阳光光照射下光解后聚合物的光敏降解


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ABSTRACT: The study and development of transient devices is an emerging field where the disposal of a device after use is desired to avoid reverse engineering and minimize the environmental impact. Polyaldehydes with phototrigger have been investigated because the radiation wavelength can be adjusted to meet the transient application. Polynuclear aromatic hydrocarbons (PAHs) were used as the optical sensitizer for photoacid generators (PAGs). Photoinduced electron transfer (PET) with an iodonium-based PAG was used to expand the spectral sensitivity range. Anthracene, tetracene, and pentacene derivatives were synthesized with appended phenylethynyl groups to improve the solubility of the sensitizer and adjust the absorption wavelength. Sensitization of the iodonium-based PAG with the PAH derivatives was found to have thermodynamically favorable PET reactions for depolymerization of poly(propylene carbonate) and poly(phthalaldehyde) (PPHA). The Rehm-Weller equation and Stern-Volmer analysis were used to study the electron transfer and the fluorescence quenching rates of the PAHs with the iodonium salts, respectively. The photosensitivity, efficiency, and byproducts of the PET reactions in the decomposable polymer films are reported. A rapid photoreaction is reported for the depolymerization of PPHA exposed to a sunlight dose of <6 J cm\(^{-2}\) (i.e., 1 min of direct sunlight) with a pentacene-based sensitizer. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2019, 136, 47141.

KEYWORDS: decomposable polymers; iodonium salt; photoinduced electron transfer; poly(phthalaldehyde); poly nuclear aromatic hydrocarbons; self-immolative polymers; sensitization; transient electronics

INTRODUCTION

Decomposable and template polymers are of use in the fabrication of integrated circuits and packages.\(^9\)\(^\text{--}\)\(^7\) Polymers that can be triggered to depolymerize or decompose into volatile, monomeric units are useful as template materials for the creation of embedded-air cavities.\(^2\)\(^\text{--}\)\(^7\) An emerging application for decomposable polymers is the phototriggered depolymerization of the polymer leading to the controlled vaporization and/or liquefaction of the component so as to eliminate device recovery.\(^8\)\(^\text{--}\)\(^\text{12}\) An optical trigger is also a reliable pathway for photopatterning transient polymers on microelectromechanical system (MEMS) devices prior to the creation of air cavities during packaging.

Poly(propylene carbonate) (PPC) is an amorphous polymer useful in the creation of embedded air cavities.\(^1\)\(^\text{--}\)\(^7\) PPC can be triggered photochemically to decompose into volatile products such as acetone, carbon dioxide, and propylene carbonate at elevated temperatures (i.e., 100–250 °C).\(^13\)\(^\text{--}\)\(^\text{15}\) It is also of interest to carry out the depolymerization reaction near ambient temperature with an optical trigger where the user can select the wavelength of the stimulus. Polyaldehydes are a family of self-immolative polymers that have been use as substrates for transient devices.\(^9\)\(^\text{--}\)\(^\text{12}\)

In particular, poly(phthalaldehyde) (PPHA) is highly sensitive to acids and will promptly depolymerize into monomer units by end-cap removal or direct chain attack at or below room temperature.\(^9\)\(^\text{--}\)\(^\text{12}\) PPHA with volatile, aldehyde copolymers have been synthesized and shown to have fast depolymerization and vaporization times.\(^13\)\(^\text{--}\)\(^\text{15}\) Photolabile protecting end groups have been used to initiate photo-depolymerization of aliphatic polyglyoxylates.\(^34\) However, the depolymerization occurs over several days and the wavelength of activation is difficult to control. Alternatively, onium salts have been used for the photocuring of coatings and photo-deblocking reactions in negative-tone, wet-developable photoresists.\(^35\)\(^\text{--}\)\(^\text{37}\) Onium salts are very soluble and can also be easily mixed with linear or cyclic decomposable polymers to form photosensitive films by solvent casting.\(^31\) Diaryliodonium and triarylsulfonium salts are efficient photoacid generators (PAGs) because of the presence of ultraviolet (UV) absorbing aryl groups on the onium cation. Upon UV excitation, the carbon-iodine or carbon-sulfur bond undergoes homolytic or heterolytic cleavage that generates cation radicals which react with monomers or solvents to produce a strong Bronsted acid. However, the photoactive spectrum

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of the onium salts is limited to the UV portion of the electromagnetic spectrum making them insensitive to sunlight. Sensitizing the onium salts to longer wavelengths of light makes a more efficient photolysis in sunlight applications.38,39

