Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Cationic-Initiated Ring-Opening Polymerization of Cyclopropenone Ketals. I. Monomer Synthesis and Polymer Structure

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To cite this Article Cook, Gregory A. and Butler, George B.(1986) 'Cationic-Initiated Ring-Opening Polymerization of Cyclopropenone Ketals. I. Monomer Synthesis and Polymer Structure', Journal of Macromolecular Science, Part A, 23: 4, 483 — 506

To link to this Article: DOI: 10.1080/00222338608063412

URL: http://dx.doi.org/10.1080/00222338608063412

J. MACROMOL. SCI.–CHEM., A22(4), pp. 483-506 (1985)

Cationic-Initiated Ring-Opening Polymerization of Cyclopropenone Ketals. I. Monomer Synthesis and Polymer Structure

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ABSTRACT

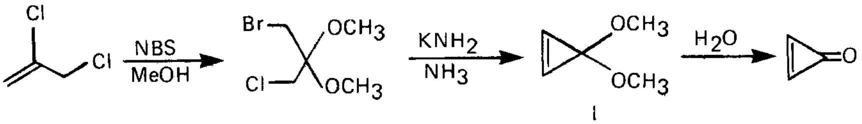
3,3-Dimethoxycyclopropene, the first of a series of cyclopropenone ketals, was initially reported from these laboratories in 1972. Polymerization of this compound, which is functionally capable of undergoing polymerization via both vinyl addition and ring opening, has not been previously studied. It was the purpose of this investigation to study this monomer as well as some of its homologs and to report their polymerization characteristics. An improved method of monomer synthesis is also reported. Among a variety of conventional cationic initiators investigated, only boron fluoride etherate was effective as a polymerization initiator. The mechanism proposed involves ring opening of the cyclopropene moiety to generate a dialkoxycarbocation intermediate, followed by propagation via several distinct and simultaneous pathways to produce a complicated polymer structure. Elucidation of the structure was aided by the synthesis of several appropriate model compounds. The reluctance of these monomers to lend themselves to normal modes of propagation is attributed to the formation of

0022-233X/85/2204-0483$3.50/0

an exceptionally stable carbocation intermediate which is relatively ineffective in further ring opening of the monomer. Isolation and characterization of these intermediates was achieved, and their low reactivity toward monomer was demonstrated. The cyclopropenone ketals studied were not converted to polymers via radical initiation.

INTRODUCTION

A relatively simple procedure for the preparation of 3,3-dimethoxycyclopropene (I) was devised by Baucom and Butler [1]. The synthesis involved treatment of 2,3-dichloropropene with N-bromosuccinimide, methanol, and acid catalyst to give 1-bromo-3-chloro-2,2-dimethoxypropane in moderate yields. Subsequent dehydrohalogenation with two equivalents of potassium amide afforded cyclopropenone ketal (I) in 50% yield (Eq. 1). I could be readily hydrolyzed in good yield to cyclopropenone, a highly sought "anti"-aromatic compound [2]. This series of reactions is presently the most widely used method of synthesis for cyclopropenone [3].



I

Albert and Butler [4] significantly improved the yield of I by reversing the order of addition of reactants in the dehydrohalogenation process. Yields in the range of 40 to 58% were obtained.

An investigation of the reactivity of I revealed it to possess an electron-deficient double bond [1, 4]. Diels-Alder reactions of the ketal with several electron-rich dienes gave the corresponding 7,7-dimethoxy-3-norcarenes in high yields [4]. In addition, a Diels-Alder adduct with the electron-rich 1,3-diphenylisobenzofuran was prepared [1].

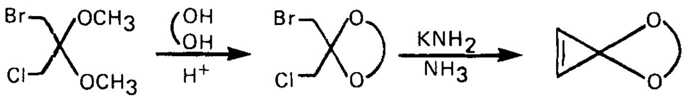
Nucleophilic attack at the electron-deficient double bond of I by secondary amines gave rise to a mixture of cyclopropylamines and β-alanine derivatives [4].

Further support for the existence of an electron-poor double bond in I was provided by charge-transfer complexation studies. Equilibrium constants for complexes formed with styrene and divinyl ether, two electron-rich olefins, were measured using NMR techniques. The magnitude of the constant obtained for the complex with styrene was significant, although comparatively lower than that obtained for the styrene-maleic anhydride complex [4].

Other methods for the preparation of cyclopropenone ketals were investigated to further simplify monomer synthesis. Dehydrohalogenation with methanolic potassium hydroxide, 1,5-diazabicyclo[3.4.0]-nonene-5, and potassium t-butoxide in dimethylsulfoxide (DMSO) were not successful. Attempts to remove the product as it formed and to trap it at Dry-Ice temperatures were also unsuccessful. In addition, a sodium amide suspension in mineral oil did not react with the precursor at 165-220°C, due to the insolubility of the starting materials in the reaction medium.

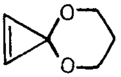
The poor stability of I caused great difficulties with its purification and handling. The monomer undergoes facile hydrolysis to cyclopropenone in the presence of water [1] and must be handled under anhydrous conditions. Despite precautions to exclude water, oxygen, and light, decomposition of the monomer was noted within 4 h at -40°C at 10^{-6} torr.

In attempts to synthesize more stable cyclopropenone ketals, several cyclic ketal analogs were prepared. Treatment of II with an appropriate diol (e.g., 1,3-dihydroxypropane) in the presence of acid catalyst gave the corresponding cyclic ketal in high yield. Subsequent dehydrohalogenation by the established procedure afforded several cyclic cyclopropenone ketals (III-V) which exhibited enhanced stability over the parent compound (Eq. 2) [5].

