Thiol-Ene Polymer Microbeads Prepared Under High-Shear and their Successful Utility as a Heterogeneous Photocatalyst via C₆₀-Capping

*Emily M. Barker and J. Paige Buchanan**

Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg,
MS. 39406

*Address correspondence to Dr. J. Paige Buchanan, Department of Chemistry and Biochemistry, University of Southern Mississippi, 118 College Drive #5043, Hattiesburg, MS 39406; Phone: (601) 266-4083; Fax: (601) 266-6075, E-mail: paige.buchanan@usm.edu

KEYWORDS C₆₀, thiol-ene, photocatalyst

ABSTRACT: A series of thiol-ene (1.1:1 equiv) polymer microbeads (PMBs) were prepared via a high-shear suspension photopolymerization method to explore the physical properties of the networks as a function of composition. 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H, 3H, 5H)-trione (TTT) and pentaerythritol tetrakis (3-mercaptopropionate) (PETMP) PMBs were selected for the synthesis of a heterogeneous photocatalyst. Particle size was characterized using DLS and OM,

and thermal stability and T_g were assessed using TGA and DSC. PMBs produced from higher functionality monomers produce smaller particles, and T_g increased with monomer rigidity. TTT-PETMP PMBs were derivatized with C_{60} to demonstrate the accessibility and reactivity of the residual thiols, successful inclusion of C_{60} as the reactive ene moiety, and overall PMB utility as a scaffold material. Upon capping with C_{60} , the T_g of the composite particles increased significantly. Most importantly, the C_{60} -capped PMBs produced singlet oxygen in direct and indirect chemical assays, and the efficiency did not decrease after recycling.

1. Introduction

The synthesis of spherical polymeric particles and their important role in applications ranging from pharmaceutical and biomedical^[1] to solid-phase synthesis^[2-3], and chromatographic separation techniques^[4-7] have been well documented. Several methods have been employed for the production of polymeric particles; however, heterogeneous polymerization methods such as emulsion/suspension and precipitation/dispersion polymerizations are the most common.^[8-10] Previously reported polymer compositions of polymeric particles include poly(vinyl chloride), polymethacrylate, and polystyrene.^[11] However, recent research interest in the synthesis of polymer microbeads (PMBs) via thiol-ene/yne “click” chemistry has exploded, due in part to the many advantages of thiol-ene “click” reactions.^[12-17] Thiol-ene polymerizations occur rapidly through a step-growth, free-radical, chain-transfer process (Scheme 1), yielding a uniform crosslinked network generally exhibiting good physical, optical, and mechanical properties. Furthermore, thiol-ene reactions are insensitive to molecular oxygen and water, making the thiol-ene reaction compatible for heterogeneous polymerization methods.^[18-19]

Scheme 1. Initiation and propagation steps of the thiol-ene photopolymerization reaction

Although thiol-ene PMBs have been prepared previously, the effect of monomer composition and functionality have not been heavily explored. Durham et al.^[13] and Amato et al.^[17] documented the effect of inhibitor and surfactant concentrations, rate of mixing, and addition of cosolvents on the formation of thiol-ene PMBs. Later, Durham explored the effect of different stabilizing agents on particle size and stability of thiol-ene PMBs.^[14] However, our efforts lie in exploring the effect of monomer composition on the physical properties and size distribution of thiol-ene PMBs prepared using a high-shear method, subsequently selecting a preferred composition for use in a follow-on, surface thiol-ene photoreaction to prepare a heterogeneous photocatalyst. Others have demonstrated the utility of the thiol-ene “click” reaction in surface modification of functionalized silica, iron oxide, and polymer particles^[15, 20-29], however, there are very few examples of thiol-ene PMBs functionalized via a follow-on thiol-ene/yne photoreaction.^[12, 16-17] Herein we describe the derivatization of thiol-ene PMBs with C_{60} to demonstrate the accessibility and reactivity of the residual thiols, successful inclusion of C_{60} fullerene as a reactive ene moiety, and overall thiol-ene PMB utility.

Fullerenes have been chemically linked to various polymeric supports for a host of applications ranging from chromatographic separation techniques to their reported use as a heterogeneous photocatalyst.^[30-31] Heterogeneous catalysis is of growing interest due to the ability to simply recover the catalyst from reaction solutions using simple filtration techniques and recycle the catalyst. In these pursuits, researchers have attached C₆₀ to amine-functionalized supports such as silica, polystyrene, polysiloxane, and dendrimers.^[32-35] However, the C₆₀-amine reaction can be low yielding and is sensitive to oxygen, which is required for singlet oxygen reactions.^[36] Our interest specifically lies in demonstrating the successful capping of thiol-ene PMBs with C₆₀ using the facile thiol-ene click reaction to create a heterogeneous photocatalyst for use in singlet-oxygen mediated reactions

