RESEARCH ARTICLE

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Time-delayed photo-induced depolymerization of poly(phthalaldehyde) self-immolative polymer via in situ formation of weak conjugate acid

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Poly(phthalaldehyde) (PPHA) can be used as a structural material in transient devices and photo-catalytically depolymerized at the end of device life by the use of a photo-acid generator (PAG). However, device degradation requires the presence of a radiation source at the end of device mission. It has been found that the onset of PPHA depolymerization after PAG photo-exposure can be delayed by incorporation of a particular weak bases in the PPHA/PAG mixture. This method of delayed PPHA depolymerization allows for PAG activation prior to or during device deployment when the device is under full user control. The basicity of specific lactams and amides was found to slow the PPHA depolymerization, giving the transient device a longer but finite mission lifetime. The weak base reacts with the photo-generated strong acid to form a weak conjugate acid, which reacts more slowly with PPHA to extend the onset of PPHA depolymerization. The addition of a molar excess of specific lactams or amides, with respect to PAG, maintains PPHA stability and mechanical properties for more than 80 minutes after photo-exposure at room temperature. The amide or lactam mediated acid activation of PPHA follows first-order kinetics. The time delay of PPHA depolymerization can allow for prelaunch photo-exposure and eliminates the need for postmission photo-exposure where reliable light-sources may not be available.

KEYWORDS

photo-transience, poly(phthalaldehyde), time delay

1 | INTRODUCTION

Polymer-based transient devices and materials are an emerging field of research where the triggered disposal of the device is required so as to avoid reverse-engineering, retrieval, or detection.[1,2] Some transient concepts involve the dissolution of the device in an aqueous solvent; however, solution-based resources may not be available.[3-6] Moore et al introduced the concept of stimuli-responsive polymers such as poly(phthalaldehyde) (PPHA) as a metastable material that can be used for a variety of transient device applications.[7,8] Low ceiling temperature polymers, such as PPHA, are thermodynamically unstable above their ceiling temperature and can be kinetically stabilized by end-capping or cyclization of the chains for use above their ceiling temperature.[9-12] The removal of the kinetic-trap can induce rapid, unzipping depolymerization at room temperature.[13,14] The PPHA backbone is susceptible to cleavage via free-acid protonation of the acetal linkage.[15] A recent study used polymeric thermal acid generators, such as poly(vinyl t-butyl carbonate sulfone), to increase the depolymerization kinetics at low temperature.[16] A specific-ion coactivation effect at the surface of cyclic PPHA microcapsules has been shown to accelerate depolymerization in acidic methanol solution.[17] Photo-acid generators (PAGs) have also been used to trigger PPHA depolymerization via sunlight and other radiation sources.[2,8,18,19] The PAG spectral response has been extended to include the entire visible spectrum

for sunlight or targeted wavelength exposure.[20-22] The use of a photo-induced electron transfer (PET) reaction between a chemical sensitizer and PAG to create a strong acid in situ upon exposure to visible light is of particular interest because it opens up device applications where visible light is available upon mission completion.

The mechanism of triggering PPHA depolymerization using visible light has been discussed[20]; however, the time-delayed, controlled depolymerization of PPHA remains largely unexplored. One limitation of the immediate, photo-initiated depolymerization of PPHA is that abundant radiant energy may not be available at the end of the device mission. Either low or uneven light radiant energy across the device can cause problems for device destruction. Also, inadvertent predeployment or in-use photo-exposure of the PAG can cause premature device destruction. Thus, it is desirable to activate the PAG just prior to deployment or during the mission where reliable exposure conditions can be guaranteed, followed by time-delayed PPHA depolymerization. This allows the one time use of transient devices during daytime hours, if the delay time can be made to match the mission lifetime. It would be especially valuable for the delay time to be predetermined by the user.

It has been found that certain amide and lactam-based compounds delay PPHA depolymerization after exposure of the PAG-loaded mixtures. The chemical interaction of the amide or lactam with the in situ, photo-generated strong acid has been explored. The depolymerization rate vs temperature shows that the delay follows first-order kinetics and an Arrhenius relationship for the activation energy. It has also been shown that the mechanical properties of the PPHA film can be maintained during the postexposure delay period.

2 | EXPERIMENTAL

2.1 | Materials

The PAG, tetrakis(pentafluorophenyl)borate-4-methylphenyl[4-(1-methylethyl)phenyl]iodonium (Rhodorsil FABA), was purchased from TCI Chemicals (Tokyo, Japan). Anthracene and dimethylacetamide (DMAc) were purchased from Alfa Aesar (Haverhill, Massachusetts). 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP TFSI) was purchased from Iolitec (Helibronn, Germany). N-methyl-pyrrolidone (NMP), 1-phenyl-2-pyrrolidinone, N-isopropylacrylamide, 1,5-dimethyl-2-pyrrolidinone, and bromothymol blue were purchased from Sigma Aldrich (St. Louis, Missouri). Tetrahydrofuran (THF) was purchased from BDH (Radnor, Pennsylvania). Cyclopentanone was purchased from EMD Millipore Corporation (Burlington, Massachusetts). All chemicals were used as received. PPHA was cationically polymerized using boron trifluoride etherate (BF$_3$) at −80°C following the procedure of Schwartz et al.[12] The PPHA number average molecular weight of the polymer used in this study was 352 kDa with a dispersity (Đ) of 1.27.

