Electronic Supplementary Material (ESI) for Polymer Chemistry.

UV-Light Crosslinked Photocatalytic Polymer Gels for Batch and Continuous Flow Reactions

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1 Materials

Methanol, ACS grade was purchased and used as received from VWR. Eosin Y disodium salt, Eosin Y (EY), 2,2'-Azobis(2-methyl-propionitrile) (AIBN), triethylamine (TEA), Aluminum oxide (activated, basic, Brockmann I), Acetonitrile (anhydrous, 99.8%), and Glass Beads (acid-washed, 212-300 μm) were purchased from Sigma Aldrich.4-Benzoylphenyl methacrylate and Pentafluorophenyl methacrylate were purchased from AmBeed. N,N-Dimethylformamide, (anhydrous, 99.8%), thioanisole (99%), Ethyl methacrylate (99%, stabilized), 3-Bromopropylamine hydrobromide (98%), and Chloroform-d (99.8 atom % D) were purchased from Thermo Scientific. Distilled water was obtained from an in-house faucet system. Unless further indicated, all materials and reagents were used as received without further processing.

2 Instrumentation and Methods

Gel Permeation Chromatography measurements were completed on a TOSOH ECOSec HLC-8320GPC using THF solvent and a pump oven at 40 ℃ with a flow rate of 1 mL/min. The samples were measured against PMMA standards purchased from Agilent (EasiVial PMMA, PL2020-0201).

Light intensity measurements were performed using a Thorlabs PM100USB equipped with a Thorlabs S120VC photodiode sensor and evaluated with Thorlabs Optical Power Monitor Software. Measurements were taken by holding the sensor in the center of the light bath.

UV/Vis Spectroscopy was performed on a Shimadzu UV-2600. Glass cuvettes with a path length of 1 cm were used. Measurements were collected against a baseline of solvent. Between measurements, cuvettes were rinsed with solvent to clean residual photocatalysts.

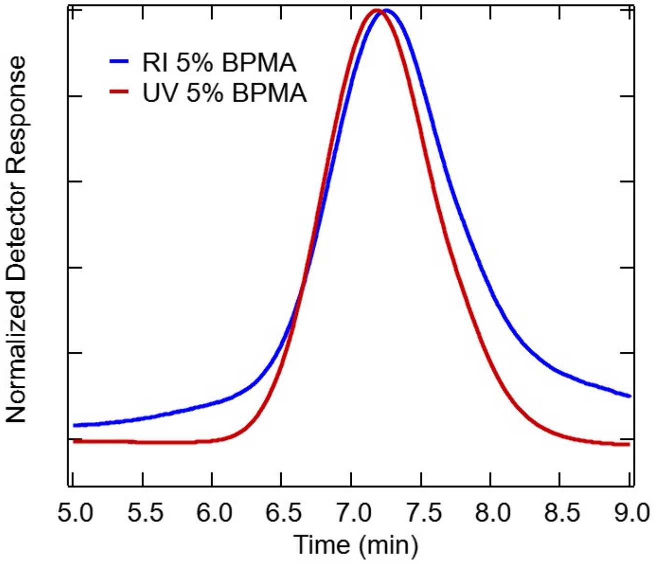
Nuclear Magnetic Resonance Spectroscopy (NMR) was performed using deuterated chloroform solvent, or in deuterated DMSO solvent if indicated. Typically, kinetic experiments were collected on a Bruker 400 mHz and polymer spectra were collected on a 500 MHz instrument.

Light Bath Materials were purchased from LEDlightinghut.com for the Green LEDs used ("Double Row 4-in-1 RGBW 5050 LED Strip, 24V"), and the light intensity was modulated with a rotary knob controller also purchased from LEDlightinghut.com (RGB LED controller). The 365 nm UV LED lights were purchased from Waveform Lighting (realUV^{TM} LED Strip Lights 365 nm) and the intensity was used without further reductions. A USB cooling fan was placed above the reactor and used as needed in case of heat generation from the LED lights, but it was observed that at the 0.5 mW/cm^2 irradiance that without a fan there was no increase in temperature above room temperature at the center of the light bath.

3 General procedures for synthesis of P(EtMA-*co*-BPMA-*co*-PFPMA)

3.1 For a target of 5 mol % incorporation of 4-Benzoylphenyl methacrylate with a 2.5 mol % target of Pentafluorophenyl methacrylate:

To a 250 mL round bottom flask equipped with a stir bar, 23.8 mg of AIBN and 1156.5 mg of 4-Benzoylphenyl methacrylate were added. A syringe plugged with cotton was filled to the 10 mL mark with basic aluminum oxide and ethyl methacrylate was added until soaked and the liquid line reached the 20 mL line and then the liquid was passed through the syringe into a vial. The vial containing ethyl methacrylate was sparged with nitrogen for 20 minutes and then the remaining materials were brought to a glove box and were also purged of air. In the glove box, 30 mL of DMF was added to the flask along with 10 mL of ethyl methacrylate and 0.4 mL of Pentafluorophenyl methacrylate. The flask was then sealed with a rubber septum and then was placed into an oil bath at 85 ℃. After 9 hours, the flask was cooled down to room temperature and opened. The polymer was then precipitated into methanol, collected, and dried under vacuum. Multiple batches were synthesized over the course of study, and the average molecular weight and dispersity among these batches was M_n=56,700 ± 9,100, with Đ= 2.03 ± 0.16.



M_n (g/mol)	**M_w (g/mol)**	**Đ**
56,500	114,300	2.02

Figure S1 Example GPC Trace data for the 5 mol % target incorporation of P(EtMA-*co*-BPMA-*co*-PFPMA)

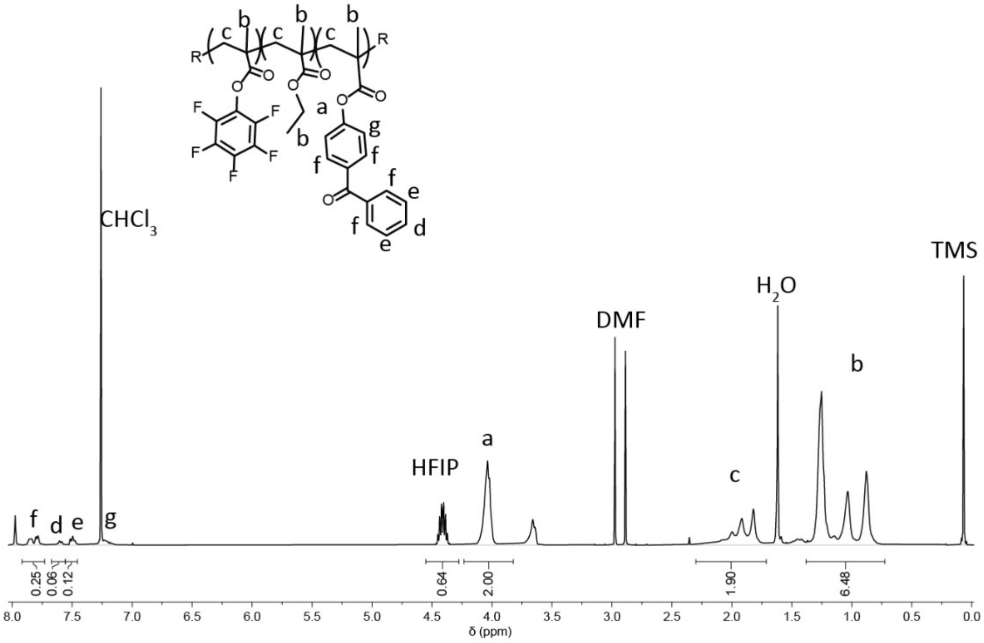


Figure S2. Example ^{1}H NMR spectrum of the 5 mol % target P(EtMA-*co*-BPMA-*co*-PFPMA) taken in $CDCl_3$, 500 MHz. Hexafluoroisopropanol (HFIP) used as internal standard.

