Functionalized and Degradable Polyphthalaldehyde Derivatives

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ABSTRACT: Polymers that depolymerize back to monomers can be repeatedly chemically recycled, thereby reducing their environmental impact. Polyphthalaldehyde is a metastable polymer that is rapidly and quantitatively depolymerized due to its low ceiling temperature. However, the effect of substitution on the physical and chemical properties of polyphthalaldehyde derivatives has not been systematically studied. Herein, we investigate the cationic polymerization of seven o-phthalaldehyde derivatives and demonstrate that judicious choice of substituents results in materials with a wide range of ceiling temperatures (< −60 to 106 °C) and decomposition temperatures (109–196 °C). We anticipate that these new polymers and their derivatives will enable researchers to access degradable materials with tunable thermal, physical, and chemical properties.
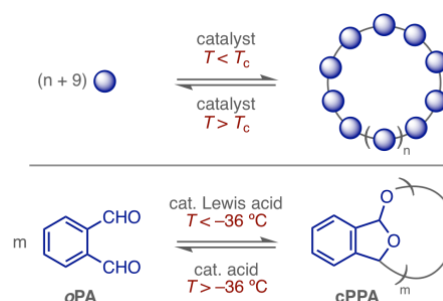
While much progress has been made in synthesizing polymers with diverse structures, considerably less attention has been paid to their fates after use. Low–ceiling temperature (T_c) polymers are a class of metastable materials that are readily triggered to depolymerize back to monomers at temperatures above their T_c (Scheme 1).[1,2] Such materials have the potential to address a grand challenge in sustainability by facilitating recycling through repeated depolymerization/repolymerization cycles, extending their useful lifetimes.[3,4] Depolymerizable polymers also have important applications in areas such as lithography,[5] triggered release,[6] and transient electronics.[7]

Polyphthalaldehyde (PPA) is among the most thoroughly studied depolymerizable polymers.[8,9] Linear or cyclic PPA (cPPA) can be obtained via anionic or cationic polymerization (respectively) of o-phthalaldehyde (oPA) below its T_c of −36 °C.[10,11] While end-capped linear PPA and cPPA are kinetically stable at room temperature, solution-phase exposure to acid results in complete depolymerization at rates too rapid to measure using standard analytical techniques (< 1 min; Scheme 1).[1] The thermodynamic instability of PPA is key to its depolymerization, but this same property has led to challenges in polymer processing.[12] For example, PPA requires plasticizers to improve its processability because its glass transition temperature (T_g) is *above* its thermal degradation temperature.[13]

A small number of substituted polyphthalaldehydes have been reported, primarily for the purpose of increasing thermal stabilities. For example, researchers at IBM found that polyphthalaldehydes bearing 4-bromo, 4-chloro, and 4-trimethylsilyl substitution exhibited higher thermal degradation temperatures than unsubstituted PPA, making them more suitable for photolithographic applications.[14] In related work, Phillips and co-workers showed that end-capped linear poly(4,5-dichlorophthalaldehyde) displayed a similar effect.[15] Poly(4-methylphthalaldehyde) has also been synthesized as a mechanistic probe,[16] but no other PPA derivatives have been reported.

Scheme 1. Low Ceiling Temperature (T_c) Cyclic Polymers

This relative lack of PPA derivatives results in part from the perception that synthesizing substituted o-phthalaldehydes is prohibitively challenging, relying on a few established, but often low-yielding, synthetic routes.[8] Furthermore, it is still unclear *a priori* whether a specific phthalaldehyde is polymerizable under experimentally accessible conditions due to a lack of quantitative data on the ceiling temperatures of known PPA derivatives. To address these deficiencies, we set out to synthesize a range of substituted oPA derivatives and evaluate their Lewis acid–catalyzed polymerizations. As a result of these studies, we identified four new cPPA derivatives with ceiling temperatures ranging from −23 to +106 °C and demonstrated that their thermal degradation temperatures positively correlate with their T_c. We anticipate that these new polymers will significantly expand the
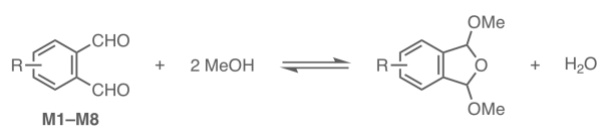
versatility of the PPA scaffold and that the structure–property relationships will serve as a roadmap for researchers to develop other PPA-based materials with varied physical and chemical properties.