The goal of this study is to extend the spectral sensitivity of PAG to longer wavelengths of light via photoinduced electron transfer (PET).36 A simplified reaction scheme, Scheme 1, uses Mtxn− as the weakly nucleophilic counterion [e.g., BF4−, PF6−, SbF6−, (CnF3)2B−] in the PAG. The PET is initiated by photosensitizer (PS) absorption of light creating the excited state [PS]*. The [PS]* undergoes energy transfer to the onium salt generating an excited complex state. The onium is reduced by a formal one-electron-transfer reaction. The electron-transfer reaction is rendered irreversible due to the rapid decay of the onium radical as shown in Scheme 1, eq. 4. The PS cation radical can decay in a number of pathways to produce a strong Bronsted acid.36

A variety of compounds, including carbazoles, phenothiazines, isozenofurans, cyanines, and conjugated olefins, can be used to photosensitize onium salts.38–40 Diaryliodonium salts are more favorable for electron-transfer reactions because the reduction potential is low compared to triarylsulfonium salts. Polynuclear aromatic hydrocarbons are an efficient class of electron-transfer PS.s.36,40 The absorption characteristics and oxidation potentials of the acenes are related to the size of their aromatic frameworks. For example, anthracene has an absorption wavelength cut-off at 390 nm while pentacene is at 585 nm. However, increasing the number of aromatic rings lowers the solvent solubility due to the higher crystallinity from π–π stacking. Pentacene suffers from poor solubility in most common organic solvents that makes it difficult for solvent casting films. The spectral absorption and solubility of acenes can be adjusted through functionalization. Incorporation of other electron-donating groups, such as alkoy groups, has been shown to improve the photosensitization process by refining the redox potentials, as well as improving the solubility.36 Electron donating groups can potentially increase the excited-state lifetime to improve energy transfer with onium salts, especially in dilute solutions.41

The sensitization of iodonium salts has been used in cationic photopolymerizations to achieve faster rate with anthracene derivatives.36 Near infrared sensitization of iodonium salts has been assessed previously with cyanines; however, the basic functionality is likely not compatible with acid-catalyzed processes.39,42–46 Wallraff et al. studied the sensitization of onium salts for acid-catalyzed deprotection of polymethacrylates as wet-developable photoresist.40 However, sensitization of onium salts has not been extensively studied for acid-catalyzed depolymerization of polymers. The aim of this study is to evaluate the sensitization of iodonium PAGs into the entire visible spectrum with anthracene, tetracene, and pentacene derivatives. It is desirable for transient polymers to have low solid residues after depolymerization. Similarly, it is desirable for the decomposable polymers to have a low chemical footprint after depolymerization to avoid detection and reverse engineering. Hence, the products of the PET reaction are studied to minimize solid residue post-depolymerization.

EXPERIMENTAL

Materials

1-Chloro-4-propoxynthioxanthone (CPTX), anthracene, n-butyllithium (2.5 M in hexane), and anhydrous dimethylformamide (DMF) at 99.8% purity were purchased from Sigma-Aldrich. Phenylacetylene was purchased from Acros Organics. Tetrahydrofuran (THF) at >99% purity was purchased from British Drug House. 3,4,5-Trimethoxyphenylacetylene was prepared from trimethoxybenzaldehyde via Corey–Fuchs reaction. 1,8-Dimethoxy-anthraquinone was prepared from reaction between iodomethane and 1,8-dihydroxanthraquinone. 5,12-Tetracenedione and 6,13-pentacenedione were prepared from literature methods.47,48 PPC was generously supplied by Novomer Inc. The weight-average molecular weight of PPC material was 160 kDa with a dispersity (D) of 1.16. PPXA was synthesized following Schwartz et al. procedure with a weight-average molecular weight of 246 kDa and a dispersity (D) of 1.57.50 The PAG used in this study was an iodonium salt, 4-isopropyl-4′-methylidiphenyliodonium tetrakis(pentafluorophenyl) borate (referred to as FABA-PAG) from Solvay Inc. Materials used in this study are shown in Figure 1.

General Synthesis Procedure for Acene Derivatives

Total of 2.05 equivalents of phenylacetylene was dissolved at 0.91 M in anhydrous THF in a flame-dried round-bottom flask under an argon atmosphere. The solution was cooled to −78 °C followed by the slow addition of 2.02 equivalents of n-butyllithium in hexane via syringe. The reaction vessel was stirred at room temperature for 30 min before being cooled to −78 °C. Total of one equivalent of the appropriate quinone was added with anhydrous THF to the reaction mixture. After stirring at room temperature for 60 min, the reaction was added dropwise into a 0.78 M solution of Sn(II) chloride dihydrate in 10% HCl solution. The solution stirred for 90 min before collecting the crystalline product via vacuum filtration. Products were recrystallized from chloroform.

