Preparation and Characterization of Singlet-Oxygen Generating Thiol-ene Networks Containing Fullerene and Metallofullerene Derivatives

Emily Matthews Barker
University of Southern Mississippi

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PREPARATION AND CHARACTERIZATION OF SINGLET-OXYGEN
GENERATING THIOL-ENE NETWORKS CONTAINING FULLERENE
AND METALLOFULLERENE DERIVATIVES

by

Emily Matthews Barker

A Dissertation
Submitted to the Graduate School
and the Department of Chemistry and Biochemistry
at The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

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August 2016
This work explores the derivatization of C₆₀ and Sc₃N@C₈₀ with S-, P-, and C-centered radicals, and is the first exploration into the functionalization of Sc₃N@C₈₀ with sulfur and phosphorous. The number of addends bound to C₆₀, as a function of reaction time and molar ratios as well as structure-property relationships including thermal stability, solubility, and singlet oxygen generation were explored. Fullerene derivatives exhibiting enhanced solubility were incorporated into two different thiol-ene polymer matrices at varying thiol-ene monomer concentrations (1:1 or 1:0.75 molar equivalents) and at different C₆₀ loadings (0, 1, 5, 10, and 20 wt %). The degree of incorporation and the dispersibility of prepared fullerenes within the thiol-ene matrix and the effect on the thermal and mechanical properties and singlet oxygen generation of the fullerene-containing thiol-ene films as a function of monomer identity and C₆₀ loading were explored, along with the characterization of photooxidized products produced upon generating singlet oxygen.

The ability of C₆₀ to produce singlet oxygen was utilized to prepare a singlet-oxygen generating heterogenous photocatalyst. A series of thiol-ene polymer microbeads (PMBs), containing residual thiols on the surface, were prepared via high-shear suspension photopolymerization, and the thermal, mechanical, and physical properties of
the networks, as a function of monomer composition, were explored. PETMP:TTT thiolene PMBs possessing the highest $T_g$ (45 °C) and greatest sample uniformity were chosen for derivatization with $C_{60}$ in a surface thiol-ene reaction to demonstrate the accessibility and reactivity of the residual thiols, the successful inclusion of $C_{60}$ as the reactive ene moiety, and overall PMB utility as a scaffold for supported photocatalysts.
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Last but not least, I would like to thank my friends and family for their support, and a special thanks to my husband, Trae Barker, and my mother, Paula Matthews, for their love and understanding during this long journey.
DEDICATION

This work is dedicated to my wonderful friends and family. In particular, I would like to thank my parents, David and Paula Matthews, my grandparents, Don and Rachel Matthews, my husband, Trae Barker, and his Parents, Edward and Denise Barker, who have always encouraged and supported my decisions.
TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................ ii

ACKNOWLEDGMENTS .................................................................................................................. iv

DEDICATION .................................................................................................................................... v

LIST OF TABLES ............................................................................................................................ ix

LIST OF ILLUSTRATIONS ............................................................................................................. xi

LIST OF SCHEMES ........................................................................................................................ xvii

LIST OF ABBREVIATIONS ............................................................................................................. xviii

CHAPTER I - INTRODUCTION ...................................................................................................... 1

CHAPTER II - SYNTHESIS AND CHARACTERIZATION OF NOVEL FULLERENE DERIVATIVES ................................................................. 11

  Introduction ..................................................................................................................................... 11

  Materials, Method, and Characterization ...................................................................................... 15

    Materials ...................................................................................................................................... 15

    Method ........................................................................................................................................ 15

      Partial oxidation of butyl 3-mercaptopropionate (BuMP) to disulfide (S-S) ...... 15

      Synthesis of thiolated C_{60} and Sc_{3}N@C_{80} fullerene derivatives ............................... 16

      Synthesis of C_{60}- and Sc_{3}N@C_{80}(TMB-PPO) fullerene derivatives ...................... 17

    Characterization ....................................................................................................................... 19

  Results and Discussion .................................................................................................................. 21

  vi
CHAPTER III - INCORPORATION OF FULLERENE DERIVATIVES INTO THIOL-ENE POLYMER MATRICES ........................................................................................................ 46

Introduction ............................................................................................................ 46

Materials, Method, and Characterization .................................................................. 48

Materials .................................................................................................................. 48

Method ...................................................................................................................... 48

Synthesis of C₆₀- and Sc₃N@C₈₀(TMB-PPO) thiol-ene films .................................. 48

Characterization ....................................................................................................... 49

Results and Discussion ............................................................................................ 50

CHAPTER IV - PREPARATION AND CHARACTERIZATION OF THIOL-ENE POLYMER MICROBEADS AND THEIR USE AS A HETEROGENEOUS PHOTOCATALYST VIA C₆₀-CAPPING ........................................................................................................ 73

Introduction ............................................................................................................ 73

Materials, Method, and Characterization .................................................................. 75

Materials .................................................................................................................. 75

Method ...................................................................................................................... 76

Preparation of thiol-ene polymer microbeads (PMBs) ............................................. 76

Preparation of C₆₀- capped thiol-ene PMBs .............................................................. 76

Characterization ....................................................................................................... 77

Results and Discussion ............................................................................................ 79
CHAPTER V - CONCLUSION ................................................................. 100

APPENDIX .......................................................................................... 105

REFERENCES ..................................................................................... 111
LIST OF TABLES

Table 1 Lifetime of Singlet Oxygen in Various Solvents .......................................................... 5
Table 2 Irradiation Time versus the Number of BuMP Addends Attached to the Fullerene Cage ........................................................................................................................................... 26
Table 3 Mole Ratios of Fullerene and TMP-PPO Versus the Number of Addends Bound to the Fullerene Cage ........................................................................................................................................... 30
Table 4 TGA Results of Prepared Fullerene Derivatives .................................................................. 33
Table 5 Solubility Studies of Fullerene Derivatives in Common Solvents at 20 °C Reported in mg mL$^{-1}$ ...................................................................................................................................................... 34
Table 6 Efficiency of Singlet Oxygen Produced from Pure C$_{60}$ Versus Fullerene Derivatives via Direct Detection ........................................................................................................................................................................ 36
Table 7 Frequencies (cm$^{-1}$) of Relevant Infrared Absorption Bands of C$_{60}$(BuMP)$_4$ and Sc$_3$N@C$_{80}$(BuMP)$_7$ Derivatives ........................................................................................................................................................................ 39
Table 8 Frequencies (cm$^{-1}$) of Relevant Infrared Absorption Bands of C$_{60}$(TMB-PPO)$_5$ and Sc$_3$N@C$_{80}$(TMB-PPO)$_3$ Derivatives ........................................................................................................................................................................ 41
Table 9 Sample Compositions of C$_{60}$(TMB-PPO)$_5$ Thiol-Ene Films ............................................. 53
Table 10 Summary of Prepared C$_{60}$(TMB-PPO)$_5$ Thiol-Ene Films ............................................... 56
Table 11 Thermal and Mechanical Properties of Prepared C$_{60}$(TMB-PPO)$_5$ Thiol-Ene Films ........................................................................................................................................................................ 59
Table 12 Monomer Composition and Primary Characterization of Prepared PMBs ......... 81
Table 13 TGA Data of Prepared PETMP:TTT PMBs Compared to a PETMP:TTT Film and Pure Chitosan ................................................................................................................................................................. 88
Table 14 Mass Balance Studies of C$_{60}$-Capped Thiol-Ene PMBs ................................................. 94
Table 15 Percent Conversion of 2M2BE as a Function of Irradiation Time from the $^1$H-NMR Analysis of Photoxygenation of 2M2BE Using C$_{60}$-Capped PMBs.......................... 98
LIST OF ILLUSTRATIONS

Figure 1. Comparison of fullerenes, metallofullerenes, and metallic nitride fullerenes. ... 1

Figure 2. Energy level diagram of singlet oxygen generation by excited-state C_{60}. ......... 4

Figure 3. Intramolecular hydrogen bonding between structures of general thiols used in thiol-ene reactions. ................................................................. 10

Figure 4. $^1$H-NMR of BuMP monomer (top) and BuMP/S-S (bottom)........................ 24

Figure 5. TGA graph showing the thermal decomposition of C_{60} and C_{60}(BuMP)_x derivatives. ................................................................. 27

Figure 6. TGA graph showing the thermal decomposition of Sc_{3}N@C_{80} and Sc_{3}N@C_{80}(BuMP)_7 derivatives. ......................................................... 27

Figure 7. $^1$H-NMR of BuMP/S-S (top) and recovered BuMP/S-S (bottom)................ 28

Figure 8. TGA graph comparing the thermal decomposition of pure C_{60}, TMB-PPO, and C_{60}(TMB-PPO)_x derivatives. ................................................................. 31

Figure 9. TGA graph comparing decomposition of pure Sc_{3}N@C_{80}, TMB-PPO, and Sc_{3}N@C_{80}(TMB-PPO)_3 derivative. ................................................................. 31

Figure 10. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C_{60} and C_{60}(TMB-PPO)_5 at $\lambda_{ex} = 346$ nm. ......................... 36

Figure 11. FT-IR spectrum of C_{60}(BuMP)_4 and BuMP starting material. ................. 38

Figure 12. FT-IR spectrum of Sc_{3}N@C_{80}(BuMP)_7 and BuMP starting material......... 38

Figure 13. FT-IR spectrum of C_{60}(TMB-PPO)_5 and TMB-PPO starting material. ....... 40

Figure 14. FT-IR spectrum of Sc_{3}N@C_{80}(TMB-PPO)_3 and TMB-PPO starting material. ................................................................. 40
Figure 15. MALDI spectrum of C₆₀ derivatives (left) and Sc₃N@C₈₀ derivatives (right).

............................................................. 42

Figure 16. MALDI isomer distribution of C₆₀(TMB-PPO)₅.

............................................................. 43

Figure 17. ¹H-NMR of TMB-PPO (top) and C₆₀(TMB-PPO)₅ (bottom).

............................................................. 44

Figure 18. Monomers used in the synthesis of fullerene containing thiol-ene films.

............................................................. 51

Figure 19. Images of thiol-ene films containing (a) 0%, (b) 1%, (c) 5%, (d) 10%, and (e) 20% C₆₀.

............................................................. 54

Figure 20. Side-by-side comparison of 1 wt % C₆₀ incorporated into a thiol-ene matrix using pure C₆₀ (left) and C₆₀(TMB-PPO)₅ (right).

............................................................. 55

Figure 21. TGA showing thermal stability of TMPMP:TMPDE-0.75 films.

............................................................. 58

Figure 22. TGA showing thermal stability of TMPMP:TMPDE-0.75 films containing 1 wt % C₆₀ and 1.5 wt % Sc₃N@C₈₀.

............................................................. 58

Figure 23. DSC graph of (a) PETMP:TTT-1; (b) PETMP:TTT-0.75; (c) TMPMP:TMPDE-1; and (d) TMPMP:TMPDE-0.75 films.

............................................................. 61

Figure 24. Capacitance graph of (a) PETMP:TTT-1; (b) PETMP:TTT-0.75; (c) TMPMP:TMPDE-1; and (d) TMPMP:TMPDE-0.75 films.

............................................................. 62

Figure 25. Capacitance comparison graph of PETMP:TTT-1; PETMP:TTT-0.75; TMPMP:TMPDE-1; and TMPMP:TMPDE-0.75 films.

............................................................. 63

Figure 26. TEM images of PETMP:TTT-1-1 films at low (left) and high (right) magnifications.

............................................................. 64

Figure 27. TEM images of PETMP:TTT-1-10 films at low (left) and high (right) magnifications.

............................................................. 64
Figure 28. TEM images of PETMP:TTT-0.75-1 films at low (left) and high (right) magnifications ................................................................. 64

Figure 29. TEM images of PETMP:TTT-0.75-10 films at low (left) and high (right) magnifications ........................................................................................................................................................................................................... 65

Figure 30. TEM images of TMPMP:TMPDE-1-1 films at low (left) and high (right) magnifications ........................................................................................................................................................................................................... 65

Figure 31. TEM images of TMPMP:TMPDE-1-10 films at low (left) and high (right) magnifications ........................................................................................................................................................................................................... 65

Figure 32. TEM images of TMPMP:TMPDE 0.75-1 films at low (left) and high (right) magnifications ........................................................................................................................................................................................................... 66

Figure 33. TEM images of TMPMP:TMPDE-0.75-10 films at low (left) and high (right) magnifications ........................................................................................................................................................................................................... 66

Figure 34. TEM images of TMPMP:TMPDE-0.75-1.5 Sc$_3$N@C$_{80}$ films at low (left) and high (right) magnifications. ........................................................................................................................................................................................................... 66

Figure 35. Phosphorescence emission spectrum of singlet oxygen generated from TMPMP:TMPDE-0.75 fullerene containing films ( $\lambda_{ex} = 433$ nm) ........................................................................................................................................................................................................... 67

Figure 36. Images of TMPMP:TMPDE-1 films prepared on IR salt plates before (top) and after (bottom) 4 hrs UV irradiation with increasing C$_{60}$ loadings of 0, 1, 5, and 10 % from left to right ........................................................................................................................................................................................................... 67

Figure 37. FT-IR spectrum of C$_{60}$(TMB-PPO)$_5$ containing TMPMP-TMPDE-1 films between 4000-2500 cm$^{-1}$ with increasing C$_{60}$ loading from 0, 1, 5, and 10 % from left to right ........................................................................................................................................................................................................... 69
Figure 38. FT-IR spectrum of C_{60}(TMB-PPO)_{5} containing TMPMP-TMPDE-1 films between 1800-1550 cm\(^{-1}\) with increasing C\(_{60}\) loading from 0, 1, 5, and 10 \% from left to right. ................................................................. 70

Figure 39. FT-IR spectrum of C_{60}(TMB-PPO)_{5} containing TMPMP-TMPDE-1 films between 1500-500 cm\(^{-1}\) with increasing C\(_{60}\) loading from 0, 1, 5, and 10 \% from left to right. ................................................................. 70

Figure 40. Structure of monomers used to synthesize thiol-ene PMBs. .................. 80

Figure 41. Optical microscope images of TMPMP:TMPDE thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm. ................................................................. 82

Figure 42. Optical microscope images of TMPMP:APE thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm. ................................................................. 82

Figure 43. Optical microscope images of TMPMP:TTT thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm. ................................................................. 82

Figure 44. Optical microscope images of PETMP:TMPDE thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm. ................................................................. 83

Figure 45. Optical microscope images of PETMP:APE thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm. ................................................................. 83

Figure 46. Optical microscope images of PETMP:TTT thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm. ................................................................. 83

Figure 47. DLS data of the thiol-ene PMBs prepared using TMPMP and PETMP thiol monomers with TMPDE. ................................................................. 84

Figure 48. DLS data of the thiol-ene PMBs prepared using TMPMP and PETMP thiol monomers with APE. ................................................................. 84
Figure 49. DLS data of the thiol-ene PMBs prepared using TMPMP and PETMP thiol monomers with TTT ................................................................. 85

Figure 50. FT-IR spectrum of thiol-ene PMBs prepared using TMPMP thiol monomer with TMPDE, APE, and TTT ene monomers................................................................. 86

Figure 51. FT-IR spectrum of thiol-ene PMBs prepared using PETMP thiol monomer with TMPDE, APE, and TTT ene monomers................................................................. 87

Figure 52. DSC graphs of the prepared thiol-ene PMBs showing the change in \( T_g \) upon varying monomer composition. ................................................................................... 88

Figure 53. TGA graph of the prepared PETMP:TTT PMBs compared to a photocured PETMP:TTT film and pure chitosan. ................................................................. 90

Figure 54. FT-IR comparing characteristic peaks of the prepared PETMP:TTT PMBs to chitosan. ................................................................................... 90

Figure 55. Image highlighting visible color change (a) before and (b) after capping the PETMP:TTT PMBs with \( C_{60} \). ................................................................................... 92

Figure 56. DLS data of the \( C_{60} \)-capped PMBs and the PETMP:TTT PMBs. .................... 93

Figure 57. DSC graph of the \( C_{60} \)-capped PMBs and the PETMP:TTT PMBs. ............... 93

Figure 58. TGA graph of the \( C_{60} \)-capped PMBs and the PETMP:TTT PMBs. ............... 94

Figure 59. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of \( C_{60} \) and \( C_{60} \)-capped PMBs (as prepared and recovered from indirect solution based assay) at \( \lambda_{ex} = 346 \) nm................................................................................... 95

Figure 60. Linear plot correlating the mass of \( C_{60} \) and the mass of \( C_{60} \)-capped PMBs yielding analogous singlet oxygen responses via direct solution based assays. ............ 96
Figure 61. Example $^1$H-NMR analysis of the % conversion of 2M2BE to its photooxygenated products, as a function of irradiation time, produced from singlet oxygen generated from the C$_{60}$-capped PMBs................................................................. 98

Figure A1. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C$_{60}$ and C$_{60}$(BuMP)$_4$ at $\lambda_{ex} = 346$ nm...................................... 105

Figure A2. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C$_{60}$ and C$_{60}$(TMB-PPO)$_2$ at $\lambda_{ex} = 346$ nm......................... 105

Figure A3. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C$_{60}$ and C$_{60}$(TMB-PPO)$_3$ at $\lambda_{ex} = 346$ nm......................... 106

Figure A4. Calibration curves correlating relative intensity to derivative concentration.
......................................................................................................................................................... 107

Figure A5. TGA showing thermal stability of PETMP:TTT-1 film series............. 108

Figure A6. TGA showing thermal stability of PETMP:TTT-0.75 film series............. 108

Figure A7. TGA showing thermal stability of TMPMP:TMPDE-1 film series.......... 109

Figure A8. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C$_{60}$ and C$_{60}$-capped PMBs (as prepared and recovered from indirect solution based assay) at $\lambda_{ex} = 346$ nm................................................................. 109

Figure A9. FT-IR spectra of 0.5 wt % C$_{60}$ doped SBS films before and after four hours of UV irradiation. ............................................................................................................. 110
LIST OF SCHEMES

Scheme 1. Initiation and propagation steps of the thiol-ene photopolymerization reaction. .............................................................................................................................................................................. 7

Scheme 2. Mechanism of molecular oxygen inhibition in thiol-ene polymerizations. ...... 9

Scheme 3. Competition reaction between BuMP monomer and PI with C₆₀. ............... 22

Scheme 4. Synthesis of S-S via oxidation of BuMP................................................................. 23

Scheme 5. Synthesis of C₆₀(BuMP)ₓ using BuMP/S-S. ............................................................ 25

Scheme 6. Synthesis of C₆₀(TMB-PPO)ₓ................................................................................ 30

Scheme 7. Common singlet oxygen reactions with sulfoxides and alkenes..................... 47

Scheme 8. Preparation of C₆₀(TMB-PPO)₅ containing thiol-ene films. ......................... 52

Scheme 9. Synthesis of thiol-ene PMBs using PETMP:TTT monomers. ......................... 81

Scheme 10. Preparation of C₆₀-capped PETMP:TTT PMBs............................................... 91

Scheme 11. Photooxygenation of 2-methyl-2-butene (2M2BE). ..................................... 97
<table>
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<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>AIBN</td>
<td>2,2’-Azobisisobutyronitrile</td>
</tr>
<tr>
<td>APE</td>
<td>Pentaerythritol Allyl Ether</td>
</tr>
<tr>
<td>BuMP</td>
<td>Butyl 3-Mercaptopropionate</td>
</tr>
<tr>
<td>DABCO</td>
<td>[1,4]Diazobicyclo(2.2.2)Octane</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DHB</td>
<td>2,5-Dihydroxybenzoic Acid</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>DMAIB</td>
<td>Dimethyl 2,2’-Azobis (Isobutyrate)</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<td>Fourier Transform-Infrared</td>
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<tr>
<td>IR</td>
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<tr>
<td>MALDI</td>
<td>Matrix-Assisted Laser Desorption/Ionization</td>
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<td>Methyl Methacrylate</td>
</tr>
<tr>
<td>MN</td>
<td>Mean Number</td>
</tr>
<tr>
<td>MNF</td>
<td>Metallic Nitride Fullerene</td>
</tr>
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<td>MRI</td>
<td>Magnetic Resonance Imaging</td>
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<td>MS</td>
<td>Mass Spectroscopy</td>
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<td>-----------</td>
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<tr>
<td>OM</td>
<td>Optical Microscopy</td>
</tr>
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<td>OPV</td>
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<td>[6,6]Phenyl C_{61}-Butyric Acid Methyl Ester</td>
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<td>PI</td>
<td>Photoinitiator</td>
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<td>Bis(2,4,6-Trimethylbenzoyl)-Phenylphosphineoxide</td>
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<tr>
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<td>TMPMP</td>
<td>Trimethylolpropane Tris-3-Mercaptopropionate</td>
</tr>
<tr>
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<td>Time of Flight</td>
</tr>
<tr>
<td>TTT</td>
<td>Triallyl-1,3,5-Triazine-2,4,6-(1H,3H,5H)-Trione</td>
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<tr>
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<td>Ultraviolet-Visible Spectroscopy</td>
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CHAPTER I - INTRODUCTION

Since the discovery of fullerenes in 1985 by the late Kroto and co-workers\textsuperscript{1}, researchers have been interested in the unique structure and properties of these molecules. Fullerenes are an allotrope of carbon and are typically synthesized by vaporizing graphite into a helium stream using a focused pulsed laser.\textsuperscript{1} The most abundant fullerene is C\textsubscript{60}, which consists of 60 sp\textsuperscript{2}-hybridized carbon atoms specifically arranged to yield an empty cage comprised of 20 hexagonal and 12 pentagonal rings (Figure 1). Though C\textsubscript{60} is the most abundant, and therefore the most common fullerene, other empty cage fullerenes have been discovered including, but not limited to, C\textsubscript{20}, C\textsubscript{36}, C\textsubscript{70}, C\textsubscript{76}, C\textsubscript{78}, C\textsubscript{82}, C\textsubscript{84}, C\textsubscript{86}, C\textsubscript{90}, and C\textsubscript{96}.

