MRS Communications (2015), 5, 191–204
© Materials Research Society, 2015
doi:10.1557/mrc.2015.28

MRS Communications

Polymers/Soft Matter Prospective Article

Depolymerizable polymers: preparation, applications, and future outlook

Joshua A. Kaitz, Olivia P. Lee, and **Jeffrey S. Moore,** Department of Chemistry and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

Address all correspondence to Jeffrey S. Moore at **jsmoore@illinois.edu**

(Received 18 March 2015; accepted 24 April 2015)

Abstract

Depolymerizable polymers are stimuli-responsive materials triggered to depolymerize rapidly and completely into their constituent monomers on command. Applications include triggerable vehicles for controlled release, restructurable materials, disappearing or sacrificial composites, and lithographic resists. Owing to their widespread utility, significant efforts have aimed to prepare and explore depolymerizable polymers and their corresponding triggers. This "Prospective" highlights advances since their discovery over a half-century ago, discusses methods in their preparation, and presents recent developments in triggered depolymerization. It also surveys applications that harness these polymers' unique properties, while offering insights into research directions that may contribute to progress in this dynamic field.

Introduction

Depolymerizable polymers and closely related self-immolative polymers are triggerable materials that respond to a specific stimulus by unzipping into small molecules. They have been developed as triggerable delivery vehicles, recyclable and restructurable materials, disappearing or sacrificial composites, and lithographic resists.[1–6] Specifically, depolymerizable polymers regenerate constituent monomers by chemically reversing propagation,[7] while self-immolative polymers afford small molecular products that differ from parent monomers.[1–3] For either case, the unzipping sequence is initiated by chemically or physically cleaving the polymer backbone, side-chains, or end-groups to expose a reactive intermediate that subsequently liberates molecular products in a stepwise fashion.[2] These steps are spontaneous under certain conditions. Although there are other approaches to polymer chain depolymerization and self-immolation, the focus herein is on polymers that fully and spontaneously unzip to monomer on demand; partial depolymerization that proceeds via radical mechanisms during thermal degradation has been comprehensively reviewed elsewhere.[8] It is important to note that "depolymerization" is a concept distinct from degradation. Many polymers have been prepared with cleavable bonds within their backbone or side-chains; however, cleaving these bonds, by hydrolysis for example, constitutes degradation and not intentionally designed, triggerable depolymerization.

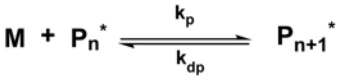
This "Prospective" highlights the discovery, preparation, and development of depolymerizable polymers with a major focus on polymers exhibiting low ceiling temperatures (T_c), the critical threshold temperature above which depolymerization and thus monomer formation are thermodynamically favored. Within this discussion, we briefly introduce another class of polymers, termed "self-immolative polymers," that unzip to small molecular products, whose role in the development of depolymerizable polymers is crucial to recent advances in the field. We also survey several applications of stimuli-responsive, low T_c polymers while providing an outlook on future technologies that will greatly benefit from continuous exploration of depolymerizable materials.

The ceiling temperature phenomenon

The concept of a ceiling temperature was first described and reported by Snow and Frey in 1943, followed by further elucidation by Dainton and Ivin in several seminal studies on poly (olefin sulfone) polymerizations.[9,10] The researchers independently discovered that copolymerizations between sulfur dioxide and olefins were paused as temperatures increased; further increasing the temperature to drive the polymerization to completion led to reduced monomer conversions and polymer molecular weights. On the contrary, decreasing polymerization temperature correlated with increasing tendency for the monomers to polymerize to high polymers.[11,12]

The authors correctly interpreted this counterintuitive result as unfavorable thermodynamics in poly(olefin sulfone) polymerizations.[13–15] With a few exceptions, polymerizations are inherently exothermic and exoentropic ($\Delta H < 0$ and $\Delta S < 0$; there are few known examples of endothermic and endoentropic polymerizations, which exhibit a floor temperature[15]). It was surmised that polymer propagation steps are reversible processes, and that there exists a temperature at which the free energy for a polymerization crosses from negative to positive (Scheme 1). At this cross-over temperature, the rate of propagation is equivalent to the rate of depropagation, establishing equilibrium. Therefore, when the polymerization temperature is raised to this point, polymer growth is halted.

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press



Scheme 1. Schematic of monomer–polymer equilibrium.

Beyond this critical temperature, however, depropagation outcompetes propagation such that further increasing the reaction temperature favors the reverse reaction and results in polymer "unzipping" (Fig. 1).[13]

The cross-over temperature was termed a ceiling temperature (T_c), and represents a critical threshold above which depropagation rate surpasses propagation rate (Fig. 1).[16,17] The T_c is an inherent thermodynamic constraint in any polymerization and depends on free energy parameters for any given monomer:

$$\Delta G_p = \Delta H_p - T\Delta S_p, \quad (1)$$

$$\Delta G = 0 \text{ at } T_c, \quad (2)$$

$$T_c = \frac{\Delta H_p}{\Delta S_p}. \quad (3)$$

Since the entropy of polymerization depends on concentration, pressure, and effects of solvation, the T_c is generally reported for any given monomer at standard pressure and for an initial monomer concentration of 1.0 mol/L.[15] A more general form of the monomer–polymer equilibrium is expressed below, where $[M]_e$ is the equilibrium monomer concentration at a given temperature:

$$T = \frac{\Delta H_p}{\Delta S_p^\circ + R\ln[M]_e}. \quad (4)$$

These relationships enable facile determination of polymer ceiling temperatures. Rearranged, a linear relationship is evident between $1/T$ and $\ln[M]_e$, with a slope of $\Delta H_p/R$ and a y-intercept of $-\Delta S_p^\circ/R$:

$$\ln[M]_e = \frac{\Delta H_p}{R}\left(\frac{1}{T}\right) - \frac{\Delta S_p^\circ}{R}. \quad (5)$$

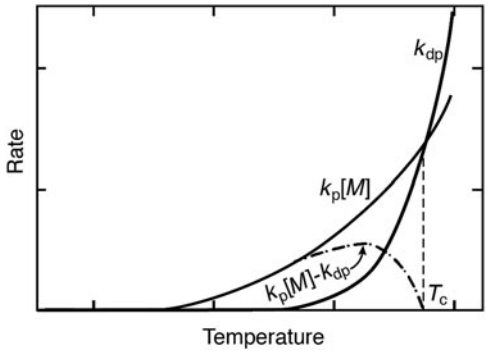


Figure 1. Polymer propagation and depropagation rates as a function of temperature. T_c is defined as the temperature at equilibrium, where the rates intersect (at $[M]_0 = 1$ M). (Reprinted with permission from Ref. 13. Copyright 1958 Royal Society of Chemistry.)

Equation (5) provides a framework for experimental determination of T_c. With increasing temperature, the monomer concentration required to meet equilibrium conditions increases. Thus, measuring monomer equilibrium concentrations at various temperatures enables accurate determination of thermodynamic parameters and gives a reliable estimate of a polymer's T_c. Alternatively, it is possible to measure the rates of polymerization or the polymer molecular weights at various temperatures, followed by extrapolation to zero in a plot of either parameter versus temperature.[15–17] While these last two techniques are less accurate than the first, they were the methods of choice in many early studies on the thermodynamics of low T_c polymer synthesis.

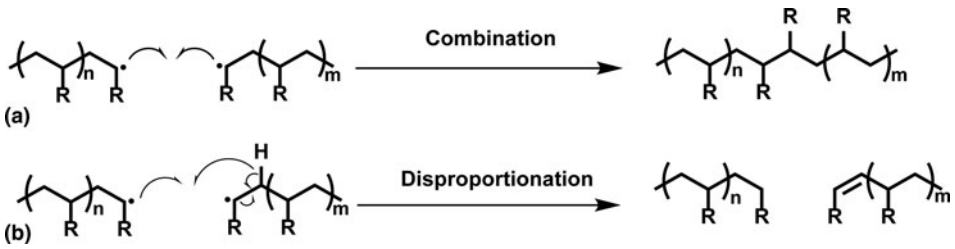
That the existence of a T_c was not discovered until the 1940s is a direct result of the fact that typical olefin polymerizations are extremely exothermic and that the resultant polyolefins exhibit impractically high T_c's.[16,17] Compared to typical olefin polymerizations known at the time, the exothermicity of poly (olefin sulfone) preparation is significantly reduced (i.e., more positive). The less exothermic polymerization results in a concomitant decrease in T_c, which was impressively recognized and interpreted by the early researchers, paving the way for the discovery of other polymers with low T_c's.

It is worth noting here that reverse propagation above T_c is one pathway that leads to depolymerization, which is a concept distinct from degradation. All polymers are theoretically capable of depolymerization if the temperature is raised above their T_c. However, the majority of common polymers have such high T_c's that thermal degradation is observed before depolymerization. Low T_c polymers are thus a special class of depolymerizable polymers with a T_c sufficiently low that depropagation is possible at or near ambient temperatures. Other commonly known depolymerizable polymers besides poly(olefin sulfone)s include many different polyaldehydes, polymers from certain cyclic ethers or acetals, and poly(α-methyl styrene). An emergent class of closely related "self-immolative" polymers that unzip will also be discussed in later sections (see Refs. 1–6 and 18–21 for reviews on these types of polymers).

Preparation of depolymerizable polymers by kinetic stabilization of chain-ends

Low T_c, depolymerizable polymers are inherently thermodynamically unstable at, or just above, room temperature. This property raises an important question: how can low T_c polymers be prepared and exploited as useful materials in ambient conditions? To prepare stable, isolable polymers based on these types of monomers, it is critical to prepare the materials below their T_c and then block or impede the depolymerization process at

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press



Scheme 2. Termination "end-capping" processes in free radical polymerizations.

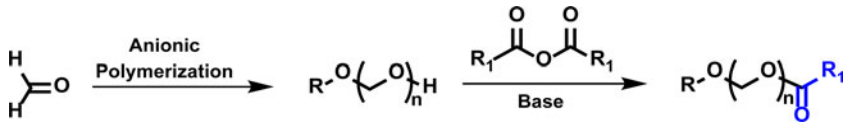
elevated temperatures. This feat has been achieved in several different manners for various polymerization methods, but all necessitate "capping" chain-ends to block the depolymerization pathway. End-capping kinetically stabilizes depolymerizable polymers above their T_c because there is not sufficient energy at room temperature to cleave capping groups and permit access to intermediates that undergo depropagation.