1,8-Dimethoxy-9,10-bis(phenylethynyl)anthracene (DMBA), 5,12-bis(phenylethynyl)tetracene (BPET), and 6,13-bis(phenylethynyl)pentacene (BPEP) were prepared according to the general procedure. 6,13-bis(3,4,5-trimethoxyphenylethynyl)pentacene (BTMP) was prepared from 3,4,5-trimethoxyphenylacetylene using the same conditions as the general procedure. Molecular structure was verified by nuclear magnetic resonance and high resolution mass spectrometry, and matched previous reports on these compounds.48,49

![Scheme 1. Mechanism for PET of onium salts.](https://example.com/scheme1.png)
Characterization

The UV–visible (vis) absorption spectrum of PSs used in this study was investigated on Hewlett Packard 8543 UV–vis spectrophotometer in solutions of degassed DMF. Formulations of all polymer solutions with sensitizer and PAG/base generator were mixed on a ball roller for 12 h. The PS-to-PAG molar ratio was 1.2:1 for all formulations. Fluorescence spectra were evaluated with a Horiba FL3-2i Fluorometer. Time-correlated single photon counting method with a Horiba NanoLed excitation source at 334, 455, 570, and 625 nm was used to obtain the fluorescence lifetimes. Stern–Volmer analysis was conducted with sensitizers maintained to approximately 4 μM solutions in degassed DMF with concentrations of PAG-FABA ranging from 0.008 to 0.3 M. Contrast curves were generated from sunlight in Atlanta, Georgia between the hours of 11 a.m. to 2 p.m. in September 2016. A variable density mask filter (Model 400 F.S.) was used from
Opto-line. Square band-pass filters of 50.8 × 50.9 mm at wavelengths of 500, 560, and 650 nm were used. All filters had a 10 ± 2 nm full-width half-max value. Formulations of PPC films, sensitizer, and PAG were spin-coated onto silicon wafers where the variable density mask filter and corresponding band-pass filter were placed on-top. PPC films were developed after exposure on a hotplate at 100 °C for 7 min. The film thickness was measured using a Veeco Dektak profilometer. The intensity of sunlight was recorded with a SM206 Solar Power Meter. UV light exposures filtered to 248 and 365 nm were exposed using an Oriel Instruments flood exposure source with a 1000 W Hg(Xe) lamp.

The electrochemical properties of the sensitizers and PAGs were evaluated by cyclic voltammetry using a Princeton PARSTAT 2263 potentiostat. Redox potentials were recorded under dry nitrogen atmosphere with a three-Et electrode electrochemical cell in an anhydrous DMF solution of 0.13 M tetrabutylammonium perchlorate. Ferrocene was used as an internal standard for determining the electrochemical potential.

Characterization of the residual products of the PET reactions within PPHA films were conducted with proton nuclear magnetic resonance (1H-NMR), matrix-assisted laser desorption/ionization–time of flight–mass spectrometry (MALDI–TOF–MS), and electrospray ionization (ESI) triple quadrupole analysis. NMR measurements were performed using a Varian Mercury Vx 400 (400 MHz) tool. Chloroform-D (CDCl3) was used for the NMR solvent and was supplied by Sigma-Aldrich at a 99.8% purity level. The concentration of residue in NMR sample tubes was held at 46 mg in 0.75 mL CDCl3. ESI measurements were performed on a Micromass Quattro LC and MALDI–TOF–MS measurements were performed on a Bruker AutoFlex III. MALDI–TOF–MS samples were prepared with a 10 mg/mL solution of the matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile in dichloromethane (DCM). The residue was prepared in a separate vial containing 10 mg/mL solution in DCM. The matrix solution and residue solution were mixed at equal parts and spotted 1 μL onto the plate for analysis.

RESULTS AND DISCUSSION

Optical Properties of PSs

The optical properties of the modified acenes were investigated by UV–vis absorption and fluorescence spectroscopy in degassed DMF. The six sensitizers, anthracene, CPTX, DMBA, BPET, BPEP, and BTMP, exhibited strong absorption bands from 312 to 673 nm, as shown in Figure 2 and listed in Table I. The fluorescence spectrum corresponding to the first excited singlet state for BPET is shown in Figure 3.

The four sensitizers that absorb in the visible region have high molar extension coefficients between 24 × 10^3 and 33 × 10^3 M−1 cm−1 which is three to four times greater than the molar extinction coefficient CPTX, 6.9 × 10^3 M−1 cm−1 at 387 nm, and anthracene, 7.1 × 10^3 M−1 cm−1 at 370 nm. However, all of the absorption bands are redshifted compared to their unmodified acene counterparts (anthracene, tetracene, and pentacene) due to the halogenation of the acene core or the extension of the π-conjugated system by the appended phenylethynyl groups. The two pentacene derivatives, BPEP and BTMP, show very similar spectra. The addition of methoxy groups to the molecules results in a redshift in the absorption spectrum by 5 nm, and markedly improved solubility in common organic solvents and polymer films. Furthermore, DMBA, BPET, and BTMP display good solid-state stability from oxidation in ambient atmosphere where only minimal degradation under fluorescent lighting and air was detected after 6 weeks via 1H-NMR (see Supporting Information).

