Decomposition of poly(propylene carbonate) with UV sensitive iodonium salts

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The decomposition characteristics of poly(propylene carbonate) containing a photoacid generator have been studied. The influence of casting solvent, photoacid concentration and type, UV exposure dose, substrate surface, and ambient gas were included in this study. Dynamic thermogravimetric analysis was used to analyze the decomposition characteristics. Kinetic parameters were extracted using the Kissinger method and the Coats–Redfern method. Fourier Transform Infrared Spectroscopy was used to analyze effects of casting solvent. The highest thermal stability was found to occur in high molecular weight, high-purity poly(propylene carbonate) samples. Cyclohexanone and trichloroethylene solvents were found to increase the thermal stability. Photoacid generators based on diphenyliodonium salts lowered the onset decomposition temperature and activation energy.

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1. Introduction

Poly(propylene carbonate) (PPC) is a soft aliphatic thermoplastic formed by the copolymerization of propylene oxide and carbon dioxide, as first reported by Inoue et al [1]. The glass transition temperature of PPC is near room temperature \( T_g \approx 25 \{\text{C} \} \text{ to } 45 \{\text{C} \} \) [2,3] and depends on molecular weight and backbone structural arrangement [4]. PPC has a relatively low decomposition temperature, with the five percent mass loss \( T_{5\%} \) widely reported to be approximately 180 °C [5]. This has limited its commercial applications as a replacement for conventional plastics but makes it attractive as a sacrificial material. Numerous efforts have been made to increase the thermal stability and mechanical properties of PPC [3.5–14]. Thermal decomposition in inert environments proceeds via unzipping into cyclic propylene carbonate (4-methyl-1,3-dioxolan-2-one) at lower temperatures (ca. 180 °C) followed by random chain scission at higher temperatures (ca. 250 °C) [15]. The decomposition mechanism depends on molecular weight [3], temperature, ambient gaseous environment [16,17], and additives [15]. Techniques to increase the thermal stability have been reported [5,6,11–13]. Methods to lower the decomposition temperature for use as a sacrificial material has also been reported [18–21].

The low decomposition temperature and volatile products make PPC an ideal sacrificial material for microelectronic applications which are constrained to temperatures between ca. 100 °C and 250 °C. This is well within the stability range of epoxy-based products. Gaseous cavities can be created by forming spatial PPC patterns followed by overcoating with a dielectric material. The PPC decomposition products can diffuse through the overcoat leaving an embedded gas cavity within the overcoat whose shape is determined by the original shape of the PPC pattern. Embedded cavities are potentially valuable in the packaging of microchips and microelectromechanical systems (MEMS).

Air cavities or other gas-filled spaces are valuable in a variety of semiconductor manufacturing and microchip packaging technologies including microfluidic channels for microprocessor cooling [22], lab-on-a-chip applications [23], air-insulated electrical signal lines [24], and vacuum packaging of MEMS resonators [25]. Air cavities surrounding a core waveguide in fiber optical cables have shown low losses [26]. Similar low losses were demonstrated in porous fiber structures with subwavelength holes [27]. Thermally decomposed PPC loaded with aluminum nitride particles has been studied for use in tape automated bonding [17,28].

A variety of polycarbonates including PPC [18–20] and polynorbornene formulations [29], have been previously studied for use as sacrificial materials. Air cavities in a variety of dimensions have been reported using polynorbornene [24] and SiO2 overcoats [30]. A small quantity of a photoacid generator (PAG), which creates a catalytic amount of an acid upon exposure to ultraviolet (UV) radiation, reduces the decomposition temperature, enabling direct
photopatterning of the material without the need for a hardmask [19]. Small amounts of residue were observed in the cavities following decomposition [19,24,25]. Improved decomposition was reported by using a combination of PAGs generating acids with different vapor pressures [18].

In this work, the thermal decomposition behavior of solvent-cast PPC is evaluated using dynamic thermogravimetric analysis (DTGA) and compared with pure species decomposition properties. PPC from two sources with different molecular weights and different impurities were compared. The effect of nitrogen and air environments in the PPC decomposition chamber was studied. The influence of casting solvent on decomposition behavior has been evaluated using six polar solvents. Acid catalyzed decomposition of the PPC film was evaluated using triflic acid and UV sensitive photoacid generators (PAGs).

The thermal decomposition data as a function of temperature and time was analyzed using Flynn–Wall–Ozawa and Coats–Redfern methods to extract values for the activation energy and pre-exponential factor. These kinetic parameters are important for predictive modeling of air cavity formation and designing controlled decomposition recipes [30]. With a sufficient amount of photoacid loading, decomposition proceeds at reduced temperatures via chain decomposition recipes [30]. With a sufficient amount of photoacid loading, decomposition proceeds at reduced temperatures via chain unzipping. The acid is created upon ultraviolet (UV) irradiation of the PAG. Without irradiation of the PAG or samples without acid loading, the PPC decomposed at temperatures above 180 °C. Residue from the non-volatile component of the PAG salts was found to be proportional to the initial PAG concentration in the PPC. Low concentrations of PAG showed anomalously slower decomposition rates after UV exposure and resulting in higher final decomposition temperatures due to foaming of the sample during decomposition.

2. Background

Poly(propylene carbonate) is synthesized via copolymerization of propylene oxide and carbon dioxide in the presence of a catalyst at elevated pressures. The primary backbone component is propylene carbonate as shown in Fig. 1. Impurities, especially ether linkages are present in the backbone as an undesired by-product of the synthesis, at typically less than 10 mol percent.

Molecular weights are typically on the order of $10^4$–$10^5$ g/mol [31] and yield of the alternating copolymer is highly dependent on catalyst and cocatalyst selection. Increased polyether content depresses the glass transition temperature by as much as 30 °C while the thermal stability increases with increasing number of ether linkages.

Depending on polymerization conditions, catalyst, and cocatalyst, the local structure of backbone components varies, affecting thermal stability and mechanical properties. Ring-opening of propylene oxide may occur at either the α or β-positions. The α-site mechanism opens the bond between the oxygen atom and the center carbon (CH group) of the propylene unit whereas the β-site mechanism opens the bond between the oxygen and the CH$_2$ group in the ring. Thus, the methyl group can be on the alpha or beta carbon with respect to the oxygen in the ring-opened propylene oxide and polymer structure depends on which ring-opening position dominates. The regiostructure of PPC can exist in three different configurations as shown in Fig. 2. These configurations have been termed head-to-head (HH), tail-to-tail (TT), and head-to-tail (HT) configurations. An important feature of the HH and TT configurations is they coexist with each other in alternating units or with chains of head-to-tail configurations. Poly(propylene carbonate) cannot exist exclusively of HH or TT configurations because they must be coupled with another configuration. PPC made from units in the head-to-tail arrangement, however, can exist solely in this configuration.

