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Synthesis of Unzipping Polyester and a Study of its Photochemistry

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ABSTRACT: Preparation of an unzipping polyester is reported. The monomer was prepared from benzoic acid in 4-step sequence. Step growth polymerization of the monomer provides the target polymer. Efficient depolymerization upon irradiation at 254 nm was confirmed with a quantum yield of > 0.8. The photolysis mechanism was investigated and the results of radical trapping experiments are consistent with an initial Norrish type I like homolysis followed by a radical mediated depropagation reaction driven by aromatization.

INTRODUCTION

Stimuli responsive materials are of great interest due to their ability to provide on-demand control of material properties.^{1,2} One class of stimuli responsive materials is those that spontaneously depolymerize (unzip) in response to stimuli. The general design of these unzipping polymers involves incorporation of a labile functional moiety on the end group or implantation of trigger-sensitive acceptor in the middle of the main chain as a linker.^{3,4} Such materials find value especially in the field of controlled drug release⁵⁻⁷ and sensor applications.^{8–10} Materials of this sort also have potential for use in the design of resists for lithographic patterning applications.^{11–13}

Several reviews on controlled depolymerization of so called "self-immolating"¹⁴ (unzipping) polymers have been published.^{1,15,16} Unzipping polymers have been reported that are sensitive to a variety of stimuli including enzymes,^{17,18} acid,^{19–21} heat,^{22,23} mechanical force^{24,25} and light.^{19,26,27} Macromolecules that are sensitive to light are of particular interest, because they enable amplification of a single stimulation reaction that is relatively easy to control.^{28,29}

The polymer community has reported the design and synthesis of several classes of photolabile, unzipping polymers including end-capped poly(phthalaldehyde), (PPA),^{30,31} various poly(benzyl carbamate)s,³² and poly(benzyl ether)s.³³ All of these materials depolymerize efficiently under certain irradiation conditions.^{11,28,34,35}

One class of such materials is based on end capped polymers with a low ceiling temperature, Tc.³¹ In some cases these polymers are end-capped with a photolabile protecting group such as *ortho*-nitrobenzyl which stabilizes them until signaled by irradiation.^{19,26} Recently polyglyoxylates were reported to be a functioning new platform for the design of such degradable polymers .^{36–38} In another approach, end capped polymers are formulated together with latent catalysts. Subsequent photoexposure generates an active catalyst that cleaves either the end group or the main chain to initiate the unzipping reaction.^{39,40} Another approach to such materials involves designing the polymer such that each repeat unit is intrinsically photo labile such that exposure results in cleavage of the backbone to generate reactive chain ends that depropagate or unzip by an irreversible pathway different from that used to prepare the polymer.^{41,42}

Unfortunately acyl end capped poly(phthalaldehyde) is not stable to storage.³¹ The poly(benzyl carbamate)s suffer from slow depolymerization rates, and poly(benzyl ether) unzipping is only successful in solution.⁴³ The benzene-based depolymerizable polymers that undergo azaguinone-methide elimination exhibit slow rates of depolymerization⁵ The stability of polymers, such as PPA has to be carefully tuned to achieve a balance between storage and handling stability and efficient unzipping.44-47 Interest in use of unzipping polymers for lithographic applications defines need for a polymer that unzips with no catalyst, but solely by exposure to radiation, is sufficiently thermally stable to survive typical photoresist processing conditions and forms homogeneous blends with base soluble matrix resins such as cresol novolac. A large number of candidates that are discussed in the previous paragraphs were auditioned for this application, but only one material has been found that meets all of the requirements. It is an aromatizing polyester. Herein, we report the preparation of this new unzipping polyester and the study of its photochemistry. The original design concept for the new unzipping polymer was inspired by the benzyl carbamates, which efficiently expel carbon dioxide upon cleavage thereby preventing any re-polymerization reaction.32

