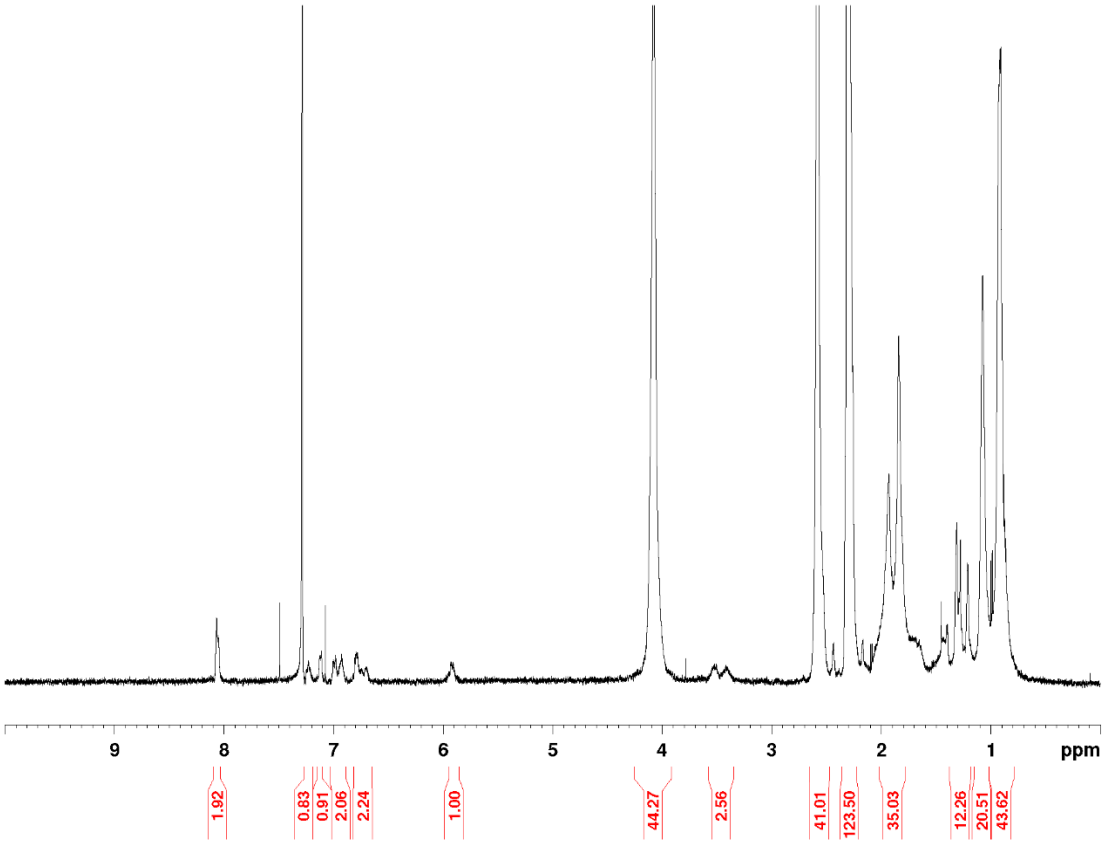
^{1}H NMR, $CHCl_3$ (500 MHz)

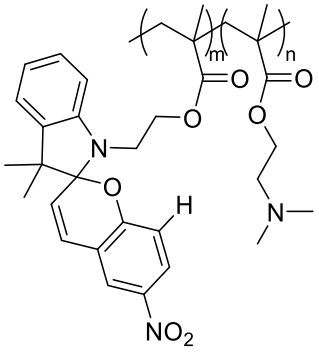




OMeSp-DMAEMA

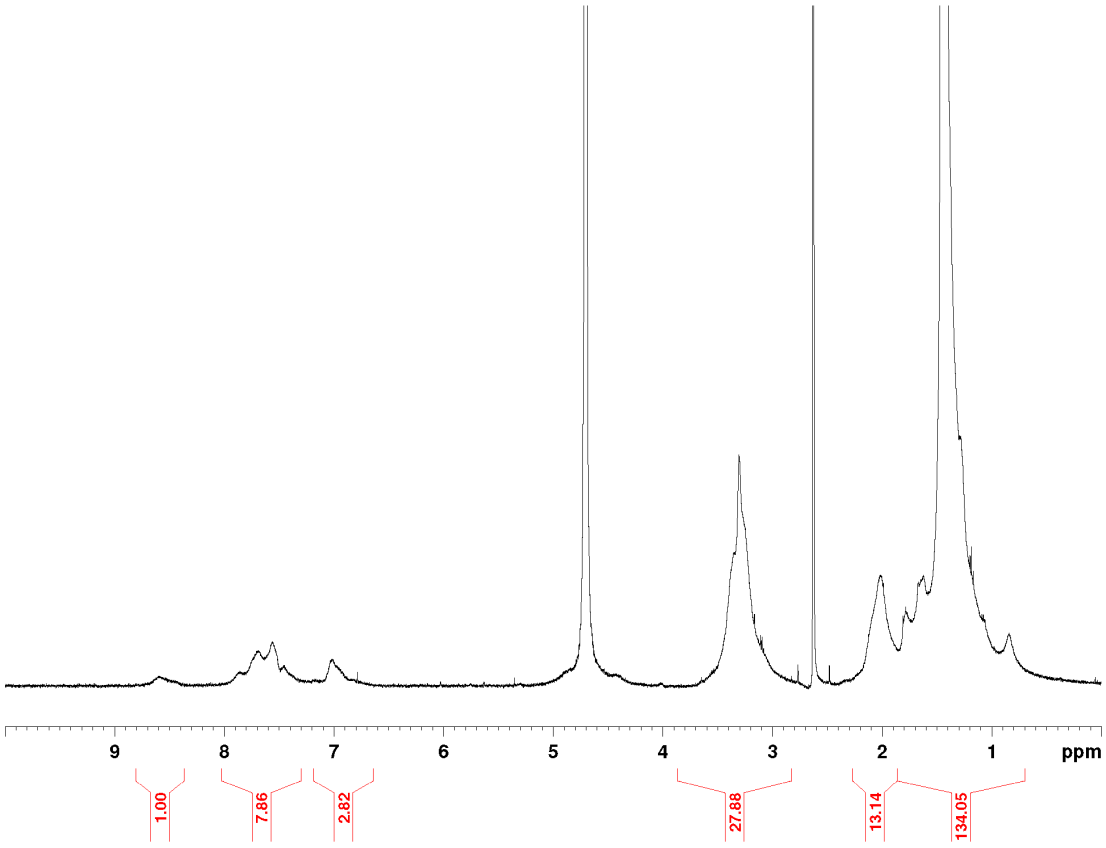
^{1}H NMR, $CHCl_3$ (300 MHz)

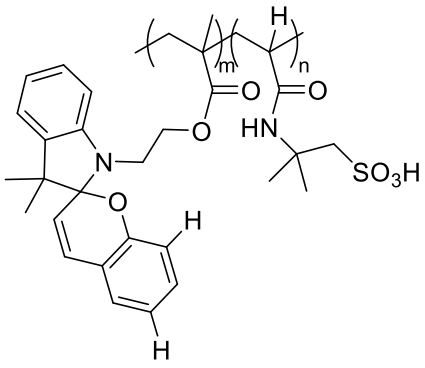




NO_2Sp-DMAEMA

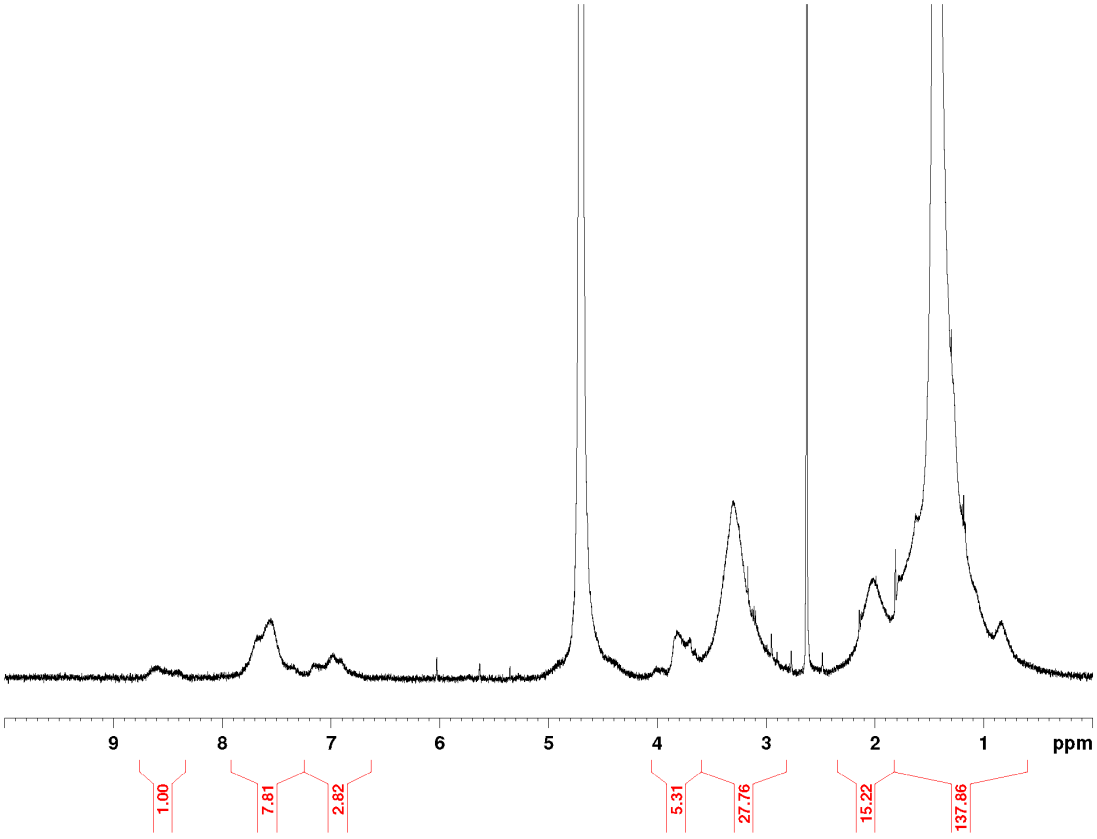
^{1}H NMR, $CHCl_3$ (500 MHz)

