Polymers

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# Self-Immolative Poly(4,5-dichlorophthalaldehyde) and its Applications in Multi-Stimuli-Responsive Macroscopic Plastics**

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***Abstract:*** *End-capped poly(4,5-dichlorophthalaldehyde) ($PCl_2PA$), which is a new self-immolative $CD_r$ polymer with the unique capability of depolymerizing continuously and completely in the solid state when an end cap is cleaved from the polymer by reaction with a specific molecular signal, is described. End-capped poly(4,5-dichlorophthalaldehyde) is sufficiently stable to enable patterning of three-dimensional macroscopic polymeric materials by selective laser sintering. These unique materials are capable of 1) autonomously amplifying macroscopic changes in the material in response to specific molecular inputs, and 2) altering their responses depending on the identity of the applied signal. Thus, not only does end-capped $PCl_2PA$ provide new and unique capabilities compared to the small subset of existing $CD_r$ polymers, but it also provides access to a new class of stimuli-responsive materials.*

**B**iological materials, such as those found in Touch-me-nots and Venus flytraps, provide amplified, macroscopic responses to local inputs. They do so by communicating the detection event to distant regions of the plant.[1,2] Other materials in plants, such as those found in the leaf system of rhododendrons, alter the shape and orientation of the leaves, where the type of macroscopic response is dictated by the identity of the environmental signal.[3] These various capabilities are achieved autonomously, and require signal amplification to increase the magnitude and rate of the response, as well as the distance that the response travels from the site of initiation.[1,4]

In contrast, typical synthetic, macroscopic, polymeric materials are far less capable, traditionally providing a single response to an abundant signal, and rarely providing an amplified or global response to a local input.[5] Herein, we describe a new self-immolative $CD_r$ polymer (i.e. poly(4,5-dichlorophthalaldehyde); abbreviated $PCl_2PA$) that enables polymeric materials to display behavior that is reminiscent of the complex responses of biological materials in plants. We refer to polymers that provide *c*ontinuous *d*epolymerization once the stimulus selectively cleaves the *r*eaction-based detection unit as $CD_r$ polymers.[6] This behavior includes amplified macroscopic responses to specific applied signals, as well as signal matching, where the output of the material is altered depending on the identity of the input signal. These dual features in materials are made possible by the thermal stability of $PCl_2PA$ (which enables selective laser sintering of the polymer to create desired macroscopic, three-dimensional materials), and by the ability of a specific signal to induce *c*ontinuous depolymerization of $PCl_2PA$ once a reaction-based detection unit (end cap) is cleaved selectively from the polymer in response to the specific signal (Figure 1).[6] In other words, a molecular detection event that occurs on the surface of a material made from $PCl_2PA$ causes macroscopic changes in the material to the depth ($z$ direction) and/or $x$,$y$ distance that the $CD_r$ polymer extends (Figure 1).

We designed $PCl_2PA$ to depolymerize within solid-state polymeric materials, which provide a nonpolar environment that limits the ability of other $CD_r$ polymers to depolymerize when exposed to specific molecular signals at ambient temperatures.[7,8] $PCl_2PA$, in contrast, depolymerizes readily in the solid state,[9] and has sufficient thermal stability to enable rapid prototyping of macroscopic plastics by additive manufacturing processes.[11,12] The resulting materials provide unique capabilities for synthetic polymeric materials, such as 1) responding selectively, often several times in sequence, in ways that match the identities of the applied signals, and 2) providing macroscopic, amplified responses.[13] Moreover, these synthetic materials can be regenerated after they respond to a specific signal if the small molecule product of the depolymerization reaction is recovered and used to prepare fresh polymer (Figure 1). Thus, $PCl_2PA$-based materials have the potential for sustainable life cycles in which their building blocks are generated from the decomposition products of aged predecessors.