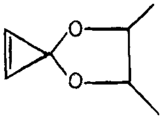


II

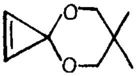
(2)



III

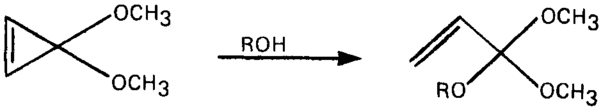


IV



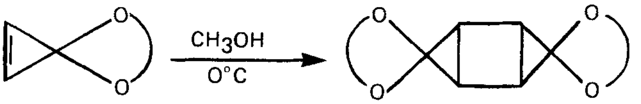
V

The reaction of methanol with I afforded trimethyl orthoacrylate as the only product (Eq. 3). Similar reactions were observed for a variety of alcohols, indicating the generality of this synthetic route to substituted orthoacrylates. In addition, several cyclic orthoacrylates were prepared from the corresponding cyclic cyclopropenone ketals [5].



(3)

Under relatively mild conditions, both in methanol at 0°C and in solid state, cyclopropenone ketals readily dimerize (Eq. 4). The mechanism of the dimerization has not been established [5].



(4)

The present research program was undertaken to investigate the polymerizability of cyclopropenone ketals and to determine the structure of the polymers.

EXPERIMENTAL

Equipment and Data

All temperatures are reported uncorrected in °C. Melting points were determined in sealed evacuated capillary tubes using a Thomas-Hoover melting point apparatus. Elemental analyses were performed by Atlantic Microlab, Atlanta, Georgia, and Schwartzkopf Laboratory, New York, New York.

Proton nuclear magnetic resonance spectra (^{1}H-NMR) were obtained using a Varian A-60 spectrometer. All chemical shifts are reported in ppm relative to the internal reference tetramethylsilane (TMS). Instrument conditions are stated for each analysis.

Infrared analysis (IR) was carried out on a Perkin-Elmer 281 spectrometer. Spectra of solid samples were obtained from a KBr disk, while those of liquids were obtained from a film.

Anhydrous solvents were obtained using the methods described by Gordon and Ford [6]. Nonsolvents for precipitation of polymers were technical grade and were used without further purification. All other solvents were reagent grade and were used as purchased. Prepurified nitrogen gas was purchased from Airco and was used without further purification.

Synthesis of Monomers and Intermediates

Preparation of 3,3-Dimethoxycyclopropene (I)

A 3-L three-necked flask was fitted with a gas inlet, mechanical stirrer, Dry-Ice condenser, and sodium hydroxide drying tower. The apparatus was flame-dried over a stream of N_2 and then cooled to a Dry-Ice/isopropanol bath with continued N_2 flow. Dry Ice was added to the condenser, and condensation of ammonia was begun. After approximately 2.4 L of liquid ammonia had been collected, the cooling bath was removed, and the solvent allowed to warm to boiling (-33°C).

Stirring was begun under a stream of N_2 and 217 g (1 mol) of 1-bromo-3-chloro-2,2-dimethoxypropane (II) was added. The N_2 flow was stopped after a solids-addition tube [7] containing 2.1 mol sodium amide (Aldrich, 97%) was attached, and base was added in small portions over a 2-h period. Vigorous boiling ensued with each addition, and the reaction mixture rapidly became dark-brown. Stirring was continued an additional 2 h, after which excess amide was neutralized by the cautious addition of 20 g of NH_4Cl. Ammonia was allowed to evaporate overnight, while 1000 mL of dry diethyl ether containing 2 mol% hydroquinone was added via an addition funnel to replace the ammonia solvent. The next morning the reaction mixture was filtered to remove by-product salts which were washed twice with ether. The solvent was removed at 20 mmHg, and the brown viscous residue was distilled at 25°C/4 mmHg. The product was collected in a trap at -78°C to give 40 g of a colorless liquid; Ref. 4, bp 36°C/33 mmHg.

Preparation of 1-Bromo-3-chloro-2,2-dimethoxypropane (II)

A 1000-mL three-necked flask equipped with a magnetic stir bar, a thermometer, and a $CaSO_4$ drying tube was charged with 600 mL anhydrous methanol, 75 mL 2,3-dichloropropene, and 8 drops of concentrated sulfuric acid. The reaction mixture was cooled to -5°C in an ice/acetone bath, and 150 g of N-bromosuccinimide was slowly added with stirring. The temperature was maintained at 0°C for at least 3 h and then gradually permitted to warm to room temperature as the ice melted. Stirring was continued for 12 h or until decolorization of the reaction mixture had occurred.

The acid catalyst was neutralized by cautious addition of 450 mL of a saturated solution of sodium bicarbonate, causing vigorous evolution of carbon dioxide and precipitation of product.

The reaction mixture was transferred to a 2-L separatory funnel using 600 mL pentane to dissolve the product and rinse the equipment. The aqueous phase was separated and extracted twice with 100 mL portions of pentane after additional water had been added to the maximum capacity of the funnel. The combined organic layer and extracts were dried over Na_2SO_4 and then decanted into a 1-L beaker. The product was frozen out of solution at -78°C in a Dry-Ice/isopropanol bath, and pentane was decanted from the white crystalline ketal. The crystals were scraped from the walls of the beaker and dried under a stream of nitrogen to give 105-115 g or 60-66% yield, mp 69-70°C; Ref. 1, mp 69.5-70.5°C.

Preparation of 2-Bromomethyl-2-chloromethyl-5,5-dimethyl-1,3-dioxane

A procedure similar to that described by Butler et al. [5] was carried out using equimolar amounts of II and 2,2-dimethyl-1,3-propanediol in the presence of a catalytic amount of H_2SO_4. Following removal of the theoretical amount of methanol by-product, the ketal was distilled directly from the reaction vessel at 56-58°C/0.01 mmHg in 85-90% yield; Ref. 5, bp 98°C/0.04 mmHg.

Preparation of 2-Bromomethyl-2-chloromethyl-4,5-dimethyl-1,3-dioxolane

The transketalization was carried out as described earlier using the corresponding 2,3-butanediol (23 mL, 0.25 mol) and 54 g (0.25 mol) of II. The cis and trans product was distilled from the reaction mixture at 47-54°C/0.01 mmHg to give 39 g of product or 64% of theory.

