

Cyclic Acetals: Synthesis and Polymerization

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ABSTRACT: Mixtures of 5-membered and 6-membered 2-vinyl (2-propenyl or 2-isopropyl)-4-hydroxymethylene or 5-hydroxy-substituted cyclic acetals were synthesized by the reaction of aldehydes with glycerol. Reesterification of the hydroxyl group in position 4 or 5 was achieved using methyl methacrylate. The compounds were subjected to radical copolymerization using different initiating systems. Both radical copolymerization and ring cleavage were observed to be dependent on the reaction conditions. The ring cleavage was confirmed on model compounds of 2-substituted 5-membered and 6-membered cyclic acetals without any polymerizable substituent. The rate of the ring opening was measured and compared to the rate of copolymerization. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2875–2880, 2001

Key words: cyclic acetals; dioxolanes; ring opening

INTRODUCTION

Cyclic acetals are used in organic synthesis for the protection of aldehyde, ketone, or glycol groups. For example, in polymer chemistry, they have been utilized for many years in poly(vinyl butyral) and poly(vinyl formal). A new possibility for the application of cyclic acetals in polymer chemistry, especially as a reaction diluent in paint vehicles, involves the reaction of cyclic acetal derivatives containing reactive loci. Using suitable substitution in the acetal ring with a group containing double reactive bonds, a monomer can be obtained which can be polymerized into polymers with interesting structures. This monomer can be also added as a reactive diluent into various compositions, such as paints, sealing compounds, or adhesives.

There are several ways to synthesize cyclic acetals. The most general one is the reaction of

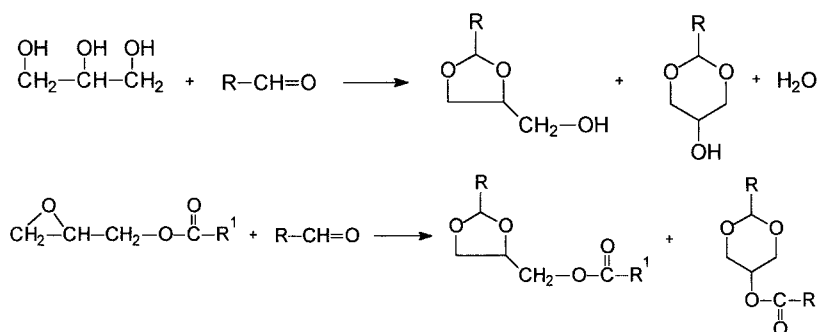
glycols with aldehydes or ketones, catalyzed by *p*-toluene sulfonic acid.¹ If an aldehyde or ketone is used which does not contain a double bond, the reaction can be catalyzed by butyltin trichloride,² which leads to higher yields and to shortening of the reaction time.

Another way of cyclic acetal synthesis is the reaction of an epoxy group with aldehyde or ketone using phosphoric acid catalysis.³ Five-membered and six-membered rings can be synthesized during the reaction of glycerol with aldehydes or ketones and during the reaction of an epoxy group with aldehydes or ketones⁴ (Scheme 1). It is further possible to introduce a substituent with a very reactive double bond into position 4 or 5 using the reaction of the hydroxy-substituted cyclic acetal prepared with methyl methacrylate¹ (Scheme 2).

The presence of reactive double bonds enables radical polymerization, when using the azoisobutyronitrile initiator or a redox initiation system with or without air. If the reaction is performed in airless conditions, only polymerization of double bonds occurs. On the contrary, in air, both acetal

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Scheme 1

ring opening and polymerization occur when a redox initiating system is used.⁵ The aim of this work was to synthesize some special cyclic acetal monomers with and without double bonds and to investigate the polymerization of double bonds and/or opening of the acetal ring with respect to the reaction conditions.

EXPERIMENTAL

Synthesis of Cyclic Acetals

All compounds prepared were identified using FTIR spectroscopy, GC-MS, and the boiling point.

2-Alkenyl-4-hydroxymethyl-1,3-dioxolane

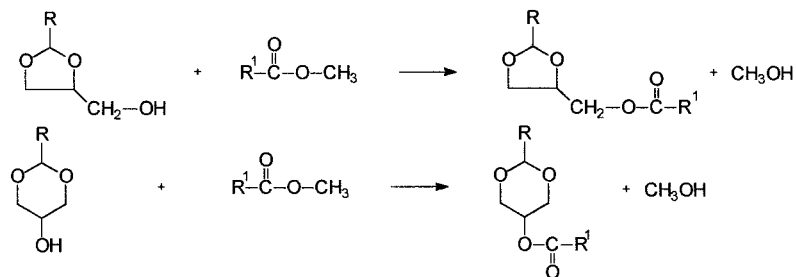
A mixture of alkenylaldehyde (1,2 mol), glycerine (1 mol), toluene (2,1 mol), toluene-4-sulfonic acid (6×10^{-4} mol), and hydroquinone (9×10^{-3} mol) was boiled for 8 h during the distillation of water. Water, 0.8 mol, was isolated. At the end of the reaction, further volatile components were distilled from the reaction mixture. The product was distilled under reduced pressure. A yield of 70–75% was obtained.

