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Tunable Thermal Degradation of Poly(vinyl butyl carbonate sulfone)s via Side-Chain Branching

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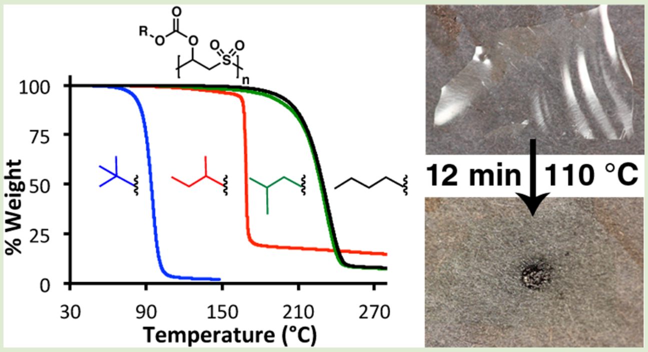
Supporting Information

ABSTRACT: Polymeric materials that depolymerize into volatiles on command may function as vanishing substrates or packaging for transient electronics. Poly(vinyl *tert*-butyl carbonate sulfone) is known to afford low-boiling byproducts upon heat-activated degradation; however, the polymer is rather unstable, even to the degree of being difficult to process and handle. Understanding the origin of this instability is important for the development of robust materials capable of programmed self-destruction. In this work, we show that poly(vinyl *tert*-butyl carbonate sulfone)s thermally decompose via carbonate elimination as the rate-determining step, indicating that its thermal instability stems from the lability of the *tert*-butyl carbonate group. We further examined the effect of isomeric butyl carbonate side chains on the thermal degradation of poly(vinyl butyl carbonate sulfone)s and found that the degradation onsets range from 91 to 213 °C, yielding as little as 2.77 ± 0.53 wt % residue. Results from our findings will aid in the development of vanishing polymers with tunable thermal degradation.



Polymers capable of programmed degradation have garnered renewed interest for use as transient electronic packaging, drug delivery vehicles, and stimuli-responsive microcapsules.[1−7] Among these applications, transient electronics are an emergent technology where the packaged devices respond to specific stimuli by self-destruction.[1,2] Ideal transient packaging needs to exhibit (1) environmental stability over the desired device lifetime without premature degradation; (2) high processability and flexibility for film fabrication and manipulation; (3) robust barrier properties that protect the electronic components; and (4) rapid, complete physical transience following a designated triggering event. Promising packaging materials include self-immolative polymers, chain-shattering polymers, and low-ceiling-temperature polyaldehydes.[8−14] While these polymers readily undergo triggered depolymerization, the resultant products often exhibit volatility that is too low for traceless, transient applications. In order for a material to disappear on demand, the triggered depolymerization event must yield highly volatile molecules to facilitate vaporization under ambient conditions.

Poly(olefin sulfone)s (POSs), synthesized by free radical polymerization of sulfur dioxide and an alkene, depolymerize into their constituent monomers upon exposure to heat, high-energy radiation or base.[15−24] In particular, Jiang and Fréchet reported that poly(vinyl *tert*-butyl carbonate sulfone) (**P1**) rapidly depolymerized at 85 °C in a single step.[25] Its thermal degradation afforded isobutylene, acetaldehyde, sulfur dioxide, and carbon dioxide, thereby leaving negligible solid residue.[25] In contrast, the homopolymer of vinyl *tert*-butyl carbonate does not degrade until 210−220 °C, yielding carbon dioxide, isobutylene, and poly(vinyl alchohol) as the thermolysis products.[26] Since **P1** degrades at a relatively low temperature and subsequently vanishes by forming volatile products, it is an attractive candidate as heat-sensitive packaging for transient electronics. However, this low thermal stability also causes **P1** to degrade under ambient conditions over time, thereby complicating its processing into films for circuit deposition.