The ^{1}H-NMR spectrum showed a six-proton triplet at 1.3 ppm, two two-proton singlets at 3.54 and 3.69 ppm, and two one-proton multiplets at 3.8 and 4.4 ppm. Major IR absorbances appeared at 2295 (s), 2900 (s), 1478 (s), 1425 (s), 1240-1020 (group of four strong bands), 940 (m), 840 (m), 800 (m), 740 (m), and 670 (m). Analysis: Calculated for $C_7H_{12}O_2BrCl$: C, 34.52; H, 4.97; Br + Cl, 47.37. Found: C, 34.62; H, 4.95; Br + Cl, 47.19.

Synthesis of 4,8-Dioxaspiro(2.5)oct-1-ene (III)

The starting material, 2-bromomethyl-2-chloromethyl-1,3-dioxane, was prepared in 85% yield from 170 g (0.78 mol) of II and 56 mL (0.78 mol) of 1,3-propanediol using the transketalization procedure described earlier; bp 65-70°C/0.1 mmHg, mp 58-60°C; Ref. 8, mp 59-60°C.

The cyclopropenone ketal (III) was synthesized in 42% yield from 157 g (0.68 mol) of 2-bromomethyl-2-chloromethyl-1,3-dioxane and 58.5 g (1.50 mol) of $NaNH_2$; bp 32-33°C/0.04 mmHg; Ref. 5, bp 35-40°C/0.3-0.4 mmHg.

Preparation of 5,6-Dimethyl-4,7-dioxaspiro(2.4)hept-1-ene (IV)

A procedure similar to that described for the preparation of I was carried out using 0.34 mol of 2-bromomethyl-2-chloromethyl-4,5-dimethyl-1,3-dioxolane and 0.38 mol of $NaNH_2$. The product was distilled at 28-33°C/0.04 mmHg to give only 5% yield of IV.

The ^{1}H-NMR spectrum showed two three-proton doublets (J = 8 Hz) at 1.52 and 1.53 ppm, two one-proton multiplets at 3.80 and 4.35 ppm, and a two-proton singlet at 7.88 ppm. Analysis: Calculated for $C_7H_{10}O_2$: C, 66.64; 7.99. Found: C, 66.48; H, 8.02.

Preparation of 6,6-Dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (V)

This compound was prepared in a manner similar to that described for the synthesis of I. Typically, 0.50-0.70 mol of 2-bromomethyl-2-chloromethyl-5,5-dimethyl-1,3-dioxane was treated with a 10% molar excess of sodium amide for 5-6 h. The product was stabilized with 2 mol% hydroquinone and isolated by distillation at 33-40°C/0.01 mmHg. The yield was 40-55% of theory; Ref. 5, bp 40-55°C/0.015 mmHg.

Synthesis of Carbocation (IX) from V

A 25-mL round-bottomed flask was charged with 1.4 g (10 mmol) of V and 10 mL of anhydrous diethyl ether. The contents were sealed

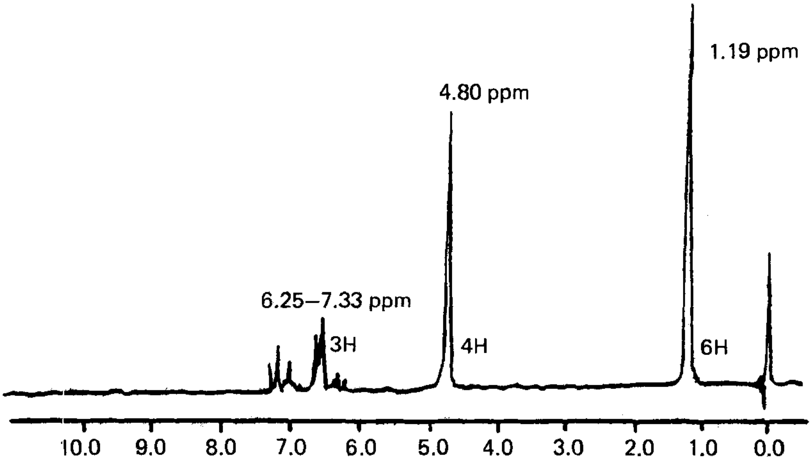


FIG. 1. NMR spectrum of cyclopropenylum ion (IX) in CD_3NO_2.

under nitrogen with a rubber septum, and the flask was cooled to -78°C, after which 10 mmol of $BF_3 \cdot OEt_2$ was slowly injected into the stirred solution. A hygroscopic solid precipitated immediately and was isolated with exclusion of moisture. The ^1H-NMR spectrum (CD_3NO_2) (Fig. 1, Table 1) confirmed the structure of this carbocation.

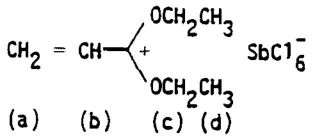
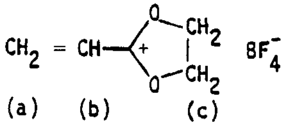
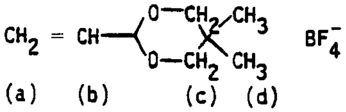
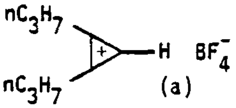
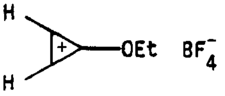
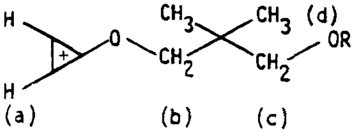
Preparation of β,β-Dimethyl-γ-bromopropylacrylate (XI)

A 250-mL three-necked flask equipped with a condenser, addition funnel, $CaCl_2$ drying tube, and N_2 inlet was charged with 73 g (0.70 mol) of 2,2-dimethyl-1,3-propanediol. The reaction vessel was purged with N_2, and heat was applied until most of the diol had melted. PBr_3 (21 mL, 0.22 mol) was then added dropwise at such a rate as to maintain a gentle reflux. The addition was completed in 45 min, and heating was continued for 2 h longer. Upon cooling, the reaction mixture was poured into 300 mL H_2O and neutralized with Na_2CO_3. The organic layer was extracted with 300 mL ether and again with 150 mL ether. The combined extracts were dried over $MgSO_4$, and ether was removed on the rotary evaporator. The brown viscous residue was fractionated at 70-80°C/8 mmHg to give 16 g or a 15% yield of 3-bromo-2,2-dimethyl-1-propanol; Ref. 9, bp 78°C/12 mmHg.