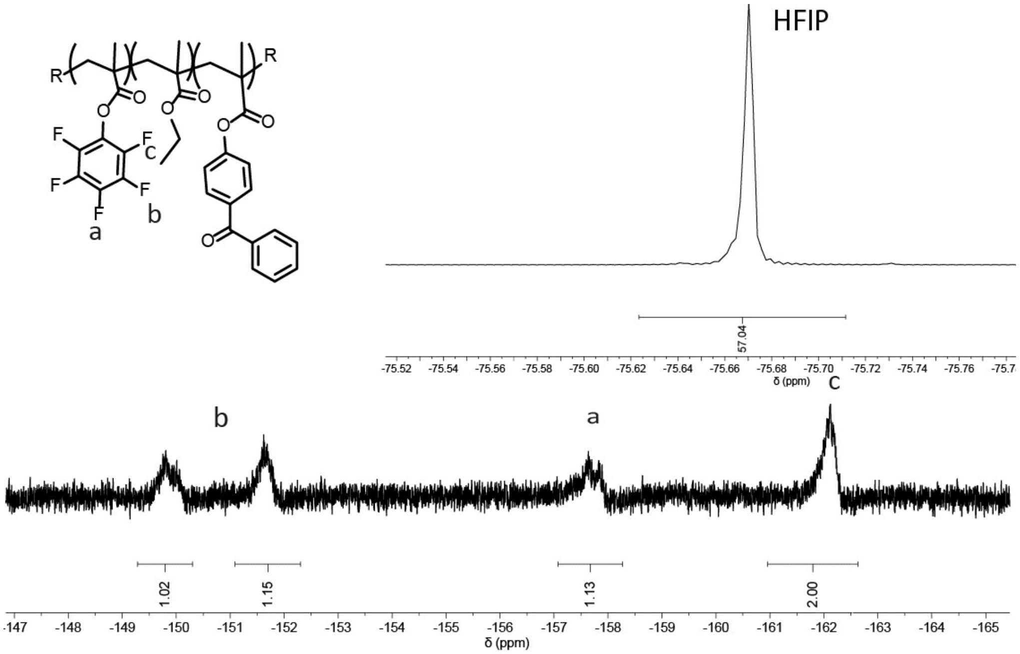
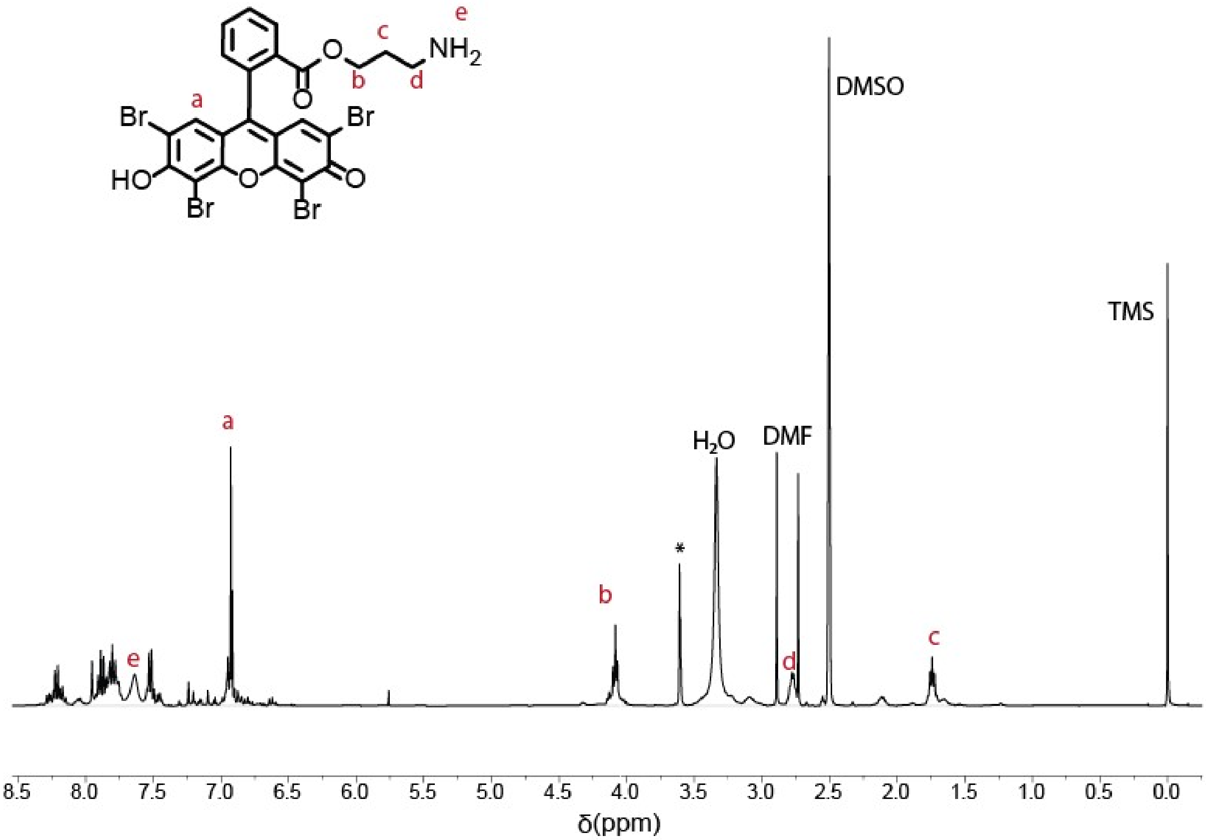


Figure S3. Example ^{19}F NMR of P(EtMA-*co*-BPMA-*co*-PFPMA) taken in $CDCl_3$. (inset) Region containing the peak from HFIP.

4 Procedure for the synthesis of EY-NH_2

The procedure for the synthesis of EY-NH_2 was adapted from Zhao et. al.[1] In a typical procedure, a 50 mL round-bottom flask was filled with 2.05 g of eosin Y disodium salt (2.96 mmol) and 973 mg (4.4 mmol) of 3-bromopropyl amine hydrobromide were added. A stir bar was also added. The flask was brought to a glove box under nitrogen environment and 15 mL of DMF was added and the flask was then sealed. The flask was then placed into a pre-heated oil bath at 85 ^{o}C and reacted for 18 hours. Afterwards, the flask was opened to air and cooled to room temperature. The product was precipitated into a mixture of 50 mL distilled water and 50 mL diethyl ether. The red powder was reprecipitated into the mixture for a second time if needed, and collected into a filter, and then dried under vacuum, additional rinsing with DCM did not appear to further purify the material.

The ^1H NMR analysis of the resulting product is shown below (DMSO-d6). The asterisk represents a potential impurity of 3-bromopropyl amine hydrobromide starting material.



5 Procedure for crosslinking amorphous P(EtMA-*co*-BPMA-*co*-PFPMA):

Typically, around 1-2 g of dried polymer was crushed as needed into smaller pieces and was placed into a petri dish. The petri dish was then placed into a light bath lined with 1.96 m of 365 nm LED light strips, with an irradiance of 4.5 mW/cm^2 under air for 2 hours. Afterwards, the polymer was collected into a vial and immersed in acetone, which was then drained, and rinsed additionally. Remaining loose chains were further removed in the functionalization step with EY-NH_2.

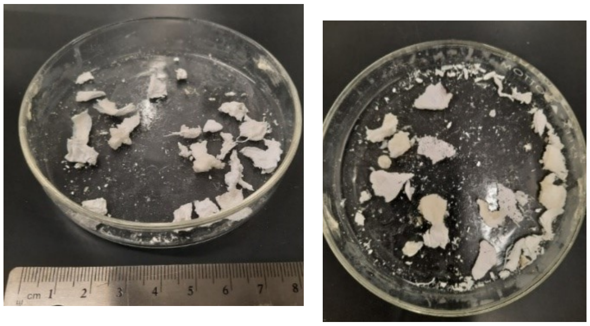
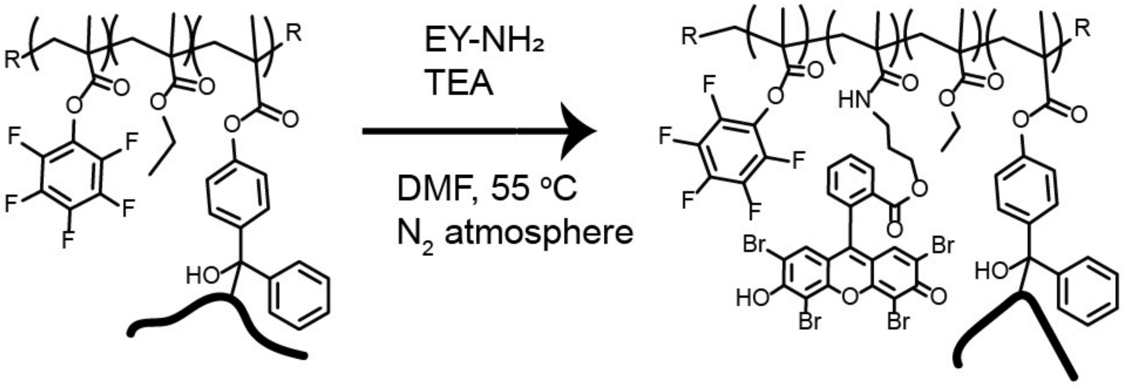


Image of P(EtMA-*co*-BPMA-*co*-PFPMA) with a target of 5 mol % incorporation of benzophenone groups as prepared for crosslinking treatment (left). Example image of a different batch of the P(EtMA-*co*-BPMA-*co*-PFPMA) with a target of 5 mol % incorporation after crosslinking treatment (right). The polymer appeared mostly the same after crosslinking treatment, but on occasion some samples exhibit small regions of a pinkish-purple color.