2.2 | Sample preparation

PPHA films were formulated in a clean scintillation vial by dissolving the solid contents and BMP TFSI in THF. A weight ratio of 12:1 for THF-to-PPHA was used in all formulations in this study. PAG and anthracene were added with a molar ratio of 1:1.2 in all formulations. Anthracene was present in all films containing PAG at the mole ratio in order to make the films sensitive to near-UV radiation. Films were cast in a PTFE petri dish and dried at room temperature at 17 psig nitrogen atmosphere for 18 hours, followed by 30 hours at 15 psig with slow bleeding of THF vapor. The films were peeled off the PTFE petri dish and allowed to dry at ambient temperature and pressure for 2 days in the dark before characterization.

2.3 | Characterization

Quartz crystal microbalance (QCM) experiments were performed at 23°C using a Stanford Research Systems QCM 200 to quantify the solid-state kinetics of PPHA depolymerization. Polymer formulations were made with 9.1 wt% polymer solids in cyclopentanone with 5 parts per hundred resin (pphr) of PAG and 1.05 pphr anthracene. The PAG and anthracene loadings were with respect to the PPHA weight. The QCM films were 1.2-μm thick and made by spin-coating onto a 2.54 cm diameter QCM substrate. The disks had a resonant frequency of 5 MHz unloaded and an active surface area of 0.4 cm^2. An open-faced holder was used to expose the polymer film to the output of a 1000 W Hg (Xe) Oriel Instruments flood exposure lamp with 365-nm bandpass filter. The exposure dose was 730 mJ/cm^2 for all samples. QCM experiments were also performed at different temperatures using a Q-Sense E4 QCM to quantify the PPHA depolymerization time vs temperature.

The PPHA depolymerization kinetics were studied using the QCM. The Butterworth-van Dyke equivalent circuit model for the QCM electrical response provided information on PPHA degradation, especially as the solid converted into a viscous liquid. The change in resonance frequency is related to the mass change of thin film, as shown in Equation 1.

$$\Delta f = -C_f m, \tag{1}$$

In Equation 1, C_f is a calibration constant, m is the mass of the film, and Δf is the change in resonance frequency. The decrease in mass resulting from evaporation of the PPHA monomer results in an increase in resonance frequency. An increase in motional resistance for the QCM in the Butterworth-van Dyke model occurs when the solid PPHA film softens or liquefies on the QCM resulting in QCM vibrational energy loss. The increase in resistance, visual inspection of the QCM and detection of PHA odor are direct evidence of PPHA depolymerization.

Dynamic mechanical analysis (DMA) of films was performed on a TA Q800 DMA instrument. All DMA samples were 30 × 8 × 0.1 mm (length-width-thickness). The measurements were performed at 23°C with 0.075% strain at 1 Hz. The samples were measured at constant temperature for 3 minutes before being exposed to a dose of 730 mJ/cm^2. This dose was chosen because it is greater than the minimum dose needed to fully expose the PAG. The storage modulus of the films was continuously measured to track the mechanical degradation of PPHA after photo-exposure.

UV-visible (UV-Vis) absorption spectroscopy was performed using Hewlett Packard 8543 UV-Vis spectrophotometer in THF solution. Attenuated total reflectance (ATR) infrared spectroscopy experiments were performed using a Nicolet iS50 FT-IR instrument. Duplicate samples prepared for DMA were examined by ATR-IR. The ATR-IR spectra were recorded before and after 730 mJ/cm^2 optical exposure. A total of 32 FT-IR scans were obtained for each sample.