To offer insights into the origin of **P1**'s instability, we considered two possible mechanistic scenarios that afforded the reported thermolysis products.[25] Literature has suggested that poly(alkyl olefin sulfone)s thermally depolymerize into sulfur dioxide and the constituent olefin via a concerted β-elimination mechanism, in which a backbone β-proton is removed by the respective sulfone through a five-membered transition state.[27−29] Functionalizing POSs with bulky, polar *tert*-butyl carbonate side groups may directly disrupt backbone stability by increasing steric demand and altering backbone proton acidity. Alternatively, the heat-induced depolymerization of **P1**

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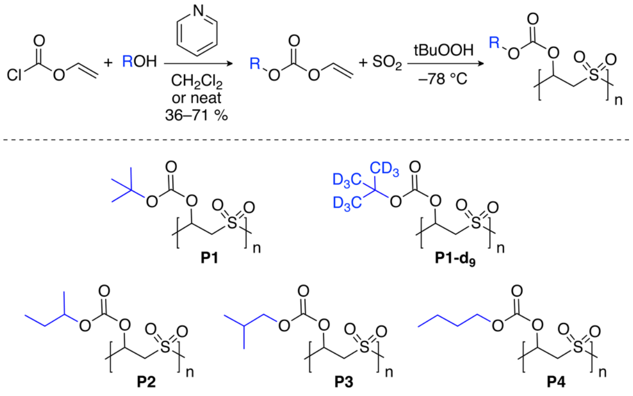
may initiate upon the elimination of the thermally labile *tert*-butyl groups, followed by decarboxylation. The intermediates generated during this process (e.g., carbonic acid and/or hydroxyl groups) may also catalyze or contribute to the rapid breakdown of polymer backbone. To offer insights into the thermolysis pathway, we performed kinetic isotope effect experiments using a deuterated **P1** analogue, **P1-d$_9$**, and investigated the thermal degradation behavior of various isomeric derivatives **P2**–**P4** (Scheme 1).

Scheme 1. Synthesis and Structures of Poly(vinyl butyl carbonate sulfone)s



In this contribution, we show that *tert*-butyl carbonate elimination is the rate-determining step (RDS) in the thermal decomposition pathway. We also demonstrate that the thermal stability of poly(vinyl butyl carbonate sulfone)s increases with decreasing degree of substitution from *tert*- to *sec*-, *iso*-, and *n*-butyl groups. Polymers **P1**, **P3**, and **P4** yield <7.5 wt % residue upon heat-activated decomposition at 91, 213, and 213 °C, respectively. Although **P2** and **P4** exhibit higher thermal depolymerization onsets than **P1** in the series, they form films that are more easily handled. Mechanical characterization shows that all polymers form films with reduced moduli in the range of 2–5 GPa. Results from our findings will aid in the development of vanishing polymers with tunable thermal degradation and the potential to serve as transient electronic substrates.

The vinyl butyl carbonate monomers were synthesized in one step via nucleophilic addition of the designated alcohol to vinyl chloroformate in the presence of pyridine (Scheme 1).[25,26] Triple distillation of the crude mixtures yielded analytically pure monomers (see Supporting Information, SI). In excess sulfur dioxide, addition of *tert*-butyl hydroperoxide (*t*BuOOH) to vinyl butyl carbonates at −78 °C initiated free radical polymerization between the olefin and SO$_2$.[25] Purification of the crude mixture was accomplished by dissolution of the polymer in chloroform, followed by precipitation into methanol. Gel-permeation chromatography (GPC; eluent: tetrahydrofuran, THF) was used to characterize the molecular weights of all poly(vinyl butyl carbonate sulfone)s investigated in this work (Table 1).