6 Post Polymerization Modification of P(EtMA-*co*-BPMA-*co*-PFPMA) to produce P(EtMA-*co*-BPMA-*co*-PFPMA-*co*-EYA)



The procedure to employ activated ester chemistry was adapted from Gibson et. al.[2]. In a typical preparation, approximately 1560 mg of dried purified polymer was placed into a 40 mL vial with approximately 297 mg of EY-NH_2 (0.19 mg EY-NH_2 per mg crosslinked polymer). The vial was brought into a glove box under nitrogen atmosphere where 39 mL of DMF (0.025 mL per mg crosslinked polymer) was added along with 57.8 µL (0.037 µL per mg crosslinked polymer) of triethylamine (TEA). The vial was then sealed under a nitrogen environment and placed onto a pre-heated heating block set to 55 °C. The reaction proceeded for 48 hours. The polymer was recovered with collection into filter paper. The gels were rinsed with additional DMF and acetone, and were then purified with Soxhlet extraction in acetone for at least 16 hours, or until the solvent in the retaining thimble appeared clear in color. The gels were then allowed to air dry before being further dried under vacuum. After treatment, the polymers appeared orange in color, indicating the presence of Eosin Y-based groups. After Soxhlet extraction for the batch size described here, the yield of EY-gel was 652 mg. The Soxhlet extraction is expected to have further helped to remove loose polymer chains from the gel, because of the increased temperature of acetone aided in increasing the swelling such that loose chains that had not been removed in earlier steps were removed.

Figure S4 below shows the UV/Vis spectra of 3 aliquots taken during each time point during the substitution process. From this data, we estimate roughly a 10 % incorporation of the EY-NH_2 into the gel.

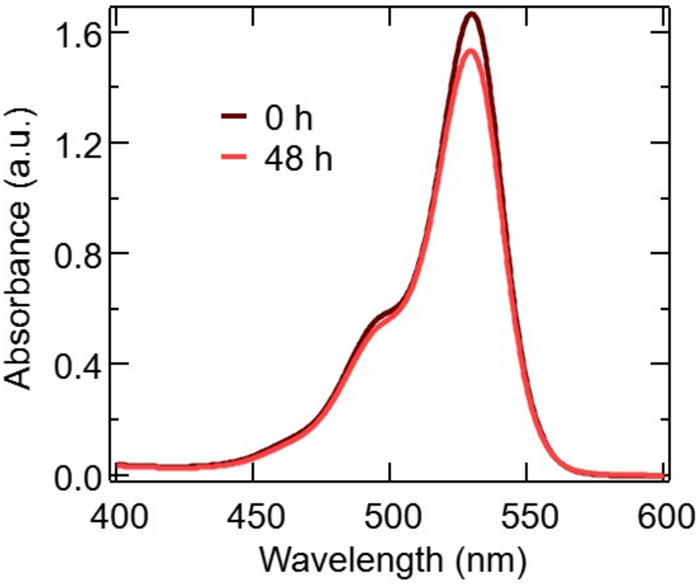


Figure S4. UV/Vis spectra of aliquots taken during the substitution, spectra are presented as the average of 3 aliquots at the timepoints indicated. From this data, roughly a 10% incorporation was estimated.

To further investigate the effects of different substitution times, the crosslinked gel was reacted in the procedure described above for 24 hours and 132 hours. Then 130 mg of the gels were tested for the oxidation of thioanisole as described in **section 8** herein, with 2 mW/cm^2 of green light irradiation. The kinetics do not suggest a major change associated with the time spent in the substitution reaction.

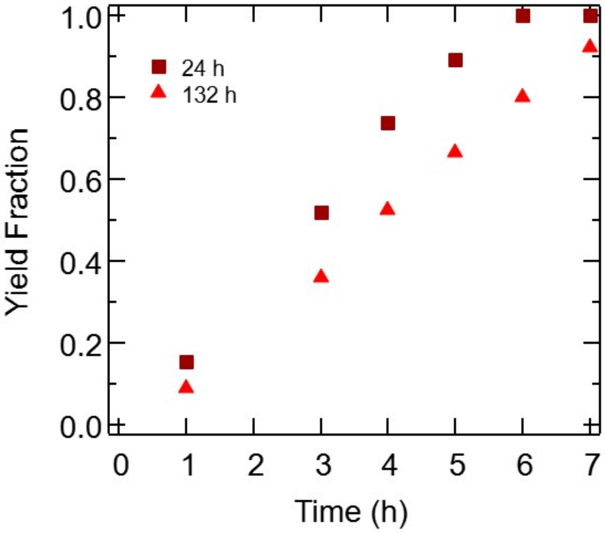


Figure S5. The oxidation of thioanisole was investigated for 130 mg of EY-gel tested at 2 mW/cm2 under the same conditions detailed in section 8.

Additionally, to investigate if the linear polymers before crosslinking result in higher substitution as a result of potentially reduced steric hinderance,, ^{19}F NMR was performed on the linear polymer P(EtMA-*co*-PFPMA-*co*-BPMA) produced before crosslinking treatment, and the collected spectra imply no major benefit from treatments to substitute the EY-NH_2 first before crosslinking treatments. The decline in the signal from the PFPMA peaks could not be reliably estimated from the collected spectra.

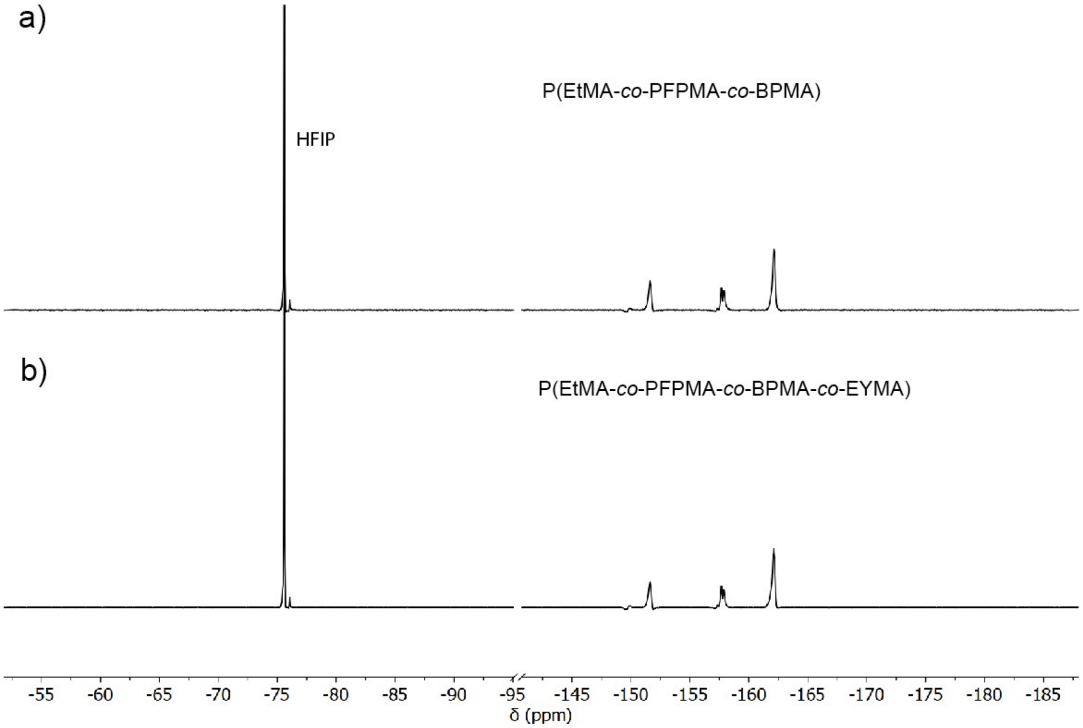


Figure S6. a) ^{19}F NMR of linear P(EtMA-co-PFPMA-co-BPMA) polymer with hexafluoroisopropanol as an internal standard. b) ^{19}F NMR of P(EtMA-co-PFPMA-co-BPMA-co-EYMA) produced after 48 hours of substitution.

7 Procedure for the Oxidation of Thioanisole Reaction with Different Reactors

The procedure for the oxidation of thioanisole was adapted from Sridhar et. al.[3]. Reaction vessels included either a 10 mL round-bottom flask, a 4 mL vial equipped with a septum cap and three 21-gauge needles of 1.5 in. length, or a 40 mL vial with a lid. The reaction was prepared by adding 2 mL of 8:2 (by volume) acetonitrile to distilled water solvent. A stir bar was added to the reaction vessel.