3 | RESULTS AND DISCUSSIONS

The PET reaction between anthracene and PAG was used to create a strong acid within the PPHA film to catalyze PPHA depolymerization after UV exposure. Figure 1 shows the QCM resistance (from the Butterworth-van Dyke model) versus time after exposure of a series of PPHA films containing different concentrations of NMP. The rapid increase in resistance in Figure 1 represents QCM energy loss due to viscoelastic damping caused by depolymerization and liquification of the PPHA film. PPHA films with no NMP had a QCM photoresponse delay of 34 seconds. This corresponds to the time needed for the strong acid to be formed and catalyze PPHA depolymerization to the point where the solid film liquefied. The addition of 0.25 and 0.5 pphr NMP in the PPHA film delayed the photoresponse by 48 and 59 seconds, respectively. Higher levels of NMP, 1 pphr, 5 pphr, and 10 pphr, delayed the photoresponse further to 195, 4034, and 6292 seconds, respectively. The mole ratio of NMP-to-PAG is 0.5:1, 1:1, 2:1, 10:1, 20:1 for films containing 0.25, 0.5, 1, 5, 10 pphr NMP and 5 pphr PAG (ie, the films giving the above-mentioned delay times). Photographs of 150-μm-thick PPHA films with and without 5 pphr NMP as a function of time after photo-exposure are shown in Figure 2. The photoresponse delay is due to the moderating effect of NMP on the acidity of the acid produced by the PET reaction.
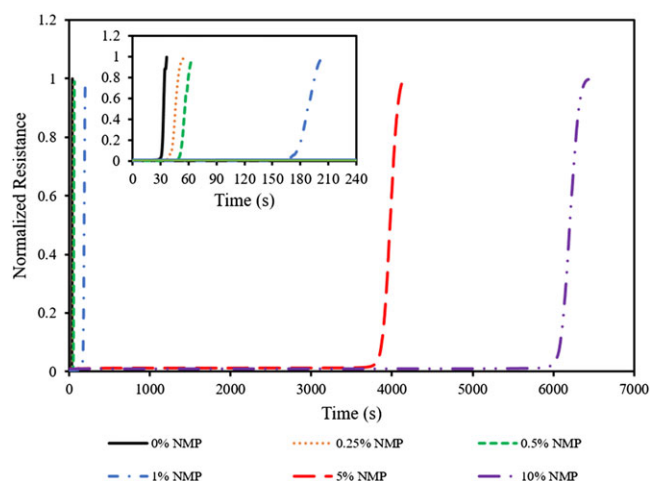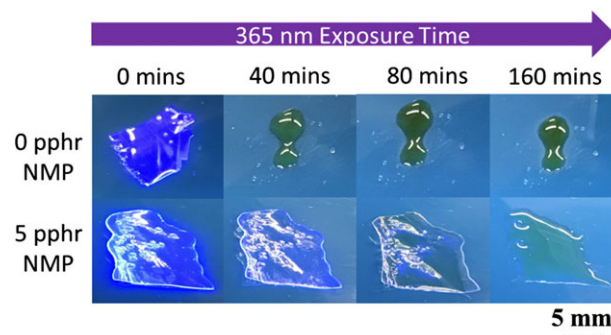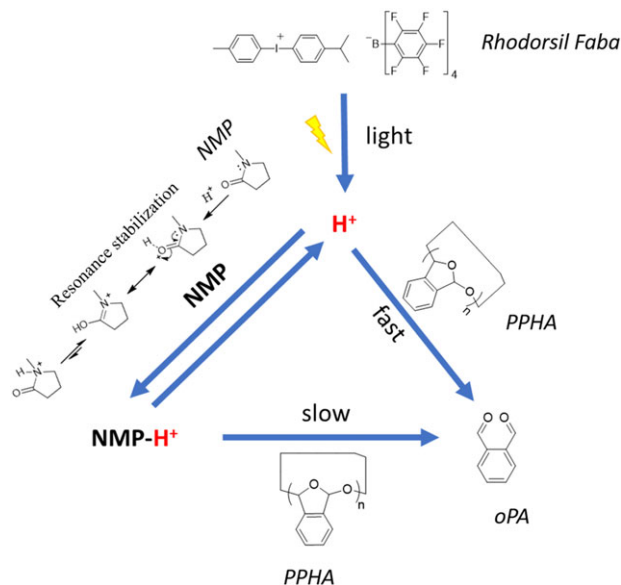

FIGURE 2 Time lapse photo comparison for depolymerizing poly(phthalaldehyde) (PPHA) films containing 0 and 5 pphr N-methyl-pyrrolidone (NMP) [Colour figure can be viewed at wileyonlinelibrary.com]

NMP is a polar, basic solvent. Its conjugate acid has a $pK_a = -0.92$ (i.e. $pK_b = 14.92$), as measured in aqueous sulfuric acid.[23] The photo-generated acid and NMP are in acid-base equilibrium, as shown in Scheme 1. In this context, the products resulting from the reaction of the superacid and weak base (NMP) is a conjugate acid (NMP-H$^+$) where the acidity of the conjugate acid (NMP-H$^+$) is less than that of the original superacid. The acid-base complex formed between NMP and the PAG-generated acid depolymerizes the PPHA polymer more slowly than the photo-generated free acid due to the higher activation energy required to depolymerize PPHA using a weak acid (NMP-H$^+$). Lactam and lactim tautomers formed with the NMP-H$^+$ protonated additive were previously investigated by FT-IR and shown to be stabilized by a resonance structure created through the organic amide functionality (ie, carbonyl adjacent to amine).[24] The acidity of the conjugate acid created by reaction of photo-generated strong acid and lactam is less than that of other photo-generated acid because of the resonance stabilization of the protonated organic amide.
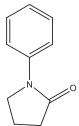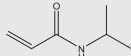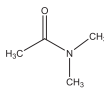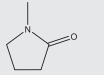

FIGURE 1 Quartz crystal microbalance (QCM) experiments for poly(phthalaldehyde) (PPHA) films containing various loadings of N-methyl-pyrrolidone (NMP). From left to right are the films containing 0%, 0.25%, 0.5%, 1%, 5%, and 10% loadings of NMP, respectively [Colour figure can be viewed at wileyonlinelibrary.com]
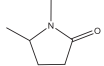