Gibbs Free Energy of PET

Molecular compounds, such as polynuclear aromatic hydrocarbon (PAH), can be used as PSs for the iodonium PAGs given that the energetics are thermodynamically feasible. PET is the oxidation–reduction process between a donor and its acceptor through molecular orbitals. A simplified diagram is shown in Scheme 2. The donor (sensitizer) is at a ground state with two paired electrons in the highest occupied molecular orbital. The oxidation potential of the donor (sensitizer) is increased, compared to the ground state value by absorption of a photon thereby promoting electron to the lowest unoccupied molecular orbital (LUMO) resulting in the formation of the first excited singlet state. The excited singlet state of the sensitizer can lose energy by fluorescence or nonradiative processes before reduction of the ion salt. The PS and ion salt can create an excited complex, as shown in Scheme 1, eq. 3, where an electron is transferred from the sensitizer to the LUMO of the PAG. A reactive cationic radical is created as a result of this electron transfer that can further react to produce a Bronsted acid. The favorability of electron transfer is determined by the oxidation and reduction potentials of the states of the compounds. In this case, the oxidation potential of sensitizer was compared to the reduction potential of the PAG to determine if the reaction is favorable. The thermodynamic favorability for the electron-transfer photosensitization of the modified PAHs with PAG/base generators can be evaluated by the Rehm–Weller equation:

\[
\Delta G(\text{eV}) = \left( E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} \right) - E_{\text{oo}}
\]

The half-wave oxidation potential (\(E_{1/2}^{\text{ox}}\)) and the optical band gap (\(E_{\text{oo}}\)) of the sensitizer was compared with the half-wave reduction potential (\(E_{1/2}^{\text{red}}\)) of the PAG/base generator. If the Gibbs free energy is less than zero (\(\Delta G < 0\)) then the PET is favorable. Another requirement is that there is no ground-state electron-
transfer between PS and PAG. In this regard, the oxidation potential of the sensitizer must be unfavorable for electron transfer until the excited state is photocreated so that the sensitizer can act as an "optical trigger." Cyclic voltammetry was used to measure the redox potentials of the sensitizers and PAG/base generators using ferrocene (Fc/Fc⁺) as an internal reference potential. UV–vis was used to evaluate the optical band gap of the sensitizers using the onset wavelength of absorbance. Redox potentials and band gaps are reported in Table II. The corresponding molecular orbitals of PAG and sensitizers are plotted in Figure 4.

PET of the acenes in this study with the iodonium PAG are thermodynamically favorable, as shown in Table II. The low reduction potential of iodonium PAG is a contributing factor. The reduction potential of iodonium PAG in this case was −1.33 V versus Fc/Fc⁺. However, electron transfer becomes less favorable as the modified acenes become more redshifted. The change in Gibbs free energy value for PET is an order of magnitude lower for BTMP (ΔG = −2.36 eV), which has an absorption onset at 700 nm, compared to anthracene (ΔG = −26.57 eV) which has an absorption onset at 385 nm. Ground-state electron transfer from all sensitizers to the PAG is thermodynamically unfavorable.

PET reactions are governed by collisional quenching where the fluorescence lifetime decay of the fluorophore (sensitizer) decreases with increasing concentration of the quencher (PAG). Thus, the effectiveness of the modified PAHs for PET reactions with iodonium salts was investigated by this method. Quenching rate constants (a measure of PET efficiency) for reducing the fluorescence lifetime of the sensitizers can be obtained from the Stern–Volmer relationship:

\[
\frac{\tau_0}{\tau} = 1 + K_{SV}[\text{PAG}], \quad K_{SV} = k_q \tau_0
\]

In eq. (7), τ₀ and τ are the fluorescence lifetimes in the absence and the presence of the quencher PAG-FABA, respectively; K_{SV} is the Stern–Volmer quenching constant; (PAG) is the concentration of the onium salt; and k_q is the bimolecular quenching rate constant. Rate constants and fluorescence lifetimes are listed in Table II. The Stern–Volmer plots of each PS with various concentrations of FABA-PAG are shown in Figure 5. The fluorescence lifetime decay of PET with quencher is also shown in Figure 6.

