SUPPORTING INFORMATION

A first study on copolymers of a methacrylate monomer containing the 2-(hydroxyimino)aldehyde group and OEGMA. RAFT polymerization and assessment of thermal and photoresponsive polymer behavior.

Martina Nardi[ab], Francesca D'Acunzo[*b], Mariangela Clemente[a], Giampiero Proietti[a], Patrizia Gentili[ab]

[a]*Dipartimento di Chimica, Università degli Studi "La Sapienza" P.le A. Moro 5, 00185 Rome, Italy.*

[b]*CNR, Istituto di Metodologie Chimiche, Sezione Meccanismi di Reazione c/o Dipartimento di Chimica,Università degli Studi "La Sapienza" P.le A. Moro 5, 00185 Roma, Italy.*

CONTENTS

S1. Spectra of HHMA

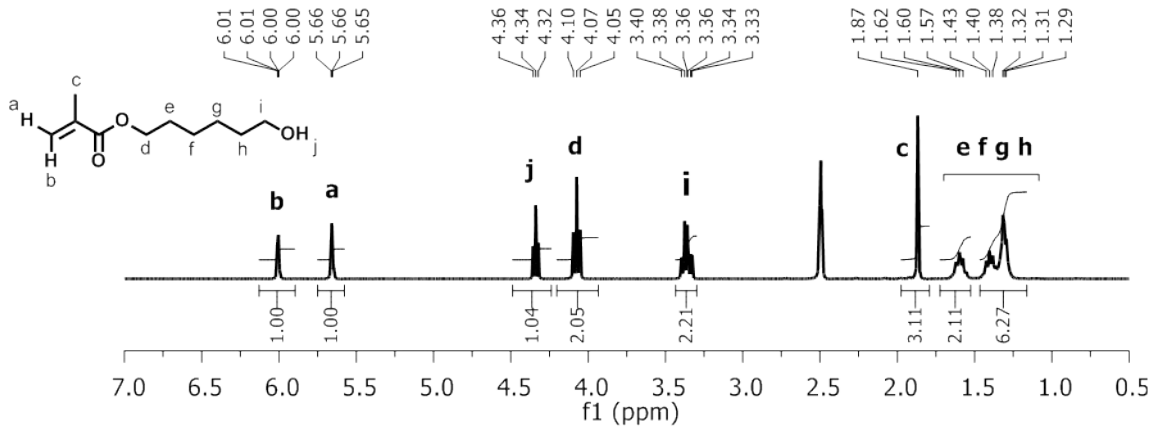

Figure S1a. ^{1}H-NMR (DMSO-d6) δ (ppm): 6.00-6.01 (m, 1H, **b**); 5.65-5.66 (m, 1H, **a**); 4.32-4.36 (t, 1H, **j**, J= 5.2 Hz); 4.05-4.10 (t, 2H, **d,** J= 6.6 Hz); 3.33-3.40 (dt, 2H, **i**, J(t)= 6.2 Hz, J(d)= 5.2 Hz); 1.87 (m, 3H, **c**); 1.57-1.62 (m, 2H, **e**); 1.29-1.43 (m, 6H, **f g h**).

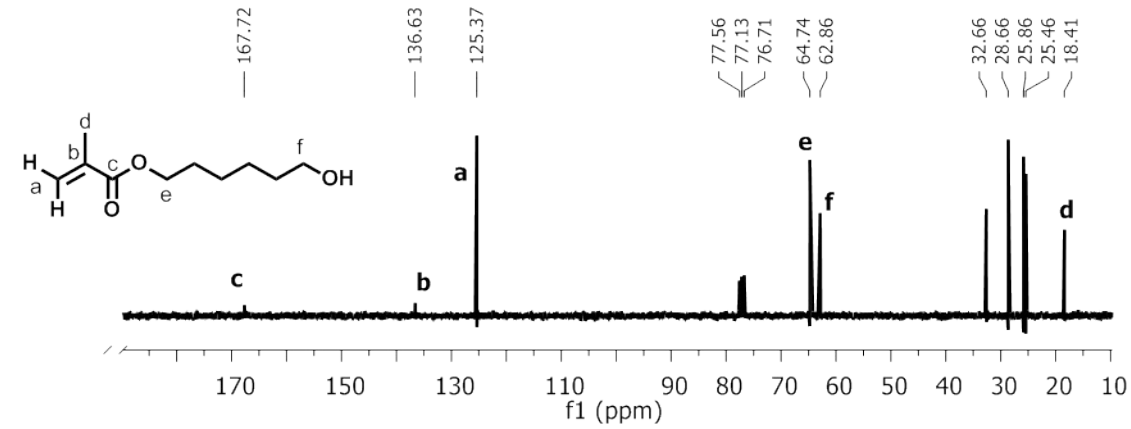

Figure S1b. ^{13}C-NMR ($CDCl_3$) δ (ppm): 167.72 (**c**), 136.63 (**b**), 125.37 (**a**), 64.74 (**e**), 62.86 (**f**), 32.66, 28.66, 25.86,25.46, 18.41 (**d**) .

