

MeMBL: Ring-opening a pathway to a renewable, chemically customizable plastic

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MeMBL (α -methylene- γ -methyl- γ -butyrolactone) is a biomass-derived compound known to be polymerizable to make an acrylic material with a high glass transition temperature. Presence of a lactone ring in the structure of MeMBL can be opened to create a pathway to modification of a MeMBL polymer. This would expand the range of uses for poly(MeMBL) as a plastic. A polymer composed of pure MeMBL and a polymer composed of MeMBL and styrene (the main component of Styrofoam) were prepared, and subjected to reactions with sodium hydroxide in alcohols, water, or dimethyl sulfoxide (DMSO). Evidence of ring-opening was determined either by observation of a change in the polymer's solubility or by NMR analysis. Both the pure MeMBL polymer and MeMBL/styrene copolymer showed evidence of ring-opening when exposed to sodium hydroxide in water, while no reaction was observed with the same treatment in alcohols. The poly(MeMBL) ring was observed to close over time. Ring-opening was found to be achievable, but ring-opening with hydroxide was found to be an ineffective pathway to further work on the opened ring.

INTRODUCTION

Renewable alternatives to petroleum-based plastics have become a topic of significant interest for the field of polymer chemistry, as they have the potential to reduce dependence upon oil for plastic products. One commercially available example is polylactic acid, or PLA, which is derived from corn and is used to make biodegradable shopping bags (Oksman, 2004) and biodegradable food packaging (Natureworks LLC, 2005). Another is the use of lactone-derived poly(esters) for use as biodegradable sutures or as "scaffolds" for use in tissue engineering (Martin, 2003). PLA and lactones are polymerized by opening the lactone ring, but lactones composed of five-member rings are known to be especially difficult to open because of the stable nature of this ring size (Moore, 2005).

In addition to ring-opening polymerization, there are also renewable polymers that are produced via free radical polymerization. While ring-opening polymerization typically occurs

by breaking an ester or amide bond on a monomer and forming a new ester or amide bond with another opened monomer, free radical polymerization occurs by inserting a "free radical" electron into a carbon-carbon double bond. This forms a new bond at the site of insertion as well as a new free radical that continues the growing polymer chain. MeMBL, or α -Methylene- γ -methyl- γ -butyrolactone, is a renewable monomer that can be polymerized via radical means, as MeMBL's methylene group permits it to polymerize without opening its lactone ring. This leads to the production of an acrylic polymer that is similar in structure to the non-renewable polymer methyl methacrylate (MMA), but with a higher glass transition temperature (Manzer, 2004). Structures of MeMBL, MMA, and the other mentioned monomers and polymers are in Figure 1. While MeMBL's lactone ring remains an unopened side group during polymerization, one could open the ring to attach various new functionalities onto the backbone polymer, and thereby change the polymer's behavior as a plastic. This would broaden the range of the polymer's potential applications beyond both replacing MMA and raising the glass transition temperatures of other polymers through copolymerization. In order to do this, a pathway for opening the lactone ring of MeMBL must be developed first. A pathway for opening a polymer with lactone

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side groups has been proposed by Pittman and Lee (2003), but to the best of the author's knowledge the pathway has not been investigated for MeMBL. This pathway is shown in Figure 2, and is of particular interest to this study.

While the Pittman and Lee paper is the only one known to suggest a ring-opening method for poly(MeMBL), others have investigated ring-opening of five-member lactone rings on different molecules. Work by Pevarello et al. (2005) and Kawahata et al. (2002) includes insertion of organo-amines into molecules containing a γ -butyrolactone (GBL) ring to produce a variety of lactam compounds. In addition, Lange et al. (2007) report a method to ring-open γ -valerolactone (GVL) in the synthesis of methyl pentaoate, under conditions of catalytic distillation. These papers may demonstrate that modification of a five-member lactone to another molecule can be done, but demonstration of ring-opening and modification of a polymer containing five-member lactone rings currently remains an open question.

MATERIALS & METHODS

Preparing Polymers

MeMBL was supplied by DuPont, and the inhibitor hydroquinone was removed by passing the monomer through an inhibitor-removing column. Styrene was purchased from Fisher Chemical and used as received. Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich and used as received.

Polymerization of MeMBL homopolymer was carried out as a free radical polymerization in chloroform. In a typical polymerization, 5.61 g of MeMBL and 0.0164 g of AIBN (a 500:1 molar ratio) were combined with 50 mL of chloroform in a round-bottom flask. The polymerization was carried out in a nitrogen-only environment at 60 °C for 24 hours. The resulting polymer was precipitated in methanol, and dried under vacuum at room temperature for 24 hours.