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Table I. Absorption and Fluorescence Maxima of Modified PAH PSs

<table>
<thead>
<tr>
<th>PS</th>
<th>Abs. ( \lambda_{max} ) (nm)</th>
<th>Abs. ( \varepsilon ) ( \times 10^3 ) M(^{-1}) cm(^{-1})</th>
<th>Emission ( \lambda_{max} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>326</td>
<td>2.8</td>
<td>381</td>
</tr>
<tr>
<td></td>
<td>342</td>
<td>5.3</td>
<td>403</td>
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<tr>
<td></td>
<td>360</td>
<td>7.6</td>
<td>427</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>7.1</td>
<td>453</td>
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<tr>
<td>CPTX</td>
<td>315</td>
<td>12</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>387</td>
<td>6.9</td>
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<tr>
<td>DMBA</td>
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<td>20</td>
<td>536</td>
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<td></td>
<td>476</td>
<td>23</td>
<td>563</td>
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<tr>
<td></td>
<td>504</td>
<td>24</td>
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<tr>
<td>BPET</td>
<td>341</td>
<td>21</td>
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</tr>
<tr>
<td></td>
<td>355</td>
<td>24</td>
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<td>3.6</td>
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<td>9.8</td>
<td>611</td>
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<tr>
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<td>556</td>
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<tr>
<td>BPEP</td>
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<td></td>
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<td>612</td>
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<tr>
<td></td>
<td>665</td>
<td>27</td>
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<tr>
<td>BTMP</td>
<td>314</td>
<td>274</td>
<td>477</td>
</tr>
<tr>
<td></td>
<td>382</td>
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<tr>
<td></td>
<td>673</td>
<td>27</td>
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</table>

BPET, 6,13-bis(phenylethynyl)pentacene; BPET, 5,12-bis(phenylethynyl)tetra- cene; BTMP, 6,13-bis(3,4,5-trimethoxyphenylethynyl)pentacene; CPTX, 1-chloro-4-propoxythioxanthone; DMBA, 1,8-dimethoxy-9,10-bis(phenylethynyl)anthracene; PAH, polynuclear aromatic hydrocarbon; PS, photosensitizer.

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Figure 3. Normalized absorbance and fluorescence emission spectra of BPET PS after excitation at 514 nm in DMF solution. [Color figure can be viewed at wileyonlinelibrary.com]
The theoretical diffusion-controlled rate constant \(k_d\) in DMF is approximately \(7.06 \times 10^9\) M\(^{-1}\) s\(^{-1}\), as estimated from a derivation from the Stokes–Einstein equation.\(^5^2\) In PET systems where the electron transfer is sufficiently exergonic, \(k_d \approx k_q\).\(^5^1\) Anthracene and DMBA are practically diffusion controlled; however, the \(k_q\) values of tetracene and pentacene derivatives (BPET, BPEP, and BTMP) are an order of magnitude lower. As expected, the decrease in \(k_q\) values can be rationalized by following the thermodynamic considerations \((\Delta G^\text{PET})\) as listed in Table II.

The Rehm–Weller equation only considers the thermodynamic favorability of the first excited singlet state for electron transfer. It is possible that upper excited state energy levels \(S_2\) of the sensitizers could contribute to more exergonic electron transfer reactions. The PSs have high molar absorptivity peaks in the near-UV region which can activate upper excited state levels. In many cases, the internal conversion from \(S_2\) to \(S_1\) is rapid, for example, picoseconds.\(^5^0\) However, it was found that the pentacene derivatives had long-lived second excited singlet states. The fluorescence spectrum of BTMP under excitation at 334 nm shows strong \(S_2\) to \(S_0\) fluorescence \(\lambda_{\text{max}}\) values at 477 and 503 nm, as well as the \(S_1\) to \(S_0\) fluorescence \(\lambda_{\text{max}}\) at 690 and 750 nm, shown in Figure 7. The response between 642 and 677 nm was removed due to emission peaks from second-order diffraction of the excitation wavelength that is unrelated to BTMP.\(^5^0\)

### Photosensitivity of Sensitized Polymer Films

The performance of the sensitizers were evaluated in solvent cast films consisting of PPC with 3 parts per hundred resin (pphr) PAG and exposed to sunlight under a variable neutral density mask and band-pass filter for wavelength selection. Sensitizers were exposed at selected wavelengths that correspond to regions near the long wavelength end of the absorption spectrum for each. Films with DMBA were exposed at 500 nm, BPET films were exposed at 560 nm, and BTMP films were exposed at 650 nm wavelength. Anthracene and CPTX were evaluated at 365 nm under a UV exposure tool. Exposed PPC films were subsequently developed at 100 °C on a hot plate for 7 min. The acid-catalyzed decomposition of PPC requires higher temperatures (100 °C) which makes characterization of photosensitivity at room-temperature possible after exposure. The normalized

![Figure 4](https://wileyonlinelibrary.com/doi/abs/10.1002/app.47141)

**Figure 4.** Energy levels of the FABA-PAG and all PS based on their redox potentials and band gaps. [Color figure can be viewed at wileyonlinelibrary.com]
thickness after development versus log exposure dose (i.e., contrast curve) was generated, Figure 8.53

The normalized thickness of the film was plotted where each point corresponds to the transmission of light from 1 to 100% through the variable neutral density mask. The full intensity of light (100% transmission) through the band-pass filters at 500, 560, and 650 nm were recorded: 1.38, 1.40, and 1.45 mW cm$^{-2}$, respectively. The linear region was extrapolated to zero on the x axis where the dosage value was taken as the minimum dose required for exposure ($D_{100}$). Films of DMBA and BPET had a similar $D_{100}$ of 284 and 270 mJ cm$^{-2}$; however, BTMP had a minimum dose of 6180 mJ cm$^{-2}$. Thus, the most redshifted BTMP peak was 22 times less sensitive than films sensitized with DMBA or BPET. The photosensitivity of all sensitized PPC films is shown in Table III.

