



Accelerated Thermal Depolymerization of Cyclic Polyphthalaldehyde with a Polymeric Thermoacid Generator

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Thermally triggerable polymer films that degrade at modest temperatures (≈ 85 °C) are created from a blend of cyclic polyphthalaldehyde (cPPA) and a polymeric thermoacid generator, poly(vinyl *tert*-butyl carbonate sulfone) (PVtBCS). PVtBCS depolymerizes when heated, generating acid which initiates the depolymerization of cPPA into volatile byproducts. The mass loss onset for 2 wt% PVtBCS/cPPA is 22 °C lower than the onset for neat cPPA alone in dynamic thermogravimetric analysis experiments. Increased concentrations of PVtBCS increase the rate of depolymerization of cPPA. Raman spectroscopy reveals that the monomer, *o*-phthalaldehyde, is the main depolymerization product of the acid-catalyzed depolymerization of cPPA. The PVtBCS/cPPA blend is a promising material for the design and manufacture of transient electronic packaging and polymers.

1. Introduction

Polyphthalaldehyde is a metastable polymer used in a variety of stimulus-responsive applications including

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photolithography,^[1–4] signal amplification,^[5–7] environmentally triggered microcapsules,^[8] and transient electronics.^[9,10] Cyclic polyphthalaldehyde (cPPA) is of great interest for transient applications because of its rapid depolymerization kinetics and facile polymerization to high molecular weight.^[9–13] cPPA has a low ceiling temperature (T_c) of -42 °C and is thermodynamically unstable at temperatures above T_c .^[14] However, the cationic polymerization results in a kinetically stabilized macrocyclic structure which does not depolymerize at room temperature.^[11,12,15,16] When cPPA is exposed to acid, protonation results in the cleavage of the acetal backbone, which destabilizes

the polymer and is followed by an unzipping reaction along the entire polymer chain.^[1,4,17]

The introduction of cPPA films doped with acid-generating moieties that activate in response to environmental triggers (e.g., temperature) can expand the utility of cPPA in transient applications. Transient electronics, in particular, would benefit from packaging with a lower degradation temperature, faster degradation kinetics, and lower energy requirements for triggering.^[11,12] For these reasons, we investigated the incorporation of a thermoacid generator (TAG) into cPPA films to lower the degradation temperature and accelerate the depolymerization kinetics. **Figure 1** shows our scheme for a thermally triggered transient cPPA film with a TAG additive. Heat activates the TAG, which in turn generates acid that catalyzes the cleavage of the acetal bonds in the polymer backbone. Upon cleavage of the acetal bond, the polymer backbone unzips into the *o*-phthalaldehyde (*o*PA) monomer. At sufficiently high temperatures (>85 °C) the *o*PA monomer will evaporate, leaving <2 wt% residue after thermal triggering. The activation temperature of the TAG is critical because it defines the triggering temperature for initiating the destabilization and depolymerization of cPPA. Herein, we report the acid-generating properties of poly(vinyl *t*-butyl carbonate sulfone) (PVtBCS) and the manufacture of transient polymeric films with lower activation temperatures and faster degradation kinetics than those of neat cPPA and other polymers reported to date.

2. Results and Discussion

PVtBCS was polymerized as reported in literature.^[18] It has been thermally degraded at temperatures as low as 75 °C into

