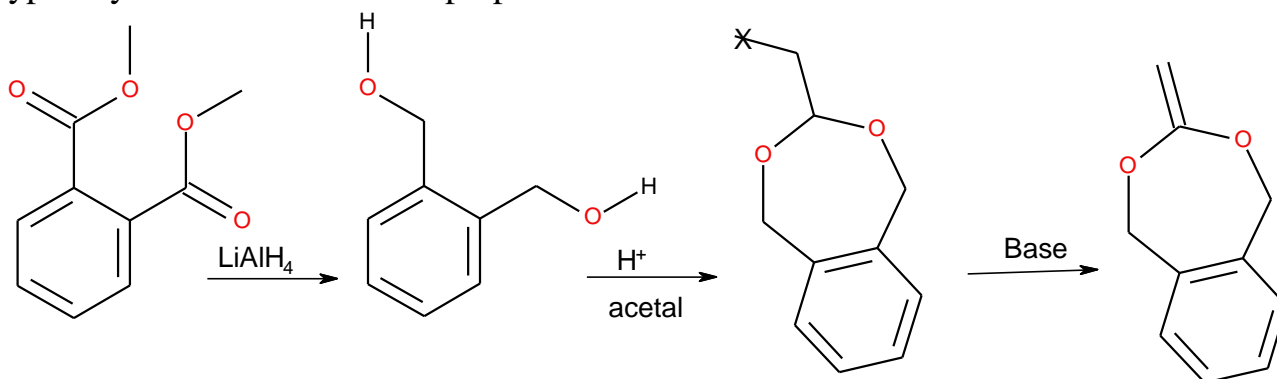


# New Monomers For Free Radical Ring Opening Polymerization(RROP)

by: Robert B. Login

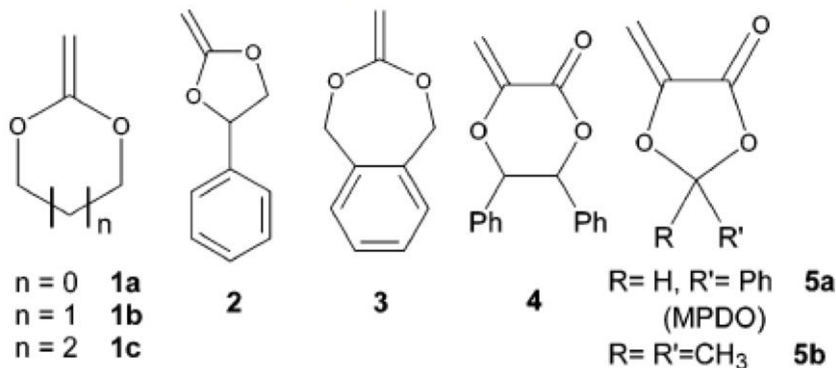
W. J. Bailey discovered that exomethylene cyclic acetals would undergo RROP especially if the resulting radical was stabilized and/or ring strain was a factor. This resulted in polyester containing polymers. Copolymerization of such monomers with vinyl or acrylic monomers results in the possibility of biodegradability based on the hydrolysis of the esters in the copolymers backbone resulting in smaller presumably degradable fragments. In addition, Bailey found that polymers of these monomers did not shrink upon polymerization unlike most typical free radically polymerized monomers. This would allow dental fillings to not shrink for example upon polymerization(*Macromolecules* **1982**, *15*, 711-714).