2-Alkyl-4-hydroxymethyl-1,3-dioxolane

Glycerol (1 mol) was cooled to 0°C, then butyltin trichloride (1.8×10^{-2} mol) was added and alkylaldehyde (1 mol) was dropped in to keep the temperature at 0°C. After the addition of alkylaldehyde to the mixture, it was allowed to reach 25°C and mixed continuously for 1 h. The product was distilled under reduced pressure. A yield of 70–75 % was obtained.

2-Alkyl(alkenyl)-4-methacryloxymethyl-1,3-dioxolane

2-Alkyl(alkenyl)-4-hydroxymethyl-1,3-dioxolane (0.7 mol), a 5% solution of sodium methanolate in methanol (0.3 mol), and hydroquinone (1.8×10^{-2} mol) were heated to 125°C with methyl methacrylate (2.6 mol) added dropwise for 3 h. A mixture of methyl methacrylate and methanol was distilled off. After the termination of the dropping, the volatile components were distilled off. The product was diluted with toluene (2.1 mol) and hexane (1 mol) and extracted using a 5% NaOH solution, a saturated NaCl solution, and water. The product was dried, and after distillation of the volatile components, it was vacuum-distilled. The yield was 70%.



Scheme 2

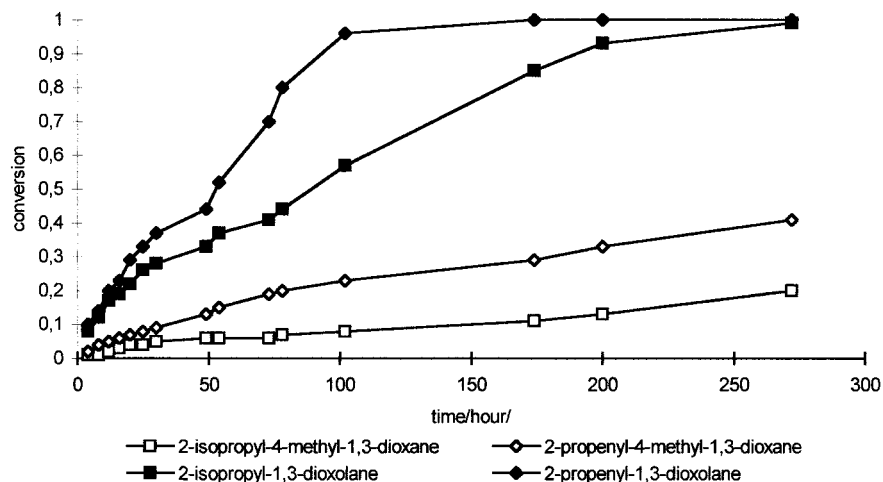


Figure 1 Opening of 5-membered and 6-membered rings.

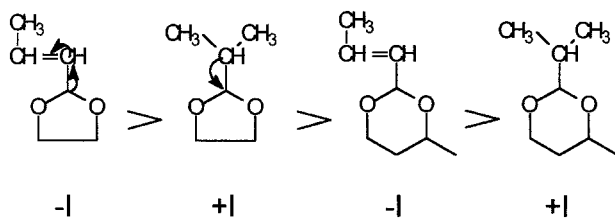
2-Alkyl(alkenyl)-4-methacryloxymethyl-1,3-dioxolane

Alkyl(alkenyl)aldehyde (5 mol), phosphoric acid (0.04 mol), and hydroquinone (1.2×10^{-2} mol) were heated to 50°C and glycidyl methacrylate (1 mol) was dropped in for 30 min. The mixture was further heated under reflux for 3 h until the temperature reached 65°C . After distillation of the volatile components, the product was obtained using vacuum distillation. The yield was 70–75%.

Radical Polymerization

Polymerization was performed using a redox initiation system [co-octoate/methyl ethyl ketone peroxide] with and without air admission or with an azoizobutyronitrile initiator. The composition of the reaction mixture with the redox initiation system was as follows: monomer, 100; methyl ethyl ketone-peroxide, 1; and co-octoate, 1. The composition of the reaction mixture with azoizobutyronitrile was as follows:

monomer, 100, and azoizobutyronitrile, 2. IR spectroscopy was used to monitor the polymerization.