Polymerization of a MeMBL/styrene copolymer was carried out as a free radical polymerization in bulk. In a typical polymerization, 2.24 g of MeMBL and 2.08 g of styrene (equimolar ratio) were placed in a small vial with 0.0164 g of AIBN (a 400:1 monomer/initiator ratio), and allowed to react in a nitrogen-only environment at 80 °C for 24 hours. The polymer was then removed from the vial, dissolved in chloroform, and the polymer was precipitated in methanol. The polymer was dried in vacuum at ambient temperature for 24 hours.

Ring Opening

Sodium hydroxide and dimethyl sulfoxide (DMSO) were purchased from Fisher Scientific, ethanol was purchased from Sigma-Aldrich, and deionized water was acquired by reverse-osmosis purification. All listed materials were used as received.

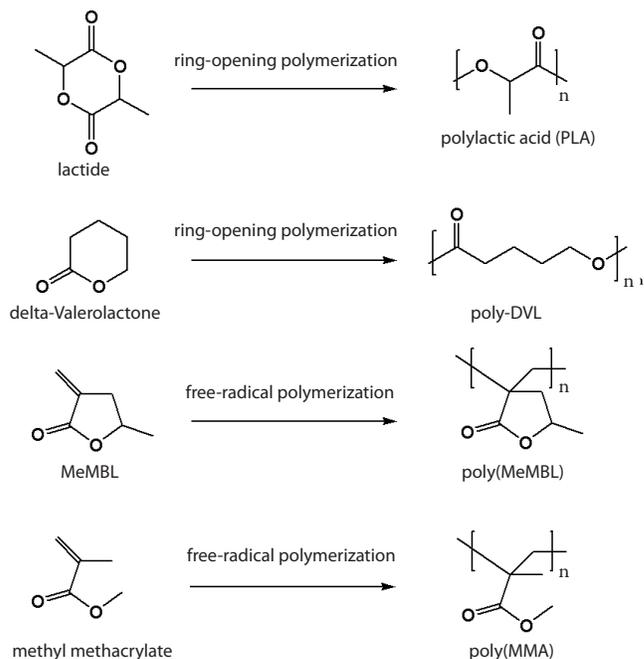


Figure 1. Structures and polymerizations of the renewable resource monomers lactide, DVL, and MeMBL, along with the non-renewable MMA. MeMBL, the molecule of interest, is currently of interest for its potential to replace MMA, and for its high glass transition temperature.

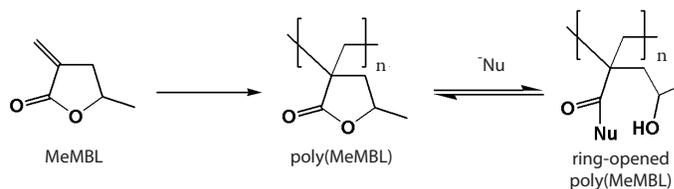


Figure 2. General pathway for polymerization and ring-opening of MeMBL. In this pathway, a nucleophile ("Nu") is inserted in the lactone ring, which opens it. Reaction pathway is adapted from pathway suggested by Pittman and Lee (2003, p.1759).

The methods for reactions using water, DMSO, and ethanol, both for the MeMBL homopolymer and MeMBL/styrene copolymer, were the same. In a typical experiment, 1.12 g (0.01 moles) of polymer, 1.2 g (0.03 moles) of NaOH, and 30 mL of solvent were combined in a round-bottom flask. The flask was sealed, but not in a nitrogen-only atmosphere. The mixture was allowed to react at the boiling point of the selected solvent for 24 hours, with the exception of DMSO, in which the reaction was carried out at 115 °C for 24 hours. This exception was made because higher temperatures under the reaction conditions for DMSO led to severe polymer degradation.

Upon completion of the reaction (noted by a change in color), the solution and any remaining solid were added to 200 mL of water, and stock HCl was added dropwise until the polymer

precipitated. The MBL/Styrene copolymer precipitated in de-ionized water only, as acid was not needed to effect precipitation. The precipitate was then filtered, and washed with a mild acid solution (<1 mL HCl per 25 mL water) three times, and allowed to dry in vacuum. Samples of the dried polymer were placed in a battery of solvents to test for changes in polymer solubility. Finally, the polymer was analyzed using ^1H nuclear magnetic resonance spectroscopy (proton NMR), to look for changes in the number and chemical shifts of protons (H atoms) on the polymer. If the ring-opening reaction proceeds according to Figure 2, one would expect a single new peak between 2 and 5 ppm in the product polymer that corresponds to the proton on the alcohol group (OH), with relatively little change on other protons.