RESULTS AND DISCUSSION

Preparation of the monomer started with a Birch reduction^{48–50} of benzoic acid, followed by alkylation, which involved quenching of the carboxylate anion by a reductive methylation. This created a quaternary center in the sixmembered ring, which served to prevent tautomeric production of the conjugated acid. Subsequently a trifluoroethyl ester group was installed via a carbodiimide mediated coupling. Trifluoroethanol was chosen because it is an excellent leaving group, which is an important factor at the propagation stage of the polymerization and it is stable to the conditions of the synthetic sequence. The diene ester **2** was

then oxidized to the dieneone 3, which was subsequently subjected to Luche's reduction to give the dienol 4 (Scheme 1).

Scheme 1. Synthesis of the unzipping monomer 4.



The synthetic route provided acceptable yields, but the last reduction step was a bit challenging in terms of both synthesis and purification. There was a need to consider 1,2 reduction to the diallylic alcohol, over 1,4 reduction to the unsaturated ketone. Many reducing reaction conditions were tried and finally Luche's reduction was found to give the desired product in a reasonable yield. The reaction was run in methanol and there was a problem of small amounts of transesterification to the methyl ester, which made the purification challenging. Silica gel column chromatography was not fully sufficient. A final vacuum distillation was required to obtain pure monomer.

A step growth polymerization of the deprotonated monomer was carried out (Scheme 2). Trifluoroethanol (TFE) forms a low boiling azeotrope with toluene⁵¹ therefore simply distilling slowly removes the alcohol by-product during the course of the reaction. Slow distillation of the azeotrope was found to be an efficient method for driving the polymerization by Le Chatelier's principle.

Scheme 2. Polymerization of the unzipping monomer 4.



The polymerization was investigated in detail (Figure 1). At first, an equivalent of a strong base such as *n*-BuLi was employed to deprotonate the acidic hydroxyl protons completely, and at the same time lithium was captured by a crown ether, to render the oxyanion more nucleophilic. This anion reacts with another ester monomer and nucleophilic acyl substitution results in propagation in a step growth fashion. The chain ends are strong bases so successful production of polymer demands careful exclusion of proton sources and electrophiles.



Figure 1. Proposed mechanism for the polymerization of 4.

The crude product of the polymerization has a GPC elution pattern that shows a shoulder peak in the low molecular weight region. It was assumed that this peak was coming from terminated growing polymer chains or from a cyclic oligomer by-product. The monomer for this polymerization is diastereomeric. One might expect that the pure *cis*-isomer has a higher probability of forming cyclic oligomers compared to *trans*-isomer. To test that hypothesis, the crude polymer was subjected to preparatory column chromatography on polystyrene resin beads. The GPC profiles of the unzipping polymer **5** before and after a chromatographic separation process are provided in figure 2. One fraction turned out to be the all cis cyclic tetramer **7**, the structure of which confirmed by X-ray crystallography (Figure S8).



Figure 2. GPC profile of the polymer before and after the chromatographic separation of cyclic tetramer 7. The red circle indicats the cyclic tetramer in the crude polymeric mixture. Before separation; Mn: 2.3 kDa, D: 2.16, after separation; Mn: 3.8 kDa, D: 1.57. The peak at 32 minutes is due to solvent.

It proved to be difficult to isolate the pure *cis* and *trans* monomers and it was also difficult to tell which one was which. No significant nuclear overhauser effect (NOE) was detected in the free alcohol form. Therefore, in order to not only achieve better separation, but also enhance the NOE, a bulky tert-butyldimethylsilyl (TBS) protecting group was attached to the alcohol group. This modification made it possible to tell which isomer is *cis* and which is *trans*. Fractions of very trans-rich monomer and very cis-rich monomer, were subjected to identical polymerization conditions. The trans-rich monomer provided a much higher molecular weight product and the cis-rich sample provided an increased yield of the cyclic tetramer (Figure 3). The yield of the cyclic tetramer was about 1.1 % when the diastereomeric monomers were used for the polymerization. The yield was increased to 6.1 % when cis-rich monomer was subjected to the same reaction conditions. There was no evidence of forming the cyclic oligomer when the reaction was run with the trans-rich monomer.