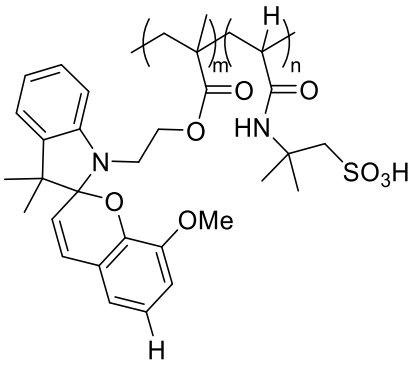




HSp-AMPS

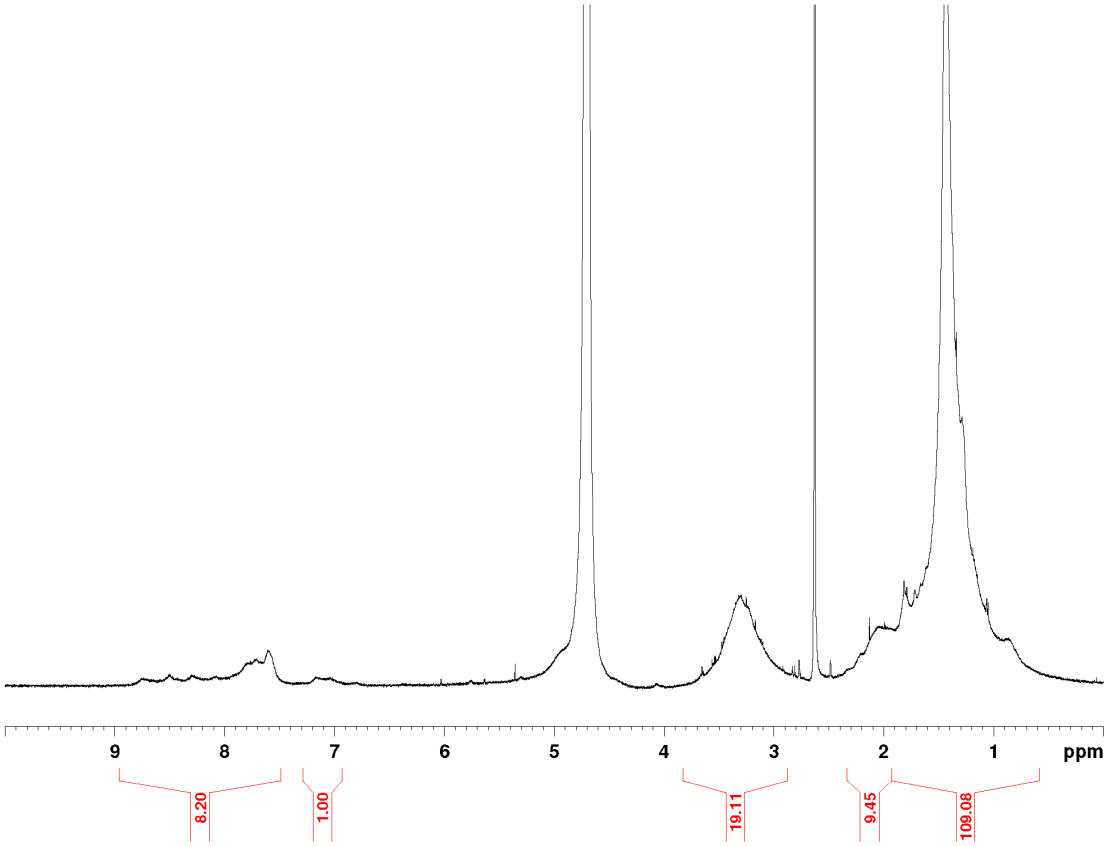
^{1}H NMR, D_2O (500 MHz)

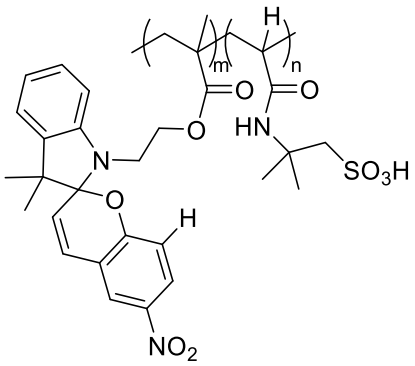




OMeSp-AMPS

^{1}H NMR, D_2O (500 MHz)

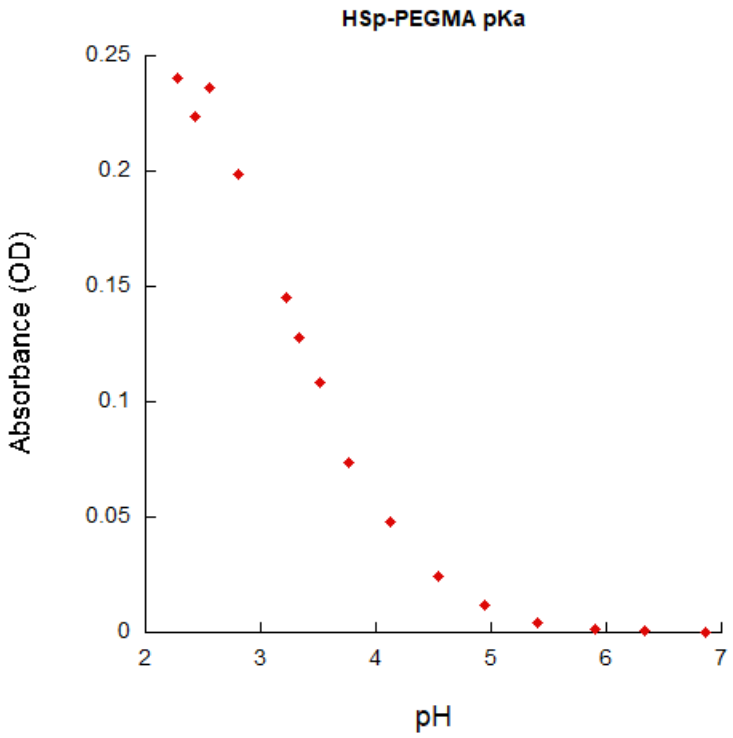


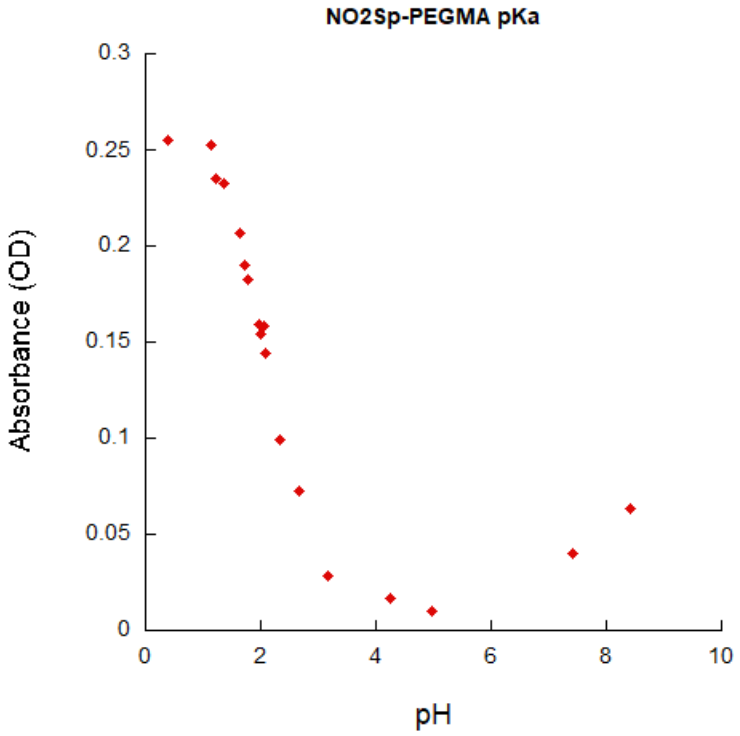


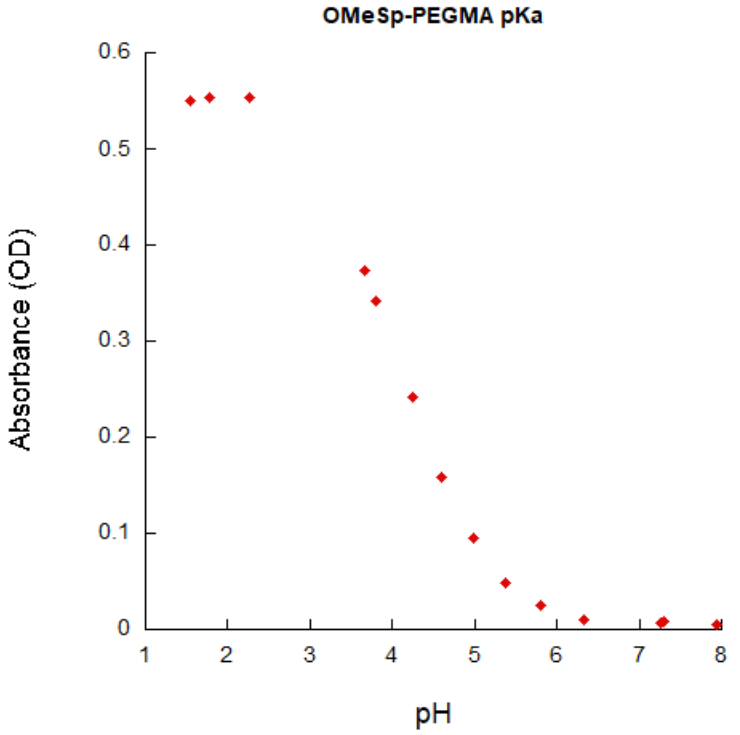
NO_2Sp-AMPS

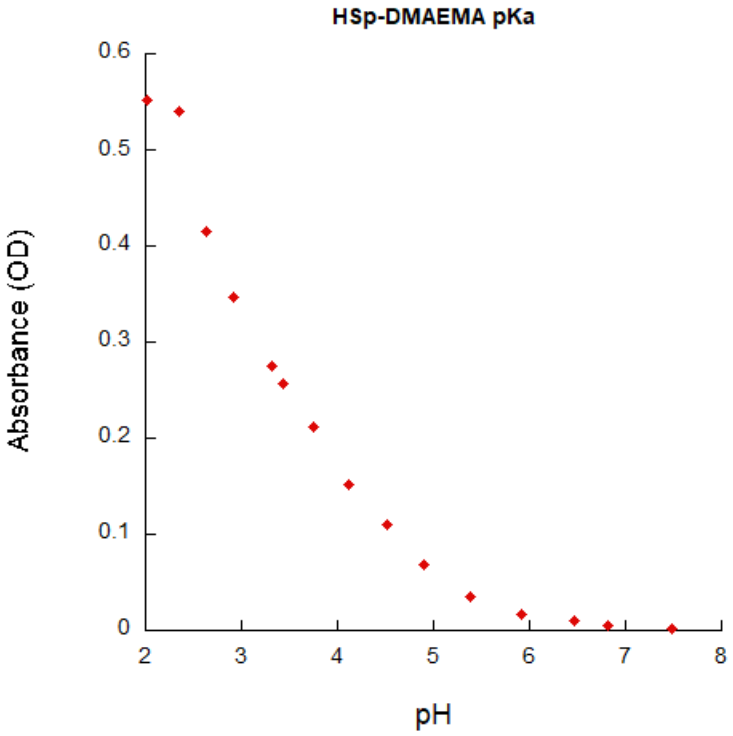
^{1}H NMR, D_2O (500 MHz)