The use of C₆₀ as a photosensitizer to generate singlet oxygen along with C₆₀'s many other remarkable photophysical properties have been well documented.^[33, 35, 37-41] An example energy diagram describing the interaction between excited-state C₆₀ and ground-state molecular oxygen is illustrated in Figure 1. Upon irradiation, excited singlet state C₆₀ is generated and quickly converts to the excited triplet state, from where efficient energy transfer to ground state molecular oxygen results in the formation of singlet oxygen. Once generated, singlet oxygen can be useful in a variety of organic reactions such as the ene reaction and the Diels-Alder reaction. Singlet oxygen can also be generated via the reaction of ozone with triphenylphosphite, hypochlorite oxidations, or hydrogen peroxide; however, the formation of singlet oxygen via energy-transfer from an electronically excited molecule, such as C₆₀, is one of the cleanest and easiest ways to yield singlet oxygen and the related photooxygenated products.^[42-43]

Figure 1. The generation of singlet oxygen via energy-transfer from excited-state C_{60}

The goal of our research is to prepare a series of thiol-ene polymer microbeads (PMBs) using a high-shear suspension photopolymerization method to explore the physical properties of the networks as a function of monomer composition, and from this group select a preferred composition for the synthesis of a singlet oxygen generating heterogeneous photocatalyst. In this effort the influence of monomer composition on the size distribution of the PMBs and the physical properties of the networks are characterized. The availability and reactivity of surface residual thiol groups is demonstrated through successful capping of the PMBs with C_{60} to generate a heterogeneous photocatalyst. Herein, we describe both the synthesis and characterization of the thiol-ene PMBs and the resulting singlet-oxygen generating heterogeneous photocatalyst using a variety of standard techniques.

2. Experimental Section

2.1. Materials

Trimethylolpropane diallyl ether (**TMPDE**) (90%), pentaerythritol allyl ether (**APE**) (triene, 70%; monoene remaining 30%), 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**TTT**) (98%), trimethylolpropane tris (3-mercaptopropionate) (**TMPMP**) (>95%), pentaerythritol tetrakis (3-mercaptopropionate) (**PETMP**) (>95%), chitosan (low molecular weight), acetic acid (>99.7%), toluene (>99.5%), benzene (99%), dichloromethane (>99.5%),

methanol (99.8%), and benzene-d₆ (99.6 % atom D) were obtained from the Sigma Aldrich Chemical Company (St. Louis, MO). Irgacure 651 was purchased from Ciba Specialty Chemicals. C₆₀ Fullerene was obtained from MER corporations. All chemicals were used as received.

2.2. Preparation of Thiol-Ene Polymer Microbeads

Thiol-ene polymer microbeads were prepared via suspension photopolymerization using low molecular weight chitosan as a low-foaming emulsifier. The thiol and ene concentrations were held constant at 1.1:1 mol equiv in the following procedure. The chitosan solution was prepared by mixing 1 g chitosan in 125 mL of a 1% (v/v) acetic acid solution. Irgacure 651 (1 wt % solids) and thiol-ene monomers (10 wt % solids) were added to the chitosan solution and premixed using the homogenizer at 16,000 rpm for 5 min. Following mixing, the solution was transferred to a 200-mL jacketed flask (Tudor Scientific Glass Co.) equipped with a condensor equilibrated to 0 °C. The flask containing the solution was then placed in a rayonet photoreactor containing sixteen 350 nm λ_{max} bulbs, and the solution was irradiated for 1 hr while mixing at 16,000 rpm. The resulting PMBs were filtered using a 0.45 μm polypropylene filter membrane, rinsed with methanol, and vacuum dried at 40 °C for at least 24 hrs.

2.3. Preparation of Fullerene-Capped Thiol-Ene Polymer Microbeads

The fullerene-capped, thiol-ene PMBs were prepared by dispersing 125 mg C₆₀, Irgacure 651 (1 wt %), and 350 mg of the prepared thiol-ene PMBs in 250 mL benzene. The dispersion was sonicated until the C₆₀ was completely dissolved in the benzene, as determined by a resulting purple dispersion. The dispersion was placed in a rayonet photochemical reactor containing sixteen 350 nm λ_{max} bulbs for 3 hrs. The resulting dispersion was filtered using a 0.45

μm polypropylene filter membrane, and the fullerene-capped, thiol-ene PMBs were washed three times with toluene (100 mL) followed by a 10% $\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$ solution (100 mL total) to remove any residuals. The purified fullerene-capped, thiol-ene PMBs were then dispersed in a 100 mL 10% $\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$ solution for 24 hr at room temperature to ensure any unreacted materials were removed before further characterization. After 24 hrs, the sample was re-filtered and dried. The resulting filtrate was colorless.

