Supporting Information

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Synthesis and On-Demand Gelation of Multifunctional Poly(ethylene glycol)-Based Polymers

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Supporting Information

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Experimental Section

Materials and Equipment

Allyl glycidyl ether (AGE), acrolein, bromobenzene, naphthalene, potassium, 2,2α-azobis(2-methylpropionitrile) (AIBN), PEG (3000 $gmol^{-1}$, 20000 $gmol^{-1}$), potassium bicarbonate were purchased from Sigma-Aldrich. Hydrazine hydrate (80% in water), hydrogen peroxide solution (35% in water), 2-hydroxy-5-methoxybenzoic acid, benzonitrile, *p*-toluenesulfonic acid (TsOH), sodium, anhydrous sodium sulfate, concentrated sulfuric acid, acetic acid were purchased from Merck KGAA. 2-Methoxyethanol, methyl mercaptoacetate were purchased from Alfa Aesar. Tetrahydrofuran (THF), n-hexane, ethyl acetate, chloroform, methanol, toluene, diethyl ether, benzene, ammonium chloride, sodium chloride were purchased from BDH Prolabo. Magnesium and anhydrous magnesium sulfate were purchased from AppliChem. THF was distilled from sodium prior to use. Naphthalene was recrystallized in methanol. Potassium naphthalenide was prepared as described elsewhere.[1] 2-Methoxyethanol and allyl glycidyl ether were freshly distilled from calcium hydride and dried by stirring in benzene at 60 °C for 15–30 min, followed by evaporation of benzene in vacuo for at least 2 h at 60–70 °C prior to polymerization. Methyl 2-hydroxy-5-methoxybenzoate (**1**) was prepared as described elsewhere[2] and purified chromatographically on silica gel with hexane/ethyl acetate (4:1 v/v) mixture as eluent.

Irradiation of the samples was performed using Bio-Link BLX 254 irradiation system with 5 × 8 W lamps, 312 nm.

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance III 500 spectrometer in $CDCl_3$ and DMSO-d_6 with working frequencies 500 MHz for ^{1}H and 125 MHz for ^{13}C NMR. Infrared (IR) spectra were recorded on Bruker Alpha spectrometer. Measurement were done using ATR-technique (ATR = Attenuated Total Reflection). Polymer structure was analyzed with Bruker Vertex 80 spectrometer, detector: LN2 cooled narrow band MCT with an 80° grazing angle and 1024 scans for each sample at a resolution of 2 cm^{-1}. Reference: deuterated 1-hexadecanethiol self-assembled monolayer on a gold wafer. Samples were prepared by spin coating of polymer solutions (in dry THF) on gold wafers. The absorption of polymers was determined on Varian Cary 50 Bio UV-Vis spectrophotometer using quartz cuvette (1 cm). Electron ionization (EI) mass spectra were

recorded on a Finnigan MAT 95 spectrometer. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were recorded on an AB SCIEX 4800 Proteomics Analyzer. α-Cyano-4-hydroxycinnamic acid and dithranol were used as the matrices and sodium iodide as an ionizing agent. Gel permeation chromatography (GPC) was performed on a Toson EcoSEC GPC system with autosampler and a differential refractive index detector in THF at 30 °C and at an elution rate of 1.0 $mLmin^{-1}$. Three PSS SDV columns (100 Å, 5 μ, 8.0 × 300 mm 1000 Å, 5 μ, 8.0 × 300 mm and 100000 Å, 5 μ, 8.0 × 300 mm) were calibrated by linear polystyrene standards (PSS).

Experimental Procedures

2-Hydroxy-5-methoxy-α,α-diphenyl benzenemethanol (2)

The synthetic procedure was adapted from that which was previously reported.[3] Briefly, the solution of bromobenzene (26.3 mL, 0.25 mol, 4.4 eq) in 65 mL of dry THF was added dropwise to magnesium (5.5 g, 0.23 mol, 4 eq) in 25 mL of dry THF and then refluxed for 1 h under an argon atmosphere. After the reaction was cooled to room temperature, a solution of methyl 2-hydroxy-5-methoxybenzoate (**1**, 10.4 g, 57 mmol, 1 eq) in 90 mL of dry THF was added dropwise thereto and the reaction was stirred overnight at room temperature. The reaction was quenched with a saturated solution of ammonium chloride and extracted with diethyl ether. The joint extracts were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The crude product was purified chromatographically on silica gel with hexane/ethyl acetate (2:1 v/v) mixture as eluent to yield 13.25 g (77%) of the title compound as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (br s, 1H, OH), 7.37–7.30 (m, 6H, H_{Ar}), 7.24–7.20 (m, 4H, H_{Ar}), 6.80 (d, J = 8.8 Hz, 1H, H_{Ar}), 6.77 (dd, J = 8.8 Hz, J = 3.0 Hz, 1H, H_{Ar}), 6.11 (d, J = 3.0 Hz, 1H, H_{Ar}), 3.71 (br s, 1H, OH), 3.61 (s, 3H, CH_3O) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.3 (C_{Ar}), 150.0 (C_{Ar}), 144.8 (2C, C_{Ar}), 131.2 (C_{Ar}), 128.4 (4C, CH_{Ar}), 128.1 (2C, CH_{Ar}), 127.9 (4C, CH_{Ar}), 118.1 (CH_{Ar}), 116.7 (CH_{Ar}), 113.9 (CH_{Ar}), 84.3 (C), 55.7 (CH_3) ppm; FTIR (Platinum ATR): ν = 3358, 3172, 1599, 1490, 1465, 1447, 1381, 1288, 1274, 1212, 1172, 1140, 1079, 1035, 1010, 936, 905, 860, 819, 770, 754, 696, 655, 645, 604, 564, 537 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{20}H_{18}O_3$: 306.1256; found 306.1259.