The composition of the test reaction was 2 mL of 8:2 ACN:H_2O, 0.33 mg/mL (0.51 μmol/mL) Eosin Y, and 83.2 μL (0.71 mmol) of thioanisole. Reaction kinetics (**Figure S4b**) showed that the 40 mL vial (closed with a lid) performed similarly to the 10 mL round-bottom flask, which was completely open to the atmosphere. Both systems reached quantitative conversion after 9 hours of irradiation time (λ_{max} = 520 nm green LED light at 1 mW/cm^2 intensity). In contrast, the 4 mL vial with 3 needles exhibited a decreased yield of 48% within the same reaction time. Two moles of O_2 are required for the oxidation of one mol of thioanisole. Using the ideal gas law, we can estimate that the headspace (2 mL) of the 4 mL vial contains approximately 0.0188 mmol of oxygen, whereas the 40 mL vial (38 mL of headspace) would contain 0.356 mmol of oxygen. Considering that 0.71 mmol of thioanisole was used in the reaction, opening the vials to take aliquots is anticipated to replenish the oxygen supply. This allows for sufficient O_2 to present for the reaction to achieve quantitative conversion in the 40 mL system. No apparent change in reaction kinetics was observed with longer sampling intervals, so it appears that the sampling intervals did not inhibit the reaction. In contrast, the 4 mL vial appeared to have insufficient head space to allow for enough oxygen to be replaced along with less effective geometry for light penetration, thereby decreasing reaction rates. Therefore, EY-gels were studied using 40 mL vials with lids for the following studies with the EY-gels.

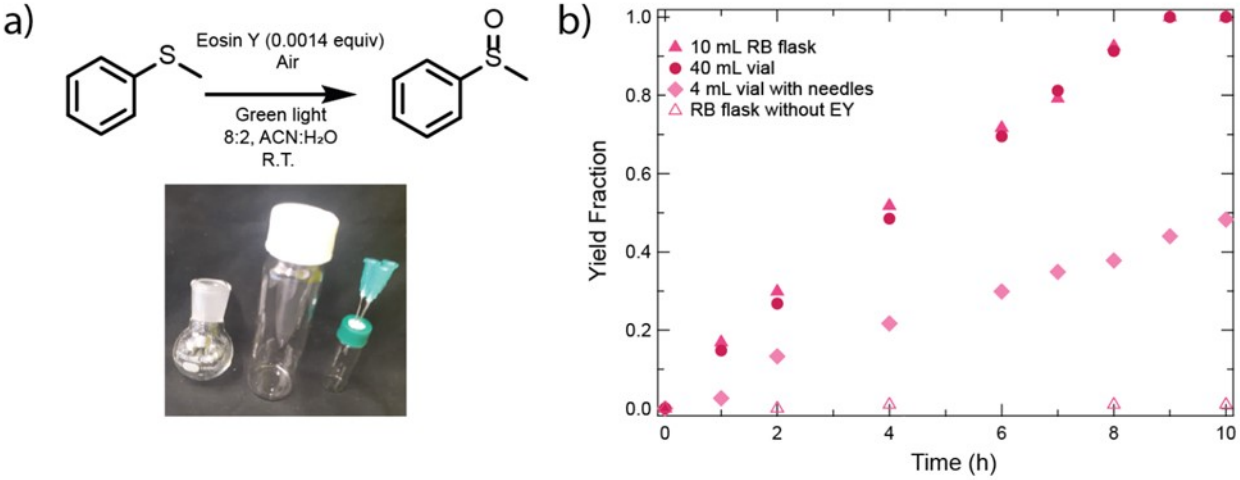


Figure S7. a) Kinetics of the oxidation of thioanisole using homogeneous Eosin Y (0.0014 mol equivalents) under green light irradiation (1 mW/cm^2) at room temperature with different reactor vessels. A control was performed using the 10 mL round-bottom flask under the same conditions except no photocatalyst was present. **b)** Reaction schematic as well as an image of the reactor vessels used.

8 Procedure for the Oxidation of Thioanisole Reaction Using EY-gels

The procedure for the oxidation of thioanisole was adapted from Sridhar et. al.[3]. A 40 mL vial equipped with a lid was used. To this vial, 130 mg of the EY-gel catalyst was added along with a stir bar and 2 mL of 8:2 by volume acetonitrile to distilled water. The vial was then placed on a stir plate and was stirred for about 24 hours to allow time for the gel to swell. Afterwards, the solvent was collected to analyze leaching amounts and fresh solvent was replaced. To the vial, 78.8 µL of thioanisole was added and the vial was placed into a light bath consisting of a crystallization dish lined with green LED lights of λ_{max}= 520 nm and an irradiance of either: 0.5 mW/cm^2, 1 mW/cm^2, 2 mW/cm^2. The reaction was allowed to proceed at room temperature. Aliquots were taken to monitor the reaction progress with ^{1}H NMR as needed and the reactor lid would be opened and resealed. To recycle the gels, the material was soaked in acetone overnight, and rinsed an additional 3 times in acetone before drying. The gel was then immersed in 2 mL of the (ACN:H_2O, 8:2) solvent for at least 16 hours before being used for an oxidation reaction again. While not in use, the gel materials were kept in a drawer in the darkness.

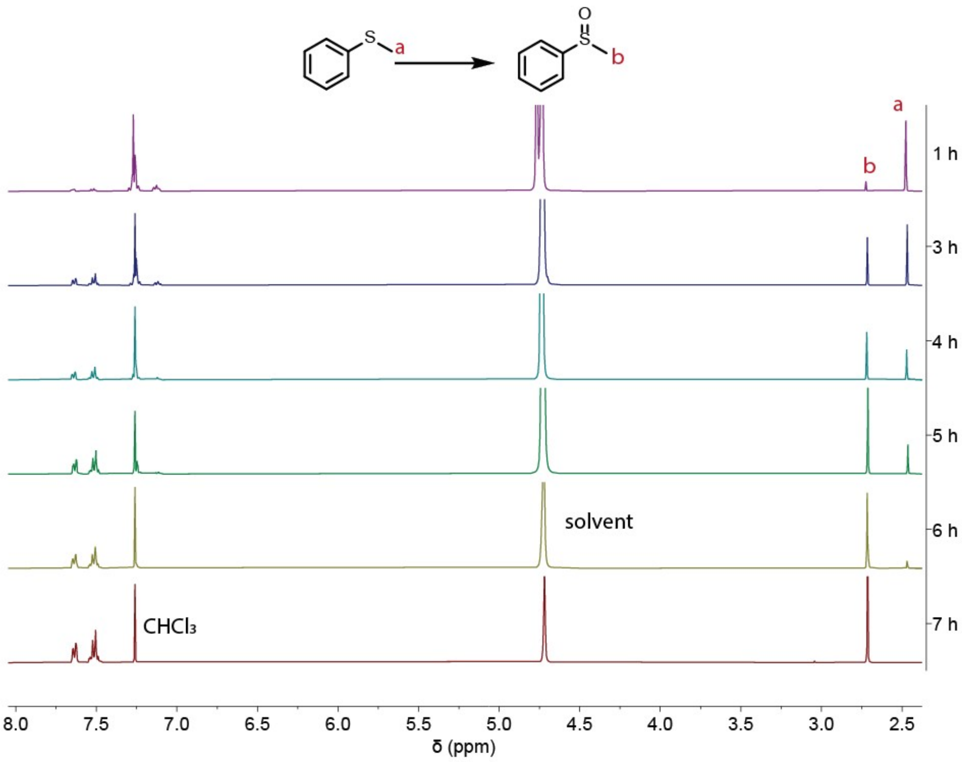


Figure S8. Example ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the resulting thioanisole conversion using 130 mg EY-gels under 2 mW/cm^2 irradiance of green light λ_{max}=520 nm with stirring.

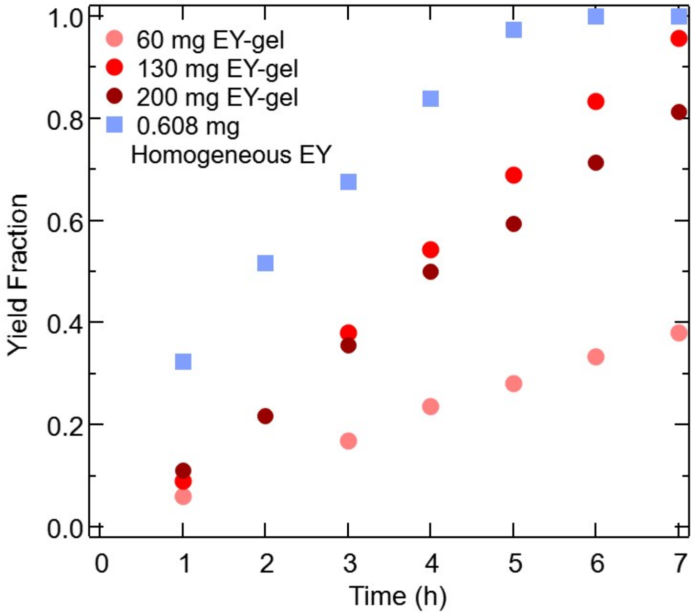
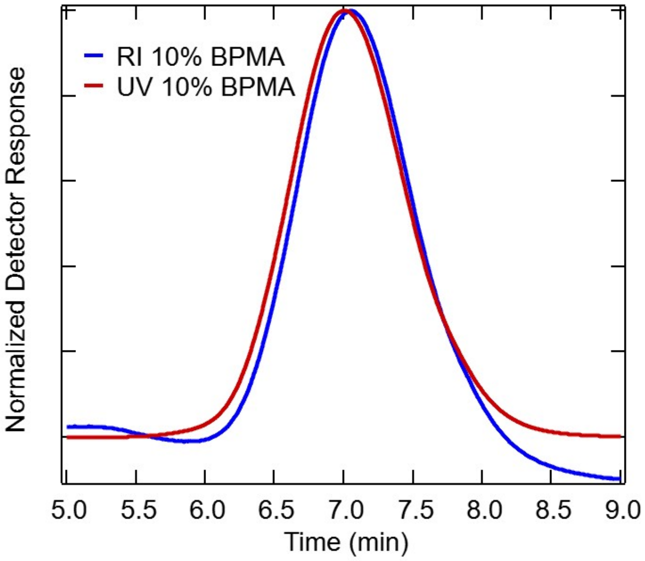