A method to normalize the sensitivity in terms of the absorbed light versus the incident light stated above was used to compare the efficiency of the PET reactions within films. The contrast-curve efficiency (Ecc) of the PET reactions in the PPC films was calculated from the ratio of the amount of photoactive compounds (PAG or PS) to the number of absorbed photons from the $D_{100}$. Quantum efficiencies approaching unity are desired. As shown in Table III, direct photolysis of the iodonium PAG at 248 nm gave a quantum efficiency of 0.42. The result is in agreement with previous measurements of iodonium salts, between 0.42 and 0.54. Efficiency dropped as the wavelength of the sensitizer was extended to higher values. The BTMP sensitizer had the lowest efficiency of 0.004. This is due to the less favorable thermodynamics of the electron transfer from BTMP to PAG compared to the other sensitizers, as discussed above.

The Ecc values show excellent agreement with the Stern–Volmer quenching rates ($K_{sv}$) as shown in Figure 9. The Ecc and $K_{sv}$ values increase with more negative value of the Gibbs energy. It is noted that the Ecc and $K_{sv}$ values for DMBA and BPET are nearly equal even though the electron transfer of iodonium salts with DMBA is 5.08 kcal mol$^{-1}$ more exergonic than with BPET. Stern–Volmer analysis shows that BPET has a longer excited-state lifetime which allows it greater opportunity to interact with and undergo electron transfer with the iodonium salt. The bimolecular quenching rate ($k_q$) of BPET is 1.39 times lower than DMBA which also follows the relationship between the PET reaction rate efficiency and the thermodynamic favorability in Table II.

Figure 5. Stern–Volmer plots of all PSs in DMF of their first excited singlet state with FABA-PAG as the quencher. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 6. The effect of various concentrations of FABA-PAG on the fluorescence lifetime decay of DMBA. Fitted to a monoexponential decay with $2.61 < \chi^2 < 2.86$. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 7. The fluorescence spectrum of BTMP at 334 nm excitation in DMF solution. The emission between 642 and 677 nm was removed due to peaks from second-order diffraction of the excitation wavelength. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 8. Contrast curves of PPC films with 3 pphr PAG with the following sensitizers: DMBA, BPET, and BTMP at 1.2 PS to 1 PAG molar ratio. [Color figure can be viewed at wileyonlinelibrary.com]
The effect of path length within the anthracene or DMBA in PPHA films was investigated, as shown in Figure 10. Light transmission versus film thickness were plotted for DMBA and anthracene at various loadings within PPHA films. The optical path length of anthracene and DMBA loaded PPHA films was investigated near the $\lambda_{\text{max}}$ absorption value.

In Figure 10, the optical path length decreased with higher loadings of DMBA within the PPHA film. The 0.52 pphr DMBA film had <1% transmittance at thickness of 35 $\mu$m. PPHA films loaded with 5.71 pphr DMBA had less than 1% transmittance of 4 $\mu$m. In Figure 10, the optical path length at 0.21 pphr anthracene (molar equivalent to 0.51 pphr DMBA) was <1% transmittance at thicknesses above 214 $\mu$m. Sensitizers with high molar absorptivity are advantageous for faster photolysis; however, this is at the expense of optical path length.

Photobleaching can mitigate problems with highly absorbent sensitizers, especially in thick films. Sensitizer photobleaching has been investigated by using UV–visible light spectroscopy, Figure 11.

A film of PPC with 3 pphr PAG and BPET was exposed to 560 nm of light at an intensity of 1.03 mW cm$^{-2}$. The PPC film is inert to acid-catalyzed degradation at ambient conditions. It was used as a control experiment to monitor the absorption properties. Changes in BPET absorbance were monitored as a function of time. Figure 11 shows the maximum absorbance of BPET occurs at 517 and 556 nm. BPET absorbance at these wavelengths decreases as a function of sunlight exposure until the absorbance is nearly zero. This experiment was repeated with DMBA and the results are similar in Figure S15. These results show that the electron-transfer process from PAH to PAG is irreversible and the sensitizer is chemically converted to a nonabsorbing species, in agreement with Scheme 1, eqs. 3 and 4. The iodonium radical produced upon activation rapidly decays and prevents back electron transfer to BPET. The absorption range of