6-Methoxy-2-vinyl-4,4-diphenyl-4*H*-1,3-benzodioxin (3)

The synthetic procedure was adapted from that which was previously reported for the synthesis of analogous acetals.[3] **2** (4.5 g, 14.7 mmol, 1.5 eq), acrolein (0.65 mL, 9.8 mmol, 1 eq) and *p*-toluenesulfonic acid (0.19 g, 0.98 mmol, 0.1 eq) were stirred in benzene (48 mL) for 3 days at room temperature. The solvent was evaporated in vacuo and the crude product was purified

chromatographically on silica gel with hexane/ethyl acetate (4:1 v/v) mixture as eluent to yield 3.2 g (95%) of the title compound as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.33 (m, 5H, H_{Ar}), 7.29–7.20 (m, 5H, H_{Ar}), 6.90 (d, J = 8.9 Hz, 1H, H_{Ar}), 6.77 (dd, J = 8.9 Hz, J = 3.0 Hz, 1H, H_{Ar}), 6.39 (d, J = 3.0 Hz, 1H, H_{Ar}), 6.06 (ddd, J = 17.4 Hz, J = 10.6 Hz, J = 4.7 Hz, 1H, CH_2=C<u>H</u>), 5.54 (ddd, J = 17.4 Hz, J = 1.2 Hz, J = 0.9 Hz, 1H, $CH(O)_2$), 5.41–5.36 (m, 2H, C<u>H</u>$_2$=CH), 3.64 (s, 3H, CH_3O) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.1 (C_{Ar}), 146.3 (C_{Ar}), 145.8 (C_{Ar}), 144.0 (C_{Ar}), 133.9 (CH_2=<u>C</u>H), 129.3 (2C, CH_{Ar}), 128.3 (4C, CH_{Ar}), 128.2 (CH_{Ar}), 128.0 (2C, CH_{Ar}), 127.7 (CH_{Ar}), 126.1 (C_{Ar}), 119.6 (<u>C</u>H_2=CH), 117.9 (CH_{Ar}), 115.1 (CH_{Ar}), 114.3 (CH_{Ar}), 94.0 ($CH(O)_2$), 84.7 (C), 55.7 (CH_3O) ppm; FTIR (Platinum ATR): ν = 2995, 2952, 2864, 1613, 1489, 1461, 1444, 1413, 1361, 1328, 1269, 1223, 1200, 1177, 1130, 1066, 1037, 994, 951, 850, 816, 802, 771, 760, 727, 700, 646, 609, 585 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{23}H_{20}O_3$: 344.1412; found 344.1415.

6-Methoxy-2-oxiranyl-4,4-diphenyl-4*H*-1,3-benzodioxin (4)

Potassium bicarbonate (57.2 mg, 0.57 mmol, 0.15 eq) was suspended in 13 mL of methanol followed by addition of **3** (1.3 g, 3.7 mmol, 1 eq), benzonitrile (0.52 mL, 5.0 mmol, 1.35 eq) and hydrogen peroxide (35%, 0.52 mL, 6.0 mmol, 1.6 eq). The reaction was stirred at 60 °C for 7 h and then at room temperature overnight. Next, 0.5 mL of hydrogen peroxide was added and the reaction was stirred at 60 °C for an additional 7 h. The reaction was quenched by addition of water, the product was extracted by chloroform and the combined organic phases were dried over anhydrous magnesium sulfate. Solvent was evaporated in vacuo. The crude product was purified chromatographically on silica gel with hexane/ethyl acetate (4:1 v/v) mixture as eluent to yield 1.0 g (74%) of **4** (mixture of diastereomers 1:1.35) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.32 (m, 5H, H_{Ar}), 7.30–7.22 (m, 5H, H_{Ar}), 6.93 and 6.88 (d, J = 8.9 Hz, 1H, H_{Ar}), 6.80–6.75 (m, 1H, H_{Ar}), 6.37 and 6.35 (d, J = 3.0 Hz, 1H, H_{Ar}), 4.84 and 4.75 (d, J = 4.3 and 4.7 Hz, 1H, $CH(O)_2$), 3.64 (s, 3H, CH_3O), 3.38–3.32 (m, 1H, CH_{epoxy}), 2.89–2.64 (m, 2H, $CH_{2\text{-}epoxy}$) ppm, ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.3 (C_{Ar}), 145.7 and 145.6 (C_{Ar}), 145.4 and 145.3 (C_{Ar}), 143.5 and 143.4 (C_{Ar}), 129.3 and 129.2 (2C, CH_{Ar}), 128.5 and 128.4 (CH_{Ar}), 128.4 and 128.4 (2C, CH_{Ar}), 128.3 (2C, CH_{Ar}), 128.1 and 128.1 (2C, CH_{Ar}), 127.9 and 127.9 (CH_{Ar}), 126.1 and 126.0 (C_{Ar}), 118.0 and 117.8 (CH_{Ar}), 115.1 and 115.0 (CH_{Ar}), 114.4 (CH_{Ar}), 94.7 and 94.2 ($CH(O)_2$), 84.8 and 84.6 (C), 55.7 (CH_3O), 51.8 and 51.7 (CH_{epoxy}), 43.8 and 43.8 ($CH_{2\text{-}epoxy}$) ppm; FTIR (Platinum ATR): ν = 3059, 2995, 2915, 2835, 1615, 1491, 1466, 1445, 1415, 1312, 1270, 1249, 1221, 1182, 1143, 1074, 1033, 989, 939, 926, 850, 831, 810, 782, 768, 756, 727, 697, 632 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{23}H_{20}O_4$: 360.1362; found 360.1360.