Choice of catalyst is important in order to minimize the ether linkages, maximize yield of the alternating copolymer, and residual catalyst may influence decomposition. Common catalysts used in PPC polymerization include heterogeneous zinc compounds, aluminum porphyrins, Cu(salen), Cr(salen). High copolymer yield results in fewer ether linkages but increases susceptibility to decomposition via chain unzipping. The unzipping mechanism occurs in highly regular PPC because terminal alcohols allow the cyclic monomer to form and detach from the backbone. Because the endgroup remains terminated with an alcohol, the cyclization continues and the backbone of the polymer unzips.

Molecular weights as low as 13,000 g/mol [32] and as high as 144,600 g/mol [15] have been synthesized in the presence of zinc glutarate, zinc-cobalt and zinc–nickel complexes [33]. Higher molecular weights are difficult to synthesize due to spontaneous depolymerization into the more thermodynamically stable cyclic propylene carbonate, especially at elevated temperatures [4], although 176,000 g/mol PPC was reported using allyl glycidyl ether as a cross-linker [34]. Catalyst and cocatalyst determine regiostructure of high molecular weight PPC with cationic initiators opening propylene oxide at both α- and β-positions, while anionic initiators, coordination initiators, and Lewis base cocatalysts open the epoxide ring primarily in the α-position. Ring-opening at the α-position gives a more regular structure with an increased number of HT linkages and reduced ether linkages [4,35,36]. Copolymer yield can be improved by vacuum activation of the catalyst prior to polymerization [3].

Residual catalyst may impact thermal stability since removal of catalyst has been suggested to increase thermal stability by inhibiting chain scission [15]. The choice of solvent for use in catalyst recovery may also influence thermal stability. Removal of catalyst after polymerization is performed by precipitation in chlorinated solvents, typically chloroform [7,8,15,37] or dichloromethane [4,34,35,38,39] and quenching with dilute hydrochloric acid in.

Fig. 1. General structure of poly(propylene carbonate). Polyether content is typically less than 10 mol%, corresponding to $x \approx 0.90$.

Fig. 2. Backbone structure configurations of PPC. It should be noted that Head-to-Head and Tail-to-Tail configurations are effectively the same monomer unit and cannot exist in exclusively one configuration. The Head-to-Tail configuration can exist solely as members of these other configurations.
methylene. Acetone has also been reported for purification/catalyst precipitation [14]. Other studies have suggested residual catalyst does not alter thermal stability.

The mechanical properties of PPC were not evaluated here but are important for sacrificial material patterning via photo-patterning and imprint lithography. Small weight percentages of PAGs used in this study and residual solvents are not expected to change mechanical properties significantly from the bulk. However, these properties will be influenced by polyether content, molecular weight, and region-structure. Chemical foaming in the presence of low quantities of PAG.

The backbone structure and influence of additives have been the subject of numerous other studies [2,6–9,40–47] and depend on polyether content [2,43] and backbone structure [4]. Glass transition temperatures of the alternating copolymer are between 35 °C and 40 °C, but are as low as 8 °C with greater polyether content. Increasing molecular weight with more HT units increases the glass transition temperature to 45 °C and improves tensile and compressive strength [4]. Tensile strength of the alternating copolymer is reported in the range of 22 MPa [6,10,48] and 32 MPa [7,8,43], but may be as low as 8 MPa [44,46,49]. The influence of small quantities of additives (less than 10 wt%) on mechanical properties has not been widely reported. Weight percentages of octadecanoic acid of 0.28–2.27% showed a slight increase in glass transition temperature. Other hydrogen-bonded complexes including clay nanoparticles reported an increase in shear modulus and viscosity at 2.5 wt% loading [13]. Glass transition temperature, tensile strength, and Young’s modulus increased at loadings between 1 wt% and 10 wt% [6,46]. Chemical foaming [42,50] will change mechanical properties from that of the bulk polymer due to porosity. Blends with poly(butylene succinate) [51], poly(3-hydroxybutyrate) [47], poly(lactic acid) [52], and glycerol stearch [49] increased storage modulus and tensile strength linearly with additive concentration. Terpolymerization with bisphenol-A [48], cyclohexene carbonate [2,43], (2-naphthoxy)methyl oxirane [8], and N-(2,3-epoxyl-propyl)carbazole [7] raised tensile strength and glass transition temperature while maleic anhydride decreased tensile strength.

The low degradation temperature of PPC has also limited broad commercial adoption. The onset of degradation is widely reported as the temperature where 5 percent weight loss occurs (T\text{d, 5%}) and is highly dependent on heating rate. Isothermal decomposition and slow heating rates (<5 °C/min) were used to obtain a degradation temperature as low as 180 °C, whereas studies using faster heating rates (10 °C/min to 25 °C/min) reported degradation temperatures above 240 °C [3,5,6,8,10,12,13,15,19,20,32,35,41,43,44,46,49,51,53]. Higher decomposition temperature reported using faster heating rates is an artifact of the measurement technique. Isothermal degradation in these studies likely occurs near 180 °C.

The decomposition mechanism of the backbone depends on decomposition environment, molecular weight of the polymer, number of ether linkages, and backbone regiostructure. In oxygenated atmospheres, decomposition primarily occurs via chain scission into combustion products. In a nitrogen environment, the backbone primarily decomposes via chain unzipping from the ends of the polymer chain or unzipping following chain scission [16,17,28]. Higher molecular weight structures decompose almost exclusively via the chain unzipping mechanism from terminal –OH groups [3,16]. Ether linkages inhibit chain unzipping and result in larger molecular weight decomposition fragments [19]. HT structured backbones most easily undergo decomposition via chain unzipping due to the highly regular structure. Although it is unclear which mechanism is dominant, unzipping into cyclic propylene carbonate can occur via either carbonate backbiting or alkoxide backbiting [44]. The chain unzipping mechanisms of highly regular head-to-tail PPC is illustrated in Fig. 3. In the alkoxide backbiting mechanism, a strong nucleophile attacks the carbonyl atom, as shown from the left side (a) of Fig. 3. In the carbonate backbiting mechanism, a weak nucleophile attacks an electrophilic carbon as shown on the right side (b) of Fig. 3. Density functional theory (DFT) simulations suggest carbonate backbiting (b) has a lower activation energy [54]. HH and TT regiostructures inhibit this mechanism but may undergo sidegroup rearrangement to allow unzipping to proceed, albeit at a slightly lower rate.