Our design of poly(4,5-dichlorophthalaldehyde) is based on the mechanistic hypothesis that electron-withdrawing groups placed *para* to benzylic acetals should increase the thermal stability of the acetals,[15,16] which otherwise are unstable functionalities, even under ambient conditions.[17] We reasoned that strategic placement of electron-withdrawing groups *para* to benzylic acetals would disfavor formation of oxocarbenium ion intermediates, which would otherwise cause nonspecific degradation. In the context of $PCl_2PA$, this predicted stabilizing effect requires placement of two *para* electron-withdrawing substituents to stabilize both acetals on each side of every repeating unit of $PCl_2PA$, since both sides contain benzylic acetals.

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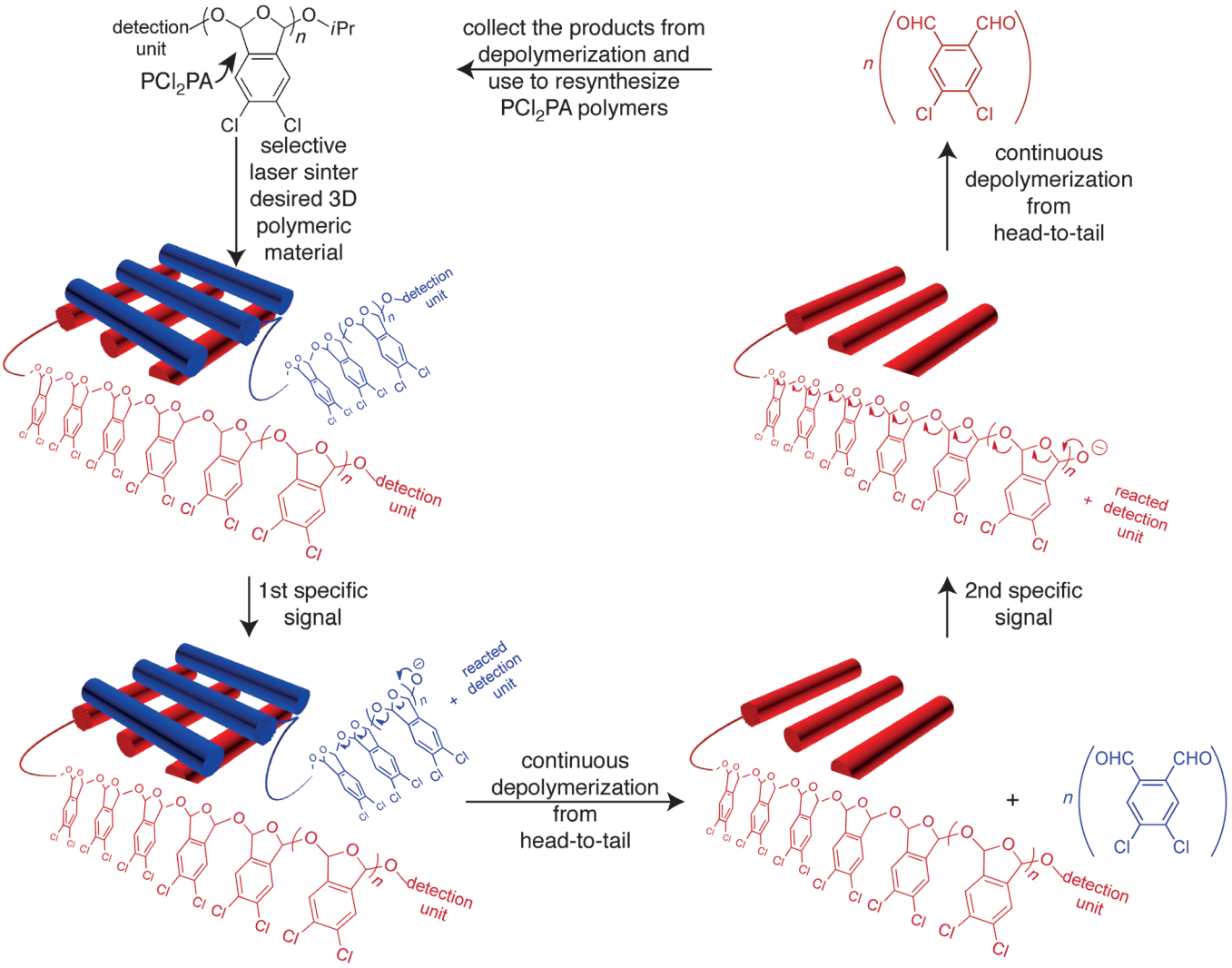