The NMR spectrum showed a six-proton singlet at 1.03 ppm, a one-proton singlet at 2.93 ppm, a two-proton singlet at 3.42 ppm, and a two-proton singlet at 3.48 ppm.

To a 250-mL round-bottomed flask was introduced 16 g (9.6 mmol) of 3-bromo-2,2-dimethyl-1-propanol, 8.1 mL (10 mmol) of acryloyl chloride, and 60 mL benzene, and the contents were refluxed for 2 h under a $CaCl_2$ drying tube. Upon cooling, the reaction mixture was washed with 100 mL saturated $NaHCO_3$ solution, followed by 100 mL

TABLE 1. NMR Spectral Data of Cationic Intermediates

Compound	Proton chemical shift (ppm)	Solvent
 (X)	a), b) 6.22-7.30 (m) c) 4.9 (q) d) 1.8 (t)	CD_3CN
 (XVI)	a), b) 6.28-7.57 (m) c) 5.35 (t)	FSO_3H[a]
 XII	a), b) 6.25-7.33 (m) c) 4.80 (s) d) 1.19 (2)	CH_3CN
 XIV	a) 10.3 (s)	CF_3CO_2H[b]
 XV	a) 9.38 (s)	$CDCl_3$[c]
 IX	a) 9.61 (s) b) 5.12 (s) c) 3.69 (m) d) 1.33 (s)	CD_3NO_2

[a] Data from Ref. 26.
[b] Data from Ref. 2.
[c] Data from Ref. 22.

water. The organic layer was dried over $MgSO_4$, and benzene was removed in vacuo. The yellow residue was fractionated at 65-66°C/1.5 mmHg to give 8.9 g or a 42% yield of the desired acrylate.

The NMR spectrum showed a six-proton singlet at 1.10 ppm, a two-proton singlet at 3.41 ppm, a two-proton singlet at 4.08 ppm, and a three-proton multiplet at 5.7-6.7 ppm.

The IR spectrum gave signals at 3040 (w), 2970 (s), 2880 (m), 1730 (s). 1635 (m), 1620 (m), 1472 (s), 1410 (s), 1390 (m), 1373 (m), 1296 (s), 1266 (d), 1210-1170 (s), 1060 (s), 985 (s), 810 (s), and 657 (s). Analysis: Calculated for $C_8H_{13}O_2Br$: C, 43.46; H, 5.93; Br, 36.14. Found: C, 43.62; H, 5.97; Br, 35.95.

Preparation of 2-Vinyl-5,5-dimethyl-1,3-dioxenium Tetrafluoroborate (XII) from XI

A 25-mL round-bottomed flask was charged with 2.2 g (10 mmol) of XI and 10 mL of anhydrous CH_2Cl_2. The reaction vessel was transferred to a dry box where 1.9 g (10 mmol) of $AgBF_4$ was weighed and added to the reaction mixture in small portions. After stirring for 45 min at room temperature, the heterogeneous mixture was filtered to remove AgBr. The salt was washed with two 5-mL portions of CH_2Cl_2, and the combined filtrate and washings were added to 200 mL of dry ether. A waxy solid precipitated immediately. The ether was decanted, and the salt was redissolved in CH_2Cl_2 and reprecipitated two more times in ether. The solid was then filtered and washed with ether under a stream of N_2. The off-white solid was dried in vacuo (10^{-6} torr) to give 0.96 g or a 40% yield.

The NMR spectrum in CD_3CN showed a six-proton singlet at 1.19 ppm, a four-proton singlet at 4.80 ppm, and a three-proton multiplet in the region 6.25-7.33 ppm.

Preparation of 2-Phenyl-4,4,5,5-tetramethyl-1,3-dioxolenium Tribromide (XIII)

A 100-mL round-bottomed flask was charged with 12 mL (0.12 mol) of benzaldehyde, 12 g (0.10 mol) of pinacol, 50 mL of toluene, and 20 mg of p-TsOH. The reaction mixture was heated to reflux, and toluene/water azeotrope was collected in a Dean-Starke trap. After approximately 2 mL of H_2O had been removed, the reaction was stopped. The solvent was removed in vacuo, and the product was distilled at 115-117°C/10 mmHg to give 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolane in 72% yield; Ref. 10, bp 120-121°C/11 mmHg.

The corresponding salt (XIII) was prepared by treating 2.1 g (0.010 mol) of the dioxolane in 25 mL of $CHCl_3$ with 2.6 mL (0.050 mol) of Br_2 at 0°C. The bromine was added in small portions, after which the reaction mixture was allowed to stir at room temperature for 1 h. The resulting orange solution was poured into 150 mL of diethyl ether, and the orange precipitate was filtered and washed thoroughly with ether.

Purification by dissolving in a minimum amount of CH_2Cl_2, and reprecipitation in ether gave pure product in 79% yield, mp 82-84°C; Ref. 10, 83-84°C.

Polymerization

Purification of Starting Materials

Cyclopropenone ketals were stabilized with 0.1 mol% hydroquinone and distilled in vacuo. The monomer was then stirred over CaH_2 for 6 h at 10^{-6} torr and subjected to two bulb-to-bulb distillations prior to use. Treatment with CaH_2 was eliminated in the case of I.

Benzoyl peroxide was dissolved in a minimum amount of CH_2Cl_2 and precipitated twice into methanol. The initiator was then dried in vacuo and stored at 0°C. AIBN was recrystallized from diethyl ether, dried, and stored at 0°C. Boron trifluoride etherate was fractionally distilled under N_2 at 124-125°C, dried over CaH_2 for 12 h, and subjected to one trap-to-trap distillation. The initiator was then sealed with a rubber septum under N_2 and stored at 0°C. The initiators, Et_3OBF_4, Ph_3CSbCl_6, and FSO_3H (Aldrich), were used as purchased. Methyl trifluoromethanesulfonate was distilled at 94-96°C and sealed in ampules.