Figure 3. GPC profiles of unzipping polymers prepared from

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trans-rich monomer (blue, Mn: 19.0 kDa, Đ: 2.55) and *cis*-rich monomer (red, Mn: 7.1 kDa, Đ: 1.53).

A level of thermal stability is important for resist application because the polymer must survive baking processes during coating. There is no absolute set point for this process temperature, but photoresists that have higher thermal stability enable wider process windows. So, thermogravimetric analysis (TGA) was performed on the unzipping polymer and a 5% weight loss was recorded at 96 °C at a 10 °C/min heating rate. Isothermal TGA was also conducted, which showed that mass was lost at a significant rate above 100 °C. (Figure S7). While not as stable as we would like, the material is sufficiently stable for processing. The application of the polymer to formulation of high sensitivity resists will be described in a subsequent submission.

In order to formulate the unzipping polymer **5** as a photoresist, it has to be blended with an acidic resin, such as *m*-cresol novolac, which is widely used to formulate positive tone photoresists. However when the unzipping polymer **5** was mixed with novolac, it slowly degraded at room temperature and the performance of the formulation varied as a function of time. It was hypothesized that the acidity of the cresol repeat unit in novolac is sufficient to trigger the depolymerization of the unzipping polymer **5**.

23 Model compounds were synthesized (Figure S₃) to study 24 the acid and base lability of the polymer. The intention was 25 first to selectively hydrolyze the ester to yield the carboxylic acid and then subject the free acid to basic conditions to 26 monitor the rate of toluene formation. Initial attempts to 27 hydrolyze the ester in basic conditions (LiOH in MeOH) 28 resulted in very rapid destruction of the starting material and 29 generation of toluene. Subsequently the use of the acid labile 30 *t*-butyl ester was explored. The methyl ether variant was 31 synthesized, treated with TFA and the reaction was monitored 32 by ¹H-NMR (Figure S₃). After 8 minutes, toluene peaks (7.25-33 7.15 ppm) started to appear together with a small down field 34 peak around 10.5 ppm that likely corresponds to the free acid 35 together with a singlet at 4.6 ppm that closely corresponds to the isobutylene. These results suggest that the monomer 36 readily decarboxylates upon hydrolysis of the ester in either 37 acid or base. The evidence also suggests that the monomer ion 38 quickly aromatizes. Clearly, the 1,4-cyclohexyldiene 39 backbone is sensitive to both acid and base conditions and 40 readily forms toluene. This also appears to be true for the 41 radical, based on experiments described below. 42

To study the stability of the unzipping polymer **5** in acid, an ethereal solution of hydrochloric acid was added to a solution of the unzipping polymer **5**. Nuclear magnetic resonance spectroscopy (NMR) was performed 1 hour after addition and it was found that the polymer had unzipped completely giving toluene as a by-product (Figure S4a). To protect the free alcohol group, the end group was acetylated and the corresponding acylated polymer **6** was subjected to the same acidic conditions. When hydrochloric acid was added to the acylated unzipping polymer **6**, there was very little production of toluene detected by NMR compared to the unzipping polymer **5** (Figure S4b).

The unzipping polymer **5** was exposed to ultraviolet (UV) light to establish its sensitivity. A small amount of the unzipping polymer was dissolved in CD₃CN and introduced into a quartz NMR tube. After 1.5 hours of exposure in a Rayonet photoreactor equipped with eight, 8 W light bulbs,

nearly all of the polymer had unzipped to generate toluene (Figure S₅). These data indicate that the polymer backbone is inherently sensitive to UV exposure, which makes it an ideal unzipping polymer for lithographic use. The quantum yield (Φ) for conversion to toluene was calculated by using KI-KIO₃ which is a well-documented chemical actinometer.⁵² and determined to be 0.85 based on monomer conversion.