Techniques to raise the decomposition temperature of PPC include blending with inorganic and organic filler materials such as calcium carbonate [9,50], starch [49,55], other polymers [14,47,52], montmorillonite [46,56] and organoclays [13], polymerizing with additional backbone components [2,7,8,10,39,43,57], and end-capping of carbonate groups [5,12]. The low degradation temperature has also been exploited for use in microelectronic cooling and packaging applications [19,20,24,25,58]. Acid catalyzed degradation lowered the decomposition temperature using UV sensitive PAG [18,19,21]. Degradation in soil and buffer solution has also been reported [16].

Techniques to improve thermal stability via the addition of fillers have been modestly successful. Blends with calcium carbonate particles showed improved thermal stability with large particles, but nanoparticles actually lowered the thermal decomposition temperature. Blends of PPC with dried starch had slightly depressed decomposition onset temperatures but further decomposition was not observed until higher temperatures [49]. Residue in these blends is attributable to the filler particles.

Blending PPC with other polymers has also been attempted to improve the thermal stability. Physical blends with poly(butylene succinate) (PBS), poly(3-hydroxybutyrate), and poly(lactic acid) with carbon black elevated the onset decomposition temperature by about 50 °C at heating rates of 20 °C/min. The thermal decomposition profile for PBS blends was segmented with an initial decomposition proportional to the weight percentage of PPC and the secondary decomposition due to the PBS content [51].

End-capping of the terminal hydroxyl groups has been described as a way to increase thermal stability to inhibit the unzipping mechanism. Small quantities of maleic anhydride, benzyol chloride, ethyl silicate, acetic anhydride, and phosphorus oxychloride were used to delay the onset of decomposition [5]. End-capping with maleic anhydride has been evaluated as a function of backbone content relative to propylene oxide [10] and blended with ethyl cellulose [53].

Hydrogen bonding between polymer blends and additives may also stabilize PPC against thermal decomposition. The addition of octadecanoic acid at weight fractions between 0.28 wt% and 2.17 wt % demonstrated improved thermal stability [12]. Calcium stearate, a derivative of octadecanoic acid, also stabilized PPC by coordinating with the metal ion [11]. Hydrogen bonding has also been observed in polymer blends [14]. Low weight fractions of organic clays capable of hydrogen bonding dispersed in PPC increased thermal stability [6,13]. Additionally, end-capping agents may be...
hydrolyzed in the presence of water to form hydrogen bonding structures which augment thermal stability in addition to suppression of the unzipping mechanism [5].

Small quantities of residue remain from the decomposed photosensitive PPC formulations. X-ray photoelectron spectroscopy (XPS) results indicated the residue contained primarily fragments of the PAG [59]. Energy dispersive x-ray fluorescence (EDS) analysis confirmed the primary residue resulted from the PAG [25]. The residue may also contain higher molecular weight products from decomposition such as alkenes and ketones as observed by mass spectroscopy [19]. These products may result from dehydrogenation in the presence of acid or due to irregularities in the backbone.

Dynamic thermogravimetric analysis (DTGA) is used to assess the thermal stability of PPC by measuring mass loss as a function of temperature at a fixed heating rate. In prior studies, heating rates have been as low as 5 °C/min and as high as 30 °C/min. Rapid heating rates are a poor indicator of overall film stability. Slow heating rates enable clearer differentiation of decomposition characteristics.

Thermal decomposition of solids as a function of time is described using the Arrhenius equation multiplied by an expression for the fractional decomposition, α, Equation (1).

\[
\frac{d\alpha}{dt} = A \cdot e^{E_{d}/RT} \cdot f(\alpha) \tag{1}
\]

where \( A \) is the pre-exponential constant, \( E_d \) is the energy of activation, \( t \) is time, \( R \) is the ideal gas constant, and \( f(\alpha) \) can be expressed by a variety of power law or logarithmic functions. Under dynamic conditions where the sample temperature is being linearly increased at a heating rate \( \dot{\gamma} \), Eq. (1) can be expressed as a function of temperature as shown in Equation (2).

\[
\frac{d\alpha}{dT} = \frac{A}{\dot{\gamma}} \cdot e^{E_{d}/RT} \cdot f(\alpha) \tag{2}
\]

The integrated quantity, \( g(\alpha) \) is shown in Equation (3).

\[
g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{T}{\dot{\gamma}} \cdot \frac{A}{e^{E_{d}/RT}} \tag{3}
\]

Numerous expressions with associated physical mechanisms have been proposed to describe thermal decomposition curves with both sigmoidal and deceleration functions. These functions can be used to describe effects of boundary conditions, diffusion limitations, and multiple nucleation sites on an individual particle [60], which are not as relevant here.

The ASTM standard technique for dynamic thermal decomposition analysis uses the method of Kissinger, which adopts Eq. (3) and defines \( f(\alpha) = (1 - \alpha)^n \), where \( n \) is the reaction order. Thus, Eq. (3) can be rearranged into Equation (4).

Fig. 4. Photoacid generator structures; a) 4-methylphenyl[4-(1-methylethyl)phenyl] tetraakis(pentafluorophenyl) borate (Rhodorsil-FABA) b) (4-tert-butylphenyl)iodonium tris (perfluoromethyl sulfonyl) methide (3M-Methide).

Fig. 5. QPAC PPC in (a) air and (c) nitrogen; Novomer PPC (\( M_w = 90,000; P_D = 1.5 \)) in (b) air and (d) nitrogen.
Table 1
Pure species kinetic parameters calculated using Coats–Redfern technique for Air and Nitrogen environments.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_a) (kJ/mol)</th>
<th>(A) (s(^{-1}))</th>
<th>(R^2)</th>
<th>(\alpha_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>QPAC – Air</td>
<td>119</td>
<td>7.22e5</td>
<td>0.9459</td>
<td>0.58</td>
</tr>
<tr>
<td>QPAC – Nitrogen</td>
<td>147</td>
<td>1.70e15</td>
<td>0.9883</td>
<td>0.41</td>
</tr>
<tr>
<td>Novomer – Air</td>
<td>120</td>
<td>3.21e5</td>
<td>0.9713</td>
<td>0.57</td>
</tr>
<tr>
<td>Novomer – Nitrogen</td>
<td>126</td>
<td>2.07e5</td>
<td>0.9569</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Thus, by plotting \(\ln \left[ -\ln(1 - \alpha)/T_{\text{max}}^2 \right] \) vs. \(-1/T\), the slope and intercept can be used to determine the activation energy and pre-exponential factor. Alternatively, kinetic parameters for higher order reactions can be determined by fitting for the best regression value at various powers. First order (linear) regression of decomposition data is indicative of single reaction mechanisms, whereas non-linear plots are indicative of complex or competing reactions [5].