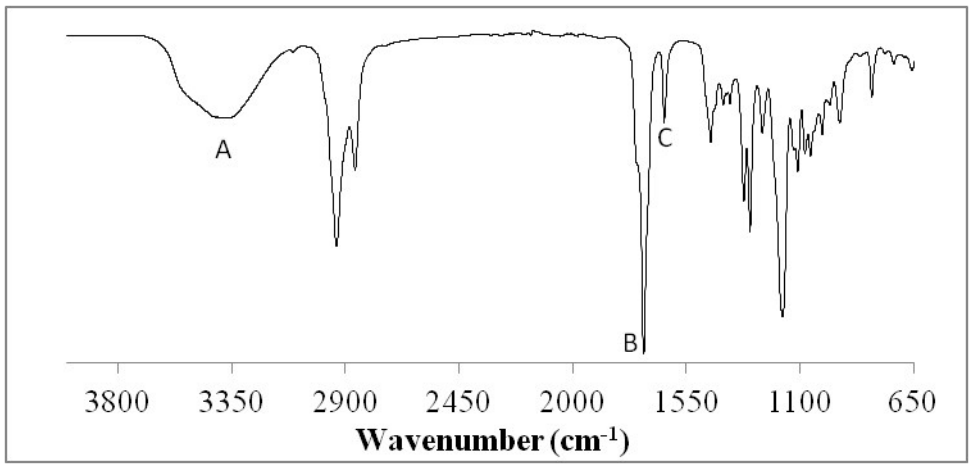

Figure S1c. FTIR of HHMA: A. O-H stretch, 3367 cm^{-1}; B. Methacrylate C=O stretch, 1718 cm^{-1}; C. C=C stretch, 1637 cm^{-1}

S2. Spectra of OHMA

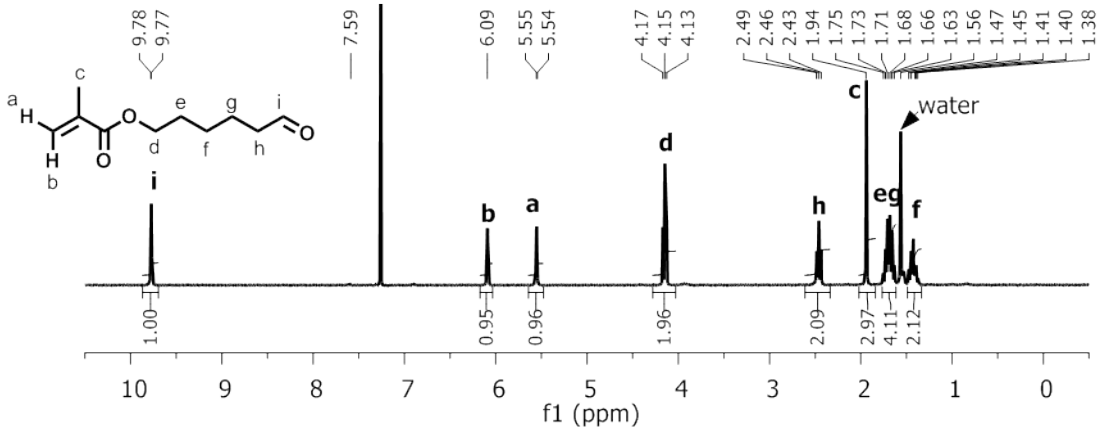

Figure S2a. ^{1}H-NMR (CDCl3) δ (ppm): 9.77-9.78 (t, 1H, **i**, J= 1.6 Hz); 6.09 (m, 1H, **b**); 5.54-5.55 (m, 1H, **a**); 4.17-4.13 (t, 2H, **d**, J= 6.5 Hz); 2.43-2.49 (dt, 2H, **h,** J(t)= 7.2 Hz, J(d)= 1.6 Hz); 1.94 (m, 3H, **c**); 1.63-1.75 (m, 4H**, e g***)*; 1.38- 1.47 (m, 2H, **f***).*

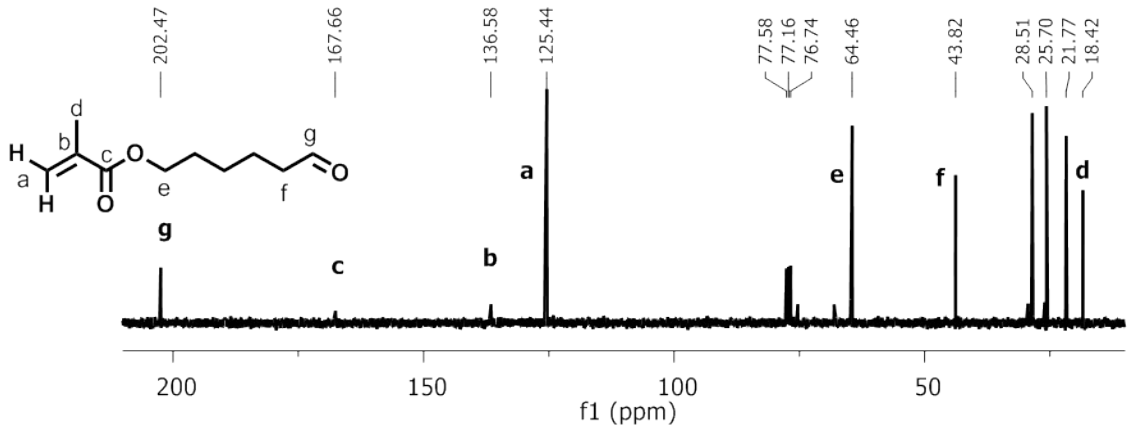

Figure S2b. ^{13}C-NMR ($CDCl_3$) δ (ppm): 202.47 (**g**), 167.66 (**c**), 136.58 (**b**), 125.44 (**a**), 64.46 (**e**), 43.82 (**f**), 28.51, 25.70, 21.17, 18.42 (**d**).