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Wavelength of exposure (nm)</th>
<th>Minimum dose (mJ cm$^{-2}$)</th>
<th>Ecc</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAG only</td>
<td>248</td>
<td>36</td>
<td>0.42</td>
</tr>
<tr>
<td>Anthracene</td>
<td>365</td>
<td>433</td>
<td>0.13</td>
</tr>
<tr>
<td>CPTX</td>
<td>365</td>
<td>573</td>
<td>0.056</td>
</tr>
<tr>
<td>DMBA</td>
<td>500</td>
<td>284</td>
<td>0.021</td>
</tr>
<tr>
<td>BPET</td>
<td>560</td>
<td>270</td>
<td>0.023</td>
</tr>
<tr>
<td>BTMP</td>
<td>650</td>
<td>6180</td>
<td>0.004</td>
</tr>
</tbody>
</table>

BPET, 5,12-bis(phenylethynyl)tetraene; BTMP, 6,13-bis(3,4,5-trimethoxyphenylethynyl)pentacene; CPTX, 1-chloro-4-propoxythioxanthone; DMBA, 1,8-dimethoxy-9,10-bis(phenylethynyl)anthracene, Ecc, contrast-curve efficiency; PAG, photoacid generator.

Figure 9. Ecc values plotted against $\Delta G_{\text{PET}}$ of sensitizers from left-to-right: anthracene, CPTX, DMBA, BPET, and BTMP. Stern–Volmer quenching rates ($K_{sv}$) plotted against $\Delta G_{\text{PET}}$ from left-to-right: anthracene, DMBA, BPET, BPEP, and BTMP. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 10. Transmittance as a function of thickness for various loadings of DMBA in PPHA films at 480 nm (top) and various loadings of anthracene in PPHA films at 363 nm (bottom). [Color figure can be viewed at wileyonlinelibrary.com]

Figure 11. UV–vis absorbance of PPC film with 3 pphr PAG and BPET exposed to 560 nm light at various time increments. [Color figure can be viewed at wileyonlinelibrary.com]
BPET’s chromophoric is related to the Π-conjugation network. Formation of the highly reactive BPET radical cation can undergo a number of reactions such as photodimerization, which will disrupt its Π-conjugation network and decreases the onset absorption wavelength. Cationic and/or radical-based photopolymerization is the common use of sensitizers with onium salts. Formation of nonvolatile residue after decomposition is undesirable for transient polymer applications. Transient polymers rely on monomer evaporation following depolymerization. However, the slow evaporation of phthalaldehyde following PPHA depolymerization gives ample opportunity for side reactions with the sensitizer byproducts because the phthalaldehyde monomer has a very low vapor pressure and may take an extended time to evaporate.

PPHA films with various PAG and DMBA loadings were formulated and cast onto glass substrates to evaluate the amount of residue formed during photoexposure, Figure 12.

Films were exposed to midday sunlight, 1034 W m$^{-2}$. PPHA can depolymerize by protonation of the PPHA ether linkage creating cationic hydroxyl groups that lead to an unzipping decomposition reaction producing phthalaldehyde. Acid-catalyzed depolymerization of PPHA can occur at temperatures above its ceiling temperature (−43 °C), which makes it suitable for transient applications at ambient conditions. The polymer transforms into liquid during depolymerization followed by evaporation or sublimation of the monomer. The three PPHA films in Figure 12 contain 1.5, 3, or 10 pphr PAG with DMBA at a 1:2:1 mol ratio of PAG to DMBA. Photoreponse time for PPHA depolymerization was dependent on PAG loading. PPHA samples with 10, 3, and 1.5 pphr PAG with DMBA began to liquefy after 10, 60, and 150 s, respectively. Yellow phthalaldehyde is easily observed upon depolymerization. Previous studies have confirmed the acid-catalyzed depolymerization of PPHA by NMR and infrared spectroscopy. A dark discoloration and presence of solid residue was visible at higher PAG/DMBA loadings. The higher PAG/DMBA loading increased the likelihood for side-reactions with the phthalaldehyde forming black, nonvolatile residue.

Crivello and Jang previously proposed multiple decomposition pathways for the PS radical cation after the PET reaction, as shown in Scheme 3. Side reactions with phthalaldehyde may occur through similar chemical pathways when PPHA depolymerizes. The sensitizer radical cation can react with the iodonium neutral radical products forming dimers, or they may directly react with phthalaldehyde during or after depolymerization. The formation of the black-colored residue may indicate that the DMBA conjugation has been extended.