2.4. Particle Size and FT-IR

Particle size was obtained on the thiol-ene PMB suspension using dynamic light scattering (DLS), which was conducted using a Microtrac S3500 instrument. A refractive index of 1.69 was used for the spherical thiol-ene particles, and a refractive index of 1.33 was used for water. The flow rate was set to 75%. Particle size is reported as mean volume (M_V) and mean number (M_N) diameter, in microns, and standard deviations are reported as the width of the measured particle size distributions. All values were obtained using the Microtrac FLEX software (v10.6.1). Optical microscope images of the PMBs were obtained using a Keyence VHX-600 digital microscope equipped with a 1000x magnification lens to support DLS data. Fourier transform infrared spectroscopy (FT-IR) was performed in the $500\text{--}4000\text{ cm}^{-1}$ range using a Nicolet Nexus 470 FT-IR spectrometer equipped with a diamond crystal ATR accessory.

2.5. Mechanical and Thermal Analysis

The glass transition temperature (T_g) of the PMBs was determined using a TA instruments Q2000 modulated differential scanning calorimetry (DSC). The photochemically cured PMBs (~10 mg) were monitored over the temperature range of -90 to $150\text{ }^\circ\text{C}$ in a heat/cool/heat cycle at a $10\text{ }^\circ\text{C}/\text{min}$ ramp rate. The T_g was obtained from the second heating

cycle. The thermal stability of the prepared PMBs was evaluated using a TA instruments Q500 series thermogravimetric analysis (TGA) instrument by monitoring change in weight as a function of temperature under a controlled atmosphere. The PMBs (~10 mg) were analyzed in aluminum pans over the temperature range of 0-600 °C at a heating rate of 10 °C/min.

2.6. Indirect and Direct Solution Based Singlet Oxygen Studies

Dispersions for the indirect singlet oxygen study were prepared using a 100 mg portion of the fullerene-capped, thiol-ene PMBs in benzene- d_6 solvent (10 mL) followed by sonication to disperse the solids. 2-Methyl-2-butene (0.1 M) and octane (4 mM, internal standard) were added to the sensitizer dispersion and transferred to a 200-mL, jacketed flask (Tudor Scientific Glass Co.) equipped with a circulating chiller equilibrated to 15 °C. The dispersion was irradiated using a rayonet photochemical reactor fitted with sixteen 350 nm λ_{max} bulbs. The dispersion was purged with reagent grade air at a rate of 120 mL/min for 30 min prior to irradiation and continued over the duration of the reaction. Aliquots (0.8 mL) were removed from the reaction vessel via syringe and centrifuged at 10,000 rpm for 1 min to settle any beads that were simultaneously captured. The supernatant was then analyzed using a 400 MHz Bruker NMR. Integration of characteristic NMR peaks for the vinyl hydrogen in the reactant (H_a = 5.2 ppm) and specific alkyl hydrogens in the products (H_b = 4.2 ppm and H_c = 5.8 ppm) were used to calculate percent conversions with time. Any peroxides produced were reduced using a 1 M triphenylphosphine solution prior to waste handling. The fullerene-capped, thiol-ene PMBs were recovered via filtration, rinsed with benzene, and recycled.

The direct singlet oxygen study was performed by adding 1.0 mg of the fullerene-capped, thiol-ene PMBs and 2 mL benzene to a fluorometer cuvette with a septum cap and stir bar. The

sample was sonicated for 5 min until beads were dispersed. The sample was excited at 346 nm, and an emission scan was obtained from 1200-1350 nm. Singlet oxygen was directly detected via the phosphorescence of singlet oxygen at 1270 nm using a Photon Technology International (PTI) FeliX32 InGaAs-TE photodiode with pre-amplifier NIR detector. After each emission scan was obtained, the dispersion was diluted by adding 1000 μL to prepare correlation data. Analogous methods were employed to obtain a dilution series and reference data for comparison for the singlet oxygen generation of pure C_{60} .