Computational T_c Estimation. To estimate the ceiling temperatures for substituted phthalaldehyde derivatives, a literature method[17] was adapted. Specifically, the acetalization of oPA with MeOH was used as the model reaction (Scheme 2, R = H). Density functional theory (B3LYP/6-31++G**)[18] was used to calculate the heat of formation for each reaction component, enabling us to determine the overall enthalpy (ΔH) for the equilibrium (SI pgs S100–S122). Using our measured T_c for oPA of –36 °C (vida infra), we computed the entropy (ΔS) from Eq. 1:

$$T_c = \frac{\Delta H}{\Delta S} \quad (1)$$

We next assumed that the ΔS determined for oPA would be similar for the substituted derivatives, given that the changes in bonding are similar for each reaction. With this assumption, the ceiling temperature was estimated by calculating the ΔH for each oPA derivative and solving Eq. 1 for T_c. We chose to focus exclusively on symmetrically substituted derivatives because nonsymmetrically substituted oPAs would have electronically distinct acetal linkages, making it difficult to disentangle the effects of different substituents.

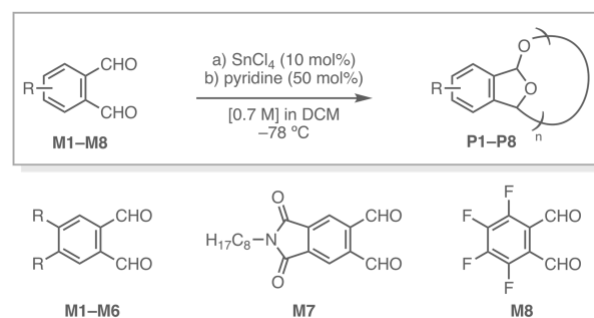**Scheme 2. Model Reaction for Phthalaldehyde Polymerization**

Our computations suggested that simple changes to oPA yield monomers with ceiling temperatures ranging from –122 °C to +98 °C (Table 1). As expected, electron-donating substituents resulted in a predicted T_c below that of oPA (M1–M3), while electron-withdrawing substituents led to higher T_c values (M6–M8), in line with these substituents' relative abilities to impact aldehyde electrophilicity.[15,17]

Monomer Synthesis and Homopolymerization. We devised and executed 2–5 step synthetic routes to substituted oPAs M1–M4 and M6–M8 (SI pgs S4–S24). Notably, during purification, monomers M6–M8 underwent carbonyl hydrate formation and oligomerization to varying extents on silica, suggesting that their ceiling temperatures were near or above room temperature. In each of these cases, the dialdehyde was obtained via vacuum sublimation.[19]

We next subjected each monomer to SnCl₄-catalyzed cationic polymerization conditions at –78 °C in DCM. The reactions were quenched by adding pyridine to sequester the Lewis acid, then the polymers were precipitated into MeOH and isolated by vacuum filtration.[10] As a baseline, the reaction of unsubstituted oPA (M5) produced cPPA (P5) in 35% isolated yield (Table 1, entry 5). Propoxy-substituted M1, butylthio-substituted M2, and hexyl-substituted M3 all possess estimated ceiling temperatures < –78 °C and were

therefore not expected to generate polymer under these conditions. Consistent with the predictions, these monomers failed to generate isolable polymers; ^{1}H NMR spectroscopic analysis following attempted precipitation from MeOH and solvent removal revealed mixtures of monomer and the corresponding dimethyl acetals (entries 1–3; see also Figure S25). In contrast to M1–M3, the estimated T_c of hexynyl-substituted M4 (–60 °C) suggested that its polymerization was feasible. Indeed, P4 was isolated in 64% yield (entry 4). Methyl ester–substituted M6, phthalimide derivative M7, and tetrafluorophthalaldehyde M8 had predicted ceiling temperatures substantially higher than that of oPA, and all three were effectively polymerized at –78 °C (entries 6–8).