Thermal gravimetric analysis (TGA) shows that **P1** thermally degrades with an onset at 91 ± 0.3 °C, comparable to the reported value (85 °C).[25] Although the original report identified the major decomposition products of **P1**, it did not provide details on the thermal degradation mechanism.[25] Given the well-known thermolysis mechanism of *tert*-butyl carbonates, we sought to investigate whether the elimination of *tert*-butyl carbonate is the rate-determining step by a kinetic isotope experiment. Upon synthesizing **P1-d$_9$**, an analogue of **P1** bearing deuterated *tert*-butyl groups, we compared the thermolysis rates between via isothermal TGA (Figures 1a and S1 and S2). The average times to reach complete degradation for **P1-d$_9$** are about three times as long as those for **P1** at 85, 80, and 75 °C, indicating a positive, primary kinetic isotope effect (PKIE; Table 2). Further plotting the instantaneous rate against time showed a bell-shaped curve for

Table 1. Molecular Weights[a] and Thermal Properties of P1–P4

	M_n (kDa)	M_w (kDa)	PDI	T_{decomp}[b] (°C)	T_g (°C)
P1[c]	108	325	3.0	91 ± 0.3[e]	
P1-d$_9$[c]	49	106	2.2	102 ± 0.2	
P2[c]	109	386	3.5	167 ± 0.4	84
P3[c]	287	644	2.2	213 ± 0.4	83
P4[c]	273	593	2.2	212 ± 0.5	63
P4[d]	101	478	4.8	213 ± 1.3	62

[a] Molecular weights reflect the isolated components after purification by precipitation. [b] Average value of *n* = 4 TGA experiments. [c] Polymerized with 40 equiv of sulfur dioxide. [d] Polymerized with 80 equiv of sulfur dioxide. [e] Lit. value = 85 °C.[25]

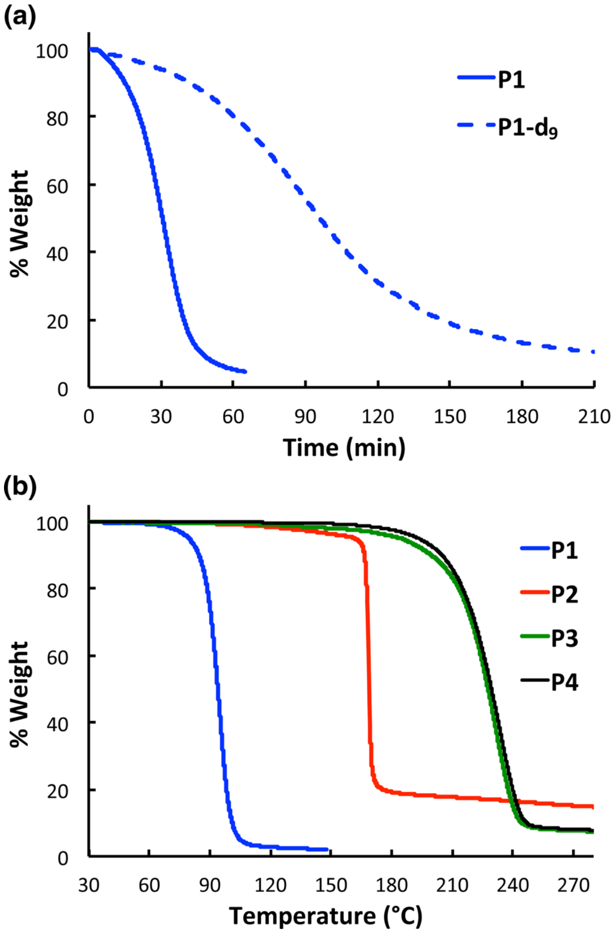


Figure 1. (a) Isothermal TGA traces of **P1** and **P1-d$_9$** at 75 °C; **P1** degrades faster than **P1-d$_9$**. (b) Ramp TGA traces (5 °C/min) of **P1**–**P4** showing that the onsets of degradation increase with decreasing side-chain branching at the carbonate *β*-carbon. Prior to analysis, materials were rigorously dried, as detailed in the SI.