For radical polymerizations such as poly(olefin sulfone) preparation, blocking the chain-ends from unzipping is relatively trivial.[11,12] Polymerization at low temperature is accompanied by termination via radical combination or disproportionation, which effectively quenches the reactive chain-ends and end-caps the polymer to inactivate it from depropagation (Scheme 2).[22] Only by re-initiating the capped chain-ends or cleaving the polymer backbone to expose new chain-ends will unzipping proceed to effect depolymerization. In this manner, low T_c polymers synthesized by free radical polymerizations essentially stabilize themselves spontaneously by termination.

However, in living chain-growth and step-growth polymerizations, termination steps that quench or otherwise inactivate chain-ends do not occur spontaneously (barring termination by cyclization or chain-transfer). It was not until the late 1950s that researchers at DuPont began to identify strategies that effectively stabilize low T_c polymers from depropagation. Polyoxymethylene (POM or polyformaldehyde) was known at the time to be thermally unstable, thereby limiting interest in its study and industrial application.[23,24] Several pioneering efforts demonstrated that anionic polymerization of formaldehyde below its T_c followed by a post-polymerization esterification greatly enhanced the thermal stability of this polymer, culminating in a series of publications that, for the first time, characterized the polymer's physical, thermal, and mechanical properties (Scheme 3).[25–29] The enhanced thermal stability is a consequence of esterification of the chain-end hemiacetal, blocking the polymer from depolymerization at elevated temperatures. Importantly, this enabled melt processing of the polymer at temperatures well above its T_c.

A later discovery introduced an alternative method to effectively stabilize depolymerizable polymers: copolymerization with small quantities of comonomers that do not depolymerize, thereby acting as "chain-stoppers" within the polymer chain.[24] Polymers formed in this way unzip until they reach a unit incapable of depropagation, subsequently stopping depolymerization and leaving the polymers end-capped. One example of such chain-stoppering approach is the cationic copolymerization of 1,3,5-trioxane—the cyclic trimer of formaldehyde—with epoxide (Scheme 4). The aldehyde units can unzip via their acetal linkages. However, the additional carbon spacer, introduced by epoxide, halts depropagation, so that the ethylene unit persists as a stable chain-end. A variety of other cyclic ethers and acetals have also been used as comonomers to stabilize polyaldehydes.[24] Although polymers prepared with this method cannot fully depolymerize from head-to-tail due to the blocking comonomers, they are activated to depolymerize into smaller subunits by cleaving sites within the backbone to create new chain-ends.

The discovery of these methods for end-capping ionic chain-growth polymerizations immediately stimulated a large outgrowth in the synthesis and study of polyaldehydes other than POM.[30–39] Vogl et al. notably embarked on the preparation of a wide range of higher aliphatic polyaldehydes, demonstrating a general approach to stabilized the polymers by post-polymerization esterification (Table I).[30–35] Later, the first aromatic polyaldehydes were discovered by the Aso group in the low-temperature cyclopolymerization of *o*-phthalaldehyde and related monomers (Scheme 5, Table I).[36–39] Advantages of aromatic polyaldehydes include enhanced monomer stability relative to aliphatic aldehydes, and improved polymer solubility due

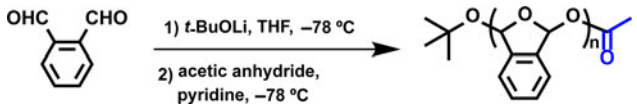


Scheme 3. End-capping POM by esterification. R depends on polymerization initiator.

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press



Scheme 4. Copolymerization of trioxane with chain-stoppering ethylene oxide. R depends on initiator.



Scheme 5. Anionic cyclopolymerization and stabilization of *o*-phthalaldehyde.[37]

to their atactic nature, unlike the highly crystalline aliphatic polyaldehydes.[18,19]

In recent years, our laboratory discovered that the cationic polymerization of *o*-phthalaldehyde surprisingly yielded macrocyclic polymer.[40] Stability is conferred to polymer chains not by capping the chain ends, but by the macrocyclization process itself, which yields "endless" polymers. The cyclic polymers are synthesized with a variety of Lewis acids as initiators, and the polymerization reaction is quenched by neutralization with base (Scheme 6). Under polymerization conditions, macrocyclization is reversible, enabling ring-expansion, ring-contraction, and ring-mixing, the latter of which was employed to produce copolymers of controlled microstructure.[40,41] We later demonstrated a similar macrocyclization mechanism in the cationic polymerization of an aliphatic aldehyde, ethyl glyoxylate, to produce another low T_c polyaldehyde.[42]

Analogous polymers prepared by step-growth polymerizations have also emerged in the literature.[4–6] The first such linear polymer, termed a "self-immolative polymer," was reported in 2008,[43] and many other classes of similar polymers have since been reported.[44–58] Synthesis of these materials is accomplished with AB-type monomers containing a blocked reactive unit. Polymerization ensues on activation of blocked functional groups, for example by catalytic activation of blocked isocyanates or exposure of reactive amines, to form linear polyurethanes and polycarbonates.[43,52] These polymers unzip via a mechanism unique from low T_c polymers, expelling gaseous byproducts to drive the unzipping process forward (discussed in the Section "Recent advances in triggered depolymerization"). However, preventing these polymers from unwanted head-to-tail self-immolation again relies on adding a reagent to end-cap the reactive polymer chains. In this case, a monofunctional nucleophilic species, which is added near the end of the polymerization reaction, is employed to serve as a chain-capping and stabilizing group (Scheme 7).

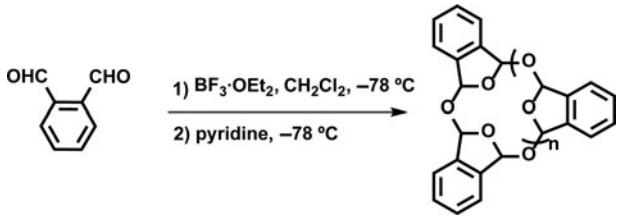
Table I. Aldehyde monomers and associated ceiling temperatures.[18]

Aldehyde	T_c (°C)
CH_2O	119
CH_3CHO	−39
$CH_3(CH_2)_2CHO$	−18
$CH_3OCOCHO$	26
$CH_3CH_2OCOCHO$	35
CF_3CHO	85
CCl_3CHO	17
CBr_3CHO	−75
CFClBrCHO	41
o-phthalaldehyde	−43

Recent advances in triggered depolymerization

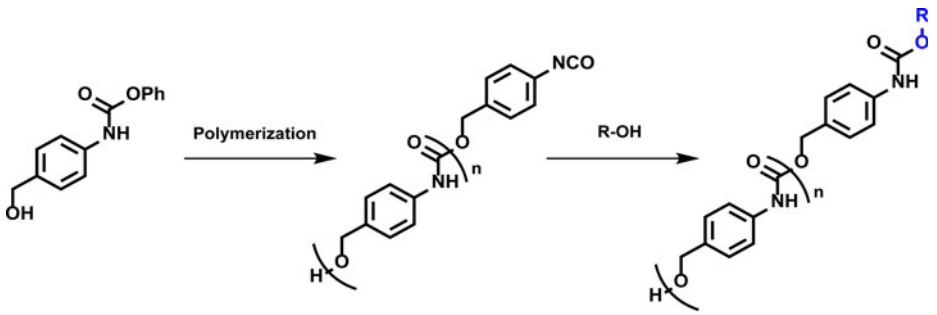
Depolymerizable polymers have witnessed a resurgence in the literature over the past decade due to their capacity to undergo triggered depolymerization.[1–3] There are numerous applications of triggered depolymerization, which will be discussed in the ensuing section. Regardless of polymer type, triggered depolymerization or self-immolation relies on a physical or chemical stimulus that reacts with either the polymer end-caps to expose chain-ends, or induces chain-scission in polymer backbones to create new chain-ends capable of unzipping. Among others, the stimuli of interest include acid, base, redox reagents, electromagnetic irradiation and heat. Polymers highlighted in this section take advantage of ionic and nucleophilic mechanisms to achieve rapid and complete unzipping to small molecules at room temperature. In contrast, general thermal degradation processes that proceed via radical mechanisms often exhibit partial unzipping of polymer chains due to competitive termination and chain-transfer events. Quantitative treatment of this pathway is beyond the scope of this Prospective and reviewed in detail elsewhere.[8] This section also discusses the comparative rates of each depolymerization or self-immolation pathway and highlights important milestones in recent progress.

Triggered head-to-tail unzipping of linear, self-immolative polymers was reported by Shabat and co-workers in 2008.[43]



Scheme 6. Cationic, macrocyclic polymerization of *o*-phthalaldehyde.[40]

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press



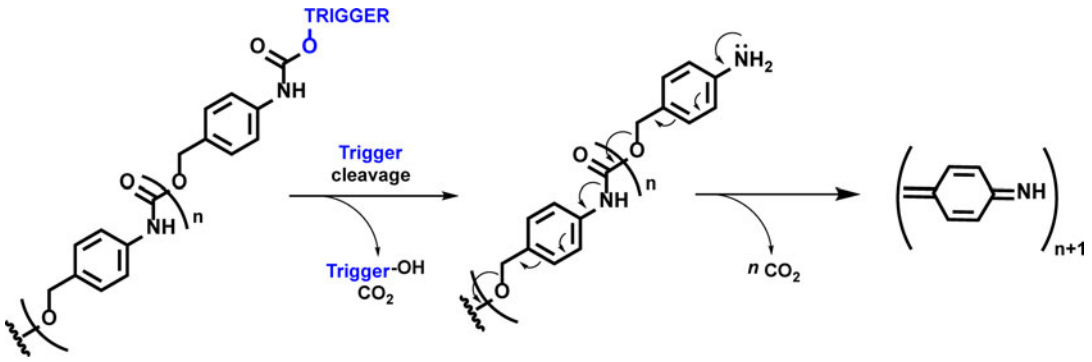
Scheme 7. Polymerization and stabilization of self-immolative polymers.[43]

For this purpose, they synthesized polymers derived from quinone-methide-based self-immolative dendrimers previously prepared by the same group.[4] They demonstrated that, to enact triggered polymer unzipping, it was necessary to end-cap the polymers with a stimulus-responsive functionality rather than the conventional, inert blocking group. When the responsive cap is removed to expose the chain-ends, head-to-tail self-immolation is initiated and driven to completion by expulsion of CO_2 (Scheme 8). Specifically, they employed 4-hydroxy-2-butanone as a trigger, which is removed by enzymatic cleavage, thereby activating the unzipping cascade. Later examples expanded the triggering modes to groups that respond to acid, base, UV light, near-IR light, heat, enzymes, and redox reagents.[44–50]

Two mechanisms are available in quinone-methide eliminations: 1,6- and 1,4-eliminations (*para* and *ortho* variants, respectively). First-generation self-immolative polymers employed 1,6-eliminations in polyurethane backbones, requiring approximately 10 h to achieve complete unzipping in physiological conditions.[43] The analogous 1,4-elimination occurred at slightly slower rates, taking about twice as long to achieve complete degradation of monomeric model compounds under identical conditions.[59] Exploiting these dual elimination mechanisms, researchers went on to develop linear polymers based on 1,6-quinone-methide backbones bearing side chains capable of further disassembly via 1,4-elimination.[44 These so-called "self-immolative comb-polymers" feature rapid backbone unzipping followed by side-chain disassembly to release multiple reporter compounds.