\textit{Figure 1.} Comparison of fullerenes, metallofullerenes, and metallic nitride fullerenes.

Not long after the discovery of the empty cage C\textsubscript{60} fullerene, researchers discovered a new class of fullerenes known as endohedral fullerenes, which contain a variety of chemical entities such as metals and atom clusters within the inner space of fullerenes (Figure 1).\textsuperscript{9-10} Encapsulating metal atoms within the fullerene cage significantly alters the electronic structure of the fullerene, making endohedral metallofullerenes potentially useful in certain applications such as charge separation, transport, and storage.\textsuperscript{11-14} The first metallofullerene discovered was La@C\textsubscript{60}, which was
determined to contain lanthanum and possess metallic properties.\textsuperscript{15} Since the discovery of La@C\textsubscript{60}, other endohedral fullerenes have been discovered, containing up to four atoms including lanthanides, Group I-III metals as well as non-metals (i.e. C, N, O, S)\textsuperscript{9, 16-19} Later, a more specific class of endohedral metallofullerenes, metallic nitride fullerenes (MNF), were discovered and were found to contain a metallic-nitride cluster (M\textsubscript{3}N) encapsulated within the fullerene cage (Figure 1).\textsuperscript{20-21} Since the discovery of the most stable and most abundant MNF, Sc\textsubscript{3}N@C\textsubscript{80}, in 1999, the use of MNFs has become increasingly popular due to their potential use in photovoltaic devices\textsuperscript{22} and biomedical applications.\textsuperscript{23-24}

Overall, the use of fullerenes has become increasingly popular due to their ability to produce singlet oxygen\textsuperscript{25} as well as their unique optical\textsuperscript{26-29}, magnetic\textsuperscript{30-31}, electronic\textsuperscript{32-33}, and photophysical\textsuperscript{25, 34-36} properties. Fullerenes have also been exploited as hydrogen stores\textsuperscript{37} and supercapacitors.\textsuperscript{38} Though fullerenes have many potential uses, they are completely insoluble in aqueous solutions and only sparingly soluble in common organic solvents, monomers, and polymers, limiting their use in many applications. Fortunately, chemical modification of fullerenes greatly enhances their solubility and processability leading to a more efficient utilization of their properties.\textsuperscript{39-40}

C\textsubscript{60} exhibits poor electron delocalization, and therefore, reacts readily with electron rich species allowing the outer surface of C\textsubscript{60} to be chemically modified.\textsuperscript{41-43} C\textsubscript{60} is known to participate in a variety addition reactions such as nucleophilic additions, cycloadditions, and free-radical additions.\textsuperscript{41-61} Numerous free-radical reactions with C\textsubscript{60} have been investigated and continue to be an important methodology for the functionalization of fullerenes. The phrase “radical sponge” is often used to emphasize
the high radical scavenging activity that C\textsubscript{60} exhibits due to their high electron affinity (ca. 2.7-2.8 eV) and the large number (30) of conjugated double bonds, which can readily react with radicals.\textsuperscript{62} Fullerene’s high reactivity for radicals allows for a higher degree of functionalization compared to other addition reactions of fullerenes. The addition of 11 phenyl groups, 15 benzyl groups, and 34 methyl groups are among the first examples of radical additions to C\textsubscript{60}.\textsuperscript{43, 60-61}

Compared to empty cage fullerenes, functionalization of MNFs is more complicated due to the stabilizing effect of the electrostatic relationship between the metal nitride cluster and the C\textsubscript{80} cage. According to a recent review by Popov et al.\textsuperscript{19}, the formal electronic structure for Sc\textsubscript{3}N@C\textsubscript{80} requires that each metal carry a \textsuperscript{+3} charge, the nitrogen a \textsuperscript{-3} charge, and the cage a \textsuperscript{-6} charge, to produce an overall neutral species, [Sc\textsubscript{3}N]\textsuperscript{6+}@[C\textsubscript{80}]\textsuperscript{6-}. Currently, only a few reactions capable of producing functionalized MNF C\textsubscript{80} adducts have been identified including cycloadditions,\textsuperscript{23, 63-64} hydroxylation,\textsuperscript{23} 1,3-dipolar addition,\textsuperscript{65-67} Diels-Alder,\textsuperscript{68-70} and Bingel-Hirsch\textsuperscript{66} adducts. To a large extent, chemical reactivity is believed to be controlled by the identity of the metal encapsulated, as demonstrated in a recent report by Echegoyen et al.,\textsuperscript{66} where the Y\textsubscript{3}N@C\textsubscript{80-diethyl malonate monoadduct was successfully prepared under conditions which would not produce the comparable Sc\textsubscript{3}N@C\textsubscript{80} adduct. This difference in chemical reactivity was attributed to the encapsulated cluster, which affected the reactivity and the regiochemistry of the addition.

Fullerenes and their derivatives are also well-known photosensitizers upon absorption of light due to their unique electronic \(\pi\)-system.\textsuperscript{25, 29, 71-72} The use of C\textsubscript{60} fullerene as a photosensitizer to generate singlet oxygen as well as C\textsubscript{60}’s photophysical
properties have been well documented. An example energy diagram illustrating the interaction between excited-state C\textsubscript{60} and ground-state molecular oxygen is provided in Figure 2. Upon irradiation the fullerene is converted to an excited triplet state though intersystem crossing. The excited fullerene triplet can then react directly with molecular oxygen via energy transfer generating singlet oxygen, a highly reactive form of molecular oxygen. Once generated, singlet oxygen can be used 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 C\textsubscript{60}, is one of the easiest and most efficient way to yield singlet oxygen and the related photooxygenated products.

![Energy level diagram of singlet oxygen generation by excited-state C\textsubscript{60}.](image)

In solution, singlet oxygen transfers its electron energy to solvent vibrations, and therefore the lifetime of singlet oxygen is highly dependent on the solvent used. The lifetime of singlet oxygen is greatly diminished in solvents with high vibrational frequencies such as water, which exhibits a strong OH vibration near 3600 cm\textsuperscript{-1}, and solvents containing CH bonds (\sim 3000 cm\textsuperscript{-1}). Replacing hydrogen molecules with
deuterium results in a vibrational shift to a lower frequency and causes an increase in the lifetime of singlet oxygen from 3-4 μs in water to 60 μs in D₂O and from 30-100 μs in organic solvent to >100 μs in deuterated organic solvents. The lifetime of singlet oxygen is significantly greater (>1 ms) in solvents that do not contain either hydrogen or deuterium. Table 1 shows the typical lifetimes of singlet oxygen in various solvents.

Table 1

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Lifetime (μs)</th>
<th>Solvent</th>
<th>Lifetime (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
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<td>(CH₃)₂C=O</td>
<td>50</td>
</tr>
<tr>
<td>D₂O</td>
<td>62</td>
<td>(CD₃)₂C=O</td>
<td>723</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>10</td>
<td>CH₃CN</td>
<td>62</td>
</tr>
<tr>
<td>Hexane</td>
<td>31</td>
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<tr>
<td>CHCl₃</td>
<td>264</td>
<td>C₆H₅CH₃</td>
<td>27</td>
</tr>
<tr>
<td>CDCl₃</td>
<td>740</td>
<td>C₆H₅CD₃</td>
<td>320</td>
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<tr>
<td>C₆H₆</td>
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</tr>
<tr>
<td>C₆D₆</td>
<td>630</td>
<td>C₆F₆</td>
<td>3,900</td>
</tr>
</tbody>
</table>

* Averaged values from Gorman and Rodgers (1989). ⁷⁹

In order to utilize the unique properties of fullerenes, many efforts have been made to incorporate fullerenes and fullerene derivatives into a polymer matrix via covalent incorporation or blending. Polymer blends and cross-linked networks containing various fullerenes show great promise in the applications of optoelectronic devices, energy conversion systems, magnetic resonance imaging (MRI) contrast agents, photovoltaic devices, oxygen sensors, and as antimicrobial and decontaminating agents. ²⁷ ⁸¹-⁸³ Recently, singlet oxygen generating fullerenes have been utilized as polymer constituents to create stimuli-responsive adhesives and antimicrobial coatings. ⁸³-⁸⁴ It has
been demonstrated that the adhesive properties of rubber-based elastomeric adhesives can be affected when blended with singlet oxygen generators, such as fullerenes, by utilizing a singlet oxygen mediated crosslinking reaction. Singlet oxygen generating fullerenes have also been exploited as potential self-decontaminating agents due to singlet oxygen’s ability to react with olefins, dienes, aromatics, peptides, and sulfur atoms, which are found in chemical warfare agents.\textsuperscript{85} Fullerenes have also been used in photovoltaic devices because of fullerene’s strong electron accepting ability, which allows it to undergo photoinduced electron transfer from an electron donating semiconductor polymer.\textsuperscript{22, 86-87}

Fullerenes have also been chemically linked to various polymeric supports for a host of applications ranging from chromatographic separation techniques to their use as a heterogeneous photocatalyst.\textsuperscript{88-89} To date, fullerenes have been incorporated into and on various polymer matrices including polystyrene (PS),\textsuperscript{84, 90} polyurethanes,\textsuperscript{91-93} and poly(methyl)methacrylate (PMMA).\textsuperscript{94} However, most of these materials yield broad glass transition temperatures making it difficult to probe subtle physical changes within the polymer matrix. The work herein, discusses the incorporation of C\textsubscript{60} and Sc\textsubscript{3}N@C\textsubscript{80} fullerene derivatives into a thiol-ene polymer matrix, which is a relatively new area of research. Furthermore, thiol-ene networks are a good model matrix due to its well-defined network with a narrow glass transition temperature, which allows us to probe subtle physical changes, such as enthalpy relaxation or aging, photodegradation due to hydrogen abstraction or scission reactions, and the consequences to network free volume, molecular weight between crosslinks, and the elasticity of the network.
“Click” chemistry is the term most often used to describe the chemistry involved in thiol-ene reactions due to the reaction’s high rate of polymerization. The term thiol-ene is a generic name for the joining of functional monomers containing a thiol group to those containing an ene (vinyl) group. Thiol-ene polymerization reactions occur via step growth radical polymerization reaction (Scheme 1) that can be initiated through the use of a thermal or photochemical initiator. Thiol-ene polymerization reactions proceed via propagation of a thyl radical through the vinyl functional groups. Through anti-Markovnikov addition, the thyl radical is added to the unsaturated alkene, creating a new carbon centered radical. The carbon centered radical then reacts with another thiol group, forming another thyl radical. Termination is believed to occur via radical-radical recombination or via radical recombination with initiating species.

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

Thiol-ene photopolymerizations occur rapidly, do not require solvents for processing, produce optically clear products, and exhibit good thermal and mechanical
properties. Furthermore, thiol-ene polymerization reactions exhibit uniform network crosslink densities due to the high conversion of thiol-ene monomers resulting in a narrow glass-transition region that does not change over time. The uniformly structured networks of thiol-ene films allow the films to be tuned to exhibit an extremely wide range of properties depending upon the chemical structures of the thiols and enes. The stable glass transition temperature indicates the thiol-ene networks are thermally and oxidatively stable. The thermal stability of the thiol-ene networks is further indicated by its stability in thermogravimetric analysis (TGA) up to 300 °C or more. Another advantage of thiol-ene polymerizations is their ability to stick to a variety of surfaces (i.e. glass, metal, plastic, etc.), which is due to delayed gelation. The delayed gelation also results in the formation of a homogeneous network since low molecular weight species are prevalent before gelation, leading to a higher gel point conversion.

Furthermore, thiol-ene photopolymerizations are unique in that they are not inhibited by oxygen and are polymerizable without the addition of photoinitiators. As shown in Scheme 2, when oxygen is present an additional chain-transfer reaction occurs in which the carbon centered radical reacts with molecular oxygen forming a peroxo radical. The peroxo radical thus formed can further react by abstracting a hydrogen form a thiol creating a thiyi radical, which can add to an unsaturated alkene continuing the main propagation steps. The reduction of oxygen inhibition in the thiol-ene polymerization is based on the ability of thiol-ene reactions to regenerate a thiyi radical by scavenging oxygen.

The step-growth nature of the product is largely influenced by monomer functionality. Only monomers with a functionality greater than two generate cross-linked polymer networks used for coatings and films. Monofunctional monomers only form single adducts while difunctional monomers generate linear polymers. In addition, these reactions allow for a wide range of thiols and enes in which different thiol-ene reactions can vary in reactivity significantly depending on the thiol-ene electron density, mechanisms, the thiol bond strength, and the solubility properties of the thiol and of the ene. The rate of polymerization of the thiol-ene reaction is directly related to the resulting electron density of the ene (norbornene > vinyl ether > propenyl > alkene ~ vinyl ester > N-vinyl amides > allyl ether ~ allyl triazine ~ allyl isocyanurate > acrylate > unsaturated ester > N-substituted maleimide > acrylonitrile ~ methacrylate > styrene > conjugated dienes). In general, ene reactivity generally decreases with decreasing electron density. Therefore, electron rich enes polymerize much faster than electron poor enes, except for norbornene, methacrylate, styrene, and conjugated dienes. The rate of polymerization of norbornene with thiols is much faster due to ring strain, which is minimized upon the
addition of the thiyl radical across the carbon-carbon double bond. Furthermore, the rates of polymerization of thiols with methacrylates, styrene, and conjugated dienes is much slower due to the stable radicals (methacrylic, benzylic, or allylic) produced upon the addition of the thiyl radical across the carbon-carbon double bond. Furthermore, the rates of polymerization of thiols can be affected by inductive resonance (Figure 3); therefore, propionate esters (a) react faster than glycolate esters (b) and both propionate and glycolate esters react much faster than alkyl thiols (c).

\[ \text{Figure 3. Intramolecular hydrogen bonding between structures of general thiols used in thiol-ene reactions.} \]

Although thiol-ene chemistry has been utilized for multiple applications ranging from the fabrication of dendrimers to the modification of existing polymer networks forming highly complex macromolecules, the incorporation of fullerenes into a thiol-ene matrix has not been widely studied. Furthermore, little is known about the consequences of incorporating singlet oxygen generating species into polymer networks. Since very little is known about the photochemistry of many fullerene derivatives, this research represents an exploration into systematically defining the ability of novel fullerene derivatives to produce singlet oxygen and the consequences of incorporating singlet oxygen generating species into various polymer networks.
CHAPTER II - SYNTHESIS AND CHARACTERIZATION
OF NOVEL FULLERENE DERIVATIVES

Introduction

Though fullerenes have many potential uses, they are completely insoluble in aqueous solutions and only sparingly soluble in common organic solvents, monomers, and polymers, limiting their use in many applications. Fortunately, chemical modification of fullerenes greatly enhances their solubility and processability leading to a more efficient utilization of their properties.\textsuperscript{39-40} Thus, over the last few decades, numerous reactions have been developed to functionalize fullerenes taking advantage of, or even enhancing, their unique physical and chemical properties. $C_{60}$ is known to participate in a variety of addition reactions such as nucleophilic additions including chlorination,\textsuperscript{44} hydroxylation,\textsuperscript{45-48} and hydrogenation,\textsuperscript{49-50} and cycloadditions including Diels-Alder, Prato, azoalkane, and Bingel-Hirsch reactions.\textsuperscript{52-54} However, the radical additions to $C_{60}$ are of more interest for this research. A recent review by Tzirakis et al.\textsuperscript{43} summarizes the radical addition of C-, Si-, O-, S-, P-, N-, and metal-centered radicals as well as hydrogen and halogen radicals to fullerenes. The addition of alkyl carbon-centered radicals such as tert-butyl, 1-adamantyl, isopropyl, ethyl, and benzyl radicals to $C_{60}$ were among the first radical additions studied, which were identified using electron paramagnetic resonance (EPR).\textsuperscript{96} Later, $C_{60}$ was discovered to undergo multiple radical additions upon prolonged irradiation with an excess of radical precursors, which was determined by line broadening in EPR and via mass spectroscopy.\textsuperscript{60-61} Some of the first multiple radical additions observed was the addition of up to 15 benzyl radicals and 34 methyl radicals to $C_{60}$.\textsuperscript{60}
The addition of O- and S- centered radicals to fullerenes has also been well documented, where alkoxy and alkylthio radicals were found to add to C\textsubscript{60} and C\textsubscript{70} via EPR studies.\textsuperscript{56, 59, 97-98} Typically, alkoxy radicals are generated via photolysis of peroxides or dialkoxy disulfides, while alkylthio radicals have been produced via photolysis of alkyl disulfides or bis(alkylthio) mercury compounds. Though the addition of S- centered radicals to fullerenes has been well documented, the alkylthiyl radical addition to C\textsubscript{60} was found to be reversible through EPR studies.\textsuperscript{98} The reversibility of the alkylthiyl radical addition to C\textsubscript{60} is believed to be due to the weaker fullerene-sulfur bond, which exhibits a binding energy half of that compared to fullerene-OH. The reversibility of the thiyl radical addition to C\textsubscript{60} was further evident by an observed color change from a light amber colored solution upon derivatizing C\textsubscript{60} to a purple colored solution indicative of pure C\textsubscript{60} upon cessation of irradiation.\textsuperscript{98}

Due to the reversibility, and therefore lack of isolation, of thiolated fullerene derivatives, the addition of S-centered radicals to fullerenes was studied using DFT calculations.\textsuperscript{59} Through DFT calculations, alkyl sulfur radicals were found to be the most reactive radical, while phenyl thiyl radicals were found to be very unreactive due to the stabilizing effect of the phenyl group. From DFT studies, it was also determined that the binding energy of the fullerene-sulfur bond doubled with an increase in radical additions to C\textsubscript{60}.

In addition to C-, O-, and S- centered radicals, a few P- centered radicals have been shown to add to C\textsubscript{60}. The addition of P- centered radicals is mainly limited to the addition of phosphoryl radicals, which were prepared via photolysis of diphosphoryl mercury compounds or hydrogen abstraction from hydrophosphoryl compounds.\textsuperscript{41, 99-103}
In 1998, Wu et al. prepared phosphine oxide functionalized fullerenes upon reacting \( C_{60} \) with trialkylphosphines. In 2011, Wang et al. demonstrated the manganese(III) acetate dihydrate catalyzed radical addition of \( C_{60} \) with phosphonates and phosphine oxides, which produced three different phosphorylated fullerenes including singly bonded fullerene dimers, hydrophosphorylated fullerenes, and acetoxylated fullerene adducts. Some phosphorylated fullerene derivatives have been shown to possess active biological activities and optical properties.

Furthermore, \( C_{60} \) was shown to readily react with commercial initiators such as 2,2'-azobisisobutyronitrile (AIBN), which was discovered during the free-radical polymerization of methyl methacrylate (MMA) and styrene in the presence of \( C_{60} \) (1 wt %). Ford et. al later demonstrated the high reactivity of \( C_{60} \) with other thermal initiators such as dimethyl 2,2'-azobis (isobutyrate) (DMAIB).

