Metastable poly(phthalaldehyde) (PPHA) can be triggered to depolymerize under visible light by incorporation of photosensitive compounds, such as a photoacid generator (PAG), which can generate a strong acid in situ. However, photosensitive compounds can be thermally unstable and have limited shelf life, causing inadvertent device triggering. It can also be difficult to fabricate components that are photosensitive because special lighting conditions are needed. In this paper, nonphotosensitive PPHA films were formed and made photosensitive at the point of use. This improved the material shelf life and manufacturability by adding a second, PAG-containing layer to the original nonphotosensitive layer at an optimal point before use. The catalytic photoacid was generated rapidly by exposure of the PAG-containing layer to radiation. Depolymerization of PPHA via the acid catalyst was followed by diffusion of the acid into the nonphotosensitive layer causing it to depolymerize. Diffusion of the photoacid into the nonphotosensitive medium was quantified at various temperatures. Photoacid diffusion in a liquid, moving-front caused depolymerization of the nonphotosensitive PPHA layer. The fabricated bilayer structure allowed for better stability of the structural material using PPHA while still achieving transience.

KEYWORDS
PAG, poly(phthalaldehyde), transient polymer

1 | INTRODUCTION

The emerging field of research into transient devices has attracted attention because of the need for disappearing electronics and other applications where device discovery, recovery, or retrieval is undesirable. The goal is to create devices that degrade and can be incorporated into the surrounding environment with little or no environmental impact.\(^1\)\(^2\) To meet the transient device goals, the material needs to degrade quickly under local stimuli and disappear completely after degradation. Cyclic poly(phthalaldehyde) (PPHA), a cationically polymerized rigid polymer, is a potential candidate material for the emerging transient device applications.\(^3\)\(^5\) PPHA is a self-immolative polymer where breaking an acetal linkage in the cyclic PPHA polymer backbone leads to cascading chain unzipping resulting in the polymer reverting back to its monomer form at temperatures above its ceiling temperature, ca. −42°C.\(^6\)\(^7\)

PPHA degradation can be triggered by different types of stimuli. These include photochemical (e.g., visible light, light emitting diode, and ultraviolet),\(^5\)\(^7\)\(^9\) chemical,\(^10\)\(^11\) thermal,\(^11\)\(^12\) and mechanical stimulus.\(^13\)\(^14\) Visible light stimulus is particularly attractive because of the availability of ambient light. Phillips et al demonstrated the use of a photo-induced electron transfer (PET) reaction between a fused-aromatic-ring sensitizer and photoacid generator (PAG) to create a strong acid that led to PPHA degradation using visible light.\(^8\) Anthracene (\(\lambda_{\text{max}} = 370\) nm) was modified to form 1,8-dimethoxy-9,10-bis(phenylethynyl)anthracene (DMBA, \(\lambda_{\text{max}} = 476\) nm and 504 nm) allowing a broader wavelength of light to be harvested, resulting in a faster rate of degradation in sunlight.\(^8\)

However, the direct addition of photosensitive compounds into PPHA presents a risk of inadvertent photo or thermal triggering of PPHA during device fabrication. Also, photo-active compounds are known to have a limited shelf-life at elevated temperatures.\(^15\) The free
acid created by PAG activation limits the ultimate shelf life of the PPHA-containing component. Therefore, it is desirable to avoid adding the photosensitive compounds when fabricating transient devices until the last possible moment before use.

The use of a photosensitive/nonphotosensitive bilayer structure to study photoacid diffusion in photoresists has been previously reported.\textsuperscript{16-21} The rate of photoacid diffusion in photoresist can be quantified by allowing the photoacid to diffuse from a photosensitive layer to a nonphotosensitive layer. Specifically, diffusion occurs through a "reaction front" mechanism. This occurs in photoresist when the temperature is below the glass transition temperature of the nonphotosensitive material. The reaction front propagates stepwise from the photosensitive layer to the nonphotosensitive layer following a layer-by-layer mechanism. In this study, the acid diffusing into the nonphotosensitive layer initiating its depolymerization. A transient, bilayer structure can be made by first fabricating a nonphotosensitive PPHA structure under visible light followed by the formation of a thin, photosensitive PPHA layer on the existing structure using lamination or spray coating. When triggered, the photoacid propagates into the nonphotosensitive layer and catalyzes PPHA depolymerization.