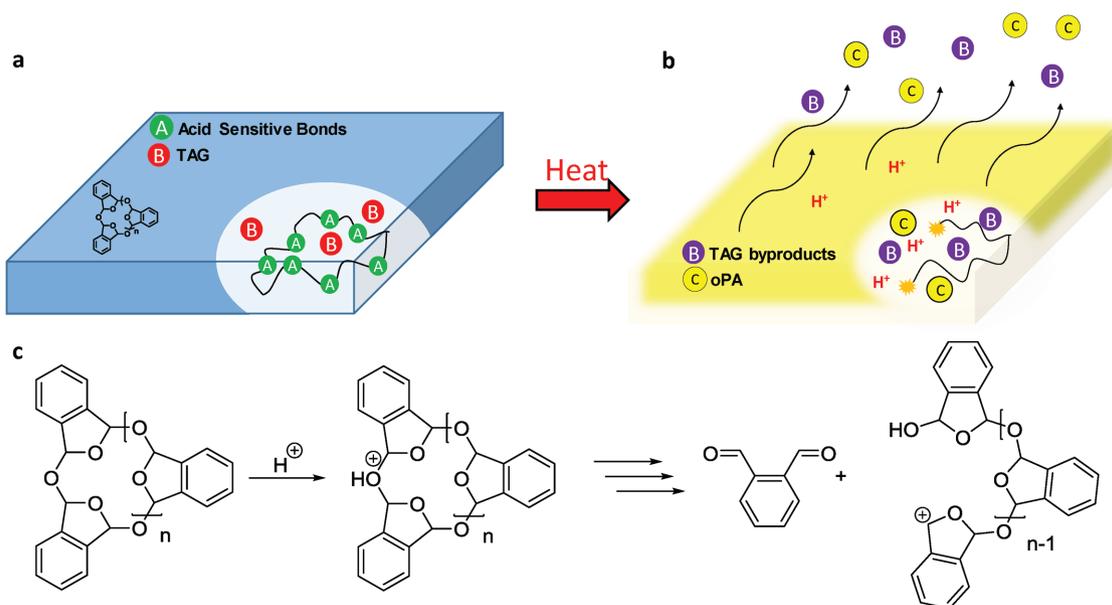


Figure 1. Thermally triggered acid catalyzed cPPA depolymerization. a) Thermoacid generator is blended and dispersed in cPPA film. b) Heating of the film produces acid which subsequently protonates the backbone oxygen in cPPA and cleaves the acetal (acid-sensitive) bonds, ultimately producing oPA monomer. c) Acid catalyzed depolymerization reaction of cPPA.

volatile byproducts via the general reaction scheme shown in **Figure 2a**.^[18] PVtBCS was previously used as a photoresist and a transient packaging material,^[18,19] yet its use as a thermoacid generator has not been reported. While PVtBCS is insoluble in water, it was discovered that heating PVtBCS for 1 h at 90 °C resulted in products that dissolved readily in water. The pH of the PVtBCS and deionized (DI) water solutions was measured after being heated at 90 °C for 1 h at three concentrations of PVtBCS (0.3, 2.1, and 20.4 mg mL⁻¹) (Figure 2b). The pH of the solutions decreased by 0.85 ± 0.17 for each 10x increase of PVtBCS concentration. No pH change was detected after 1 h for control solutions that were not heated. PVtBCS is an excellent TAG for initiating the depolymerization of cPPA because it has a low thermal degradation temperature, evaporates completely after thermal degradation, and readily generates acid when heated in the presence of water. It was expected that residual water in the polymer film would be sufficient to allow for acid generation by the depolymerization of PVtBCS (Figure S1, Supporting Information).

cPPA was synthesized by cationic polymerization as described in literature with $M_n = 120$ kDa and polydispersity index (PDI) = 1.64 (see Table S1, Supporting Information).^[9,11] Blended PVtBCS/cPPA films were solvent cast from solution by first dissolving cPPA in chloroform and then adding 0.5–2.0 wt% PVtBCS. After the PVtBCS dissolved, the solution was poured into a polytetrafluoroethylene mold. Free standing PVtBCS/cPPA polymer films of ≈ 40 μm thicknesses were obtained after complete solvent evaporation (24 h).

The thermal degradation of cPPA, PVtBCS, and PVtBCS/cPPA blends was evaluated by thermogravimetric analysis (TGA). **Figure 3a** shows the results for isothermal TGA experiments on neat cPPA films. TGA results for isothermal experiments of pure oPA from 55 to 105 °C are shown in Figure S2 in the Supporting Information. Without the TAG additive, the cPPA films thermally degraded and evaporated completely (<2 wt%) within 72 min at 95 °C and 175 min at 90 °C, demonstrating a temperature dependent degradation rate that follows an Arrhenius relationship (Figure S3, Supporting Information).

