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Patterned Plastics That Change Physical Structure in Response to Applied Chemical Signals

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Abstract: This Communication describes a strategy for designing stimuli-responsive plastics that are capable of responding to chemical signals in the environment by changing shape. The plastics consist of patterned mixtures of poly(phthalaldehyde) polymers in which each polymer contains a different end-capping group, or “trigger”. Each polymer within the plastic is capable of responding to a different signal and depolymerizing once the signal reacts with the trigger. This process of depolymerization enables the plastic to alter its physical features quickly and with a magnitude that depends on the length of the responsive polymer.

This Communication describes a first generation design strategy for preparing plastics that are capable of altering their macroscopic appearance autonomously in response to specific external chemical signals. These plastics are prepared by patterning derivatives of poly(phthalaldehyde) (Figure 1) into defined regions within the plastic, where each region contains a derivative of poly(phthalaldehyde) with a different end-capping group (i.e., trigger). These triggers are cleaved from the polymer when they sense and react with specific chemical signals; the resulting hemiacetal-terminated polymer (Figure 1) then depolymerizes rapidly to effect a structural change in the plastic.

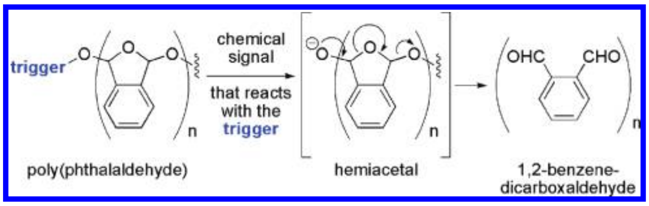


Figure 1. Design of signal-responsive polymers that depolymerize selectively in the presence of a specific chemical signal.

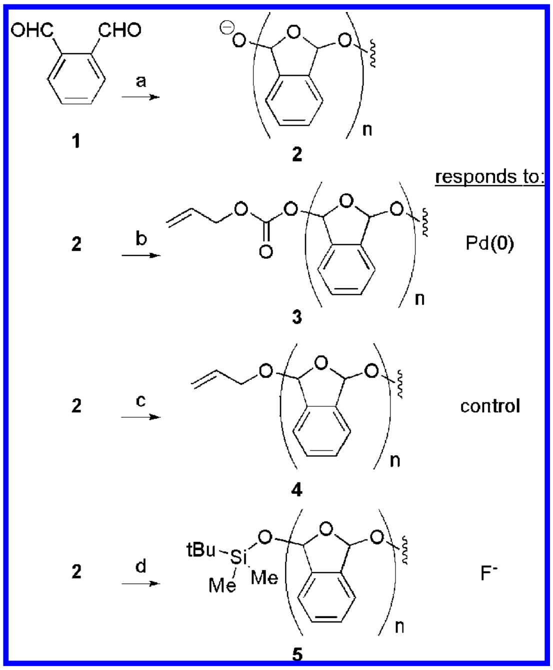
The design strategies presented in this Communication offer a starting point for preparing new types of *macroscopic* “smart” materials that are capable of adjusting their shape, structure, or surface properties in response to *specific* chemical signals. Such materials may prove useful in a variety of applications including smart coatings, casings, packaging, and diagnostics.

Our first effort in preparing these types of responsive polymers is based on poly(phthalaldehyde), a polymer that was used by Fréchet and Willson and further developed by Ito and Willson as a creative solution to a problem of sensitivity in photoresist chemistry.[1] When exposed to UV light in the presence of a photoacid, poly(phthalaldehyde) depolymerizes:[1] the photoacid cleaves one of the acetal linkages in the polymer, and the resulting truncated polymer depolymerizes readily and completely. This depolymerization occurs because the ceiling temperature of poly(phthalaldehyde) without an end-capping group (i.e., the hemiacetal form in Figure 1) is −40 °C.[1] In the presence of an end-capping group (e.g., acetate), however, the polymer is stable up to 180 °C.[1]

We recognized that the end-capping group in poly(phthalaldehyde) could serve an important role in controlling whether the polymer remained intact or depolymerized.[2] By end-capping the polymer with the functionality that reacts with a specific chemical signal, we reasoned that we could design polymers (and ultimately plastics) that respond selectively and autonomously to chemical signals in the environment. We also recognized that only one reaction of a trigger with a chemical signal would be needed to cause an entire polymer to depolymerize, which would result in a much larger structural change in a responsive plastic than otherwise would be expected for a single reaction between two functional groups.