Solvents used as precipitants for separation of polymeric products were methanol, water, diethyl ether, petroleum ether or hexanes, carbon tetrachloride, and benzene. Solvents typically used to dissolve polymers were benzene, acetone, dimethylsulfoxide, dimethylformamide, carbon tetrachloride, methylene chloride, tetrachloroethylene, and water.

Reaction of I with $SnCl_4$

A polymer tube was flushed with N_2 and charged with 6 mL of anhydrous CH_2Cl_2 and 12 μL (0.10 mol) of $SnCl_4$. The tube was connected to the high vacuum line, and the contents were degassed 3 times. Previously purified and degassed I (1.0 g, 10 mmol) was introduced into the reaction vessel via a trap-to-trap distillation and subsequently sealed in vacuo. The frozen contents were allowed to warm to -78°C in a Dry-Ice/isopropanol bath, producing a dark-green solution. The color remained for 1 h, then became blue and then red as the temperature warmed to -40°C. As the temperature approached 0°C, the solution turned brown but remained homogeneous. The tube was opened, and some of the contents were dripped into several nonsolvents with no precipitation occurring. The remaining solution was added to 25 mL of CH_3OH, and solvents were removed in vacuo. The residual liquid was analyzed by ^{1}H-NMR and was shown to be a mixture of dimer and unidentifiable products.

Reaction of I with BF_3 Gas

A 25-mL round-bottomed flask was flushed with N_2 and charged with 6 mL of anhydrous CH_2Cl_2 and 1.0 g (10 mmol) of I. The contents were sealed under N_2 with a rubber septum and cooled to -78°C. The gaseous initiator (4.5 μL, 0.1 mmol) was injected into the stirred reaction mixture. A faint-yellow color appeared within 5 min, but no other change was observed over a 2-h period. A small portion of the polymerization mixture was removed with a syringe and added to several nonsolvents, with no precipitate being observed. The reaction temperature was increased to 0°C for 1 h, and an additional 0.1 mmol of BF_3 was injected. Once again, no precipitation of polymer in various nonsolvents was observed. The remaining solution was treated with ammoniacal methanol, and the solvents were removed to give a yellow oil. NMR analysis revealed the presence of predominantly unreacted starting material.

Reaction of I with $BF_3 \cdot OEt_2$, Et_3OBF_4, and $TiCl_4$

A procedure similar to that described for the reaction of I with $SnCl_4$ was carried out using 10 mmol of monomer and 0.1 mmol initiator in 6 mL anhydrous CH_2Cl_2. No polymer was produced in any of the experiments, although a colored species similar to that obtained in the I/$SnCl_4$ system was observed for I in the presence of $TiCl_4$.

Reaction of V with $BF_3 \cdot OEt_2$, Et_3OBF_4, ϕ_3CSbCl_6, CF_3SO_3,CH_3, and FSO_3H

A procedure similar to that described for the reaction of I with $SnCl_4$ was carried out using monomer and initiator in a 100:1 molar ratio. In the case of $CF_3SO_3CH_3$, a small ampule containing a weighed amount of initiator was broken in a solution of V in CH_2Cl_2 at -78°C. All other initiators were weighed and transferred with solvent to a polymer tube prior to introduction of monomer in the high vacuum line. No significant reaction of any kind was observed in any of the experiments at -78 to 0°C.

Polymerization of V with a Large Excess of $BF_3 \cdot OEt_2$

A 25-mL round-bottomed flask was charged with 1.4 g (10 mmol) of V and 10 mL anhydrous solvent. The contents were sealed under N_2 with a rubber septum, and the appropriate reaction temperature was attained in a water bath. The prescribed quantity of purified $BF_3 \cdot OEt_2$ (see Table 2) was injected into the stirred polymerization mixture. The solution immediately became brown, and precipitation of an elastomeric solid ensued. After stirring for 1 h, the mixture was poured into 150 mL petroleum ether. The tan precipitate was filtered and dried in vacuo. The polymer was insoluble in all organic solvents tried and in 1 N KOH.

TABLE 2. Polymerization[a] Data for Monomer (V)/$BF_3 \cdot OEt_2$ System

Monomer (mmol)	$BF_3 \cdot OEt_2$ (mmol)	Solvent (mL)	Temperature (°C)	% Conversion
10	0.54	ϕH (10)	25	3.8
10	0.40	ϕCH_3 (10)	25-50	5.2
10	0.10	CH_2Cl_2 (10)	40	0
10	0.50	Isohex (10)	30	7.4

[a] Carried out under a N_2 atmosphere; initiator was injected into a solution of monomer and diluent.

Reaction of V with Carbonium Ions (XII) and IX)

A 25-mL round-bottomed flask was charged with 0-5 mmol of XII and 10 mL CH_2Cl_2 in the dry box. The contents were sealed under N_2 with a rubber septum, and the reaction vessel was transferred to the hood. The homogeneous solution of the carbonium ion was stirred at room temperature, and 1.4 g (10 mmol) of V was injected in one portion. Following a 3-h reaction period, analysis of the reaction mixture revealed the presence of nearly pure starting material.

A similar procedure was carried out using 0.5 mmol of IX dissolved in 10 mL CH_3CH. No reaction occurred after 3 h.

Reaction of V with XIII

A polymer tube was charged with 45 mg (0.1 mmol) initiator and connected to the high vacuum line, followed by introduction via separate trap-to-trap distillations of 1.4 g (10 mmol) of V and 7 mL anhydrous CH_2Cl_2. The frozen mixture was sealed in vacuo and allowed to warm to -78°C in a Dry-Ice/isopropanol bath. No changes were observed after 1 h, and the polymerization mixture was slowly warmed to 25°C. After 2 h at room temperature the initiator was quenched with $NaOCH_3$, and solvent was removed to give nearly pure starting material.