3. Experimental

3.1. Film preparation

Poly(propylene carbonate) was obtained from QPac-Aldrich and Novomer Inc. and studied as received without purification. Solutions of polymer, PAG, and solvent were mixed for one week on a bottle roller. The films were spin-cast to 10 \(\mu\)m thickness on glass slides. The PPC film was soft baked at 110 °C for 20 min to evaporate the solvent. Following solvent volatilization, film samples were removed from the glass slide using a razor blade and tweezers before being loaded into TGA weighing pans.

Films were also decomposed under glass on a hotplate to observe film decomposition with various PAG loadings. The samples were placed under glass and the chamber was purged for 1 h with nitrogen. The hotplate temperature was increased at a rate of 1 °C/min to a final temperature of 220 °C. This provided a supplement to quantitative results and allowed for better understanding of the decomposition mechanism for different photoacid concentrations.

3.2. Thermogravimetric analysis (TGA)

DTGA was performed using a Seiko TG/DTA 320 system. The TGA scale was re-zeroed for each weighing tin before every experiment.

![Fig. 6. QPAC PPC dissolved in g-butyrolactone decomposed in a nitrogen purged environment at (a) 0.5 °C/min, (b) 2 °C/min, and (c) 10 °C/min.](image-url)
Samples between 10 mg and 15 mg were loaded onto the microbalance and the system purged for 30 min with nitrogen at a flow rate of 100 mL/min. The thin PPC films were cut into large sections (ca. 10 cm²) and folded several times to the size of the TGA weighing tin in order to achieve the large masses (10–15 mg) required for accurate weight loss measurement. Oxygen content for nitrogen purged decomposition was below 100 ppm. Samples were decomposed at heating rates of 0.5 °C/min, 2 °C/min, and 10 °C/min. The temperature was increased from 30 °C to 300 °C and data were sampled at a frequency of 0.2 Hz for most studies. After decomposition, residue in the pan was observed qualitatively.

3.3. Solvent comparison

PPC was dissolved in solvent to allow spincoating of thin films on a substrate. The primary solvent used in this study was γ-butyrolactone (GBL). Additional polar solvents including acetone, anisole, cyclohexanone, trichloroethylene, and dichloromethane...
were analyzed in this study. All solvents were obtained from Sigma-Aldrich. Samples dissolved in GBL were analyzed at heating rates of 0.5 °C/min, 2 °C/min, and 10 °C/min. Experiments using different solvents were heated at 0.5 °C/min for clearer differentiation of decomposition effects.

3.4. PPC films with photoacid generator (PAG)

Acid catalyzed decomposition of polycarbonates has previously been reported for photopatterning of sacrificial materials [19]. In this study, triflic acid catalyzed decomposition was compared with two photoacid generators which generate equivalent strength super-acids (i.e. entirely dissociated). The PAGs investigated in this study were the iodonium salts 4-methylphenyl [4-(1-methylethyl)phenyl] tetrakis(pentafluorophenyl) borate (referred to hereafter as Rhodorsil-FABA) and bis(4-tert-butylphenyl)iodonium tris(perfluoromethyl sulfonyl) methide (referred to hereafter as 3M-Methide). These photoacids were investigated because they had been previously identified as the most effective for acid catalyzed decomposition of PPC [59]. The structure of the Rhodorsil-FABA PAG is illustrated in Fig. 4a. The structure of the Methide PAG is illustrated in Fig. 4b.

Proper comparison of the PAGs requires equivalent molar acid content after UV exposure. The molecular weight of the Rhodorsil-FABA is 1016.26 g/mol and the molecular weight of the 3M-Methide is 804 g/mol. More importantly, the weight difference is primarily due to the structure of the anion, which correlates to the vapor pressure of the conjugate acid formed upon exposure to UV light. Tetrakis-pentafluorophenyl boric acid (generated by Rhodorsil-FABA) has essentially no vapor pressure at room temperature, whereas triflic acid (generated by 3M-Methide) has a vapor pressure of 8 torr at 25 °C. Consequently, it is expected the Rhodorsil-FABA PAG will remain present in ever increasing concentration during decomposition, while the 3M-Methide PAG will decrease in concentration as the reaction proceeds due to evaporation.

3.5. Fourier transform infrared (FTIR) spectroscopy characterization

Fourier Transform Infrared (FTIR) spectroscopy was used in an effort to identify influences of casting solvent and photoacid generators. FTIR data were collected using a Nicolet Magna IR 560 spectrometer. Data were collected in transmission mode in a nitrogen purged chamber under a nitrogen flowrate of 50 mL/min with 2 cm⁻¹ resolution and averaged over 512 scans. Films were cast on a KBr disk at a thickness of approximately 1 um. Background scans of the KBr disk were performed prior to data collection for each polymer film.

4. Results

4.1. Bulk polymer comparison (no solvent)

QPac and Novomer PPC were used as-received and decomposed in nitrogen and air environments. The heating rate for all samples was 2 °C/min. The TGA curves are shown in Fig. 5. Kinetic parameters of activation energy (Ea) and pre-exponential factor (A) were calculated for a first order reaction using the Coats–Redfern method. These results, including the linear regression correlation value (R²) and the decomposition completion fraction at the maximum weight loss rate (∑max), are listed in Table 1.

4.2. TGAs of cast films in γ-butyrolactone and M.W. comparison

QPac and Novomer PPC dissolved in γ-butyrolactone with no additional additives were spin-coated as films 10 μm thick and the solvent was evaporated by softbaking on a hotplate at 100 °C. Films were decomposed in a nitrogen purged environment at heating rates of 0.5 °C/min, 2 °C/min, and 10 °C/min. The dynamic thermogravimetric analysis plot for the QPac PPC is shown in Fig. 6. DTGA curves of two different molecular weight PPCs of 90,000 g/mol and 100,000 g/mol from Novomer are shown in Figs. 7 and 8, respectively. Activation energies (Ea), pre-exponential factor, and correlation factor (R²) obtained using the Coats–Redfern method for γ-butyrolactone dissolved blends at all heating rates are listed in Table 2 as well as the maximum completion fraction (∑max).

4.3. TGAs of solvent-cast films with photoacid generator

The two photoacid generators used in this study, (4-tert-butylphenyl)iodonium tris(perfluoromethyl sulfonfonyl) methide (3M-Methide) and 4-methylphenyl[4-(1-methylethyl)phenyl] tetrakis(pentafluorophenyl) borate (Rhodorsil-FABA), were heated at 0.5 °C/min and decomposed at in a nitrogen purged environment.