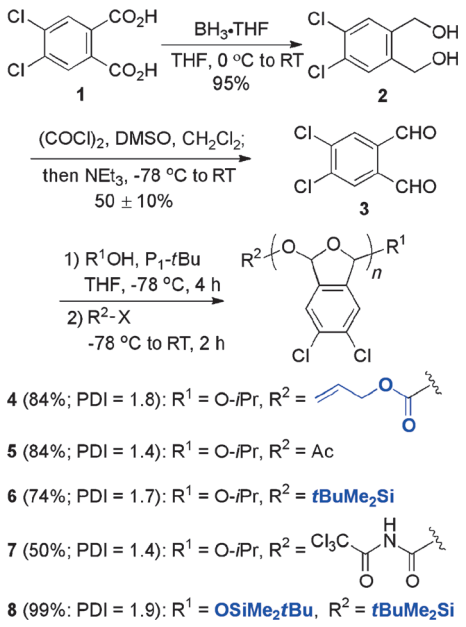

***Figure 1.*** Illustration of a multi-stimuli-responsive, self-powered, 3D polymeric material with amplified global responses to specific local signals. The entire material is composed of patterned poly(4,5-dichlorophthalaldehyde) ($PCl_2PA$), but portions of the material contain $PCl_2PA$ with different detection units. This arrangement enables certain portions of the material to respond to one stimulus, while other portions respond to a different stimulus. When the material responds, $PCl_2PA$ depolymerizes continuously and completely from head to tail, which provides an amplified response that translates a specific detection event into a macroscopic response in the material. Recovery of the products after depolymerization enables regeneration of the $PCl_2PA$ polymers, thereby providing a pathway for realizing sustainable stimuli-responsive materials.

To test this idea, we compared the thermal stability of $PCl_2PA$ versus poly(phthalaldehyde) (PPA). We prepared $PCl_2PA$ by first generating the monomer (**3**; Scheme 1), and using anionic polymerization conditions ($R^1$-OH as initiator) followed by end capping with an electrophilic detection reagent ($R^2$-X) to access stimuli-responsive polymers, where the detection reagent, and in some cases the initiator, provide a stimuli-responsive detection unit to $PCl_2PA$. Thus, the synthetic route for preparing $PCl_2PA$ derivatives that respond to different external signals requires only changing the electrophilic detection reagent or initiator, rather than developing a new synthesis for each new desired response. Example detection units include those that respond to $Pd^0$ (**4**, Scheme 1),[18] fluoride (**6** and **8**),[19] and 254 and 365 nm light (see Figure S1 in the Supporting Information),[20] as well as control units that are inert to applied signals (**5** and **7**).

End-capped $PCl_2PA$ (e.g. Alloc-$PCl_2PA$-O*i*Pr; **4**) is bench stable at 23 °C, open to the air, with $<1\,\%$ degradation occurring over 130 days (Figure S9).[21] In contrast, Alloc-end-capped poly(phthalaldehyde)[22] (abbreviated Alloc-PPA-O*i*Pr), which lacks the hypothesized stabilizing effects of the electron-withdrawing *para*-chloro groups, degraded by 95 % under the same conditions (Figure S2). Thermal gravimetric analysis (TGA) of Alloc-$PCl_2PA$-O*i*Pr (**4**) and Alloc-PPA-O*i*Pr confirms[23] that **4** is stable at temperatures approximately 40 °C higher than Alloc-PPA-O*i*Pr (Figure S3), with the onset of thermal degradation of Alloc-$PCl_2PA$-O*i*Pr occurring at $205 \pm 2$ °C.