It is known that the anthracene radical cation can undergo phenylation with the aryl radical from the iodonium to produce 9-phenylanthracene and a proton. The 9-phenylanthracene can absorb another photon and act as an electron donor with another iodonium salt. It was proposed that poly(arenes) can be generated in this manner. The modified PAHs used in this study may also react with aryl radicals or phthalaldehyde in a similar way. The modified PAH appears to induce a larger amount of solid residue at a faster rate than the unmodified parent compound during the PET reaction. Appending phenylethynyl groups onto the acene core likely provides more resonance stability of the radical cation of the sensitizer. The long-lived radical cation may diffuse and form stable products by reaction with phthalaldehyde or other aryl compounds creating an extended conjugated network.

The nonvolatile, black residue from the PHA film with 10 pphr PAG and DMBA was analyzed by 1H-NMR to investigate the chemical structure, as shown in Figure S16. The residue was baked at 175 °C on a hotplate for 4 h to evaporate phthalaldehyde while remaining below the melting point of DMBA. The residue had broad peaks from 6 to 8 ppm indicative of possible aromatic derivatives. Furthermore, the mass of the postexposure residue was less than the original mass of PAG and DMBA in the film. This suggests that phthalaldehyde participates in reactions with the DMBA cation radical.

Figure 12. Sunlight-induced depolymerization of 100 μm thick PPHA films with various loadings of FABA-PAG with DMBA over glass substrate over an 18 min sunlight exposure at noon. [Color figure can be viewed at wileyonlinelibrary.com]
Figure 13. MALDI–TOF–MS analyses of residue after full sunlight-induced depolymerization of PPHA film with 10 pphr PAG and DMBA. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 14. Time-lapse photos of PPHA films with 1 pphr PAG and anthracene, CPTX, DMBA, BPET, and BTMP exposed to natural sunlight at noon over a 20 min period. [Color figure can be viewed at wileyonlinelibrary.com]
the participation of PAG in the side reactions after PET. The results show that the iodonium cation was no longer present (i.e., the absence of 337 m/z peak); however, the borate anion was present (i.e., 679.1 m/z) suggesting that it does not play a significant role in the side reactions. MALDI TOF MS was used to determine the molecular mass of the poly(aromatic) products to evaluate the extent of the conjugated framework, Figure 13.

The MS spectrum shows a number of aromatic derivatives as a result of the side reactions with the DMBA radical cation. A series of main peaks (denoted in the spectrum) with their corresponding fragmentations were observed. The product formed in the side reaction extends to nearly 1.5 kDa, which is 3.6 times the molar mass of DMBA. The separation between these peaks corresponds to about the molar mass of a phthalaldehyde monomer, about 134 Da. It is evident that lower loadings of the PAG and modified PAHs are necessary to mitigate the undesirable side reactions with phthalaldehyde that form nonvolatile, solid poly(aromatics). Faster evaporating copolymers of aldehydes, such as with butanal, could also potentially mitigate side reactions.

The sunlight-induced “transience” of the PPHA films with optimal loading of photocatalysts with PSs was exposed midday sunlight, as shown in Figure 14. Formulations of 1 pphr PAG with anthracene, CPTX, DMBA, BPET, and BTMP (1.2:1 PS to PAG ratio) were solution cast into film. BTMP loaded films remarkably began to depolymerize in less than 1 min and underwent complete depolymerization in 5.5 min. The PET efficiency (Ecc) of BTMP with iodonium salts are one to two orders of magnitude lower than the other sensitizers according to Table III. However, it is likely the higher near-UV absorbance excites BTMP to an upper excited state where electron transfer is more efficient. This is shown in Table II and Figure S14 where the bimolecular quenching rate increased by an order of magnitude when evaluated at the second singlet excited state. PPHA only, PPHA with anthracene, and PPHA with 1 pphr PAG films did not undergo depolymerization in sunlight after 1 h. The PPHA with PAG film did not significantly depolymerize because of the limited amount of UV radiation absorbed by PPHA in sunlight. Thus, a sensitizer is needed to activate the PAG in sunlight. All of the sensitized PPHA films with PAG eventually lose their mechanical integrity during depolymerization and absorb into the texwipe.

CONCLUSIONS

PAHs with disubstituted phenylethynyl groups were found to be efficient sensitizers of onium salts to induce acid-catalyzed depolymerization of PPHA and PPC films. Thermodynamically favorable sensitizers for PET reaction, as evaluated by the Rehm–Weller equation, show a strong correlation with the fluorescence quenching rates in solution and Ecc within films. Pentacene derivatives showed long fluorescence lifetimes and high quenching rates in the upper excited singlet state levels. The soluble anthracene, tetracene, and pentacene derivatives were effective in the photodegradation of polymers with short sunlight exposure times. This study has provided a pathway of developing a class of photochemical triggers whose exposure wavelength can be tuned from the UV region into the entire visible light region for the purpose of initiating the depolymerization of polymers for a wide variety of transient applications.

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