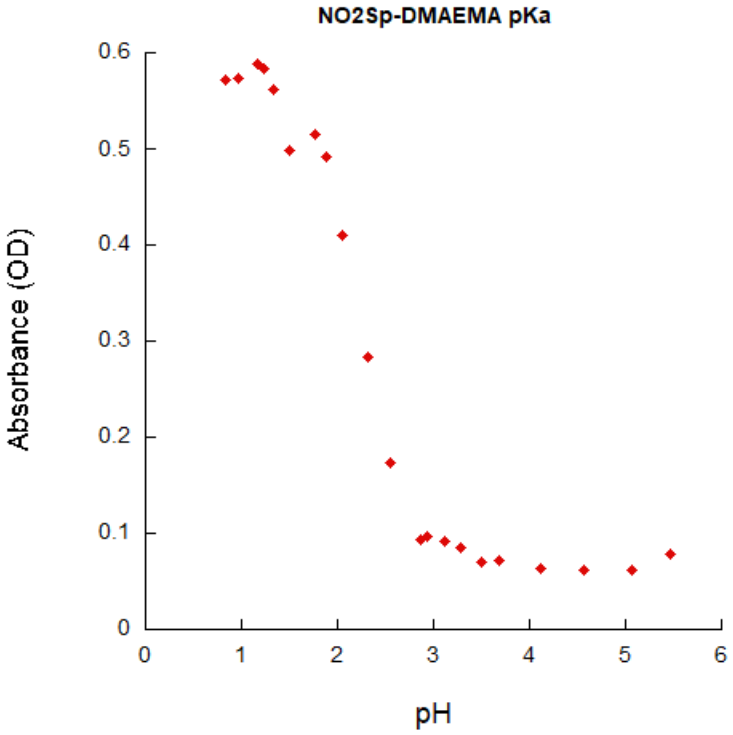
2. Absorbance data for pKa determinations of DMAEMA, AMPS polymers.

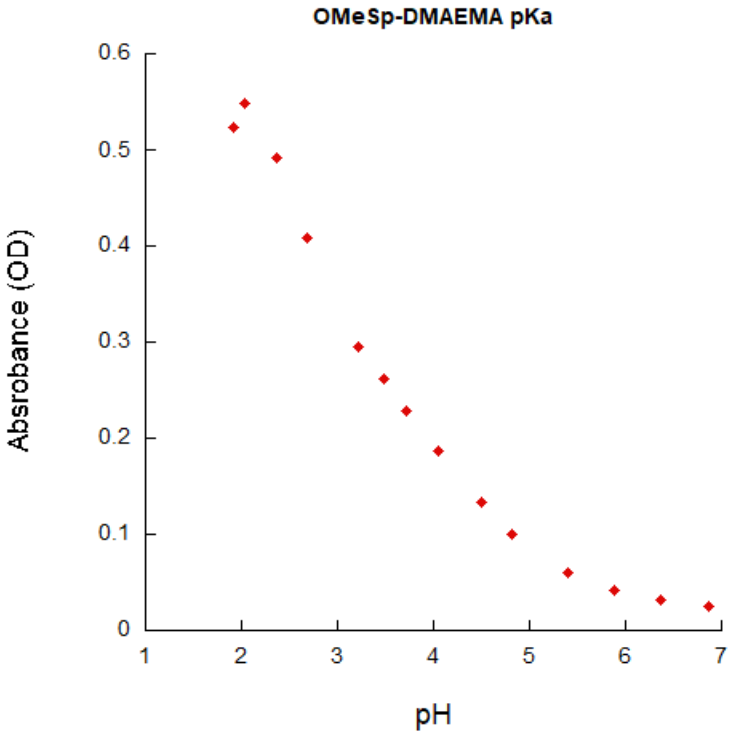


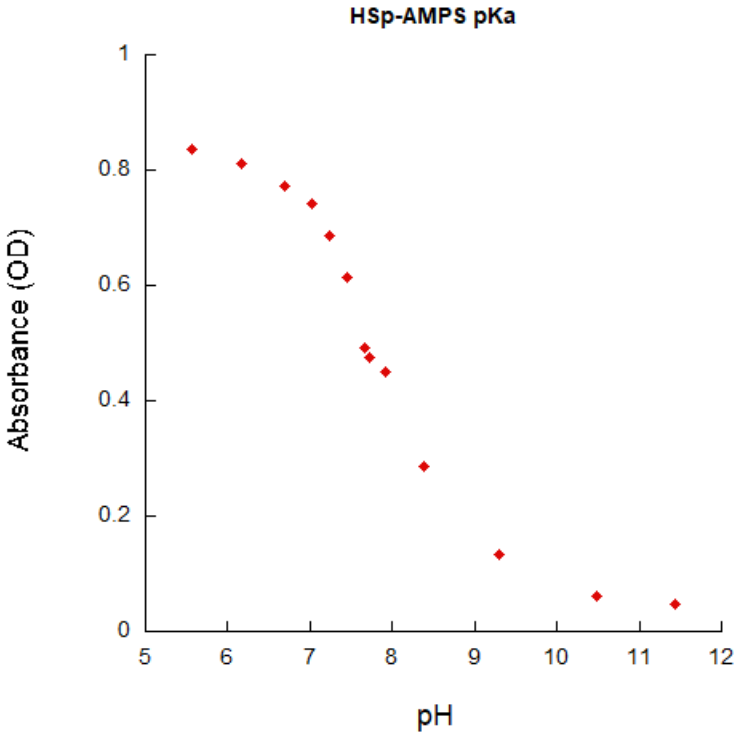

NO2Sp-PEGMA pKa
Absorbance (OD)
0.3
0.25
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10
pH

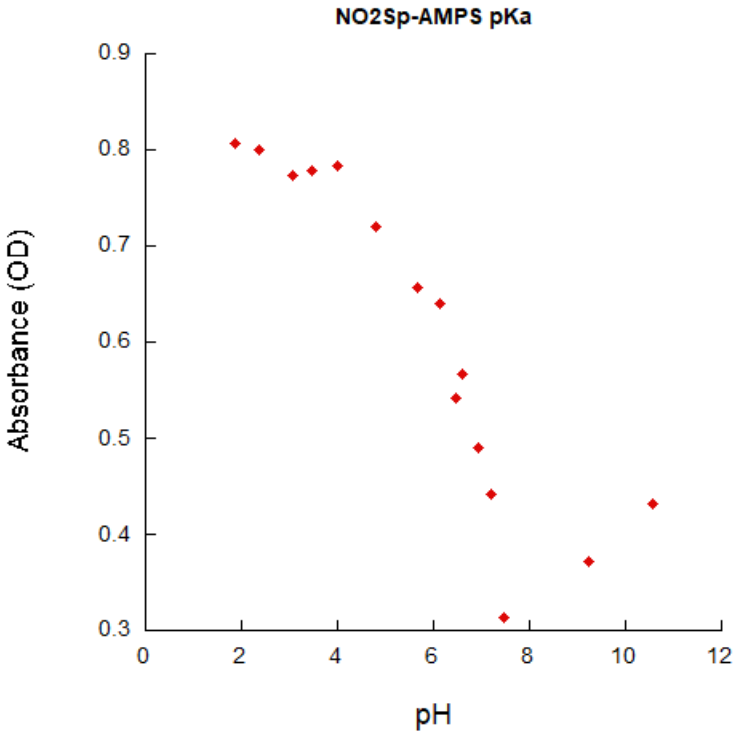

OMeSp-PEGMA pKa
Absorbance (OD)
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
7
8
pH

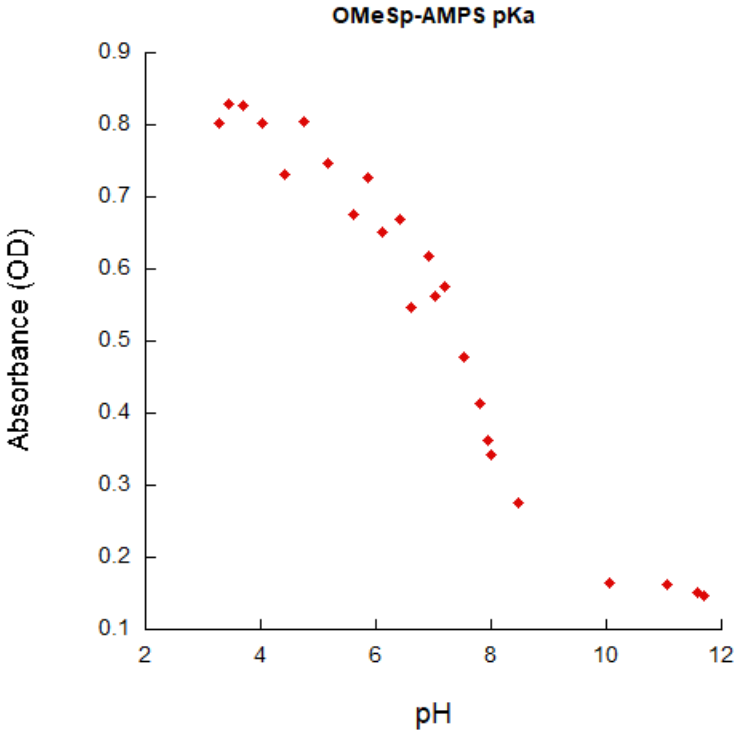

HSp-DMAEMA pKa
Absorbance (OD)
0.6
0.5
0.4
0.3
0.2
0.1
0
2
3
4
5
6
7
8
pH


NO2Sp-DMAEMA pKa
Absorbance (OD)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
pH


OMeSp-DMAEMA pKa
Absrobance (OD)
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
7
pH

