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Depolymerization of Trityl End-capped Poly(ethyl glyoxylate): Potential Applications in Smart Packaging^a

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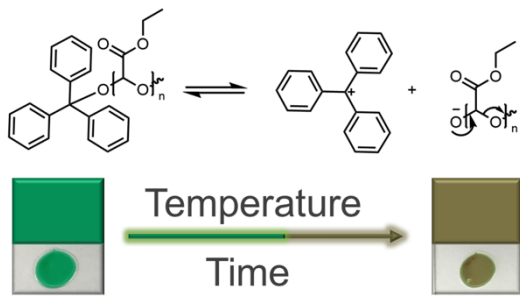
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Abstract: The temperature-dependent depolymerization of self-immolative poly(ethyl glyoxylate) (PEtG) capped with triphenylmethyl (trityl) groups was studied and its potential application for smart packaging was explored. PEtGs with four different trityl end-caps were prepared and found to undergo depolymerization to volatile products from the solid state at different rates depending on temperature and the electron-donating substituents on the trityl aromatic rings. Through the incorporation of hydrophobic dyes including Nile red and IR-780, the depolymerization was visualized as a color change of the dye as it changed from a dispersed to aggregated state. The ability of this platform to provide information on thermal history through an easily readable signal makes it promising in smart packaging applications for sensitive products such as food and other cargo that is susceptible to degradation.

^a **Supporting Information** is available online from the Wiley Online Library or from the author.



1. Introduction

Stimuli-responsive polymers, which respond to stimuli with changes in chemical or physical properties, have been intensively researched over the past couple of decades.^[1] Their unique behavior relative to conventional non-responsive polymers has inspired their use in a wide variety of applications including biosensors,^[2] smart coatings,^[3] drug delivery vehicles,^[4, 5] as well as self-healing and shape-memory materials.^[6, 7] However, conventional stimuli-responsive polymers that contain many responsive moieties along the polymer backbone usually require a large number of stimuli-mediated events to bring about significant changes in properties.^[8, 9] This may result in limitations for some applications.

Self-immolative polymers (SIPs), a recently developed class of stimuli-responsive materials, consist of a polymer backbone and a stimuli-responsive end-cap at one or both polymer termini.^[9, 10] Upon detection of an external signal that can cleave the end-cap, complete collapse of the polymer backbone via end-to-end depolymerization occurs. Compared with traditional stimuli-responsive polymers, SIPs can be easily modified to achieve responsiveness to different stimuli via alterations of the end-cap rather than complete re-engineering of the polymer backbone. Using this strategy, SIPs that respond to stimuli including light,^[11-13] heat,^[14, 15] changes in pH,^[16, 17] oxidation,^[18] and reduction^[19, 20] have been developed. In addition, the response mechanism of SIPs allows signal amplification, as one equivalent of stimulus can lead to complete polymer degradation and generation of many monomers or degradation products. SIPs have also been explored as transient materials.^[21, 22] In the past several years, SIP backbones including polycarbamates,^[23] polycarbonates,^[19, 24] poly(benzyl ether)s,^[25] and polyacetals^[11, 26-28] have been reported.

We recently reported polyglyoxylates as a class of polyacetal-based SIPs.^[11] They can be prepared from commercial monomers including ethyl glyoxylate and degrade to

environmentally benign products such as glyoxylic acid and ethanol.^[29, 30] Unlike other SIPs, polyglyoxylates can also degrade to volatile products (e.g., ethyl glyoxylate), so they undergo rapid depolymerization in the solid state.^[31] We reported the polymerization of different glyoxylate monomers that enabled the properties of the polymers to be tuned^[11] and also the incorporation of different end-caps that enable poly(ethyl glyoxylate) (PEtG) to respond to different stimuli.^[16] As part of this work, we reported a 4-methoxytriphenylmethyl (MMT) end-capped PEtG that was responsive to acid in aqueous-organic solvents and the rate of end-cap cleavage was increased by the introduction of additional electron-donating methoxy groups to the aromatic ring (e.g., in dimethoxytriphenylmethyl, DMT) (**Figure 1a**).^[16] While PEtG-DMT and PEtG-MMT were stable for days to weeks in aqueous-organic solvent mixtures in the absence of acid, in further exploring these polymers, we unexpectedly found that they disappeared into the air when cast as films and stored in the dry state in the absence of any acid, even for only a few days. This result contrasted with our previous work on PEtG films with UV light-responsive end-caps which only degraded when their end-caps had been actively cleaved off.^[31] We describe here our exploration of this phenomenon for four different triphenylmethyl (trityl) end-capped PEtGs and their potential application in smart packaging. To the best of our knowledge, this is the first observation of this type of behavior for the well-known trityl group and the first example of SIPs applied in this manner.