In this study, a quantitative determination of the activation energy for the thermally induced depolymerization of PPHA powder, and PPHA films (with and without photosensitive compounds) were compared. The activation energy provided the basis for estimating the shelf life of the transient PPHA device based on the storage temperature. Bilayer PPHA structures were fabricated and the diffusivity of the acid was studied to determine the PPHA degradation rate based on acid diffusion.

\textbf{SCHEME 1} Preparation of bilayer photosensitive poly(phthalaldehyde) (PPHA) film using solvent bonding [ Colour figure can be viewed at wileyonlinelibrary.com ]

\textbf{FIGURE 1} Thermogravimetric analysis (TGA) result for weight fraction versus time at several isothermal temperatures for A, poly(phthalaldehyde) (PPHA) polymer powder thermally stressed at 358 K, 363 K, 368 K, and 373 K; B, PPHA film with 60 pphr bis(trifluoromethyl)sulfonylimide (BMP TFSI) was thermally stressed at 353 K, 358 K, 363 K, and 368 K; and C, PPHA film with 60 pphr BMP TFSI and photosensitive compounds were thermally stressed at 323 K, 333 K, 343 K, and 373 K [ Colour figure can be viewed at wileyonlinelibrary.com ]
Materials: 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (BMP TFSI) was purchased from IoLiTec (Heilbronn, Germany). The PAG, Tetrakis (pentafluorophenyl)borate 4-methylphenyl[4-(1-methylethyl)phenyl]iodonium (Rhodorsil FABA), was purchased from Alfa Aesar (Haverhill, Massachusetts) and tetrahydrofuran (THF) was purchased from TCI Chemicals (Chennai, India). Anthracene was purchased from Alfa Aesar (Haverhill, Massachusetts) and tetrahydrofuran (THF) was purchased from BDH (Radnor, Pennsylvania). All chemicals bought were used as received. Cyclic PPHA was cationically polymerized below its ceiling temperature (~42°C) following previous synthesis procedure. The resulting PPHA has a number average molecular weight of 397 kDa with a dispersity (D) of 1.18.

All PPHA films were solvent cast with 60 part per hundred (pphr) BMP TFSI with respect to PPHA. Polymer formulations were prepared in a clean glass vial with addition of all solid contents (PPHA, PAG, and anthracene) and BMP TFSI dissolved in THF, with a 12:1 weight ratio for THF:PPHA. The films were cast onto Polytetrafluoroethylene (PTFE)-lined petri dishes and dried at room temperature with a 15-psig nitrogen overpressure for 18 hours, followed by 12 hours at 15-psig nitrogen with a slow THF vapor bleed rate. The films were peeled off the PTFE substrates and allowed to dry in the dark for 2 days.

Thermogravimetric analysis (TGA) was performed with a TA Q50 Instrument. All samples prepared were dried for over a month to ensure low solvent content. All samples tested were isothermally aged in a nitrogen-rich environment for 24 hours. TGA pan was cleaned by ramping to 900°C to remove organic residue. The time for 2% weight change for each sample was recorded as an indication of the onset of decomposition of the polymer and film.

To study the photoacid diffusivity from the photosensitive layer to the nonphotosensitive layer, the films were held in place using double-sided tape on a quartz substrate and flattened using 300 kPa hydraulic pressure to ensure sample flatness for later thickness measurement. Bilayer PPHA films were prepared by laminating two PPHA film layers using solvent bonding. Bilayer PPHA films were then exposed at a total dose of 3.6 J/cm² from a Xe lamp to ensure complete activation of the PAGs. This dose was chosen because it is greater than the minimum dose needed for full PAG activation. Scheme 1 describes the preparation of a bilayer PPHA film. Films were post-exposure baked (PEB) at various temperatures for different times. The depolymerization product, phthalaldehyde (PHA), was removed by dissolution in methanol. The resulting films were again dried under nitrogen. A Veeco Dektak 150 Surface profilometer was used to measure the depth of the pit formed. The profilometer was operated at a scan rate of 1.11 μm/s with a stylus tip force of 1 g.