3. Results and Discussion

A series of thiol-ene PMBs were prepared via high-shear suspension photopolymerization techniques. The structure-property relationships among thermal, mechanical, and physical properties of PMBs related to monomer composition were explored. Due to the reported high monomer conversion and physical uniformity of thiol-ene networks^[44-45], photocured thiol-ene PMBs prepared from the diverse monomer group in Figure 2 are ideal to investigate how basic features such as rigidity and network density can influence the resulting PMB characteristics, such as particle size and size distributions.^[18, 44, 46]

Figure 2. Chemical structures of monomers used in this study to synthesize thiol-ene polymer microbeads: trimethylolpropane diallyl ether (**TMPDE**), allyl pentaerythritol ether (**APE**), 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H, 3H, 5H)-trione (**TTT**), trimethylolpropane tris (3-mercaptopropionate) (**TMPMP**), and pentaerythritol tetrakis (3-mercaptopropionate) (**PETMP**)

In general, thiol-ene PMBs were prepared by combining a 1.1:1 molar equivalent of thiol and ene functional groups, 1 wt % Irgacure 651 photoinitiator, and low molecular weight chitosan as a low-foaming emulsifier (Scheme 2). Compositions prepared during this study along with characterization results are provided in Table 1. Monomer and chitosan solutions were mixed separately and then combined and homogenized at 16,000 rpm for 5 min prior to irradiation. Following mixing, the solution was placed in a rayonet photoreactor and irradiated for 1 hr at 0 °C with continued mixing at 16,000 rpm. The thermal management for the heat evolved during reaction was mitigated by the low reaction temperature, and the high shear condition was found to yield small, uniform PMBs, which correlates with literature.^[13] Optical microscope images of prepared thiol-ene PMBs are illustrated in Figure 3 and in Supporting Information (Figure S1). All compositions yielded uniform spherical, translucent particles, which produce a bulk white powder after filtering and solvent removal.

Scheme 2. Synthesis of thiol-ene PMBs

Table 1. Monomer composition and primary characterization of prepared PMBs

Sample ID	MV (μm) ^a	MN (μm) ^a	T_g Exp ($^\circ\text{C}$) ^b	T_g Ref ($^\circ\text{C}$)	Thermal degradation onset ($^\circ\text{C}$) ^c	Thermal degradation onset Ref	% char ^d
TMPDE-TMPMP	27 (± 9)	3 (± 6)	-28	-30; Mackey 2012 ^[47]	-	-	-
APE-TMPMP	12 (± 5)	5 (± 3)	-20	-20; Shin 2008 ^[44]	-	-	-
TTT-TMPMP	25 (± 12)	5 (± 2)	20	22, Shin 2008 ^[44]	-	-	-
TMPDE-PETMP	17 (± 5)	3 (± 1)	-22	-19; Durham 2015 ^[15]	-	-	-
APE-PETMP	9 (± 4)	3 (± 1)	-5	-5; Shin 2008 ^[44]	-	-	-
TTT-PETMP	17 (± 6)	4 (± 2)	45	3; Prasath 2010 ^[48] 45; Li 2009 ^[45] -1; Durham 2012 ^[13] 26; Durham 2015 ^[15]	346	-	6
TTT-PETMP film ^e	-	-	45	45; Li 2009 ^[45]	353	-	8
C ₆₀ -Capped TTT-PETMP ^e	17 (± 4)	4 (± 2)	58	-	342	-	9
Chitosan	-	-	-	-	258	255; Arora 2011 ^[49]	36

^a MV = mean average diameter of the volume distribution and MN = mean average diameter of the number distribution and standard deviations obtained from the combined DLS measurements of 6 sample batches; ^b T_g obtained from DSC measurements; ^c calculated from TGA plots as the temperature corresponding to 10% mass loss; literature references for T_g and thermal degradation onset temperatures are provided for comparison; ^d % char is reported as the mass remaining above 600 $^\circ\text{C}$ from TGA analysis; ^e control thiol-ene film and C₆₀-capped PMBs used in photocatalytic studies.

Figure 3. Optical microscope images of prepared thiol-ene PMBs at 1000x magnification with scale bar set to 50 μm

Particle size information was obtained for the thiol-ene PMBs using dynamic light scattering techniques. Volume and number-weighted averages are reported in Table 1, where M_V represents the mean diameter of the volume distribution and is more sensitive to the presence of large particles and M_N is the population average particle size. DLS provided interesting results, as shown in Figure 4 (also Supporting Information, Figure S2). At a constant shear rate and emulsifier concentration, monomer composition was found to affect particle size and size distributions, with a M_V and M_N range of 9-27 and 3-5 μm in diameter. PMBs prepared using TMPMP (F=3) thiol monomer yielded larger PMBs than those prepared with PETMP (F=4), which was attributed to the increased functionality and resulting cross-link density. Analogous results were observed in the incorporation of the TMPDE (F=2) flexible ene monomer, which

yielded larger particles than APE ($F=3$). Recent reports by Durham et. al.^[15] and Li et. al.^[50] suggest that other factors such as concentration, polarity, monomer viscosity, and surfactant may contribute to polymer particle size variations.^[15, 50] A good correlation was found between DLS data and optical microscope images of PMBs.