Scheme 3

GC-MS Measurements

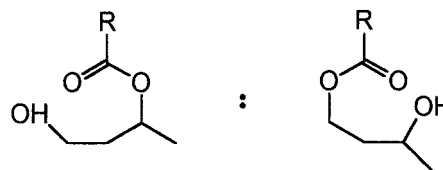
A gas chromatograph Hewlett-Packard Model 5890 Series II Plus coupled with a mass selective detector Hewlett-Packard Model 5972 MSD was used for the identification of individual reaction components and products. A capillary column HP-5-MS (Hewlett-Packard), length 30 m, internal diameter 0.25 mm, and a stationary phase of 5% phenyl siloxane, and 95% methyl siloxane with a film thickness of $0.25 \mu\text{m}$, with helium as the carrier gas, was used for the separation. The obtained EI and CI mass spectra were compared with the ones of raw materials and with catalog data.

GC-FID Measurements

A gas chromatograph Hewlett-Packard Model 5890 with a split-splitless injector and FID detection was used for estimation of the product purity. The same column as for the GC-MS was used. Nitrogen was the carrier gas.

IR Spectra

IR spectra of dioxolanes were measured between two KBr plates using a Perkin-Elmer Model 283.



Scheme 4

Polymerization of cyclic acetals in airless conditions

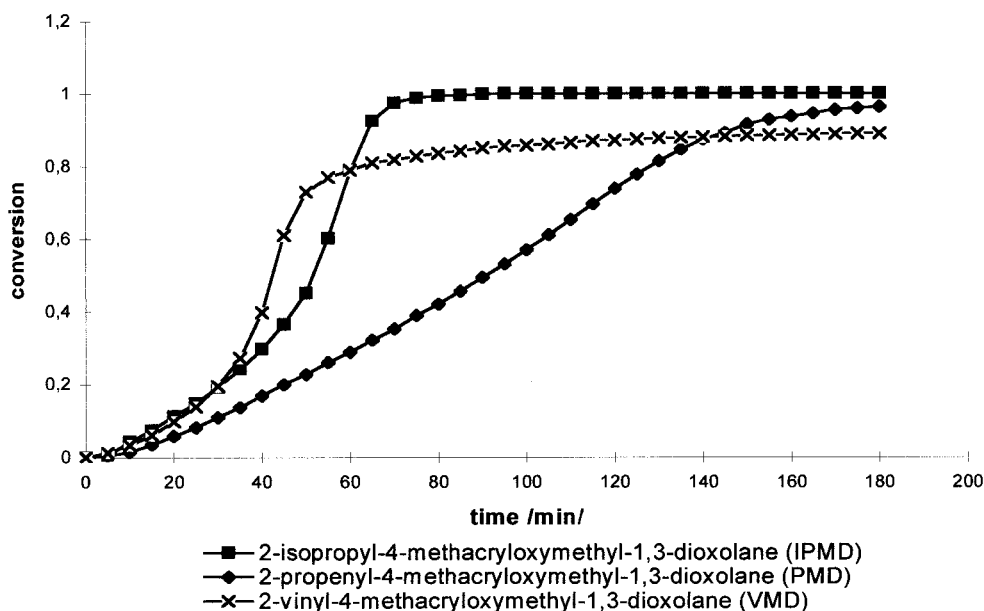


Figure 2 Polymerization of methacrylate double bond in airless conditions.

Changes in the absorption bands of the double bonds, ester carbonyls, and OH groups were chosen to follow the reactions during polymerization or copolymerization. Those measurements were performed both in airless conditions (between two KBr plates) and in air using the specular reflection method.

RESULTS AND DISCUSSION

Ring Opening of Cyclic Acetals

For determination of the influence of the cyclic acetal structure on the velocity of the ring opening, the following compositions were chosen:

- 2-Isopropyl-1,3-dioxolane
- 2-Isopropyl-4-methyl-1,3-dioxane

- 2-Propyl-1,3-dioxolane
- 2-Propyl-4-methyl-1,3-dioxane.

The above compounds do not contain reactive double bonds and, therefore, it was possible to use GC to study acetal ring opening under the application of the redox initiation system.

From the results obtained, it was evident that the 5-membered ring was less stable than was the 6-membered ring (Fig. 1). It was also possible to observe the influence of the substituent in position 2 on the rate of the ring opening (Scheme 3). The $-I$ effect of unsaturated alkyl accelerated the origin of the radical and ring opening in comparison to the saturated isopropyl substituent. From the mass chromatogram, it was observed that the ring split between the 1–2 or 2–3 ring atoms, namely, in the ratio 1:1, as demonstrated in 2-propenyl-4-methyl-1,3-dioxane (Scheme 4).