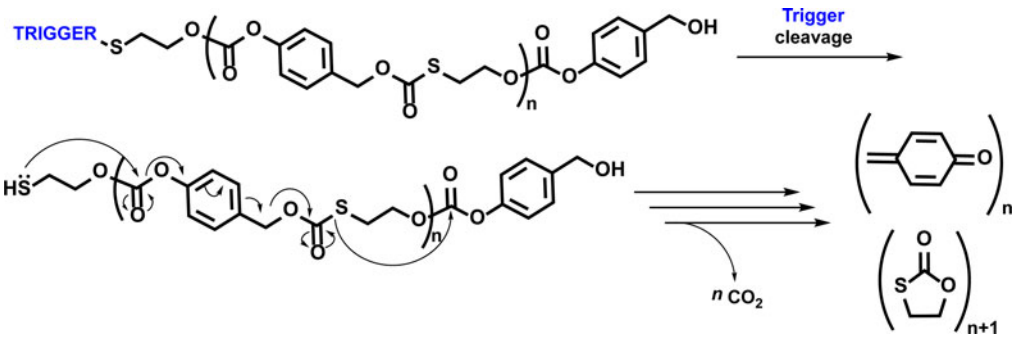
The Gillies group successfully expanded the scope of linear self-immolative polymers and modulated the rates of their head-to-tail unzipping by designing analogs with cyclizing spacers and alternative main-chain atoms.[50–53] They demonstrated this approach by incorporating a cyclizable thiol spacer into a polycarbonate backbone such that self-immolation rates were amplified by over an order of magnitude compared with analogs containing amine spacers (Scheme 9).[52] Complete transformation of thiol-spaced polymers into small molecular products occurred in 5 h in a neutral buffer at 37 °C, compared with several days for the corresponding polymers with amine spacers. The researchers further prepared small, monodisperse self-immolative oligomers and polymers by stepwise synthesis to demonstrate conclusively that, as expected, the rate of unzipping is directly related to the overall chain-length for this class of polymers.[53] Times to reach 50% self-immolation (polymer "half-lives") ranged from under 10 min for dimer, 24 min for octamer, and up to 40 min for a polydisperse polymer sample with average degree of polymerization ~50.

An analogous class of polymers, the "chain-shattering" polymers, also undergoes triggered degradation by a similar quinone-methide elimination mechanism. However, rather



Scheme 8. Triggered unzipping of self-immolative polymers.[43]

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press

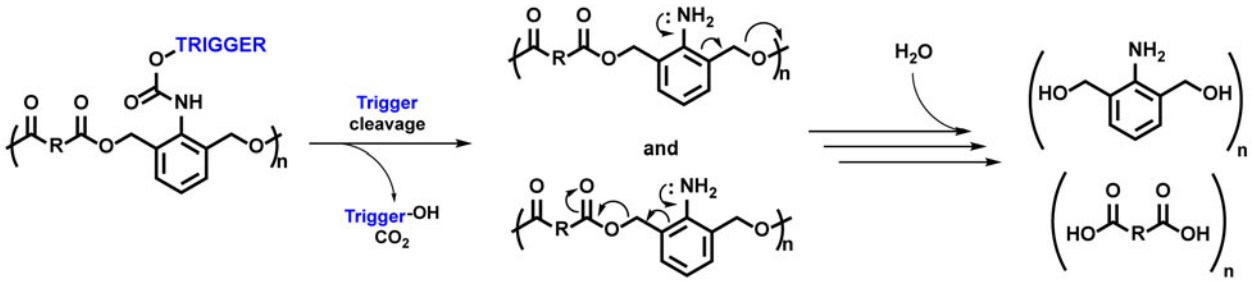


Scheme 9. Triggered self-immolation with enhanced rates by alternating cyclization-elimination.[52]

than head-to-tail unzipping proceeding from chain-ends, these polymers cleave from alternating sites within the backbone (Scheme 10).[60–66] Since the degradation cascade does not proceed along polymer chains and requires multiple initiation events, the reaction rates are notably governed by triggering conditions and stimuli. Complete degradation has been observed on time scales of several minutes for UV-sensitive polymers, several hours for near-IR-, acid-, and base-sensitive polymers, and even days for oxidation-sensitive polymers.[60–62,65,66] Advantages of chain-shattering polymers include their facile preparation by step-growth copolymerization between activated, bifunctional quinone-methide moieties and bifunctional comonomers, thereby enabling integration of a wide variety of functional motifs into polymer chains.[60,65] In fact, the Cheng group demonstrated that copolymerization with a reactive therapeutic allows for direct insertion of target drugs into polymer backbones for on-demand release.[66] One could further envision the incorporation of multiple unique, stimuli-responsive triggers to afford chain-shattering polymers responsive to multiple stimuli.

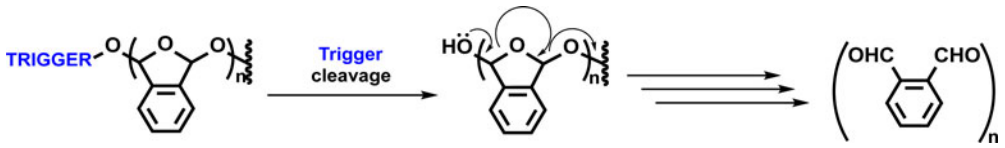
For low T_c polyaldehydes, triggered depolymerization from head-to-tail was first demonstrated in 2010[67] and further expanded in subsequent years.[68–71] It was already known that acid exposure was a viable route to achieve polyaldehyde depolymerization by random chain-scission along the acetal backbone.[72] However, triggering stimuli were limited to acidic reagents capable of backbone cleavage. Taking inspiration from the self-immolative polymer literature, Seo and Phillips demonstrated that end-capping poly(phthalaldehyde) with a responsive functionality enabled triggered depolymerization (Scheme 11).[67] They employed protective groups that are cleavable by palladium sources or fluoride ions and showed that complete depolymerization to monomer is nearly instantaneous upon exposure to the chemical stimulants. In this case, polymer unzipping at room temperature is not driven by expulsion of gaseous byproducts but rather results from the extremely low T_c of the poly(phthalaldehyde) (−43 °C). Using available thermodynamic data,[36] it can be estimated that the equilibrium monomer concentration for this polymer at room temperature is 14 mol/L (at 25 °C), so depolymerization continues until reaching this condition, which is unachievable in practice. Poly(phthalaldehyde) exhibits the most rapid depolymerization rates observed for any class of depolymerizable polymers. In fact, the extremely rapid unzipping speeds have hindered attempts to monitor reaction progress in solution, as complete reversion to monomer is observed on analytical time scales. In the solid state, total degradation has been observed within 15 min.[67]

Triggered depolymerization of low T_c polyaldehydes, specifically poly(phthalaldehyde), has many advantages compared to self-immolative polymers that have made this class of materials a system of choice for continued research over several decades. High molecular weight poly(phthalaldehyde) is prepared



Scheme 10. Triggered degradation of chain-shattering polymers.[65]

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press

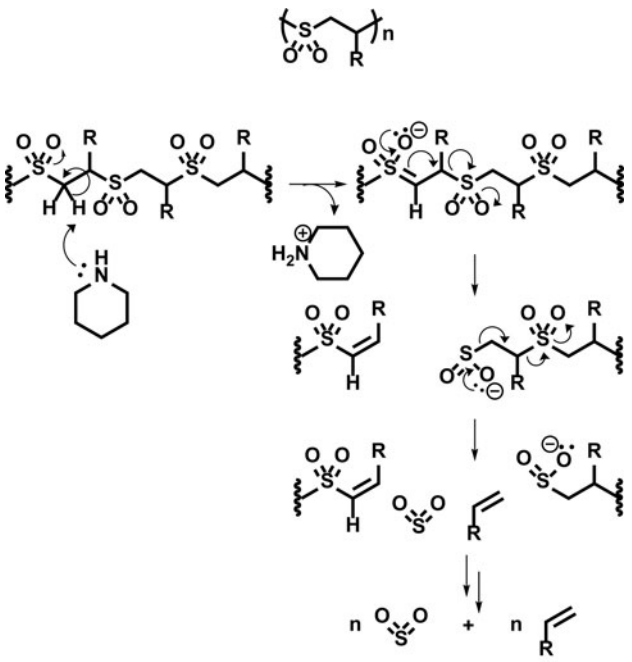


Scheme 11. Triggered depolymerization of poly(phthalaldehyde).[67]

and end-capped with a variety of stimuli-responsive triggers from commercially available reagents, although rigorous purification of *o*-phthalaldehyde monomer is required for anionic polymerizations.[68,69] Furthermore, it is possible to functionalize related polymers by post-polymerization modification to achieve cross-linking or tailor the polymer with specific moieties.[70,71] Most importantly, the depolymerization process of polyaldehydes is nearly instantaneous on exposure to acid, heat, or triggering reagents. Even macrocyclic poly(phthalaldehyde), which lacks triggering end-groups, depolymerizes rapidly by main-chain scission on exposure to acid.[72] As a result, polyaldehydes have found widespread use in a variety of applications.[2,19]