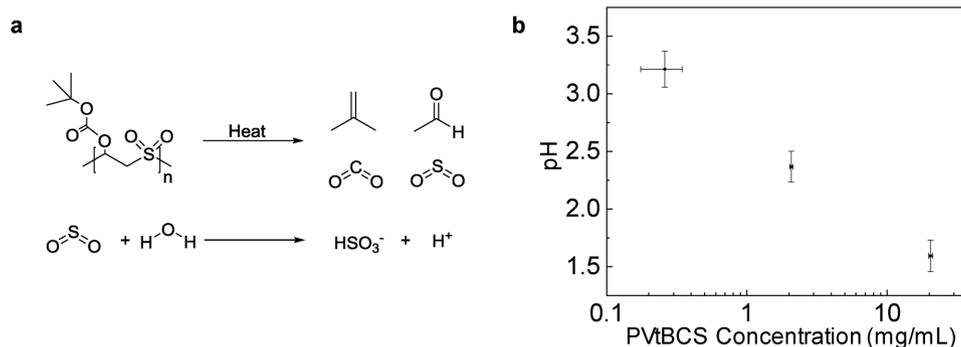


Figure 2. Thermoacid generation with PVtBCS. a) Degradation reaction for PVtBCS upon heating produces several volatile byproducts, including sulfur dioxide (SO₂), which reacts with water to produce acid. b) Solution pH of PVtBCS in DI water (0.3–20.4 mg mL⁻¹) after exposure to 90 °C for 1 h.

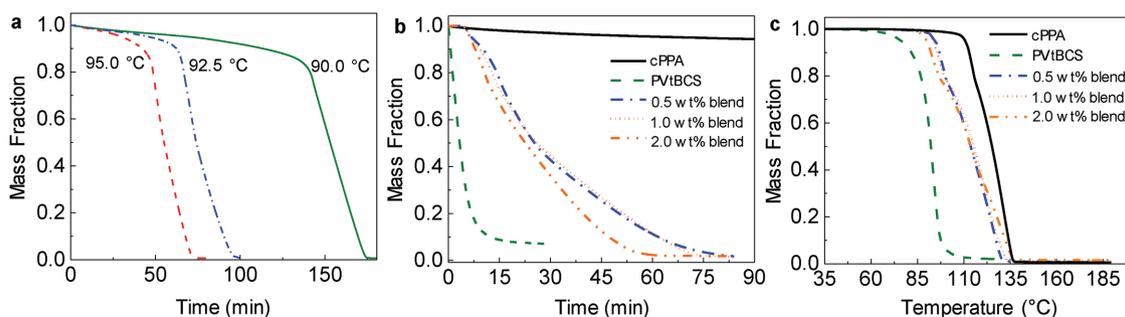


Figure 3. Results of thermogravimetric analysis. a) Isothermal experimental results for neat cPPA at 90, 92.5, and 95 °C. b) 85 °C isothermal experimental results for all materials tested. (Note: Isothermal results are the average response for three replicates.) c) Dynamic TGA scans at 5 °C min⁻¹ for all materials tested.

The addition of PVtBCS into the cPPA film drastically increased the thermal degradation rate at 85 °C (Figure 3b). As expected, neat cPPA degraded slowly with a 6% mass loss within 90 min while, in great contrast, the composite films of PVtBCS/cPPA fully evaporated within that period. Figure S1 in the Supporting Information shows the depolymerization of a 2 wt% PVtBCS/cPPA film, where evaporation of the film is clearly observed.

A series of dynamic TGA experiments were performed to characterize the degradation behavior of the polymer films. The experiments were performed at 5 °C min⁻¹ and the degradation onset temperature of the polymer films was calculated from the intersection of tangent lines fit to the data before and after rapid degradation begins (Figure 3c). Neat cPPA had the highest degradation onset temperature at 110 °C, PVtBCS has the lowest at 85 °C, and the blended films have degradation onset temperatures between these two temperatures. An increase in amount of PVtBCS reduced the degradation onset temperature from 94 °C (0.5 wt%) to 92 °C (1.0 wt%) and finally 88 °C (2.0 wt%). Degradation onset temperatures found by dynamic TGA are dependent on heating rate and are greater than those used in isothermal experiments because of the continuously increasing temperature and lack of incubation time at lower temperatures. Interestingly, an increase in concentration of PVtBCS in the cPPA films resulted in only minor increases of the isothermal degradation rate and decreases of the degradation onset temperature. Since PVtBCS acts by initiating the depolymerization of cPPA and does not accelerate the evaporation rate of oPA, degradation rate measurements by TGA are limited by the evaporation rate. In all TGA experiments (both isothermal and dynamic) for the PVtBCS/cPPA blends, the residual mass of the polymer films was less than 2 wt%.