SCHEME 1 Schematic for competitive reaction of H$^+$ and NMP-H$^+$ react with poly(phthalaldehyde) (PPHA) [Colour figure can be viewed at wileyonlinelibrary.com]

The effect of conjugate acid acidity on the PPHA depolymerization delay time was investigated by using various amides and lactams with different basicity. Table 1 shows the chemical structures of additives (ie, amides and lactams) used. Figure 3 shows the UV-Vis spectrum for several of the compounds shown in Table 1 and anthracene, the photosensitizer used to activate the PAG. Anthracene has near-UV absorption from 365 to 390 nm. This is the radiation used to induce electron transfer to the PAG and create the photo-acid. The amide and lactam additives do not interfere with photo-acid creation because they do not absorb UV radiation between 365 to 390 nm, the spectral region where anthracene absorbs. Thus, the time delay in PPHA depolymerization was not due to attenuation of UV radiation in the activation of the PAG.

Figure 4 shows the QCM resistance change after exposure of PPHA films with the five different amides and lactams (Table 1) in the PPHA at a 10:1 base-to-PAG mole ratio. A 10:1 mole ratio of

TABLE 1 Chemical structures of weakly basic additives used for time-delayed photo-depolymerization of PPHA

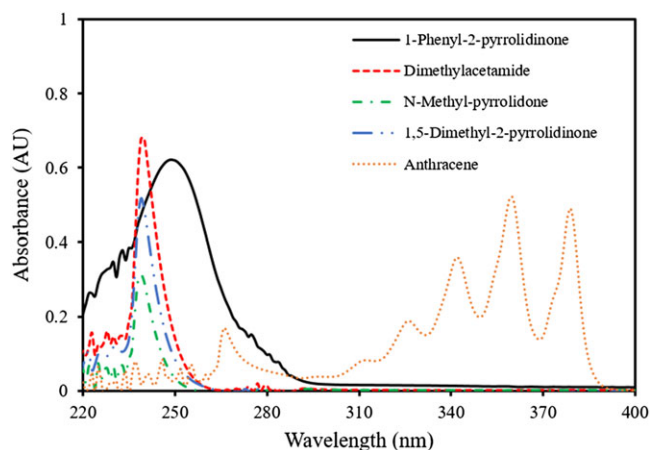| Additive	Chemical Structure
1-Phenyl-2-pyrrolidinone	
N-Isopropylacrylamide	
Dimethylacetamide (DMAc)	
N-methyl-pyrrolidone (NMP)	
1,5-Dimethyl-2-pyrrolidinone	

FIGURE 3 UV-Vis spectrum for anthracene and additive used for time-delayed photo-depolymerization of poly(phthalaldehyde) (PPHA) [Colour figure can be viewed at wileyonlinelibrary.com]
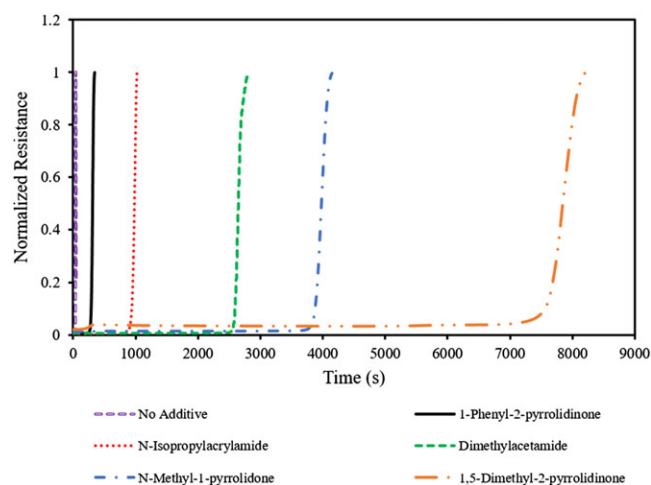

FIGURE 4 Quartz crystal microbalance (QCM) experiments for poly(phthalaldehyde) (PPHA) films containing equal molar of different lactam/amide additives to 5 pphr N-methyl-pyrrolidone (NMP) [Colour figure can be viewed at wileyonlinelibrary.com]