Typically these monomers are prepared as illustrated in scheme 1:



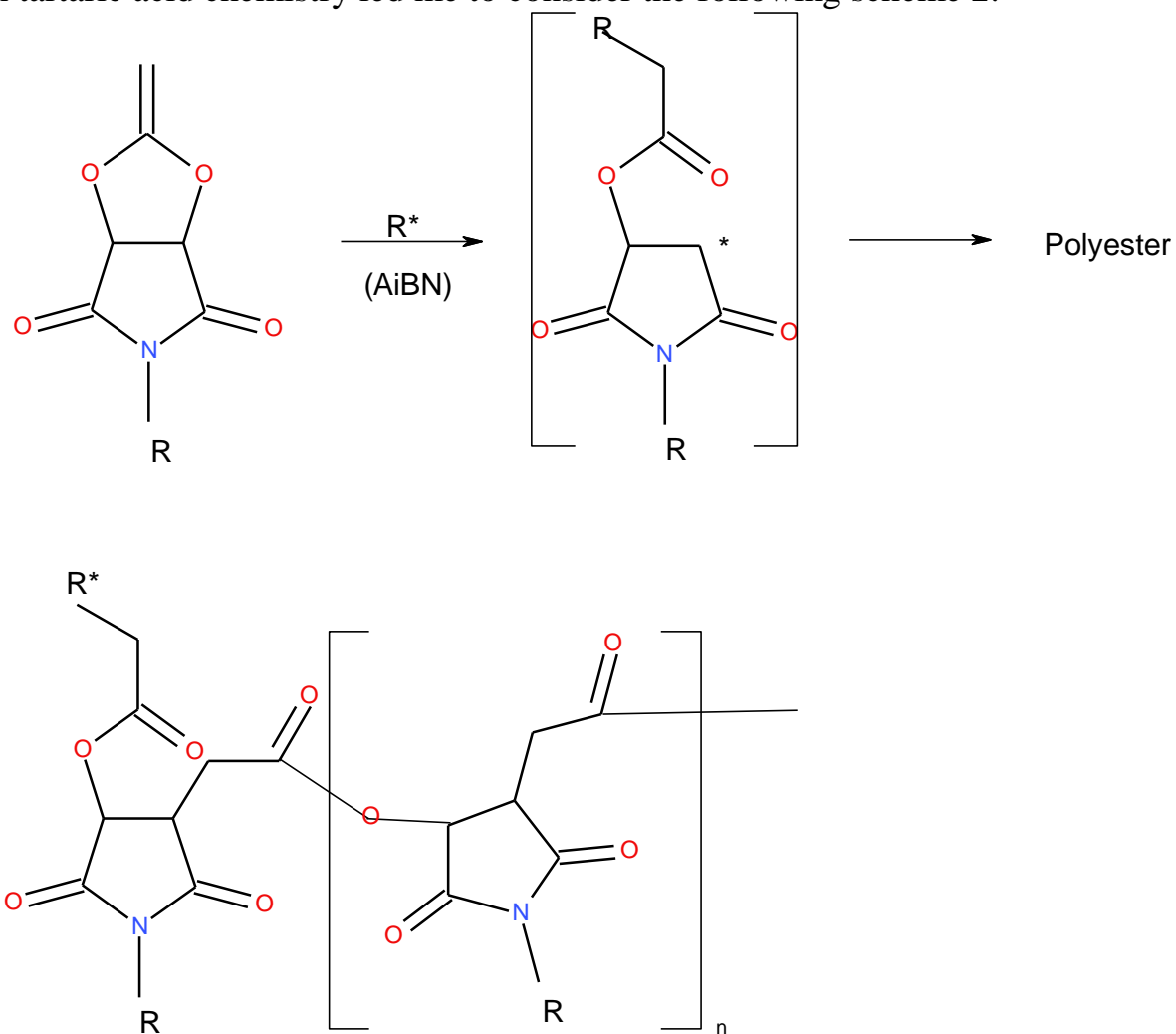
Scheme 1 Preparation of BMBO

## Scheme 1. Cyclic Monomers that undergo Ring-Opening and/or Addition Free Radical Polymerization



*Macromolecules* **2005**, *38*, 5581–5586

Polymerization can occur in two ways, RROP or 1,2-vinyl addition. RROP is favored by ring strain and/or resonance stabilization of the propagating radical. Therefore, my interest in tartaric acid chemistry led me to consider the following scheme 2:

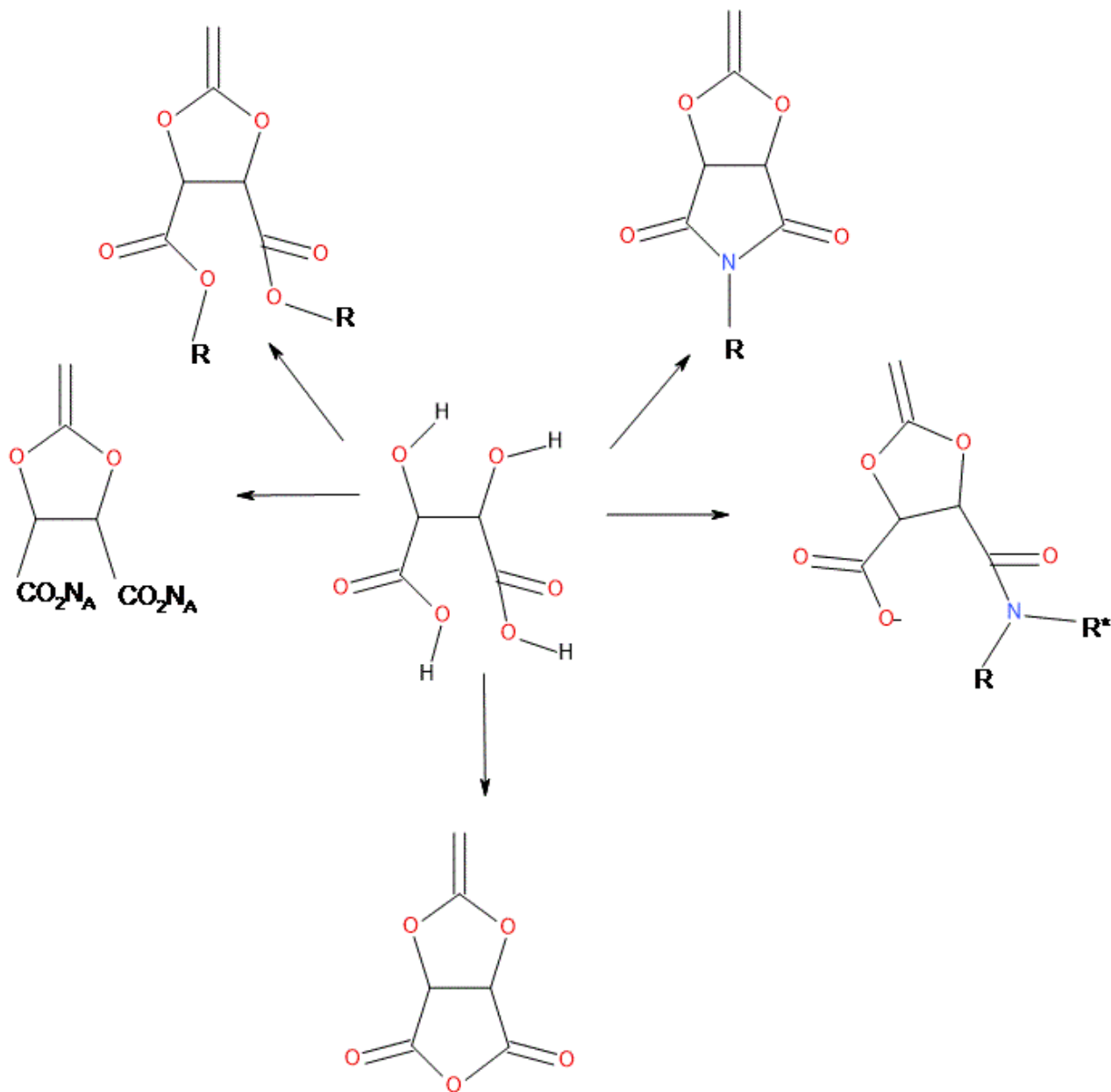


Scheme 2 This also shows the mechanism of RROP(R=methyl, R\*= initiator fragment)