Figure S9. Kinetics of thioanisole oxidation for different loadings of the EY-gel and homogeneous Eosin Y at 2 mW/cm^2. The 130 mg data is presented as the average of three trials whereas the other traces represent a single trial.

9 Characterization Data of P(EtMA-*co*-BPMA-*co*-PFPMA), 10 % and 15 % BPMA feed ratios

9.1 For a target of 10 mol % incorporation of 4-Benzoylphenyl methacrylate with a 2.5 mol % target of Pentafluorophenyl methacrylate:

To a 100 mL round-bottom flask equipped with a stir bar, 11.8 mg of AIBN and 1222.5 mg of 4-Benzoylphenyl methacrylate were added. A syringe plugged with cotton was filled to the 5 mL mark with basic aluminum oxide and ethyl methacrylate was added until the liquid line reached the 10 mL line and then the liquid was passed through the syringe into a vial. The vial containing ethyl methacrylate was sparged with nitrogen for 20 minutes and then the remaining materials were brought to a glove box and were also purged of air. In the glove box, 15 mL of DMF was added to the flask along with 5 mL of ethyl methacrylate and 0.21 mL of Pentafluorophenyl methacrylate. The flask was then sealed with a rubber septum and then was placed into an oil bath at 85 ^{o}C. After 1 hour, the flask was cooled down to room temperature and opened. The polymer was then precipitated into methanol, collected, and dried under vacuum. The conversion with respect to the ethyl methacrylate was calculated to be 16% at the end of the hour of reaction time.



M_n (g/mol)	M_w (g/mol)	**Đ**
77,000	166,900	2.16

Figure S10. GPC Traces of the 10% target incorporation of BPMA in the P(EtMA-*co*-BPMA-*co*-PFPMA) polymers.

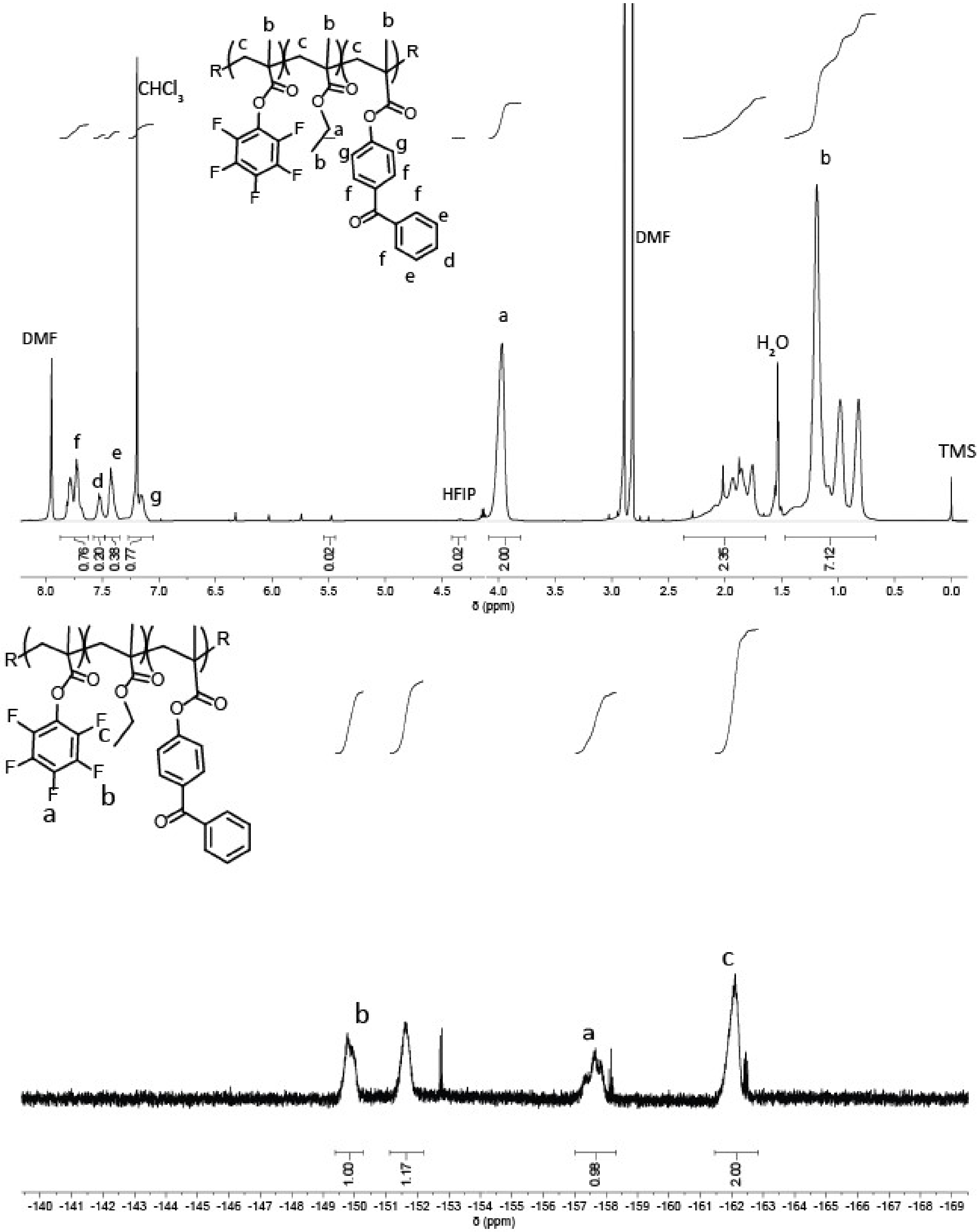
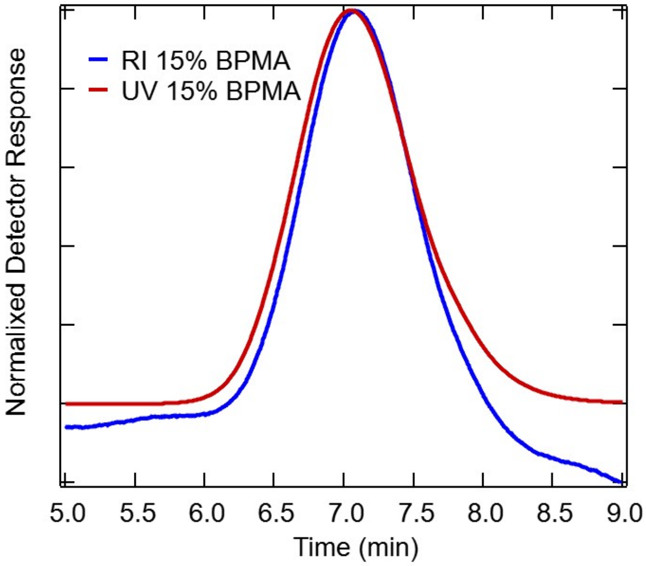


Figure S11. ^{1}H NMR spectrum (top) and ^{19}F NMR spectrum of P(EtMA-*co*-BPMA-*co*-PFPMA) polymer synthesized with a target of 10 mol % of 4-benzoylphenyl methacrylate after purification by precipitation in methanol.