Though numerous radical additions have been shown with \( C_{60} \), only a few radical additions of MNFs, such as \( \text{Sc}_3\text{N}@\text{C}_{80} \), have been documented. In 2007, Shustova et. al derivatized \( \text{Sc}_3\text{N}@\text{C}_{80} \) via radical addition of CF. Later Shu et al. derivatized \( \text{Sc}_3\text{N}@\text{C}_{80} \) with carbon-centered radicals generated from diethyl malonate catalyzed by manganese(III) acetate. Shu et al. also demonstrated the reaction of \( \text{Sc}_3\text{N}@\text{C}_{80} \) with photochemically generated benzyl radicals producing a benzyl adduct, \( \text{Sc}_3\text{N}@\text{C}_{80}(\text{CH}_2\text{C}_6\text{H}_5)_2 \), in 82% yield.

Numerous functionalization methods have been employed to increase the solubility, and therefore, the processability of fullerenes. An important breakthrough in polymer photovoltaics was achieved upon functionalizing pristine \( C_{60} \), yielding phynyl-C\(_{61}\)-butyric acid methyl ester (PCBM), which exhibits enhanced solubility (~ 50 mg mL\(^{-1}\)).
in chlorobenzene) compared to pristine C\textsubscript{60}.\textsuperscript{114} In 2009, Troshin et al.\textsuperscript{87} prepared various C\textsubscript{60} and C\textsubscript{70} methanofullerenes closely resembling the structure of PCBM to determine structure-property relationships as a function of functionality. The solubilities of the resulting methanofullerenes was found to vary greatly, ranging from 4 to \(~\text{130 mg mL}^{-1}\), however, a correlation between functionality and solubility was not determined. Furthermore, both empty cage fullerenes and MNFs have been highly hydroxylated yielding water soluble fullerols exhibiting biological activity\textsuperscript{115-119} and radical-scavenging ability\textsuperscript{120-124} with negligible toxicity.\textsuperscript{125-126} Therefore, fullerols have attracted much attention for their use in medical and cosmetic applications.

The ability of a few fullerene derivatives to produce singlet oxygen upon derivatization has also been explored, and was found to decrease with an increase in the number addends bound but was independent of addend functionality.\textsuperscript{71, 127-129} Functionalized fullerenes that generate singlet oxygen have been exploited for their use in biological applications such photodynamic therapy and antimicrobial coatings.\textsuperscript{128, 130}

In this work, derivatization of C\textsubscript{60} and Sc\textsubscript{3}N@C\textsubscript{80} with S-, P-, and C- centered radicals using easy synthetic strategies was investigated. To the best of our knowledge, this is the first report of functionalizing Sc\textsubscript{3}N@C\textsubscript{80} with sulfur and phosphorous. Successful functionalization of C\textsubscript{60} and Sc\textsubscript{3}N@C\textsubscript{80} was supported through a combination of techniques including FT-IR, MALDI-MS, elemental analysis, \textsuperscript{1}H-NMR, and TGA. The number of addends bound to C\textsubscript{60} as a function of reaction time and molar ratios as well as structure-property relationships including thermal stability, solubility, and singlet oxygen generation as a function of increasing number of addends bound to C\textsubscript{60} were explored.
Materials, Method, and Characterization

Materials

Materials used in the preparation, purification, and characterization of fullerene derivatives were butyl 3-mercaptopropionate (BuMP, 98%), 1,4-diazabicyclo[2.2.2]octane (DABCO, >99%), hydrochloric acid (HCl, 37%), anhydrous magnesium sulfate (MgSO₄), methanol (MeOH, >99.8%), ethanol (EtOH, >99.5%), acetone (>99.5%), chloroform (>99.8%), benzene-d₆ (99.6 atom % D), chloroform-d₁ (99.6 atom % D), α-cyano-4-hydroxycinnamic acid (>99%), 2,5-dihydroxybenzoic acid (DHB, 98%), trifluoroacetic acid (TFA, 99%), and ProteoMass™ MALDI calibration kit purchased from Sigma Aldrich Chemical Company (St. Louis, MO); benzene (99.0%) and dichloromethane (DCM, >99.5%) obtained from EMD Chemicals (Gibbstown, NJ); bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (TMB-PPO) purchased from Ciba Specialty Chemicals; and C₆₀ (99.6%) and Sc₃N@C₈₀ (MNF) (95%) fullerenes obtained from SES Research (Houston, TX). All chemicals were obtained commercially and used as received.

Method

Partial oxidation of butyl 3-mercaptopropionate (BuMP) to disulfide (S-S).

BuMP (11.5 mL, 70.9 mmol) and DABCO (4 g, 35.7 mmol) were dissolved in benzene (100 mL) and aerated for 48 hours at room temperature. Benzene was removed from the resulting S-S monomer solution under reduced pressure, and the concentrated solution was purified via liquid-liquid extraction with DCM. DABCO was removed from the solution by washing three times with 0.1M HCl followed by distilled water. The organic layer was dried over anhydrous MgSO₄, which was removed via filtration using 0.25 μm
nylon syringe filter membranes. Following filtration, DCM was removed from the dry S-S solution under reduced pressure, and the resulting S-S product was characterized using $^1$H-NMR to determine conversion of S-H to S-S. BuMP $^1$H-NMR (C$_6$D$_6$, 400 MHz): $\delta$ 3.94 (t, 2H, $J = 6.6$ Hz, CH$_2$), 2.41 (q, 2H, CH$_2$), 2.25 (t, 2H, $J = 6.5$ Hz, CH$_2$), 1.45 (t, 1H, $J = 8.5$ Hz, SH), 1.36 (quin, 2H, CH$_2$), 1.16 (sex, 2H, CH$_2$), 0.75 (t, 3H, $J = 7.5$ Hz, CH$_3$). BuMP/S-S (~30% S-S) $^1$H-NMR (C$_6$D$_6$, 400 MHz): $\delta$ 3.94 (m, 4H, CH$_2$), 2.70 (t, 1.2H, $J = 7.0$ Hz, CH$_2$), 2.46 (t, 1.2H, $J = 7.2$ Hz, CH$_2$), 2.40 (q, 2.8H, CH$_2$), 2.24 (t, 2.8H, $J = 6.8$ Hz, CH$_2$), 1.44 (t, 1.4H, $J = 8$ Hz, SH), 1.36 (m, 4H, CH$_2$), 1.16 (m, 4H, CH$_2$), 0.75 (t, 6H, $J = 7.5$ Hz, CH$_3$).

**Synthesis of thiolated C$_{60}$ and Sc$_3$N@C$_{80}$ fullerene derivatives.** Thiolated fullerene derivatives, C$_{60}$(BuMP)$_x$, were prepared by mixing C$_{60}$ (50 mg, 0.07 mmol) and BuMP/S-S (2.25 mL, 13.9 mmol) in 100 mL benzene. The sample was sonicated until C$_{60}$ was dissolved, as determined by a resulting clear purple solution. The solution was then placed in a Rayonet photochemical reactor containing nine 250 nm bulbs, at varying time intervals, resulting in a purple-red solution. The solution was then concentrated under reduced pressure and methanol (20 mL) was added to the concentrated sample, dissolving any unreacted BuMP/S-S, and forming a precipitate of brick red solids. The precipitate was collected via filtration, using 0.45 µm polypropylene filter membranes, and dried at 50 °C for 10 min. The resulting sample was further purified via gravity column chromatography using 40-63 µm silica gel (SiliCycle®) and a gradient solvent mixture from 100% DCM to 10% MeOH:90% DCM to remove unreacted C$_{60}$ and to narrow the isomer distribution of the crude product. An amber colored band was isolated.
at 10% MeOH:90% DCM and vacuum dried at 50 °C. The purified C$_{60}$(BuMP)$_x$ derivatives were characterized via TGA, FT-IR, and MALDI.

Sc$_3$N@C$_{80}$(BuMP)$_y$ derivatives were synthesized using a similar method. Sc$_3$N@C$_{80}$ (5 mg, 0.005 mmol) and BuMP/S-S (225 µL, 1.4 mmol) were dissolved in 100 mL benzene. The resulting solution was placed in a Rayonet photoreactor and irradiated at 250 nm for 6 hr. Solids formed during the reaction were collected via filtration using 0.45 µm nylon filter membranes and dried at 50 °C overnight, yielding brick red solids. Sc$_3$N@C$_{80}$(BuMP)$_y$ was characterized via TGA, FT-IR, and MALDI. BuMP FT-IR: 2957, 2875 (ν C-H, s), 2573 (ν S-H, w), 1735 (ν C=O, s), 1487, 1250 (δ C-H, m), 1165, 1066 (ν C-O, m) cm$^{-1}$. C$_{60}$(BuMP)$_x$ FT-IR: 2957, 2875 (ν C-H, m), 1735 (ν C=O, s), 1610 (ν C=C, m), 1458, 1250 (δ C-H), 1165, 1066 (ν C-O, s), 853, 752, 694 (δ C-H, w), 530 (δ C-S, w) cm$^{-1}$; MALDI-MS m/z = 720. Sc$_3$N@C$_{80}$(BuMP)$_7$ FT-IR: 2957, 2875 (ν C-H, m), 1735 (ν C=O, s), 1653 (ν C=C, w), 1458, 1250 (δ C-H, m), 1165, 1066 (ν C-O, w), 836, 759, 725 (δ C-H, w) cm$^{-1}$; MALDI-MS m/z = 1109.

Synthesis of C$_{60}$- and Sc$_3$N@C$_{80}$(TMB-PPO) fullerene derivatives. C$_{60}$(TMB-PPO)$_x$ fullerene derivatives were synthesized by dissolving C$_{60}$ (75 mg, 0.1 mmol) and TMB-PPO (261 mg, 0.6 mmol) in 150 mL benzene and irradiating for 1 hr using a Rayonet photochemical reactor containing sixteen 350 nm bulbs. A resulting dark brown heterogeneous solution was obtained. Benzene was removed under reduced pressure, then methanol (100 mL) was added to the concentrated sample, one, to dissolve any unreacted TMB-PPO starting material, and two, to precipitate the C$_{60}$(TMB-PPO)$_x$ product. Starting material was removed and product was collected via filtration using 0.45 µm nylon filter membranes. The resulting sample was then dried at 50 °C overnight.
yielding \( \text{C}_{60}(\text{TMB-PPO})_5 \) in crude isolated yields of \( \sim 95\% \). Resulting solids were further purified via gravity column chromatography using 40-63 μm silica gel (SiliCycle®) and a gradient solvent mixture from 100% DCM to 10% MeOH:90% DCM to narrow the isomer distribution of the resulting crude product. A coffee colored band was isolated at 7% MeOH:93% DCM and vacuum dried at 50 °C overnight yielding black crystals in \( \sim 80\% \) yield. The purified \( \text{C}_{60}(\text{TMB-PPO})_5 \) derivative was characterized via TGA, FT-IR, MALDI, and \(^1\)H-NMR.

The \( \text{Sc}_3\text{N}@\text{C}_{80}(\text{TMB-PPO})_y \) derivatives were synthesized using a similar method, in which case \( \text{Sc}_3\text{N}@\text{C}_{80} \) (5 mg, 4.5 μmol) and TMB-PPO (11.5 mg, 27.5 μmol) were dissolved in 100 mL benzene. The resulting solution was placed in the Rayonet photoreactor and irradiated at 350 nm for 1 hr resulting in a light amber heterogeneous solution. The sample was then filtered and dried yielding \( \text{Sc}_3\text{N}@\text{C}_{80}(\text{TMB-PPO})_3 \) in crude isolated yields of \( \sim 95\% \). The \( \text{Sc}_3\text{N}@\text{C}_{80}(\text{TMB-PPO})_3 \) derivative was characterized via TGA, FT-IR, and MALDI. TMB-PPO FTIR: 2929, 2861 (\( \nu\ C-\text{H}, \text{s} \)), 1680 (\( \nu\ C=\text{O}, \text{s} \)), 1608 (\( \nu\ C=\text{C}, \text{s} \)), 1437, 1381 (\( \delta\ C-\text{H}, \text{m} \)), 1218, 1201, (\( \nu\ P=\text{O}, \text{s} \)), 1149 (\( \nu\ P-\text{Ar}, \text{m} \)), 850, 750, and 694 (\( \delta\ C-\text{H}, \text{m} \)) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\)): 7.86 (m, 2H, CH), 7.53 (dt, 1H, \( J = 1.5 \) and 7.5 Hz, CH), 7.40 (dt, 2H, \( J = 3.2 \) and 7.9 Hz, CH), 6.77 (s, 4H, CH), 2.23 (s, 6H, CH\(_3\)), 2.12 (s, 12H, CH\(_3\)); \( \text{C}_{60}(\text{TMB-PPO})_5 \) (FTIR): 2929, 2861 (\( \nu\ C-\text{H}, \text{s} \)), 1707 (\( \nu\ C=\text{O} \)), 1608 (\( \nu\ C=\text{C}, \text{s} \)), 1437, 1381 (\( \delta\ C-\text{H}, \text{m} \)), 1242, 1222, (\( \nu\ P=\text{O}, \text{s} \)), 1154 (\( \nu\ P-\text{Ar}, \text{s} \)), 850, 750, and 694 (\( \delta\ C-\text{H}, \text{m} \)) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\)): 7.57 (m, 5H), 6.88 (m, 12H), 2.13 (m, 54H); elemental analysis (experimental) C 78.6, H 4.4, O 15.6, P 1.4; \( \text{Sc}_3\text{N}@\text{C}_{80}(\text{TMB-PPO})_3 \) FT-IR: 2911, 2852 (\( \nu\ C-\text{H}, \text{s} \)), 1731 (\( \nu\ C=\text{O}, \text{w} \)), 1606 (\( \nu\ C=\text{C}, \text{s} \))
w), 1437, 1381 (δ C-H, m), 1259 (ν P=O, s), 1141 (ν P-Ar, s), 800, and 694 (δ C-H, m) cm⁻¹

**Characterization**

_Nuclear magnetic resonance (NMR)_ - ¹H-NMR spectrums were obtained using a Bruker 400 MHz NMR in either benzene-d₆ or chloroform-d₁. Therefore, all shifts are reported relative to benzene-d₆ or chloroform-d₁ at 7.16 ppm or 7.24 ppm, respectively.

_Thermogravimetric analysis (TGA)_ - The average number of addends attached to the fullerene cage was approximated using a TA instruments Q500 series TGA by calculating the ratio of the weight loss between 115-570 °C to the weight loss at temperatures above 570 °C as reported by Singh et al.¹³¹ Samples (~10 mg) were analyzed at a heating rate of 10 °C min⁻¹ under nitrogen in either aluminum or platinum pans over a temperature range of 25-600 °C or 25-800 °C, respectively.

_Solubility studies_ - The solubility of the fullerene derivatives in common solvents was determined using a method adapted from Troshin et al.⁸⁷ In general, saturated solutions of the fullerene derivatives were prepared by mixing an excess amount of solid (at least 25 mg) in 1 mL solvent (MeOH, EtOH, acetone, DCM, chloroform, and benzene) at room temperature (~ 20 °C) for 24 hrs. Following mixing, the prepared saturated solutions were filtered using 0.25 μm PTFE syringe filters into glass vials of a known mass. Solvent was removed at 45 °C under reduced pressure.

_Fourier transform-infrared spectroscopy (FT-IR)_ - The FT-IR spectrums were obtained on the fullerene derivatives in the 500-4000 cm⁻¹ range using a Nicolet Nexus 470 FT-IR spectrometer equipped with a diamond crystal ATR accessory.
Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) -

The mass spectra of the fullerene derivatives were obtained using a Bruker Microflex matrix-assisted laser desorption/ionization- time of flight (MALDI-TOF) mass spectrometer with a laser power of ~90%. A quadratic calibration was obtained using a ProteoMassTM mix containing bradykinin fragment 1-7 (757.3997 Da), angiotensin II (human) (1,046.5423 Da), and insulin (bovine) (5,730.6087 Da). The matrix for the calibrant was prepared by dissolving 10 mg α-cyano-4-hydroxycinnamic acid in 1 mL of a mixed solvent of 0.1% trifluoroacetic acid (TFA)/DCM (1:2, v/v). The calibrant (0.5 µL) along with the prepared matrix (0.5 µL) were spot mixed onto a 96-well polished steel target. The analyte was prepared by dissolving the fullerene derivative (1 mg mL\(^{-1}\)) in DCM, and the matrix for the analyte was prepared by dissolving 2,5-dihydroxybenzoic acid (DHB)(1mg mL\(^{-1}\)) in a mixed solvent of 0.1% (TFA)/DCM (1:2, v/v). The matrix and analyte solutions were premixed at a 1:2000 molar analyte-to-matrix ratio, and 1 µL of the mix was added to the 96-well polished steel target.

Elemental analysis (EA) - Elemental Analysis of the C\(_{60}\)(TMB-PPO)\(_x\) derivative was obtained to determine the C, H, O, and P content of the derivative. Dry samples were sent to a commercial analytic company, Galbraith Laboratories Inc. (Knoxville, TN).

Inductively-coupled plasma mass spectrometry (ICP-MS) - Digested samples were sent to a commercial analytic company, Bonner Analytical Testing Co. (Hattiesburg, MS) for ICP-MS. Prior to ICP-MS analysis, a known mass of sample (~ 1.5 mg) was added to a digestion tube containing concentrated sulfuric acid (3.5 mL) and H\(_2\)O\(_2\) (30%, 3.5 mL). The resulting mixture was heated to 200 °C until no solids were visual and solutions were clear (~6 hrs). Upon cooling to room temperature, resulting
solutions were filtered using a 0.2 µm PTFE syringe filter and diluted yielding a 50 mL sample.

Direct singlet oxygen studies - Direct singlet oxygen solution based studies were performed using a method adapted by Barker et al.\textsuperscript{132} Samples were prepared by dissolving fullerene derivatives in benzene and sonicating for 5 min until fully dissolved. Benzene (2 mL) was added to a fluorometer cuvette with a septum cap and stir bar, then 1-10 µL of the prepared sample was added via syringe. The resulting sample was then excited at 350 nm, and an emission scan was obtained from 1200-1350 nm. Any singlet oxygen produced 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. Following each emission scan obtained, more sample (10-100 µL) was added to the cuvette to prepare calibration curves. Analogous methods were employed to obtain a calibration curve for the singlet oxygen generation of pure C\textsubscript{60} for comparison.

Results and Discussion

The first fullerene derivatives synthesized in this study, C\textsubscript{60}(BuMP)\textsubscript{x}, were prepared by mixing a monothiol monomer, BuMP, in a C\textsubscript{60} solution with the addition of a photoinitiator, PI, (1 wt %) to initiate the reaction. The functionalization of C\textsubscript{60} with the BuMP monomer was later optimized using a disulfide initiator, S-S, prepared from the BuMP monomer due to an observed competition reaction between C\textsubscript{60} and the PI, C\textsubscript{60}(PI)\textsubscript{x}, shown in Scheme 3. The occurrence of the side reaction with the PI is not surprising considering C\textsubscript{60}’s high affinity for radicals.\textsuperscript{62} However, the % yield of C\textsubscript{60}(PI)\textsubscript{x} was significantly higher (~ 99%) than that of C\textsubscript{60}(BuMP)\textsubscript{x} (~1%), even though the
concentration of the PI was only 1 wt % of the sample. The high reactivity of C\textsubscript{60} with PI compared to the thiol monomer is due to the weaker fullerene-sulfur bond (C-S BDE = 260 kJ mol\(^{-1}\) versus C-C BDE = 350 kJ mol\(^{-1}\)), which is supported by previous EPR studies.\textsuperscript{59,98}

Scheme 3. Competition reaction between BuMP monomer and PI with C\textsubscript{60}.

The use of the BuMP/S-S prepared via oxidation of the desired monothiol BuMP monomer (Scheme 4) was twofold. First, to prevent the competition between C\textsubscript{60} and the carbon-centered radicals produced from the photoinitiator. Secondly, to improve the yield of the C\textsubscript{60}(BuMP)\(_x\) reaction by enhancing the probability of the addition of the thiol-centered radicals to the fullerene. Furthermore, the use of the BuMP/S-S is ideal since disulfides are known to undergo homolytic cleavage upon irradiating, yielding thiyI radicals, which has previously been shown to react with C\textsubscript{60} and C\textsubscript{70} via EPR.\textsuperscript{56,98}
Scheme 4. Synthesis of S-S via oxidation of BuMP.