We were interested in elucidating the mechanism of the photolysis of the unzipping polymer 5. Tony Kaiser and Hanns Fischer studied the photo-cleavage of aliphatic carboxylic acids and esters in solution and concluded that the Norrish type I reaction was the most reasonable scission pathway.53 The Norrish type I reaction has been extensively studied and is well known for ketone and aldehyde functional groups, but not many studies have been conducted on ester moieties. It is possible that cleavage could occur at the ester O-alkyl bond. However, Kaiser and Fischer documented that homolysis of aliphatic carboxylic acids and esters primarily occurs at C (α) to carbonyl carbon bond. This implies that the ester bond of the unzipping polymer might undergo homolysis upon irradiation to generate radical intermediates that could initiate a depolymerization reaction of the polymer fragments.

The first strategy to test this hypothesis involved attempting to capturing a radical intermediate with a stable radical trapping reagent, such as the 2,2,6,6-tetramethyl-1piperidinyloxy free radical (TEMPO). Neither any generated radicals nor the TEMPO radical can be detected by NMR spectroscopy. But, if radicals are formed in the reaction, recombination with TEMPO would trap these radicals to form a covalent carbon-oxygen bond (Figure 4a). The products of such a coupling would have distinctive peaks in NMR coming from the methyl group of the TEMPO moiety (Figure S6). The NMR spectra of the products of the TEMPO trapping experiment do indeed show coupling to the TEMPO.



Figure 4. Proposed photolysis mechanism of the unzipping polymer **6** and trapping of radical intermediates by (a) TEMPO and (b) DMPO. Conditions: $[6]_0 = 0.5$ mM, [TEMPO or DMPO]₀/[**6**]₀ = 1.0, acetonitrile-*d*, or toluene.

Spin trapping is another powerful tool that can provide evidence for radical intermediates.⁵⁴ Thus, 5,5-dimethyl-1pyrroline N-oxide (DMPO) was chosen for this study. If radicals are formed by photolysis of the unzipping polymer **6**, coupling with DMPO should give distinctive signals in electron paramagnetic resonance (EPR) spectroscopy because the DMPO spin state would change (Figure 4b).

Figure 5 shows the EPR spectra obtained by the DMPO trapping experiment and by computational simulation. The two spectra match very well. The results from these two

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trapping experiments provide strong evidence that the unzipping polymer undergoes homolytic chain cleavage upon photolysis *via* the Norrish type I like reaction.



Figure 5. Experimental (black line) and simulated (blue line) EPR spectra of spin-trapped nitric oxide radical in the presence of DMPO in toluene. Conditions: $[6]_o = 0.5$ mM, $[DMPO]_o/[6]_o = 1.0$, toluene.

CONCLUSION

In conclusion, we have successfully synthesized and studied an intrinsically photosensitive, unzipping, aromatizing polyester. A step growth polymerization of the monomer anion provided the desired polymer. The formation of a cyclic tetramer side product during step growth polymerization was documented and a method for removing it from the polymer was established. The stability of the unzipping polymer 5 toward acid was increased by acylation of the free alcohol end group. The unzipping polymer 5 was found to be labile to UV irradiation and depolymerized rapidly upon exposure at 254 nm to yield toluene and CO2. Trapping experiments are consistent with the hypothesis that the photolysis proceeds via a Norrish type I like reaction. This type of photolabile material is of great interest for lithographic applications since it enables a photochemical cleavage with "gain" that does not involve a catalyst. Such a polymer is considered as a strong candidate for the design of a next generation of lithography resists. A patterning study based on this material will be reported separately.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic procedures, spectra data, compound characterization data and quantum yield calculation (PDF)

Crystallographic data of cyclic tetramer (CIF)

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Notes

The authors declare no competing financial interests.

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