Table 1. Cationic Polymerization of oPA Derivatives[a]

monomer	R =	est. T_c[b] (°C)	Yield[c] (%)	M_n (kg/mol)	Đ
M1	OPr	–122	0	–	–
M2	SBu	–86	0	–	–
M3	n-C₆H₁₃	–80	0	–	–
M4	C≡CBu	–60	64	12.3	2.2
M5	H	–36[d]	35	3.2	2.2
M6	CO₂Me	–2	48	11.7	1.7
M7	–	+43	83	25.1	1.9
M8	–	+98	53	16.2	2.0

[a]Entries 4–8 represent the average of two runs. [b]At 1 M. [c]Isolated yield. [d]Experimentally determined.

Ceiling Temperature Measurement and Thermal Analysis. While the results of the polymerizations were qualitatively consistent with our T_c estimations, we sought to evaluate these predictions quantitatively. To do so, a variable-temperature ^{1}H NMR spectroscopic method was adapted from a protocol by Kohl and co-workers (SI pgs 72–97).[20] Solutions with known initial concentrations of monomer ([M]₀) and catalyst were prepared. Then, the monomer concentration ([M]) was measured at different temperatures by integrating the aldehyde C–H resonance versus an internal standard. Consistent with the predicted ceiling temperatures, we observed dramatic differences in monomer conversion based on the phthalaldehyde substitution: hexyl-substituted M3 showed <5% conversion at –60 °C, whereas tetrafluorophthalaldehyde M8 reached >95% conversion at rt (Figure 1). In the absence of a Lewis basic quenching agent, the polymerizations were reversible; warming the reactions to the starting temperatures
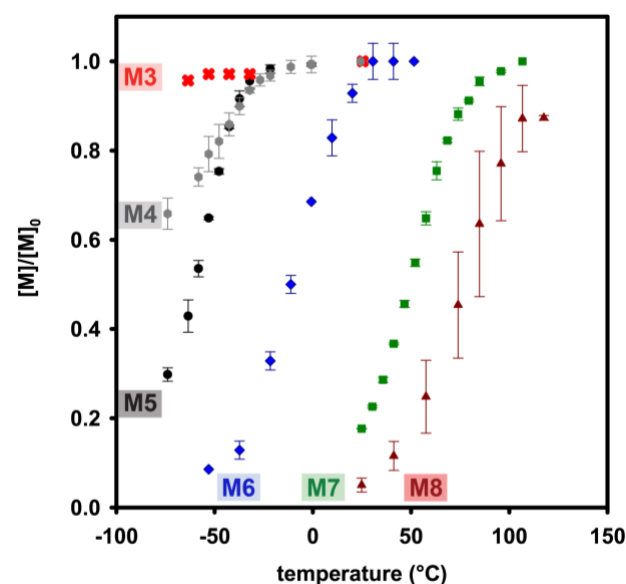
regenerated the dialdehyde monomers.

Figure 1. Plot of the normalized monomer concentrations versus temperature in the presence of 10 mol% SnCl$_4$. ([**M6**]$_0$ = 0.35 M; [M]$_0$ = 0.70 M for all other monomers.)

To quantitatively determine the ceiling temperature, the data from each reaction were plotted as $R \cdot \ln[M]$ versus $1/T$, where R is the universal gas constant. The slope and intercept of the resulting line correspond respectively to the ΔH and ΔS for the polymerization. From these two values, Eq. 2 was used to calculate the experimental T_c.[21] Performing this analysis on oPA provided a ceiling temperature of −36 °C (Table 2, entry 5), in close agreement with the results of Kohl and co-workers.[20] We could not measure T_c values for **M1**–**M3** due to the limited temperature range of the NMR probe; however, −60 °C provides an upper limit (entries 1–3).