Photosensitive protected aldehyde poly(ethylene glycol) (5)

2-methoxyethanol solution in THF was placed into a flame dried Schlenk flasks via a gastight syringe (Hamilton) under an argon atmosphere and freshly prepared potassium naphthalenide was added thereto dropwise till the green color remained. Next, **4** was introduced into the reaction vessel with a gastight syringe and the reaction was stirred for a given period of time at a defined temperature. Polymerization was terminated by the addition of methanol and concentrated in vacuo. Monomer conversion was calculated based on ^{1}H NMR spectra of crude polymer. The polymer was purified chromatographically on a silica gel column with gradient elution (chloroform to chloroform/methanol 10:0.7 v/v mixture as an eluent) to yield the product as a light beige solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–6.75 (10H, H_{Ar}), 6.75–6.36 (2H, H_{Ar}), 6.28 (1H, H_{Ar}), 4.91 (1H, $CH(O)_2$), 4.25–3.20 (6H, $CH_{2\text{-}PEG}$ + CH_{PEG} + CH_3OAr), 3.16 (CH_3O) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.0–152.6 (C_{Ar}), 146.5–145.5 (2C, C_{Ar}), 143.8–143.2 (C_{Ar}), 129.5–129.1 (2C, CH_{Ar}), 128.1 (5C, CH_{Ar}), 127.9 (2C, CH_{Ar}), 127.6–127.2 (CH_{Ar}), 126.2–125.8 (C_{Ar}), 118.3–118.0 (CH_{Ar}), 115.1–114.7 (CH_{Ar}), 114.2–113.7 (CH_{Ar}), 94.3–93.8 ($CH(O)_2$), 84.5–84.1 (C), 80.9–79.7 (CH_{PEG}), 70.9–70.1 ($CH_{2\text{-}PEG}$), 55.6 ($\underline{C}H_3OAr$) ppm; FTIR (spin coated film on a gold wafer): ν = 3252, 3060, 3032, 2932, 1617, 1600, 1496, 1465, 1447, 1274, 1230, 1144, 1124, 1077, 1046, 998 cm^{-1}.

Triblock copolymer of poly(ethylene glycol) and photosensitive protected aldehyde poly(ethylene glycol) (6)

The polymerization was performed as described for **5**, except PEG/potassium naphthalenide was used as the initiating system and polymerization was carried out at 50°C. For chromatographic purification of the crude polymer chloroform to chloroform/methanol, 10:1.5 v/v elution system was used to yield the pure polymer as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.20 (m, 10H, H_{Ar}), 6.92 and 6.88 (d, 1H, H_{Ar}), 6.78–6.74 (m, 1H, H_{Ar}), 6.35–6.33 (m, 1H, H_{Ar}), 5.01 and 4.96 (d, 1H, $CH(O)_2$), 4.08–4.02 (m, 1H, CH_{PEG}), 3.80–3.46 (m, $CH_{2\text{-}PEG}$ + CH_3OAr) ppm.

(6-Methoxy-4,4-diphenyl-4*H*-1,3-benzodioxin-2-yl)-2-(2-methoxyethoxy)ethanol (7)

The synthesis was performed as described for **5**, except initiator to monomer feed ratio was 1:0.9. The crude product was purified chromatographically on silica gel with hexane/ethyl acetate (1:2 v/v) mixture as eluent to yield the title compound (70%) (mixture of diastereomers D1 and D2 in a ratio 1:2.3 correspondingly) as a slightly yellow viscous oil. The diastereomers were separated chromatographically and analyzed.

D1: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 5H, H_{Ar}), 7.29–7.21 (m, 5H, H_{Ar}), 6.89 (d, J = 8.9 Hz, 1H, H_{Ar}), 6.76 (dd, J = 8.9 Hz, J = 3.0 Hz, 1H, H_{Ar}), 6.35 (d, J = 3.0 Hz, 1H, H_{Ar}), 5.02 (d, J

= 3.8 Hz, 1H, $CH(O)_2$), 4.09–4.04 (m, 1H, C<u>H</u>OH), 3.77–3.68 (m, 2H, OC<u>H</u>$_2$CH), 3.66–3.56 (m, 5H, CH_3OAr + 2×OCH_2CH_2O), 3.52–3.42 (m, 2H, 2×OCH_2CH_2O), 3.32 (s, 3H, C<u>H</u>$_3OCH_2$), 2.79 (br s, 1H, OH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.2 (C_{Ar}), 146.0 (C_{Ar}), 145.6 (C_{Ar}), 143.6 (C_{Ar}), 129.4 (2C, CH_{Ar}), 128.3 (CH_{Ar}), 128.2 (4C, CH_{Ar}), 128.1 (2C, CH_{Ar}), 127.8 (CH_{Ar}), 125.9 (C_{Ar}), 118.0 (CH_{Ar}), 115.0 (CH_{Ar}), 114.3 (CH_{Ar}), 93.9 ($CH(O)_2$), 84.6 (C), 72.0 (CH_2), 71.6 (CHOH), 71.1 (CH_2), 70.9 (CH_2), 59.1 (<u>C</u>H_3OCH_2), 55.7 (<u>C</u>H_3OAr) ppm.