9.2 For a target of 15 mol % incorporation of 4-Benzoylphenyl methacrylate with a 2.5 mol % target of Pentafluorophenyl methacrylate:

To a 100 mL round-bottom flask equipped with a stir bar, 11.8 mg of AIBN and 1945 mg of 4-Benzoylphenyl methacrylate were added. A syringe plugged with cotton was filled to the 5 mL mark with basic aluminum oxide and ethyl methacrylate was added until the liquid line reached the 10 mL line and then the liquid was passed through the syringe into a vial. The vial containing ethyl methacrylate was sparged with nitrogen for 20 minutes and then the remaining materials were brought to a glove box and were also purged of air. In the glove box, 15 mL of DMF was added to the flask along with 5 mL of ethyl methacrylate and 0.22 mL of Pentafluorophenyl methacrylate. The flask was then sealed with a rubber septum and then was placed into an oil bath at 85 ^{o}C. After 1 hour, the flask was cooled down to room temperature and opened. The polymer was then precipitated into methanol, collected, and dried under vacuum. The conversion with respect to the ethyl methacrylate was calculated to be 25% at the end of the hour of reaction time.



M$_n$ (g/mol)	**M$_w$** (g/mol)	**Đ**
78,300	151,100	1.93

Figure S12. GPC Traces of the 15% target incorporation of BPMA in the P(EtMA-*co*-BPMA-*co*-PFPMA) polymers.

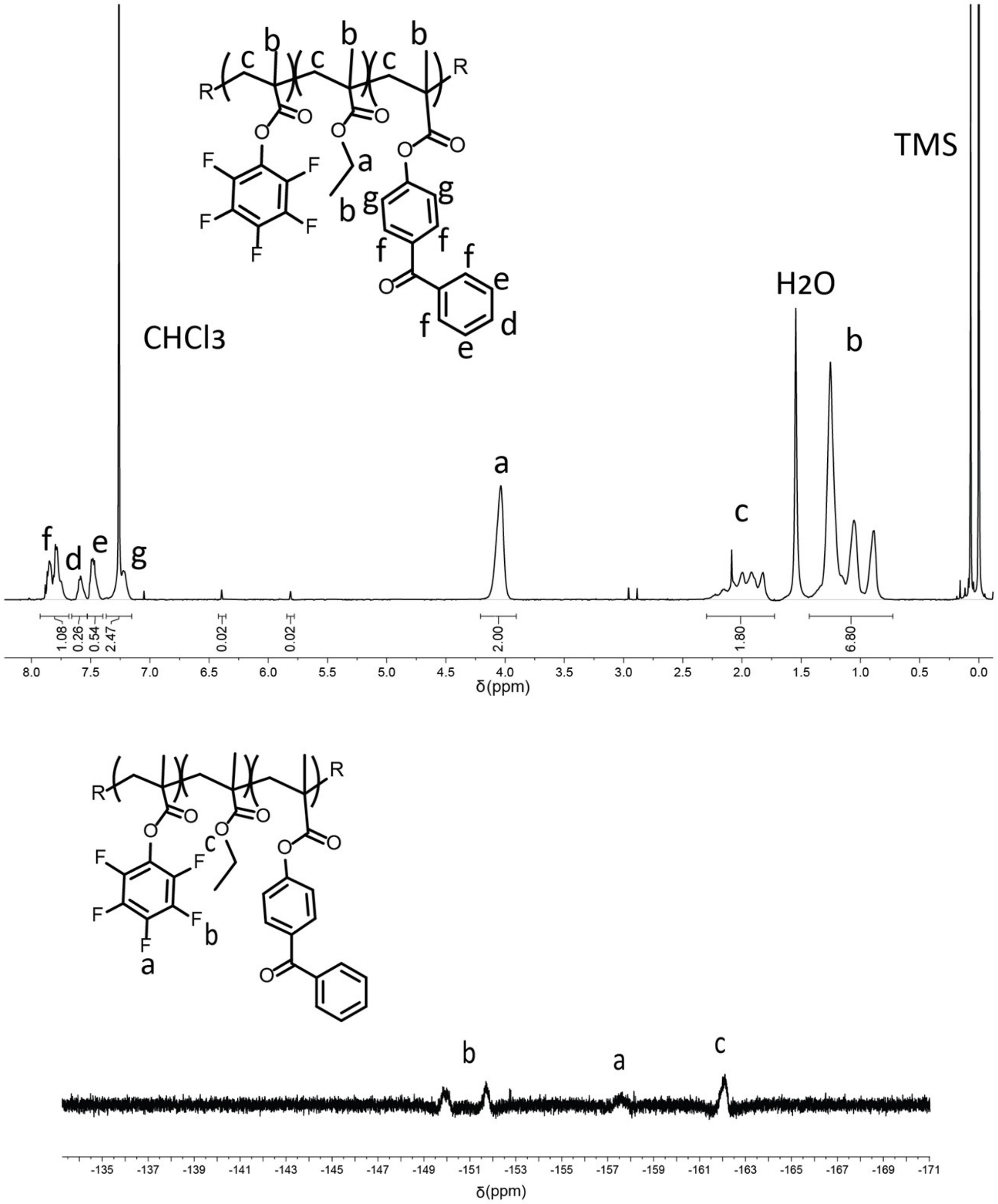


Figure S13. ^1H NMR spectrum (top) and ^{19}F NMR spectrum (bottom) of P(EtMA-*co*-BPMA-*co*-PFPMA) polymer synthesized with a target of 15 mol % of 4-benzoylphenyl methacrylate after purification by precipitation in methanol.

10 Swelling Tests for Crosslinked Polymer Gels in acetone

After crosslinking treatment, the polymer gels were placed into acetone and were allowed to swell for several hours. To determine the swelling ratios, a piece of polymer gel was removed from immersion in acetone with tweezers and was blotted on a KimWipe such that the polymer piece no longer had acetone dripping from it. The mass of polymer was then measured while wet to determine W_{wet} and the acetone was allowed to evaporate such that no additional loss of acetone was measured with increasing time. At this point the polymer was weighed again to determine W_{dry}.

Table S1. Swelling test results for different feed ratios of BPMA.

Sample	W_{wet}/W_{dry} (1)	W_{wet}/W_{dry} (2)	W_{wet}/W_{dry} (3)	Average	Standard Deviation
5 mol %	7.29	5.92	9.78	7.67	1.96
10 mol %	9.06	8.08	10.41	9.18	1.17
15 mol %	14.02	10.03	10.56	11.54	2.17

11 EY-gel Leaching Analysis

Figure S14 shows images before and after the EY-gels were tested at the light intensities indicated. The vials on the right of each image show the vials tested for the effects of leached EY-NH_2, and the estimated leaching was studied for their reaction kinetics in **Figure S15** herein.

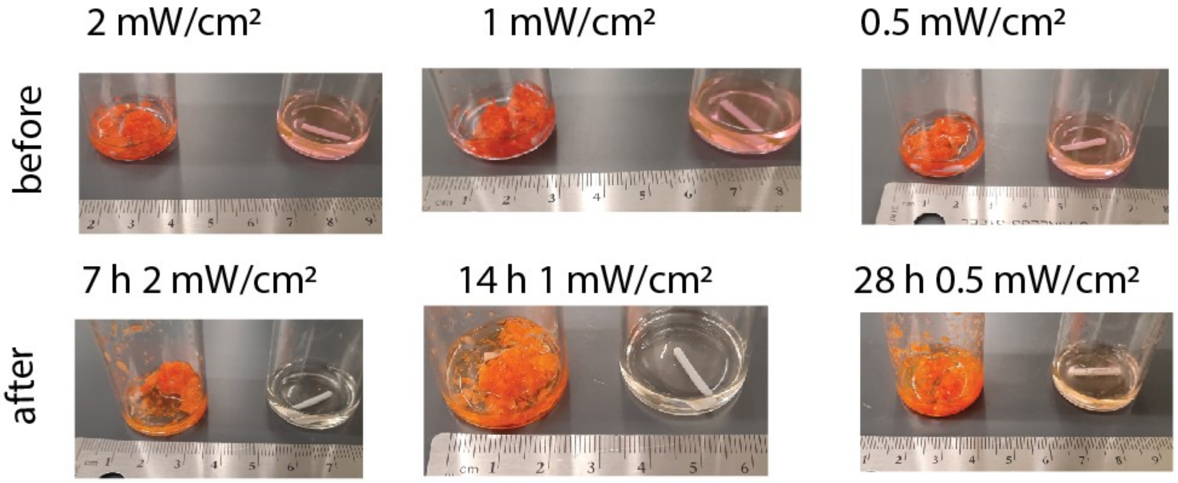


Figure S14. Images of EY-gel photocatalysts (left) before and after the indicated reaction times for the oxidation of thioanisole. Homogeneous EY-NH_2 (right) solutions prepared as well indicate that small amounts of the photocatalyst exhibit a significant loss of the characteristic pink color, whereas the lowest light intensity indicates some retention of this color even after 28 hours of irradiation.