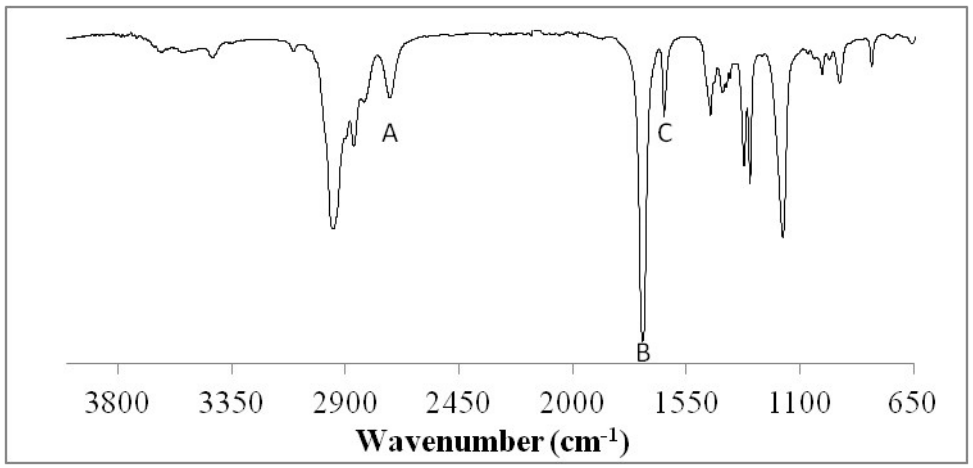

Figure S2c. FTIR of OHMA: A. C(O)-H stretch, 2724 cm^{-1}; B. C=O stretch, methacrylate and unconjugated aldehyde, 1723 cm^{-1}; C. C=C stretch, 1638 cm^{-1}

S3. Spectra of HIHMA

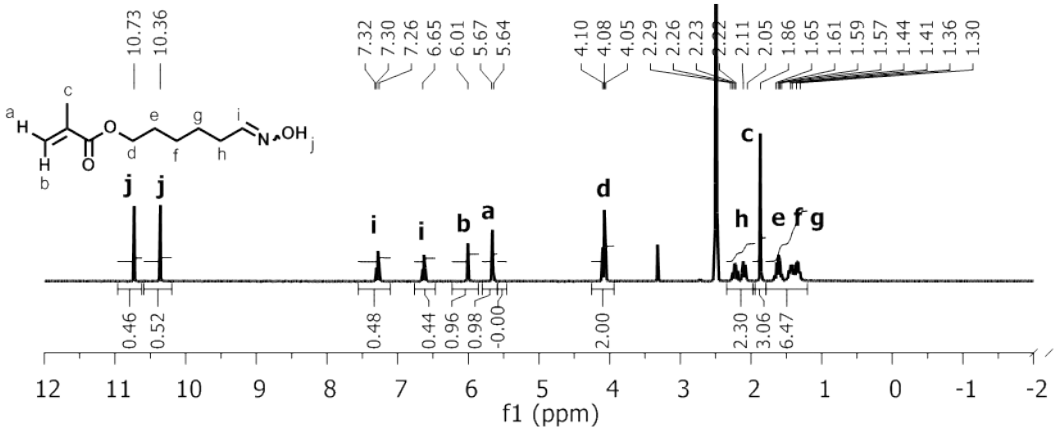

Figure S3a. ^{1}H -NMR (DMSO-d6) δ (ppm): 10.73 (s, 1H, **j**, Z isomer); 10.36 (s, 1H, **j**, E isomer); 7.26-7.32 (t, 1H, **i**, E isomer, J= 5.9 Hz); 6.61-6.65 (t, 1H, **i**, Z isomer, J= 5.4 Hz); 6.01 (m, 1H, **b**) ; 5.64-5.67 (m, 1H, **a**); 4.05-4.12 (t, 2H, **d**, J= 6.5 Hz); 2.22-2.29 (dt, 2H, **h**, Z isomer, J(t)= 7.2 Hz, J(d)= 5.5 Hz); 2.05-2.11 (dt, 2H, **h**, E isomer, J(t)= 7.0 Hz, J(d)= 6.0 Hz); 1.86 (m, 3H, **c**); 1.30-1.65 (m, 6H, **e f g**).

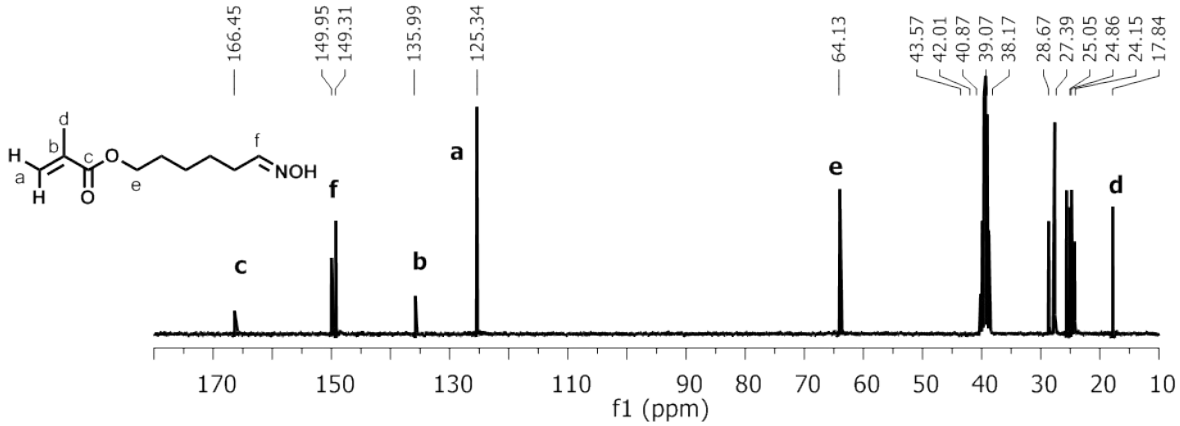

Figure S3b. ^{13}C-NMR (DMSO) δ (ppm): 166.45 (**c**), 149.95 (**f**), 149.31 (**f**), 135.99 (**b**), 125.34 (**a**), 64.13 (**e**), 28.67, 27.39, 25.05, 24.86, 24.15, 17.84 (**d**).