We synthesized poly(phthalaldehyde) using anionic polymerization conditions that were modified from those reported by Ito and Willson (Scheme 1).[1] Responsive polymers **3** and **5** were designed to respond to Pd(0) or fluoride, respectively. Polymer **4** was prepared as a control to demonstrate that the triggers in polymers **3** and **5** are responsible for the selective response characteristics.

Scheme 1. Synthesis of Signal-Responsive Poly(phthalaldehyde) Polymers[a]



[a] (a) *n*-BuLi (0.003 equiv), THF, −80 °C, 10−14 days; (b) allyl chloroformate, −80 °C, 72 h, 94%; (c) allyl triflate, −80 °C, 96 h, 83%; (d) TBSCl, −80 °C, 72 h, 86%.

Polymers **3**−**5** are stable for up to 15 h (i.e., they show no signs of depolymerization over the period that we monitored them) as 0.01 M solutions in tetrahydrofuran (THF) at 25 °C under an atmosphere of

10.1021/ja104420k

Table 1. Solution-Phase Response Rates of Polymers **3**−**5** to Various Signals[a]

Line	Polymer	Signal	Equiv of Signal[h]	Exposure Time (min)	Polymer Remaining (%)[I]
1	**3**[b]	none	−	930	95
2	**3**[b]	Pd(0)[e]	0.40	5	0
3	**3**[b]	Pd(0)[e]	0.08	5	10
4	**3**[b]	Pd(0)[e]	0.01	5	89
5	**4**[c]	none	−	960	99
6	**4**[c]	Pd(0)[e]	0.5	320	95
7	**4**[c]	F^-[f]	0.5	25	97
8	**5**[d]	none	−	1310	97
9	**5**[d]	none[g]	−	1080	96
10	**5**[d]	F^-[f]	0.5	1	0

[a] All experiments were performed at 0.01 M concentrations of polymer in THF and at 25 °C, unless noted otherwise. [b] $M_n = 19.9$ kDa. [c] $M_n = 21.7$ kDa. [d] $M_n = 15.3$ kDa. [e] $Pd(PPh_3)_4$. [f] Delivered by adding 0.4 μL of 0.3 M TBAF in 1:2 THF−phosphate buffer (0.1 M, pH 7.1) to polymer **4** in 260 μL of THF. [g] 1:2 THF−phosphate buffer (0.1 M, pH 7.1). [h] Molar equivalents in relation to the polymer. [I] Calculated from GPC data using the area (A) of peaks and the equation $[A_{polymer}/(A_{polymer} + A_{monomer})] \times 100$.

air (Table 1, entries 1, 5, and 8). However, when polymer **3** is exposed to catalytic quantities of $Pd(PPh_3)_4$, the polymer depolymerizes within minutes in a dose-dependent manner (entries 2−4). Time-dependent ^1H NMR spectra in the Supporting Information reveal that this Pd(0)-triggered depolymerization is quantitative and rapid and occurs without generation of byproducts; the only peaks apparent in the ^1H NMR spectrum correspond to the monomer, 1,2-benzenedicarboxaldehyde. Gel permeation chromatography (GPC) chromatograms reveal similar trends (see the Supporting Information).

Control polymer **4** showed negligible levels of depolymerization after exposure to 0.5 equiv of $Pd(PPh_3)_4$ for >5 h, which was expected based on the known relative reactivities of allyl ethers versus allyl carbonates.[3] In the presence of fluoride, control polymer **4** also showed negligible levels of depolymerization (entry 7). Polymer **5**, in contrast, depolymerized completely in <1 min when exposed to 0.5 equiv of fluoride.