Table 2. **Thermal Degradation Times and Calculated Rate Constants of P1 and P1-d$_9$ at Various Temperatures**

T^a (°C)	polym.^{b}	decomp. time^c (min)	$k_1 \times 10^{-2d}$ (min^{-1})	$k_2 \times 10^{-2d}$ (min^{-1})	$k_2^{\mathrm{H}}/k_2^{\mathrm{D}}$
85	**P1**	17 ± 0.6	3.26	40.4	3.1
	P1-d$_9$	40 ± 0.7	0.548	13.1	
80	**P1**	24 ± 0.4	1.18	28.3	3.8
	P1-d$_9$	70 ± 1.6	0.227	7.53	
75	**P1**	42 ± 0.3	0.259	16.0	4.1
	P1-d$_9$	140 ± 2.8	0.0930	3.91	

[a]TGA temperature was ramped at 10 °C/min and held at target isothermal temperature. [b]Polymers were rigorously dried by lyophilization. [c]Average value of $n = 3$ TGA experiments. [d]Obtained from fitting with an autocatalytic kinetic model (see SI).

both polymers at all three temperatures, suggesting that the thermal degradation proceeds through an autocatalytic pathway.

To quantify the extent of the KIE, we determine the thermolysis rate constants of **P1** and **P1-d$_9$** by fitting polymer conversion over time to an autocatalytic kinetic model.[30,31] In this model, rate constants k_1 and k_2 describe the noncatalytic and autocatalytic steps, respectively. The rate constant k_2 is at least 1 order of magnitude greater than that of k_1 at all temperatures, showing that the autocatalytic step proceeds faster than the noncatalytic step. Comparing the values of k_2 shows that **P1-d$_9$** thermally depolymerizes at a much lower rate than **P1**, thereby leading to a large primary kinetic isotope effect where the temperature-dependent $k_\mathrm{H}/k_\mathrm{D}$ = 4.1, 3.8, and 3.1 at 75, 80, and 85 °C, respectively (comparing k_2 in Table 2). In addition, **P1-d$_9$** shows a degradation onset of 11 °C higher than that of **P1** in a ramp TGA experiment (Table 1). All of these results suggest that the elimination of *tert*-butyl carbonate moiety is indeed the RDS, followed by rapid polymer main-chain scission.

Based on the apparent thermolysis mechanism for **P1** (Scheme S1), we anticipated that changing the degree of substitution at the carbonate *β*-position will vary the degradation onset temperatures of poly(vinyl carbonate sulfone)s. Thus, we synthesized derivatives of **P1** with isomeric butyl carbonates for systematic thermal analyses. Using the aforementioned synthetic procedures, we obtained **P1**, **P2**, and **P4** with similar M_n, while **P3** displayed a high M_n of 287 kDa (Table 1). Rigorous monomer purification and decreasing initiator loading to 2.5 mol % allowed for the synthesis of **P1** with M_n of 108 kDa, higher than the previously reported M_n of 11 kDa.[25] The polymerization of **P4** performed with 40 equiv of sulfur dioxide afforded polymer with an M_n of 273 kDa, while decreasing the polymerization concentration by using 80 equiv of sulfur dioxide reduces the M_n to 101 kDa. The M_n of **P3** remained high when the polymerization was performed with both 40 and 80 equiv of sulfur dioxide. In addition, elemental analyses of **P1**−**P4** show that each polymer contains a 1:1 ratio of olefin:sulfone, as expected for polymers that are perfectly alternating (see SI).[22]