2. Results and Discussion

In addition to the previously reported MMT and DMT end-capped PEtGs, we also synthesized and studied trityl end-caps containing a propargyl ether with zero or one methoxy groups (Scheme S1) and used these to prepare the corresponding trityl end-capped polymers PEtG-AT and PEtG-AMT (Figure 1). These polymers had initially been designed to provide an alkyne coupling site for the preparation of amphiphilic block copolymers, but were

included in the current study because of the subtle electronic effects introduced by the alkyne group. Polymerization and end-capping were performed at -20 °C in the presence of triethylamine and with initiation by trace hydrate of the monomer as previously reported.^[11] Molar masses of the polymers ranged from 19 to 35 kg mol⁻¹ (details in SI).

To measure their solid-state depolymerization, the polymers were dissolved in CH₂Cl₂ and drop-cast onto glass slides to form coatings. The coatings were then stored at different temperatures and their mass loss was measured. At 6 °C, all the polymer coatings were relatively stable for ~30 days (**Figure 2**). PEtG-DMT and PEtG-AMT began to depolymerize after 30 days. At 10 °C, PEtG-DMT began depolymerizing almost immediately and PEtG-AMT after ~5 days. This result suggests that the DMT end-cap may be slightly less stable compared with the AMT end-cap. The propargyl ether of the AMT may be less electron-donating than the methoxy due to the modest electronegativity of the alkyne. PEtG-MMT and PEtG-AT were stable at 10 °C for the first ~15 days and then began to depolymerize. At 22 °C, PEtG-DMT and PEtG-AMT lost ~50% of their mass over 5 days, while PEtG-MMT and PEtG-AT lost 50% of their mass over 15-20 days. Finally, at 30 °C PEtG-DMT and PEtG-AMT rapidly depolymerized, losing more than 50% of their mass over the first day and PEtG-MMT and PEtG-AT lost 50% of their mass over 3-5 days. At the highest temperatures, most systems reached essentially no mass remaining over the time period of the experiment. PEtG-AT has ~10% remaining mass, which might be attributed to some trapping of the ethyl glyoxylate as its non-volatile hydrate through reaction with water vapour in the air. A small residual mass due to the non-volatile trityl end-cap would also be expected. A control PEtG with a benzyl carbonate end-cap (PEtG-control, Figure S1) did not undergo any significant mass loss at any of the studied temperatures over 35 days.

To further demonstrate the effect of temperature and confirm the depolymerization, PEtG-AMT and PEtG-control were dissolved in DMSO- d_6 and sealed in NMR tubes, then variable temperature ^1H NMR spectroscopy was performed. After the first spectrum was taken at 25 °C, the temperature was increased at intervals of 25 °C to 125 °C. Each increment took ~15 minutes and spectra were acquired at each temperature. Over the time period of the study, PEtG-AMT was relatively stable below 100 °C, as indicated by broad peaks corresponding to the PEtG backbone and pendant esters (**Figure 3a**). However, when the temperature reached 100 °C, a singlet at 9.1 ppm emerged, indicating depolymerization to ethyl glyoxylate. With a further increase to 125 °C, the singlet at 9.1 ppm increased greatly in intensity and the broad peak at 5.4 ppm corresponding to the PEtG backbone methine proton decreased. After 1 h at 125 °C, the peak at 5.4 ppm had almost completely disappeared, indicating complete depolymerization of PEtG-AMT. For PEtG-control carried through the same experimental conditions, only a small degree of degradation was observed (Figure 3b). This result demonstrates that the depolymerization of PEtG-AMT was induced by end-cap removal at elevated temperature.

Overall, the above studies showed that trityl end-capped PEtGs underwent depolymerization in a temperature-dependent manner and that the rate could be tuned based on the electronics of the trityl groups. In addition, this behavior was specific to the trityl end-caps compared to carbonate end-caps. We attribute it to an equilibrium existing between the capped and uncapped forms of the PEtG (Figure 1c). The position of this equilibrium depends on the stability of the trityl cation, with electron-donating groups more strongly favoring the uncapped polymer. In the uncapped state, PEtG can depolymerize, releasing the volatile monomer ethyl glyoxylate (boiling point ~110 °C) and continually shifting the equilibrium to the right, particularly for solid state samples. At higher temperatures, this depolymerization and monomer evaporation occurs more rapidly, and is also more highly favored

thermodynamically due to the entropic contributions of depolymerization and evaporation. In contrast, in conventional small molecule chemistry involving trityl groups, the product is often not volatile and there are no onwards reactions affecting the equilibrium. Thus, the combination of factors leading to the observed thermal instability are quite unique to self-immolative polymers.