Attempted Polymerization of Cyclopropenone Ketals with Radical Initiators

In a typical procedure, pure monomer, initiator, and solvent (if required) were charged to a polymer tube, and the contents were degassed three times. The prescribed quantities of starting materials and reaction conditions were used according to standard practice. The reaction mixture was sealed in vacuo (10^{-6} torr) and heated for an appropriate time period. In the case of photolysis the degassed sample was irradiated with light of appropriate wavelength in a quartz cell.

Work-up involved dripping the reaction mixture into various nonsolvents to precipitate any polymeric products. When no solid precipitate was detected, solvent (if present) was evaporated, and the residue was analyzed by NMR.

Radical Initiation of V in the Presence of a Trapping Agent

The trapping agent, 2,2,6,6-tetramethylpiperidine-1-oxyl, was prepared by the oxidation of 2,2,6,6-tetramethylpiperidine (10 g) in the presence of 12 mL of 30% hydrogen peroxide and a catalytic amount of phosphotungstic acid [11].

A polymer tube was charged with 2.9 g (21 mmol) of V, 1.09 g (4.2 mmol) of benzoyl peroxide, and 0.66 g (4.2 mmol) of the trapping agent, and the contents were degassed several times and sealed in vacuo. After heating for 22 h at 60 ± 0.1°C, a black viscous product was obtained which was not examined further.

RESULTS AND DISCUSSION

Synthesis of Cyclopropenone Ketals

The previous method for preparation of cyclopropenone ketals involving dehydrohalogenation with potassium amide [1, 4] suffered from the necessity of handling large quantities of potassium metal and liquid ammonia in a tedious and time-consuming procedure. The commercially available sodium amide was chosen as an alternative dehydrohalogenating agent. As a result, handling of potassium metal was eliminated, and the volume of liquid ammonia required was reduced by one-half.

In a typical procedure (see Experimental), an appropriate volume of liquid ammonia was condensed, and finely ground sodium amide was added in small portions. Typical additions required 2 h and were followed by a 2-h reaction period. Work-up was similar to that described previously [1, 4], except that anhydrous diethyl ether containing 2 mol% of hydroquinone was added to replace the evaporating ammonia. The hydroquinone inhibited decomposition of the product during isolation and purification. Yields were 10-30% lower than those reported for dehydrohalogenation with potassium amide. However, the decrease in time and the enhanced safety of the procedure compensated for the decrease in yield.

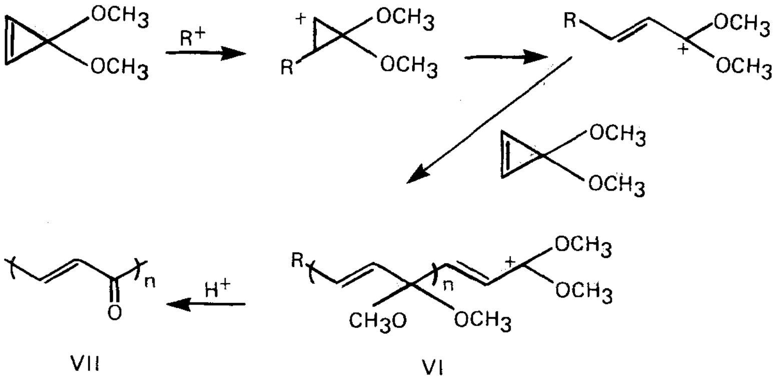
The cyclic cyclopropenone ketals exhibited a marked increase in stability over I, particularly V, which could be treated with calcium hydride without substantial decomposition. The resulting anhydrous monomer was stored at -40°C in a sealed tube at 10^{-6} torr for several days with no noticeable color formation.

Several sources in the chemical literature point out that 2-substituted 1,3-dioxolanes and 1,3-dioxanes are susceptible to ring-opening in the presence of cationic and radical species, and can be polymerized under suitable conditions [12-15]. As a result, the cyclization of the ketal moiety in cyclopropenone ketals introduced an additional mode of polymerization into the monomer which could greatly complicate the mechanistic and structural features of its polymerization. In order to prevent ring-opening of the 1,3-dioxo-heterocycle, the α-methylene carbon atoms could be sterically protected by the attachment of various substituents [12, 16].

The secondary diol, 2,3-butanediol, underwent transketalization with II to form 2-bromo-2-chloro-4,5-dimethyl-1,3-dioxolane in 64% yield, which could be cyclized to IV (Eq. 3).

Polymerization Studies

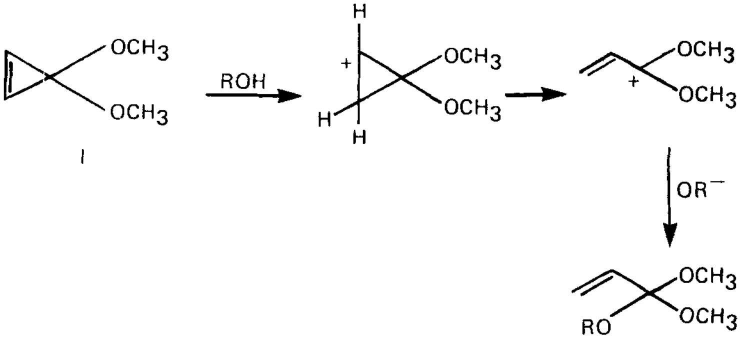
Numerous polymerization initiators were considered for initiation of polymerization of I and other cyclic ketal analogues which might induce propagation through an allylic propagating species:



(5)

The polymer (VI) predicted via Eq. (5) could be subsequently hydrolyzed to give structure VII comprised of α,β-unsaturated carbonyl units. Such a novel polymer may exhibit semiconduction or light-sensitive properties due to its unusual cross-conjugation.

The above mechanism was proposed on the basis of an earlier reaction mechanism designed to account for the formation of orthoacrylates by treatment of cyclopropenone ketals with excess anhydrous alcohol [4] to yield the previously unreported orthoacrylates. This scheme (Eq. 6) was applicable to most alcohols due to the possession of a weakly acidic proton. Because the mechanism was believed to involve a cationic intermediate, polymerization via a cationic pathway was initially investigated.