This increase in the thermal stability for $PCl_2PA$ versus PPA does not prevent end-capped $PCl_2PA$ from depolymerizing completely and continuously from head to tail at room temperature when dissolved in THF and exposed to a specific applied signal. For example, Alloc-$PCl_2PA$-O*i*Pr (**4**) depoly-




***Scheme 1.*** Synthesis of 4,5-dichlorophthalaldehyde (**3**) and poly(4,5-dichlorophthalaldehyde). Reactive detection units are highlighted in blue. The yield of **2** to **3** is provided as the average and standard deviation from nine experiments. PDI = polydispersity index.

merizes completely and selectively when exposed to $Pd^0$ for 30 min at 23 °C in THF (Figure S4), whereas control polymer Ac-$PCl_2$PA-O*i*Pr (**5**), which contains acetate (Ac) as an end cap that does not respond to $Pd^0$, shows no degradation under the same conditions (Figure S4). Similarly, TBS-$PCl_2$PA-O*i*Pr (**6**) depolymerizes completely when exposed to fluoride in a THF/water mixture, whereas a control polymer (**7**), which contains an unresponsive end cap, shows negligible depolymerization (Figure S5).

End-capped $PCl_2$PA also depolymerizes in the solid state. Exposure of solid cylinders (3.5 mm diameter × 1.8 mm tall), made from either TBS-$PCl_2$PA-OTBS (**8**) or Ac-$PCl_2$PA-O*i*Pr (**5**) (Figure S6), to 12 mM fluoride in a 160:1 mixture of MeCN/phosphate buffer (0.1M, pH 7.1; the monomers are soluble in this solution, while the polymers are not) caused the cylinder made from TBS-$PCl_2$PA-OTBS (**8**) to disappear over a period of 5 h (Figure S6, Video S1). In contrast, and as predicted, the cylinder made from Ac-$PCl_2$PA-O*i*Pr (**5**) did not change significantly in size (Figure S6, Video S2).

We verified the selective solid-state depolymerization results by concentrating the solvents (after 5 h of exposure to fluoride) and re-dissolving the residues in THF (polymers and monomers both are soluble in this solvent). Gel permeation chromatography (GPC) analysis of the THF solution from the reaction of the cylinder composed of TBS-$PCl_2$PA-OTBS (**8**) with fluoride revealed small molecule products (Figure S7), which confirms that the solid object made from **8** depolymerized rather than simply dissolving once a TBS detection unit was cleaved from the polymer. In contrast, the GPC chromatogram from the reaction of the cylinder made from Ac-$PCl_2$PA-O*i*Pr (**5**) with fluoride revealed polymer with a retention time that is identical to the retention time of the original sample (Figure S7). These combined GPC results demonstrate that depolymerization of $PCl_2$PA occurs in the solid state, and exhibits selectivity that is consistent with the selectivity observed in solution-phase experiments.

Consequently, we used $PCl_2$PA and selective laser sintering[10,11,25] to prepare 3D, multi-stimuli-responsive macroscopic plastics to demonstrate the ability to pre-pattern 3D objects that are capable of responding in different ways (and, presumably resulting in different functions) depending on the identity of the applied molecular signal. Video S3 depicts this selective laser sintering process in real time using an inexpensive $CO_2$ laser cutter (on low power) and irregularly