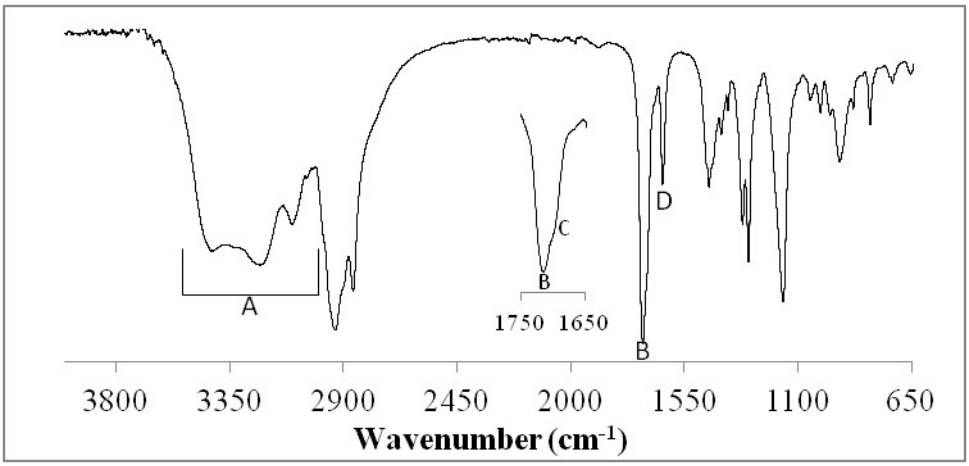

Figure S3c. FTIR of HIHMA: A. NO-H stretch, 3423-3101 cm^{-1}; B. C=O stretch, methacrylate 1714 cm^{-1}; C. C=N(OH) stretch, shoulder at ≈1690 cm^{-1}; D. C=C stretch, 1637 cm^{-1}

S4. Spectra of HIABMA

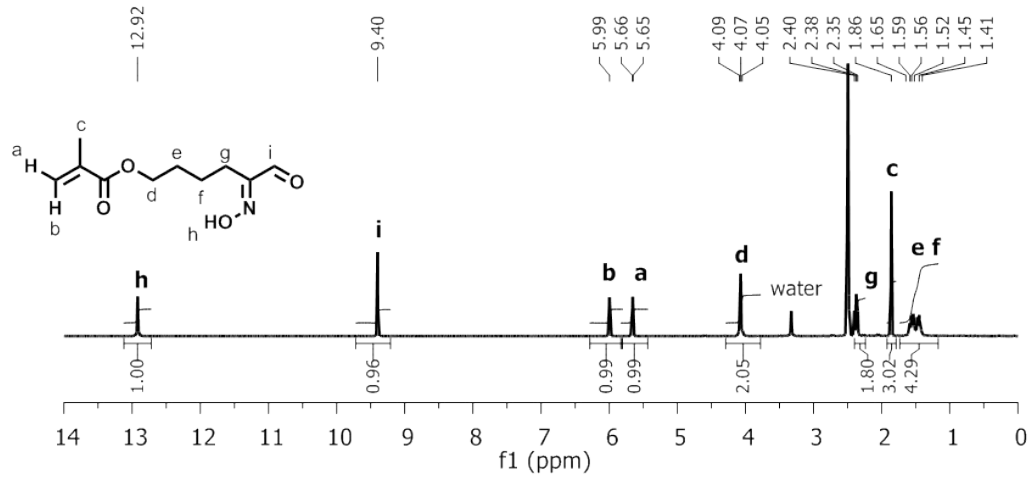

Figure S4a. ^{1}H-NMR (DMSO-d6) δ (ppm): 12.92 (s, 1H, **h**, *E* isomer); 9.40 (s, 1H, **i**, *E* isomer); 5.99 (m, 1H, **b**), 5.65-5.66 (m, 1H, **a**); 4.05-4.09 (t, 2H, **d**, J = 6.2 Hz); 2.35-2.40 (t, 2H, **g**, J= 7.3 Hz); 1.86 (m, 3H, **c**); 1.41-1.65 (m, 4H, **e f**).

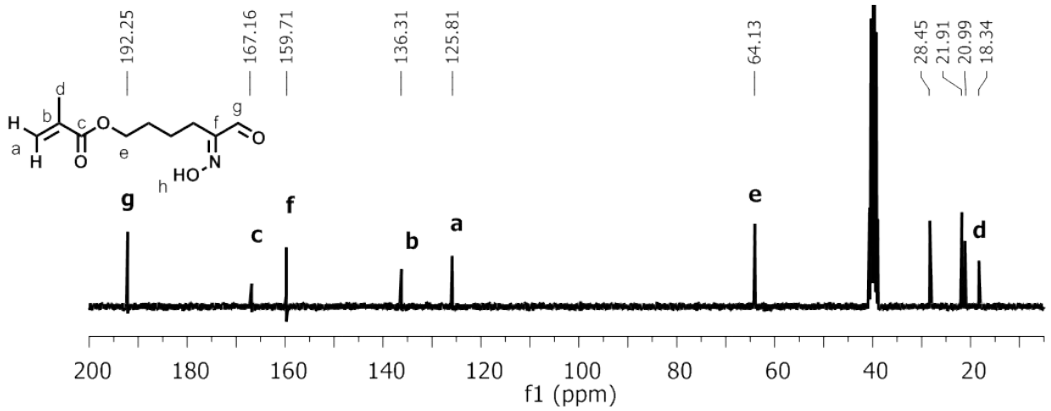

Figure S4b. ^{13}C-NMR (DMSO) δ (ppm): 192.25 (**g**), 167.16 (**c**), 159.71 (**f**), 136.31 (**b**), 125.81 (**a**), 64.13 (**e**), 28.45, 21.91, 20.99, 18.34 (**d**).