### Table 2

<table>
<thead>
<tr>
<th>TGA Conditions</th>
<th>Ea (kJ/mol)</th>
<th>A (s⁻¹)</th>
<th>R²</th>
<th>∑max</th>
</tr>
</thead>
<tbody>
<tr>
<td>QPAC - 0.5 °C/min</td>
<td>285</td>
<td>2.66e25</td>
<td>0.9334</td>
<td>0.53</td>
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<td>QPAC - 2 °C/min</td>
<td>407</td>
<td>1.89e39</td>
<td>0.9312</td>
<td>0.57</td>
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<tr>
<td>QPAC - 5 °C/min</td>
<td>233</td>
<td>9.39e19</td>
<td>0.7973</td>
<td>0.55</td>
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<tr>
<td>Novomer 90k - 0.5 °C/min</td>
<td>295</td>
<td>5.82e26</td>
<td>0.9889</td>
<td>0.43</td>
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<tr>
<td>Novomer 90k - 2 °C/min</td>
<td>247</td>
<td>5.90e20</td>
<td>0.9958</td>
<td>0.47</td>
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<tr>
<td>Novomer 90k - 10 °C/min</td>
<td>234</td>
<td>9.36e19</td>
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<td>0.46</td>
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<td>Novomer 100k - 0.5 °C/min</td>
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<td>Novomer 100k - 2 °C/min</td>
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<tr>
<td>Novomer 100k - 10 °C/min</td>
<td>399</td>
<td>2.04e37</td>
<td>0.9515</td>
<td>0.60</td>
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**Table 2** Kinetic parameters calculated using Coats–Redfern technique for PPC dissolved in γ-butyrolactone and for photoacid generators used in this study.

### Table 3

<table>
<thead>
<tr>
<th>TGA Conditions</th>
<th>Ea (kJ/mol)</th>
<th>A (s⁻¹)</th>
<th>R²</th>
<th>∑max</th>
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<td>Rhodorsil-FABA</td>
<td>155</td>
<td>1.33e13</td>
<td>0.9776</td>
<td>0.69</td>
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<tr>
<td>3M-Methide</td>
<td>303</td>
<td>5.61e30</td>
<td>0.9876</td>
<td>0.58</td>
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</table>

**Table 3** Kinetic parameters calculated using Coats–Redfern technique for photoacid generators used in this study heated at 0.5 °C/min.
The PAGs were used in their as-received state without drying. The PAGs were examined by thermal analysis either neat or dissolved in solvent and dried in a TGA pan. The DTGA curves for these PAGs are shown in Fig. 9. The activation energy ($E_a$), pre-exponential factor, and regression correlation ($R^2$) obtained using the Coats–Redfern method are listed in Table 3 with the maximum completion fraction ($\alpha_{\text{max}}$).

4.4. TGAs of photoacid generators

The thermal decomposition of the PAG is important because it can facilitate the acid activated decomposition mechanism of the PPC. Acid is generated upon thermal dissociation in a manner similar to UV exposure. Both PAGs exhibit five percent mass loss at temperatures near the decomposition temperature of PPC ($T_d$). 5\%-Methide = 182 °C; $T_d$ 5\%-FABA = 187 °C). The 3M-Methide PAG completely decomposes rapidly and thus may completely volatilize with little effect on PPC films while Rhodorsil-FABA does not decompose completely until 210 °C, allowing the thermally generated acid to play an active role in decomposition of unexposed films.

4.5. TGAs of Novomer films cast from different solvents

Dissolving PPC in solvent allows control of film thickness by varying spin speed. PPC dissolves readily in numerous polar solvents including methylene chloride, anisole, acetone, γ-butyrolactone, trichloroethylene, and cyclohexanone. Novomer PPC with a molecular weight of 100,000 g/mol was dissolved in each of these solvents, spun as a 10 μm thick film, and decomposed in a nitrogen environment at a heating rate of 0.5 °C/min. The DTGA curves for these films are shown in Fig. 10. Table 4 shows the kinetic parameters extracted using the Coats–Redfern technique. Residual solvent or interaction with PPC has a notable effect on the temperature for the onset of decomposition, as reflected in the activation energy and pre-exponential factor. No easily discernible trend can be seen on how the casting solvent may impact the thermal decomposition of PPC. Comparison of physical properties such as dipole moment, heat of vaporization, and boiling point show no pattern to the change in decomposition temperature. This suggests a more complex interaction between solvent and polymer backbone and may be an interaction with the terminal alcohol groups to suppress initiation or at the carbonyl sites to inhibit unzipping propagation. End-capping at the chain terminations seem most likely as this has been observed in other systems [5] where no evidence of hydrogen bonding was reported. All solvents in this study are readily hydrolyzed in the presence of water and these products may also be responsible for end-capping of the polymer backbone. These effects may depend highly on molecular weight, polydispersity, and degree of film drying.

4.6. TGAs of PPC films with different photoacid generator concentrations

The effects of two different photoacid generators (3M-Methide and Rhodorsil-FABA) were studied by varying concentration and UV exposure. The Novomer PPC with a molecular weight of 90,000 g/mol and QPac PPC with a molecular weight of 50,000 g/mol were investigated by first dissolving the PAG in γ-butyrolactone with the polymer and mixing on a bottle roller. The photoacid concentrations by weight were 3.00 percent 3M-Methide and 3.75 percent Rhodorsil-FABA, which corresponds to an acid loading of approximately 1 mol of acid to 440 monomer units of the polymer. The average chain length of the Novomer PPC with a molecular weight of 90,000 g/mol is approximately 880 monomer units, which means there are 2 acid molecules per polymer chain. Upon UV exposure or

![Fig. 10. Solvent-cast Novomer (MW = 100k) PPC Weight Fraction vs. Temperature in nitrogen heated at 0.5 °C/min compared with as-received sample: (a) methylene chloride, (b) anisole, (c) acetone, (d) as-received (no solvent added), (e) γ-butyrolactone, (f) trichloroethylene, and (g) cyclohexanone.](image)

Table 4

<table>
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<tr>
<th>Solvent</th>
<th>$E_a$ (kJ/mol)</th>
<th>$A$ (s$^{-1}$)</th>
<th>$R^2$</th>
<th>$\alpha_{\text{max}}$</th>
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<td>No solvent added</td>
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<td>2.07e47</td>
<td>0.997</td>
<td>0.60</td>
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</table>

*The poor correlation factor for the kinetic parameters of the acetone dissolved sample is due to inversion of the curve in the middle of the decomposition range, seen as a step backwards in the TGA plot in Fig. 10.*
thermal activation, the organic cation of the PAG decomposes. The remaining anion has a highly dispersed negative charge and thus generates a strong Brønsted acid. Since the acid is regenerated after each propylene carbonate decomposition, there is sufficient acid to initiate decomposition from each end of the backbone.