D2: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 5H, H_{Ar}), 7.28–7.21 (m, 5H, H_{Ar}), 6.92 (d, J = 8.9 Hz, 1H, H_{Ar}), 6.76 (dd, J = 8.9 Hz, J = 3.0 Hz, 1H, H_{Ar}), 6.34 (d, J = 3.0 Hz, 1H, H_{Ar}), 6.97 (d, J = 5.3 Hz, 1H, $CH(O)_2$), 4.11–4.05 (m, 1H, C<u>H</u>OH), 3.80 (dd, J = 10.3 Hz, J = 3.3 Hz, 1H, OC<u>H</u>$_2$CH), 3.65–3.53 (m, 6H, 1×OC<u>H</u>$_2$CH + CH_3OAr + 2×OCH_2CH_2O), 3.46 (t, J = 4.8 Hz, 2H, 2×OCH_2CH_2O), 3.35 (s, 3H, C<u>H</u>$_3OCH_2$), 2.14 (br s, 1H, OH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.2 (C_{Ar}), 145.9 (C_{Ar}), 145.7 (C_{Ar}), 143.6 (C_{Ar}), 129.5 (2C, CH_{Ar}), 128.4 (CH_{Ar}), 128.2 (4C, CH_{Ar}), 128.0 (2C, CH_{Ar}), 127.8 (CH_{Ar}), 125.9 (C_{Ar}), 118.0 (CH_{Ar}), 115.0 (CH_{Ar}), 114.3 (CH_{Ar}), 94.2 ($CH(O)_2$), 84.6 (C), 71.9 (CH_2), 71.8 (CHOH), 71.0 (CH_2), 70.8 (CH_2), 59.1 (<u>C</u>H_3OCH_2), 55.7 (<u>C</u>H_3OAr) ppm.

FTIR (Platinum ATR): ν = 3405, 2903, 1599, 1492, 1446, 1272, 1224, 1198, 1101, 1035, 995, 947, 871, 849, 809, 758, 700, 647, 629, 585 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{26}H_{28}O_6$: 436.1886; found 436.1884.

Poly(allyl glycidyl ether) (12)

The polymerization was performed as described for **5**, except it was carried out in bulk at 30°C. The monomer to initiator ratio was 1:100. Polymerization was terminated by the addition of acidified methanol and concentrated in vacuo. Monomer conversion was 97%. The polymer was purified chromatographically on a silica gel column with gradient elution (chloroform to chloroform/methanol 10:0.7 v/v mixture as an eluent) yielding slightly yellow oil (90%). GPC (THF): M_n 11600 gmol^{-1}, M_w 12400 gmol^{-1}, PDI 1.07. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.93–5.82 (m, 1H, C<u>H</u>=CH_2), 5.25 (d, 1H, CH=C<u>H</u>$_2$), 5.14 (d, 1H, CH=C<u>H</u>$_2$), 3.98 (d, 2H, OC<u>H</u>$_2$CH=CH_2), 3.67–3.43 (m, 5H, $CH_{2\text{-PEG}}$ + CH_{PEG} + CH_{PEG}C<u>H</u>$_2$O), 3.36 (s, 3H, CH_3O) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.1 (CH_2=<u>C</u>H), 116.9 (<u>C</u>H_2=CH), 79.0–78.8 (CH_{PEG}), 72.4 (O<u>C</u>H_2CH=CH_2), 70.4–69.9 (2C, $CH_{2\text{-PEG}}$ + CH_{PEG}<u>C</u>H_2O), 59.2 (CH_3O) ppm.

Ester poly(ethylene glycol) (13)

Polymer **12** (0.2 g, 1.75 mmol of C=C, 1 eq) was dissolved in 1 mL of dry THF under an argon atmosphere followed by the addition of methyl mercaptoacetate (0.79 mL, 8.7 mmol, 5 eq) and

AIBN (43 mg, 0.26 mmol, 0.15 eq). The reaction was refluxed for 5 h. Completion of the reaction was confirmed by ^{1}H NMR spectrometry by disappearance of allyl group signal. The solvent was removed in vacuo and the residue was purified on silica gel column with gradient elution (chloroform to chloroform/methanol 10:0.7 v/v mixture as an eluent) to yield 0.29 g (76%) of the pure product as a yellow oil. GPC (THF): M_n 15100 gmol^{-1}, M_w 16000 gmol^{-1}, PDI 1.07. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.73 (s, 3H, $CH_3OC{=}O$), 3.64–3.40 (m, 7H, $CH_{2\text{-}PEG}$ + CH_{PEG} + $CH_{PEG}C\underline{H}_2O$ + $OC\underline{H}_2CH_2$), 3.37 (s, 3H, CH_3O), 3.23 (s, 2H, $SCH_2C{=}O$), 2.70 (t, 2H, $SC\underline{H}_2CH_2$), 1.85 (m, 2H, $CH_2C\underline{H}_2CH_2$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.9 (C=O), 79.0–78.8 (CH_{PEG}), 71.1–70.0 (2C, $CH_{2\text{-}PEG}$ + $CH_{PEG}\underline{C}H_2O$), 69.6 ($O\underline{C}H_2CH_2$), 52.4 ($\underline{C}H_3OC{=}O$), 33.4 ($S\underline{C}H_2C{=}O$), 29.5 ($S\underline{C}H_2CH_2$), 29.2 ($CH_2\underline{C}H_2CH_2$) ppm.