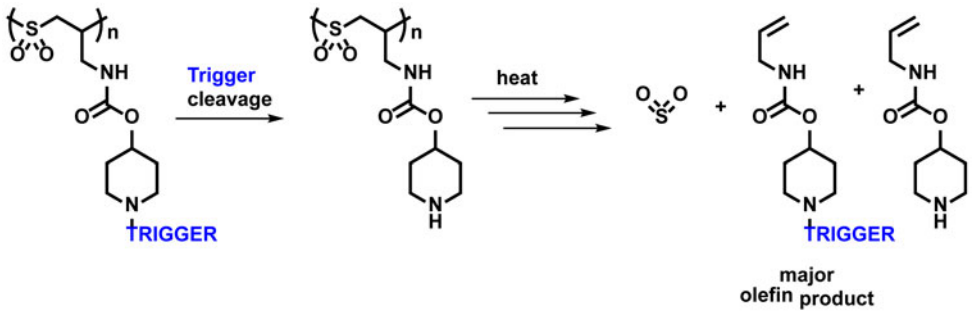
Like self-immolative polymers and polyaldehydes, triggered depolymerization has also been explored in low T_c poly(olefin sulfone)s. In the 1930s, researchers found that heating poly(olefin sulfone)s in aqueous alkaline solutions yielded the constituent olefin monomers and sulfur dioxide, which was isolated in the form of sodium sulfite.[73–75] Removing the backbone protons by base led to random backbone scission, creating new chain-ends that initiate the depolymerization cascade (Scheme 12).[76] Lobez and Swager later investigated amine-initiated depolymerization of poly(2-methyl-1-pentene sulfone) using ammonium hydroxide, *n*-butylamine, and piperidine.[77] At 25 °C, depolymerization reached completion within 30 min in 0.7 M of amine bases and after 24 h in 0.7 M ammonium hydroxide. The researchers also compared the depolymerization of poly(2-methyl-1-pentene sulfone) and poly(1-hexene sulfone) triggered by 0.3 molar equivalents (relative to repeat units) of piperidine. While both polymers remained intact after 60 min at 25 °C, heating the samples to 80 °C for 30 min led to depolymerization, with poly(1-hexene sulfone) degrading to a greater extent than poly(2-methyl-1-pentene sulfone) due to less side-chain steric hindrance and thus ease of deprotonation.[77] Despite these observations, there have yet to be any reports on rigorous kinetic treatment of base-triggered poly(olefin sulfone) depolymerization. Besides base as a triggering stimulus, it has also been known since 1960s that poly(olefin sulfone)s exhibit high sensitivity to gamma-ray and electron-beam exposure and depolymerize upon irradiation.[78–82]

The limited ability to functionalize poly(olefin sulfone)s with stimuli-responsive end-groups during free radical polymerizations has narrowed the scope of triggering modes available to activate their head-to-tail depolymerization (See the Section "Preparation of depolymerizable polymers by kinetic stabilization of chain-ends"). This limitation in poly(olefin sulfone) synthesis also presents a great opportunity in their preparation via controlled radical polymerization methodologies. In 2007, Yaguchi and Sasaki partially addressed the challenge of expanding triggering modes and developed UV-sensitive poly(olefin sulfone)s by functionalizing the polymer side chains with a UV-responsive photobase generator.[83] Exposure to UV irradiation first generated amine base from the side chains, and subsequent heating of the irradiated polymer at 150 °C for 15 min induced base-triggered depolymerization (Scheme 13). The researchers later enhanced the UV-sensitivity of these poly(olefin sulfone)s by additionally grafting base amplifiers onto the polymer backbone.[84] One could envision employing other amine protecting groups in future designs of poly(olefin sulfone)s to sensitize polymers to additional stimuli. Although the olefin monomers are regenerated as the major products in these systems, triggered depolymerization of poly(olefin sulfone)s also produces a variety of side products. Furthermore, activating the depolymerization cascade requires both UV light and heat rather than a single stimulus. To optimize poly(olefin sulfone) depolymerization



Scheme 12. Base-triggered depolymerization of poly(olefin sulfone)s.[76]

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press



Scheme 13. UV-triggered depolymerization of photobase-functionalized poly(olefin sulfone)s.[83]

efficiency, future exploration will focus on developing triggerable side-chains that respond to a single stimulus and lead to direct backbone cleavage when removed.

Applications of depolymerizable, low T_c polymers

Lithographic materials

One of the earliest applications of depolymerizable polymers was for lithographic purposes. The high sensitivity of poly(olefin sulfone)s to high-energy radiation was an attractive feature for the development of electron-beam resists. Poly(1-butene sulfone), for instance, is more sensitive to electron-beam radiation than the standard poly(methyl methacrylate) resists by nearly one order of magnitude.[82] Following the initial discovery, other aliphatic and aromatic poly(olefin sulfone)s were extensively investigated for application in lithography.[85–88] Despite their rapid depolymerization rates on exposure, only poly(1-butene sulfone) has been used commercially, while most of the other polymers display poor film-forming properties and low thermal stability.[88] Poly(1-butene sulfone) has also been used as a wet-etch mask instead of a dry-etch electron-beam resist due to its lack of resistance to plasma and reactive ion etching environments.[89]

In the 1980s, researchers at IBM began to explore the use of low T_c polyaldehydes as photoresist materials for lithography.[90–93] Poly(phthalaldehyde) was chosen for research due to its ease of preparation and solubility in common organic solvents. When combined with photoacid generators, exposure of poly(phthalaldehyde) films to light triggers acid-catalyzed depolymerization, permitting fabrication of patterned films.[90] Depolymerization was found to be a particularly effective mechanism in lithography because of the drastic and rapid physical changes between polymer and monomer that occur on exposure.[90–93] More recently, IBM has shown probe-based nanolithography to be a useful tool for patterning poly(phthalaldehyde) by thermal depolymerization. A heated scanning probe is used to stimulate depolymerization and evaporation of the resultant monomer, allowing for rapid patterning with high resolution. Remarkable two-dimensional (2D) and three-dimensional (3D) architectures were fabricated with unprecedented resolution (Fig. 2).[94,95]

Responsive composites

Incorporation of depolymerizable polymers into composite materials allows for a dramatic change in physical or chemical properties upon exposure to specific stimuli. Lobez and Swager developed a gamma-ray sensor containing a network of multiwalled carbon nanotubes coated with poly(1-hexene sulfone), which served as insulting materials to separate the conductive carbon nanotubes from one another.[96] Irradiating the network with ionizing gamma rays led to rapid depolymerization of the polymer matrix and permitted the carbon nanotubes to form conductive contacts, thereby increasing the conductance of the sensor (Fig. 3). The authors further found that functionalizing poly(1-hexene sulfone) with pyrene and triphenylbismuth moieties via "click" chemistry resulted in a fivefold conductance improvement when the device was exposed to low-dose radiation (5×10^3 rad). This result was attributed to the favorable π–π interactions between pyrene and the carbon nanotubes and to the enhanced radiation absorption from the presence of bismuth.

One major advantage of depolymerizable polymers is the capacity to transform into small molecular units, thereby facilitating the breakdown and recycling of bulk materials. The Swager group demonstrated rapid disassembly of a polymer composite consisting of poly(dimethylsiloxane) and poly(1-hexene sulfone).[77] Poly(dimethylsiloxane) is a common elastomer that exhibits high thermal stability and tunable mechanical properties[97–99]; however, its robust nature also inhibits its degradation and recycling. By chemically incorporating poly(1-hexene sulfone) into segments of poly(dimethylsiloxane), the researchers developed composites that exhibited similar mechanical properties to poly(dimethylsiloxane) but were capable of undergoing disassembly in the presence an amine base (Fig. 4).[77] From a sustainability standpoint, continued development of depolymerizable composites facilitates the fabrication of recyclable materials, thereby reducing waste production. As carrier materials, the stimuli-responsive composites presented in this example also apply to the transport, delivery and triggered release of active compounds.

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press

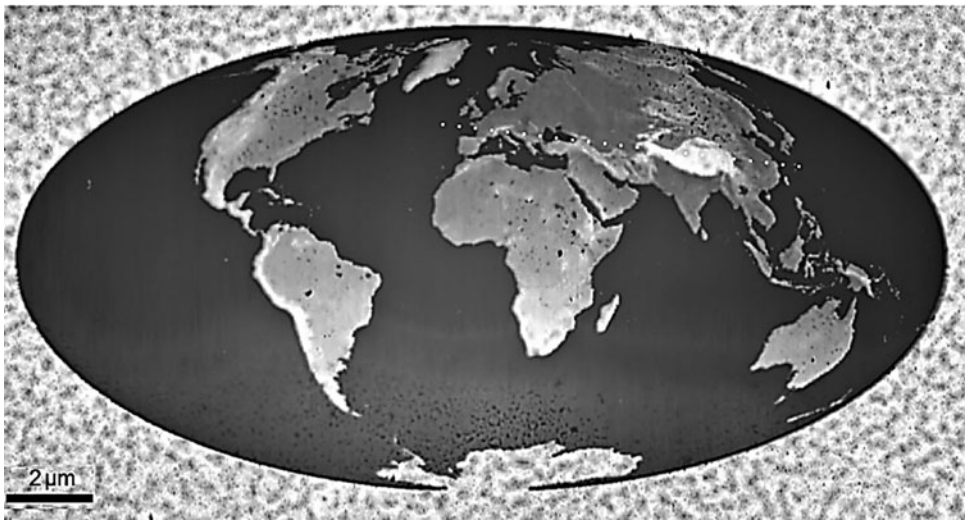


Figure 2. AFM topographic image of a 3D world map written into a poly(phthalaldehyde) layer by thermally induced depolymerization via probe-based nanolithography (Reprinted with permission from Ref. 95. Copyright 2010 John Wiley and Sons).