Ether linkages consume the acid upon decomposition by terminating the backbone with an alcohol group which does not allow polymer unzipping or acid regeneration. A lower acid concentration of 0.200 wt% 3M-Methide or 0.250 wt% Rhodorsil-FABA was also studied. This lower acid concentration corresponds to a mole ratio of 6600 monomer units per acid molecule. All UV exposures used a dose of 1 J/cm² at λ = 248 nm.

The DTGA curves for UV exposed and unexposed films with 3.75 wt% Rhodorsil-FABA in QPac and Novomer (M.W. = 90,000 g/mol) at heating rates of 0.5 °C/min, 2 °C/min, and 10 °C/min in a nitrogen environment are shown in Fig. 11. The UV exposed samples exhibit a low temperature, gradual decomposition while the unexposed films show a sharp decomposition at higher temperature. The shift in the decomposition temperature to lower values reflects the acid activation step. Additionally, the mass loss occurs over a broad temperature range in the exposed case, compared with a relatively narrow temperature range in the unexposed case. Decomposition of QPac and Novomer (M.W. = 90,000) loaded with 3.00 wt% 3M-Methide PAG at heating rates of 0.5 °C/min, 2 °C/min, and 10 °C/min

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with and without UV exposure is shown in Fig. 12. Shown in Fig. 13 are the low acid loading of the Rhodorsil-FABA PAG (0.25 wt%) for the exposed and unexposed cases at the heating rates listed above for QPac and Novomer (M.W. = 90,000). Fig. 14 shows the low acid loading of the 3M-Methide PAG (0.20 wt%) for QPac and 90,000 g/mol Novomer with UV exposure and without UV exposure at the same heating rates.

The 3M-Methide PAG had a lower decomposition onset temperature than the Rhodorsil-FABA PAG for the UV exposed samples. Similar mass loss rates were observed in all exposed cases, consistent with a decomposition and steadily increasing rate of product loss. This is consistent with depolymerization into the cyclic monomer and a mass loss due to the evaporation of the liquid. In the unexposed cases, the films with the FABA PAG had a slightly lower decomposition onset temperature and all samples exhibited behavior consistent with rapid decomposition and volatilization. This is consistent with depolymerization followed by immediate evaporation although chain scission may be competing.

Table 5 summarizes the Coats–Redfern kinetic parameters for a first order reaction and completion fraction at the maximum decomposition rate ($\alpha_{max}$) for the UV exposed cases for both base polymers, both photoacid concentrations of each PAG, and all
heating rates. Table 6 lists the Coats–Redfern kinetic parameters and $\alpha_{\text{max}}$ for the unexposed cases of these same films.

4.7. TGA of PPC films with different PAG concentrations and solvents

The influence of casting solvent on Rhodorsil-FABA PAG was studied at concentrations of 3.75 wt% and 0.25 wt%. The UV exposure dose was 1 J/cm$^2$ at $\lambda = 248$ nm. All samples were decomposed at a heating rate of 0.5 °C/min. Several casting solvents were compared including: γ-butyrolactone, acetone, anisole, and methylene chloride. The DTGA curves for these samples are shown in Fig. 15. The kinetic parameters were calculated using the Coats–Redfern method. The first order reaction parameters are listed in Table 7 along with the completion fraction at the point of maximum decomposition rate. A second set of samples were prepared with 0.25 wt% PAG examining the solvent effect including: γ-butyrolactone, acetone, anisole, and methylene chloride. The DTGA curves for these samples are shown in Fig. 16. The Coats–Redfern kinetic parameters are listed in Table 8.

4.8. TGAs of high PAG concentration and triflic acid

Novomer material loaded with 10.0 wt%, 3.75 wt%, and 0.25 wt% of Rhodorsil-FABA PAG is compared in Fig. 17. The residue remaining at temperatures above 180 °C is primarily attributable to the initial PAG loading. This remaining fraction decomposes between 190 °C and 230 °C. Although not illustrated here, the decomposition curve of the Rhodorsil-FABA PAG from Fig. 9 almost exactly overlays the "foot" observed in the decomposition range of the PAG.

Fig. 18 shows the comparison between the equivalent molar acid loadings (wt% adjusted to achieve the same molar concentration) of 3M-Methide and Rhodorsil-FABA PAGs after UV exposure. PAG decomposition using triflic acid was examined to compare the effect of a strong acid which did not need to be UV exposed to form the acid. A 1.0 wt% solution of triflic acid was and PAG was made by using previously dried triflic acid and acetone as the solvent, as shown in Fig. 19. It was not possible to use γ-butyrolactone as the solvent because at the softbake temperature, 100 °C, the triflic acid containing film catalyzed the decomposition of the PPC polymer. The slightly higher temperature for weight loss with the triflic acid is consistent with the elevated weight loss temperature seen in Fig. 15 for the acetone-solvent effect with Rhodorsil-FABA PAG.

The decomposition of PPC via chain unzipping into the monomer means that the decomposition profile, temperatures, rates, and calculated activation energies should be similar to that of the pure monomer. If the decomposition products are only the monomer, the TGA curves for PPC should match that of propylene carbonate, perhaps with a slight temperature lag due to the unzipping of the monomer. If, however, the polymer splits into lighter molecular weight fragments (i.e. acetone and carbon dioxide), then weight loss should occur more rapidly because these are more volatile products. To compare the monomer with polymer decomposition products, propylene carbonate was volatilized at heating rates of 0.5 °C/min, 2 °C/min, and 10 °C/min. Propylene carbonate loaded with 3.75 wt% Rhodorsil-FABA and exposed to UV light was also studied at these heating rates. The DTGA curves for these experiments are shown in Fig. 19. The general shape is nearly identical at each heating rate, except for the foot on the PAG loaded liquid. This foot is present at the same wt% as the initial PAG loading and exhibits a second decomposition region as the PAG decomposes. Kinetic parameters extracted using the Coats–Redfern method are summarized in Table 9.

4.9. Kinetic analysis by Kissinger method

The kinetic parameters were calculated using the Kissinger method for all polymer blends evaluated in this study at multiple
heating rates. The results of these calculations are summarized in Table 10. Additionally, the kinetic parameters extracted for the monomer with PAG and without PAG are included. Without PAG, the QPac PPC had a higher activation energy (165 kJ/mol) than the Novomer materials (136 kJ/mol and 142 kJ/mol). The mixtures containing QPac or Novomer with a high concentration of PAG before UV exposure had activation energies between 154 kJ/mol and 166 kJ/mol. UV exposure of the blends with a high concentration of PAG had lower activation energies between 45 kJ/mol and 71 kJ/mol. QPac showed a higher activation energy than the Novomer PPC. Low acid concentrations exhibited a mixed effect on the activation energies for both exposed and unexposed films with no easily distinguished trend.