Hydrazide poly(ethylene glycol) (14)

Water solution of hydrazine hydrate (80%, 2.2 mL, 45 mmol, 100 eq) was added to the solution of polymer **13** (0.1 g, 0.45 mmol, 1 eq of ester groups) in THF (11 mL) and the reaction was refluxed for 5 h. The solvent was evaporated, the crude product was dialyzed against water for 48 h and dried in vacuo to yield 87 mg (87%) of the title polymer as a colorless viscous oil. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.11 (s, 1H, $NH_2N\underline{H}$), 4.29 (broad, s, 2H, $N\underline{H}_2NH$), 3.65–3.20 (m, 7H, $CH_{2\text{-}PEG}$ + CH_{PEG} + $CH_{PEG}C\underline{H}_2O$ + $OC\underline{H}_2CH_2$), 3.25 (s, 3H, $C\underline{H}_3O$), 3.04 (s, 2H, $SCH_2C{=}O$), 2.60 (t, 2H, $SC\underline{H}_2CH_2$), 1.76 (m, 2H, $CH_2C\underline{H}_2CH_2$) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.5 (C=O); 78.3–78.0 (CH_{PEG}), 70.4–69.3 ($CH_{2\text{-}PEG}$), 69.5–69.2 ($CH_{PEG}\underline{C}H_2O$), 69.1 ($O\underline{C}H_2CH_2$), 32.6 ($S\underline{C}H_2C{=}O$), 28.9 ($S\underline{C}H_2CH_2$), 28.6 ($CH_2\underline{C}H_2CH_2$) ppm.

Cleavage of acetal protecting groups in polymer 5

The samples were prepared by spin coating of polymer **5** solution (20 mgmL^{-1} in dry THF) on gold wafers at approximately 100 rps for 30 sec using Lot-Oriel SCV-20 spin coater. The prepared samples were exposed to 312 nm light for different periods of time and analyzed by IR spectroscopy.

Hydrazones 9

7-D2 (10 mg, 0.023 mmol, 1 eq) and acetohydrazide (10 mg, 0.135 mmol, 5.9 eq) were dissolved in 1 mL of acetonitrile-d_3/deuterated water (9:1 v/v) mixture. The prepared solution was placed in a quartz cuvette (1 cm) and exposed to 312 nm light for 2 h while stirring. The product was analyzed by ^{1}H NMR spectroscopy, which confirmed the formation of a mixture of isomers in a ratio 1.7:1.

Hydrazones 11

Reaction of polymer **6d** (M_n 4700 $gmol^{-1}$, 20 mg, ~ 0.011 mmol of protected aldehyde groups, 1 eq) and acetohydrazide (10 mg, 0.135 mmol, 13.5 eq) was performed as described for **9**, except the irradiation time was 30 min (incomplete conversion).

Hydrogel Fabrication

The hydrogel was prepared from polymer **6d** (M_n 4700 $gmol^{-1}$, 45 mg, ~ 0.024 mmol of protected aldehyde groups, 1 eq) and polymer **14** (M_n ~ 18900 $gmol^{-1}$, 6.75 mg, ~ 0.03 mmol of hydrazide groups, 1 eq) in 0.52 mL of distilled water by irradiation for 2 h (stirring was performed for the first 30 min) followed by washing with distilled water.

References

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[2] D. Petrovi, R. Brückner, *Org. Lett.* **2011**, *13*, 6524–6527.

[3] P. Wang, H. Hu, Y Wang. *Org. Lett.* **2007**, *9*, 1533–1535.

Figures

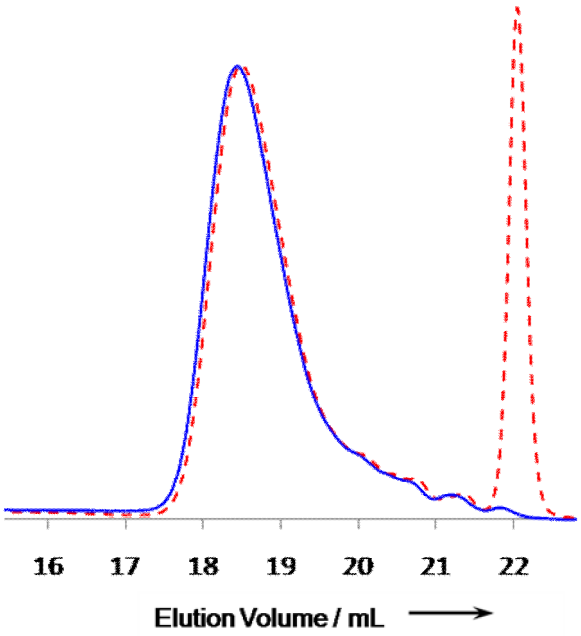

Figure S1 Gel permeation chromatograms of polymer **5** obtained in the conditions corresponding to Table 1, Entry 4 before (red dashed line) and after (blue solid line) chromatographic purification on silica gel.