Triggered release

Perhaps the most ubiquitous application of depolymerizable polymers is their use in triggered release.[1–3,100–103] Several methods to achieve triggered release are possible and have been reported with depolymerizable polymers. The monomer itself may serve as the compound of interest or disassemble further to release a compound of interest; alternatively, the depolymerizable material may serve as a structural container that releases sequestered active agents on triggered destruction. Triggered release itself is further categorized according to the function of the released additive. For example, liberated compounds may serve as reporter molecules for signal-amplified sensing, fluorescent probes, active drug components for drug delivery, healing agents in autonomic self-healing, or many other functions.[100,101] The focus herein is given to reports of depolymerizable polyaldehydes used in triggered release.

Two different low T_c polyaldehydes have been reported thus far for application in triggered release: poly(phthalaldehyde)[102] and poly(glyoxylate)s.[103] In either case, the polyaldehyde serves as a structural container that encapsulates the active compounds (Fig. 5). Phillips and co-workers demonstrated the fabrication of core–shell microcapsules with poly(phthalaldehyde) shell walls. Subjecting the capsules to chemical reagents that cleave polymer end-groups triggers shell-wall depolymerization and leads to successful release of encapsulated actives.[102] Gillies and co-workers later reported the preparation of micellar nanoparticles formed from amphiphilic poly(ethyl glyoxylate)-poly(ethylene glycol) block copolymers. Triggered release was achieved via photolysis of poly(glyoxylate) end-groups to induce depolymerization and initiate nanoparticle decomposition, thereby liberating core contents.[103]

Unlike self-immolative polymers, generating active or reporter molecules directly from depolymerized polyaldehydes has not yet been reported.[4] One could envision that future systems will take advantage of the inherently amplified response in depolymerizable polyaldehydes by incorporating a monomer designed for a targeted purpose such as drug delivery or sensing. Alternatively, monomers could undergo further disassembly to produce an active agent in an autonomic fashion, as has been reported for self-immolative comb polymers.[44]

Adaptive structural materials

One remarkable feature of depolymerizable polymers is their capacity to serve as dynamic structural materials. By selectively triggering their depolymerization, structural materials can be designed to erode at specified times to permit recycling, patterning, regeneration, or other relevant shape-shifting transformations. Phillips and co-workers capitalized on this application by fabricating a patterned plastic block composed of poly(phthalaldehyde) with two distinct and responsive end-groups. Exposure to one triggering condition selectively etched the corresponding polymers, thereby disintegrating portions of the plastic to reveal predesigned patterns while leaving the remainder polymer intact.[67]

Researchers later extended the concept of adaptive polyaldehyde materials by demonstrating a reversible cycle of depolymerization followed by repolymerization, mimicking regenerative biomaterials such as bone (Fig. 6).[104] It was found that depolymerization of poly(phthalaldehyde) is mechanically activated by ultrasonication, which cleaves polymer chains that subsequently unzip to monomer. Incredibly, the monomer thus generated was directly repolymerized to poly(phthalaldehyde), albeit by first cooling below its T_c and adding initiator. This finding highlights the potential for poly(phthalaldehyde) to serve as a recyclable or regenerative synthetic material. While these studies served merely as preliminary proof-of-concept demonstrations, they

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press

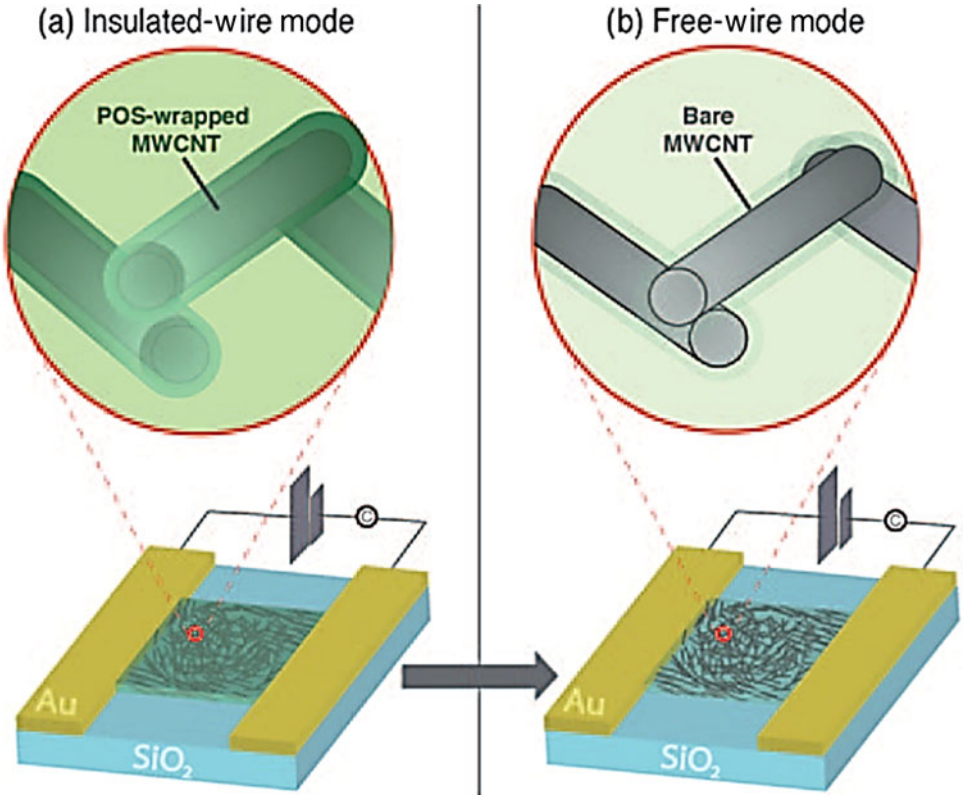


Figure 3. Gamma-ray irradiation depolymerizes the insulating poly(1-hexene sulfone) coating on the carbon nanotubes (a) and allows the carbon nanotubes to form low-resistance contacts (b), thereby increasing sensor conductance (Reprinted with permission from Ref. 96. Copyright 2009 John Wiley and Sons).

emphasize the potential importance of adaptive, dynamic structural materials in future material designs.

Transient substrate and template materials

A final key application of depolymerizable polyaldehyde materials has been their use as temporary substrate or template materials. While most prior polymer research has focused on preparing permanent, mechanically and thermally robust structures, there is a growing interest in depolymerizable substrates that could serve as temporary barrier materials, transient substrate materials, or other adaptive structures. In one example, triggered depolymerization of poly(phthalaldehyde) films was employed to activate a microfluidic pumping system on command.[105] It was shown that modifying polymer end-group polarity allows the chain-end triggers to be exposed at interfaces between film and water rather than buried within polymer layers; this approach was a productive means to enhance solid-state depolymerization capabilities in the microscale pumps.[106] Toward depolymerizable packaging, it was shown that, in conjunction with photoacid generators, light-sensitive

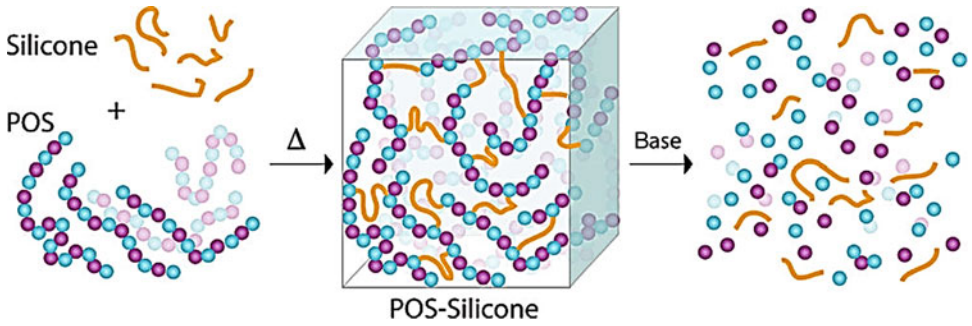


Figure 4. Schematic representation of poly(olefin sulfone)-poly(dimethylsiloxane) composite assembly and base-triggered decomposition (Reprinted with permission from Ref. 77. Copyright 2010 American Chemical Society).

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press

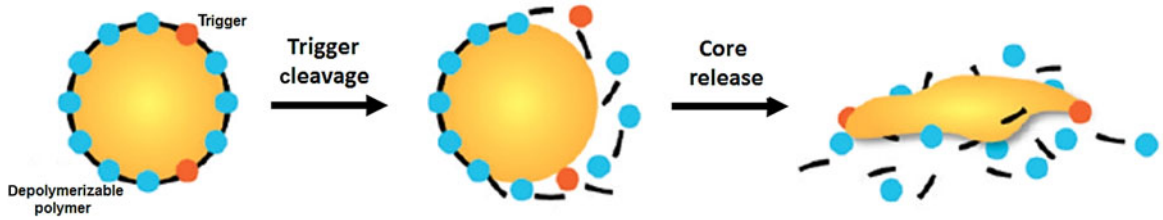


Figure 5. Schematic representation of triggered release: core-shell containers are disassembled by triggering shell-wall depolymerization or self-immolation to release sequestered actives (Reprinted with permission from Ref. 101. Copyright 2011 American Chemical Society).

poly(phthalaldehyde) films are fabricated and employed as substrate materials for transient electronics.[107] When suitably irradiated, film depolymerization induces loss of mechanical integrity and concomitant electronic device destruction (Fig. 7). One could envision expanding this concept to other applications where triggered destruction is desirable.

In analogous efforts, depolymerizable polyaldehydes have been utilized as removable templating materials to drive nanostructure formation. Patterned poly(phthalaldehyde) films were shown to be effective, removable scaffolds for directed gold nanoparticle assembly.[108] Likewise, poly(phthalaldehyde)-polystyrene block copolymers were shown to self-assemble under suitable conditions, and subsequent acid treatment depolymerized and etched away the poly(phthalaldehyde) blocks, leaving behind porous nanochannels.[109] With the growing importance of nanostructured and nanoporous materials, there is a clear opportunity for additional utilization of depolymerizable polymers as sacrificial templating scaffolds.