Characterization of the partially oxidized BuMP/S-S was afforded though $^1$H-NMR (Figure 4). For ease of comparison, following integrations of BuMP/S-S are normalized to pure BuMP monomer. Synthesis of BuMP/S-S was supported by the formation of two triplets ($e'$ and $f'$) at $\delta$ 2.46 (0.6H) and $\delta$ 2.70 (0.6H) due to the deshielding effect of the new S-S bond formed upon oxidizing S-H to S-S. The partial oxidation of BuMP/S-S was further supported by the decrease in the integration of peaks e and f from 2H (BuMP monomer) to 1.4H (BuMP/S-S) as well as the decrease in integration of the thiol peak (d) at $\delta$ 1.44 from 1H (BuMP monomer) to 0.71H (BuMP/S-S). The % conversion of S-H to S-S was determined by dividing the relative integration of $f'$ (0.6H) by the total integration of $f'$ and f (2H). The % conversion of S-H to S-S can also be calculated by using $e'$ and e instead of $f'$ and f or by subtracting the relative integration of the thiol peak (d) in the BuMP/S-S $^1$H-NMR spectrum from the thiol peak (d) in the BuMP monomer spectrum. The % conversion calculations suggest that approximately 30% of the BuMP monomer was converted to the S-S product.
* indicates impurity

Figure 4. $^1$H-NMR of BuMP monomer (top) and BuMP/S-S (bottom).

To prevent the formation of a side reaction in the presence of a commercial photoinitiator, the $C_{60}(\text{BuMP})_x$ derivative was remade using the resulting BuMP/S-S initiator according to Scheme 5. The reaction of $C_{60}$ with alkylthio radicals has previously been studied via EPR. However, the reaction was found to be reversible, which was observed by the color change from a red-purple solution to purple upon cessation of light. The reversibility of the reaction was found to be corrected by adding pure BuMP monomer as a hydrogen source.
Scheme 5. Synthesis of $C_{60}(\text{BuMP})_x$ using BuMP/S-S.

Structure-property relationships as a function of increasing BuMP addends bound to $C_{60}$ were explored by varying reaction times from 6-12 hrs, as reported in Table 2. The number of BuMP addends bound to $C_{60}$ was approximated using TGA by analyzing the mass lost between 115-570 °C. Representative TGA plots are provided in Figure 5 and the number of addends calculated from TGA is reported in Table 2. Any mass lost between room temperature and 115 °C is attributed to the loss of secondary bound water; between 115-570 °C, decomposition of BuMP attached to the cage; and the remaining mass lost above 570 °C is attributed to the decomposition of the fullerene cage. From the TGA data obtained, it was determined that upon increasing the reaction time, the number of BuMP addends bound to $C_{60}$ decreased from nine addends to four after 24 hrs. To enhance the probability of functionalizing $\text{Sc}_3\text{N}@[C_{80}]$ with BuMP monomers, the
Sc$_3$N@C$_{80}$ BuMP reaction was allowed to react for 6 hrs. According to TGA data, the resulting Sc$_3$N@C$_{80}$(BuMP) derivative was functionalized with ~ 7 BuMP addends and isolated in higher % yields (~50%) compared to C$_{60}$(BuMP)$_x$ derivatives (20-45%). The higher number of addends and the higher % yields were not expected considering previous reports indicate that Sc$_3$N@C$_{80}$ is much less reactive compared to C$_{60}$, indicating that our radical addition method result in Sc$_3$N@C$_{80}$ derivatives in higher yields over C$_{60}$ derivatives prepared under similar reaction conditions. Furthermore, the synthesis of Sc$_3$N@C$_{80}$(BuMP)$_7$ demonstrates the first report of thiolated Sc$_3$N@C$_{80}$.

Table 2

*Irradiation Time versus the Number of BuMP Addends Attached to the Fullerene Cage*

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Irradiation Time (hrs)</th>
<th>Avg. # Addends$^a$</th>
<th>Avg. Molecular Weight (g mole$^{-1}$)$^b$</th>
<th>% Yield$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$(BuMP)$_9$</td>
<td>6</td>
<td>9</td>
<td>2180</td>
<td>20</td>
</tr>
<tr>
<td>C$_{60}$(BuMP)$_7$</td>
<td>12</td>
<td>7</td>
<td>1856</td>
<td>32</td>
</tr>
<tr>
<td>C$_{60}$(BuMP)$_4$</td>
<td>24</td>
<td>4</td>
<td>1370</td>
<td>45</td>
</tr>
<tr>
<td>Sc$<em>3$N@C$</em>{80}$(BuMP)$_7$</td>
<td>6</td>
<td>7</td>
<td>2245</td>
<td>50</td>
</tr>
</tbody>
</table>

Experiments were conducted using a Rayonet photoreactor and irradiated at 250 nm. $^a$calculated from TGA plots as reported by Singh et al.$^{131}$; $^b$calculated based on number of addends determined from TGA; and $^c$ determined based on amount of product obtained after purification.
Figure 5. TGA graph showing the thermal decomposition of C\textsubscript{60} and C\textsubscript{60}(BuMP)\textsubscript{x} derivatives.

Figure 6. TGA graph showing the thermal decomposition of Sc\textsubscript{3}N@C\textsubscript{80} and Sc\textsubscript{3}N@C\textsubscript{80}(BuMP)\textsubscript{7} derivatives.

Furthermore, as seen in Figure 7, the recovered BuMP/S-S analyzed via \textsuperscript{1}H-NMR was found to consist of ~100% S-S. The increase in S-S from 30 - ~100% suggests that

27
over time, the concentration of the BuMP monomer decreases and the S-S concentration increases, indicating that the initial increase in the number of BuMP addends bound to C\textsubscript{60} occurs due to the excess of pure BuMP monomer to aid as a hydrogen source. As the reaction continues, and since the C\textsubscript{60}-thiol reaction is reversible, BuMP monomer is converted to S-S and C\textsubscript{60} doesn’t recapture the thiol since it is starved for a hydrogen source.\textsuperscript{98}

* indicates impurity

Figure 7. \textsuperscript{1}H-NMR of BuMP/S-S (top) and recovered BuMP/S-S (bottom).

A second derivative, C\textsubscript{60}(TMB-PPO), was prepared according to Scheme 6, utilizing the high reactivity of C\textsubscript{60} with the radicals produced from the commercial photoinitiator, bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (TMP-PPO). Structure-property relationships based on number of addends bound to C\textsubscript{60} was
determined by varying the molar ratio of C\textsubscript{60} to TMB:PPO from 1:1 to 1:12. Derivatives prepared during this study and corresponding fullerene:TMB-PPO molar ratios are reported in Table 3. TGA was used to determine the number of TMB-PPO addends bound to C\textsubscript{60}. Representative TGA plots are provided in Figure 8 and Figure 9, including C\textsubscript{60}, Sc\textsubscript{3}N@C\textsubscript{80}, TMB-PPO and fullerene derivatives prepared during this study. The maximum number of TMB-PPO derivatives bound to C\textsubscript{60} was calculated to be five, where the number of TMB-PPO addends bound to C\textsubscript{60} did not further increase upon increasing the fullerene:TMB-PPO ratio from 1:6 to 1:12. However, a decrease in the % yield was observed upon increasing the fullerene:TMB-PPO ratio due to removal of C\textsubscript{60}(TMB-PPO)\textsubscript{5} with unreacted TMB-PPO during purification. Therefore, Sc\textsubscript{3}N@C\textsubscript{80} was functionalized with TMB-PPO using the fullerene:TMB-PPO ratio of 1:6, which resulted in the addition of ~3 TMB-PPO addends to Sc\textsubscript{3}N@C\textsubscript{80}. Moreover, this work represents the first exploration of functionalizing Sc\textsubscript{3}N@C\textsubscript{80} with P- centered radicals and was obtained in >95 % yield.
Scheme 6. Synthesis of $C_{60}(\text{TMB-PPO})_x$.

Table 3

Mole Ratios of Fullerene and TMP-PPO Versus the Number of Addends Bound to the Fullerene Cage

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>C$_{60}$:TMB-PPO Molar Ratio</th>
<th>Avg. # Addends$^a$</th>
<th>Avg. Molecular Weight (g mole$^{-1}$)$^b$</th>
<th>% Yield$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$(TMB-PPO)$_2$</td>
<td>1:1</td>
<td>2</td>
<td>1000</td>
<td>&gt; 95</td>
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<tr>
<td>C$_{60}$(TMB-PPO)$_3$</td>
<td>1:3</td>
<td>3</td>
<td>1139</td>
<td>&gt; 95</td>
</tr>
<tr>
<td>C$_{60}$(TMB-PPO)$_5$</td>
<td>1:6</td>
<td>5</td>
<td>1400</td>
<td>&gt; 95</td>
</tr>
<tr>
<td>C$_{60}$(TMB-PPO)$_5$</td>
<td>1:12</td>
<td>5</td>
<td>1400</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>Sc$<em>3$N@C$</em>{80}$(TMB-PPO)$_3$</td>
<td>1:6</td>
<td>3</td>
<td>1586</td>
<td>&gt; 95</td>
</tr>
</tbody>
</table>

Experiments were conducted using a Rayonet photoreactor and irradiated at 350 nm for 1 h. $^a$calculated from TGA plots as reported by Singh et al.$^{131}$; $^b$calculated based on number of addends determined from TGA; and $^c$determined based on amount of product obtained after filtration.
The thermal stability of the $C_{60}(TMB-PPO)_x$ derivatives was also analyzed using TGA. Thermal degradation onset temperatures are defined as the temperature at 10%
mass loss and are observed in Figure 8 and Figure 9 and reported in Table 4. The thermal degradation onset temperatures of the fullerene derivatives were found to be between 190 and 236 °C, indicating an expected lower thermal stability compared to $C_{60}$ (642 °C) and Sc$_3$N@C$_{80}$ (719 °C) alone. However, the thermal stability of the fullerene derivatives is higher, compared to TMB-PPO alone (191 °C). The thermal stability of the derivatives was also found to decrease with an increase in TMB-PPO addends, where $C_{60}$(TMB-PPO)$_2$ exhibits a much higher thermal stability (37 °C) compared to $C_{60}$(TMB-PPO)$_5$. Furthermore, the thermal stability of $C_{60}$(TMB-PPO)$_3$ is higher (18 °C) compared to Sc$_3$N@C$_{80}$(TMB-PPO)$_3$, indicating a slightly elevated thermal stability for $C_{60}$ derivatives compared to Sc$_3$N@C$_{80}$ derivatives. Furthermore, pristine $C_{60}$ was found to decompose at temperatures above 800 °C, whereas, $C_{60}$(TMB-PPO)$_x$ derivatives were found to be stable at temperatures up to 800 °C. The stability of the $C_{60}$(TMB-PPO)$_x$ derivatives up to 800 °C, is believed to be due to the decomposition of the TMB-PPO addends resulting in a char and stabilizing $C_{60}$. 
Table 4

*TGA Results of Prepared Fullerene Derivatives*

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>C&lt;sub&gt;60&lt;/sub&gt;-TMB-PPO Molar Ratio</th>
<th>Thermal Degradation Onset (°C)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>% Char&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;60&lt;/sub&gt;(TMB-PPO)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1:1</td>
<td>236</td>
<td>68</td>
</tr>
<tr>
<td>C&lt;sub&gt;60&lt;/sub&gt;(TMB-PPO)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1:3</td>
<td>208</td>
<td>61</td>
</tr>
<tr>
<td>C&lt;sub&gt;60&lt;/sub&gt;(TMB-PPO)&lt;sub&gt;5&lt;/sub&gt;</td>
<td>1:6</td>
<td>199</td>
<td>48</td>
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<tr>
<td>Sc&lt;sub&gt;3&lt;/sub&gt;N@C&lt;sub&gt;80&lt;/sub&gt;(TMB-PPO)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1:6</td>
<td>190</td>
<td>63</td>
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<tr>
<td>TMB-PPO</td>
<td>-</td>
<td>191</td>
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<td>719</td>
<td>86</td>
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</table>

Experiments were conducted using a Rayonet photoreactor and irradiated at 350 nm for 1 h. *calculated from TGA as the temperature corresponding to 10% mass loss; *reported as the mass remaining above 800 °C from TGA analysis.

The solubility of the prepared fullerene derivatives in common solvents was investigated to determine how solubility is affected as a function of both the identity and the number of addends bound to C<sub>60</sub> and Sc<sub>3</sub>N@C<sub>80</sub>. Solubilities of the fullerene derivatives obtained in common solvents are reported in Table 5. Varying the identity and the number of addends bound to the fullerene was found to affect the solubility of both C<sub>60</sub> and Sc<sub>3</sub>N@C<sub>80</sub>. In general, adding four BuMP addends to C<sub>60</sub> increased the solubility of C<sub>60</sub> from 0.16 mg mL<sup>-1</sup> to 6 mg mL<sup>-1</sup> in chloroform, and the addition of seven increased the solubility to 12 mg mL<sup>-1</sup> in chloroform. However, the addition of nine BuMP addends resulted in a derivative that exhibited poor solubilities in all solvents. It is possible that the decrease in solubility of C<sub>60</sub>(BuMP)<sub>9</sub> is due to polymerization of or the higher molecular weight (~2180 g mol<sup>-1</sup>) of the fullerene derivative.
Table 5

*Solubility Studies of Fullerene Derivatives in Common Solvents at 20 °C Reported in mg mL⁻¹*

<table>
<thead>
<tr>
<th></th>
<th>MeOH</th>
<th>EtOH</th>
<th>Acetone</th>
<th>DCM</th>
<th>CHCl₃</th>
<th>Benzene</th>
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<tbody>
<tr>
<td>Dielectric constant</td>
<td>33</td>
<td>24.3</td>
<td>21</td>
<td>9.1</td>
<td>4.8</td>
<td>2.28</td>
</tr>
<tr>
<td>C₆₀¹³³</td>
<td>0</td>
<td>0.001</td>
<td>0.001</td>
<td>0.26</td>
<td>0.16</td>
<td>1.7</td>
</tr>
<tr>
<td>C₆₀(BuMP)₄</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>0.3</td>
</tr>
<tr>
<td>C₆₀(BuMP)₇</td>
<td>0.1</td>
<td>0.7</td>
<td>7</td>
<td>9</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>C₆₀(BuMP)₉</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>C₆₀(TMB-PPO)₂</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
<td>18</td>
<td>14</td>
<td>8</td>
</tr>
<tr>
<td>C₆₀(TMB-PPO)₃</td>
<td>0.4</td>
<td>1</td>
<td>1.3</td>
<td>19</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td>C₆₀(TMB-PPO)₅</td>
<td>6</td>
<td>3</td>
<td>40</td>
<td>260</td>
<td>219</td>
<td>91</td>
</tr>
<tr>
<td>Sc₃N@C₈₀</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Sc₃N@C₈₀(BuMP)y</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.9</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Sc₃N@C₈₀(TMB-PPO)₃</td>
<td>1.5</td>
<td>1.4</td>
<td>1.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Average of triplicate measurements, all values within ±10.

The solubility of C₆₀ was also affected upon the addition TMB-PPO addends to C₆₀. The addition of TMB-PPO was found to increase the solubility of C₆₀ in all common organic solvents studied over C₆₀ alone. The addition of five TMB-PPO addends was found to dramatically increase C₆₀’s solubility to remarkably high value of ~260 mg mL⁻¹ in DMC. However, the addition of two and three TMB-PPO addends only increased the solubility up to ~18-19 mg mL⁻¹ in DMC. Interestingly, there wasn’t much of a difference in the solubilities of C₆₀ containing two TMB-PPO addends versus three; however, a huge increase in solubility was observed with the addition of five TMB-PPO addends. The increase in solubility upon functionalizing fullerenes with TMB-PPO addends is
attributed to the addition of carbonyl and phosphine oxide functional groups, which exhibit more polar functionalities. However, there is no reported explanation regarding the solubility of fullerene derivatives in organic solvents as a function of addend functionality.

Upon derivatization of fullerenes, direct singlet oxygen studies were performed by directly detecting the phosphorescence of singlet oxygen at 1270 nm produced upon exciting a catalytic amount of fullerene derivatives at 345 nm using a fluorometer equipped with a NIR detector. Emission spectrums were obtained for pristine $C_{60}$ and fullerene derivatives to obtain normalized responses yielding $C_{60}$ equivalent correlation concentrations, and are plotted in Figure 10 as well as Figure A1-Figure A4 and are reported in Table 6. In general, an expected trend was observed where emission intensity increased with increasing concentration, and the generation of singlet oxygen decreased upon increased derivatization of $C_{60}$ independent of functionality. A previous study by Hamano et al.\textsuperscript{71} showed a similar trend where the efficiency of fullerene derivatives to produce singlet oxygen was not dependent on the type of addend, but was found to be depended on the number of addends, where efficiency decreased with an increase in the number of addends bound to $C_{60}$.
Figure 10. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C\textsubscript{60} and C\textsubscript{60}(TMB-PPO)\textsubscript{5} at λ\textsubscript{ex} = 346 nm.

Table 6

Efficiency of Singlet Oxygen Produced from Pure C\textsubscript{60} Versus Fullerene Derivatives via Direct Detection

<table>
<thead>
<tr>
<th>Derivatives</th>
<th>Derivatives (µM)</th>
<th>C\textsubscript{60} (µM)</th>
<th>Relative Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc\textsubscript{3}N@C\textsubscript{80}</td>
<td>0.3</td>
<td>0.1</td>
<td>-3</td>
</tr>
<tr>
<td>C\textsubscript{60} (BuMP)\textsubscript{4}</td>
<td>14</td>
<td>1</td>
<td>-14</td>
</tr>
<tr>
<td>C\textsubscript{60}(TMB-PPO)\textsubscript{2}</td>
<td>9</td>
<td>0.9</td>
<td>-10</td>
</tr>
<tr>
<td>C\textsubscript{60}(TMB-PPO)\textsubscript{3}</td>
<td>13</td>
<td>1</td>
<td>-13</td>
</tr>
<tr>
<td>C\textsubscript{60}(TMB-PPO)\textsubscript{5}</td>
<td>26</td>
<td>1</td>
<td>-25</td>
</tr>
</tbody>
</table>

Singlet oxygen was directly detected via phosphorescence at 1270 nm at λ\textsubscript{ex} = 350 nm.
Singlet oxygen studies were also performed on Sc₃N@C₈₀ derivatives. Sc₃N@C₈₀(TMB-PPO)₃ exhibits poor solubility in benzene, so the singlet oxygen response obtained upon exciting Sc₃N@C₈₀(TMB-PPO)₃ was compared to that of C₆₀(TMB-PPO)₅ in acetone. Interestingly, though Sc₃N@C₈₀ itself was shown to produce singlet oxygen, derivatizing Sc₃N@C₈₀ with either BuMP or TMB-PPO was found to greatly hinder the singlet oxygen generating ability of Sc₃N@C₈₀, where the presence of singlet oxygen was not observed at all upon exciting Sc₃N@C₈₀ derivatives.

Further characterization was afforded on C₆₀(BuMP)₄, C₆₀(TMB-PPO)₅, Sc₃N@C₈₀(BuMP)₇ and Sc₃N@C₈₀(TMB-PPO)₃, which resulted in higher solubilities in common organic solvents and higher yields. As seen in Figure 11 and Figure 12 as well as Table 7, the purified C₆₀(BuMP)₄ and Sc₃N@C₈₀(BuMP)₇ derivative possess characteristic IR peaks of the BuMP starting material (2957, 2875 (ν C-H, s), 1735 (ν C=O, s), 1487, 1250 (δ C-H, m), 1165, 1066 (ν C-O, m) cm⁻¹). Furthermore, the thiol peak at 2570 cm⁻¹ present in the BuMP spectrum is not observed for either C₆₀(BuMP)₄ or Sc₃N@C₈₀(BuMP)₇. The characteristic IR peaks of the BuMP starting material along with the disappearance of the thiol peak observed in the spectrum of the purified C₆₀(BuMP)₄ and Sc₃N@C₈₀(BuMP)₇ derivative supports the successful functionalization of C₆₀ and Sc₃N@C₈₀ with BuMP.
Figure 11. FT-IR spectrum of C₆₀(BuMP)₄ and BuMP starting material.