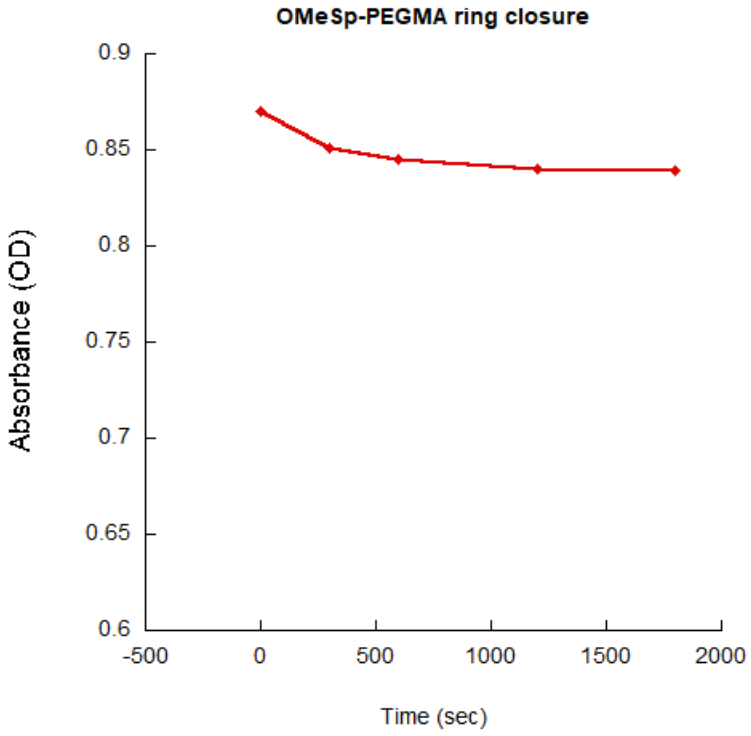

HSp-AMPS pKa
Absorbance (OD)
1
0.8
0.6
0.4
0.2
0
5
6
7
8
9
10
11
12
pH

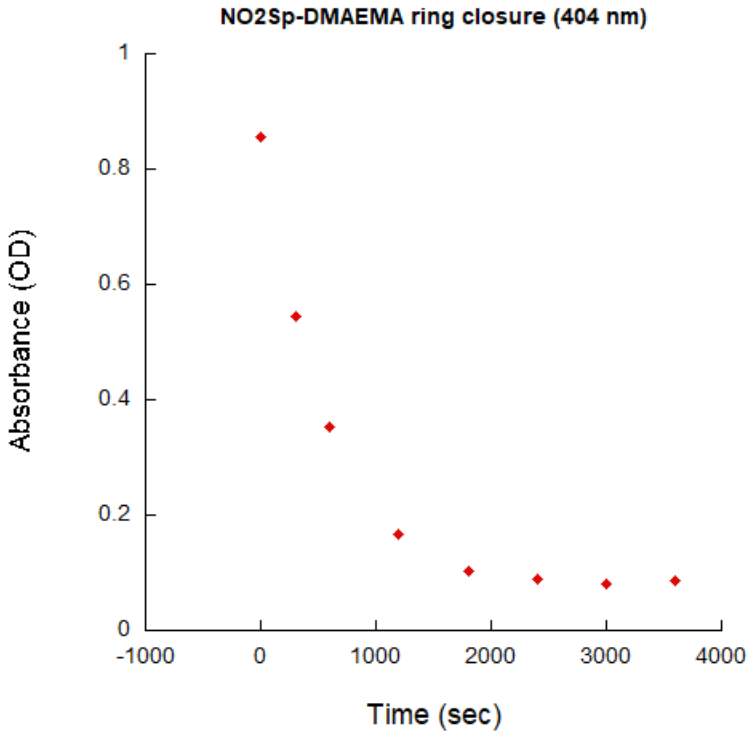

NO2Sp-AMPS pKa
Absorbance (OD)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0
2
4
6
8
10
12
pH

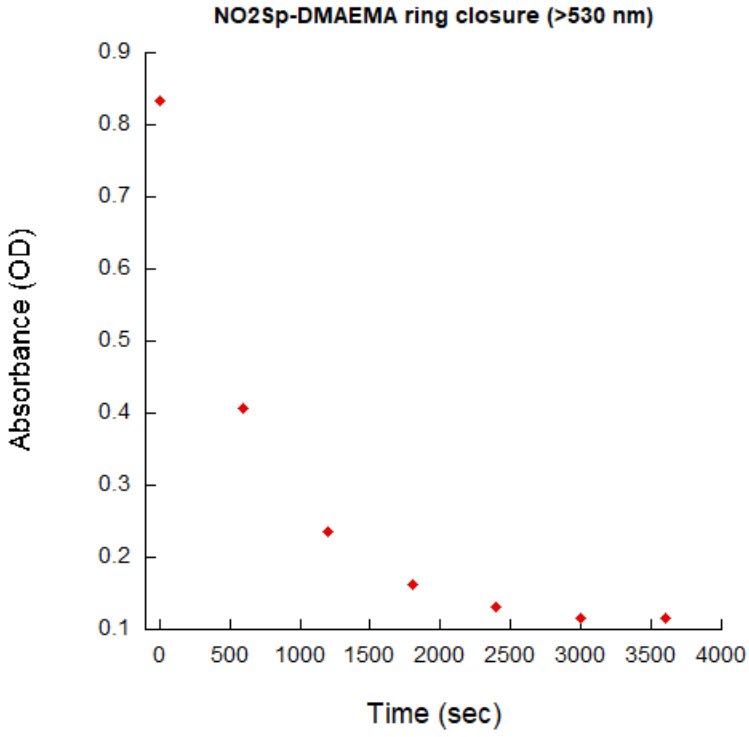

OMeSp-AMPS pKa
Absorbance (OD)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
2
4
6
8
10
12
pH

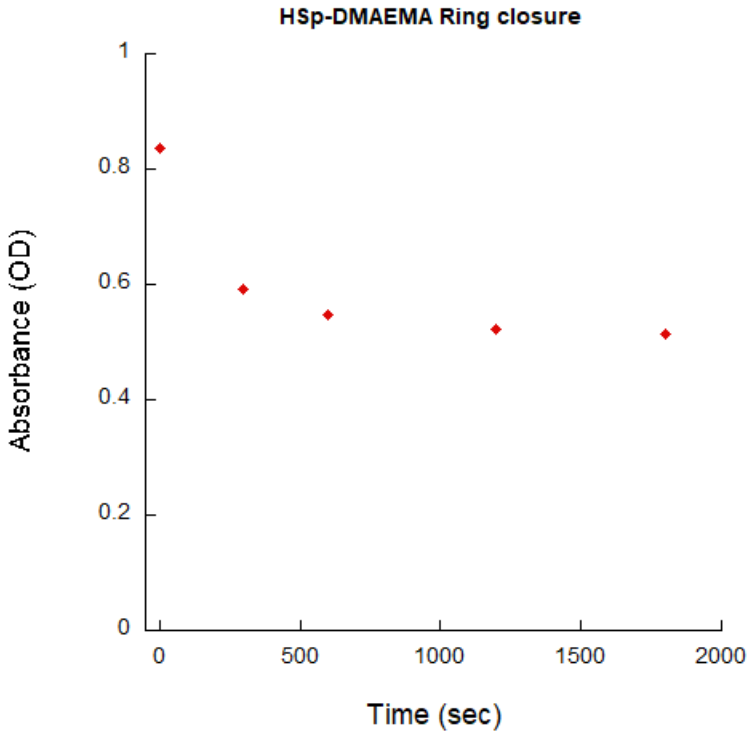
3. Photo ring closing absorbance data

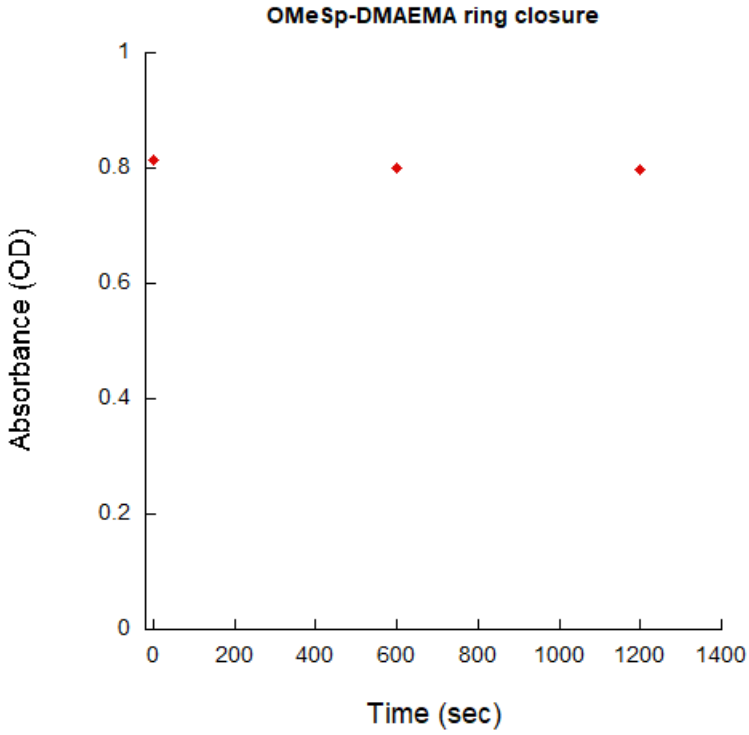
All irradiation experiments shown were performed using 3 mW/cm^2 at 404 nm (unless otherwise noted), with specific conditions specified in manuscript.