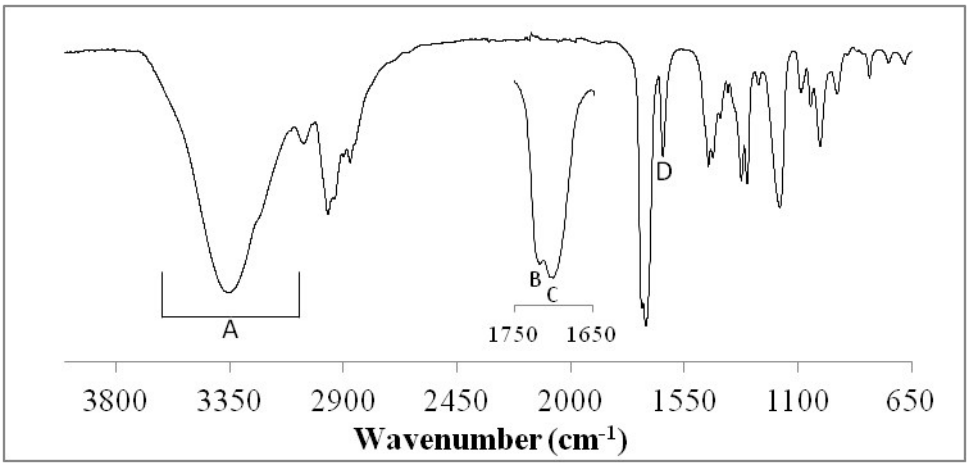

Figure S4c. FTIR of HIABMA: A. NO-H stretch, 3553-3053 cm^{-1}; B. C=O stretch, methacrylate 1718 cm^{-1}; C. C=N(OH) and C=O conjugated aldehyde stretch, 1704-1700 cm^{-1}; D. C=C stretch, 1634 cm^{-1}

S5. Calculation of conversion and monomers incorporation through ^{1}H-NMR

During the polymerization reactions, samples were drawn at fixed time-points under a nitrogen stream, transferred directly in an NMR tube and subjected to high vacuum to remove DMF prior to dilution with $CDCl_3$.

S5a. Calculations for poly(OHMA-*co*-OEGMA$_{475}$)