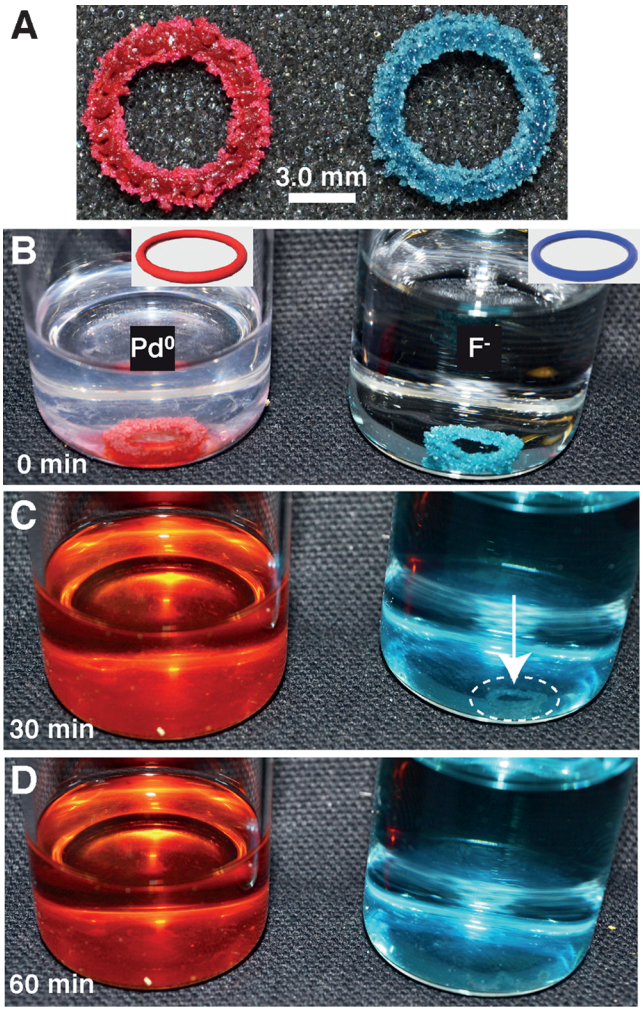



***Figure 2.*** Solid-state depolymerization of laser-sintered 3D rings in response to specific signals. a) Photographs of two rings made from either Alloc-$PCl_2$PA-O*i*Pr (**4**) and red dye (left ring) or TBS-$PCl_2$PA-OTBS and blue dye (right ring). The left ring was exposed to 2.7 mM $[Pd(PPh_3)_4]$ and 143 mM benzenesulfinic acid sodium salt in 7.5:7.5:1 benzene/MeOH/$CH_2Cl_2$, and the right ring was exposed to 111 mM tetrabutylammonium fluoride (TBAF) in 17:1 MeCN/100 mM pH 7.1 phosphate buffer. Time-lapsed photographs of the rings show b) initial exposure of the rings to the signal, as well as rapid degradation of the rings after c) 30 min and d) 60 min. The dotted ellipse in (c) depicts the location of small quantities of the ring made from **8** that remain after 30 min exposure to fluoride. The photographs also illustrate the ability of the 3D rings to release admixed dye upon depolymerization in response to an applied signal.

shaped $PCl_2PA$ granules[26] with average lengths of $26 \pm 16$ μm (Figure S8).[27]

Figure 2 A shows examples of 7.5 mm diameter 3D rings that we prepared from either TBS-$PCl_2PA$-OTBS (**8**) or Alloc-$PCl_2PA$-O*i*Pr (**4**) using the selective laser sintering process. We verified the fidelity of the fabrication procedure first by using GPC to analyze the polymers before and after sintering.[28] The data reveal negligible levels of depolymerization caused by the sintering method for both TBS-$PCl_2PA$-OTBS (**8**) and Alloc-$PCl_2PA$-O*i*Pr (**4**; Figure S9). Moreover, the sintering process reproduces the intended width of the objects, albeit with $0.50 \pm 0.06$ mm increased line width compared to the dimensions in the electronic image (Table S1) of objects with millimeter-sized lines.

Exposure of the 3D rings to their respective signals (i.e. $Pd^0$ along with benzenesulfinic acid sodium salt—an additive—for rings made from **4**, and fluoride for rings made from **8**) caused rapid solid-state depolymerization that was complete in less than one hour (Figure 2, B–D). Control experiments reveal that rings constructed from Alloc-$PCl_2PA$-O*i*Pr (**4**) do not change in shape or size when exposed only to benzenesulfinic acid sodium salt (Figure S10). Likewise, rings composed of TBS-$PCl_2PA$-OTBS (**8**) do not change when exposed to tetrabutylammonium chloride instead of tetrabutylammonium fluoride (the source of fluoride) under the same conditions (Figure S11). These two control experiments demonstrate that the ability of $PCl_2PA$ to depolymerize selectively in the solid state is retained, even after selective laser sintering to create 3D materials. Finally, Figure 2 illustrates that 3D materials made from sintering end-capped $PCl_2PA$ are capable of releasing admixed contents (dyes in this case) when they depolymerize in response to specific signals (Figure 2, B–D).