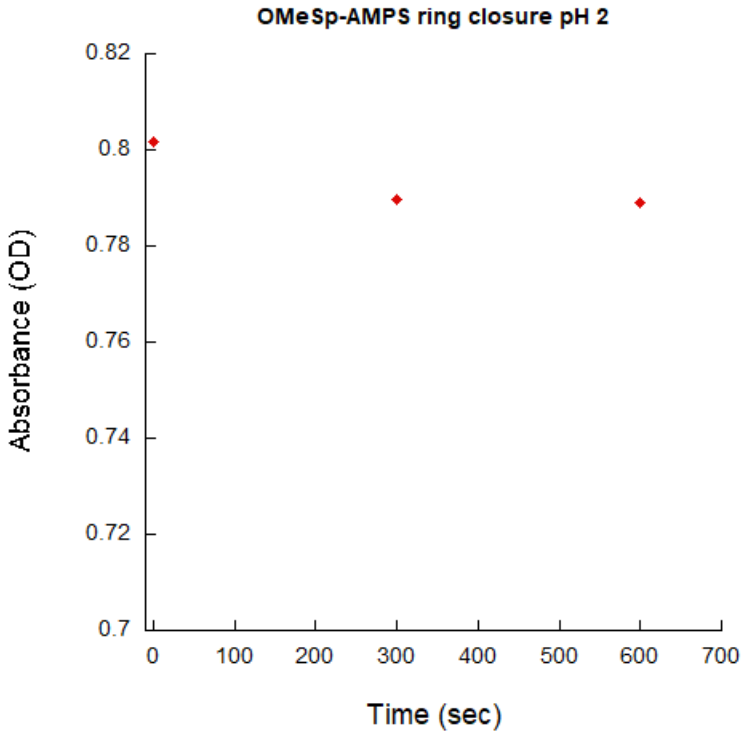


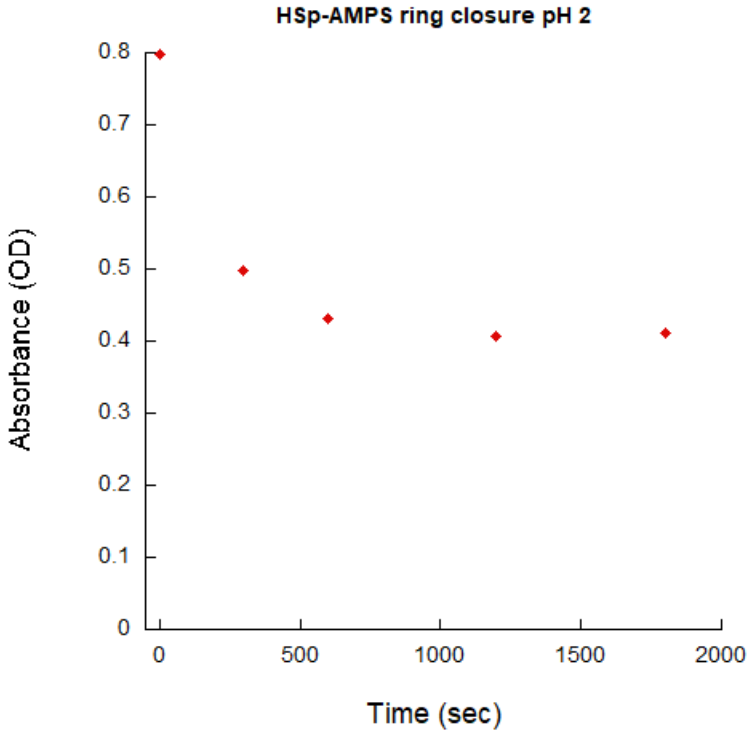

NO2Sp-DMAEMA ring closure (404 nm)
Absorbance (OD)
1
0.8
0.6
0.4
0.2
0
-1000
0
1000
2000
3000
4000
Time (sec)

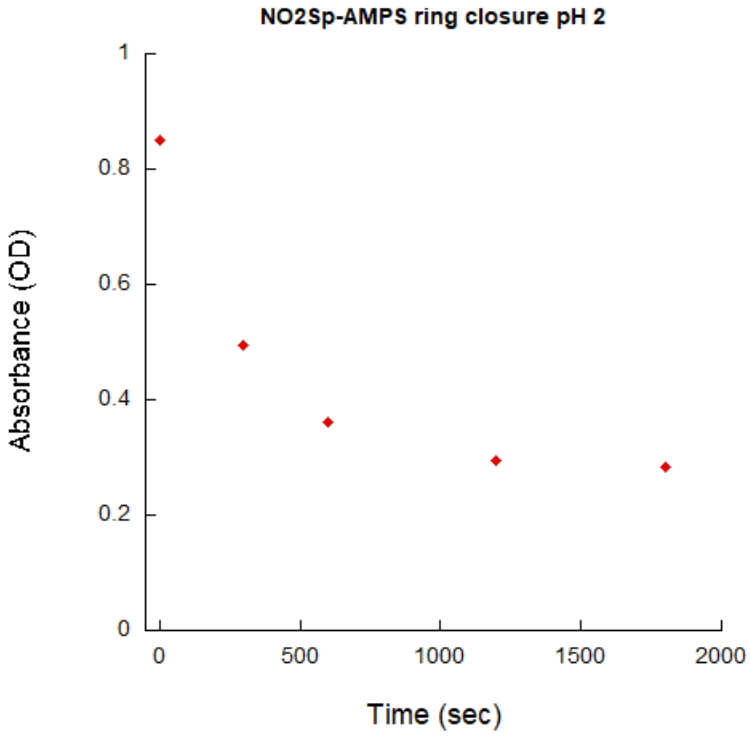

NO2Sp-DMAEMA ring closure (>530 nm)
Absorbance (OD)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
500
1000
1500
2000
2500
3000
3500
4000
Time (sec)

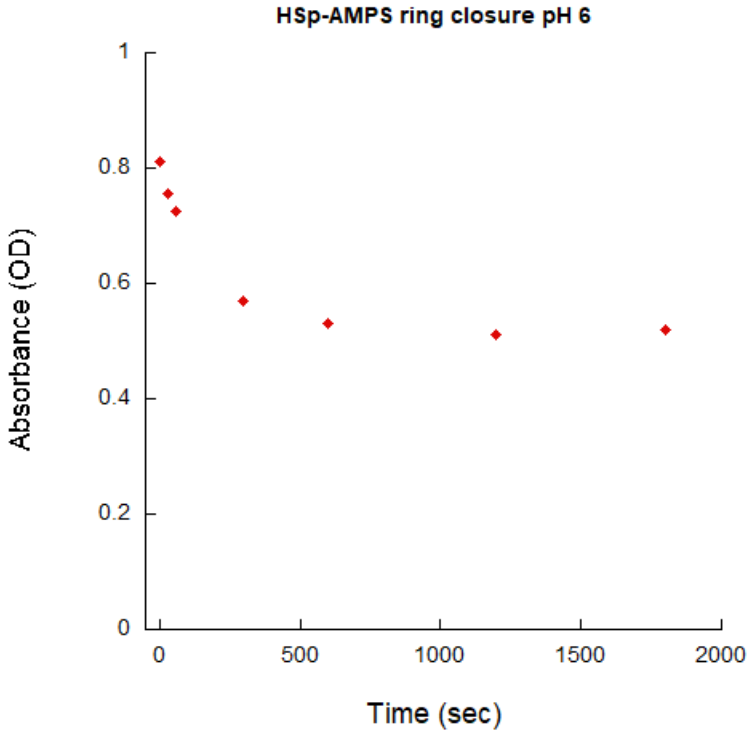

HSp-DMAEMA Ring closure
Absorbance (OD)
1
0.8
0.6
0.4
0.2
0
0
500
1000
1500
2000
Time (sec)

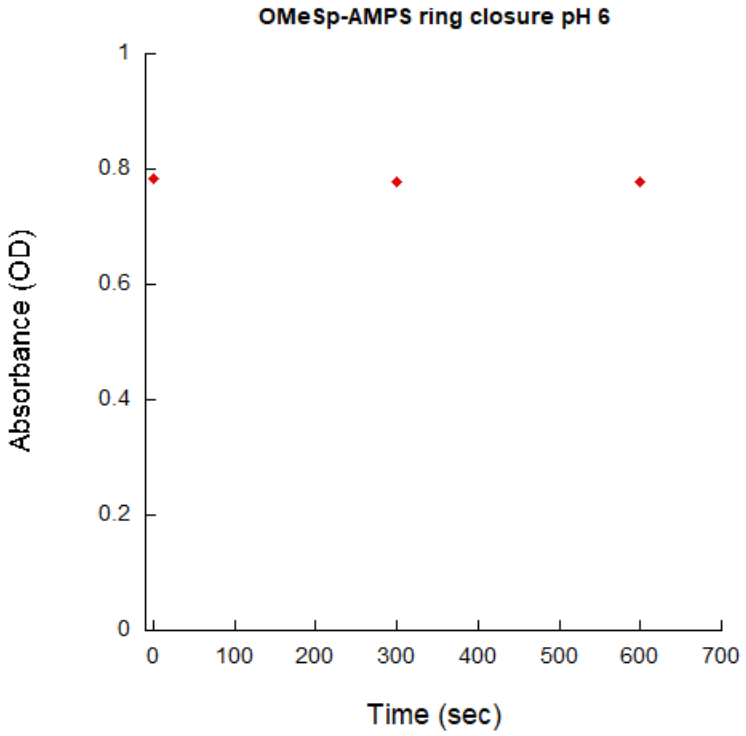

OMeSp-DMAEMA ring closure
Absorbance (OD)
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
1000
1200
1400
Time (sec)

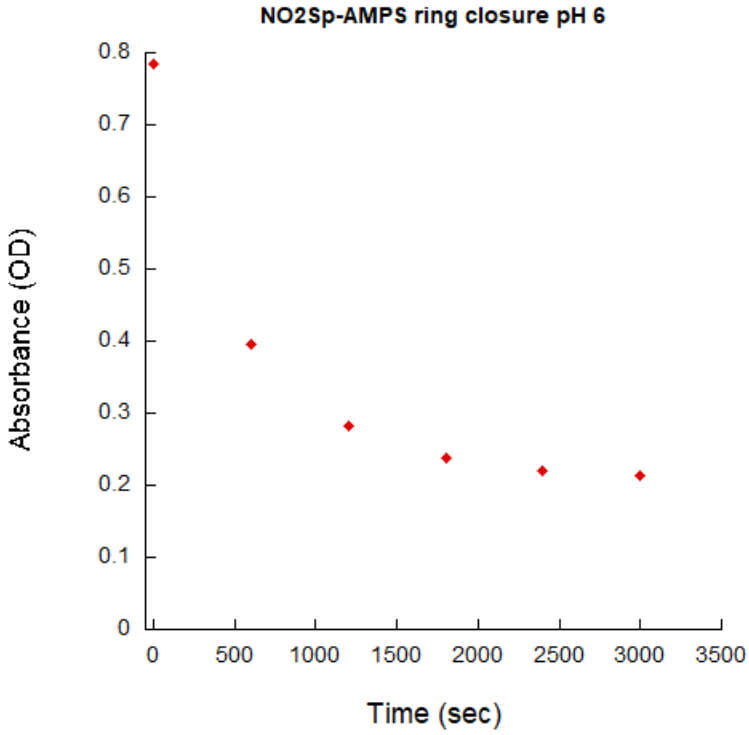

OMeSp-AMPS ring closure pH 2
Absorbance (OD)
0.82
0.8
0.78
0.76
0.74
0.72
0.7
0
100
200
300
400
500
600
700
Time (sec)


HSp-AMPS ring closure pH 2
Absorbance (OD)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
500
1000
1500
2000
Time (sec)

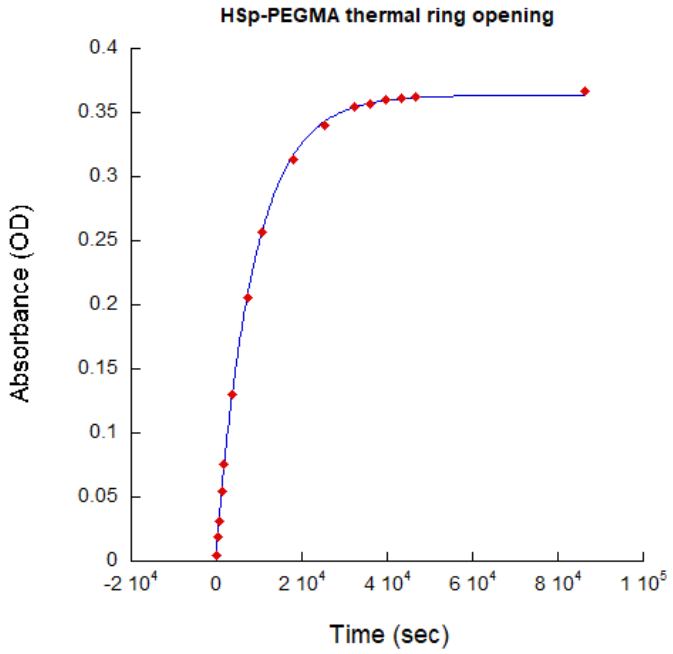

NO2Sp-AMPS ring closure pH 2
Absorbance (OD)
Time (sec)
0
0.2
0.4
0.6
0.8
1
0
500
1000
1500
2000