Figure 4. DLS analysis of thiol-ene PMB samples prepared using TMPMP (F=3) and PETMP (F=4) with (a) TMPDE (F=2), (b) APE (F=3), and (c) TTT (F=3)

Differential scanning calorimetry (DSC) obtained glass transition temperatures, T_g 's, combined with fourier transform infrared spectroscopy (FT-IR) analysis of PMB networks support a high conversion of monomers, representing essentially completely cured networks. FT-IR spectrums were acquired on prepared PMBs, revealing the disappearance of the thiol (2500 cm^{-1}) and ene (1600 cm^{-1}) monomer peaks (Supporting Information Figure S3) upon polymerization. T_g 's from DSC measurements are reported in Table 1 and Figure 5 and are consistent with PMB chemical composition. In general, T_g 's were found to correlate well with literature values where available. Interestingly, the high-shear photopolymerization method reported herein yields TTT-PETMP PMBs possessing the T_g of the analogous bulk material in contrast to reports of other methods ($-1\text{ }^{\circ}\text{C}$ and $26\text{ }^{\circ}\text{C}$).^[13, 15] A general and expected trend of increasing T_g with monomer rigidity exists. Moreover, a refining of the particle size distribution is apparent with increasing T_g , where the number of particles at a given size increases and the distribution narrows.

Figure 5. DSC analysis of prepared PMBs using monomer compositions from Figure 1 and after capping TTT-PETMP PMBs with C₆₀

Thermal stability of PMBs was analyzed using TGA, which monitors sample weight loss as a function of time and temperature. Representative TGA plots are provided in Figure 6, including TTT-PETMP PMBs, a photocured TTT-PETMP film, chitosan for comparison, and C₆₀-capped TTT-PETMP PMBs. Thermal degradation onset temperatures are defined as the temperature at 10% mass loss (allowing for water loss from chitosan) and are reported in Table 1. For the TTT-PETMP PMBs and a control TTT-PETMP film prepared through standard methods, the thermal degradation onset temperatures were determined to be 346 and 353 °C, respectively, indicating a slightly elevated thermal stability for the bulk material. There is no indication of chitosan incorporation into prepared PMBs through FT-IR, TGA, or DSC results. Chitosan is known to both absorb water and produce char as indicated by the mass lost at T<100 °C and remaining at higher temperatures.^[49]

Figure 6. (a) TGA analysis of prepared PMBs and controls: a TTT-PETMP film radiation cured at 350 nm for 5 min, pure chitosan, TTT-PETMP PMBs, and C₆₀-capped PMBs; (b) expanded to reflect thermal degradation onset temperatures

The surface of TTT-PETMP PMBs was derivatized with C₆₀ - in a follow-on, thiol-ene reaction - to (1) demonstrate the accessibility and reactivity of the residual thiols and (2) illustrate thiol-ene PMB utility as a scaffold for supported photocatalysts. Of the PMBs produced, the TTT-PETMP PMBs were chosen as the preferred composition due to the increased sample uniformity and higher T_g . Another outcome of this work was the demonstration that C₆₀ may serve as the reactive ene in a typical thiol-ene reaction, despite its reputation as an electron-

deficient polyene. Therefore, our approach for capping C_{60} to thiol-ene PMBs is to perform the post-polymerization surface thiol-ene reaction described in Scheme 3. The C_{60} -capped, TTT-PETMP PMBs were prepared by dispersing TTT-PETMP PMBs in a C_{60} solution containing 1 wt % Irgacure 651 photoinitiator and irradiating for 3 hrs in the rayonet photoreactor, which results in the isolation of a brick-red powder, Supporting Information Figure S4. Capping the thiol-ene PMBs with C_{60} did not affect the particle size of the PMBs as observed from the DLS data reported in Table 1. PMBs with an average diameter in the 20 μm -range result, leading to a photocatalyst with a balance of ease of isolation and high catalytic surface area, i.e. compared to the amine-coated polystyrene beads (150-300 μm) prepared by Jensen et. al.^[33] In general smaller beads having comparable surface coverage of photocatalyst would be expected to be more reactive due to the increased surface area.

Scheme 3. Preparation of C_{60} -capped thiol-ene PMBs

Capping of the TTT-PETMP PMBs with C_{60} was found to have a dramatic impact on the glass transition temperatures as determined by DSC (Figure 5) and thermal degradation onset temperatures using TGA (Figure 6). An expected increase in T_g is observed with the incorporation of C_{60} , from 45 $^{\circ}\text{C}$ to 58 $^{\circ}\text{C}$. A 13 $^{\circ}\text{C}$ increase in T_g between the unmodified and modified PMBs is significant and supports successful capping of the thiol-ene PMBs via the creation of a more heavily crosslinked rigid network. Furthermore, for the C_{60} -capped TTT-PETMP PMBs, the thermal degradation onset temperature was determined to be 342 $^{\circ}\text{C}$,

indicating a slightly lower thermal stability upon capping the TTT-PETMP PMB with C_{60} when compared to controls and suggesting that the S- C_{60} bonds are the first to break during thermal decomposition process, thereby liberating C_{60} . A 3% increase in the % char, determined from TGA (Table 1) was observed upon capping the PMBs with C_{60} , suggesting that approximately 3% of the total mass of the C_{60} -capped PMBs corresponds to bound C_{60} . This 3% value correlates with the mass percent of C_{60} added to the PMBs during derivatization, as determined by mass balance studies (Supporting Information, Table S1).