### 3 | RESULT AND DISCUSSION

The rate-limiting step is PPHA depolymerization after the initial chain scission ring-opening reaction. Chain scission ring opens the cyclic polymer and activates (deprotects) the newly created chain ends, initiating the rapid depolymerization of PPHA back to monomer. First order reaction kinetics and an Arrhenius relationship for the rate constant was used to describe the PPHA degradation rate, Equation 1.

\[
\ln k(T) = \ln A + \frac{E_A}{R T}
\]

In Equation 1, \(k(T)\) is the reaction rate at a specific temperature \(T\), \(A\) is a pre-exponential factor for the reaction, \(E_A\) is the activation energy for the reaction, and \(R\) is the gas constant. Equation 1 can be linearized to obtain \(E_A\) and \(A\) from gradient and interception, Equation 2.

\[
\ln(k) = \frac{E_A}{R T} + \ln(A).
\]

The stability of PPHA polymer powder, PPHA polymer film without photosensitive compounds, and PPHA polymer film with photosensitive compounds (10 pphr PAG, 2.1 pphr anthracene) were evaluated. The fractional weight change under isothermal conditions for each sample at a specific temperature was recorded, shown in Figure 1. Figure 2 shows a plot of natural logarithm of reaction rate versus inverse temperature. Table 1 summarizes \(E_A\) and \(A\) values from the linear data fit for each sample, Equation 2. The pre-exponential factor for the reaction is extrapolated from the Arrhenius equation for PPHA polymer powder, PPHA film with and without photosensitive compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy (J/Mol)</th>
<th>Pre-exponential Factor (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPHA powder</td>
<td>3.32*10⁵</td>
<td>1.95*10⁴⁴</td>
</tr>
<tr>
<td>PPHA film—no photosensitive compounds</td>
<td>2.23*10⁵</td>
<td>2.95*10²⁸</td>
</tr>
<tr>
<td>PPHA film—photosensitive compounds</td>
<td>9.23*10⁴</td>
<td>2.41*10¹⁰</td>
</tr>
</tbody>
</table>

Abbreviation: PPHA, poly(phthalaldehyde).
has been used to express the collision frequency of molecules at different temperatures. It was calculated from the y-intercept in Figure 2. No specific physical interpretation was given to the pre-exponential factor. The results show that high-purity, high-molecular weight PPHA polymer is extremely stable with a high activation energy, \(3.32\times10^5\) J/mol. The PPHA polymer was cationically polymerized using boron trifluoride etherate as the catalyst. A strong Lewis acid can catalyze the depolymerization of PPHA at room temperature through attack of the PPHA ether linkage in the polymer backbone. Purification of the PPHA after synthesis is critical to achieving stable polymer. This includes removing the BF\(_3\) catalyst to a level below one part per million, as measured by inductively coupled plasma mass

**FIGURE 3** Photoacid penetration depth for exposed 100 \(\mu\)m poly(phthalaldehyde) (PPHA) film with 10 pphr photoacid generator (PAG), 2.1 pphr anthracene, and 60 pphr BMP TFSI against increasing post-exposure baked (PEB) time under various PEB temperatures [Colour figure can be viewed at wileyonlinelibrary.com]

**SCHEME 2** Explanation of reaction front propagation mechanism for photoacid diffusion in depolymerized poly(phthalaldehyde) (PPHA) medium into reaction interface [Colour figure can be viewed at wileyonlinelibrary.com]

**FIGURE 4** A, Square of penetration depth of photoacid versus time for exposed 100 \(\mu\)m PPHA film with 10 pphr photoacid generator (PAG) under various post-exposure baked (PEB) temperatures for different length. Linear regression line was fit for data points at each temperature, assuming a Fickian diffusion model. B, Natural log of diffusion constant at various temperatures [Colour figure can be viewed at wileyonlinelibrary.com]
spectrometry (ICP-MS). It is noted that this concentration is lower than the previously documented safe BF₃ level.²² Inclusion of 60 pphr BMP TFSI into the PPHA film lowered the activation energy slightly to 2.23*10⁵ J/mol. The decrease in activation energy may be due to the higher chain segment and impurity (e.g., BF₃) mobility within the mixture caused by the BMP TFSI plasticizing effect on the polymer film. Nevertheless, the expected stability of PPHA films with no photosensitive compounds should be about 400 days at 50°C, based on extrapolation of the Arrhenius data.