In this case the propagating radical is stabilized by being adjacent to the imide carbonyl, the same stabilization of the readily polymerized maleimide monomers. Such monomers can be readily prepared as illustrated in scheme one from the well known tartrimes ( Tartaric and Malic acids in Synthesis by Gawronski and Gawronska; Wiley 1999). This book also reviews the extensive literature for transforming said tartaric acid to other RROP monomers.

In addition ester, amide and anhydride monomer versions are also very possible. They would also exhibit resonance stabilization and thus also be capable of RROP.

Not shown are the enantiomeric possibilities of optically active tartaric acid with the l-isomer being commercially available.



Scheme 3

Not only can these monomers homopolymerize they can also copolymerize affording a large variety of polyester containing copolymers. The anhydride monomer can be polymerization and post reacted to form diacids or with diamines or diols to form cross-linked resins such as gels or cured coatings.

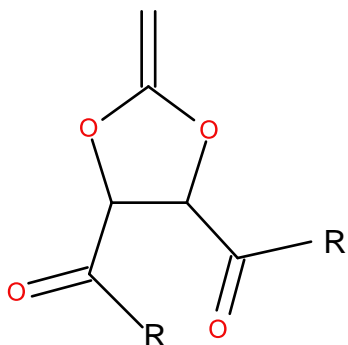
RROP monomers have been employed with CRP techniques such as ATRP, RAFT, etc. to prepare block copolymers and other well controlled structures (Chem. Rev. **2007**, 107, 2270-2299). For example high VP can be copolymerized with these monomers so that the resulting polymers can be easily degraded to fragments that can more easily biodegraded or be easily excreted from the body (Zhong et al. USP 5,912,312 Jun. 15, 1999).

The resulting succinic moiety is extreme flexible because it can be readily derivatised or hydrolyzed to be ionic or as an ester derivative, oil soluble or surface active. Long chain amine generated amides or imides can be sprinkled in PVP chains for example to afford surface active polymers. The ability to hydrolyze the resulting backbone esters can afford more easily removed personal care products avoiding undesired build-up. Even as a homopolymer, the succinic anhydride or imide structures are stiffening moieties and film formers. Reduction to the pyrrolidone structure can be achieved at the monomer stage as reviewed in Gawronski and Gawronska's book, where they show this reaction with closely analogous compounds.

There is a significant literature concerning RROP but I have searched (Scifinder structure search) for my idea and cannot find it in the literature? Please let me know if my idea is already in the literature.

Claims:

1. Free radical ring opening (RROP) monomers comprising compounds of the following structure;



Where R= the alcohol or amine required to form ester groups or amide groups or each R is the same oxygen or nitrogen atom thus forming an anhydride or imide moiety.

2. A free radical polymerization process comprising the monomers of claim 1.
3. The process of claim 2 wherein copolymers are formed in various ratios.

4. The process of claim 2 wherein said polymerizations are performed in solvents such as those in which said monomers are soluble.
5. The process of claim 2 wherein said copolymers are selected from vinyl pyrrolidone, or vinyl acetate or alkyl acrylate or methacrylate or acrylamide or methacrylamide or styrene or ethylene or propylene or butadiene and the like.
6. The process of claim 5 wherein more than two monomers are employed to prepare terpolymers.
7. Polymers containing said RROP monomers subsequently hydrolyzed forming biodegradable or easily excretable fragments.
8. The polymers of claim 7 wherein said monomers are polymerized to form tablets or capsules and so forth that contain active ingredients where said actives are released in the gut.
9. The polymers of claim 7 wherein said polymers form useful objects that do not pollute the environment because they hydrolyze to biodegradable fragments.

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