To investigate the ability of the C_{60} -capped PMBs to photochemically generate singlet oxygen, direct and indirect solution based assays were performed. Direct solution based assays were performed using a fluorometer equipped with a NIR detector to directly detect the phosphorescence of singlet oxygen at 1270 nm produced from exciting a catalytic amount of C_{60} -capped PMBs at 346 nm (Figure 7 and Supporting Information Figure S5). Analogous experiments were performed with C_{60} and C_{60} -capped PMBs to obtain normalized responses leading to a C_{60} equivalent correlation mass. The mass ratio of C_{60} -capped PMBs and C_{60} yielding analogous singlet oxygen responses increases linearly, with pure C_{60} producing the most singlet oxygen as expected, Figure 8. Considering that ~3 wt% of the C_{60} -capped PMBs can be attributed to C_{60} , this study would have us conclude that the C_{60} chemically bound to the PMBs is approximately half as active as free C_{60} , attributable to the loss of conjugation caused by the surface-binding event affecting the energy levels of the orbitals involved and reduced access to the C_{60} within the network.

Figure 7. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C₆₀ and C₆₀-capped PMBs (as prepared and recovered from indirect solution based assay) at 346 nm

Figure 8. Linear plot correlating the mass of C₆₀ and the mass of C₆₀-capped PMBs yielding analogous singlet oxygen responses via direct solution based assays

The indirect solution based assay was performed using a procedure originally reported by Tagmatarchis et al.^[51] and modified by McCluskey et. al.^[38] In this process, evidence for singlet oxygen generation is detected by the photooxygenation of 2-methyl-2-butene to the allylic hydroperoxides shown in Scheme 4.

Scheme 4. Photooxygenation of 2-Methyl-2-butene

A catalytic amount of C_{60} -capped, thiol-ene PMBs were dispersed in a 0.1 M 2-methyl-2-butene solution. As observed by McCluskey et al., this reaction produced ~ 1:1 ratio of the two hydroperoxide products, **1** and **2**, with each possessing a well-resolved and unique hydrogen chemical shift (H_a , δ 5.2; H_b , δ 4.2; H_c δ 5.8) in the 1H -NMR, corresponding to the area of one hydrogen and leading to the ready analysis of reaction mixtures using integration of 1H -NMR peak areas. The reaction was monitored by taking aliquots with time. Figure 9 and Table S2 in the Supporting Information summarizes the solution photochemistry of the C_{60} -capped PMBs for the photooxygenation of 2-methyl-2-butene via in situ generated singlet oxygen. In the absence of the C_{60} -capped TTT-PETMP PMBs, no photooxygenated products were observed; however, in the presence of the C_{60} -capped PMBs, 98% of 2-methyl-2-butene was converted to its photooxygenated products within 90 min. The C_{60} -capped PMBs were recovered and reused in the direct assay, where no reduction of singlet oxygen production was observed, supporting the use of the C_{60} -capped PMBs as a heterogeneous singlet-oxygen generating photocatalyst.

Figure 9. Example ^1H -NMR analysis of the % conversion of 2-methyl-2-butene to its photooxygenated products, as a function of irradiation time, produced from singlet oxygen generated from the C_{60} -capped PMBs

4. Conclusion

A series of thiol-ene PMBs were prepared via suspension photopolymerization techniques under high shear with chitosan as a low foaming surfactant to explore the thermal, mechanical, and physical properties of the resulting PMBs as a function of monomer composition. Particle size of the thiol-ene PMBs was determined using DLS, and it was observed that monomer composition does affect particle size, with smaller particles produced from higher functionality monomers. Furthermore, it was observed that T_g increased upon increasing monomer rigidity and resulted in particles with a more uniform size distribution. The thermal stability of the thiol-ene PMBs was determined using TGA, which indicated a slightly elevated thermal stability for the bulk material and supports the lack of chitosan incorporation during photopolymerization.