The addition of 10 pphr Rhodorsil FABA and 2.1 pphr anthracene caused the activation energy to drop to 9.23*10⁴ J/mol. The expected shelf life dropped to as low as 15 hours at 50°C. This is because of the acid impurities in Rhodorsil FABA caused by prior thermal degradation or in situ degradation. Cold storage greatly extends the shelf life of all samples. PPHA structures without photosensitive compounds are clearly easier to store and handle compared with Rhodorsil FABA containing polymer. This creates the opportunity for fabricating nonphotosensitive PPHA structures in any ambient lighting conditions followed by long term storage and addition of a photo-sensitive layer at a time near the point of deployment.

The bilayer structure composed of a nonphotosensitive core and (later added) photosensitive layer was investigated. Various thicknesses of photosensitive PPHA films with different PAG and anthracene loadings were laminated onto 600-μm thick nonphotosensitive PPHA films using the solvent in the polymer film as the bonding agent. No additional adhesive was applied to bond the films together. The PPHA depolymerization mechanism in the nonphotosensitive layer is by acid diffusion from the PAG-containing layer into the 600-μm thick nonphotosensitive PPHA films. Sufficient BMP TFSI was added to photosensitive layer to keep the depolymerized PPHA liquid so that acid diffusion was high during the whole depolymerization process.¹⁸

Table 2 Diffusion coefficient of photoacid from a fully exposed 100 μm PPHA film containing 5 pphr PAG at various temperatures into depolymerized PPHA

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>293</th>
<th>308</th>
<th>313</th>
<th>323</th>
<th>338</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient (μm²/s)</td>
<td>4.23</td>
<td>38.0</td>
<td>73.5</td>
<td>139</td>
<td>331</td>
</tr>
</tbody>
</table>

Abbreviations: PEB, post-exposure baked; PPHA, poly(phthalaldehyde).

Figure 5 Penetration depth of photoacid in poly(phthalaldehyde) (PPHA) film versus post-exposure baked (PEB) time at room temperature for (A) PPHA films containing 5 pphr and 10 pphr photoacid generator (PAG); (B) PPHA films containing 5 pphr PAG with thickness of 100 μm, 130 μm, and 167 μm [Colour figure can be viewed at wileyonlinelibrary.com]

Figure 6 A, Comparison of square of penetration depth of photoacid versus post-exposure baked (PEB) time for exposed 100 μm poly(phthalaldehyde) (PPHA) film with 5 pphr and 10 pphr photoacid generator (PAG). B, Comparison of square of penetration depth of photoacid versus PEB time for exposed PPHA films containing 5 pphr PAG with various thickness of 100 μm, 130 μm, and 167 μm [Colour figure can be viewed at wileyonlinelibrary.com]
PAG-containing film into the 600-μm thick nonphotosensitive PPHA layer at different temperatures. A clear trend showing an increase in the rate of penetration by the photoacid with PEB temperature can be seen. Both the rate of acid reaction with the PPHA and increase in diffusion rate occurred at higher temperature. Glassy PPHA decomposes below its glass transition temperature (T_g). Therefore, the resulting penetration of acid into a nonphotosensitive PPHA occurred through a liquid reaction front propagation mechanism,\textsuperscript{17} as explained in Scheme 2. The PAG was uniformly distributed in the photosensitive film prior to photo-exposure. Once the PAG was photo-activated, PPHA depolymerization occurred and the photo-active layer liquefied. The photoacid-containing depolymerized liquid front moved into the fresh (nonphotosensitive) PPHA material on a layer-by-layer basis. The reaction front continued to move until all the PPHA was mixed with the acid-loaded material, the PAG was consumed, or the PAG was diluted to such extent that it was no longer able to depolymerize PPHA. Although the PAG is a catalyst, impurities in the film, such as water and residual solvent, can consume a fraction of the in situ created photoacid.