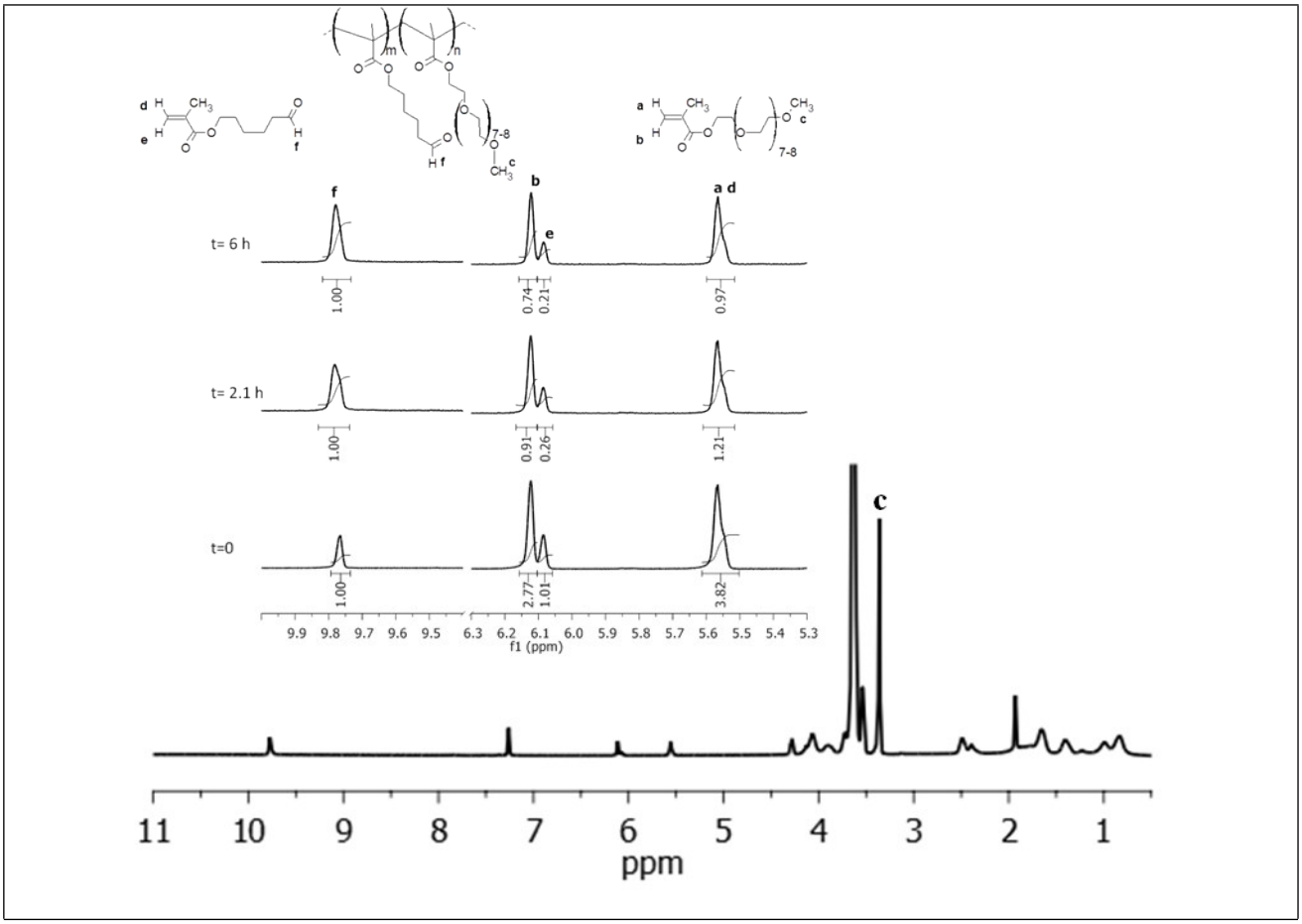

Figure S5a. ^{1}H-NMR ($CDCl_3$) of polymerization mixture for OHMA/OEGMA$_{475}$ 3:7 at reaction time 4h. Inset: expansion at different reaction timepoints.

The aldehyde signal (9.77 ppm, $CDCl_3$) is the sum of monomer and polymer C*H*O intensities and, therefore, is used as internal standard.

- Ratio (R_t) of incorporated monomers at time *t* (equation 2 in the Experimental Section of the paper):

$$R_t = \frac{S_0^{OEGMA} - S_t^{OEGMA}}{S_0^M - S_t^M}, \text{ where } S_{0,t}^{OEGMA} = \frac{I(6.12\ ppm)}{I(9.77\ ppm)} \text{ and } S_{0,t}^{OHMA} = \frac{I(6.09\ ppm)}{I(9.77\ ppm)}$$

- Overall monomers conversion (equation 1 in the Experimental Section of the paper)

$$Conv\% = 100 \times \frac{(I_0 - I_t)}{I_0}, \text{ where } I_{0,t} = \frac{I(5.57\ ppm)}{I(9.77\ ppm)}$$

S5b. Calculations for poly(HIHMA-*co*-OEGMA$_{475}$)

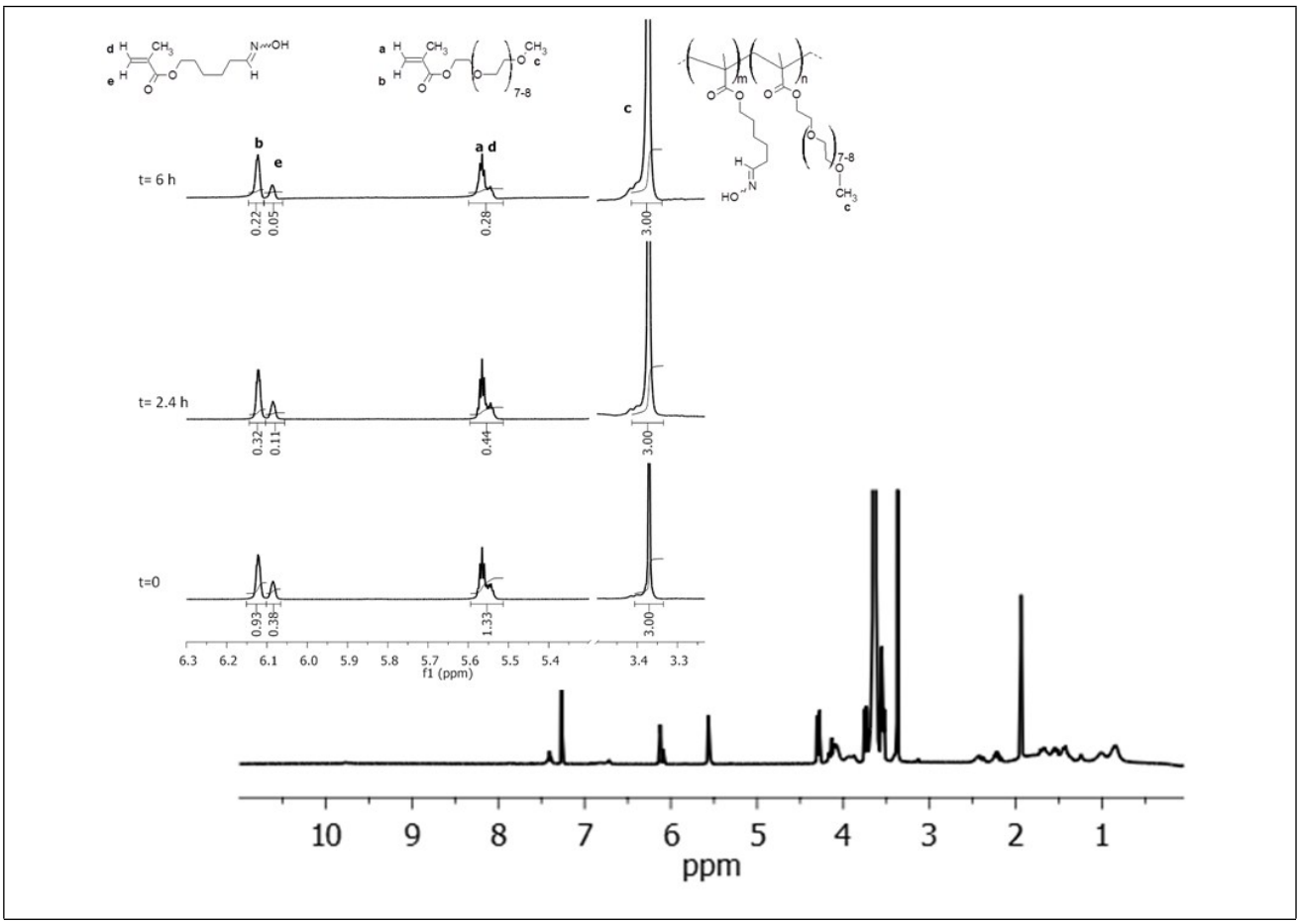

Figure S5b. ^{1}H-NMR ($CDCl_3$) of polymerization mixture for HIHMA/OEGMA$_{475}$ 3:7 at reaction time 2.4h. Inset: expansion at different reaction timepoints.