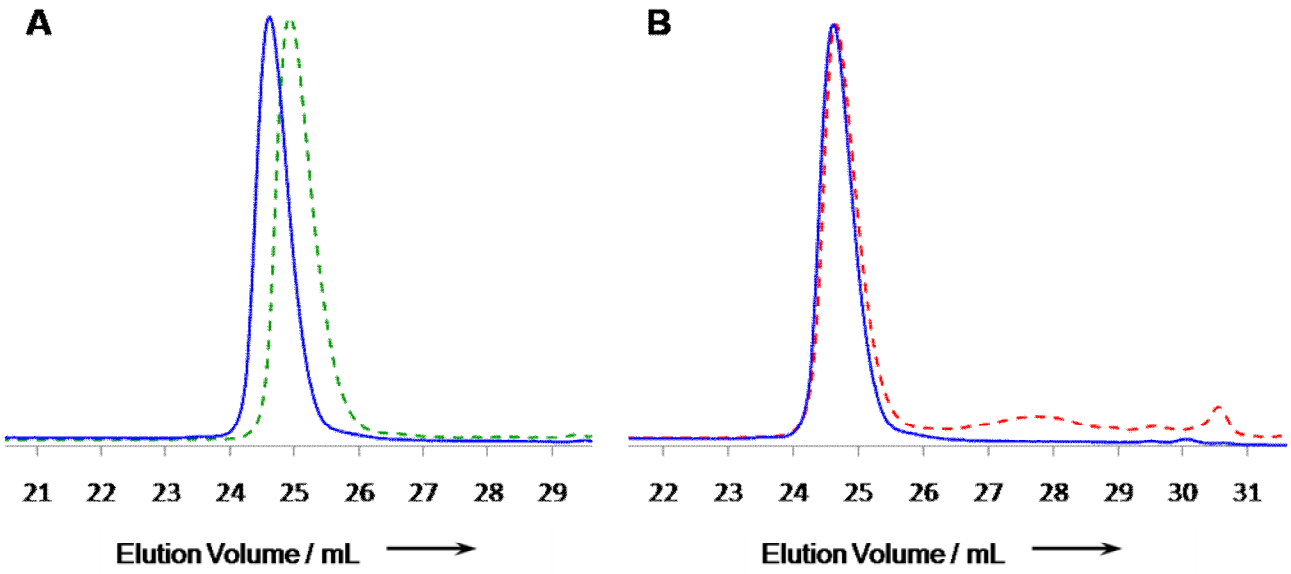

Figure S2 Comparative gel permeation chromatograms of PEG 3000 used as macroinitiator (dashed line) and copolymer **6d** (solid line) (A) and this polymer before (dashed line) and after (solid line) chromatographic purification on silica gel (B).

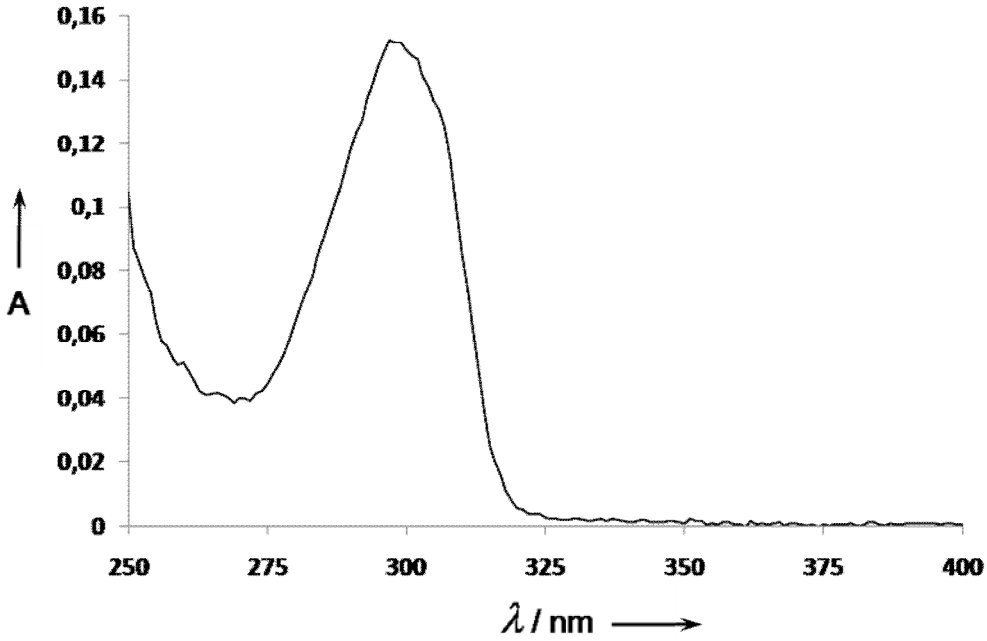

Figure S3 UV spectrum of polymer **5**.