Figure 12. FT-IR spectrum of Sc₃N@C₈₀(BuMP)₇ and BuMP starting material.
Table 7

_Frequencies (cm\(^{-1}\)) of Relevant Infrared Absorption Bands of C\(_{60}(BuMP)_4\) and Sc\(_3N@C\(_{80}(BuMP)_7\) Derivatives_

<table>
<thead>
<tr>
<th>Assignments</th>
<th>BuMP</th>
<th>C(_{60}(BuMP)_4)</th>
<th>Sc(<em>3N@C(</em>{80}(BuMP)_7)</th>
<th>C(_{50})</th>
<th>Sc(<em>3N@C(</em>{80})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu) C-H</td>
<td>2957(s)</td>
<td>2957(m)</td>
<td>2957(m)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2875(s)</td>
<td>2875(m)</td>
<td>2875(m)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) S-H</td>
<td>2573(w)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) C=O</td>
<td>1735(s)</td>
<td>1735(s)</td>
<td>1735(s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) C=C</td>
<td>-</td>
<td>1610(m)</td>
<td>1653(w)</td>
<td>1428(m)</td>
<td>1380(m)</td>
</tr>
<tr>
<td>(\delta) C-H</td>
<td>1487(m)</td>
<td>1487(m)</td>
<td>1458(m)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1250(m)</td>
<td>1250(s)</td>
<td>1250(m)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) C-C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1180(m)</td>
<td>1200(w)</td>
</tr>
<tr>
<td>(\nu) C-O</td>
<td>1165(m)</td>
<td>1165(s)</td>
<td>1165(w)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1066(m)</td>
<td>1066(s)</td>
<td>1066(w)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\delta) C-H</td>
<td>-</td>
<td>853(w)</td>
<td>836(w)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>752(w)</td>
<td>759(w)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>694(w)</td>
<td>725(w)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) Sc-N</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>600(m)</td>
</tr>
<tr>
<td>(\delta) C-C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>575(m)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>526(m)</td>
<td>-</td>
</tr>
</tbody>
</table>

\(s=\text{strong, } m=\text{medium, } w=\text{weak}\)

C\(_{60}(\text{TMB-PPO})_5\) and Sc\(_3N@C\(_{80}(\text{TMB-PPO})_3\) samples were also characterized via FT-IR. As seen in Figure 13 and Figure 14 as well as Table 8, purified C\(_{60}(\text{TMB-PPO})_5\) and Sc\(_3N@C\(_{80}(\text{TMB-PPO})_3\) samples contain characteristic IR peaks of TMB-PPO (2929, 2861 (\(\nu\) C-H, s), 1608 (\(\nu\) C=C, s), 1437, 1381 (\(\delta\) C-H, m), 1149 (\(\nu\) P-Ar, m), 850, 750, and 694 (\(\delta\) C-H, m) \(\text{cm}^{-1}\)). An apparent shift in the C=O\(_{\text{TMB}}\) from 1680 to 1707 \(\text{cm}^{-1}\) is observed for both C\(_{60}(\text{TMB-PPO})_5\) and Sc\(_3N@C\(_{80}(\text{TMB-PPO})_3\). Furthermore, a shift in the P=O\(_{\text{PPO}}\) peaks from 1201 and 1222 \(\text{cm}^{-1}\) to 1223 and 1242 \(\text{cm}^{-1}\) was observed upon the binding of PPO to C\(_{60}\) and a shift to 1261 \(\text{cm}^{-1}\) was observed upon binding PPO to Sc\(_3N@C\(_{80}\).
Figure 13. FT-IR spectrum of C₆₀(TMB-PPO)₅ and TMB-PPO starting material.

Figure 14. FT-IR spectrum of Sc₃N@C₈₀(TMB-PPO)₃ and TMB-PPO starting material.
Table 8

*Frequencies (cm\(^{-1}\)) of Relevant Infrared Absorption Bands of C\(_{60}\)(TMB-PPO)\(_5\) and Sc\(_3\)N@C\(_{80}\)(TMB-PPO)\(_3\) Derivatives*

<table>
<thead>
<tr>
<th>Assignments</th>
<th>TMB-PPO</th>
<th>C(_{60})(TMB-PPO)(_5)</th>
<th>Sc(<em>3)N@C(</em>{80})(TMB-PPO)(_3)</th>
<th>C(_{60})</th>
<th>Sc(<em>3)N@C(</em>{80})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu) C-H</td>
<td>2929(s)</td>
<td>2929(s)</td>
<td>2911(s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2861(s)</td>
<td>2861(s)</td>
<td>2852(s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) C=O</td>
<td>1680(s)</td>
<td>1707(s)</td>
<td>1731(w)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) C=C</td>
<td>1608(s)</td>
<td>1608(s)</td>
<td>1606(w) 1428(m) 1380(m)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\delta) C-H</td>
<td>1437(m)</td>
<td>1437(m)</td>
<td>1437(m)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1381(m)</td>
<td>1381(m)</td>
<td>1381(m)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) P=O</td>
<td>1218(s)</td>
<td>1242(s)</td>
<td>1259(s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1201(s)</td>
<td>1222(s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) C=C</td>
<td>-</td>
<td>-</td>
<td>1180(m) 1200(w)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) P-Ar</td>
<td>1149(m)</td>
<td>1154(s)</td>
<td>1141(s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\delta) C-H</td>
<td>850(m)</td>
<td>850(m)</td>
<td>800(m)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>750(m)</td>
<td>750(m)</td>
<td>694(m)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>694(m)</td>
<td>694(m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\nu) Sc-N</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>600(m)</td>
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</tr>
<tr>
<td>(\delta) C-C</td>
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<td>575(m)</td>
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<td>526(m)</td>
<td>-</td>
</tr>
</tbody>
</table>

\(s=\text{strong, } m=\text{medium, } w=\text{weak}\)

C\(_{60}\)(BuMP)\(_4\), C\(_{60}\)(TMB-PPO)\(_5\), Sc\(_3\)N@C\(_{80}\)(BuMP)\(_y\) and Sc\(_3\)N@C\(_{80}\)(TMB-PPO)\(_3\), were also analyzed using MALDI-MS to observe the presence of the fullerene, which is difficult to detect in FT-IR due to overlapping C-H and C=C peaks present for both the fullerene and TMB-PPO. As seen in Figure 15, MALDI analysis on each C\(_{60}\) derivative yielded a parent ion peak at \(m/z\) 720 and each Sc\(_3\)N@C\(_{80}\) derivative yielded a parent ion peak at \(m/z\) 1109. Further MALDI analysis of C\(_{60}\)(TMB-PPO)\(_5\) yielded an isomer distribution centered around \(m/z\) 1368 corresponding to C\(_{60}\) with ~ 5 TMB-PPO addends and further suggesting a population of isomers present (Figure 16). The higher molecular weights of the C\(_{60}\)(BuMP)\(_4\) and Sc\(_3\)N@C\(_{80}\)(BuMP)\(_7\) derivatives were not observed due to
the favorable breaking of the weaker fullerene-sulfur bonds, allowing the fullerene to re-establish conjugation

C\textsubscript{60}(TMB-PPO)\textsubscript{5} was also analyzed using elemental analysis (EA), which resulted in experimental percent compositions of C 78.6, H 4.4, O 15.6, P 1.4. Using the obtained EA experimental percent compositions, the formula for C\textsubscript{60}(TMB-PPO)\textsubscript{5} was corrected to C\textsubscript{60}(TMB)\textsubscript{4.3}(PPO)\textsubscript{0.7}(O)\textsubscript{4}(H\textsubscript{2}O)\textsubscript{7}. EA suggests the attachment of 5 TMB-PPO addends at a ratio of 0.7 PPO to 4.3 TMB (1PPO:6TMB) addends per C\textsubscript{60}, which correlates well with TGA and MALDI. ICP-MS was obtained for both C\textsubscript{60}(TMB-PPO)\textsubscript{5} and Sc\textsubscript{3}N@C\textsubscript{80}(TMB-PPO)\textsubscript{3}, and suggests that 1.6% of the C\textsubscript{60}(TMB-PPO)\textsubscript{5} sample consists of phosphorous, which further correlates with EA. ICP also suggests the binding of ~2.25 phosphorous addends per Sc\textsubscript{3}N@C\textsubscript{80}, and TGA suggested a total of 3 addends bound to Sc\textsubscript{3}N@C\textsubscript{80}, indicating a higher binding of phosphorous to Sc\textsubscript{3}N@C\textsubscript{80} compared to C\textsubscript{60}. ICP data was also found to correlate well with FT-IR, where phosphine oxide peaks were stronger than the carbonyl peaks for the Sc\textsubscript{3}N@C\textsubscript{80}(TMB-PPO)\textsubscript{3} sample.

![MALDI spectrum of C\textsubscript{60} derivatives (left) and Sc\textsubscript{3}N@C\textsubscript{80} derivatives (right).](image)

\textit{Figure 15.} MALDI spectrum of C\textsubscript{60} derivatives (left) and Sc\textsubscript{3}N@C\textsubscript{80} derivatives (right).
Figure 16. MALDI isomer distribution of C₆₀(TMB-PPO)₅.

Since the cleavage of TMB-PPO at 350 nm yields a 2:1 ratio of TMB and PPO radicals, both of which can readily react with C₆₀, ¹H-NMR was performed to determine the relative ratio of TMB and PPO addends bound to C₆₀(TMB-PPO)₅. As observed in Figure 17, the TMB-PPO starting material possesses well-resolved and unique hydrogen chemical shifts for both TMB (Hₐ, 7.86 δ; Hₖ, 7.53 δ; Hₖ, 7.40 δ) and PPO (Hₐ, 6.77 δ; Hₖ, 2.23 δ; Hₖ, 2.12 δ), allowing for the easy integration of ¹H-NMR peak areas. Unlike the starting material, the C₆₀(TMB-PPO)₅ adduct yields broad peaks for TMB (Hₐ, Hₖ, Hₖ, 7.57 δ) and PPO (Hₐ, Hₖ, Hₖ, 2.13 δ) addends, which is suggestive of a population of isomers and not a single isomer. However, though broad peaks are present in the ¹H-NMR spectrum of the C₆₀(TMB-PPO)₅ derivative, overlapping of the TMB and PPO regions were not observed, allowing for the integration of the ¹H-NMR peak areas. To determine the ratio of TMB and PPO addends, the total area of TMB (Hₐ, Hₖ, and Hₖ =
22) and PPO (H_d, H_e, H_f = 5) of the starting material was compared to the total area of TMB (H_a, H_b, and H_c = 66) and PPO (H_d, H_e, H_f = 5) of C_{60}(TMB-PPO)_{5}. The $^1$H-NMR data suggests that there are six TMB groups for every PPO group, indicating that not every C_{60} contains a PPO group, which correlates well with EA.

Figure 17. $^1$H-NMR of TMB-PPO (top) and C_{60}(TMB-PPO)_{5} (bottom).

In summary, thiolated C_{60} and Sc_{3}N@C_{80} fullerene derivatives were synthesized via radical addition of the thyl radical produced upon photolysis of BuMP/S-S and isolated when pure BuMP monomer was added as a hydrogen source. Furthermore, other C_{60} and Sc_{3}N@C_{80} derivatives were prepared via radical addition of the resulting
products produced upon photolysis of the commercial photoinitiator TMB-PPO. Resulting fullerene derivatives were shown to exhibit enhanced solubility in common solvents over C\textsubscript{60} alone, allowing for easier processing. Furthermore, functionalizing C\textsubscript{60} or encapsulating metals within the fullerene cage was found to depress the production of singlet oxygen but did not completely hinder it. Moreover, the singlet oxygen production of resulting derivatives was found to be independent of addend identity but dependent on the number of addends attached to C\textsubscript{60}, where the singlet oxygen production of derivatives decreased with an increase in addends. However, the depressed production of singlet oxygen is compensated for by the tremendous increase in solubility in organic solvents and miscibility with monomers.

Further characterization was afforded on the preferred soluble derivatives, C\textsubscript{60}(BuMP)\textsubscript{4}, Sc\textsubscript{3}N@C\textsubscript{80}(BuMP)\textsubscript{7}, C\textsubscript{60}(TMB-PPO)\textsubscript{5} and Sc\textsubscript{3}N@C\textsubscript{80}(TMB-PPO)\textsubscript{3} obtained in higher yields, using standard techniques and supported the successful functionalization of C\textsubscript{60} and Sc\textsubscript{3}N@C\textsubscript{80} with BuMP or TMB-PPO addends. Furthermore, an overall ratio of 1PPO:6TMB was determined for C\textsubscript{60}(TMB-PPO)\textsubscript{5}, indicating an expected increased radical reactivity of the carbon radical. However, a higher percentage of PPO was observed for the Sc\textsubscript{3}N@C\textsubscript{80}(TMB-PPO)\textsubscript{3} adduct, which may be due to the reversed electronic requirements of Sc\textsubscript{3}N@C\textsubscript{80} compared to C\textsubscript{60}.
CHAPTER III - INCORPORATION OF FULLERENE DERIVATIVES INTO THIOL-ENE POLYMER MATRICES

Introduction

The low solubility and the high crystallinity of C\textsubscript{60} render C\textsubscript{60} useless for numerous material applications. Therefore, to utilize the unique properties of fullerenes, many efforts have been made to incorporate fullerenes and fullerene derivatives into a polymer matrix via covalent incorporation or upon blending with compatible polymers to produce a processable fullerene-containing material\textsuperscript{134}. Fullerene derivatives, such as phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM) have been blended into various polymer networks for their use as an organic photovoltaic (OPV) cell. Recently, fullerene-polymer blends of C\textsubscript{60} and Sc\textsubscript{3}N@C\textsubscript{80} containing polystyrene-\textit{block}-polybutadiene-\textit{block}-polystyrene (SBS) and polystyrene-\textit{block}-polyisoprene-\textit{block}-polystyrene (SIS) were prepared for use as a stimuli-responsive adhesive and as an antimicrobial coating due to the ability of the blended polymer film to produce singlet oxygen\textsuperscript{83,135}. The singlet oxygen generating ability of C\textsubscript{60} has also been utilized to prepare self-cleaning photocatalytic coatings upon blending C\textsubscript{60} and C\textsubscript{60} derivatives into a polyurethane matrix\textsuperscript{85}.

However, little is known about the consequences of incorporating singlet oxygen generating species into polymer networks. There are a number of known reactions of singlet oxygen with chemical moieties present in common polymer networks. Alkyl sulfides are known to readily react with singlet oxygen, resulting in the formation of new functional groups that can be detected via FT-IR\textsuperscript{136}. As seen in Scheme 7, singlet oxygen can react with sulfides producing a peroxysulfoxide and thiadioxirane intermediates,
which can decay yielding sulfones or decay to ground-state triplet oxygen and the sulfide starting material. The formation of sulfones can be detected by FT-IR due to their strong IR absorption bands near 1400-1300 cm\(^{-1}\) and 1200-1300 cm\(^{-1}\). Singlet oxygen can also react with sulfides, yielding sulfoxides, which exhibit strong IR absorption bands near 1225-980 cm\(^{-1}\). Additionally, singlet oxygen can react with residual alkene monomers producing hydroperoxides, which can further react forming ketones. Hydroperoxides exhibit O-O-H and strong C-O-O stretching IR absorption bands between 3450-3200 cm\(^{-1}\) and 1200-1000 cm\(^{-1}\), respectively. Furthermore, ketones and other carbonyl groups exhibit strong stretching IR absorption bands near 1800-1650 cm\(^{-1}\).

Scheme 7. Common singlet oxygen reactions with sulfoxides and alkenes.

In this chapter, fullerene derivatives exhibiting enhanced solubility were incorporated into two very different thiol-ene polymer matrices at varying thiol-ene monomer concentrations (1:1 or 1:0.75 molar equivalents) and at different loadings of C\(_{60}\) (0-20 wt %). The dispersibility of prepared fullerenes as a function of monomer identity and C\(_{60}\) loading, along with the effect on the thermal and mechanical properties of the fullerene-doped films were explored. Furthermore, the ability of the resulting C\(_{60}\)
containing thiol-ene networks to generate singlet oxygen as well as characterization of potential photooxidized products produced upon generating singlet oxygen were explored.

Materials, Method, and Characterization

Materials

Materials used in the preparation, purification, and characterization of the fullerene containing thiol-ene films were C_{60}(TMB-PPO)_{5} and Sc_{3}N@C_{80}(TMB-PPO)_{3} prepared in previous study; trimethylolpropane diallyl ether (TMPDE, 90%), 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT, 98%), trimethylolpropane tris (3-mercaptotropolionate) (TMPMP, >95%), pentaerythritol tetrakis (3-mercaptotropolionate) (PETMP, >95%), 2,2’-azobis(2-methylpropionitrile) (AIBN, 98%) purchased from Sigma Aldrich Chemical Company (St. Louis, MO); dichloromethane (DCM, ≥99.5%) obtained from EMD Chemicals (Gibbstown, NJ). All commercial chemicals were used as received.

Method

Synthesis of C_{60}- and Sc_{3}N@C_{80}(TMB-PPO) thiol-ene films. Fullerene containing thiol-ene films were prepared by adding a known mass of the C_{60}(TMB-PPO)_{5} or Sc_{3}N@C_{80}(TMB-PPO)_{3} derivative to a thiol-ene monomer mix of either PETMP:TTT or TMPMP:TMPDE monomers at varying thiol-ene monomer concentrations of 1:1 to 1:0.75 molar equivalents. AIBN thermal initiator (1 wt % solids) was added to the sample, and the resulting mixture was combined in a high shear mixer (FlackTec Inc SpeedMixer™) at 2,400 rpm for 5 min. DCM (2-10 mL) was added to the sample to aid in uniform mixing. Any residual solvent was removed under reduced pressure, and the
resulting sample was added to a 10 g Teflon release mold and placed in a 50-65 °C oven for 24-96 hrs to ensure complete polymerization. Five different sets of fullerene-TE films were prepared: the C₆₀(TMB-PPO)₅ films prepared using PETMP:TTT and TMPMP:TMPDE monomers at 1:1 and at 1:0.75 molar equivalents at four different loadings of C₆₀ (1,5,10, and 20 wt %) and an Sc₃N@C₈₀(TMB-PPO)₃ film using TMPMP:TMPDE monomers at 1:0.75 molar equivalents with a Sc₃N@C₈₀ loading of 1.5 wt % for a total of 21 films. The resulting films were characterized using DSC, TEM, and dielectric spectroscopy.

**Characterization**

*Gel fractions* - Gel fractions of the prepared films were obtained by adding a known mass of the film in benzene, allowing the samples to rest at room temperature for 24 hrs, and recovering the remaining film. Residual solvent was removed at 80 °C under reduced pressure, and the final mass of the residual dry film was obtained to determine the gel fractions, which is recorded as the final mass of the film after solvent removal over the initial mass and is expressed as a percent. UV-Vis was obtained on the resulting benzene solution to determine the amount of extractable C₆₀-TMB-PPO through comparisons to known standards.

*Differential scanning calorimetry (DSC)* - The glass transition temperature (T_g) of the films (~10 mg) was obtained using a TA instruments Q2000 modulated DSC over the temperature range of -90 to 150 °C in a heat/cool/heat cycle at a 10 °C min⁻¹ ramp rate.

*Dielectric measurements* - Dielectric properties were measured using a Keithley 4200 Semiconductor Characterization System (SCS) connected to a custom designed parallel plate electrode assembly at room temperature under nitrogen. Two types of
permittivity tests were performed. The first test measured permittivity at frequencies spanning from 10 kHz to 10 MHz in graduated logarithmic steps with 0 VDC (volts dc) bias. For the second test, the DC offset voltage was swept from -30 to +30 VDC in 1 VDC steps at a constant frequency. Both tests calculated capacitance by measuring the root mean squared (rms) current at the given frequency and rms voltage.

*Transmission electron microscopy (TEM)* - The dispersion of C$_{60}$(TMB-PPO)$_5$ and Sc$_3$N@C$_{80}$(TMB-PPO)$_3$ in the thiol-ene matrix was visualized using a Zeiss EM-900 TEM at 50kV. TEM samples were prepared using a Leica EM FC6 ultramicrotome with cryochamber cooled to -60 °C and sliced using glass knives. Samples were applied to 300 mesh copper grids, purchased from Electron Microscopy Sciences.