The OCH_3 signal of OEGMA$_{475}$ (3.37 ppm, $CDCl_3$) is the sum of monomer and polymer OCH_3 intensities and, therefore, can be used as internal standard.

- Ratio (R_t) of incorporated monomers at time *t* (equation 2 in the Experimental Section of the paper):

$$R_t = \frac{S_0^{OEGMA} - S_t^{OEGMA}}{S_0^M - S_t^M}, \text{ where } S_{0,t}^{OEGMA} = \frac{I(6.12\ ppm)}{I(3.37\ ppm)/3} \text{ and } S_{0,t}^{HIHMA} = \frac{I(6.06\ ppm)}{I(3.37\ ppm)/3}$$

- Overall monomers conversion (equation 1 in the Experimental Section of the paper)

$$Conv\% = 100 \times \frac{(I_0 - I_t)}{I_0}, \text{ where } I_{0,t} = \frac{I(5.57 - 5.54\ ppm)}{I(3.37\ ppm)/3}$$

S5c. Calculations for poly(HIABMA-*co*-OEGMA$_{475}$)

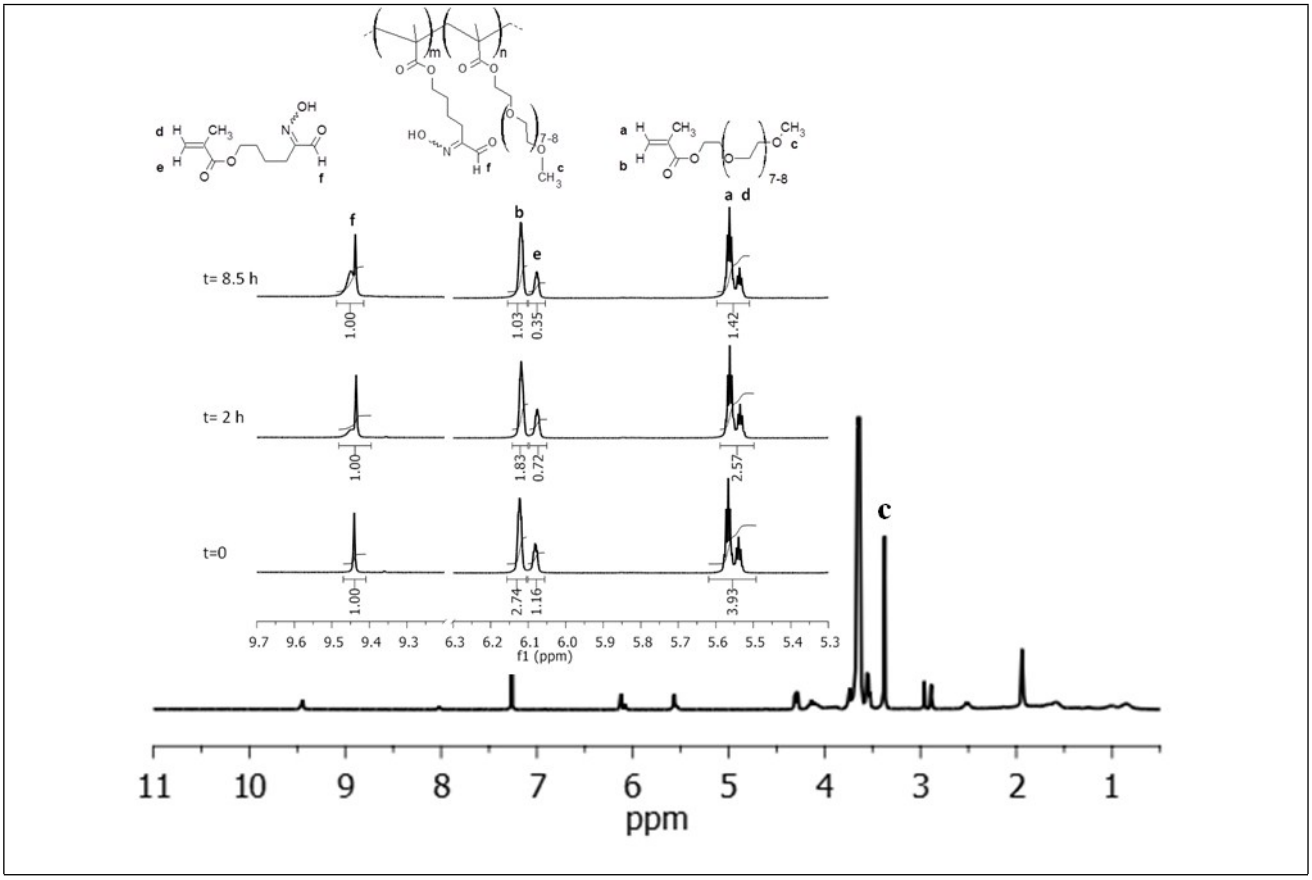

Figure S5c. ^{1}H-NMR ($CDCl_3$) of polymerization mixture for HIABMA/OEGMA$_{475}$ 3:7 at reaction time 4h. Inset: expansion at different reaction timepoints.