We prepared stimuli-responsive plastics using these polymers, as shown in Figure 2. Polymer **5** was patterned as a cylinder within a film of polymer **4** (the overall dimensions of the sheet are 14.6 mm ×13.4 mm × 490 μm). Since polymers **4** and **5** are almost identical in chemical composition (they differ only in end-capping groups), they do not phase segregate, and the sheet appears homogeneous upon visual inspection (Figure 2B). When the film is immersed in ethyl acetate (4 mL) and exposed to a solution of tetrabutylammonium fluoride (TBAF) (1.8 mL, 0.3 M in 1:2 THF−0.1 M phosphate buffer, pH 7.1), polymer **5** depolymerizes completely within 15 min to reveal a cylindrical hole in the plastic sheet (Figure 2C).

In conclusion, we have demonstrated a new design strategy for preparing plastics that are capable of altering their physical structure in a predefined way when exposed to an external chemical signal. The polymers used in this study are more sensitive to nonspecific changes in external conditions (e.g., pH) than more traditional structural plastics, but we expect that macroscopic materials composed of these types of responsive polymers will find applications in settings where rapid and selective response characteristics are more important than long-term structural stability. We also anticipate that the modular construction strategy we describe for preparing these materials will facilitate the fabrication of plastics that respond to a variety of signals, including enzymes, small molecules, and metals.

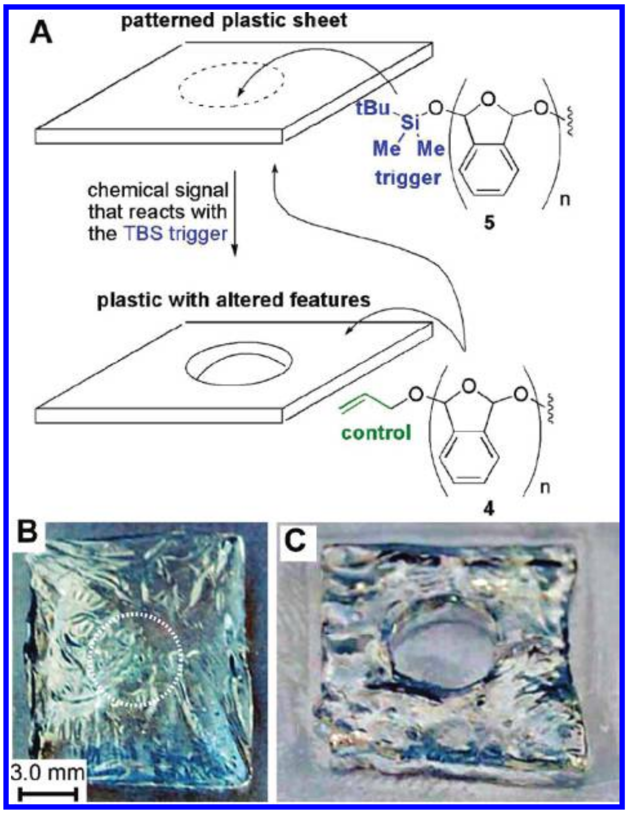


Figure 2. A patterned plastic film that reveals a cylindrical hole when exposed to fluoride. (A) Design strategy for a prototype stimuli-responsive plastic. (B) Photograph (top view) of a film consisting of polymer **5** patterned as a cylinder in a film of polymer **4**. The dotted white line indicates the approximate position of polymer **5**. (C) Photograph (oblique view) of the film after 15 min of exposure to fluoride and after washing the film with diethyl ether to remove 1,2-benzenedicarboxaldehyde after depolymerization. The colors in the photographs were enhanced in Adobe Photoshop using the "auto levels" function. The original photographs are in the Supporting Information.

Acknowledgment. This work was supported in part by DARPA (N66001-09-1-2111), the Arnold and Mabel Beckman Foundation, the Camille and Henry Dreyfus Foundation, 3M, Mr. Louis Martarano, and The Pennsylvania State University.

Supporting Information Available: Experimental procedures and supporting spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA104420K