The rate of photoacid diffusion and degradation of the PPHA is dominated by four factors: (a) rate of photoacid generation, (b) rate of PPHA depolymerization and liquefication, (c) rate of photoacid quenching (ie, consumption), and (d) rate of photoacid diffusion into the solid PPHA.\textsuperscript{23} In this study, a high exposure dose was used to activate the PAG in a short time eliminating photoacid generation from being the rate-limiting step. Moreover, the photoacid is known to be a very strong acid (pK_a < -14) that will depolymerize PPHA rapidly.\textsuperscript{24} The only consumption of acid that would occur is from trace alkaline impurities or side reactions, of which none have been identified. Since there are no alkaline additives in the PPHA films, photoacid quenching can be assumed negligible. Therefore, the rate-limiting step for depolymerization of nonphotosensitive PPHA using the two-layer structure is the rate of photoacid diffusion into the solid PPHA medium. Figure 4A shows the square of the penetration thickness versus PEB time at various temperatures. A linear relationship is expected for Fickian diffusion, assuming a constant diffusion coefficient vs concentration. Linear regression lines were fitted to estimate diffusion coefficient of the photoacid into PPHA, following classical Fickian diffusion. Table 2 summarizes the photoacid diffusivity into depolymerized PPHA vs temperature. Higher temperature led to an increase in the diffusion coefficient. The relationship of the diffusion coefficient and temperature was assumed to follow the usual Arrhenius relationship. The activation energy and pre-exponential factor for acid diffusion was calculated. Figure 4B shows the plot of the temperature dependence of the photoacid diffusion coefficient into depolymerized PPHA medium. The activation energy for the photoacid diffusion was found to be 79 kJ/mol with a pre-exponential factor of 7.6*10^{14} s^{-1}. By knowing these two parameters, an amount of time for complete degradation of a PPHA film using a 100-μm photosensitive film with 5 pphr PAG can be estimated.

The PAG concentration in the photo-active layer and photosensitive layer thickness were varied to see their influence on acid diffusion. The penetration depth and standard deviation are summarized in Figure 5. Figure 6A compares the square of the penetration thickness vs PEB time at room temperature for films containing 5 pphr PAG and 10 pphr PAG. A higher diffusivity, 8.9 μm^2/s, was observed for the film containing 10 pphr PAG, compared with 4.2 μm^2/s for the film containing 5 pphr PAG. Figure 6B compares the square of penetration thickness versus PEB time at room temperature for films containing 5 pphr of PAG at various thicknesses. The diffusivity was also evaluated with a thicker photo-active film. The diffusivity increased from 4.2 μm^2/s to 8.6 μm^2/s when the photo-active film thickness increased from 100 μm to 167 μm. In both cases, acid diffusivity increased with the thickness of the photosensitive layer or PAG concentration. Acid-catalyzed degradation of PPHA is known to be an exothermic reaction.\textsuperscript{8} The addition of more polymer and more PAG resulted in greater local heating to facilitate acid diffusion. In addition, a higher concentration of PAG or greater thickness of the photosensitive layer produced a higher local concentration of acid during liquefication of the underlying layers. Thus, the diffusivity increased for both cases, concentration and thickness.

To demonstrate the utility of a bilayer transient PPHA film, a formulation of 0.3 g PPHA containing 60 pphr BMP TFSI, 10 pphr PAG, and 2.1 pphr anthracene was prepared and spray coated onto a 150-μm thick PPHA film. Figure 7 shows time-lapse pictures of exposed bilayer PPHA transient films at room temperature. The transient bilayer PPHA film completely disappeared after 1 hour and soaked into the surrounding environment.

### 4 | SUMMARY

The need for and advantages of using a photo-active/nonphotoactive bilayer structure in the fabrication of PPHA-based transient devices is described. Nonphotosensitive PPHA films have a long shelf-life at room temperature and can be safely handled in any lighting condition.
By addition of a photosensitive layer near the time of deployment, the risk of accidental device triggering can be lowered. Once irradiated, the photoacid propagates following a Fickian diffusion mechanism and a layer-by-layer liquid reaction front.

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