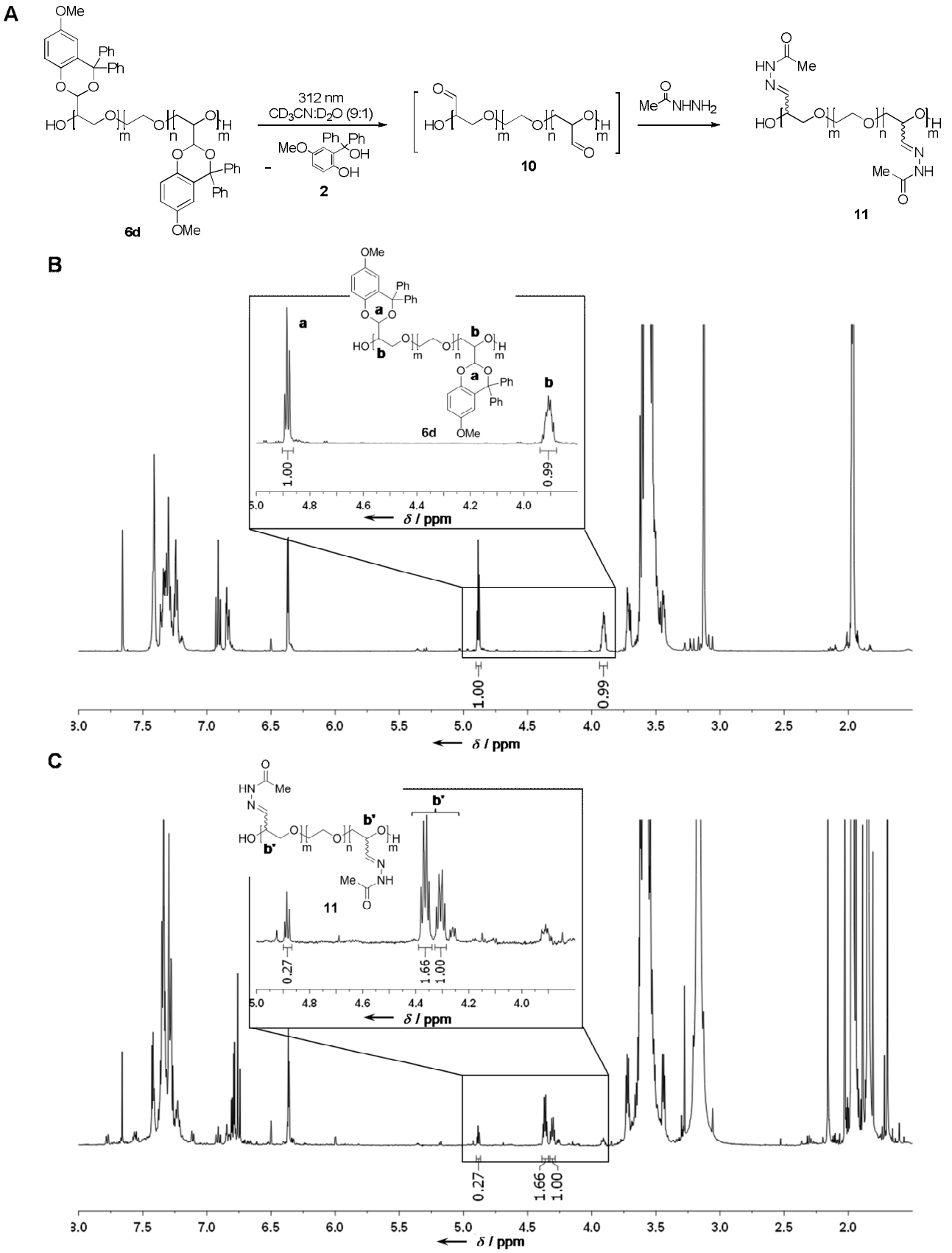

Figure S4 Photodeprotection of copolymer **6d** upon irradiation with 312 nm light followed by in situ reaction with acetohydrazide (A). ^{1}H NMR spectra of polymer **6d** (B) and hydrazones **11** obtained by photodeprotection of aldehyde groups in copolymer **6d** followed by their in situ reaction with acetohydrazide (C). Solvent $CD_3CN:D_2O$ (9:1).