Table I Concentration of Elastically Active Network Chains

Compound	b_{110} (mol m ⁻³)	b_{130} (mol m ⁻³)	b_{150} (mol m ⁻³)	M_C (g mol ⁻¹)
PMD	91.8	81.5	86.2	13,500
IPMD	0.52	0.44	0.35	2,500,000
VMD	1308.7	1309	1253	840

b_i , concentration of elastically active network chains (EANC); t , temperature of measurements (110, 130, 150°C); M_C , average molecular weight of network strand.

Reaction of cyclic acetals under the access of air

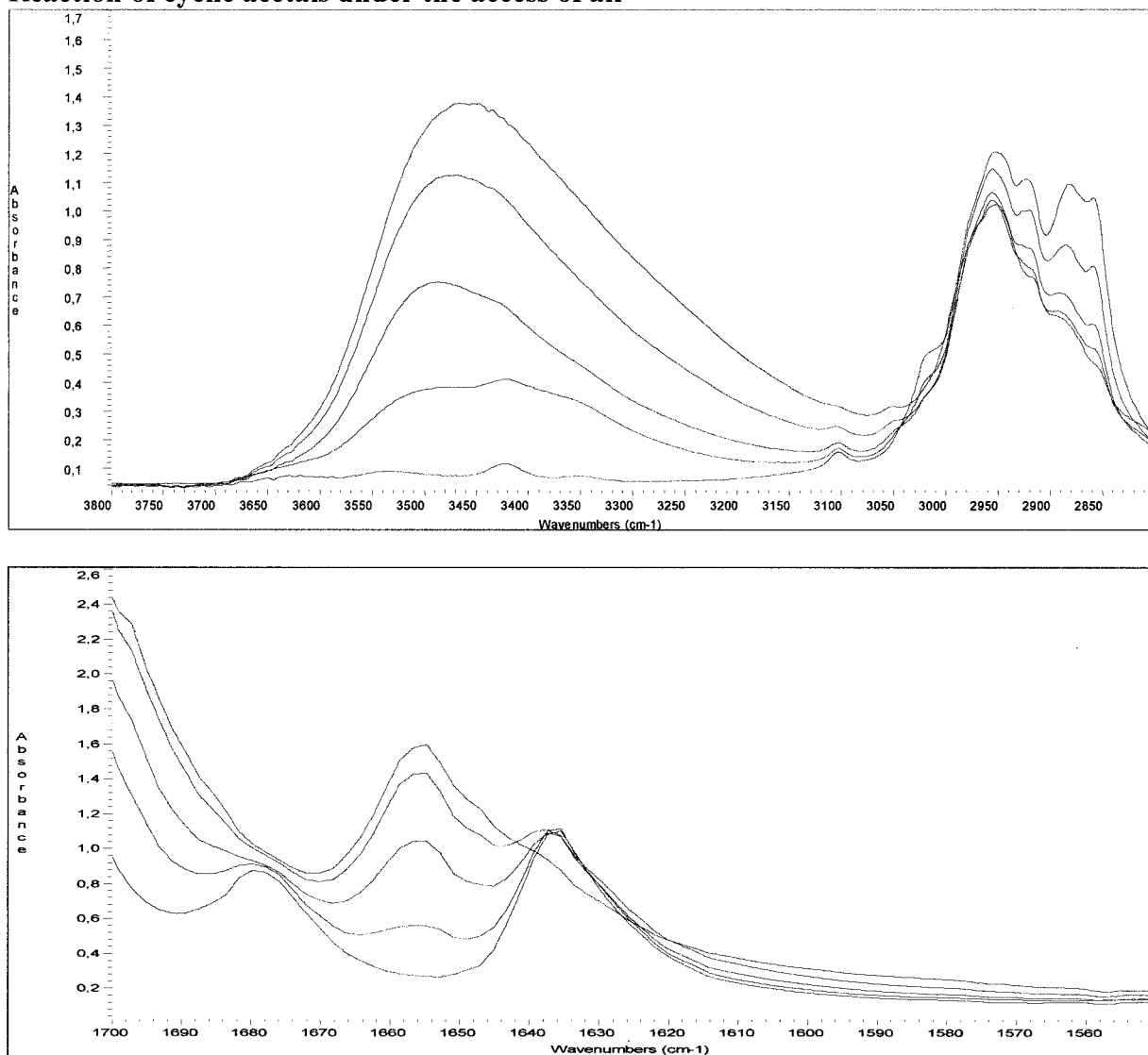
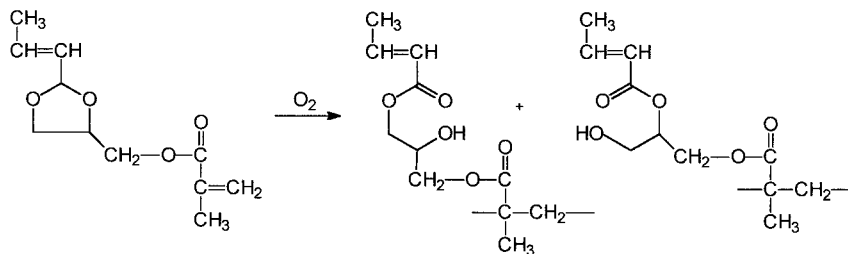