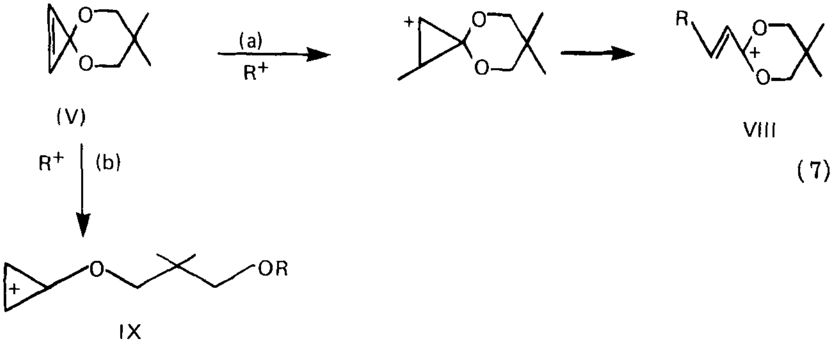
(6)

Cationic Initiation of Cyclopropenone Ketals

Attempted polymerization of cyclopropenone ketals with several cationic initiators was carried out with no evidence of polymer formation. Boron trifluoride gas (BF_3), boron trifluoride etherate ($BF_3\cdot OEt_2$), triethyl oxonium tetrafluoroborate (Et_3OBF_4), triphenylmethyl hexachloroantimonate (ϕ_3CSbCl_6), fluorosulfonic acid (FSO_3H), and methyl trifluoromethylsulfonate ($CH_3SO_3CH_3$) are all known to initiate polymerization of cationically polymerizable monomers. However, none of these initiators gave linear polymer from cyclopropenone ketal monomers under established conditions for polymerization.

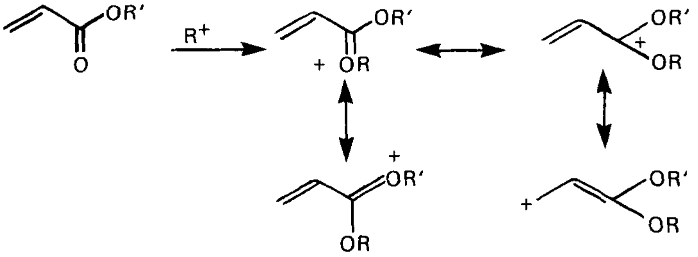
The low reactivity of cyclopropenone ketals in the presence of various cationic species was not consistent with that expected for the highly strained cyclopropene double bond. The sluggish reactivity of the monomers suggested the formation of a very stable intermediate which exhibited little inclination to propagate with monomer. Similar behavior had been reported for vinyl amine, where cationic initiation produced a carbocation which was not sufficiently reactive to sustain propagation [17]. The low reactivity of the cationated species was attributed to resonance stabilization of the positive charge.

Two resonance stabilized carbocations that are derivable from cyclopropenone ketals were proposed to explain the sluggish reactivity of these monomers in the presence of cationic initiators. The first intermediate postulated was a vinyl dialkoxycarbocation (VIII) (Eq. 7). Alternatively, since most cationic initiators are good alkoxide abstraction agents [18], a cyclopropenylium ion (IX), arising from abstraction of alkoxide anion from the sp^3 carbon atom of the cyclopropenone ketal, is conceivable:



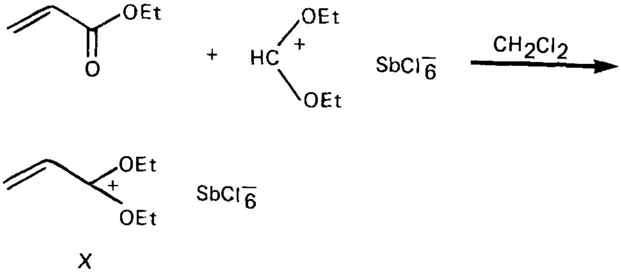
(7)

Allen and Plesch [19] postulated the formation of a vinyl dialkoxycarbocation intermediate to account for the inability of acrylate monomers to polymerize in the presence of cationic initiators. Presumably, the carbonyl oxygen is the site of highest nucleophilicity, and the monomer irreversibly undergoes reaction with the cationic initiator to produce the proposed vinyl dialkoxycarbocation:



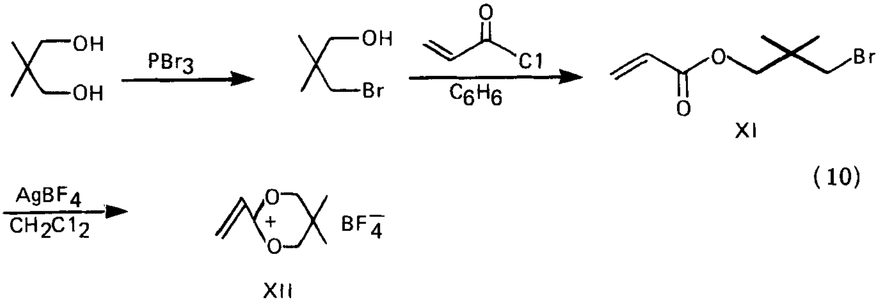
(8)

Stabilization through resonance with the double bond and the two adjacent oxygen atoms generates a highly delocalized carbocation which is sufficiently stable to prohibit propagation. Thus, acrylate monomers must have scavenged the initiator ions without regenerating a chain carrier. Evidence for the formation of vinyl dialkoxycarbocations from acrylates was provided in this study via the synthesis and isolation of an analogous carbocation from the reaction of ethyl acrylate with diethoxymethyl carbocation:



(9)

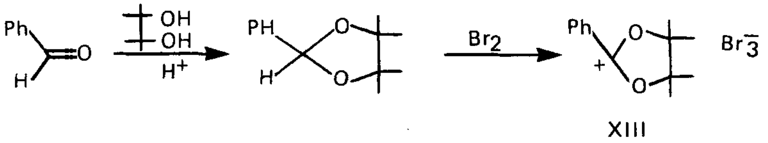
Likewise, 2-vinyl-5,5-dimethyl-1,3-dioxonium tetrafluoroborate (XII) was synthesized by an intramolecular alkylation at the carbonyl oxygen atom when β,β-dimethyl-γ-bromo propylacrylate (XI) was treated with $AgBF_4$:



(10)

The low reactivity of the vinyl dialkoxycarbocation (X) was illustrated in a reaction with V in CH_2Cl_2 solvent. No reaction was observed at -78 to 0°C when the salt was present in 1 mol% concentration. In accordance with the earlier proposal, X was presumably unreactive toward the cyclopropenone ketal due to its high resonance-derived stability. Thus, the proposed cationic intermediate generated by the rearrangement of the cationated cyclopropenone ketals (Eq. 7) appears to have little inclination to add monomer and is essentially inert under the reaction conditions described.