Films decomposed under nitrogen exhibited widely varying behavior depending on the acid type and concentration. Samples without PAG and those which contained PAG but were not UV exposed demonstrated similar behavior. The PPC decomposed into a clear liquid product which quickly evaporated at the decomposition temperature. This decomposition occurred at approximately 190 °C and appears to be consistent with depolymerization into a liquid product, which is likely propylene carbonate.

Films loaded with higher concentrations of photoacid (3.0 wt% 3M-Methide, 3.75 wt% Rhodorsil-FABA, and 10 wt% Rhodorsil-FABA) exhibited a somewhat similar decomposition mechanism as the unloaded and unexposed samples. The onset of decomposition was much lower (by about 100 °C) and the reaction occurred over a wide temperature range (from 100 °C to 140 °C). The films decomposed into a liquid with a dark tint which subsequently volatilized and left a dark-brown and/or black residue in the TGA pans. These samples were also observed to form bubbles in the pan, which was not seen with PPC films in the absence of PAG.

Films loaded with a low concentration of PAG (0.20 wt% and 0.25 wt% of 3M-Methide and Rhodorsil-FABA, respectively) showed very different decomposition characteristics than the unloaded, unexposed, or high PAG concentration samples. At these low concentrations, the nucleation and growth of gas bubbles in the polymer were clearly visible when the film was UV irradiated. In this case, the entrapped bubbles continuously expanded after formation, which caused the polymer to foam and expand in volume.

4.10. FTIR analysis

FTIR was used to examine the thin polymer films deposited on KBr. Fig. 20 shows the spectra of PPC films cast in different solvents after solvent evaporation. Fig. 21 shows the PPC spectra for films cast in γ-butyrolactone in the presence of a small quantity of Rhodorsil-FABA. Additional spectra were gathered for UV exposed films and UV exposed films heated to 120 °C. However, these spectra exactly overlay the unexposed spectra shown in Fig. 21 but with a lower intensity due to the decreased film thickness. When the peaks are normalized for intensity around the C=O peak at 1750 cm⁻¹, they accurately overlay each other and are therefore not shown because no significant information can be discerned from them. Similar results were experienced in attempts to track film decomposition using UV—Visible light spectroscopy. Complete decomposition of the film leaves very weak, nearly indistinguishable peaks, as has previously been reported [19].
Films with and without PAG and in different solvents exhibited very similar spectral peaks, as would be expected since the residual solvent is mostly removed and the PAG and only accounts for a few weight percent of the mixture. The broad peak at ca. 3000 cm$^{-1}$ is attributable to C–H bond stretching in the propylene units. There may also be an OH peak hidden within this peak. The peak at 1760 cm$^{-1}$ is attributed to the C=O of the carbonate groups. The broad peak at 1250 cm$^{-1}$ is due to the C–O bond of the carbonate groups but also may be due to any irregularities (ether linkages) in the backbone of the polymer. The peak at 1475 cm$^{-1}$ is due to C=C bonding in the propylene groups. The additional peaks in the 1350–1450 cm$^{-1}$ range are due to scissoring and bending of the C–H bonds.

As seen in Fig. 20, the FTIR spectra of solvent-cast PPC films do not distinguish the essential differences between various solvents used to cast the films. The C–H stretching (2850–2960 cm$^{-1}$), and bending and scissoring (1350–1470 cm$^{-1}$) modes exhibit slight variations between solvents. Very slight differences are seen at 1575 cm$^{-1}$, which may be attributed to carboxylate groups present at the ends of the polymer chains.

The influence of the Rhodorsil-FABA on the FTIR spectra is shown in Fig. 21. Novomer PPC was dissolved in γ-butyrolactone and cast on KBr slides from solutions containing different weight percentages of Rhodorsil-FABA PAG. Additionally, the PAG alone was dissolved in γ-butyrolactone and cast on KBr. The primary peak in the Rhodorsil-FABA spectrum is seen at 1470 cm$^{-1}$, C–C bonding. Secondary peaks are seen at 975 cm$^{-1}$ from the methyl groups and at 1514 cm$^{-1}$ from benzene ring stretching. The peaks at 1470 cm$^{-1}$ and 975 cm$^{-1}$ are obscured by PPC peaks. The benzene ring peak at 1514 cm$^{-1}$ is with higher PAG loadings and is the only clear difference between the spectra. No evidence of hydrogen bonding as observed in other PPC studies at 1550 cm$^{-1}$ was observed here.

### 5. Discussion

#### 5.1. Enthalpy of vaporization by Kissinger method

The enthalpy of vaporization of propylene carbonate has been reported to be between 49 kJ/mol [64] and 51 kJ/mol [65]. The propylene carbonate data analyzed using the Kissinger method yielded an activation energy in the same range as the as these literature values. The similar activation energies for the monomer with no additives (50.5 kJ/mol) and with 3.75% Rhodorsil-FABA PAG (48.8 kJ/mol) indicate that the photoacid does not decompose the monomer into smaller fragment products and has little effect on the overall vapor pressure.

The activation energies calculated by the Kissinger method for the Novomer PPC with UV exposed photoacid at high concentrations (3.0% 3M-Methide or 3.75% Rhodorsil-FABA) are very close to that of the heat of vaporization of the cyclic monomer. This suggests the formation of propylene carbonate via the chain unzipping mechanism and subsequent volatilization. The chain unzipping mechanism has been reported to be due to the formation of terminal –OH groups upon acid activation [19] and is the dominant decomposition mechanism in high molecular weight PPC [15]. Because the Novomer polymer had both higher molecular weight and higher regularity of repeat units (HT), the lower activation...
energy of the Novomer material was consistent with chain unzipping into the monomer.

5.2. Photoacid consumption by impurities

For the QPac material, fragmentation into larger molecular weight products likely competed with chain unzipping. Polyether groups present in the QPac PPC prevented acid regeneration by forming an alcohol termination unable to propagate the unzipping mechanism. The quenching of the unzipping mechanism by the ether groups is likely the reason for the higher activation energies calculated using kinetic analysis. This is particularly true at low concentration of PAG where acid regeneration is critical because the number of acid molecules is less than the number of polymer chains. The higher molecular weight decomposition products that result from the ether impurities may also contribute to the higher activation energy.