base-to-PAG corresponds to the 5 pphr NMP experiment described above. All samples were exposed to a 730 mJ/cm^2 radiation dose, which is above the threshold needed to activate the anthracene-sensitized PAG. The PPHA depolymerization time increased with the basicity of the amide or lactam additive. As the basicity of the amide/lactam additive increased, the acidity of the resulting conjugate acid decreased, thus increasing the activation energy for the conjugate acid to depolymerize PPHA. It is noted that the shift in PPHA depolymerization time shown in Figure 4 corresponds to the case of excess base with respect to the PAG-generated acid. The PPHA film containing 1-phenyl-2-pyrrolidinone resulted in the most rapid PPHA depolymerization after exposure among five amide or lactams shown in Figure 4.1-Phenyl-2-pyrrolidinone is a weaker base than NMP due to the strong electron withdrawing nature of the aromatic ring on the nitrogen. The weaker base results in the formation of a stronger conjugate acid. Thus, the depolymerization of PPHA occurred faster than the film containing NMP. N-isopropylacrylamide had a slightly longer delay time than 1-phenyl-2-pyrrolidone due to the absence of the strong electron withdrawing phenyl ring, making it a stronger base or better electron pair donor. N-isopropylacrylamide is less effective in delaying depolymerization than DMAc due to its less basic secondary amine compared with the tertiary amine of DMAc in a nonaqueous PPHA film. Moreover, the disappearance of the electron withdrawing acryloyl group in N-isopropylacrylamide also led to higher basicity for the nitrogen atom in DMAc. DMAc has less affinity for H$^+$ (less basic) compared with NMP, making it a weaker base than NMP in an acidic environment.[25] Therefore, the conjugate acid of DMAc is more acidic than NMP-H$^+$, leading to a shorter delay time. The inductive effect of alkyl chain length increases the basicity of the compound (creates a weaker conjugate acid), as can be seen in the longer delay time with 1,5-dimethyl-2-pyrrolidinone compared with NMP. 1,5-Dimethyl-2-pyrrolidone has an additional methyl group resulting in greater electron donating, compared with NMP. This makes 1,5-dimethyl-2-pyrrolidone a stronger base than NMP (ie, weaker conjugate acid),

resulting in longer PPHA depolymerization delay time. It is also noted that strong bases inhibit any PPHA depolymerization, and weaker bases have no effect on PPHA depolymerization time, as described below.

The shift in acidity of the photo-generated acid by use of a lactam or amide additive was confirmed by incorporation of an acid/base color indictor in the PPHA film. Bromothymol blue is magenta at pH < 0 and progressively more yellow as the pH is increased from 0 to 6.[26] Figure 5 shows the color change of PPHA films containing bromothymol blue, PAG, and anthracene. The three samples on the left side of Figure 5 contained 0.5 wt% (with respect to PPHA) bromothymol blue and also contained (left to right): (1) no amide/lactam additive, (2) NMP, and (3) 1,5-dimethyl-2-pyrrolidinone. After UV exposure (picture on the right side of Figure 5), all three samples were liquid due to PPHA depolymerization. The time to depolymerize the PPHA was longer for the samples containing NMP and 1,5-dimethyl-2-pyrrolidinone, as described above. The liquid remnant of film with no additive turned magenta upon UV exposure showing that the bromothymol blue was in its most acidic state. The remnant of the films with NMP and 1,5-dimethyl-2-pyrrolidinone were orange after UV exposure with the NMP appearing more orange than the 1,5-dimethyl-2-pyrrolidinone-containing sample. This test proves that the pH is lower in the sample containing no lactam/amide additive and the conjugate acid formed by reaction of the photo-acid with the NMP or 1,5-dimethyl-2-pyrrolidinone is less acidic. In addition, these tests show that the conjugate acid formed from NMP is more acidic than the formed from 1,5-dimethyl-2-pyrrolidinone. It was also noted that the PPHA films with and without the lactam/amide additive changed color at the same time after UV exposure showing that the additives did not simply delay the creation of an acid, rather, inclusion of the additives with PAG form a weaker acid than PAG by itself.

Bases that were either stronger or weaker than the lactams and amides discussed above had a more extreme effect on depolymerization time than the ones shown in Table 1. Bases weaker than NMP had little or no effect on PPHA depolymerization time because the conjugate acid was effectively not different from the photo-generated acid. For example, bis(2-ethylhexyl) phthalate had no effect on PPHA depolymerization delay time.[22] Bases that were stronger than the ones listed in Table 1, such as 1-octyl-2-pyrrolidone, had extremely long delay times because the conjugate acid was weaker. It is noted that 1-octyl-pyrrolidone is a stronger base because of the electron donating effect of the long alkyl chain attached to the nitrogen atom. Similarly, the addition of tetramethyl-1,6-hexanediamine also resulted in a near-infinite delay time due to its higher basicity. The tertiary

amine structures on each end of the molecule and its long alkyl group in the middle makes it a stronger base than NMP.

The activation energy for the NMP-H$^+$ catalyzed PPHA depolymerization was determined in order to estimate the delay time for PPHA after UV exposure at different temperatures. Figure 6 shows the depolymerization time, as determined by the rise in QCM resistance, for the PAG (5 pphr) and NMP (5 pphr) loaded films at different temperatures. At 28°C, it took 2700 seconds for the film to start depolymerizing. At 33°C and 38°C, the onset of depolymerization was only 1920 and 1200 seconds, respectively. First-order reaction kinetic and an Arrhenius relationship for the rate were used, Equations 2 and 3.

$$k(T) = Aexp\left(-\frac{E_A}{RT}\right). \tag{2}$$

In Equation 2, $k(T)$ is the reaction rate (s^{-1}) at a specific temperature, A is the pre-exponential factor, E_A is the activation energy, R is the gas constant (8.314 J/mol-K), and T is the reaction temperature (K). The equation can be linearized, as shown in Equation 3.