Based on the mass loss profiles, we envisioned that the temperature-dependent behavior of the trityl end-capped PEtGs could be harnessed for applications where the thermal history of the material is important. For example, storage temperatures are critical in the transport of food and other perishable materials. Thus far, there are two main classes of food quality sensors. One type of sensor can directly measure the quality of the food product inside the packaging by detecting the chemicals associated with food spoilage, such as amines, ethanol and hydrogen sulfide. This can be done through the interaction of these chemicals with pH sensitive dyes, proteins and enzymes^[32-34] Another type of sensor provides information on the conditions of the package exterior by integrating the temperature and time associated with food storage. This type of sensor is usually based on diffusion or chemical reactions.^[35, 36] As the depolymerization of trityl end-capped PEtG is directly associated with storage temperature and time, this material has the potential to serve as a simple, low-cost component in smart packaging for food and other sensitive products.

To use the depolymerization reaction of PEtG for smart packaging, it is critical to translate the depolymerization into a clear signal. To achieve this, we investigated the incorporation of hydrophobic dyes, whose optical properties can change, depending on their environments. First, Nile red was investigated as it can exhibit variable color depending on its environment.^[37] It was mixed with the trityl end-capped PEtGs through co-dissolution in CH_2Cl_2 , then the solvent was evaporated to form a deep pink coating containing 0.1 wt% of

the dye (**Figure 4a**). After 24 h at 22 °C, the PEtG-DMT and PEtG-AMT coatings had changed from deep pink into deep purple with a noticeable loss of polymer. To clearly display this color change, squares corresponding to computer generated color samples that were sub-sampled from digital pixels of the pictures of PEtG coatings are included in Figure 4a. For PEtG-MMT, the color change occurred over ~4 days, and for PEtG-AT over ~6 days. In contrast, PEtG-control coatings didn't show any significant color change during their incubation at 22 °C for 6 days. To examine this change spectroscopically, thinner films of both PEtG-AMT and PEtG-control were prepared, then the absorption spectra of the films before and after incubation were measured. Before incubation, both films had Nile red absorptions centered at 544 nm with a bandwidth of ~85 nm (width at half-peak height) (Figure 4c-d). After incubation for 24 h, the baseline of the PEtG-AMT sample significantly increased due to scattering arising from Nile red aggregation after the disappearance of the polymer. In addition, the bandwidth increased to ~115 nm (after subtraction of the baseline). This presumably results in the color change. PEtG-control didn't exhibit any significant change in the absorption profile.

While incorporated Nile red underwent a color change upon depolymerization, it was subtle in some cases. Thus, the incorporation of IR-780 was also explored. This dye appeared as green when well dispersed in the hydrophobic polymer environment (Figure 4b). However, upon incubation at 22 °C, the coatings turned brown over 3-10 days, corresponding to dye aggregation. The time over which the color changed was again dependent on the specific trityl end-cap but overall it took longer than the Nile red color change as we observed. Thus, the time for the response signal depends to some extent on the specific dye.

3. Conclusions

In conclusion, we have demonstrated that PEtGs with trityl end-caps having electron-donating groups undergo solid state depolymerization in a temperature-dependent manner. This process is driven by the evaporation of monomer under ambient conditions. The rate of depolymerization could be tuned based on the structures of the trityl groups. By mixing the polymer with trace amounts of hydrophobic dye, we showed proof of the principle that these molecules can serve as smart coatings that can indicate the thermal history of materials. Using color matching, it is anticipated that such coatings could be read and analyzed directly by visual color changes or using an application on a hand-held device such as a cell phone. This would enable their use as simple smart packaging labels. To the best of our knowledge, this is the first application of depolymerization as a sensor for smart packaging and capitalizes on the unique ability of PEtG to degrade to volatile products.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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Figure Captions

Figure 1. a) Structures of trityl end-capped PEtGs; b) Synthesis of PEtG-AT and PEtG-AMT; c) Mechanism for temperature-dependent depolymerization of trityl-capped PEtG.

Figure 2. Mass loss profiles for end-capped PEtGs at different temperatures: a) PEtG-DMT; b) PEtG-MMT; c) PEtG-AMT; d) PEtG-AT; e) PEtG-control. In each experiment, the error bars represent the standard deviation of the measurements for three samples.

Figure 3. Variable temperature ^1H NMR spectra of a) PEtG-AMT and b) PEtG-control at different temperatures (15 min per temperature increment unless otherwise indicated). Spectra are offset to allow the progression over time to be clearly observed.

Figure 4. a) and b) Color changes of different PEtG coatings containing either a) 0.1 wt% Nile red or b) 0.5 wt% IR-780 incubated at 22 °C for different time periods. The rectangular color patches are computer generated color samples that were sub-sampled from digital pixels to display color changes of the coating. c) and d) UV-Vis spectra of c) PEtG-AMT and d) PEtG-control thin films containing 0.1 wt% Nile red before and after incubation at 37 °C for 24 h; the inserted pictures in c) are the thin films before and after incubation.