$$T_c = \frac{\Delta H}{\Delta S + R \cdot \ln[M]_0} \qquad (2)$$

Hexynyl-substituted **M4** displayed a T_c of −23 °C, slightly *above* that of oPA. This result is consistent with the weak electron-withdrawing nature of alkynyl groups[22] (σ_m = 0.21, σ_p = 0.03 for −C≡CMe).[23] Ester-substituted **M6** exhibited a T_c of 13 °C, in line with the stronger electron-withdrawing abilities of esters (σ_m = 0.36, σ_p = 0.45 for −CO$_2$Me).[24] Both phthalimide **M7** and tetrafluorophthalaldehyde **M8** had ceiling temperatures significantly higher than room temperature (74 and 106 °C, respectively) due to the even stronger resonance- and inductive-withdrawing effects of these substituents.

While our estimations of ceiling temperatures were qualitatively accurate and useful in identifying a range of substrates to examine, there are substantial quantitative differences between computed and experimental values. Examining the thermodynamic parameters in Table 2 reveals that a contributing factor in this discrepancy was our flawed assumption that the ΔS would remain approximately constant for the different monomers. In fact, a ~7-fold difference in ΔS was observed for **M4** versus **M8**.[25]

Table 2. Thermodynamic Parameters for Polymerizing M1–M8[a]

monomer	est. T_c[b] (°C)	ΔH (kcal/mol)	ΔS (cal/mol•K)	expt. T_c (°C)
M1[d]	−122	–	–	< −60
M2[d]	−86	–	–	< −60
M3[d]	−80	–	–	< −60
M4[d]	−60	−0.90	−2.9	−23
M5[d]	n/a	−3.0	−11.9	−36
M6[e]	−2	−4.9	−14.9	+13
M7[f]	+43	−7.0	−19.3	+74
M8[f]	+98	−7.9	−20.1	+106

[a]Entries 4–8 represent the average of two runs. [b]At 1 M. [c]Corrected to 1 M. [d]CD$_2$Cl$_2$ solvent. [c]CDCl$_3$ solvent. [d]1,1,2,2-Tetrachloroethane-d_2 solvent.

Following purification,[12] the polymers' thermal decomposition temperatures (T_d) were measured by differential scanning calorimetry (DSC; SI pgs S49–S71).[26] A positive relationship between T_c and T_d was apparent, with T_d ranging from 109 °C for **M5** to 196 °C for **M8** (Figure 2A). Interestingly, polymer **P8** was the only polymer to exhibit a glass transition *below* its decomposition temperature (Figure 2B), suggesting that **P8** could have processing advantages over unsubstituted PPA.
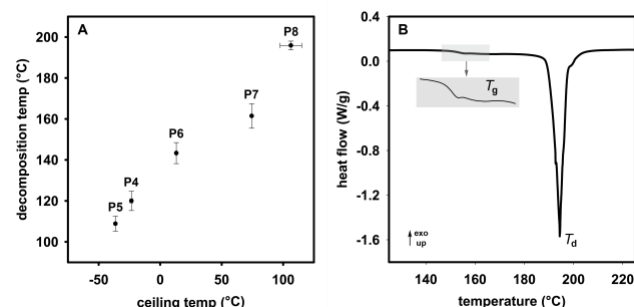

Figure 2. (A) Plot of decomposition temperature (via DSC) versus the experimental ceiling temperature for **P4**–**P8** (via ^{1}H NMR spectroscopy). (B) DSC thermogram for **P8**.

Cationic Copolymerization. To elucidate the impact of copolymer composition on thermal stabilities, we copolymerized **M5** with **M6** at feed ratios ranging from 0–100 mol% **M6** (SI pgs S54–S62).[27] Following purification, the cumulative copolymer composition was estimated via ^{1}H NMR spectroscopy. A linear trend between copolymer composition and feed ratio was evident (Figure 3A), suggesting either an alternating or statistical sequence. Thermal analysis of the copolymers revealed a near-linear relationship between copolymer composition and T_d (Figure 3B). The slight non-linearity is likely a result of differing levels of residual Lewis acid remaining in the (co)polymers after purification.[12,28] A similar trend in decomposition temperature has been reported for copolymers of oPA with ethyl glyoxylate.[13] These results demonstrate that PPA substitution patterns and incorporation ratios can be