The PMBs prepared from TTT-PETMP monomers resulted in PMBs with the highest T_g and sample uniformity and were therefore selected for derivatization with C_{60} to demonstrate the accessibility and reactivity of the residual thiols and general PMB utility as a scaffold for supported photocatalysts. Following capping the TTT-PETMP PMBs with C_{60} , direct and indirect solution based assays were performed to support the ability of the C_{60} -capped PMBs to photochemically generate singlet oxygen. From analogous experiments using both pure C_{60} and C_{60} -capped PMBs in a direct solution based assay, a C_{60} mass equivalence was determined for the C_{60} -capped PMBs, leading to the conclusion that the efficiency of C_{60} -capped PMBs in generating singlet oxygen is modestly suppressed relative to untethered C_{60} . However, the C_{60} -capped PMBs are readily recovered from reaction vessels using simple filtration techniques, and the efficiency of the recycled beads to generate singlet oxygen was not diminished when compared to the as-prepared sample. An overriding conclusion of this work is that the facile preparation of uniform thiol-ene PMBs using a high-shear method and successful thiol-ene PMB use as a scaffolding material to attach a singlet-oxygen generating photocatalyst has been achieved.

Acknowledgments

Financial support for this work was provided through the NSF GK-12 Program-University of Southern Mississippi, “Connections in the Classroom: Molecules to Muscles” award #0947944, the National Science Foundation (NSF) CAREER program award #CHE-0847481, and the NSF instrumentation grant #CHE-0840390.

References

- [1] L. Liu, R. Spindler, S. J. Urbanec, R. Vakili, A. K. Sengupta, K. Cureton, AMCOL International Corporation, USA . **2008**, p. 37 pp.
- [2] A. R. Vaino, K. D. Janda, *J. Comb. Chem.* **2000**, 2, 579-596.
- [3] M. Orzaez, P. Mora, L. Mondragon, E. Perez-Paya, M. J. Vicent, *Int. J. Pept. Res. Ther.* **2007**, 13, 281-293.
- [4] W.-H. Li, H. D. H. Stover, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, 36, 1543-1551.
- [5] I. Bunia, V. Neagu, C. Luca, *React. Funct. Polym.* **2006**, 66, 871-883.
- [6] N. Fontanals, R. M. Marcé, P. A. G. Cormack, D. C. Sherrington, F. Borrull, *J. Chromatogr.* **2008**, 1191, 118-124.
- [7] N. Miletić, Z. Vuković, A. Nastasović, K. Loos, *J. Mol. Catal. B: Enzym.* **2009**, 56, 196-201.
- [8] M. T. Gokmen, F. E. Du Prez, *Prog. Polym. Sci.* **2012**, 37, 365-405.
- [9] P. J. Dowding, B. Vincent, *Colloids Surf., A* **2000**, 161, 259-269.
- [10] G. L. Li, H. Mohwald, D. G. Shchukin, *Chem. Soc. Rev.* **2013**, 42, 3628-3646.
- [11] B. Brooks, *Chem. Eng. Technol.* **2010**, 33, 1737-1744.
- [12] M. T. Gokmen, J. Brassinne, R. A. Prasath, F. E. Du Prez, *Chem. Commun.* **2011**, 47, 4652-4654.
- [13] O. Z. Durham, S. Krishnan, D. A. Shipp, *ACS Macro Lett.* **2012**, 1, 1134-1137.
- [14] O. Z. Durham, D. A. Shipp, *Polymer* **2014**, 55, 1674-1680.
- [15] O. Z. Durham, H. R. Norton, D. A. Shipp, *RSC Adv.* **2015**, 5, 66757-66766.
- [16] D. N. Amato, D. V. Amato, J. Narayanan, B. R. Donovan, J. R. Douglas, S. E. Walley, A. S. Flynt, D. L. Patton, *Chem Commun (Camb)* **2015**, 51, 10910-10913.
- [17] D. V. Amato, D. N. Amato, A. S. Flynt, D. L. Patton, *Polym. Chem.* **2015**, 6, 5625-5632.
- [18] C. E. Hoyle, T. Y. Lee, T. Roper, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, 42, 5301-5338.
- [19] C. E. Hoyle, A. B. Lowe, C. N. Bowman, *Chem Soc Rev* **2010**, 39, 1355-1387.
- [20] Y. Kotsuchibashi, M. Ebara, T. Aoyagi, R. Narain, *Polym. Chem.* **2012**, 3, 2545-2550.
- [21] T. B. Mai, T. N. Tran, M. Rafiqul Islam, J. M. Park, K. T. Lim, *Journal of Materials Science* **2013**, 49, 1519-1526.
- [22] B. Korthals, M. C. Morant-Miñana, M. Schmid, S. Mecking, *Macromolecules* **2010**, 43, 8071-8078.
- [23] V. S. Khire, T. Y. Lee, C. N. Bowman, *Macromolecules* **2008**, 41, 7440-7447.
- [24] L. A. Connal, C. R. Kinnane, A. N. Zelikin, F. Caruso, *Chemistry of Materials* **2009**, 21, 576-578.
- [25] L. Cheng, X. Zhang, Z. Zhang, H. Chen, S. Zhang, J. Kong, *Talanta* **2013**, 115, 823-829.