RESULTS & DISCUSSION

For the MeMBL polymer, a change of solubility (from insoluble starting material to a product fully soluble in water) was noted after reaction with sodium hydroxide in water. After the reaction of poly(MeMBL), which is insoluble in water, the polymer/water mixture became a yellow solution, indicating a change in solubility. However, in the 24 hours taken to dry the product, the polymer's solubility changed to that of the original polymer, and NMR revealed that the starting polymer had been reformed. This is believed to be caused by ring-closing after ring-opening, and subsequent tests revealed the ring-opened polymer, when dissolved in methanol, would precipitate out of solution after approximately one hour. The recovered precipitated product was identified by ^1H NMR as the original, closed-ring polymer. This pattern was found to be repeatable over several (>5) reactions. When DMSO was used as a solvent, MeMBL again underwent a change in solubility, indicating a ring-opening. However, this ring-opened polymer also underwent ring-closing and reformed the original, closed-ring polymer within an hour. This was confirmed over several repetitions. No reaction was observed with the use of ethanol as a solvent.

The failure of the reaction in ethanol has a number of possible causes. First is the issue of temperature. Ring-opening experiments in water were found not to proceed at 60 or 70 °C, and since the reaction in ethanol was carried out at its boiling point of just 78.5 °C, the temperature may have been too low for the reaction to proceed. Meanwhile, higher temperatures used with water (100 °C) and DMSO (115 °C) appeared sufficient. A second possible cause for failure stems from ethanol's properties as a protic solvent. During the reaction, ethanol may have reacted with sodium hydroxide to form water and sodium ethoxide, in which case the nucleophilic attack shown in Figure 2 would be one of ethoxide instead of hydroxide. Since ethoxide is a larger nucleophile, and MeMBL's lactone ring is very small, steric hindrance could have prevented ring-opening by ethoxide.

Also of interest were two solutions of ring-opened poly(MBL) that were not precipitated immediately after the reaction. These solutions were held for approximately one week before the precipitation step. Upon neutralization with acid (in accordance with the experimental method), the ring-opened products would revert to the ring-closed form quickly.

Reaction of the MeMBL/Styrene copolymer in DMSO yielded no change in solubility, and ^1H NMR revealed a new peak at a chemical shift of 2.9 ppm, which should correspond to the alcohol group seen in Figure 2. The new peak was consistently observed for approximately one week. After that time, ^1H NMR of the copolymer revealed a polymer equivalent to the starting material, and this is again hypothesized to be due to ring-opening followed by ring-closing. Reactions of the copolymer in water or ethanol did not proceed.

Literature shows that GBL, which has the same five-membered rings as MeMBL, heavily favors a closed-ring state (Duda, 1996 and Houk, 2008). This may help explain the fleeting nature of the ring-opened compound observed in this experiment. Work by Carothers et al. also indicates that ring-opened GBL is most likely to close if the end groups on the open ring are a carboxylic acid and alcohol, while other end groups are less likely to undergo ring closing (1962). Combining this information with the observation that the ring-closing phenomenon occurs rapidly upon addition of acid suggests that a more stable product than an alcohol and carboxylic acid are formed during the ring-opening reaction. A likely candidate is a sodium salt on one of the end groups of the open ring, as no other reactive molecules are present in water or DMSO to create other groups. Furthermore, ^1H NMR of the copolymer reveals the creation of an alcohol group during the ring-opening reaction, which would imply the creation of the carboxylic sodium salt shown in Figure 3. The acid used during the precipitation step, therefore, plays an important role in the ring-closing of poly(MeMBL). Upon exposure to water or acid, the salt is converted to a carboxylic acid. This permits a ring-closing reaction to take place, yielding the original polymer.

Future work on ring-opening, therefore, should avoid using precipitation in acid as a method to purify ring-opened poly(MeMBL). Other reactions to investigate include using

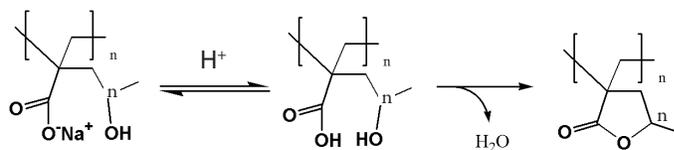


Figure 3. Ring-closing of MeMBL in the presence of acid. Here, an acid proton (H^+) attaches to the carboxylate group of the open ring, giving a carboxylic acid. The alcohol ($-\text{OH}$) and carboxylic acid ($-\text{OOH}$) groups react with each other to reform the closed lactone ring.

nucleophiles other than hydroxide, which may lend some resistance to ring-closing.

CONCLUSIONS

Lactone ring-opening of poly(MeMBL) has been demonstrated by the solubility changes observed in poly(MeMBL), and by ¹H NMR in poly(MeMBL+Styrene). The opened lactone ring was found to be unstable over time and rapidly closed in the presence of an acid. The goal of this research, to find a pathway to an open lactone ring for further chemical reactions, was met using hydroxide as a ring-opening nucleophile, although the ring reformed after a relatively short time. Nonetheless, the evidence of ring-opening in the presence of hydroxide indicates that a pathway is plausible, and should be tried using other nucleophiles, particularly amine nucleophiles. Once this can be done, further side group modification of the polymer can be carried out, and MeMBL's candidacy as a renewable, chemically customizable plastic can be evaluated.

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