$$\ln(k) = -\frac{E_A}{R}\frac{1}{T} + \ln(A) \tag{3}$$

Figure 7 shows the linearized plot of ln(k) vs 1/T for PPHA films containing 5 pphr NMP and 5 pphr PAG (in addition to anthracene). The value of k(T) for each sample was taken as the inverse of onset
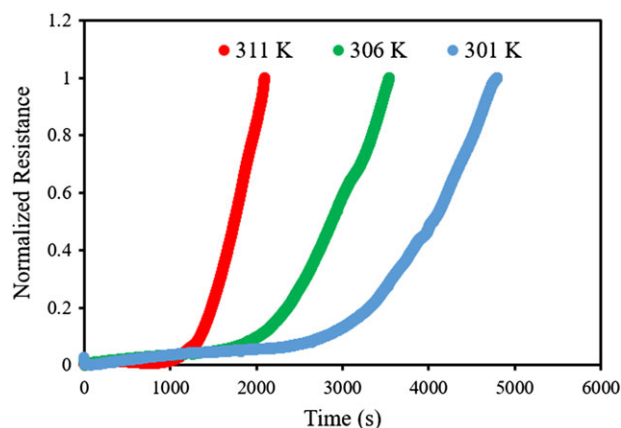
FIGURE 6 Quartz crystal microbalance (QCM) experiments at different temperatures for poly(phthalaldehyde) (PPHA) films containing 5 pphr N-methyl-pyrrolidone (NMP) [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 5 pH test for in situ generated acid strength inside poly(phthalaldehyde) (PPHA) films with and without addition of 5 pphr N-methyl-pyrrolidone (NMP) using bromothymol blue as indicator [Colour figure can be viewed at wileyonlinelibrary.com]
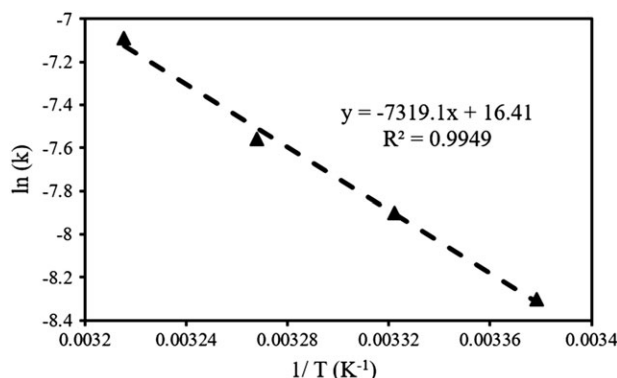
FIGURE 7 Plot of ln(k) vs 1/T for poly(phthalaldehyde) (PPHA) films containing 5 pphr N-methyl-pyrrolidone (NMP). Arrhenius type response was assumed, and linear fitting was used to extrapolate activation energy and pre-exponential factor

time for depolymerization in the QCM. The resulting E_A for the reaction is 61 kJ/mol and A is $1.3*10^7$ s^{-1}.

Depolymerization of PPHA leads to the formation of phthalaldehyde (PHA) monomers, which can be monitored by following the carbonyl peak height in infrared spectroscopy. The carbonyl peak height was monitored for films containing 0, 1, and 5 pphr NMP (ie, mole ratio of NMP-to-PAG of 0:1, 2:1, and 10:1) using the C-F stretch at 1352 cm^{-1} from BMP TFSI as the reference peak for total internal reflectance FT-IR after photo-exposure. Figure 8 shows the absorbance of PHA monomers vs time after PPHA film exposure. The rate of formation of the carbonyl peak, corresponding to PPHA depolymerization (ie, PHA monomer formation), was slower for films containing higher NMP content, which confirms slower PPHA depolymerization rate when more NMP is present in the film.

The mechanical properties of the films containing NMP after exposure were investigated. Figure 9 shows the storage modulus for films with different NMP loadings after photo-exposure. The PAG in the PPHA films was fully exposed to ensure complete PET activation. With the addition of 5 pphr NMP in PPHA, no significant loss of
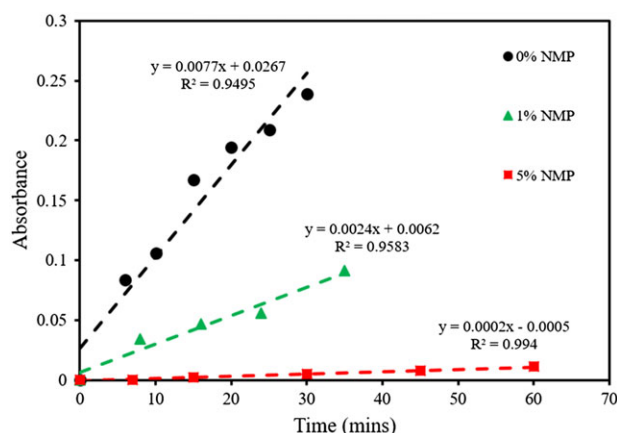