Figure 3 Time changes in IR spectrum of 2-propenyl-4-methacryloxymethyl-1,3-dioxolane.

Polymerization of Cyclic Acetals in Airless Conditions

It follows from Figure 2 that the fastest polymerization was observed for VMD. However, due to

the polymerization of the vinyl double bond and the copolymerization of methacrylic and vinyl double bonds located on one monomer molecule, a network is formed by crosslinking and the system



Scheme 5

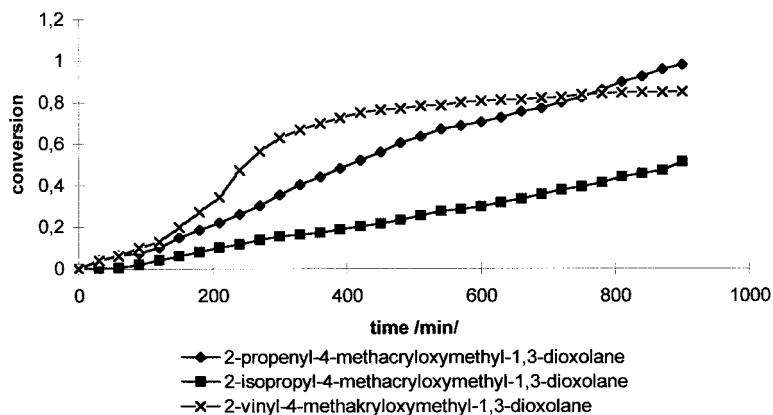


Figure 4 Polymerization of methacrylate double bond under the access of air.

reaches the gel point (freezes) around 80% of conversion. An interesting difference in the polymerization velocities was observed for IPMD and PMD. Very slow polymerization of PMD seemed to be caused by the formation of relatively stable propenyl radicals, which decreased the polymerization rate of the methacrylic double bond. The formation of radicals on the propenyl double bond was proven by measurements of the network density, as seen in Table I.

As shown by IR spectra of 2-propenyl-4-methacryloxymethyl-1,3-dioxolane in the presence of the redox initiating system (Fig. 4), the polymerization of double bonds and acetal ring opening occur. From the spectra, it is possible to identify the OH bond groups (3400 cm^{-1}) and the change of the propenyl double bonds to a crotonate double bond ($1680\text{--}1655\text{ cm}^{-1}$) (Scheme 5).

From Figure 4, it was shown that the same order of reactivities as in the case of ring opening (see Fig. 1) occurred for the polymerization of the methacrylate double bond in air. This follows from Figures 1 and 4, where the rate of ring opening was significantly lower than was the rate of polymerization, making the ring opening the rate-determining step of the reaction. We expect the same $-I$ effect of vinyl and propenyl groups. A significant drop in the reaction rate of the vinyl derivative to 70–75% of conversion was caused by the copolymerization of vinyl and methacryl double bonds. Due to this copolymerization, the polymer network is formed and reaction begins to be controlled by diffusion.

CONCLUSIONS

The synthesis of cyclic acetals led, in all cases, to the mixtures of 5-membered and 6-membered rings in the ratio 6:4. Two reactions of cyclic acetals were observed under the conditions of radical polymerization. In airless conditions, the polymerization and copolymerization of double bonds of substituents in positions 2 and 4 were observed. When the reaction with the redox initiation system was carried out under an access of air, the polymerization of double bonds and acetal ring opening occur. In this case, acetal ring opening was the rate-determining step of the overall reaction. The velocity of the ring cleavage was found to depend on both the substituent in position 2 and on the ring size. As was expected, the 5-membered rings were less stable. The tendency to ring cleavage was also supported when the substituent in position 2 showed the $-I$ effect.

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