To further understand the stability of the incorporation of the EY-NH_2, the gel was tested through heating in DMF (a good solvent). 100 mg of EY-gel was placed into a 40 mL vial and the vial was filled with DMF. The vial was periodically shaken and heated to 80 °C for the first wash, representing about 26 hours of heated immersion. Washes #2-4 represent a total of about 72 hours of 100 °C heating in DMF. Lastly, the EY-gel was placed into a vial filled with DMF at room temperature. As is shown, only slight amounts of pink coloration are visible to the eye in each wash, with the final vial showing the room temperature DMF having no visible trace of leaching. This test suggests that some degree of leaching is observed, perhaps through the diffusion of loose chains, however, the bright orange color remains in the gel, suggesting that the majority of the EY-NH_2 remains in the gel and is not merely physiosorbed.

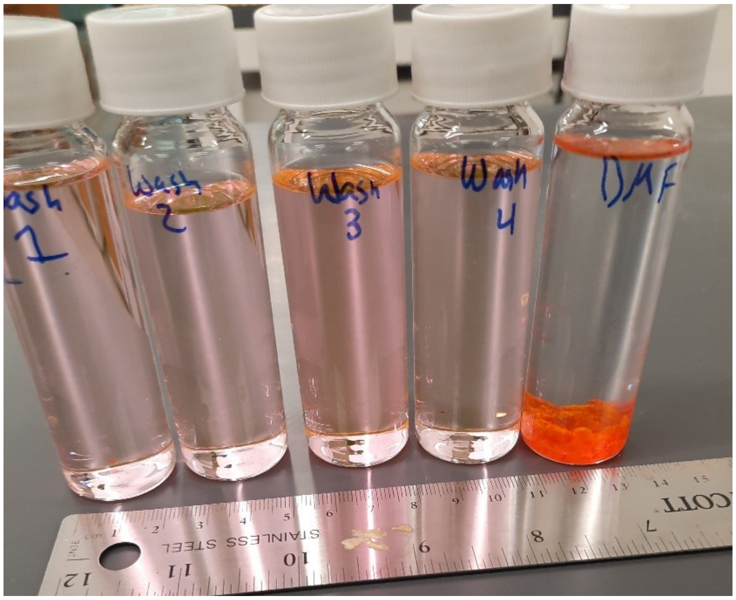


Figure S15. Image of heating test results, where wash 1 represents the solvent recovered from heating the gel in DMF at 80 °C for about 26 hours, and the remaining washes #2-4 represent about 72 hours of heating in DMF at 100 °C. The last vial on the right shows the gel after immersion in room temperature DMF after recovery from the 4th wash.

The amount of EY leached was analyzed using UV-Vis spectroscopy. To determine the amount of EY leeched, 130 mg of EY-gel was soaked in 3 mL of 8:2 ACN to H_2O for 24 hours and was stirred in the dark. Afterwards, the solvent was collected and additional solvent was added as needed to ensure enough sample was filled into the 1 cm path length cuvette. A calibration curve was created using serial dilutions of a 0.5 mg/mL stock solution of EY-NH_2 in the same 8:2 ACN to H_2O solvent used for the gels. Using the calibration curve, it was estimated that about 9.5 µg/mL EY-NH_2 had leached from the gel into the solution.

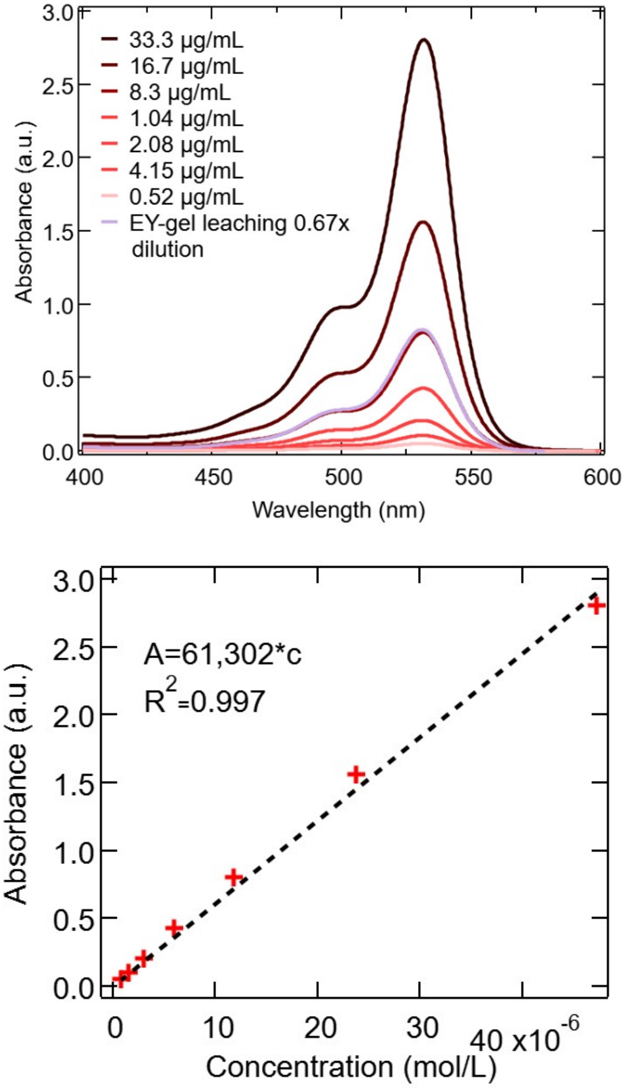


Figure S16. UV/Vis absorbance spectra of EY-NH_2 at different dilutions in 8:2 ACN:H_2O solvent, along with the observed EY-NH_2 leached into solvent from the EY-gel (top). A calibration curve was constructed to determine the leached amount (bottom).

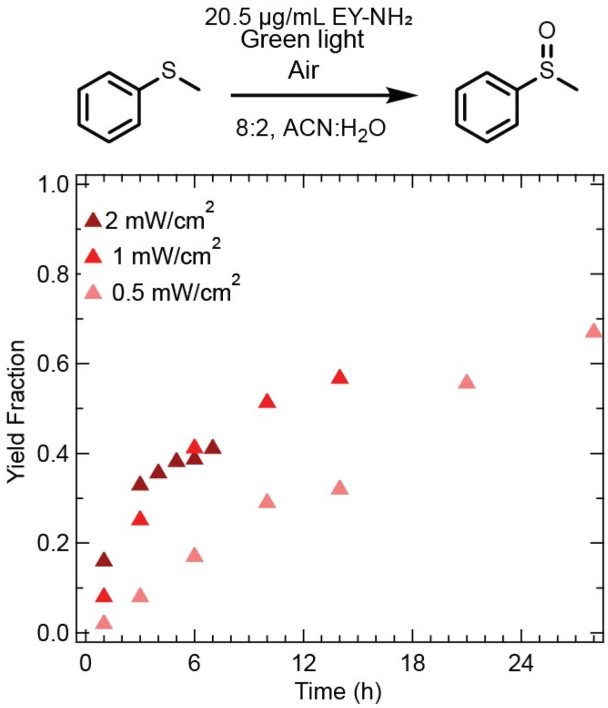


Figure S17. Kinetic study using 20.5 µg/mL EY-NH_2 in 2 mL of solvent under varied light intensities under Green LED light exposure at the indicated irradiances. This concentration was used to simulate leached amounts of EY-NH_2 photocatalyst in order to understand the impact of leeched amounts on the apparent kinetics of the oxidation of thioanisole.

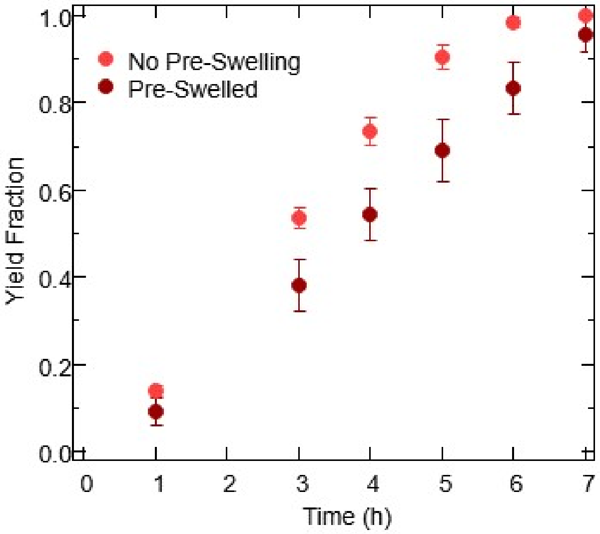


Figure S18. Kinetic study at 2 mW/cm^2 520 nm green light comparing the effects of swelling for at least 16 hours before running the experiment. The leached material that occurred during the swelling time was removed and the solvent was replaced before running the experiments in the case of the swelled gels, whereas for the gels that were not pre-swelled were used right after adding reaction solvent and reactant. These results indicate that leached catalyst can result in around an average of 15% more yield. The Pre-swelling set is the same as the kinetic studies seen for the 2 mW/cm^2 data in Figure 2 as it is the same set of conditions and treatments.