The thermal properties of polymers **P1**−**P4** were evaluated by TGA and differential scanning calorimetry (DSC). The TGA traces show that the thermal decomposition of **P1**−**P4** proceeds in one step (Figure 1b). The onset temperature for polymer degradation increases from 91 to 167 °C and 213 °C with decreasing substitution at the carbonate's *β*-carbon from quaternary (**P1**) to tertiary (**P2**) and to secondary (**P3** and **P4**), respectively. The difference in the M_n of **P4** does not contribute significantly to the degradation onset (Table 1). It is important to note that 91 °C is the lower threshold of the target degradation onset temperature as **P1** still maintains sufficient stability for processing at room temperature. The increased onset temperatures of **P2**−**P4** simplify material handling under ambient conditions due to improved polymer stability. Polymer **P1** thermally degrades to yield an average of 2.77 ± 0.53 wt % residual mass. Polymers **P3** and **P4** also thermally degrade to less than 7.5% of the original mass; however, significant residual mass remains upon **P2** decomposition. Heating **P2** at 170 °C for 1 h reproducibly yields 13% residue unidentified by NMR spectroscopy or mass spectrometry. The similarity between the TGA profiles of **P3** and **P4** suggests that the substitution at the carbonate *β*-carbon determines the thermal degradation behavior of the polymers.

DSC measurements show that polymers **P2**, **P3**, and **P4** exhibit glass transition temperatures (T_g) at 84, 83, and 63 °C, respectively, while **P1** does not exhibit a T_g prior to thermal decomposition. Although **P3** and **P4** degrade at similar temperatures, the T_g of **P3** is closer to that of **P2**, suggesting that increasing side-chain branching raises T_g regardless of substitution position.

Mechanical characterization of the polymer films provides some insight into the polymers' potential use as electronic substrates or encapsulants. Free-standing films of **P1**−**P4** were solvent-cast from chloroform onto PTFE-lined Petri dishes. Films of **P2** and **P4** are easily handled and manipulated. In comparison, films of **P3** are slightly brittle but can still be handled relatively easily, while **P1** forms the most brittle film, requiring careful handling. Determined by nanoindentation, films of **P1**−**P4** display reduced moduli of 4.8, 2.4, 4.6, and 2.9 GPa, respectively (Figure S13). The stiffness of these polymers makes them candidates as stiff polymeric substrates for transient electronics. To demonstrate the physical transience of these polymers, a film of **P1** was heated at 110 °C on a hot stage; it disappeared within 12 min as the volatile products bubbled away (Figure 2).

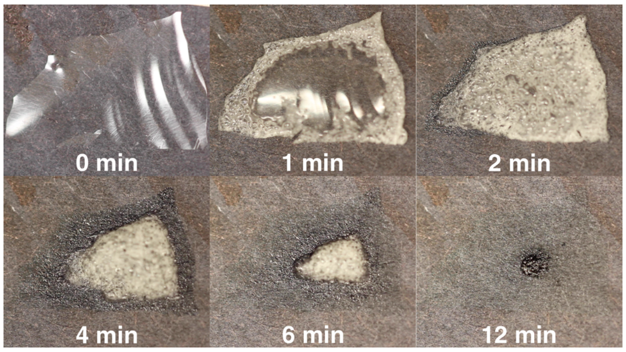


Figure 2. Heat-activated degradation of a film fabricated from **P1** over 12 min at 110 °C on a hot stage.

In summary, preliminary mechanistic studies show that poly(vinyl butyl carbonate sulfone)s thermally decompose via carbonate elimination as the rate-determining step. We used these results to guide polymer design; by modulating side-chain substitutions, we demonstrate control over thermal depolymerization of these polymers. Consistent with the proposed mechanism, polymers **P1**−**P4** exhibit increasing thermal stability with decreasing side-chain branching at the *β*-carbon to the carbonyl group. Thermally triggering the depolymerization of **P1**, **P3**, and **P4** affords little solid residue, a characteristic that is desirable for the development of transient materials. Mechanical characterization of the polymers reveals that films of **P2** and **P4** are more easily manipulated than those of **P1** and **P3**. We further show the complete physical transience of a film fabricated from **P1**, which rapidly vanishes at 110 °C within 12 min. The design and synthesis of these thermally degradable poly(olefin sulfone)s represent the first step toward developing transient substrates and packaging materials that will completely vanish on demand.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Monomer synthesis, polymerization conditions, polymer characterization, and film processing and characterization. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00234.

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Notes

The authors declare no competing financial interest.

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