- [26] M. Taghavikish, S. Subianto, N. K. Dutta, N. R. Choudhury, *ACS Appl Mater Interfaces* **2015**, 7, 17298-17306.
- [27] R. D. Rutledge, C. L. Warner, J. W. Pittman, R. S. Addleman, M. Engelhard, W. Chouyyok, M. G. Warner, *Langmuir* **2010**, 26, 12285-12292.
- [28] A. Pfaff, A. Schallon, T. M. Ruhland, A. P. Majewski, H. Schmalz, R. Freitag, A. H. Muller, *Biomacromolecules* **2011**, 12, 3805-3811.
- [29] C. Kuttner, P. C. Maier, C. Kunert, H. Schlaad, A. Fery, *Langmuir* **2013**, 29, 16119-16126.
- [30] K. I. Guhr, M. D. Greaves, V. M. Rotello, *J. Am. Chem. Soc.* **1994**, 116, 5997-5998.
- [31] B. Nie, K. Hasan, M. D. Greaves, V. M. Rotello, *Tetrahedron Lett.* **1995**, 36, 3617-3618.
- [32] T. Hino, T. Anzai, N. Kuramoto, *Tetrahedron Letters* **2006**, 47, 1429-1432.
- [33] A. W. Jensen, C. Daniels, *J. Org. Chem.* **2003**, 68, 207-210.
- [34] A. W. Jensen, USA . **2005**, pp. 20 pp., Cont.-in-part of U.S. Ser. No. 126,308.
- [35] A. W. Jensen, B. S. Maru, X. Zhang, D. K. Mohanty, B. D. Fahlman, D. R. Swanson, D. A. Tomalia, *Nano Lett* **2005**, 5, 1171-1173.
- [36] A. Hirsch, *Chemistry of the Fullerenes*, Thieme, **1994**.
- [37] J. W. Arbogast, A. P. Darmanyan, C. S. Foote, F. N. Diederich, R. L. Whetten, Y. Rubin, M. M. Alvarez, S. J. Anz, *J. Phys. Chem.* **1991**, 95, 11-12.
- [38] D. M. McCluskey, T. N. Smith, P. K. Madasu, C. E. Coumbe, M. A. Mackey, P. A. Fulmer, J. H. Wynne, S. Stevenson, J. P. Phillips, *ACS Appl. Mater Inter.* **2009**, 1, 882-887.
- [39] V. A. Nadtochenko, I. V. Vasil'ev, N. N. Denisov, I. V. Rubtsov, A. S. Lobach, A. P. Moravskii, A. F. Shestakov, *J. Photochem. Photobiol., A* **1993**, 70, 153-156.
- [40] R. Sun, C. Jin, X. Zhang, Z. Cai, *Wuli* **1994**, 23, 83-87.
- [41] C. S. Foote, *Top. Curr. Chem.* **1994**, 169, 347-363.
- [42] C. S. Foote, S. Wexler, W. Ando, *Tetrahedron Letters* **1965**, 6, 4111-4118.
- [43] J. R. Williams, G. Orton, L. R. Unger, *Tetrahedron Letters* **1973**, 14, 4603-4606.
- [44] J. Shin, S. Nazarenko, C. E. Hoyle, *Macromolecules* **2008**, 41, 6741-6746.
- [45] Q. Li, H. Zhou, C. E. Hoyle, *Polymer* **2009**, 50, 2237-2245.
- [46] T. M. Roper, C. A. Guymon, E. S. Jonsson, C. E. Hoyle, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, 42, 6283-6298.
- [47] N. M. Mackey, Ph.D. Dissertation thesis, The Univeristy of Southern Mississippi, Hattiesburg, MS, May 2012 **2012**.
- [48] R. A. Prasath, M. T. Gokmen, P. Espeel, F. E. Du Prez, *Polym. Chem.* **2010**, 1, 685.
- [49] S. Arora, S. Lal, S. Kumar, M. Kumar, M. Kumar, *Arch. Appl. Sci. Res.* **2011**, 3, 188-201.
- [50] B.-z. Li, L.-j. Wang, D. Li, Y. L. Chiu, Z.-j. Zhang, J. Shi, X. D. Chen, Z.-h. Mao, *Journal of Food Engineering* **2009**, 92, 255-260.
- [51] N. Tagmatarchis, H. Shinohara, *Org. Lett.* **2000**, 2, 3551-3554.