The aldehyde signal (9.77 ppm, $CDCl_3$) is the sum of monomer and polymer C*H*O intensities and is, therefore, used as internal standard.

- Ratio (R_t) of incorporated monomers at time *t* (equation 2 in the Experimental Section of the paper):

$$R_t = \frac{S_0^{OEGMA} - S_t^{OEGMA}}{S_0^M - S_t^M}, \text{ where } S_{0,t}^{OEGMA} = \frac{I(6.12\ ppm)}{I(9.44\ ppm)} \text{ and } S_{0,t}^{HIABMA} = \frac{I(6.08\ ppm)}{I(9.44\ ppm)}$$

- Overall monomers conversion (equation 1 in the Experimental Section of the paper)

$$Conv\% = 100 \times \frac{(I_0 - I_t)}{I_0}, \text{ where } I_{0,t} = \frac{I(5.55\ ppm)}{I(9.44\ ppm)}$$

S6. Full ^{1}H NMR spectra of poly(HIABMA-*co*-OEGMA$_{475}$) 3:7 in the photostimulation experiment

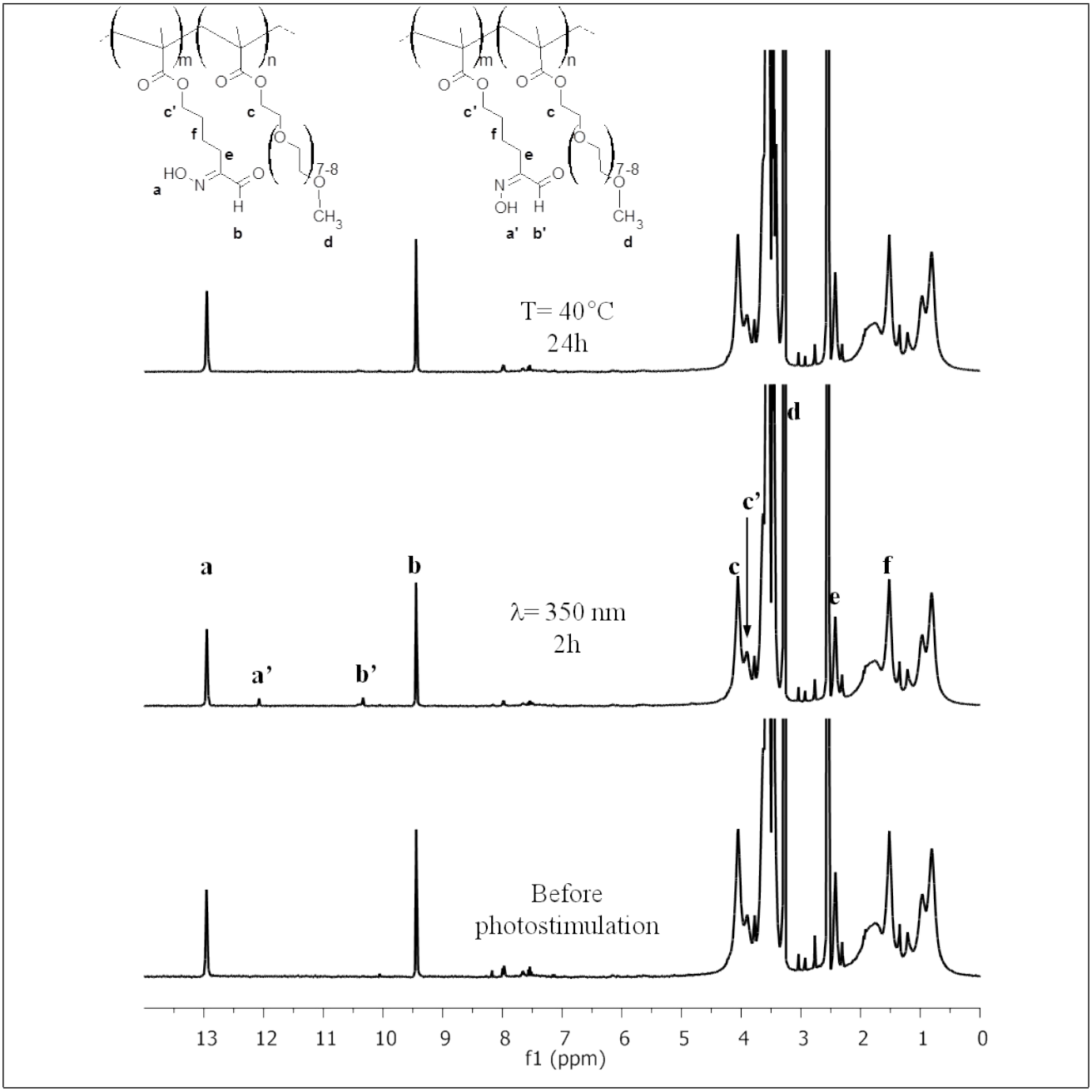

Figure S6. Bottom: ^{1}H -NMR (DMSO-d6) of pristine poly(HIABMA-*co*-OEGMA$_{475}$) 3:7. δ (ppm); 12.92 (s, **a**, *E* isomer); 9.40 (s, **b**, *E* isomer); 4.01 (br, **c**), 3.85 (br, **c'**); 3.24 (s, **d**); 2.38 (br, **e**); 1.48 (br, f). **Middle**: Spectrum of the copolymer after 2h irradiation at 350 nm; 12.03 (s, **a'**, *Z* isomer); 10.29 (s, **b'**, *Z* isomer). **Top**: Spectrum of the copolymer after 24h in the dark at 40°C, following irradiation at 350 nm.