The molecular weight of neat cPPA, PVtBCS/cPPA blends, and neat PVtBCS films was measured with gel permeation chromatography (GPC) after heating at 85 °C for 15, 30, and 60 min. After heating for the requisite time, the films were dissolved in tetrahydrofuran (THF) and analyzed by GPC. Figure 4a shows the normalized integrated peak areas of the polymer elution peaks for each specimen after heating for the indicated time, which are proportional to the amount of polymer remaining for each specimen. The rate of loss of polymer as heating progresses is highly dependent on the concentration of PVtBCS. While 90% of the neat cPPA remained after 30 min, at 85 °C, 0% of the 2 wt% PVtBCS/cPPA remained under the same conditions. In addition, analysis of the elution

curve in Figure 4b reveals that the significant reduction in polymer concentration is not accompanied by the appearance of lower molecular weight peaks, which would be expected for fragmented polymers, because the depolymerization of cPPA yields small molecular monomers that elude with the solvent. These data are consistent with the previously reported unzipping mechanism in which the polymer chains of cPPA unzip to monomer upon cleavage.^[11,15]

Analysis of the molecular weight degradation reveals a significant disparity in transience time between GPC and TGA measurements. It is quite evident, by GPC, that the depolymerization rates of PVtBCS/cPPA films are highly dependent on the wt% of PVtBCS. For example, the 2 wt% PVtBCS/cPPA films depolymerize within 15 min, but the depolymerization of 0.5 wt% PVtBCS/cPPA films takes over 30 min. These data suggest that TGA measurements are dominated by oPA evaporation after PVtBCS/cPPA depolymerization and not representative of the depolymerization reaction itself. For transience applications, both methods provide valuable information. The measurement of evaporative rate (TGA) provides a more accurate measure of the time required for the polymer to vanish. Conversely, measuring the molecular weight (GPC) provides a better measure of how long the material retains its polymer character and mechanical integrity.

The mechanical integrity of 2 wt% PVtBCS/cPPA and neat cPPA films was measured by dynamic mechanical analysis during a temperature ramp from 35 to 85 °C at 10 °C min⁻¹ and an isothermal hold at 85 °C (Figure S8, Supporting Information). At 85 °C the neat cPPA film had a stable response for 55 min with a slight increase in the storage modulus due to loss of plasticizing solvent and ultimately failed because of crack formation. In stark contrast, the 2 wt% PVtBCS/cPPA film completely failed within 1.5 min at 85 °C and a yellow crystalline residue, characteristic of oPA, was recovered after the experiment, indicating depolymerization of the cPPA. Rapid loss of mechanical properties for 2 wt% PVtBCS/cPPA at 85 °C is consistent with the rapid depolymerization measured by GPC, suggesting that the depolymerization kinetics measured by GPC are representative of the lifetime for the mechanical integrity of cPPA.

The 2 wt% PVtBCS/cPPA blended film and its degradation products were characterized by Raman spectroscopy (Figure 4C). The Raman spectrum of the volatile products is characteristic of oPA, confirming the depolymerization of cPPA into gaseous