5.3. Additional decomposition products

Deviations from the enthalpy of the monomer may also be attributed to the formation of hydrolysis products. 1,2-propanediol

Fig. 17. Exposed and unexposed Novomer with Rhodorsil-FABA at different concentrations. Shown in (a) and (d) are 3.75 wt%. Shown in (b) and (c) are 10.0 wt%. Shown in (e) and (f) are 0.25 wt%.

Fig. 18. Exposed Novomer PPC with (a) 3.0 wt% 3M-Methide and (b) 3.75 wt% Rhodorsil-FABA and (c) an unexposed, air-dried film with a 1.0 wt% triflic acid.
has been observed in PPC pyrolysates via FTIR [15] and may form in the presence of water, although most of the water was likely removed during film drying on a hotplate. It is possible that some water remained bound within the polymer matrix and may have contributed to formation of minor products including 1,2-propanediol. Activation energies calculated using the techniques cited in this paper cannot distinguish between the cyclic monomer and the alcohol product because 1,2-propanediol has an enthalpy of vaporization close to that of propylene carbonate [66].

Decomposition of the monomer into carbon dioxide and acetone with additional heating has been reported, but this does not occur until higher temperatures than evaluated in this study. These products may result from decomposition in an oxygenated atmosphere or at extremely fast ramp rates, but appear to be only minor products in this study. The TGA curves shown in Fig. 19 suggest that the addition of photoacid to cyclic propylene carbonate does not dimerize or degrade the monomer. Thus, it is likely that the PAG has little or no impact after degradation of the polymer into cyclic propylene carbonate.

5.4. Residual solvent influence on decomposition

The exact influence of residual solvent on the decomposition behavior is very subtle. Some of the solvents evaluated in this study are capable of hydrogen bonding and thus stabilizing the PPC backbone, but no evidence of this is observed in the FTIR spectra. Additionally, the solvents evaluated in this study, with the notable exception of γ-butyrolactone, are not capable of undergoing polymerization. Although γ-butyrolactone has been copolymerized with PPC [47] and may undergo homopolymerization [67], it is difficult to polymerize except under controlled conditions [68], despite high ring strain [69]. No change in the viscosity of γ-butyrolactone was observed when photoacid was added to the solvent and UV exposed in the absence of PPC. Deviations in thermal stability due to residual solvent or interaction will depend highly on molecular weight, polydispersity, and film drying conditions and temperatures.

Table 9

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<th>Solvent Type</th>
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<th>A (s⁻¹)</th>
<th>R²</th>
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<tr>
<td>0.5 °C/min</td>
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Table 10

<table>
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</table>
5.5. Confounding effects on kinetic analysis

Without adequate photoacid loading (i.e. low weight percentages of PAG), decomposition proceeds slowly via the unzipping mechanism before proceeding via random chain scission at higher temperatures and subsequent unzipping. This results in a segmented and complex degradation curve as seen in Figs. 13 and 14. The irregularity in the decomposition curves at these acid loadings levels is also likely the result of bubble entrapment of decomposition products during heating. Such effects are not accounted for in the kinetic models. TGA data and results of the open-face decomposition observed under glass both indicate complex, multiphase behavior of the decomposition mechanism in the presence of PAG. Intumescent flame retardants (IFRs) are multicomponent systems where an acidic source chars a carbonization agent to form a low thermal conductivity layer while a blowing agent is converted to a gas and expands with heat. Consequently heat transfer into the sample and mass transfer out of the polymer are inhibited. The photoacid in our system coupled with the polymer backbone fragments potentially provide acid and carbonization agent, while the decomposition products act as a blowing agent. Chemical foaming of PPC has been reported to raise the thermal stability as measured by TGA [41,42]. The foaming effect observed for the UV exposed acid samples decomposed under glass are consistent with this expectation. Under sufficient acid loading, the polymer matrix decomposes to the liquid product and does not allow bubble entrapment. At low acid concentrations, the decomposition of the polymer matrix decomposes to the liquid product and does not allow bubble entrapment. At low acid concentrations, the decomposition of the polymer matrix is incomplete allowing liquid decomposition products to convert into vapor which foams the polymer. These effects are responsible for the elevated activation energies at low acid loading as well as the complex and segmented degradation curves at these acid concentrations.

Differences in the calculated activation energies may be influenced by numerous other factors not previously discussed. Although every effort was made to mix a homogenous blend of solid polymer with photoacid generators, the local concentration of photoacid generator may have been greater than or less than the nominal concentration of the blend. The oxygen content in the TGA atmosphere may also have impacted the decomposition behavior. Although the TGA was purged with nitrogen for 1 h before heating, reducing oxygen content to below 100 ppm, some experiments at 10 °C/min exhibited characteristics consistent with an oxygenated environment (i.e. rapid decomposition with the absence of the “foot” observed in nitrogen environments).

6. Conclusions

The acid catalyzed decomposition of PPC significantly reduces the activation energy as calculated by Coats–Redfern and Kissinger methods. The activation energies calculated using these techniques are similar to those calculated for cyclic propylene carbonate when sufficient quantities of acid are present. In these cases, the decomposition appears to occur via chain unzipping into cyclic propylene carbonate. Under insufficient acid loading, decomposition occurs via a composite decomposition mechanism where part of the polymer decomposes at low temperature and the remaining portion decomposes at higher temperatures.

Polymer purity and molecular weight impact the observed activation energy. Higher molecular weight products of the alternating copolymer most likely decompose via the chain unzipping mechanism. The high molecular weight, high-purity polymer in this study (Novomer) decomposed with UV exposed PAG and had activation energies close to that of cyclic propylene carbonate. The similar activation energies suggest the acid generated upon UV
exposure is sufficient to initiate chain unzipping, which is nearly identical to the reported values of the heat of vaporization. This suggests that upon acid activation, chain unzipping occurs at or below the temperature where cyclic propylene carbonate exhibits significant vapor pressure. Chain unzipping may occur at room temperature after acid activation but is not observed in thermogravimetric analysis because of the negligible vapor pressure of propylene carbonate at room temperature. However, this is unlikely (or unzipping proceeds very slowly) as no liquid product is observed upon UV exposure without heating.

Residual solvent clearly impacts the decomposition, especially in the presence of UV activated PAG. The amount of solvent remaining in the polymer matrix was not measured and likely varied between samples and casting solvents. Because of the uncertainty regarding the presence of UV activated PAG, the amount of solvent remaining in the polymer matrix was not measured and likely varied between samples and casting solvents. Because of the uncertainty regarding the presence of UV activated PAG, the amount of solvent remaining in the polymer matrix was not measured and likely varied between samples and casting solvents.

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