FIGURE 8 Attenuated total reflectance (ATR) absorbance of phthalaldehyde (PHA) monomer peak after periods of time for films containing 0, 1, and 5 pphr N-methyl-pyrrolidone (NMP) [Colour figure can be viewed at wileyonlinelibrary.com]
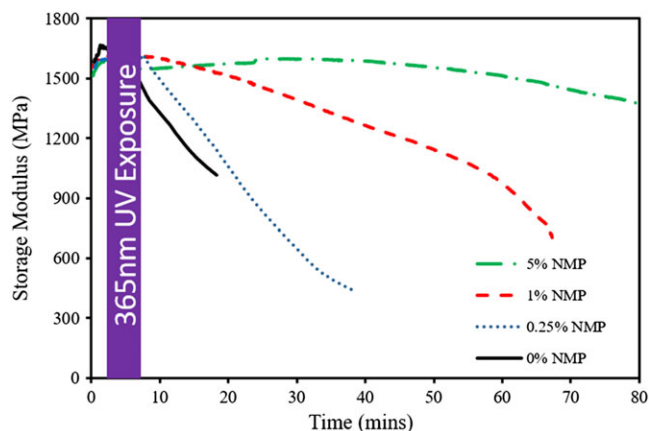

FIGURE 9 In situ dynamic mechanical analysis (DMA) measurement of films storage modulus change over time with different loadings of N-methyl-pyrrolidone (NMP) after UV exposure [Colour figure can be viewed at wileyonlinelibrary.com]

mechanical stiffness before UV exposure was observed. The average storage modulus was 1600 MPa. Upon UV exposure, the immediate mechanical degradation was observed for films without NMP. Films containing higher loadings of NMP maintained mechanical integrity longer. Films with 5 pphr NMP and 5 pphr PAG had similar mechanical stiffness for the first 80 minutes after exposure. The delay time for a significant drop in modulus approximately matched the QCM liquefaction time. Therefore, the addition of 5 pphr NMP helped delay the photoresponse of PAG loaded PPHA films while can still maintaining similar mechanical properties during the transition period.

4 | CONCLUSION

A class of lactam- and amide-based additives was found to effectively delay the photo-depolarization of PAG loaded PPHA phototransient materials. The fundamental cause of the delayed depolymerization was attributed to the formation of a weaker conjugate acid when the lactam/amide additive was present. The delay time was related to the basicity of the additive. By incorporating a suitable amount of lactam or amide additive into the PPHA film (molar excess compared with the photo-generated acid), the mechanical property integrity could be maintained for more than 80 minutes at room temperature without sacrificing the initial mechanical stiffness. The delay time was considerably longer at lower temperature. By tuning the amount of additive in the film, the depolymerization time of PPHA-based transient devices can be tuned to specific mission lifetimes. The time-delayed photo-induced depolymerization of PPHA enables phototransient devices to degrade without the need for postmission photo-exposure. For example, there is interest in single-use delivery vehicles (eg, gliders and parachutes) and electronic devices (eg, small sensors) that can be used once and do not have to be retrieved or cannot be found after use. This work provides a wider operation window for which day-time deployment of transient devices is possible.

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REFERENCES

1. Fu KK, Wang Z, Dai J, Carter M, Hu L. Transient electronics: materials and devices. *Chem Mater*. 2016;28(11):3527-3539. https://doi.org/10.1021/acs.chemmatter.5b04931.

2. Phillips O, Schwartz JM, Engler A, Gourdin G, Kohl PA. Phototriggerable transient electronics: materials and concepts, in: IEEE 67th Electron. Components Technol. Conf., 2017: pp. 772–779. doi:10.1109/ECTC.2017.174.

3. Yin L, Cheng H, Mao S, et al. Dissolvable metals for transient electronics. *Adv Funct Mater*. 2014;24(5):645-658. https://doi.org/10.1002/adfm.201301847.

4. Hwang S, Song J, Huang X, et al. High-performance biodegradable/transient electronics on biodegradable polymers. *Adv Mater*. 2014;26(23):3905-3911. https://doi.org/10.1002/adma.201306050.

5. Jin SH, Shin J, Cho I, et al. Solution-processed single-walled carbon nanotube field effect transistors and bootstrapped inverters for disintegratable, transient electronics. *Appl Phys Lett*. 2014;105(1):013506. https://doi.org/10.1063/1.4885761

6. Acar H, Çınar S, Thunga M, Kessler MR, Hashemi N. Study of physically transient insulating materials as a potential platform for transient electronics and bioelectronics. *Adv Funct Mater*. 2014;24(26):4135-4143. https://doi.org/10.1002/adfm.201304186.

7. Park CW, Kang S, Hernandez HL, et al. Thermally triggered degradation of transient electronic devices. *Adv Mater*. 2015;27(25):3783-3788. https://doi.org/10.1002/adma.201501180.

8. Hernandez HL, Kang S, Lee OP, et al. Triggered transience of metastable poly (phthalaldehyde) for transient electronics. *Adv Mater*. 2014;26(45):7637-7642. https://doi.org/10.1002/adma.201403045.