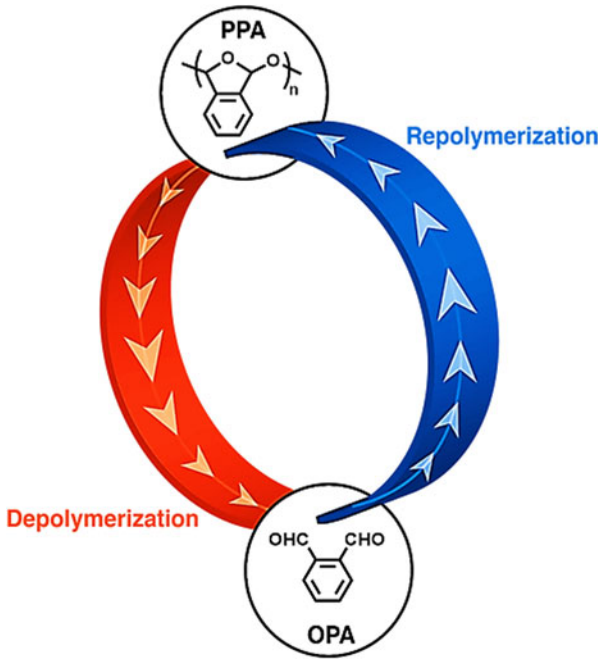


Figure 6. Adaptive polyaldehyde material exhibiting reversible cycle of depolymerization and orthogonal repolymerization. Poly(phthalaldehyde) was mechanically depolymerized by exposure to high-intensity ultrasonication, and resulting monomer (*o*-phthalaldehyde) repolymerized by anionic polymerization.[104]

Current status and future directions

A great deal of research effort has been invested into the field of depolymerizable and self-immolative polymers. While a number of depolymerizable and self-immolative polymer scaffolds have been prepared and studied, there is still demand for novel and versatile materials. For one, new materials need to be mechanically and chemically stable toward environmental conditions; polyaldehydes are exceedingly sensitive to acidic conditions, while self-immolative polymers are known to undergo unwanted side reactions with nucleophiles.[1] There is undoubtedly a great challenge in preparing materials that can be triggered to fall apart on command, yet are stable to any orthogonal conditions. The Phillips group has begun exploring new materials to address this need and pioneered a class of poly(benzyl ether)s that depolymerize on triggering but are stable to both acid and base.[110] The window for achieving these contrasting properties in synthetic polymers is exceedingly small, leaving a high demand for similar types of robust yet depolymerizable structures.

Opportunities also exist in the rational design of aldehyde monomers with programmed function. As detailed in the preceding section, the development of polyaldehyde materials where the generated monomer performs a function could be exploited, as in the case for self-immolative polymers. Likewise, small molecules released by further disassembly of aldehyde monomers would be an effective means to add functionality to depolymerizable polyaldehydes.

In the context of biomaterials and drug delivery, there is an increasing demand for biocompatible materials and triggers sensitive to biologically relevant small molecules, receptors, and enzymes. New triggers will need to be developed and evaluated in terms of their capability to initiate stimuli-responsive depolymerization in complex biological environments. Furthermore, it is crucial to expand the availability and scope of biocompatible polyaldehyde materials. While poly(phthalaldehyde) depolymerizes to the toxic *o*-phthalaldehyde monomer, the poly(glyoxylate) family represents a biocompatible class of depolymerizable polyaldehydes that merits further exploration for biological applications.[103,111–116]

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press

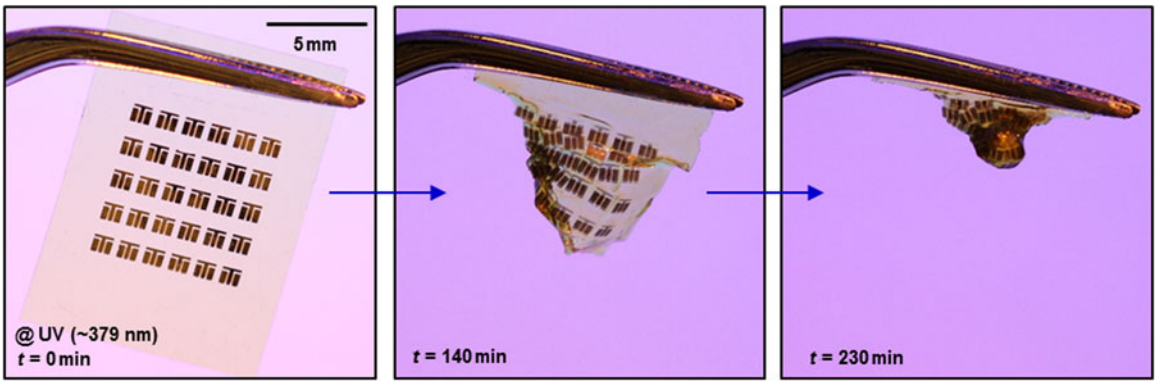


Figure 7. Triggered depolymerization of poly(phthalaldehyde) films for transient electronics. Films are embedded with photoacid generators such that UV irradiation initiates acid-catalyzed depolymerization of substrate followed by electronic destruction (Reprinted with permission from Ref. 107. Copyright 2014 John Wiley and Sons).

Finally, with further refinement in the preparation of depolymerizable polymers, the materials will undoubtedly find expanded use in diverse, and perhaps unexpected, applications. The use of sacrificial templates for the fabrication of nanoporous materials or degradable elastomer composites, and the use of these polymers for transient or other adaptive structures will almost surely continue. One might additionally expect new depolymerizable materials developed specifically to address the rising challenge of finding green, recyclable materials that minimally impact the environment. Depolymerizable polymers, notably those prepared from renewable resources, would represent an ideal way to achieve materials capable of recycling on command. Beyond that, could these reversible materials be used for energy storage and delivery? It remains to be seen how this field will grow and into which areas it will expand, but the prospects certainly look bright that the coming years will witness major progress in this dynamic field.

Acknowledgments

This work was supported as part of Defense Advanced Research Project Agency Air Force Contract FA8650–15-C-7522. J. A. K. thanks the Springborn Endowment for a graduate fellowship.

References

1. G.I. Peterson, M.B. Larsen, and A.J. Boydston: Controlled depolymerization: stimuli-responsive self-immolative polymers. *Macromolecules* **45**, 7317 (2012).
2. S.T. Phillips and A.M. DiLauro: Continuous head-to-tail depolymerization: an emerging concept for imparting amplified responses to stimuli-responsive materials. *ACS Macro Lett.* **3**, 298 (2014).
3. S.T. Phillips, J.S. Robbins, A.M. DiLauro, and M.G. Olah: Amplified responses in materials using linear polymers that depolymerize from end-to-end when exposed to specific stimuli. *J. Appl. Polym. Sci.* **131**, 40992 (2014).
4. S. Gnaim and D. Shabat: Quinone-methide species, a gateway to functional molecular systems: from self-immolative dendrimers to long-wavelength fluorescent dyes. *Acc. Chem. Res.* **47**, 2970 (2014).
5. M. Avital-Scmilovici and D. Shabat: Self-immolative dendimers: a distinctive approach to molecular amplification. *Soft Matter* **6**, 1073 (2010).
6. A.D. Wong, M.A. DeWit, and E.R. Gillies: Amplified release through the stimulus triggered degradation of self-immolative oligomers, dendrimers, and linear polymers. *Adv. Drug Deliv. Rev.* **64**, 1031 (2012).
7. A.D. Jenkins, P. Kratochvíl, R.F.T. Stepto, and U.W. Suter: Glossary of basic terms in polymer science. *Pure Appl. Chem.* **68**, 2287 (1996).
8. C. David: Thermal degradation of polymers, in *Comprehensive Chemical Kinetics Volume 14: Degradation of Polymers*, edited by C.H. Bamford and C.F.H. Tipper (Elvesier Scientific Publishing Company, New York, 1975), pp. 1–173.
9. R.D. Snow and F.E. Frey: The reaction of sulfur dioxide with olefins: the ceiling temperature phenomenon. *J. Am. Chem. Soc.* **65**, 2417 (1943).
10. F.S. Dainton and K.J. Ivin: Reversibility of the propagation reaction in polymerization processes and its manifestation in the phenomenon of a 'ceiling temperature'. *Nature* **162**, 705 (1948).
11. F.S. Dainton and K.J. Ivin: The kinetics of polysulphone formation. II. The formation of 1-butene polysulphone in the region of the ceiling temperature. *Proc. R. Soc. Lond. A* **212**, 207 (1952).
12. R.E. Cook, F.S. Dainton, and K.J. Ivin: Effect of olefin structure on the ceiling temperature for olefin polysulfone formation. *J. Polym. Sci.* **26**, 351 (1957).
13. F.S. Dainton and K.J. Ivin: Some thermodynamic and kinetic aspects of addition polymerisation. *Q. Rev. Chem. Soc.* **12**, 61 (1958).
14. K.J. Ivin: Thermodynamics of addition polymerization processes. *Angew. Chem. Int. Ed.* **12**, 487 (1973).
15. K.J. Ivin: Thermodynamics of addition polymerization. *J. Polym. Sci. A, Polym. Chem.* **38**, 2137 (2000).
16. H. Sawada: Thermodynamics of polymerization. I. *J. Macromol. Sci. C, Polym. Rev.* **3**, 313 (1969).
17. H. Sawada: Thermodynamics of polymerization. IV. Thermodynamics of equilibrium polymerization. *J. Macromol. Sci. C, Polym. Rev.* **8**, 235 (1972).
18. O. Vogl: Addition polymers of aldehydes. *J. Polym. Sci. A, Polym. Chem.* **38**, 2293 (2000).
19. S. Kostler: Polyaldehydes: homopolymers, block copolymers and promising applications. *Polym. Int.* **61**, 1221 (2012).
20. P. Kubisa, K. Neeld, J. Starr, and O. Vogl: Polymerization of higher aldehydes. *Polymer* **21**, 1433 (1980).
21. O. Vogl: Kinetics of aldehyde polymerization. *J. Macromol. Sci. C, Polym. Rev.* **12**, 109 (1975).
22. G. Odian: *Principles of Polymerization*, 4th ed. (Wiley-Interscience, New York, 2004), pp. 204–206.
23. N. Brown: Polymerization of formaldehyde. *J. Macromol. Sci. A, Pure Appl. Chem.* **1**, 209 (1967).
24. J. Masamoto: Modern polyacetals. *Prog. Polym. Sci.* **18**, 1 (1993).
25. C.E. Schweitzer, R.N. MacDonald, and J.O. Punderson: thermally stable high molecular weight polyoxymethylenes. *J. Appl. Polym. Sci.* **1**, 158 (1959).
26. T.A. Koch and P.E. Lindvig: Molecular structure of high molecular weight acetal resins. *J. Appl. Polym. Sci.* **1**, 164 (1959).