12 Continuous Flow Reactor with Packed EY-gel

The continuous flow reactor was constructed using AWG #13 PTFE tubing purchased from TefCap Industries, the nominal inner diameter specified is 0.076 inches, and the wall thickness is 0.012 inches, further details may be found at: www.tefcap.com/awg-13-thin-wall-ptfe-tubing/. 1.5m (5 ft) of tubing was measured with a ruler and was cut with scissors. Next, one end was blocked and glass beads of 212-300 μm diameter were poured in through the opened end, leaving 13 cm (5 in.) unpacked at the front of the tubing. In small batches, pieces of the dried EY-gel were packed into the tubing, and after short segments, more glass beads were packed such that there were not long stretches of gel that could form a blockage. A total of about 100 mg of EY-gel was added to the tubing. For the homogeneous condition, 23 mL of solvent was prepared with a concentration of 0.304 mg/mL of Eosin Y.

Masterflex^{TM} Polypropylene luer fittings were used one with a female end, and one with a male end. The inlet end with the female fitting was connected to a 25 mL SGE air-tight glass syringe. The male end was connected to a needle with a small plug of cotton placed into it, and the needle was pierced through a septum cap connected to a 40 mL vial which was placed inside the beaker. The septum cap on the vial was left slightly loose to prevent pressure changes in the outlet, and the vial was wrapped in aluminum foil.

A Chemyx Fusion 4000-X syringe pump was used to push reaction liquid through the tubing. The feed syringe was loaded with 226.6 μL of thioanisole and 23 mL of solvent. The tubing was connected to a syringe secured onto a syringe pump and solvent was pushed through the tubing at a flow rate of 0.2 mL/min and the final injection volume displayed on the syringe pump was recorded once the first drop of liquid had been released from the outlet, the flow rate was then changed to 2.1 μL/min and solvent was run through the reactor overnight to allow time for the gels to reach equilibrium swelling. Then to begin the experiment, the packed tubing was injected completely with the reaction solution containing thioanisole, and the LED lights were turned on to 0.5 mW/cm^{2,} which was measured from the center of the crystallization dish. The flow rate was set at 2.1 μL/min to conduct the experiment. The flow rate was confirmed through measurement after a set amount of time. Yields were measured through aliquots for ^{1}H NMR, and these aliquots were taken by placing the needle directly into an NMR tube which was wrapped in aluminum foil, and the NMR tube was left to collect product output for 8 minutes before deuterated chloroform was added for analysis.

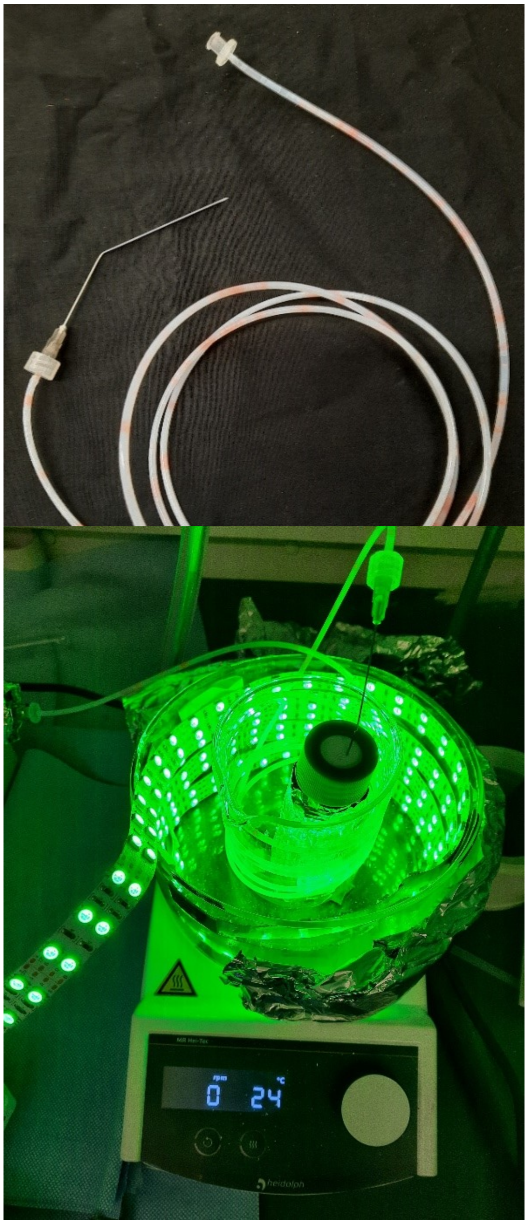


Figure S19. Image of the packed reactor after 108 hours of use, the orange segments are the EY-gel. The ruler displays units in inches (left). Image of the reactor set up with the beaker placed in the center of the light bath and a 40 mL vial covered in foil to collect the product output (right).

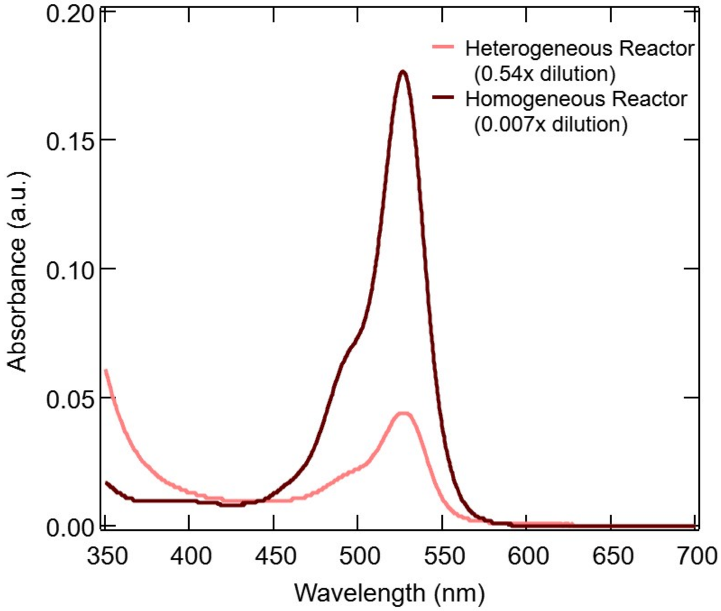


Figure S20. UV/vis spectra of the collected fractions shown in Figure 5c.

The collected fractions were measured against a baseline of ACN:H_2O 8:2 solvent in a cuvette of pathlength 1 cm. It is important to note that for analysis the homogeneous sample was diluted to a factor of 0.007 times the initial concentration, that is 20 µL of sample in 2.98 mL of solvent. For the heterogeneous reactor, 1.34 mL of sample was added to 1.16 mL of solvent, representing a factor of 0.54 times the initial concentration. Therefore the homogeneous sample represents about a 323-fold increase in the amount of Eosin Y. The homogeneous concentration of Eosin Y used was 304 µg/mL. Using the calibration curve in would suggest a concentration of 0.94 µg/mL of EY-NH_2 in the heterogeneous product output, the calculation is provided below.

$$A = \varepsilon l c$$

$$from\ page\ 15{:}A = 61{,}302 \times x\frac{mol}{L}$$

$$from\ Figure\ S16, A\ of\ heterogeneous\ sample = \ .044$$

$$x\frac{mol}{L} = 7.18 \times 10^{-7}$$

$$EY - NH_2\ MW = 704.99\,\frac{g}{mol}$$

$$\frac{7.18 * 10^{-7}\,mol}{L} \times \frac{1\,L}{1000\,mL} \times \frac{704.99\,g}{mol} \times \frac{10^6 \mu g}{g} \times \frac{1}{.54\ dilution\ factor} = \frac{0.94\,\mu g}{mL}$$

13 Comparison of Turnover Numbers and Turnover Frequencies

Finally, a comparison of turnover numbers (TON) and turnover frequencies is (TOF) made to compare the homogeneous Eosin Y and the EY-gel in batch and flow conditions. The batch conditions are 130 mg of EY-gel or 0.608 mg of Eosin Y at 2 mW/cm^2 with 0.67 mmol of thioanisole reactant. The flow conditions are as described in the previous section detailing the continuous flow reactor conditions, notably using 0.5 mW/cm^2 intensity.

Table S2. Summary of estimated TON and TOF values for batch and flow conditions for the homogeneous Eosin Y and heterogeneous EY-gels using the 2 mW/cm^2 green light irradiance conditions for batch experiments, and 0.5 mW/cm^2 for flow conditions..

Batch	TON	TOF	Flow	TON	TOF
Eosin Y	712	142	**Eosin Y**	142	9
EY-gel	180	26	**EY-gel**	229	15

Overall, the homogeneous Eosin Y shows higher efficacy as a result of the superior mass transfer and even dispersion of the photocatalyst in the reaction liquid. The heterogeneous EY-gel performs reasonably well compared to alternate Eosin Y-based heterogeneous catalysts, which are summarized by Peng et. al., who found a range of TONs from 544 to 12.5, and TOF values from 11.3 to 0.4.[4]

References

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