9. Schwartz JM, Engler A, Phillips O, Lee J, Kohl PA. Determination of ceiling temperature and thermodynamic properties of low ceiling temperature polyaldehydes. *J Polym Sci A Polym Chem*. 2018;56(2):221-228. https://doi.org/10.1002/pola.28888.

10. Kaitz JA, Lee OP, Moore JS. Depolymerizable polymers: preparation, applications, and future outlook. *MRS Commun*. 2018;5(02):191-204. https://doi.org/10.1557/mrc.2015.28.

11. Kaitz JA, Diesendruck CE, Moore S. End group characterization of poly (phthalaldehyde): surprising discovery of a reversible, cationic macrocyclization mechanism. *J Am Chem Soc*. 2013;135(34):12755-12761. https://doi.org/10.1021/ja405628g.

12. Schwartz JM, Phillips O, Engler A, Sutlief A, Lee J, Kohl PA. Stable, high-molecular-weight poly (phthalaldehyde). *J Polym Sci A Polym Chem*. 2017;55(7):1166-1172. https://doi.org/10.1002/pola.28473.

13. Phillips ST, Robbins JS, Dilauro AM, Olah MG. Amplified responses in materials using linear polymers that depolymerize from end-to-end when exposed to specific stimuli. *J Appl Polym Sci*. 2014;131 40992 (19):1-12. https://doi.org/10.1002/app.40992.

14. Dilauro AM, Zhang H, Baker MS, Wong F, Sen A, Phillips ST. Accessibility of responsive end-caps in films composed of stimuli-responsive, depolymerizable poly (phthalaldehydes). *Macromolecules*. 2013;46(18):7257-7265. https://doi.org/10.1021/ma401463e.

15. Tsuda M, Hata M, Nishida RIE, Oikawa S. Acid-catalyzed degradation mechanism of poly (phthalaldehyde): unzipping reaction of chemical. *J Polym Sci A Polym Chem*. 1997;35(1):77-89.

16. Hernandez HL, Lee OP, Casey CMP, et al. Accelerated thermal depolymerization of cyclic polyphthalaldehyde with a polymeric thermoacid generator. *Macromol Rapid Commun*. 2018;39(11):1800046 (1–5). https://doi.org/10.1002/marc.201800046.

17. Tang S, Tang L, Lu X, Liu H. Programmable payload release from transient polymer microcapsules triggered by a specific ion coactivation effect. *J Am Chem Soc*. 2018;140(1):94-97. https://doi.org/10.1021/jacs.7b11022.

18. Schwartz JM, Gourdin G, Phillips O, et al. Cationic polymerization of high-molecular-weight phthalaldehyde-butanal copolymer. *J Appl Polym Sci* 46921. 2018;volume 136, no issue number(volume 136, no issue number2volume 136, no issue number):1-7. https://doi.org/10.1002/app.46921.

19. Jiang J, Phillips O, Engler A, Vong MH, Kohl PA. Photodegradable transient bilayered poly (phthalaldehyde) with improved shelf-life. *Polym Adv Technol*. 2019;1-7. https://doi.org/10.1002/pat.4552

20. Phillips O, Engler A, Schwartz JM, et al. Sunlight photo-depolymerization of transient polymers. *J Appl Polym Sci*. 2019;(136):47141(1-12). https://doi.org/10.1002/APP.47141

21. Lee KM, Phillips O, Engler A, Kohl PA, Rand BP. Phototriggered depolymerization of flexible poly (phthalaldehyde) substrates by integrated organic light-emitting diodes. *ACS Appl Mater Interfaces*. 2018;10(33):28062-28068. https://doi.org/10.1021/acsami.8b08181.

22. Jiang J, Warner M, Phillips O, Engler A, Kohl PA. Tunable transient and mechanical properties of photodegradable poly (phthalaldehyde), In Preparation; 2018.

23. Gold V, Bethell D. *Advances in Physical Organic Chemistry APL*. New York, NY: Academic Press Inc.; 1975.

24. Rad-moghadam K, Ali S, Mousazadeh R, Roudsari ST. N-methyl-2-pyrrolidonium chlorosulfonate: an efficient ionic-liquid catalyst and mild sulfonating agent for one-pot synthesis of δ-sultones. *J Mol Liq*. 2016;218:275-280. https://doi.org/10.1016/j.molliq.2016.02.082

25. Lequestel M, Laurence JY, Lachkar C, Helbert A, Berthelot M. Hydrogen-bond basicity of secondary and tertiary amides, carbamates, ureas and lactams. *J Chem Soc Perkin Trans 2*. 1992;0:2091-2094. https://doi.org/10.1039/P29920002091

26. El Nahhal IM, Zourab SM, Kodeh FS, Qudaih AI. Thin film optical BTB pH sensors using sol–gel method in presence of surfactants. *Int Nano Lett*. 2012;2(16): 1-9. https://doi.org/10.1186/2228-5326-2-16