HSp-AMPS ring closure pH 6
Absorbance (OD)
Time (sec)
0
0.2
0.4
0.6
0.8
1
0
500
1000
1500
2000


OMeSp-AMPS ring closure pH 6
Absorbance (OD)
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
600
700
Time (sec)

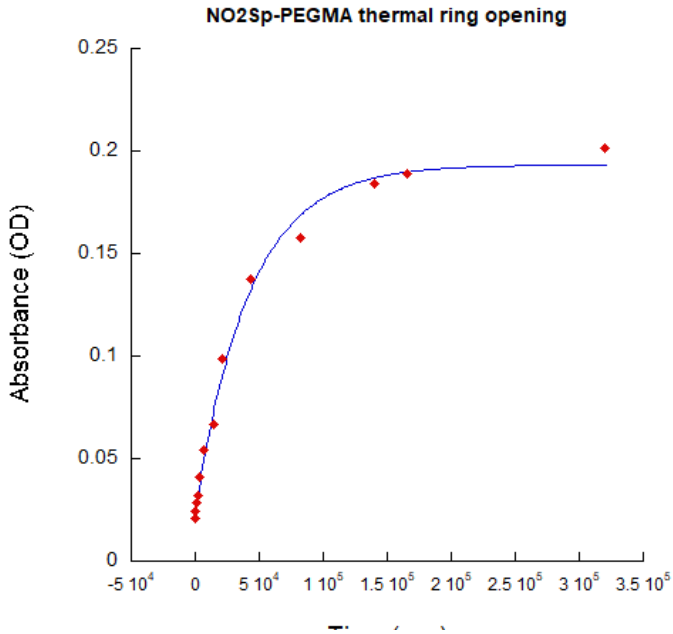

NO2Sp-AMPS ring closure pH 6
Absorbance (OD)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
500
1000
1500
2000
2500
3000
3500
Time (sec)

4. Thermal ring opening absorbance data with exponential decay fits.



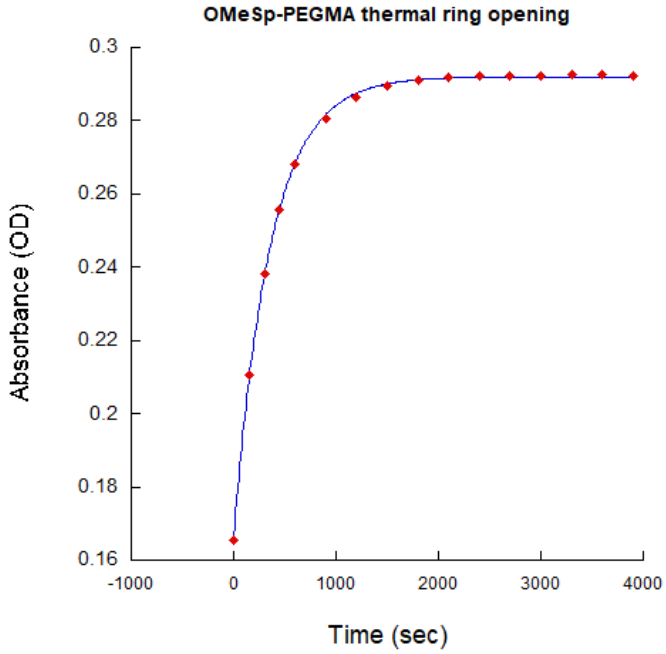
Curve fit:

$y = 8.6x10^{-3}+0.35(1-e^{-kt})$



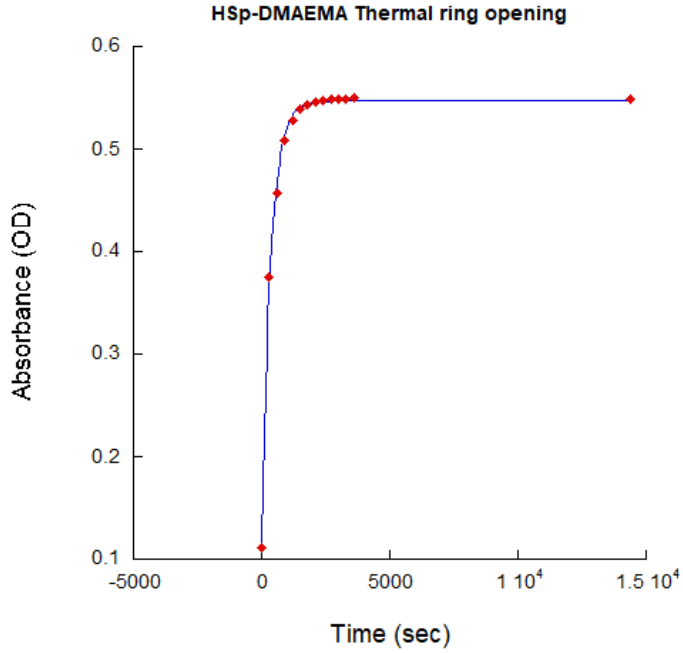
Curve fit:

$y = 0.0245+0.17(1-e^{-kt})$



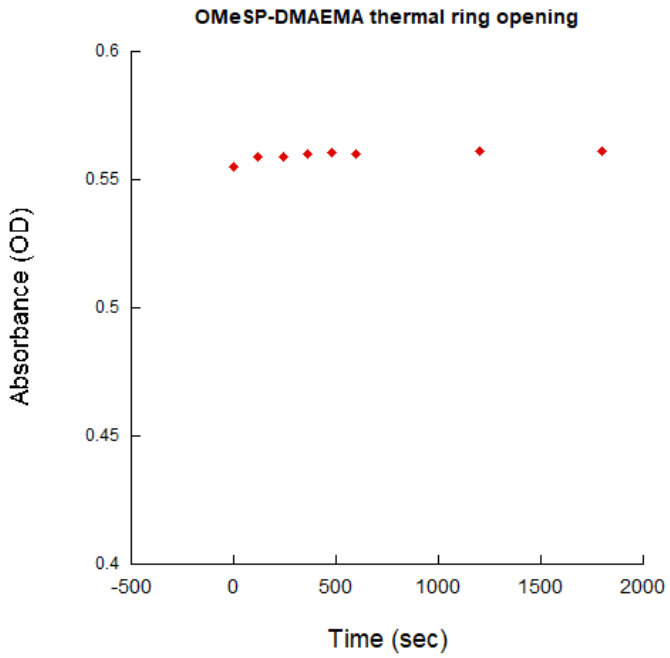
Curve fit:

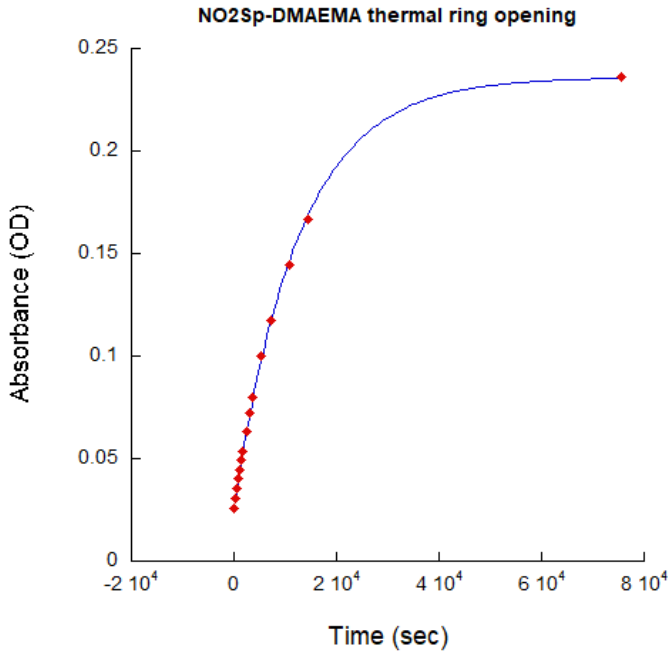
$y = 0.17+0.13(1-e^{-kt})$



Curve fit:

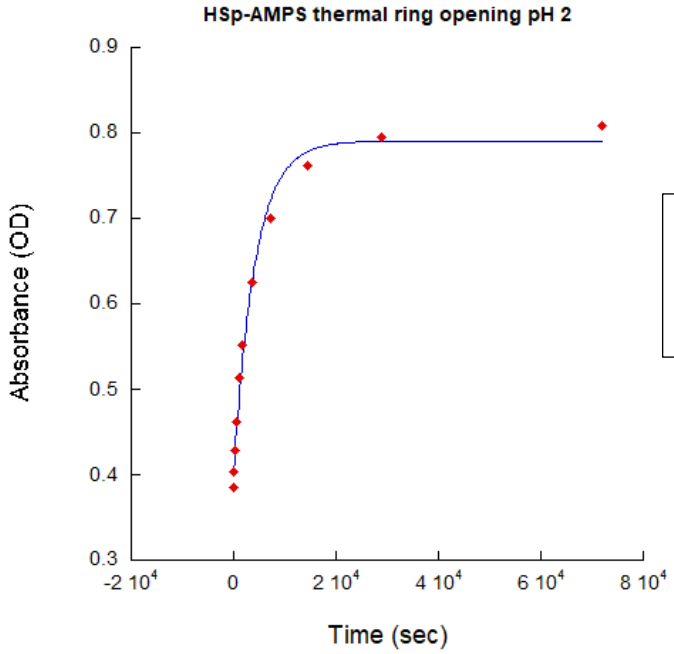
$y = 0.11+0.43(1-e^{-kt})$





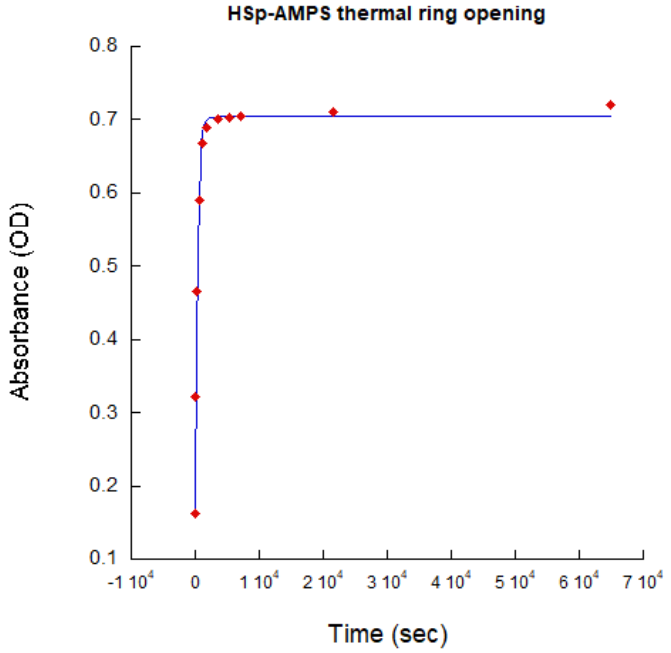
Curve fit:

$y = 0.026+0.21(1-e^{-kt})$



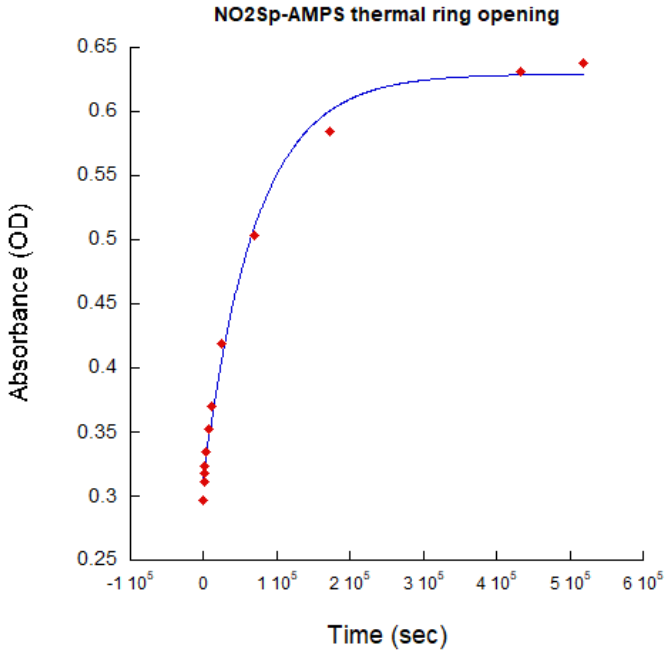
Curve fit:

$y = 0.40+0.39(1-e^{-kt})$



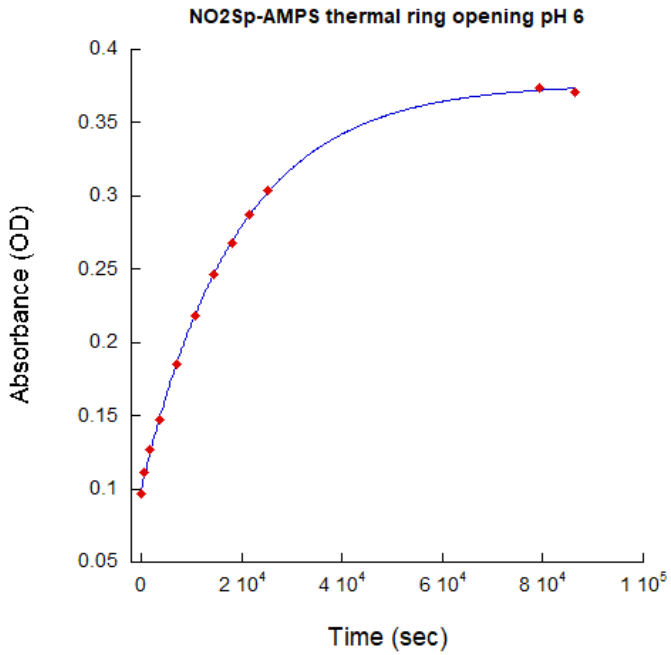
(pH 6) Curve fit:

$y = 0.17+0.53(1-e^{-kt})$



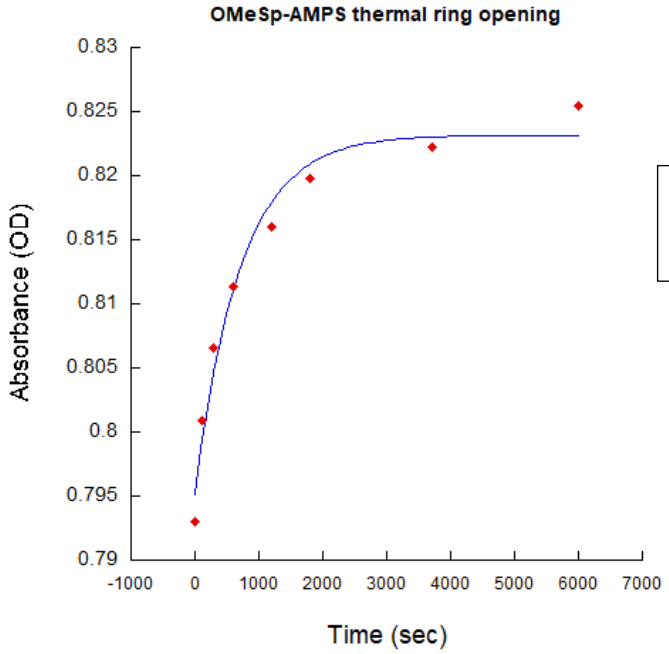
(pH 2) Curve fit:

$y = 0.31+0.31(1-e^{-kt})$



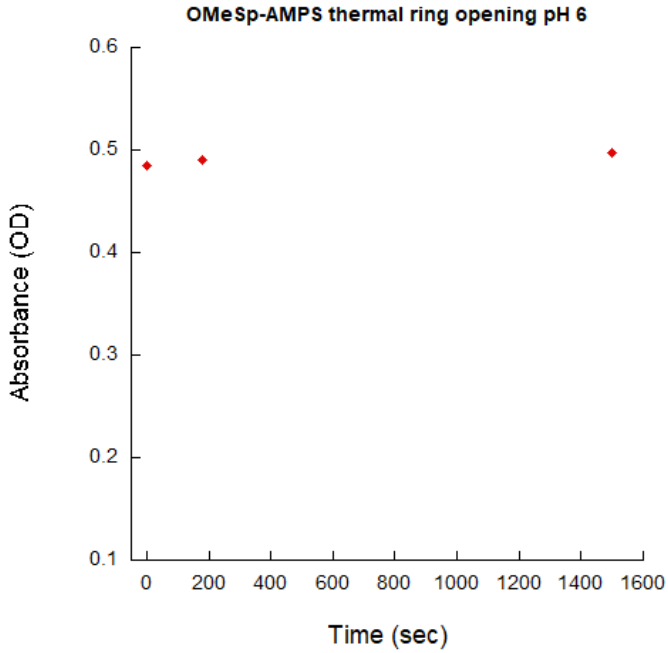
(pH 6) Curve fit:

$y = 0.10+0.28(1-e^{-kt})$



(pH 2) Curve fit:

$y = 0.80+0.028(1-e^{-kt})$



5. Supporting figures

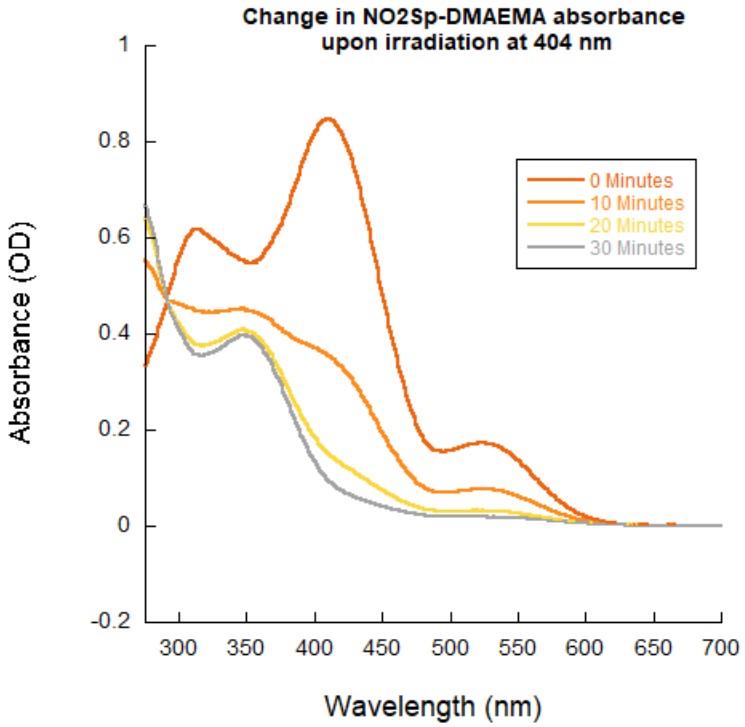


Figure S1. Decrease in both MCH^+ and MC absorbance upon exposure of NO_2Sp-DMAEMA to 3 mW/cm^2 at 404 nm, where only MCH^+ absorbs.

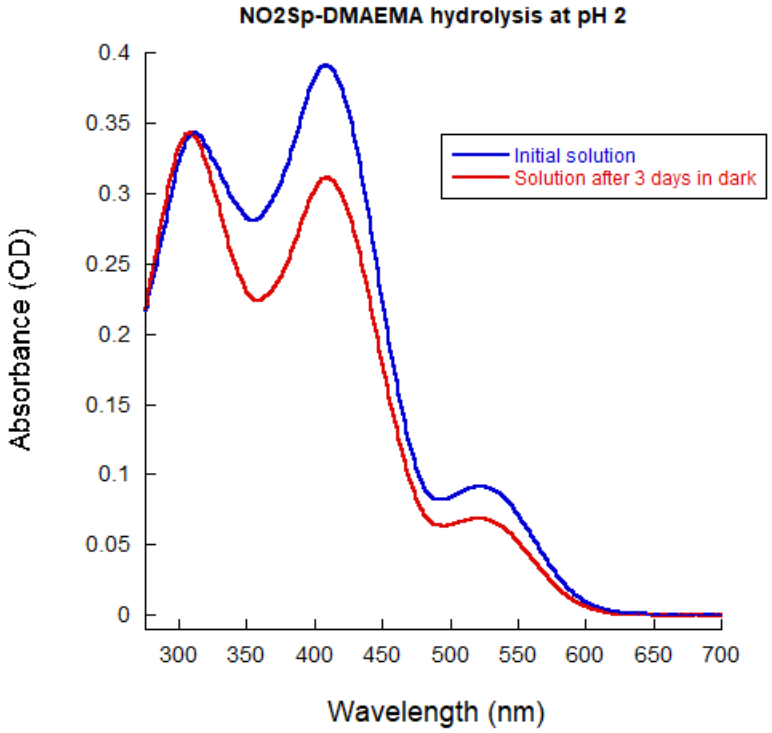


Figure S2. Decrease in absorbance of **NO_2Sp-DMAEMA** at pH 2 over 3 days in the dark.