**Results and Discussion**

The solubility of C$_{60}$ was greatly enhanced from having poor solubility (0.26 mg mL$^{-1}$) to having exceptional solubility (260 mg mL$^{-1}$) in DCM, and an increase in Sc$_3$N@C$_{80}$ solubility from 0 mg mL$^{-1}$ to 1.5 mg mL$^{-1}$ in methanol was observed upon derivatizing with TMB-PPO. The increase in solubility of both C$_{60}$ and Sc$_3$N@C$_{80}$ allowed for the easy incorporation into a thiol-ene polymer matrix. Fullerene containing thiol-ene films were prepared according to Scheme 8, where fullerene derivatives, C$_{60}$(TMB-PPO)$_5$ and Sc$_3$N@C$_{80}$(TMB-PPO)$_3$, were added to a thiol-ene monomer mix of either PETMP:TTT or TMPMP:TMPDE monomers, shown in Figure 18, at varying thiol-ene monomer concentrations of 1:1 or 1:0.75 molar equivalents. The molar ratio of the ene monomer was varied to determine the ability of the C$_{60}$(TMB-PPO)$_5$ derivative to react as a reactive ene allowing for the covalent incorporation of C$_{60}$ into the thiol-ene polymer matrix. Other film compositions were prepared with an ene deficiency (0.25:1
and 0.5:1 alkyl ene: thiol) to determine the least amount of alkyl ene needed to produce a film with good mechanical integrity. Films prepared with an alkyl ene: thiol molar ratio less than 0.75:1 exhibited poor film quality evident by gel % values lower than 50 %. Furthermore, the monomer composition was varied from a very rigid monomer system, PETMP:TTT \((T_g \, 56)\), to a very flexible monomer system, TMPMP:TMPDE \((T_g \, -32)\), to determine how the incorporation of \(C_{60}\) into the polymer matrix changes the thermal and mechanical properties of the extremes in thiol-ene systems. Overall, five different sets of fullerene-thiol-ene films were prepared and are reported in Table 9. Representative images of the resulting thiol-ene films with an increase in \(C_{60}\) loading are pictured in Figure 19.

\[ \text{TMPDE} \]
\[ \text{TTT} \]

Trimethylolpropane
diallyl ether

1,3,5-triallyl-1,3,5-triazine-
2,4,6(1H, 3H, 5H)-trione

\[ \text{TMPMP} \]
\[ \text{PETMP} \]

Trimethylolpropane tris
(3-mercaptopropionate)
Pentaerythritol tetrakis
(3-mercaptopropionate)

*Figure 18.* Monomers used in the synthesis of fullerene containing thiol-ene films.
Scheme 8. Preparation of $C_{60}(TMB-PPO)_5$ containing thiol-ene films.
Table 9

Sample Compositions of C₆₀(TMB-PPO)₅ Thiol-Ene Films

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Weight % C₆₀</th>
<th>Weight % C₆₀(TMB-PPO)₅</th>
<th>Monomer Composition</th>
<th>Ene/Thiol ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETMP:TTT-1-0</td>
<td>0</td>
<td>0</td>
<td>PETMP:TTT</td>
<td>1</td>
</tr>
<tr>
<td>PETMP:TTT-1-1</td>
<td>1</td>
<td>2</td>
<td>PETMP:TTT</td>
<td>1</td>
</tr>
<tr>
<td>PETMP:TTT-1-5</td>
<td>5</td>
<td>10</td>
<td>PETMP:TTT</td>
<td>1</td>
</tr>
<tr>
<td>PETMP:TTT-1-10</td>
<td>10</td>
<td>19</td>
<td>PETMP:TTT</td>
<td>1</td>
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<tr>
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<td>20</td>
<td>39</td>
<td>PETMP:TTT</td>
<td>1</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-0</td>
<td>0</td>
<td>0</td>
<td>PETMP:TTT</td>
<td>0.75</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-1</td>
<td>1</td>
<td>2</td>
<td>PETMP:TTT</td>
<td>0.75</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-5</td>
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<td>10</td>
<td>PETMP:TTT</td>
<td>0.75</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-10</td>
<td>10</td>
<td>19</td>
<td>PETMP:TTT</td>
<td>0.75</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-20</td>
<td>20</td>
<td>39</td>
<td>PETMP:TTT</td>
<td>0.75</td>
</tr>
<tr>
<td>TMPMP:TMPDE-1-0</td>
<td>0</td>
<td>0</td>
<td>TMPMP:TMPDE</td>
<td>1</td>
</tr>
<tr>
<td>TMPMP:TMPDE-1-1</td>
<td>1</td>
<td>2</td>
<td>TMPMP:TMPDE</td>
<td>1</td>
</tr>
<tr>
<td>TMPMP:TMPDE-1-5</td>
<td>5</td>
<td>10</td>
<td>TMPMP:TMPDE</td>
<td>1</td>
</tr>
<tr>
<td>TMPMP:TMPDE-1-10</td>
<td>10</td>
<td>19</td>
<td>TMPMP:TMPDE</td>
<td>1</td>
</tr>
<tr>
<td>TMPMP:TMPDE-1-20</td>
<td>20</td>
<td>39</td>
<td>TMPMP:TMPDE</td>
<td>1</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-0</td>
<td>0</td>
<td>0</td>
<td>TMPMP:TMPDE</td>
<td>0.75</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-1</td>
<td>1</td>
<td>2</td>
<td>TMPMP:TMPDE</td>
<td>0.75</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-5</td>
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<td>10</td>
<td>TMPMP:TMPDE</td>
<td>0.75</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-10</td>
<td>10</td>
<td>19</td>
<td>TMPMP:TMPDE</td>
<td>0.75</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-20</td>
<td>20</td>
<td>39</td>
<td>TMPMP:TMPDE</td>
<td>0.75</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-1.5% Sc₃N@C₈₀</td>
<td>1.5% Sc₃N@C₈₀</td>
<td>2.4</td>
<td>TMPMP:TMPDE</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Figure 19. Images of thiol-ene films containing (a) 0%, (b) 1%, (c) 5%, (d) 10%, and (e) 20% C<sub>60</sub>.

As seen in Figure 20, the incorporation of C<sub>60</sub>(TMB-PPO)<sub>5</sub> into the thiol-ene films resulted in a visually more uniform and continuous film compared to the addition of pure C<sub>60</sub>. Furthermore, a general and expected trend was observed where the films prepared with higher loadings of C<sub>60</sub> (>5%) resulted in an increase in color (Figure 19). It should also be noted that curing time was found to be greatly dependent on monomer identity and C<sub>60</sub> loading, where curing times increased with an increase in C<sub>60</sub> loading and with a decrease in monomer rigidity. The increased curing times as a function of C<sub>60</sub> loading is due to the radical scavenging ability of fullerenes. Furthermore, the increased curing time for TMPMP:TMPDE compared to the PETMP:TTT monomers is due to the decreased monomer functionality of the TMPMP:TMPDE monomers versus the PETMP:TTT monomers.
Figure 20. Side-by-side comparison of 1 wt % C$_{60}$ incorporated into a thiol-ene matrix using pure C$_{60}$ (left) and C$_{60}$(TMB-PPO)$_5$ (right).

The gel percents and the amount of C$_{60}$(TMB-PPO)$_5$ extracted from the resulting films were analyzed to obtain an initial insight into the degree of incorporation of the derivatives into the thiol-ene films. As seen in Table 10, all films at low loadings of C$_{60}$ (<5%) yield good gel percent values (>90%). Furthermore, all films prepared using the flexible monomers (TMPMP:TMPDE) yield similar gel percents, all above 90%.

However, a very different trend was observed with films prepared using the rigid (PETMP:TTT) monomers with higher loadings of C$_{60}$ (>10%), where the ene deficient PETMP:TTT-0.75 films exhibit significantly higher gel percent values (99% and 98%) compared to the PETMP:TTT-1 film series (88% and 47%). Furthermore, the PETMP:TTT-0.75-20 films yielded higher gel percent values (98%) compared to PETMP:TTT-1-20 (47%), which suggests an increase in the incorporation of C$_{60}$(TMB-PPO)$_5$ in the ene deficient films at higher C$_{60}$ loadings.
### Table 10

**Summary of Prepared C\textsubscript{60}(TMB-PPO)\textsubscript{5} Thiol-Ene Films**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Weight % C\textsubscript{60}</th>
<th>Gel %</th>
<th>% Extractable C\textsubscript{60}(TMB-PPO)\textsubscript{5}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETMP:TTT-1-0</td>
<td>0</td>
<td>99</td>
<td>-</td>
</tr>
<tr>
<td>PETMP:TTT-1-1</td>
<td>1</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>PETMP:TTT-1-5</td>
<td>5</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>PETMP:TTT-1-10</td>
<td>10</td>
<td>88</td>
<td>15</td>
</tr>
<tr>
<td>PETMP:TTT-1-20</td>
<td>20</td>
<td>47</td>
<td>63</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-0</td>
<td>0</td>
<td>99</td>
<td>-</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-1</td>
<td>1</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-5</td>
<td>5</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-10</td>
<td>10</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>PETMP:TTT-0.75-20</td>
<td>20</td>
<td>98</td>
<td>5</td>
</tr>
<tr>
<td>TMPMP:TMPDE-1-0</td>
<td>0</td>
<td>99</td>
<td>-</td>
</tr>
<tr>
<td>TMPMP:TMPDE-1-1</td>
<td>1</td>
<td>97</td>
<td>1</td>
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<td>TMPMP:TMPDE-1-5</td>
<td>5</td>
<td>95</td>
<td>2</td>
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<tr>
<td>TMPMP:TMPDE-1-10</td>
<td>10</td>
<td>93</td>
<td>3</td>
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<td>20</td>
<td>93</td>
<td>7</td>
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<tr>
<td>TMPMP:TMPDE-0.75-0</td>
<td>0</td>
<td>91</td>
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<tr>
<td>TMPMP:TMPDE-0.75-1</td>
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<td>99</td>
<td>0</td>
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<tr>
<td>TMPMP:TMPDE-0.75-5</td>
<td>5</td>
<td>95</td>
<td>2</td>
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<tr>
<td>TMPMP:TMPDE-0.75-10</td>
<td>10</td>
<td>94</td>
<td>5</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-20</td>
<td>20</td>
<td>93</td>
<td>6</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-1.5%</td>
<td>1.5 %</td>
<td>96</td>
<td>0</td>
</tr>
</tbody>
</table>

The amount of C\textsubscript{60}(TMB-PPO)\textsubscript{5} extracted during gel percent studies was also analyzed and is reported in Table 10. In general, the amount of C\textsubscript{60}(TMB-PPO)\textsubscript{5} extracted was found to compare well with the gel percent values obtained. For all samples, an expected trend in the amount of C\textsubscript{60}(TMB-PPO)\textsubscript{5} extracted increased as a function of C\textsubscript{60} loading, where little (<2%), if any, C\textsubscript{60}(TMB-PPO)\textsubscript{5} was extracted from films with low loading.
loadings of $C_{60}$. Furthermore, all samples prepared with TMPMP:TMPDE monomers as well as the PETMP:TTT-0.75 films resulted in films with moderately low (<7%) amounts of extracted $C_{60}(\text{TMB-PPO})_5$. However, the amount of $C_{60}(\text{TMB-PPO})_5$ extracted from the PETMP:TTT-1 film series increased significantly with higher loadings of $C_{60}$, where 15% and 63% of the $C_{60}(\text{TMB-PPO})_5$ added was extracted from PETMP:TTT-1-10 and PETMP:TTT-1-20 films, respectively. Both gel percent values and the amount of $C_{60}(\text{TMB-PPO})_5$ extracted from the prepared films suggests that $C_{60}$ is being covalently incorporated into the films, as observed by high gel percent values and a low amount of $C_{60}(\text{TMB-PPO})_5$ extracted from all films except the PETMP:TTT-1 10 and 20 wt % film series.

The thermal and mechanical properties of the resulting thiol-ene films were explored as a function of $C_{60}$ loading, alkyl ene concentration, and monomer rigidity. Thermal stability of the resulting films was determined using TGA, and representative TGA plots are provided in Figure 21 as well as Figure A5-Figure A7. Thermal degradation onset temperatures and % char were calculated from TGA and are recorded in Table 11. In general, the thermal stability decreases (50-100 °C) with an increase in $C_{60}$ loading and is slightly higher (~ 15 °C) for the rigid PETMP:TTT films series compared to the flexible TMPMP:TMPDE films. The thermal stability was also found to be higher for the 1:1 films series containing low loadings of $C_{60}$ (<5%) while the thermal stability is higher for the ene deficient films at higher loadings of $C_{60}$ (>5%), which further supports the incorporation of the fullerene derivatives into the thiol-ene matrix.
Figure 21. TGA showing thermal stability of TMPMP:TMPDE-0.75 films.

Figure 22. TGA showing thermal stability of TMPMP:TMPDE-0.75 films containing 1 wt % C$_{60}$ and 1.5 wt % Sc$_3$N@C$_{80}$. 
Table 11

*Thermal and Mechanical Properties of Prepared C\textsubscript{60}(TMB-PPO\textsubscript{5}) Thiol-Ene Films*

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Thermal Degradation Onset (°C)</th>
<th>% Char</th>
<th>Glass Transition Temperature ((T_g)) DSC</th>
<th>Step Width</th>
</tr>
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<tbody>
<tr>
<td>PETMP:TTT-1-0</td>
<td>352</td>
<td>7.2</td>
<td>56</td>
<td>11</td>
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<tr>
<td>PETMP:TTT-1-1</td>
<td>349</td>
<td>8.8</td>
<td>60</td>
<td>11</td>
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<tr>
<td>PETMP:TTT-1-5</td>
<td>339</td>
<td>13.8</td>
<td>42</td>
<td>16</td>
</tr>
<tr>
<td>PETMP:TTT-1-10</td>
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<td>20.5</td>
<td>19</td>
<td>19</td>
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<td>29.6</td>
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<td>7.7</td>
<td>31</td>
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<td>8.9</td>
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<td>13.8</td>
<td>49</td>
<td>14</td>
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<td>18.2</td>
<td>42</td>
<td>16</td>
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<td>274</td>
<td>27.7</td>
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<td>20</td>
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<tr>
<td>TMPMP:TMPDE-1-0</td>
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<td>4</td>
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<tr>
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<td>2.9</td>
<td>-28</td>
<td>4</td>
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<td>309</td>
<td>3.1</td>
<td>-28</td>
<td>4</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-5</td>
<td>294</td>
<td>10.1</td>
<td>-27</td>
<td>8</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-10</td>
<td>293</td>
<td>15.2</td>
<td>-20</td>
<td>14</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-20</td>
<td>263</td>
<td>28.8</td>
<td>-4</td>
<td>25</td>
</tr>
<tr>
<td>TMPMP:TMPDE-0.75-1.5% Sc@C\textsubscript{80}</td>
<td>296</td>
<td>5.7</td>
<td>-33</td>
<td>4</td>
</tr>
</tbody>
</table>

All films were also analyzed using differential scanning calorimetry (DSC) and represented glass transition temperature \((T_g)\) values, along with the step width of the \(T_g\), obtained from DSC are reported in Table 11 and graphed in Figure 23. The \(T_g\) of a film is defined as the temperature region where the film transitions from a hard, glassy state to a
soft, rubbery material. For the flexible films series, a general trend was observed where the $T_g$ increases (~28 °C) and a broadening of step width of the $T_g$ (~20 °C) was observed as a function of C$_{60}$ loading independent of alkyl ene concentration. However, the $T_g$ for the rigid film series was found to be dependent on both C$_{60}$ loading and alkyl ene concentration, where the $T_g$ of the control (0% C$_{60}$) PETMP:TTT films decreased significantly (25 °C) with a decrease in alkyl ene concentration. The change in $T_g$ of the control films for the rigid system, as a function of alkyl ene concentration, suggests that small changes in the network of the PETMP:TTT films yield significant changes in the $T_g$. Furthermore, an interesting trend is observed with the PETMP:TTT-1 film series where the $T_g$ increases initially (4 °C) with C$_{60}$ loading (1 wt %), then declines (51 °C) as C$_{60}$ loading continues to increase. However, with the PETMP:TTT-0.75 film series, the $T_g$ increases (10 °C) and remains constant (±3 °C) up to 20 wt % loading, at which time the $T_g$ decreases (8 °C). Though the $T_g$ decreases from the PETMP:TTT-1-10 to the PETMP:TTT-1-20 film, the $T_g$ of the PETMP:TTT-1-20 film is still higher (33 °C) than that of the control, PETMP:TTT-1-0 (31 °C). Furthermore, the step width of the PETMP:TTT film series was found to only vary ~5 °C. Another trend was observed with DSC, where the enthalpy relaxation peak is only observed for the TMPMP:TMPDE films up to 5 wt % C$_{60}$ loading and for the rigid ene deficient control (PETMP:TTT-0.75-0) film. This is not surprising considering enthalpy relaxation is known to decrease with increasing monomer rigidity.$^{137}$ The variations in the observed $T_g$, broadening of the $T_g$ step width, and the loss of enthalpy relaxation as a function of C$_{60}$ loading, alkyl ene concentration, and monomer rigidity, further supports the covalent incorporation of C$_{60}$ into the thiol-ene matrix.
Further characterization was afforded on the prepared films except for the PETMP:TTT-1-20 film, which exhibited poor gel fractions (47%) and a higher percentage (63%) of $C_{60}$(TMB-PPO)$_5$ extracted from the film. Capacitance of the prepared films were explored to obtain initial insight of the dispersibility of $C_{60}$(TMB-PPO)$_5$ within the polymer matrix. Capacitance values were obtained using a Keithley 4200-SCS instrument and custom electrode assembly$^{92}$ over the frequency range of 0-10 MHz. Overall, the capacitance for the TMPMP:TMPDE film (Figure 24 c and d) series was found to be higher than that of the rigid PETMP:TTT film (Figure 24 a and b) series, where the rigid PETMP:TTT films exhibited capacitance values between 2-4 pF and the flexible TMPMP:TMPDE films exhibited capacitance values between 2-12 pF. As seen
in Figure 24 and Figure 25, the ene deficient films for each monomer composition exhibited higher capacitance values over the 1:1 films, suggesting that the dispersibility of C₆₀(TMB-PPO)₅ is more uniform for the TMPMP:TMPDE films and in ene deficient films. A general trend was also observed for all films where an initial increase in capacitance was observed with an initial increase in C₆₀ loading (1 wt %), then decreased as C₆₀ loading continued to increase (>5 wt %). The decrease in capacitance upon increasing C₆₀ loading above 1 wt % suggests that aggregation of the fullerene derivatives within the matrix is occurring.

**Figure 24.** Capacitance graph of (a) PETMP:TTT-1; (b) PETMP:TTT-0.75; (c) TMPMP:TMPDE-1; and (d) TMPMP:TMPDE-0.75 films.
Figure 25. Capacitance comparison graph of PETMP:TTT-1; PETMP:TTT-0.75; TMPMP:TMPDE-1; and TMPMP:TMPDE-0.75 films.

To visually analyze the dispersibility of the C$_{60}$(TMB-PPO)$_5$ adducts within the polymer matrix, images of the resulting 1 and 10 wt % films were obtained using transmission electron microscopy (TEM) (Figure 26-Figure 34). A very interesting phenomena was observed where large aggregates were present within the rigid PETMP:TTT film series; however, the fullerene containing TMPMP:TMPDE films appeared continuous throughout. The large aggregates present in the PETMP:TTT films were surprising considering the visual uniformity and dispersibility of the films as seen in Figure 19. Though aggregates are present in the ene deficient PETMP:TTT films, the aggregates are smaller and more dispersed. The aggregation of C$_{60}$(TMB-PPO)$_5$ within the PETMP:TTT films could be due to the higher functionality of the PETMP and TTT monomers, where the monomers are reacting with themselves instead of with C$_{60}$(TMB-PPO)$_5$, resulting in phase segregation. Furthermore, the aggregation present within the PETMP:TTT system helps explain the low capacitance values obtained.
Figure 26. TEM images of PETMP:TTT-1-1 films at low (left) and high (right) magnifications.

Figure 27. TEM images of PETMP:TTT-1-10 films at low (left) and high (right) magnifications.

Figure 28. TEM images of PETMP:TTT-0.75-1 films at low (left) and high (right) magnifications.
Figure 29. TEM images of PETMP:TTT-0.75-10 films at low (left) and high (right) magnifications.

Figure 30. TEM images of TMPMP:TMPDE-1-1 films at low (left) and high (right) magnifications.

Figure 31. TEM images of TMPMP:TMPDE-1-10 films at low (left) and high (right) magnifications.
To determine the ability of the fullerene containing thiol-ene films to produce singlet oxygen, direct singlet oxygen studies were performed on the TMPMP:TMPDE-0.75 films containing 1 and 10 wt% C$_{60}$ and 1.5 wt% Sc$_3$N@C$_{80}$. As seen in Figure 35,
the emission spectrum of the fullerene containing films shows a phosphorescence peak centered around 1270 nm, supporting the formation of singlet oxygen.

![Phosphorescence emission spectrum](image)

**Figure 35.** Phosphorescence emission spectrum of singlet oxygen generated from TMPMP:TMPDE-0.75 fullerene containing films (λ<sub>ex</sub> = 433 nm).