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press

27. C.F. Hammer, T.A. Koch, and J.F. Whitney: Fine structure of acetal resins and its effect on mechanical properties. *J. Appl. Polym. Sci.* **1**, 169 (1959).
28. W.H. Linton and H.H. Goodman: Physical properties of high molecular weight acetal resins. *J. Appl. Polym. Sci.* **1**, 179, (1959).
29. R.G. Alsup, J.O. Punderson, and G.F. Leverett: the effect of solvents on high molecular weight, stable acetal resins. *J. Appl. Polym. Sci.* **1**, 185 (1959).
30. O. Vogl: The polymerization of aldehydes. *J. Polym. Sci.* **46**, 261 (1960).
31. O. Vogl: Polymerization of higher aldehydes. III. Elastomeric polyacetaldehyde. *J. Polym. Sci. A, Polym. Chem.* **2**, 4591 (1964).
32. O. Vogl: Polymerization of higher aldehydes. IV. Crystalline isotactic polyaldehydes: anionic and cationic polymerization. *J. Polym. Sci. A, Polym. Chem.* **2**, 4607 (1964).
33. O. Vogl: Polymerization of higher aldehydes. V. End-capped crystalline isotactic polyaldehydes: characterization and properties. *J. Polym. Sci. A, Polym. Chem.* **2**, 4621 (1964).
34. O. Vogl and W.M.D. Bryant: Polymerization of higher aldehydes. VI. Mechanism of aldehyde polymerization. *J. Polym. Sci. A, Polym. Chem.* **2**, 4633 (1964).
35. E.G. Brame Jr., R.S. Sudol, and O. Vogl: Polymerization of higher aldehydes. VII. Tacticity of elastomeric polyacetaldehyde. *J. Polym. Sci. A, Polym. Chem.* **2**, 5337 (1964).
36. C. Aso, S. Tagami, and T. Kunitake: Polymerization of aromatic aldehydes. II. Cationic cyclopolymerization of phthalaldehyde. *J. Polym. Sci. A, Polym. Chem.* **7**, 497 (1969).
37. C. Aso and S. Tagami: Polymerization of aromatic aldehydes. III. The cyclopolymerization of phthalaldehyde and the structure of the polymer. *Macromolecules* **2**, 414 (1969).
38. C. Aso: Cyclopolymerization of bifunctional monomers. *Pure Appl. Chem.* **23**, 287 (1970).
39. S. Tagami, T. Kagiyama, and C. Aso: Polymerization of aromatic aldehydes. VII. Cyclopolymerization of *o*-formylphenylacetaldehyde and formation of a cyclic trimer. *Polym. J.* **2**, 101 (1971).
40. J.A. Kaitz, C.E. Diensendruck, and J.S. Moore: End group characterization of poly(phthalaldehyde): surprising discovery of a reversible, cationic macrocyclization mechanism. *J. Am. Chem. Soc.* **135**, 12755 (2013).
41. J.A. Kaitz, C.E. Diensendruck, and J.S. Moore: Dynamic covalent macrocyclic poly(phthalaldehyde)s: scrambling cyclic homopolymer mixtures produces multi-block and random cyclic copolymers. *Macromolecules* **46**, 8121 (2013).
42. J.A. Kaitz, C.E. Diesendruck, and J.S. Moore: Divergent macrocyclization mechanisms in the cationic initiated polymerization of ethyl glyoxylate. *Macromolecules* **47**, 3603 (2014).
43. A. Sagi, R. Weinstain, N. Karton, and D. Shabat: Self-immolative polymers. *J. Am. Chem. Soc.* **130**, 5434 (2008).
44. R. Weinstain, A. Sagi, N. Karton, and D. Shabat: Self-immolative comb-polymers: multiple-release of side-reporters by a single stimulus event. *Chem. Eur. J.* **14**, 6857 (2008).
45. R. Weinstain, P.S. Baran, and D. Shabat: Activity-linked labeling of enzymes by self-immolative polymers. *Bioconjugate Chem.* **20**, 1783 (2009).
46. A.P. Esser-Kahn, N.R. Sottos, S.R. White, and J.S. Moore: Programmable microcapsules from self-immolative polymers. *J. Am. Chem. Soc.* **132**, 10266 (2010).
47. C. de Gracia Lux, C.L. McFearin, S. Joshi-Barr, J. Sankaranarayanan, N. Fomina, and A. Almutairi: Single UV or near IR triggering event leads to polymer degradation into small molecules. *ACS Macro Lett.* **1**, 922 (2012).
48. G.I. Peterson, D.C. Church, N.A. Yakelis, and A.J. Boydston: 1,2-Oxazine linker as a thermal trigger for self-immolative polymers. *Polymer* **55**, 5980 (2014).
49. H. Okada, K. Tanaka, W. Ohashi, and Y. Chujo: Photo-triggered molecular release based on auto-degradable polymer-containing organic-inorganic hybrids. *Bioorg. Med. Chem.* **22**, 3435 (2014).
50. M.A. DeWit, A. Beaton, and E.R. Gillies: A reduction sensitive cascade biodegradable linear polymer. *J. Polym. Sci. A, Polym. Chem.* **48**, 3977 (2010).
51. M.A. DeWit and E.R. Gillies: A cascade biodegradable polymer based on alternating cyclization and elimination reactions. *J. Am. Chem. Soc.* **131**, 18327 (2009).
52. E.K.Y. Chen, R.A. McBride, and E.R. Gillies: Self-immolative polymers containing rapidly cyclizing spacers: toward rapid depolymerization rates. *Macromolecules* **45**, 7364 (2012).
53. R.A. McBride and E.R. Gillies: Kinetics of self-immolative degradation in a linear polymeric system: demonstrating the effect of chain length. *Macromolecules* **46**, 5157 (2013).
54. A.D. Wong, T.M. Gungor, and E.R. Gillies: Multi-responsive azobenzene end-cap for self-immolative polymers. *ACS Macro Lett.* **3**, 1191 (2014).
55. M.A. DeWit, A. Nazemi, S. Karamdoust, A. Beaton, and E.R. Gillies: Design, synthesis and assembly of self-immolative linear block copolymers. *ACS Symp. Ser.* **1066**, 9 (2011).
56. J.S. Robbins, K.M. Schmid, and S.T. Phillips: Effects of electronics, aromaticity, and solvent polarity on the rate of azaquinone–methide-mediated depolymerization of aromatic carbamate oligomers. *J. Org. Chem.* **78**, 3159 (2013).
57. G.G. Lewis, J.S. Robbins, and S.T. Phillips: Phase-switching depolymerizable poly(carbamate) oligomers for signal amplification in quantitative time-based assays. *Macromolecules* **46**, 5177 (2013).
58. G. Liu, X. Wang, J. Hu, G. Zhang, and S. Liu: Self-immolative polymersomes for high-efficiency triggered release and programmed enzymatic reactions. *J. Am. Chem. Soc.* **136**, 7492 (2014).
59. R. Erez, D. Shabat: The azaquinone-methide elimination: comparison study of 1,6- and 1,4-eliminations under physiological conditions. *Org. Biomol. Chem.* **6**, 2669 (2008).
60. N. Fomina, C. McFearin, M. Sermsakdi, O. Edigin, and A. Almutairi: UV and near-IR triggered release from polymeric nanoparticles. *J. Am. Chem. Soc.* **132**, 9540 (2010).
61. N. Fomina, C.L. McFearin, M. Sermsakdi, J.M. Morachis, and A. Almutairi: Low power, biologically benign NIR light triggers polymer disassembly. *Macromolecules* **44**, 8590 (2011).
62. C. de Gracia Lux, S. Joshi-Barr, T. Nguyen, E. Mahmoud, E. Schopf, N. Fomina, and A. Almutairi: Biocompatible polymeric nanoparticles degrade and release cargo in response to biologically relevant levels of hydrogen peroxide. *J. Am. Chem. Soc.* **134**, 15758 (2012).
63. C. de Gracia Lux and A. Almutairi: Intramolecular cyclization for stimuli-controlled depolymerization of polycaprolactone particles leading to disassembly and payload release. *ACS Macro Lett.* **2**, 432 (2013).
64. J. Olejniczak, J. Sankaranarayanan, M.L. Viger, and A. Almutairi: Higher efficiency two-photon degradable copolymer for remote controlled release. *ACS Macro Lett.* **2**, 683 (2013).
65. Y. Zhang, L. Ma, X. Deng, and J. Cheng: Trigger-responsive chain-shattering polymers. *Polym. Chem.* **4**, 224 (2013).
66. Y. Zhang, Q. Yin, L. Yin, L. Ma, L. Tang, and J. Cheng: Chain-shattering polymeric therapeutics with on-demand drug-release capability. *Angew. Chem. Int. Ed.* **52**, 6435 (2013).
67. W. Seo and S.T. Phillips: Patterned plastics that change physical structure in response to applied chemical signals. *J. Am. Chem. Soc.* **132**, 9234 (2010).
68. A.M. DiLauro, J.S. Robbins, and S.T. Phillips: Reproducible and scalable synthesis of end-cap-functionalized depolymerizable poly(phthalaldehydes). *Macromolecules* **46**, 2963 (2013).
69. J.D. Winter, A.P. Dove, A. Knoll, P. Gerbaux, P. Dubois, and O. Coulembier: Control over molar mass, dispersity, end-groups and kinetics in cyclopolymerization of *ortho*-phthalaldehyde: adapted choice of phosphazene organocatalyst. *Polym. Chem.* **5**, 706 (2014).
70. J.A. Kaitz and J.S. Moore: Functional phthalaldehyde polymers by copolymerization with substituted benzaldehydes. *Macromolecules* **46**, 608 (2013).
71. J.A. Kaitz, C.M. Possanza, Y. Song, C.E. Diesendruck, A.J.H. Spiering, E.W. Meijer, and J.S. Moore: Depolymerizable, adaptive supramolecular polymer nanoparticles and networks. *Polym. Chem.* **5**, 3788 (2014).
72. M. Tsuda, M. Hata, R. Nishida, and S. Oikawa: Acid-catalyzed degradation mechanism of poly(phthalaldehyde): unzipping reaction of chemical amplification resist. *J. Polym. Sci. A, Polym. Chem.* **35**, 77 (1997).
73. D.S. Frederick, H.D. Cogan, and C.S. Marvel: The reaction between sulfur dioxide and olefins. Cyclohexene. *J. Am. Chem. Soc.* **56**, 1815 (1934).
74. M. Hunt and C.S. Marvel: The reaction between sulfur dioxide and olefins. II. Propylene. *J. Am. Chem. Soc.* **57**, 1691 (1935).