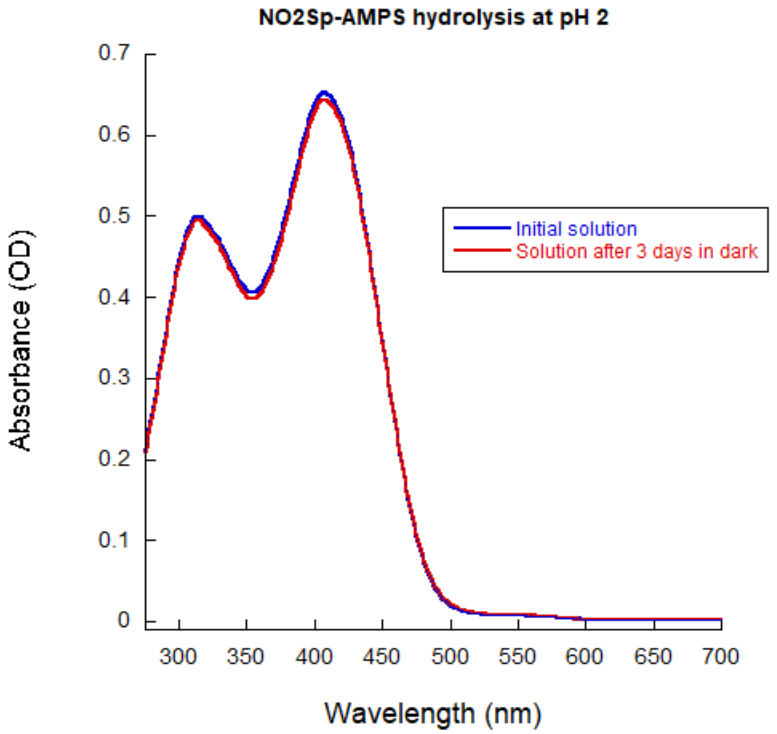


Figure S3. Minimal decrease in MCH^+ absorbance of **NO_2Sp-AMPS** at pH 2 over 3 days in the dark.

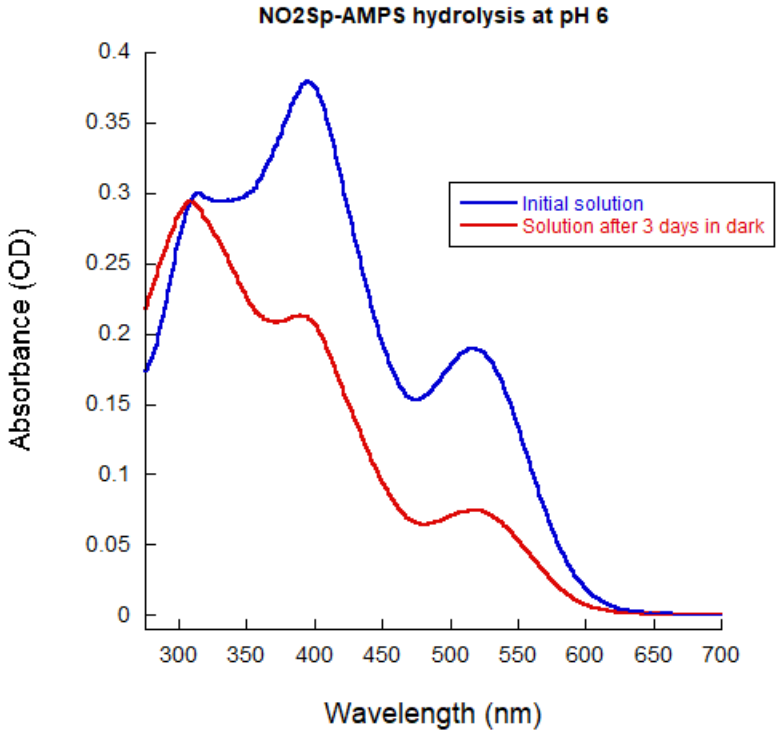


Figure S4. Decrease in absorbance of **NO_2Sp-AMPS** at pH 6 over 3 days in the dark.

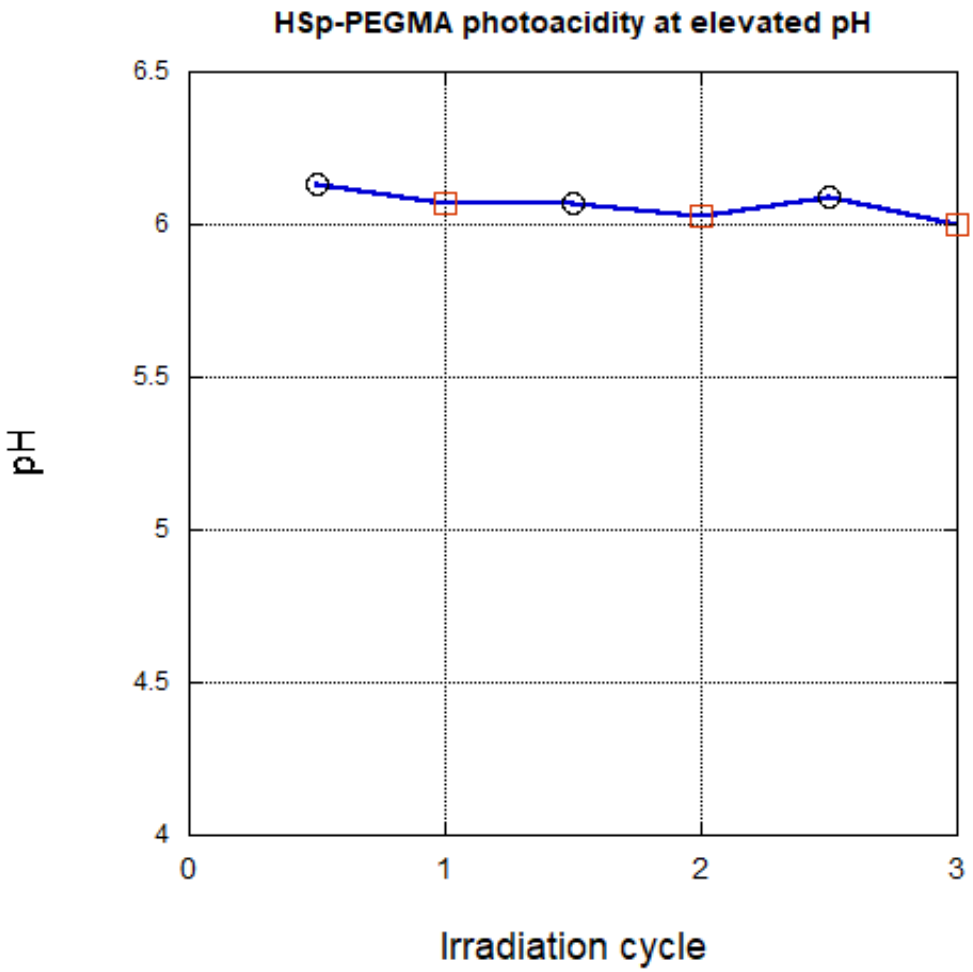


Figure S5. Ineffective photoacidity of **HSp-PEGMA** at pH > 6. Irradiations were performed with $\lambda > 295$ nm, for 10 minutes (yellow sqyares). Samples were allowed to recover solution pH in the dark over at minimum two hours (black circles).

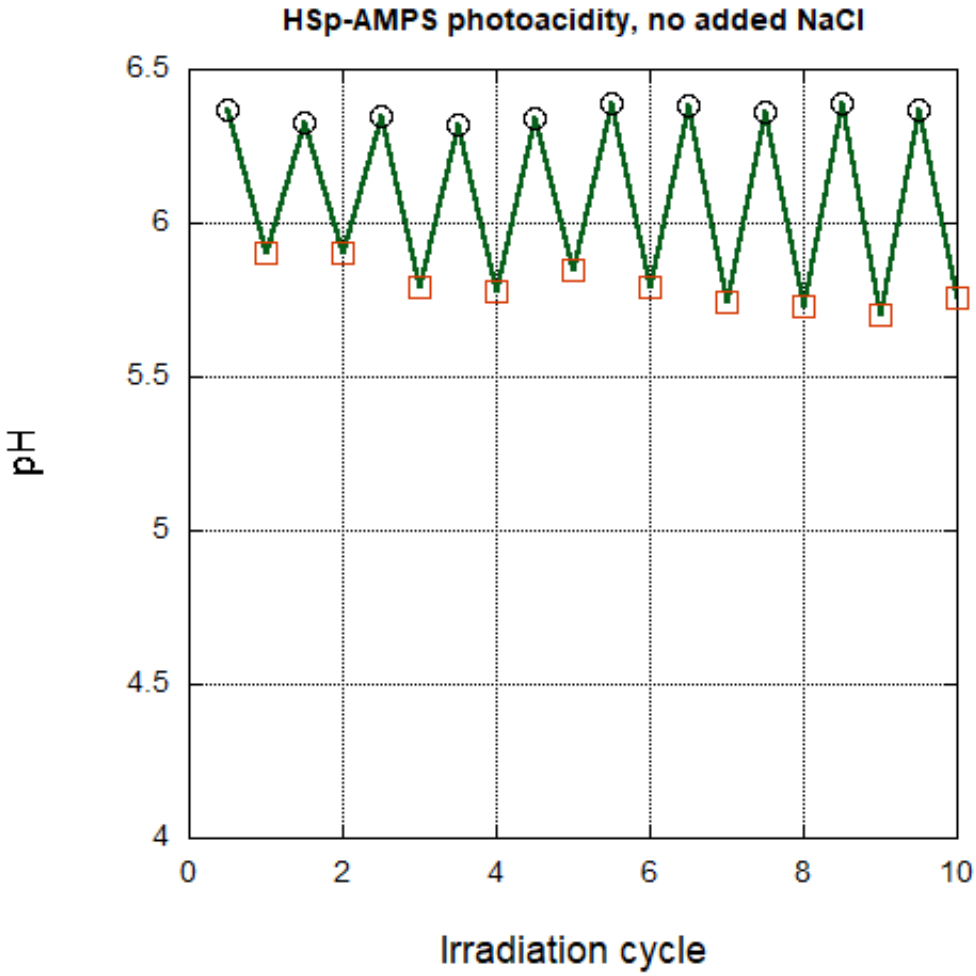


Figure S6. Photoacidity of **HSp-AMPS** in the absence of added NaCl. Irradiations were performed for 10 minutes with $\lambda > 295$ nm (yellow squares). Samples were allowed to recover solution absorbance in the dark for at minimum 30 minutes (black circles).

6. Extinction coefficients for PEGMA polymers

	ε MCH$^+$ ($M^{-1}cm^{-1}$)
HSp-PEGMA	31000
NO_2Sp-PEGMA	23000
OMeSp-PEGMA	27000