rationally designed to obtain copolymers with targeted thermal properties, though improvements to the purification process will likely be required to ensure consistent results.
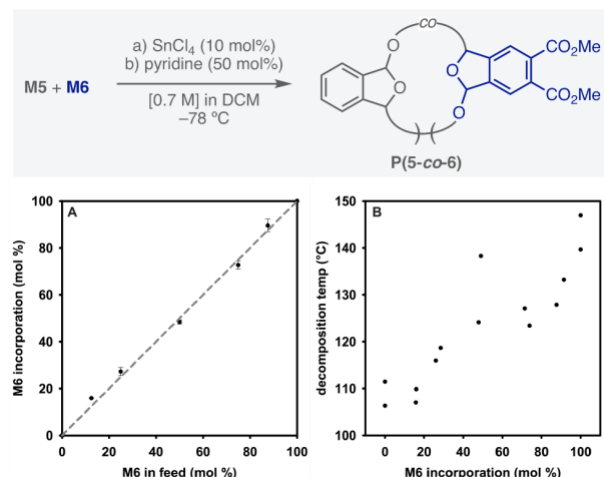

Figure 3. (A) Plot of **M6** incorporation in **P(5-*co*-6)** (via ^{1}H NMR spectroscopy) versus **M6** composition in the feed. The dashed line is for a 1:1 relationship. (B) Plot of decomposition temperature (via DSC) versus **M6** incorporation in **P(5-*co*-6)**.

Microcapsule fabrication. In previous work, cPPA was used to form triggerable core–shell microcapsules.[29] The new PPA derivatives described herein could generate capsules that exhibit different surface functionalities, specific ion coactivators,[29b] and rates of payload release. For a preliminary study, **P6** was prepared on gram scale in 76% yield (SI pg S71) and subjected to the previously described microencapsulation conditions optimized for unsubstituted cPPA (SI pgs S98–S99).[29a] Briefly, oil-in-water emulsions comprised of **P6**/jojoba oil/DCM in aqueous poly(vinyl alcohol) were generated via a microfluidic flow focusing device. Rapid evaporation of the DCM followed by filtering and washing furnished microcapsules with an average diameter of 228 ± 5 μm. Scanning electron microscopy (SEM) confirmed these capsules exhibited a core–shell architecture, with an estimated shell-wall thickness of 11 μm (Figure 4). These **P6** microcapsules represent a potential starting point to generate anionic, cationic, and labelled depolymerizable capsules via post-encapsulation functionalization reactions.
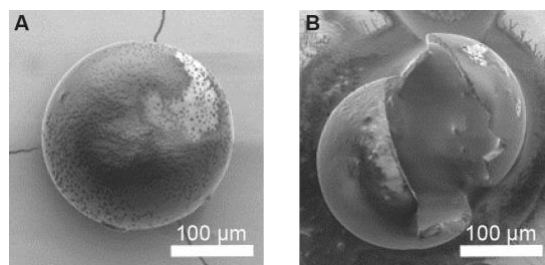

Figure 4. SEM images of (A) intact and (B) ruptured **P6** microcapsules.

To summarize, seven substituted *o*-phthalaldehyde derivatives were synthesized and subjected to cationic polymerization conditions. As predicted computationally, several of these compounds were unreactive at −78 °C due to their low ceiling temperatures; however, four new polyphthalaldehydes bearing alkyne, ester, imide, and fluorine substituents were successfully synthesized due to their higher ceiling temperatures. Remarkably, poly(tetrafluorophthalaldhyde) is both highly stable and likely thermally processable. We anticipate that these (co)polymers, as well as derivatives synthesized via post-polymerization modification, will enable researchers to access degradable materials with tunable thermal, physical, and chemical properties. Moreover, the combined computational and experimental method to predict and measure ceiling temperatures should help guide the synthesis of new PPA derivatives.

ASSOCIATED CONTENT

Supporting Information. Experimental details, characterization data, synthetic procedures.

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structure–property relationships

cat.
Lewis acid

T_c range ≥ 165 °C

R—

8 examples

Δ

T_d range = 87 °C