![Images of films](image)

**Figure 36.** Images of TMPMP:TMPDE-1 films prepared on IR salt plates before (top) and after (bottom) 4 hrs UV irradiation with increasing C<sub>60</sub> loadings of 0, 1, 5, and 10 % from left to right.
The characterization of potential photooxidized products produced upon generating singlet oxygen was explored using FT-IR. Samples were spin casted onto salt plates and images were taken before and after irradiation. As seen in Figure 36, an increase in film color was observed with an increase in C<sub>60</sub> loading. Furthermore, after irradiation, all samples, including the control 0 wt % C<sub>60</sub> sample, resulted in an amber colored film. For ease of comparison, the FT-IR spectrums of C<sub>60</sub>(TMB-PPO)₅ containing TMPMP-TMPDE thiol-ene films are shown from 4000-2500 cm<sup>-1</sup> in Figure 37, from 1800-1550 cm<sup>-1</sup> in Figure 38, and from 1500-500 cm<sup>-1</sup> in Figure 39. Overall, very little photodegradation is observed for the C<sub>60</sub>(TMB-PPO)₅ containing TMPMP-TMPDE-1 films compared to those previously prepared by Phillips et al. As seen in Figure A9, a strong, broad absorption band was observed around 3400 cm<sup>-1</sup>, along with a decrease in the aliphatic stretching bands between 3000 and 2840 cm<sup>-1</sup>, indicating the presence of hydroperoxide products. A growth in the absorption bands between 1650 and 1750 cm<sup>-1</sup> was observed and is evidence of the formation of new carbonyl moieties by reaction of peroxides with free double bonds of the butadiene segments incorporated in the SBS block copolymer. Furthermore, the absorption band associated with out-of-plane deformations of trans-internal double bonds around 970 cm<sup>-1</sup> and that of the terminal vinyl groups around 910 cm<sup>-1</sup> decreased in intensity following UV irradiation of C<sub>60</sub> doped SBS films, indicative of photodegradation via singlet oxygen.

In all figures, C<sub>60</sub> loading increases from 0, 1, 5, and 10 % from left to right. As seen in Figure 37, the growth of broad absorption bands centered around 3300 cm<sup>-1</sup> suggests the formation of hydroperoxide products. Furthermore, the 3300 cm<sup>-1</sup> absorption band increases with C<sub>60</sub> loading indicating that the film containing 10 wt % C<sub>60</sub> generates
more singlet oxygen compared to lower loaded films, as expected. Furthermore, the increase in C₆₀ could result in an increase in unreacted ene due to the reaction of C₆₀(TMB-PPO)₅ with the thiol monomer. The increase in unreacted ene will allow for the formation of more hydroperoxide products. For the C₆₀(TMB-PPO)₅ containing TMPMP-TMPDE-1 films, an increase in the intensity and a broadening of the carbonyl stretching at 1739 cm⁻¹ is observed with an increase in C₆₀ loading suggesting the formation of new carbonyl moieties upon generating singlet oxygen.

Figure 37. FT-IR spectrum of C₆₀(TMB-PPO)₅ containing TMPMP-TMPDE-1 films between 4000-2500 cm⁻¹ with increasing C₆₀ loading from 0, 1, 5, and 10 % from left to right.
Figure 38. FT-IR spectrum of C₆₀(TMB-PPO)₅ containing TMPMP-TMPDE-1 films between 1800-1550 cm⁻¹ with increasing C₆₀ loading from 0, 1, 5, and 10 % from left to right.

As seen in Figure 39, after irradiating the C₆₀(TMB-PPO)₅ containing TMPMP-TMPDE-1 films for 4 hrs, an increase in the absorption between 1500-500 cm⁻¹ was
observed the with an increase in C$_{60}$ loading. The increase in the absorbance between 1200-1000 cm$^{-1}$ post irradiation further supports the formation of hydroperoxide products. Furthermore, the increase in the absorbance between 1420-1300 cm$^{-1}$ post irradiation suggests the possible formation of sulfones.

In summary, visually dispersed thiol-ene-fullerene nanocomposites with low extractables and high gel percents were prepared using two monomer compositions of PETMP:TTT ($T_g$ 56) and TMPMP:TMPDE ($T_g$ -32) with increased fullerene loading (0, 1, 5, 10, 20 wt %) and at two different thiol-ene molar equivalents (1:1 or 1:0.75) to probe network structure-property relationships. The thermal and mechanical properties of the resulting thiol-ene films were explored as a function of C$_{60}$ loading, alkyl ene concentration, and monomer rigidity. Thermal stability of the derivatives and the resulting networks was determined using TGA and was found to decrease with an increase in monomer functionality and at high fullerene loadings, which is attributed to the favorable breaking of the fullerene-addend bond, allowing the fullerene to re-establish conjugation. All films were also analyzed using DSC and $T_g$ values were obtained. The $T_g$ of the flexible film series was found to increase as a function of C$_{60}$ loading, independent of alkyl ene concentration. Whereas, the $T_g$ of the rigid film series was found to be dependent on both C$_{60}$ loading and alkyl ene concentration. Furthermore, enthalpic relaxations observed with DSC decreased with an increase in C$_{60}$ loading and monomer rigidity. TMPMP:TMPDE composite networks show well-dispersed derivatives via TEM imaging, and PETMP:TTT composites show phase separation in TEM, which is supported by the observed $T_g$'s. Furthermore, singlet oxygen generated from the
nanocomposite films increased with an increase in $\text{C}_{60}$ loading, and good photostability of the networks was observed.
CHAPTER IV - PREPARATION AND CHARACTERIZATION OF THIOL-ENE POLYMER MICROBEADS AND THEIR USE AS A HETERogeneous PHOTOCATALYST VIA C\textsubscript{60}-CAPping

Introduction

The synthesis of spherical polymeric particles and their important role in various devices and applications ranging from pharmaceutical and biomedical applications\textsuperscript{138} to cosmetics,\textsuperscript{139} solid-phase synthesis,\textsuperscript{140-141} and chromatographic separation techniques\textsuperscript{142-145} have been well documented. Though several methods have been used for the synthesis of polymeric particles, heterogeneous polymerization methods including emulsion/suspension and precipitation/displacement polymerizations are the most common.\textsuperscript{146-148} In emulsion polymerizations, hydrophobic monomers are dispersed in an aqueous solution containing water-soluble initiators and surfactants.\textsuperscript{146-149} In suspension polymerizations, the initiator is soluble in the monomer phase, which is dispersed into an aqueous phase to form monomer droplets where initiation and free-radical polymerization occurs yielding polymer microbeads (PMBs) ranging from 5-1000 μm in diameter.\textsuperscript{147, 150-151} Particle size is greatly influenced by factors such as agitation rate, viscosity, and surfactant identity and concentration.\textsuperscript{146} Unlike emulsion and suspension polymerizations, dispersion and precipitation polymerizations begin as a homogeneous solution, in which the monomer and the initiator are soluble in the continuous phase. Upon initiation, the polymer particles formed precipitate out. Dispersion polymerizations are considered a type of precipitation reaction, but unlike precipitation reactions, which do not contain stabilizers or surfactants, stabilizers are added to dispersion polymerizations to stabilize the polymer particles and prevent coalescence.\textsuperscript{148, 152}
Polymeric particles have previously been prepared using polymer compositions such as poly(vinyl chloride), polymethacrylate, and polystyrene.\textsuperscript{153} However, recent research interest in the preparation of PMBs via thiol-ene/yne “click” chemistry has exploded, due to the numerous advantages of thiol-ene “click” reactions.\textsuperscript{154-159}

Although thiol-ene PMBs have previously been prepared, the effect of monomer composition and functionality on the physical properties and size distribution of thiol-ene PMBs has not been heavily explored. Durham et al.\textsuperscript{155} and Amato et al.\textsuperscript{159} studied the effect of inhibitor and surfactant concentrations, rate of mixing, and addition of cosolvents on the synthesis of thiol-ene PMBs. Later, Durham explored the effect of different stabilizing agents on the stability and the resulting particle size of thiol-ene PMBs.\textsuperscript{156} The work herein explores the effect of monomer composition and functionality on the physical properties and size distribution of thiol-ene PMBs prepared using a high-shear method, subsequently selecting a preferred composition for secondary surface functionalization via a thiol-ene photoreaction for the preparation of a heterogeneous photocatalyst.

Heterogeneous catalysis has become increasingly popular due to the ability to simply recover and recycle the catalyst via filtration. C\textsubscript{60} has previously been attached to amine-functionalized supports such as silica, polystyrene, polysiloxane, and dendrimers.\textsuperscript{73-74, 160-161} However, the C\textsubscript{60}-amine reaction results in low yields and is sensitive to oxygen, which is needed for singlet oxygen reactions.\textsuperscript{162} Though others have functionalized polymeric supports with C\textsubscript{60} to create a singlet oxygen generating heterogeneous photocatalyst, our efforts demonstrate the successful derivatization of thiol-ene PMBs with C\textsubscript{60} using a secondary thiol-ene click reaction.
Others have demonstrated the utility of the thiol-ene “click” reaction in surface modification of functionalized silica, iron oxide, and polymer particles\textsuperscript{157, 163-172}, however, there are only a few examples where thiol-ene PMBs have been functionalized via a follow-on thiol-ene/yne “click” photoreaction.\textsuperscript{154, 158-159} This work describe the derivatization of thiol-ene PMBs with C\textsubscript{60} to demonstrate the accessibility and reactivity of the residual thiols, successful inclusion of C\textsubscript{60} fullerene as a reactive ene moiety, and overall thiol-ene PMB utility.

In this chapter, a series of thiol-ene PMBs were prepared via high-shear suspension photopolymerization to explore the thermal, mechanical, and physical properties of the networks as a function of monomer composition. Thiol and ene concentrations were held constant at 1.1:1 molar equivalents to create PMBs with residual thiols on the surface for secondary functionalization. Particle size was characterized using dynamic light scattering (DLS) and the glass transition temperature ($T_g$) was determined using differential scanning calorimetry (DSC). The PMBs that possessed the highest $T_g$ and greatest sample uniformity were chosen for derivatization with C\textsubscript{60} in a surface thiol-ene reaction to demonstrate the accessibility and reactivity of the residual thiols, the successful inclusion of C\textsubscript{60} as the reactive ene moiety, and overall PMB utility as a scaffold for supported singlet-oxygen generating photocatalysts.

\textbf{Materials, Method, and Characterization}

\textit{Materials}

Materials used in the preparation, purification, and characterization of the thiol-ene PMBs and C\textsubscript{60}-capped thiol-ene PMBs were 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%), methanol (MeOH, >99.8%), toluene (>99.5%), methanol (MeOH, >99.8%), and benzene-d₆ (99.6 atom % D) purchased from Sigma Aldrich Chemical Company (St. Louis, MO); benzene (99.0%) and dichloromethane (DCM, >99.5%) obtained from EMD Chemicals (Gibbstown, NJ); 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE® 651) purchased from Ciba Specialty Chemicals; and C₆₀ (99.6%) fullerene obtained from SES Research (Houston, TX). All commercial chemicals were used as received.

**Method**

**Preparation of thiol-ene polymer microbeads (PMBs).** The thiol-ene PMBs were prepared using suspension photopolymerization techniques with chitosan as a low-foaming emulsifier. The thiol and ene monomer concentrations were held constant at 1.1:1 molar equivalent in the following procedure. To prepare the chitosan solution, chitosan (1 g) was added to a 1% (v/v) acetic acid solution (125 mL). IRGACURE® 651 photoinitiator (1 wt % solids) and thiol-ene monomers (10 wt % solids) were combined and added to the chitosan solution. The resulting solution was homogenized at 16,000 rpm for 5 min then transferred to a 200-mL jacketed flask (Tudor Scientific Glass Co.) equipped with a condenser equilibrated to 0 °C. The resulting PMBs were filtered using a 0.45 μm polypropylene filter membrane, rinsed with methanol to remove any residuals, and vacuum dried at 40 °C for at least 12 hrs.

**Preparation of C₆₀- capped thiol-ene PMBs.** The fullerene-capped thiol-ene PMBs were prepared by dispersing 350 mg of the prepared PETMP:TTT PMBs in a C₆₀
solution, which was prepared by dissolving 125 mg C$_{60}$ with IRGACURE® 651 (1 wt %) in 250 mL benzene. The dispersion was sonicated until the C$_{60}$ was completely dissolved, then placed in a Rayonet photochemical reactor containing sixteen 350 nm bulbs for 3 hrs. The resulting C$_{60}$-capped PMBs were collected via filtration using a 0.45 µm polypropylene filter membrane and washed three times with toluene (100 mL total) followed by a 10% MeOH:CH$_2$Cl$_2$ solution (100 mL total) to remove any residuals. The purified C$_{60}$-capped thiol-ene PMBs were then dispersed in a 10% MeOH:CH$_2$Cl$_2$ (100 mL) solution for 24 hrs at room temperature to ensure any unreacted materials were removed before further characterization. After 24 hrs, C$_{60}$-capped PMBs were recollected via filtration and dried at 50 °C. The resulting C$_{60}$-capped PMBs were analyzed using DLS, DSC, and TGA along with indirect and direct solution based singlet oxygen studies to determine their ability to produce singlet oxygen.

**Characterization**

*Dynamic light scattering (DLS)* - The particle size and standard deviations of the thiol-ene PMB suspension was determined using a Microtrac S3500 DLS instrument. A refractive index of 1.69 was used for the thiol-ene particles and 1.33 was used for water. All particles were treated as spherical and analyzed with a 75% flow rate. Particle size values are reported as mean volume (MV) and mean number (MN) diameter, in microns, and standard deviations (SD) are reported as the width of the measured particle size distributions.

*Optical microscopy (OM)* - Optical microscope images of the PMBs were collected using a Keyence VHX-600 digital microscope with a 1000x magnification lens.
*Fourier transform-infrared spectroscopy (FT-IR)* - FT-IR spectrums of the prepared PMBs were obtained in the 500-4000 cm\(^{-1}\) range using a Nicolet Nexus 470 FT-IR spectrometer equipped with a diamond crystal ATR accessory.

*Differential scanning calorimetry (DSC)* - The glass transition temperature \((T_g)\) of the prepare PMBs (~10 mg) was obtained using a TA instruments Q2000 modulated DSC over the temperature range of -90 to 150 °C in a heat/cool/heat cycle at a 10 °C min\(^{-1}\) ramp rate.

*Thermogravimetric analysis (TGA)* - The thermal stability of the PMBs was determined using a TA instruments Q500 series TGA instrument by monitoring change in weight as a function of temperature. The PMBs (~10 mg) were analyzed using aluminum pans over the temperature range of 25-600 °C at a heating rate of 10 °C min\(^{-1}\) under nitrogen.

*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 \(\lambda_{\text{max}}\) bulbs. The dispersion was purged with reagent grade air at a rate of 120 mL min\(^{-1}\) 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 one 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 \((H_a, \delta 5.2)\) and specific alkyl hydrogens in the products \((H_b, \delta 4.2 \text{ and } H_c, \delta 5.8)\) 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 \(\mu\)L benzene to prepare calibration curves. Analogous methods were employed to obtain a dilution series and calibration curve for the singlet oxygen generation of pure \(C_{60}\) for comparison.

Results and Discussion

To obtain micron size PMBs with a narrow size distribution exhibiting good thermal and mechanical properties, a series of thiol-ene PMBs was prepared and the structure-property relationships of the PMBs were explored as a function of monomer composition. Monomer compositions were varied and investigated to determine how basic features such as monomer rigidity and network density influence both particle size and size distributions of the resulting PMBs. The monomers shown in Figure 40 were
chosen for this study due to the reported high monomer conversion and physical uniformity of the thiol-ene polymer networks.

Figure 40. Structure of monomers used to synthesize thiol-ene PMBs.

Thiol-ene PMBs were prepared according to Scheme 9 using a high-shear photopolymerization method. PMBs prepared during this study along with characterization results are provided in Table 12. In general, the high-shear method chosen produced spherical, translucent particles, as observed in the optical microscope images (Figure 41–Figure 46). The prepared PMBs were further analyzed using DLS to determine particle size and size distributions. Volume (MV) and number (MN) weighted averages along with standard deviations obtained from DLS are reported in Table 12 and representative plots are provided in Figure 47–Figure 49.

Table 12 *Monomer Composition and Primary Characterization of Prepared PMBs*

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MV (µm)(^a)</th>
<th>MN (µm)(^b)</th>
<th>(T_g) Exp (°C)(^c)</th>
<th>(T_g) Ref (°C)(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMPMP:TMPDE</td>
<td>27 (±9)</td>
<td>3 (±6)</td>
<td>-28</td>
<td>-30(^{173})</td>
</tr>
<tr>
<td>TMPMP:APE</td>
<td>12 (±5)</td>
<td>5 (±3)</td>
<td>-20</td>
<td>-20(^{174})</td>
</tr>
<tr>
<td>TMPMP:TTT</td>
<td>25 (±12)</td>
<td>5 (±2)</td>
<td>20</td>
<td>22(^{174})</td>
</tr>
<tr>
<td>PETMP:TMPDE</td>
<td>17 (±5)</td>
<td>3 (±1)</td>
<td>-22</td>
<td>-19(^{175})</td>
</tr>
<tr>
<td>PETMP:APE</td>
<td>9 (±4)</td>
<td>3 (±1)</td>
<td>-5</td>
<td>-5(^{174})</td>
</tr>
<tr>
<td>PETMP:TTT</td>
<td>17 (±6)</td>
<td>4 (±2)</td>
<td>45</td>
<td>45(^{177})</td>
</tr>
<tr>
<td>PETMP:TTT film</td>
<td>-</td>
<td>-</td>
<td>45</td>
<td>45(^{177})</td>
</tr>
</tbody>
</table>

\(^a\) MV = mean volume diameter and \(^b\) MN = mean number diameter particle size averages and standard deviations obtained from DLS measurements; \(^c\) \(T_g\) obtained from DSC measurements; \(^d\) literature references for \(T_g\) for comparison; and \(^e\) control thiol-ene film.
Figure 41. Optical microscope images of TMPMP:TMPDE thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm.

Figure 42. Optical microscope images of TMPMP:APE thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm.

Figure 43. Optical microscope images of TMPMP:TTT thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm.
Figure 44. Optical microscope images of PETMP:TMPDE thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm.

Figure 45. Optical microscope images of PETMP:APE thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm.

Figure 46. Optical microscope images of PETMP:TTT thiol-ene PMBs at 1000x magnification with scale bar set to 50 µm.
Figure 47. DLS data of the thiol-ene PMBs prepared using TMPMP and PETMP thiol monomers with TMPDE.

Figure 48. DLS data of the thiol-ene PMBs prepared using TMPMP and PETMP thiol monomers with APE.
In general, from the DLS data it was determined that the high-shear method chosen yielded particles ranging from 9-27 µm (MV) and 3-5 µm (MN) in diameter. In general, an expected trend was observed where particle size decreased with an increase in monomer functionality and rigidity. Whereby the PMBs prepared using the tri-thiol (TMPMP) monomer yielded larger particles than those prepared with the tetra-thiol (PETMP) monomer, and the PMBs prepared using the flexible di-ene (TMPDE) monomer yielded larger particles than those prepared using the flexible tri-ene (APE) monomer. The observed decrease in particle size with increasing monomer functionality and rigidity, when shear rate and emulsifier concentrations are held constant, suggests that monomer composition affects both particle size and size distribution.

Though PMBs have been produced using the suspension photopolymerization methods, complete polymerization of PMBs was not observed as evident by low $T_g$ values (-1 °C and 26 °C) reported by Durham et al.\textsuperscript{175, 178} Therefore, to support high
polymerization conversion of the prepared PMBs using the high-shear method chosen, the PMBs were first analyzed using FT-IR (Figure 50 and Figure 51). High conversions of the prepared PMBs are supported by the absence of the thiol and alkyl ene peaks at 2500 cm\(^{-1}\) and 1600 cm\(^{-1}\), respectively.

*Figure 50.* FT-IR spectrum of thiol-ene PMBs prepared using TMPMP thiol monomer with TMPDE, APE, and TTT ene monomers.
High polymerization conversion of the prepared PMBs was further supported by obtaining the glass transition temperatures ($T_g$’s) of the PMBs and a photocured PETMP:TTT film for comparison (Table 13 and Figure 52). The $T_g$ of the prepared PMBs obtained using DSC was found to correlate well with literature values as seen in Table 13. Furthermore, a deviation between the $T_g$ of the bulk film and the PETMP:TTT PMBs was not observed supporting complete polymerization of the prepared PMBs unlike other recent published methods. Moreover, monomer composition was also found to affect the $T_g$ of the resulting PMBs as observed by an increase in $T_g$ upon increasing monomer rigidity, which is expected considering the same trend is observed for the bulk material. A refining of the particle size distribution was also observed with increasing $T_g$, where the number of particles at a given size increased and the distribution narrowed.
Table 13

*TGA Data of Prepared PETMP:TTT PMBs Compared to a PETMP:TTT Film and Pure Chitosan*

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Thermal degradation onset (°C)c</th>
<th>Thermal degradation onset Ref</th>
<th>% chard</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETMP:TTT</td>
<td>346</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>PETMP:TTT filme</td>
<td>353</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>Chitosan</td>
<td>258</td>
<td>255179</td>
<td>36</td>
</tr>
</tbody>
</table>

`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 °C from TGA analysis; `e`control thiol-ene film and C$_{60}$-capped PMBs used in photocatalytic studies.