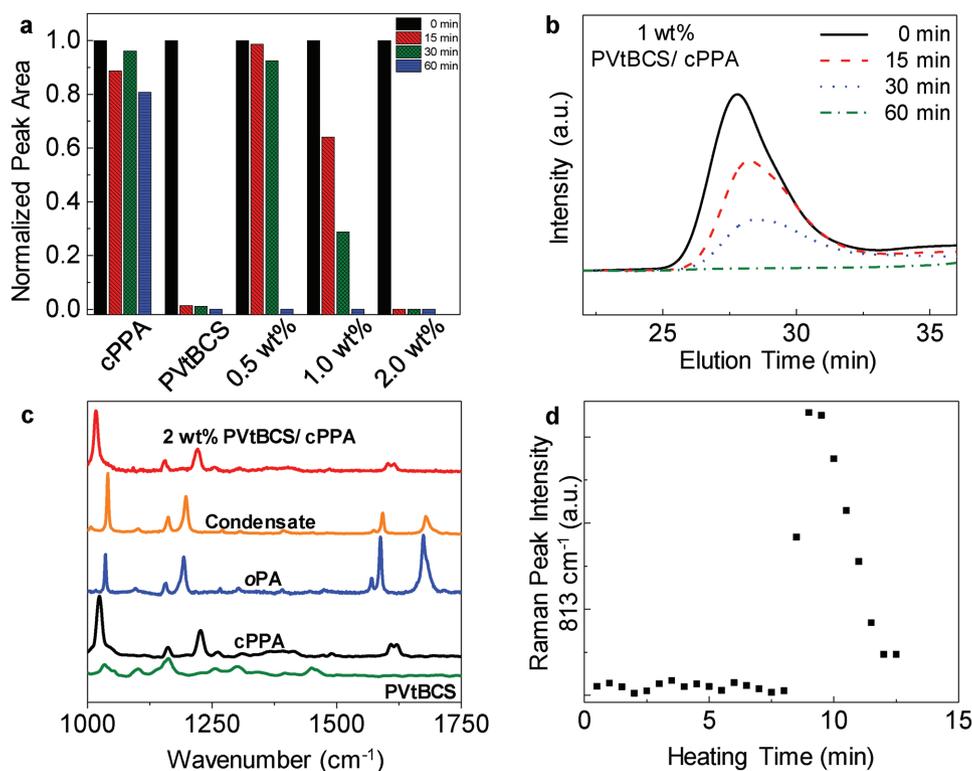


Figure 4. Chemical analysis of acid-catalyzed cPPA depolymerization. a) Normalized GPC peak area versus time under isothermal conditions at 85 °C. Peak areas are normalized by the area of the polymer peak before heating. b) GPC elution curves for 1 wt% PVtBCS/cPPA under isothermal conditions at 85 °C. (Note: GPC results for other materials can be found in Figures S4–S7, Supporting Information.) c) Raman spectra of the condensed evaporative products from the depolymerization of 2 wt% PVtBCS/cPPA at 85 °C for 15 min. The condensate shows a clear signature of oPA product. d) Time evolution of oPA characteristic Raman peak (813 cm⁻¹) for monitoring the onset and completion of depolymerization of 2 wt% PVtBCS/cPPA at 85 °C.

oPA. This is consistent with several prior reports of cPPA depolymerizing to oPA in quantitative yields.^[9–11,14,15,20] No significant differences were detected between the Raman spectra of cPPA and PVtBCS/cPPA films, likely due to the low concentration of PVtBCS in the film. More importantly, the addition of the PVtBCS did not depolymerize cPPA before heating as confirmed by the absence of oPA peaks. Characterization of the nonvolatile residual products was unsuccessful due to the presence of background fluorescence and an absence of diagnostic peaks (Figure S9, Supporting Information). It may be possible that the depolymerization products from PVtBCS are reacting with the oPA to form fluorescent and nonvolatile byproducts.^[21]

Raman spectroscopy was performed at 85 °C on a continuous basis to detect the onset of depolymerization for 2 wt% PVtBCS/cPPA blended films. The onset of depolymerization was detected by the appearance of the oPA Raman peak at 813 cm⁻¹. The peak was monitored to track the formation of oPA from the depolymerization of cPPA until complete evaporation of oPA (Figure 4d). The onset of depolymerization occurred rapidly (\approx 8 min) at 85 °C and evaporation was complete by 12 min.

3. Conclusions

A thermally depolymerizable polymer blend made from the thermoacid generator PVtBCS and cPPA was developed.

PVtBCS depolymerizes when heated at 85 °C to form acidic and volatile byproducts. PVtBCS was blended with cPPA, an acid sensitive polymer with a low ceiling temperature (–42 °C), at 0.5, 1.0, and 2.0 wt% to drastically increase the thermal depolymerization rate. PVtBCS/cPPA films depolymerize into products that evaporate within 80 min at 85 °C leaving <2 wt% of residue. Gel permeation chromatography measurements reveal that an increase in the thermoacid generator concentration greatly increases the rate of depolymerization for the PVtBCS/cPPA blended films with full depolymerization of 2 wt% PVtBCS/cPPA films within 15 min. Dynamic mechanical analysis confirms that all mechanical integrity for 2 wt% PVtBCS/cPPA films is rapidly lost at 85 °C.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

ceiling temperature, metastable polymers, polyphthalaldehyde, transient electronics, triggered depolymerization

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