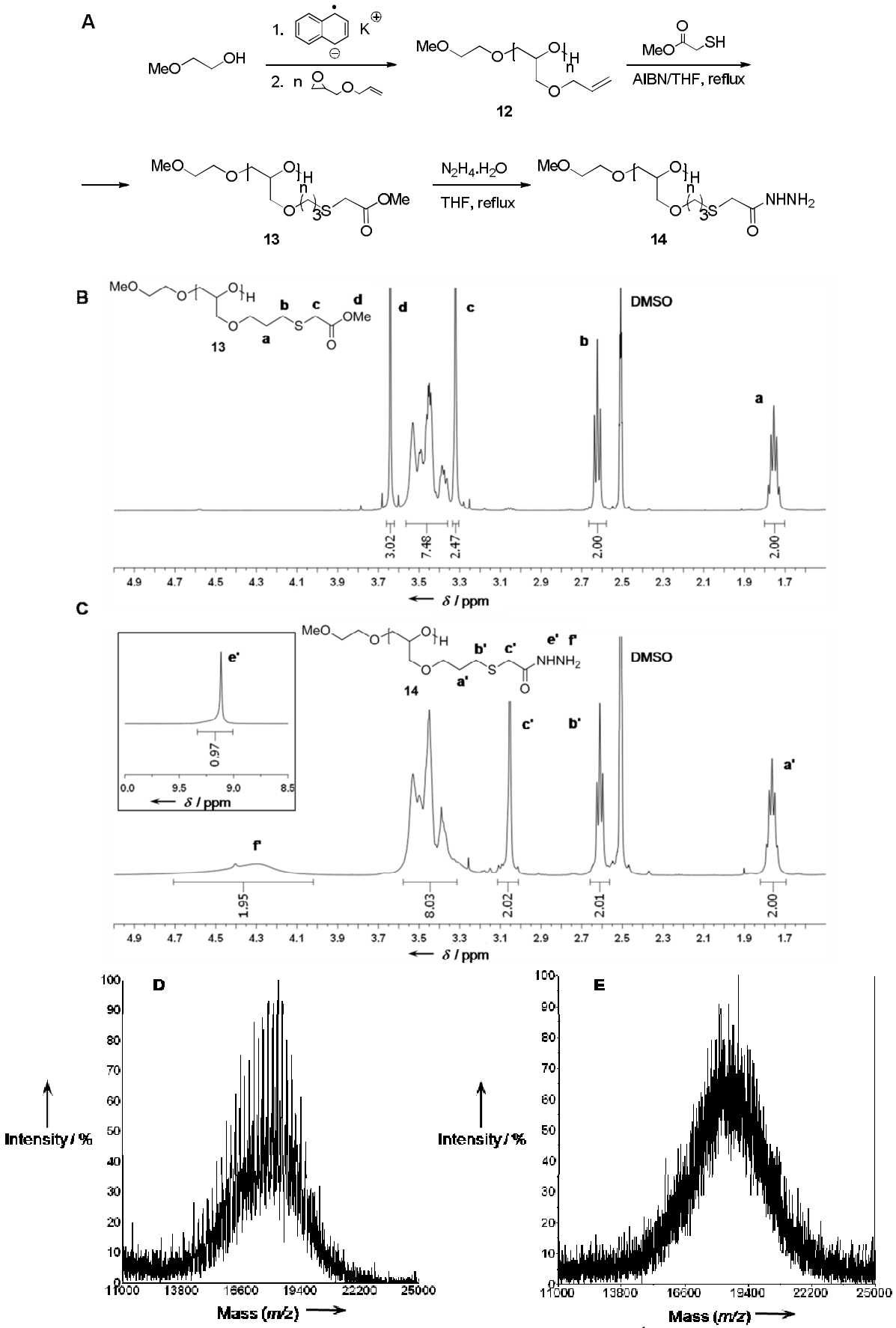

Figure S5 Synthesis of homomultifunctional hydrazide PEG (A). ^{1}H NMR spectra of polymers **13** (B) and **14** (C) confirming complete conversion of ester into hydrazide groups (solvent DMSO-d_6). MALDI-TOF-MS spectra of polymers **13** (D) and **14** (E) confirming maintenance of the polymer molecular weight after modification.

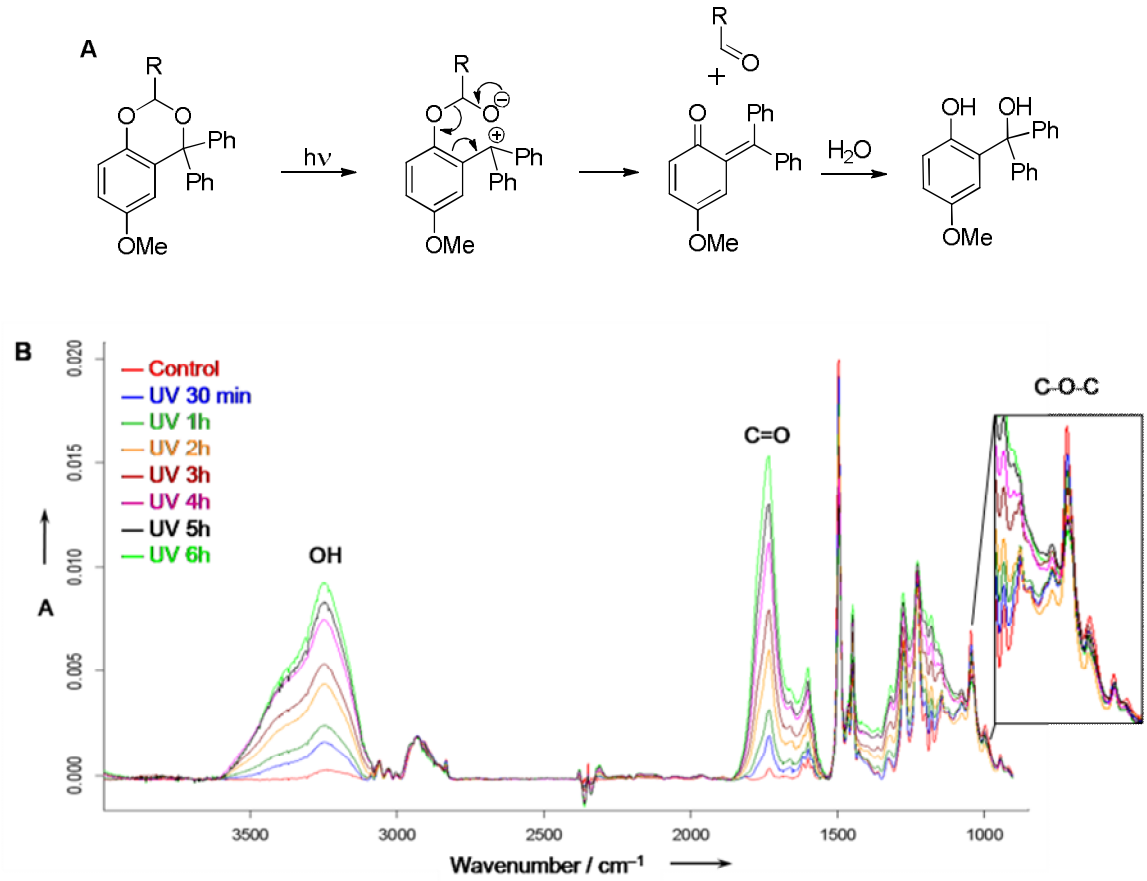

Figure S6. Mechanism of photoinduced cleavage of the acetal protecting groups (A). IR spectra of polymer **5** before (control) and after for times UV treatment times at 312 nm ranging from 30 min to 6 hrs (B). Polymer **5** was spin coated on gold wafers prior to UV treatment.