Multi-stimuli-responsive macroscopic materials that are inspired by the input-output matching behavior of rhododendrons also are readily accessible. In this case, $PCl_2PA$ polymers with different end caps are incorporated into a single 3D object. The backbones of the polymers remain the same, but the composition of the detection units differ, which provides regions of 3D materials that respond to different signals. Figure 3 shows two examples of 3D gratings to illustrate this concept.

The first grating has square pores (Figure 3 A) and, when exposed to fluoride, converts into freestanding, horizontal cylinders through depolymerization of TBS-$PCl_2PA$-OTBS (**8**, blue; Figure 3 A). These cylinders (made from Alloc-$PCl_2PA$-O*i*Pr (**4**) and red dye) depolymerize when exposed to a second specific signal (i.e. $Pd^0$), thus completing a dramatic macroscopic change in the grating in response to multiple stimuli.

The second grating (Figure 3 B) is similar to the first in its mechanism of response, but has three layers, which allows it to switch shapes and sizes of the pores (and, hence, function) sequentially in response to multiple applied signals (Figure 3 C). For example, exposure of this three-layer grating to $Pd^0$ causes depolymerization of the red triangles (made from Alloc-$PCl_2PA$-O*i*Pr (**4**) and red dye), which reveals a two layer grating and pores with new shapes and sizes (Figure 3 C). Exposure of this two-layer grating to fluoride causes the blue rings (made from TBS-$PCl_2PA$-OTBS (**8**) and blue dye) to depolymerize, to leave a one-layer grating with square pores (Figure 3 C). This final layer is made from orange dye and Ac-$PCl_2PA$-O*i*Pr (**5**), the latter of which is inert to fluoride and $Pd^0$ and does not depolymerize when exposed to these specific signals. Other examples of multi-stimuli-responsive 3D polymeric materials are possible as well,