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press

75. L.L. Ryden and C.S. Marvel: The reaction between sulfur dioxide and olefins. III. Higher olefins and some limitations of the reaction. *J. Am. Chem. Soc.* **57**, 2311 (1935).
76. T. Shinoda, T. Nishiwaki, and H. Inoue: Decomposition of poly (4-hydroxystyrene sulfone) in alkaline aqueous solutions. *J. Polym. Sci. A, Polym. Chem.* **38**, 2760 (2000).
77. J.M. Lobez and T.M. Swager: Disassembly of elastomers: poly(olefin sulfone)–silicones with switchable mechanical properties. *Macromolecules* **43**, 10422 (2010).
78. T.N. Bowmer and J.H. O'Donnell: Radiation degradation of poly(olefin Sulfone)s: a volatile product study. *J. Macromol. Sci. A, Pure Appl. Chem.* **17**, 243 (1982).
79. J.R. Brown and J.H. O'Donnell: The degradation of poly(butene-1 sulfone) during γ irradiation. *Macromolecules* **3**, 265 (1970).
80. J.R. Brown and J.H. O'Donnell: γ Radiolysis of poly(butene-1 sulfone) and poly(hexane-1 sulfone). *Macromolecules* **5**, 109 (1972).
81. P.B. Ayscough, K.J. Ivin, and J.H. O'Donnell: Electron spin resonance spectra of γ-irradiated sulphones and polysulphones. *J. Chem. Soc. Faraday Trans.* **61**, 1110 (1965).
82. M.J. Bowden and L.F. Thompson: Electron irradiation of poly(olefin sulfones). Application to electron beam resists. *J. Appl. Polym. Sci.* **17**, 3211 (1973).
83. H. Yaguchi and T. Sasaki: Photoinduced depolymerization of poly(olefin sulfone)s possessing photobase generating groups in the side chain. *Macromolecules* **40**, 9332 (2007).
84. T. Sasaki and H. Yaguchi: Photoinduced unzipping depolymerization of poly(olefin sulfone)s possessing photobase generator and base amplifier. *J. Polym. Sci. A, Polym. Chem.* **47**, 602 (2009).
85. L.F. Thompson and M.J. Bowden: A new family of positive electron beam resists—poly(Olefin Sulfones). *J. Electrochem. Soc.* **120**, 1722 (1973).
86. E. Gipstein, W. Moreau, G. Chiu, and O.U. Need: The synthesis and evaluation of cyclic olefin sulfone copolymers and terpolymers as electron beam resists. *J. Appl. Polym. Sci.* **21**, 677 (1977).
87. M.J. Bowden and E.A. Chandross: Poly(Vinyl Arene Sulfones) as novel positive photoresists. *J. Electrochem. Soc.* **122**, 1370 (1975).
88. C.G. Willson: Organic resist materials—theory and chemistry, in *Introduction to Microlithography—Theory, Materials, and Processing,* edited by L.F. Thompson, C.G. Wilson and M.J. Bowden (American Chemical Society, Washington, D.C., 1983), pp. 126.
89. C.G. Willson, G.N. Taylor, and T.M. Wolf: Oxygen plasma removal of thin polymer films. *Polym. Eng. Sci.* **20**, 1087 (1980).
90. H. Ito and C.G. Willson: Chemical amplification in the design of dry developing resist materials. *Polym. Eng. Sci.* **23**, 1012 (1983).
91. C.G. Willson, H. Ito, J.M.J. Fréchet, T.G. Tessier, and F.M. Houlihan: Approaches to the design of radiation-sensitive polymeric imaging systems with improved sensitivity and resolution. *J. Electrochem. Soc.* **133**, 181 (1986).
92. H. Ito and R. Schwalm: Thermally developable, positive resist systems with high sensitivity. *J. Electrochem. Soc.* **136**, 241 (1989).
93. H. Ito, M. Ueda and A.F. Renaldo: Thermally developable, positive tone, oxygen RIE barrier resist for bilayer lithography. *J. Electrochem. Soc.* **136**, 245 (1989).
94. O. Coulembier, A. Knoll, D. Pires, B. Gotsmann, U. Duerig, J. Frommer, R.D. Miller, P. Dubois, and J.L. Hedrick: Probe-based nanolithography: self-amplified depolymerization media for dry lithography. *Macromolecules* **43**, 572 (2010).
95. A.W. Knoll, D. Pires, O. Coulembier, P. Dubois, J.L. Hedrick, J. Frommer, and U. Duerig: Probe-based 3-D nanolithography using self-amplified depolymerization polymers. *Adv. Mater.* **22**, 3361 (2010).
96. J.M. Lobez and T.M. Swager: radiation detection: resistivity responses in functional poly(Olefin Sulfone)/Carbon nanotube composites. *Angew. Chem. Int. Ed.* **49**, 95 (2010).
97. N. Grassie and I.G. Macfarlane: The thermal degradation of polysiloxanes—I. Poly(dimethylsiloxane). *Eur. Polym. J.* **14**, 875 (1978).
98. W. Patnode and D.F. Wilcock: Methylpolysiloxanes. *J. Am. Chem. Soc.* **68**, 358 (1946).
99. L. Cademartiri and G.A. Ozin: *Concepts of Nanochemistry* (Wiley-VCH, Weinheim, 2009), pp. 113–139.
100. C.A. Blencowe, A.T. Russell, F. Greco, W. Hayes, and D.W. Thornthwaite: Self-immolative linkers in polymeric delivery systems. *Polym. Chem.* **2**, 773 (2011).
101. A.P. Esser-Kahn, S.A. Odom, N.R. Sottos, S.R. White, and J.S. Moore: triggered release from polymer capsules. *Macromolecules* **44**, 5539 (2011).
102. A.M. DiLauro, A. Abbaspourrad, D.A. Weitz, and S.T. Phillips: Stimuli-responsive core–shell microcapsules with tunable rates of release by using a depolymerizable poly(phthalaldehyde) membrane. *Macromolecules* **46**, 3309 (2013).
103. B. Fan, J.F. Trant, A.D. Wong, and E.R. Gillies: Polyglyoxylates: a versatile class of triggerable self-immolative polymers from readily accessible monomers. *J. Am. Chem. Soc.* **136**, 10116 (2014).
104. C.E. Diesendruck, G.I. Peterson, H.J. Kulik, J.A. Kaitz, B.D. Mar, P.A. May, S.R. White, T.J. Martinez, A.J. Boydston, and J.S. Moore: Mechanically triggered heterolytic unzipping of a low-ceiling-temperature polymer. *Nat. Chem.* **6**, 623 (2014).
105. H. Zhang, K. Yeung, J.S. Robbins, R.A. Pavlick, M. Wu, R. Liu, A. Sen, and S.T. Phillips: Self-powered microscale pumps based on analyte-initiated depolymerization reactions. *Angew. Chem. Int. Ed.* **51**, 2400 (2012).
106. A.M. DiLauro, H. Zhang, M.S. Baker, F. Wong, A. Sen, and S.T. Phillips: Accessibility of responsive end-caps in films composed of stimuli-responsive, depolymerizable poly(phthalaldehydes). *Macromolecules* **46**, 7257 (2013).
107. H. Lopez Hernandez, S.-K. Kang, O.P. Lee, S.-W. Hwang, J.A. Kaitz, B. Inci, C.W. Park, S. Chung, N.R. Sottos, J.S. Moore, J.A. Rogers, and S.R. White: Triggered transience of metastable poly(phthalaldehyde) for transient electronics. *Adv. Mater.* **26**, 7637 (2014).
108. F. Holzner, C. Kuemin, P. Paul, J.L. Hedrick, H. Wolf, N.D. Spencer, U. Duergi, and A.W. Knoll: Directed placement of gold nanorods using a removable template for guided assembly. *Nano Lett.* **11**, 3957 (2011).
109. A.P. Vogt, J.D. Winter, P. Krolla-Sidenstein, U. Geckle, O. Coulembier, and C. Barner-Kowollik: Polyphthalaldehyde-*block*-polystyrene as a nanochannel template. *J. Mater. Chem. B* **2**, 3578 (2014).
110. M.G. Olah, J.S. Robbins, M.S. Baker, and S.T. Phillips: End-capped poly (benzyl ethers): acid and base stable polymers that depolymerize rapidly from head-to-tail in response to specific applied signals. *Macromolecules* **46**, 5924 (2013).
111. J.P. Vairon, E. Muller, and C. Bunel: The ionic polymerizations of methyl glyoxylate. *Macromol. Symp.* **85**, 307 (1994).
112. C.H. Brachais, J. Huguet, and C. Bunel: Synthesis, characterization and stabilization of poly(methyl glyoxylate). *Polymer* **38**, 4959 (1997).
113. C.H. Brachais, R. Duclos, C. Vaugelade, J. Huguet, M.L. Capelle-Hue, and C. Bunel: Poly(methyl glyoxylate), a biodegradable polymeric material for new drug delivery systems. *Int. J. Pharm.* **169**, 23 (1998).
114. F. Burel, L. Rossignol, P. Pontvianne, J. Hartman, N. Couesnon, and C. Bunel: Synthesis and characterization of poly(ethyl glyoxylate)—a new potentially biodegradable polymer. *e-Polymers* **3**, 407 (2003).
115. B. Belloncle, F. Burel, H. Oulyadi, and C. Bunel: Study of the in vitro degradation of poly(ethyl glyoxylate). *Polym. Degrad. Stab.* **93**, 1151 (2008).
116. J.A. Kaitz and J.S. Moore: Copolymerization of *o*-phthalaldehyde and ethyl Glyoxylate: cyclic macromolecules with alternating sequence and tunable thermal properties. *Macromolecules* **47**, 5509 (2014).

https://doi.org/10.1557/mrc.2015.28 Published online by Cambridge University Press