*Figure 52.* DSC graphs of the prepared thiol-ene PMBs showing the change in $T_g$ upon varying monomer composition.

To ensure chitosan wasn’t incorporated into the thiol-ene matrix upon polymerization of the PMBs, the thermal stability including the thermal degradation onset...
temperature and the % char of the PETMP:TTT PMBs was analyzed using TGA and compared to that of a photocured PETMP:TTT film and pure chitosan (Figure 53). The thermal degradation onset temperature is reported as the temperature at which 10% of the sample mass is lost and the % char is reported as the mass remaining at 600 °C. Chitosan is known to both absorb water and char, which is observed by the mass lost below 100 °C and the mass remaining at higher temperatures (T >600 °C) as seen in Figure 53 and reported in Table 13. Furthermore, the thermal degradation onset temperature of chitosan (258 °C) is much lower than that of the PETMP:TTT network (~350 °C). A slight decrease in the thermal onset degradation temperature (7 °C) and % char (2 °C) is also observed for the PMBs compared to the films prepared from the same PETMP:TTT monomer composition. The slight decrease in the thermal onset degradation temperature and the % char observed for the PMBs compared to the film does not support the incorporation of chitosan in the prepared PMBs, which is further supported by the absence of characteristic chitosan peaks in the FT-IR spectrum of the prepared PMBs (Figure 54).
Figure 53. TGA graph of the prepared PETMP:TTT PMBs compared to a photocured PETMP:TTT film and pure chitosan.

Figure 54. FT-IR comparing characteristic peaks of the prepared PETMP:TTT PMBs to chitosan.
Of the PMBs produced, the particles prepared using PETMP:TTT monomers yielded PMBs with the highest $T_g$ (45 °C) and increased sample uniformity. Therefore, the PETMP:TTT PMBs were chosen for derivatization with $C_{60}$ via a follow-on thiol-ene click reaction to demonstrate the accessibility and reactivity of the residual thiols, the successful inclusion of $C_{60}$ as the reactive ene moiety, and overall PMB utility as a scaffold for supported singlet-oxygen generating photocatalyst.

The approach for capping $C_{60}$ to the PETMP:TTT PMBs was performed using a post polymerization surface thiol-ene reaction shown in Scheme 10. In general, the $C_{60}$-capped PMBs were prepared by dispersing PETMP:TTT PMBs in a $C_{60}$ solution containing IRGACURE® 651 photoinitiator (1 wt %), which was added to initiate the reaction. The sample was placed in a Rayonet photoreactor and irradiated at 350 nm for 3 hrs. The resulting $C_{60}$-capped PMBs were collected via filtration and washed yielding a brick-red powder seen in Figure 55.

Scheme 10. Preparation of $C_{60}$-capped PETMP:TTT PMBs.
Figure 55. Image highlighting visible color change (a) before and (b) after capping the PETMP:TTT PMBs with C$_{60}$.

To determine if aggregation occurs upon capping the PMBs with C$_{60}$, the particle size of the C$_{60}$-capped PMBs was collected and compared to PETMP:TTT PMBs alone. As seen in Figure 56, capping the PETMP:TTT PMBs with C$_{60}$ did not greatly change the particle size of the PMBs. However, capping the thiol-ene PMBs with C$_{60}$ was found to have a dramatic impact on the $T_g$ and the thermal degradation onset temperatures as seen in Figure 57 and Figure 58. Upon capping the PETMP:TTT PMBs with C$_{60}$, the $T_g$ increased from 45 °C to 58 °C, which is a significant increase and supports successful capping of the PETMP:TTT PMBs with C$_{60}$. Furthermore, upon capping the PMBs with C$_{60}$, the thermal degradation onset temperature decreased 4 °C from 346 °C to 342 °C, indicating a slightly lower thermal stability for the C$_{60}$-capped PMBs. However, a 3% increase in the % char was observed upon capping the PETMP:TTT PMBs with C$_{60}$. The 3% increase in the mass remaining at 600 °C upon capping the PETMP:TTT PMBs, suggests that C$_{60}$ accounts for 3% of the total mass of the C$_{60}$-capped PMBs, which is supported by the mass balance studied performed (Table 14).
Figure 56. DLS data of the C\textsubscript{60}-capped PMBs and the PETMP:TTT PMBs.

Figure 57. DSC graph of the C\textsubscript{60}-capped PMBs and the PETMP:TTT PMBs.
Figure 58. TGA graph of the C\textsubscript{60}-capped PMBs and the PETMP:TTT PMBs.

Table 14

Mass Balance Studies of C\textsubscript{60}-Capped Thiol-Ene PMBs

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>PETMP:TTT PMBs (mg)\textsuperscript{a}</th>
<th>C\textsubscript{60} (mg)\textsuperscript{b}</th>
<th>Recovered C\textsubscript{60}-Capped PETMP:TTT (mg)\textsuperscript{c}</th>
<th>Average Mass Increase Post Functionalization (%)\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{60}-Capped PETMP:TTT PMBs</td>
<td>350</td>
<td>125</td>
<td>361.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Experiments were conducted using a Rayonet photoreactor and irradiated at 350 nm for 3 h. Samples prepared using \textsuperscript{a}PETMP:TTT PMBs and \textsuperscript{b}C\textsubscript{60} dispersed in 250 mL benzene; \textsuperscript{c}mass of C\textsubscript{60}-capped PMBs recovered; \textsuperscript{d}average percent mass increase post functionalization calculated by dividing the increase in mass of the collected C\textsubscript{60}-capped PMBs by the original mass of the PETMP:TTT PMBs and averaged over three samples.
Figure 59. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of $C_{60}$ and $C_{60}$-capped PMBs (as prepared and recovered from indirect solution based assay) at $\lambda_{ex} = 346$ nm.

To determine the ability of the $C_{60}$-capped thiol-ene PMBs to generate singlet oxygen, direct and indirect solution based singlet oxygen studies were performed. In general, direct solution based assays were performed by directly detecting the phosphorescence of singlet oxygen at 1270 nm produced, upon exciting the $C_{60}$-capped PMBs at 346 nm, using a fluorometer equipped with a NIR detector. Excitation spectrums were obtained for both $C_{60}$ and the $C_{60}$-capped PMBs to obtain normalized responses yielding a $C_{60}$ equivalent correlation mass (Figure 59 and Figure A8). As expected, $C_{60}$ was found to produce the most singlet oxygen; however, the mass ratio of $C_{60}$ and the $C_{60}$-capped PMBs, resulting in analogous singlet oxygen responses, was found to increase linearly as seen in Figure 60.
Figure 60. Linear plot correlating the mass of C\textsubscript{60} and the mass of C\textsubscript{60}-capped PMBs yielding analogous singlet oxygen responses via direct solution based assays.

To further assess the use of the C\textsubscript{60}-capped PMBs as a heterogeneous photocatalyst, the PMBs used in the direct study were collected via filtration and used in the indirect study. For the indirect solution based singlet oxygen assay, a method originally reported by Tagmatarchis et al.\textsuperscript{180} and modified by McCluskey et al.\textsuperscript{83} was used. For this study, evidence for any singlet oxygen produced was detected via \textsuperscript{1}H-NMR by monitoring the photooxygenation of 2-methyl-2-butene (2M2BE) to the allylic hydroperoxides as seen in Scheme 11. In the presence of singlet oxygen, 2M2BE is oxidized yielding an ~ 1:1 ratio of hydroperoxide products, 1 and 2, both of which possess well-resolved and unique hydrogen chemical shifts (\textsuperscript{H}a, \(\delta\) 5.2; \textsuperscript{H}b, \(\delta\) 4.2; \textsuperscript{H}c \(\delta\) 5.8) in the \textsuperscript{1}H-NMR, corresponding to the area of one hydrogen and leading to the ready analysis of reaction mixtures using integration of \textsuperscript{1}H-NMR peak areas.
Scheme 11. Photooxygenation of 2-methyl-2-butene (2M2BE).

In general, the indirect solution based singlet oxygen study was conducted by dispersing the C$_{60}$-capped PMBs in a 2M2BE solution and irradiating in a Rayonet photoreactor at 350 nm. The photooxygenation of 2M2BE in the presence of the C$_{60}$-capped PMBs was monitored by taking aliquots with time and obtaining $^1$H-NMR (Table 15 and Figure 61). From $^1$H-NMR, it was determined that 98% of the 2M2BE present was oxidized within 90 min when the C$_{60}$-capped PMBs were added, whereas no photooxygenated products were produced in the absence of the C$_{60}$-capped PMBs.

To further support the use of the C$_{60}$-capped PMBs as a heterogeneous photocatalyst, the C$_{60}$-capped PMBs used in the indirect study were recollected and used in another direct singlet oxygen assay. As seen in Figure 61, a decrease in the production of singlet oxygen was not observed, supporting the use of the C$_{60}$-capped PMBs as a heterogeneous photocatalyst.
Table 15

Percent Conversion of 2M2BE as a Function of Irradiation Time from the \(^1\)H-NMR Analysis of Photoxygenation of 2M2BE Using C\(_{60}\)-Capped PMBs

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Octane (Internal Standard)</th>
<th>2M2BU (5.2 ppm)</th>
<th>P1 (4.25 ppm)</th>
<th>P2 (5.8 ppm)</th>
<th>% conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0.1444</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>0.0674</td>
<td>0.0019</td>
<td>0.0026</td>
<td>6</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0.0296</td>
<td>0.0035</td>
<td>0.0046</td>
<td>21</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>0.0169</td>
<td>0.0062</td>
<td>0.0066</td>
<td>43</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>0.0021</td>
<td>0.0079</td>
<td>0.0095</td>
<td>89</td>
</tr>
<tr>
<td>90</td>
<td>1</td>
<td>0.0003</td>
<td>0.0088</td>
<td>0.0099</td>
<td>98</td>
</tr>
</tbody>
</table>

\(^1\)H-NMR chemical shifts and corresponding areas calculated for \(^1\)H-NMR peak areas. Experiments were conducted using a catalytic amount of C\(_{60}\)-Capped PETMP:TTT PMBs suspended in a 0.1 M 2M2BE solution in benzene-D\(_6\) solvent and irradiated at 350 nm in an oxygen-rich environment.

Figure 61. Example \(^1\)H-NMR analysis of the % conversion of 2M2BE to its photooxygenated products, as a function of irradiation time, produced from singlet oxygen generated from the C\(_{60}\)-capped PMBs.
In summary, a series of thiol-ene (1.1:1 molar equivalent) PMBs were prepared via a high-shear suspension photopolymerization method and the physical properties of the networks as a function of composition were explored. 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. Of the PMBs produced, the particles prepared using PETMP:TTT monomers yielded PMBs with the highest \( T_g \) (45 °C) and increased sample uniformity. Therefore, PETMP:TTT PMBs were chosen for secondary 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 the PMBs with C\(_{60}\), the \( T_g \) of the composite particles increased significantly supporting the successful functionalization of PMBs with C\(_{60}\). Most importantly, the C\(_{60}\)-capped PMBs were shown to produce singlet oxygen in both direct and indirect solution based singlet oxygen assays, where the efficiency did not decrease after recycling.
CHAPTER V - CONCLUSION

Derivatization of C\textsubscript{60} and Sc\textsubscript{3}N@C\textsubscript{80} with S-, P-, and C- centered radicals using easy synthetic strategies was investigated in this work. To our knowledge, this is the first report of the functionalization of Sc\textsubscript{3}N@C\textsubscript{80} with S- and P- centered radicals. Thiolated C\textsubscript{60} and Sc\textsubscript{3}N@C\textsubscript{80} derivatives were prepared upon functionalizing with monothiol BuMP monomer upon photolysis of the prepared BuMP/S-S (~30% S-S). The reversibility of the fullerene-thiol reaction was corrected with the addition of pure BuMP monomer as a hydrogen source. Derivatization of C\textsubscript{60} and Sc\textsubscript{3}N@C\textsubscript{80} with P-, and C- centered radicals was demonstrated, utilizing the high reactivity of C\textsubscript{60} with the commercial photoinitiator, TMB-PPO. Successful functionalization of C\textsubscript{60} and Sc\textsubscript{3}N@C\textsubscript{80} was supported from through a combination of techniques including FT-IR, MALDI-MS, elemental analysis, XPS, \textsuperscript{1}H-NMR, and TGA.

The number of addends bound to C\textsubscript{60} as a function of reaction time and molar ratios were explored. Interestingly, the number of BuMP addends bound to C\textsubscript{60} was found to decrease from 9-4 and the % yield was found to increase with an increase in reaction time. As expected, the number of TMB:PPO addends increased from 1-5 with an increase in the molar ratio of C\textsubscript{60}:TMB-PPO.

Structure-property relationships as a function of increasing number of addends bound to C\textsubscript{60} were explored. Thermal stability of the fullerene derivatives was found to decrease with an increase in the number of addends; however, the derivatives exhibited a higher thermal stability compared to BuMP and TMB-PPO alone. The solubility of the prepared fullerene derivatives in common solvents was investigated to determine how solubility is affected based on the identity and number of addends bound to C\textsubscript{60} and
The solubility of C₆₀ and Sc₃N@C₈₀ was found to increase with an increase in the number of addends bound to C₆₀, and was found to be dependent on addend functionality. TMB-PPO functionalized derivatives yielded adducts exhibiting much higher solubilities in common organic solvents compared to C₆₀(BuMP)ₓ derivatives. More interestingly, Sc₃N@C₈₀(BuMP)₇ exhibited higher solubilities in more non-polar organic solvents (DCM, CHCl₃, and benzene) compared to Sc₃N@C₈₀(TMB-PPO)₃, which exhibited higher solubilities in more polar solvents (MeOH, EtOH, and acetone).

The ability of the prepared fullerene derivatives to produce singlet oxygen as a function of addend functionality and number of addends bound to C₆₀ and Sc₃N@C₈₀ was investigated. An expected trend was observed where emission intensity increased with increasing concentration and the generation of singlet oxygen decreased upon derivatizing C₆₀. However, derivatizing Sc₃N@C₈₀ was found to greatly hinder the singlet oxygen generating ability of Sc₃N@C₈₀, where the presence of singlet oxygen was not observed at all upon exciting Sc₃N@C₈₀ derivatives.

Upon enhancing the solubility of fullerenes via derivatization with TMB-PPO addends, prepared C₆₀(TMB-PPO)₅ and Sc₃N@C₈₀(TMB-PPO)₃ were incorporated into two different thiol-ene polymer matrices (PETMP:TTT or TMPMP:TMPDE) at varying thiol-ene monomer concentrations (1:1 or 1:0.75 molar equivalents) and at different loadings of C₆₀ (0, 1, 5, 10 and 20 wt %). The dispersibility of prepared fullerenes as a function of monomer identity and C₆₀ loading, along with the effect on the thermal and mechanical properties of the fullerene-doped films, were explored.

The gel percents and the amount of C₆₀(TMB-PPO)₅ extracted from the resulting films were analyzed to obtain an initial insight into the degree of incorporation of the
derivatives into the thiol-ene films. Both gel percent values and the amount of C\textsubscript{60}(TMB-PPO\textsubscript{5} extracted from the prepared films suggests that C\textsubscript{60} is being covalently incorporated into the films, as observed by high gel percent values and a low amount of C\textsubscript{60}(TMB-PPO\textsubscript{5} extracted from all films except the PETMP:TTT-1 10 and 20 wt % film series.

The thermal and mechanical properties of the resulting thiol-ene films were explored as a function of C\textsubscript{60} loading, alkyl ene concentration, and monomer rigidity. Thermal stability of the resulting films was found to decrease with an increase in C\textsubscript{60} loading, further supporting the incorporation of the fullerene derivatives into the thiol-ene matrix. The \( T_\sigma \) of the resulting films was also obtained, and a general trend was observed for the flexible films series where \( T_\sigma \) increased and a broadening of step width was observed as a function of C\textsubscript{60} loading independent of alkyl ene concentration. Whereas the \( T_\sigma \) for the rigid film series was found to be depended on both C\textsubscript{60} loading and alkyl ene concentration. The variations in the observed \( T_\sigma \), broadening of the \( T_\sigma \) step width, and the loss of enthalpy relaxation as a function of C\textsubscript{60} loading, alkyl ene concentration, and monomer rigidity, further supports the covalent incorporation of C\textsubscript{60} into the thiol-ene matrix.

Capacitance of the prepared films were explored to obtain initial insight of the dispersibility of C\textsubscript{60}(TMB-PPO\textsubscript{5} within the polymer matrix and suggests that the dispersibility of C\textsubscript{60}(TMB-PPO\textsubscript{5} is more uniform for the TMPMP:TMPDE films and in ene deficient films. Transmission electron microscopy of the resulting 1 and 10 wt % films was obtained to visually analyze the dispersibility of the C\textsubscript{60}(TMB-PPO\textsubscript{5} adducts within the polymer matrix. A very interesting phenomenon was observed where large
aggregates were present within the rigid PETMP:TTT film series; however, the fullerene containing TMPMP:TMPDE films appeared continuous throughout. The aggregation of C$_{60}$(TMB-PPO)$_5$ within the PETMP:TTT films suggests the monomers are reacting with themselves instead of with C$_{60}$(TMB-PPO)$_5$, resulting in phase segregation.

The ability of the TMPMP:TMPDE-0.75 films containing 1 and 10 wt % C$_{60}$ and 1.5 wt % Sc$_3$N@C$_{80}$ to produce singlet oxygen was determined using direct singlet oxygen studies, and each films was found to produce singlet oxygen. The characterization of potential photooxidized products produced upon generating singlet oxygen was explored using FT-IR. Overall, very little photodegradation was observed for the C$_{60}$(TMB-PPO)$_5$ containing TMPMP-TMPDE-1 films compared to those previously prepared by Phillips et al.$^{135}$ However, FT-IR did suggest the presence of hydroperoxide products and new carbonyl moieties upon generating singlet oxygen. Furthermore, the presence of photooxidized products was found to increase with an increase in C$_{60}$ loading.

The ability of C$_{60}$ to produce singlet oxygen was also utilized to prepare a heterogenous photocatalyst upon covalently linking C$_{60}$ to the surface of thiol-ene polymer microbeads (PMBs). First, a series of thiol-ene PMBs were prepared via high-shear suspension photopolymerization, with chitosan as a low foaming surfactant, and the thermal, mechanical, and physical properties of the networks as a function of monomer composition were explored. Thiol and ene concentrations were held constant at 1.1:1 molar equivalents to create PMBs with residual thiols on the surface for secondary functionalization. Particle size of the resulting thiol-ene PMBs was characterized using DLS and found to decrease slightly with increasing monomer functionality. The $T_g$ of the
thiol-ene PMBs was determined using DSC, and as expected, was found to increase with increasing monomer rigidity. Of the PMBs prepared, those from PETMP:TTT monomers possessed the highest $T_g$ and greatest sample uniformity. Therefore, the PETMP:TTT PMBs were derivatized with $C_{60}$ in a surface thiol-ene reaction and the accessibility and reactivity of the residual thiols, the successful inclusion of $C_{60}$ as the reactive ene moiety, and overall PMB utility as a scaffold for supported singlet oxygen generating photocatalysts were demonstrated. Upon capping the PETMP:TTT PMBs with $C_{60}$, the $T_g$ of the composite particle increased significantly, by 23 °C, while a more modest increase in thermal stability was observed from TGA. Most importantly, the $C_{60}$-capped PMBs were observed to produce singlet oxygen via direct and indirect solution based assays, and the efficiency of these new heterogeneous photocatalysts did not decrease after recycling.
**APPENDIX**

*Figure A1.* Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C$_{60}$ and C$_{60}$(BuMP)$_4$ at $\lambda_{ex} = 346$ nm.

*Figure A2.* Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C$_{60}$ and C$_{60}$(TMB-PPO)$_2$ at $\lambda_{ex} = 346$ nm.
Figure A3. Analogous responses from the direct detection of singlet oxygen upon exciting a catalytic amount of C₆₀ and C₆₀(TMB-PPO)₃ at $\lambda_{\text{ex}} = 346$ nm.
Figure A4. Calibration curves correlating relative intensity to derivative concentration.
Figure A5. TGA showing thermal stability of PETMP:TTT-1 film series.

Figure A6. TGA showing thermal stability of PETMP:TTT-0.75 film series.
Figure A7. TGA showing thermal stability of TMPMP:TMPDE-1 film series.

Figure A8. 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 λₑₓ = 346 nm.
Figure A9. FT-IR spectra of 0.5 wt % C$_{60}$ doped SBS films before and after four hours of UV irradiation.

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