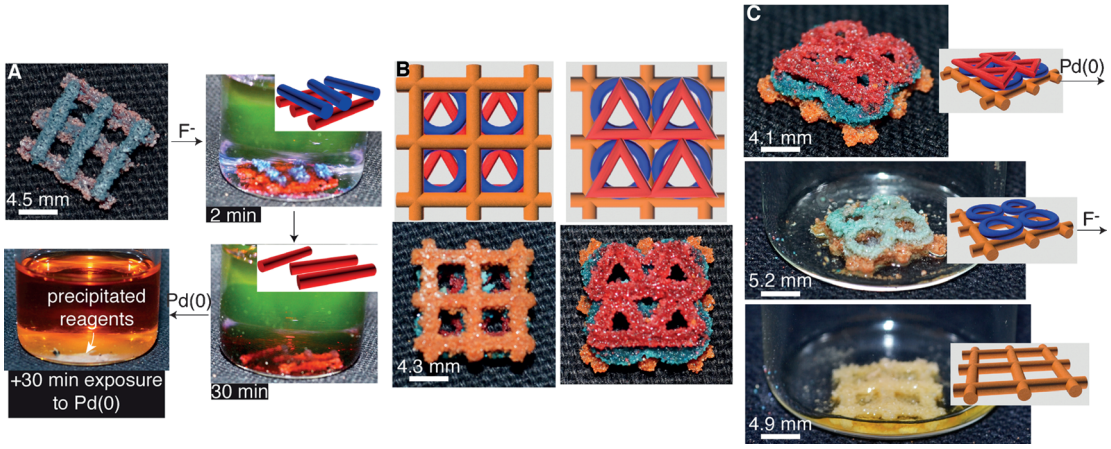



***Figure 3.*** Selective laser-sintered 3D gratings that display orthogonal repsonses to multiple stimuli. a) A two-layer grating made from Alloc-$PCl_2PA$-O*i*Pr (**4**) and red dye (bottom cylinders), and TBS-$PCl_2PA$-OTBS (**8**) and blue dye (top cylinders). Exposing the grating to a 111 mM TBAF solution (17:1 MeCN/100 mM pH 7.1 phosphate buffer) causes rapid depolymerization of TBS-$PCl_2PA$-OTBS (**8**) and dissolution of the blue cylinders. Likewise, exposure of the remaining red cylinders to 2.7 mM [$Pd(PPh_3)_4$] and 143 mM benzenesulfinic acid sodium salt (7.5:7.5:1 benzene/MeOH/$CH_2Cl_2$) for 30 min results in conversion of the red cylinders into soluble products. b) A three-layer grating—made from Alloc-$PCl_2PA$-O*i*Pr (**4**) and red dye (triangles), TBS-$PCl_2PA$-OTBS (**8**) and blue dye (rings), and Ac-$PCl_2PA$-O*i*Pr (**5**) and orange dye (squares)—responds to fluoride and $Pd^0$ in the opposite order as the two-layer grating in (a). In this second case (c), exposing the grating to $Pd^0$ causes selective depolymerization of the triangles, and subsequent exposure of the resulting two-layer grating to fluoride causes depolymerization of the rings. The final layer of squares is unreactive to either $Pd^0$ or fluoride, and therefore remains as a grid with new shapes and sizes of pores (and function) compared with its two- and three-layer predecessors.

simply by varying the composition of the detection units on $PCl_2PA$. Such materials should display selective and orthogonal responses to a variety of applied signals, such as UV light,[20,22] heat,[29] inorganic species (other than $Pd^0$ and fluoride), and possibly even enzymes.[30]

Finally, $PCl_2PA$ can be regenerated by recovery of the product of depolymerization (i.e. 4,5-dichlorophthalaldehyde, **3**), which is the monomer for preparing $PCl_2PA$ (Scheme 1). Direct purification of 4,5-dichlorophthalaldehyde (**3**) after depolymerization proved inefficient,[31] so instead we reduced the dialdehyde to diol **2** directly after the depolymerization reaction, and purified the diol to intersect the synthesis and polymerization scheme in Scheme 1. By using this process, we recovered 65 % of pure diol **2** when 1) $PCl_2PA$-based stimuli-responsive materials depolymerized completely, 2) the dialdehyde was reduced, and 3) the resulting diol (**2**) was purified. This recovery and regeneration process offers an opportunity for a sustainable life cycle for $PCl_2PA$-based materials.

In conclusion, this ability to create 3D, macroscopic, self-powered, sustainable, multi-stimuli-responsive polymeric materials with amplified global responses to specific applied molecular signals provides a step forward towards the goal of creating materials that resemble the remarkable response properties of plants. These advances in stimuli-responsive materials are made possible by the development of $PCl_2PA$, which, when outfitted with other detection units (see Figure S1 for examples), should enable use of $PCl_2PA$-based materials in a variety of contexts, including low-energy recycling of plastics, multiuse plastics, controlled release, and smart coatings and materials. Importantly, the procedure for preparing the $PCl_2PA$ polymers for these applications remains the same; only the composition of the detection reagent or initiator need be altered to change the signal to which the polymer responds. This synthetic simplicity and versatility should make $PCl_2PA$ a privileged, new $CD_r$ polymer for applications in a variety of contexts, including for creating advanced stimuli-responsive polymeric materials.

**Keywords:** depolymerization · materials science · polymerization · polymers · selective laser sintering

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Figure S12), which is consistent with similar observations for PPA.[24] Additional TGA experiments on Ac-$PCl_2$A-O*i*Pr and Ac-PPA-O*i*Pr, which contain ester rather than carbonate end caps (Alloc-$PCl_2$A-O*i*Pr and Alloc-PPA-O*i*Pr contain carbonate end caps), reveal a similar 40 °C increase in the stability of the $PCl_2$PA derivative over the PPA derivative, as well as 8–14 °C increases in stability for the Ac-end-capped derivatives relative to the Alloc-end-capped variants (i.e. Ac-PPA-O*i*Pr is 14 °C more stable than Alloc-PPA-O*i*Pr, and Ac-$PCl_2$A-O*i*Pr is 8 °C more stable than Alloc-$PCl_2$A-O*i*Pr). This consistent trend in stability between $PCl_2$PA and PPA, as well as Ac versus Alloc suggests that the TGA measurements reflect the thermal stability of the polymers, rather than differences in the boiling points of the thermal decomposition products.

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