A similar dialkoxycarbocation was prepared during this study using the method of Goosen and McCleland [16] whereby treatment of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolane with bromine afforded the corresponding 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolonium tribromide (XIII):



(11)

The benzyl dialkoxycarbocation (XIII) would be expected to exhibit comparable stability to the allyl analogue (XII) and should behave similarly in the presence of cyclopropenone ketals. As predicted, treatment of V with XIII at -78 to 25°C resulted in no reaction.

The proposed cyclopropenylium intermediate (IX) would likewise be expected to exhibit high stability due to the aromaticity of the 2π-electron system. Other instances of cyclopropenylium ion formation via an alkoxide abstraction mechanism have been reported involving hydrogen bromide [20, 21]. In addition, stable alkoxy and hydroxy cyclopropenylium ions have been prepared and isolated from cyclopropenone precursors [22].

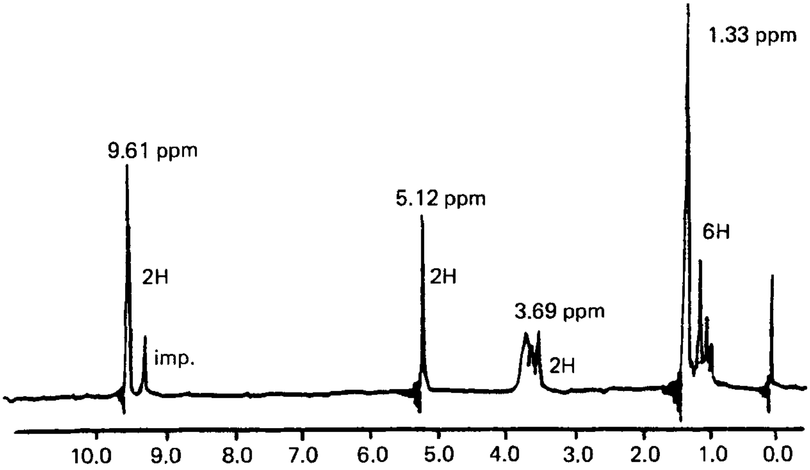


FIG. 2. NMR spectrum of 2-vinyl-1,3-dioxenium tetrafluoroborate (XII) in CD_3CN.

In an effort to isolate a cation intermediate directly from cyclopropenone ketals, monomer V was treated with one equivalent of $BF_3 \cdot OEt_2$ in diethyl ether at -78°C. A hygroscopic solid precipitated immediately and was isolated with exclusion of moisture. The NMR spectrum exhibited by the cationated species was not similar to that of the vinyl dialkoxycarbocation (XII) (Eq. 10 and Fig. 2) synthesized earlier, but was consistent with the spectral data expected for the cyclopropenylium ion (IX) (Eq. 7 and Fig. 1). The NMR spectral data for the carbocations are tabulated along with data for other similar cationated species for comparison (Table 1).

Breslow [2] ascribed a singlet at 10.3 ppm to the ring proton of dipropylcyclopropenylium tetrafluoroborate (XIV) in trifluoroacetic acid medium. The considerable shift downfield was attributed to the relatively large amount of positive charge on the carbon atom to which the proton is attached. The proposed cyclopropenylium ion produced from V possesses two ring protons which appear as a singlet at 9.61 ppm in CD_3NO_2. A similar chemical shift of 9.30 ppm was reported for ethoxycyclopropenylium tetrafluoroborate (XV) in $CDCl_3$ [22]. Variation of observed chemical shifts for the above-mentioned cyclopropenylium ions was attributed to the different media employed for NMR analysis [23] and the slightly diminished positive charge on the alkoxycyclopropenylium carbon atoms due to resonance with the adjacent oxygen atom. In the NMR spectra of typical carbocations, the chemical shift of a proton was found to be directly proportional to the charge on the carbon to which the hydrogen in question was attached [24, 25].

When a solution of the proposed cyclopropenylium ion in CD_3NO_2

was treated with a small amount of deuterium oxide (D_2O), a quantitative conversion to cyclopropenone occurred. The singlet at 9.61 ppm disappeared and was replaced with a singlet at 9.1 ppm which was ascribed to the cyclopropenone protons [27]. Similar conversions to cyclopropenones upon hydrolysis with water were reported for several other cyclopropenylium ions [22, 27].

Thus, cyclopropenone ketal (V) underwent an alkoxide abstraction in the presence of $BF_3 \cdot OEt_2$ under the prescribed reaction conditions. The resulting carbocation (IX) ($R = BF_3$) was not sufficiently reactive to sustain propagation, and polymerization was essentially terminated. Presumably, other cationic initiators such at Et_3OBF_4 and FSO_3H generated a similar cyclopropenylium species which was inert under the conditions of the reaction.

When cyclopropenone ketal (V) was allowed to react with at least 4 mol% $BF_3 \cdot OEt_2$ at temperatures above 25°C, a low conversion to a cross-linked polymer resulted (Table 2). No polymerization was observed in the presence of 1 mol% $BF_3 \cdot OEt_2$ or at temperatures below 20°C. The formation of polymer could be rationalized in two ways: 1) the stable cyclopropenylium intermediate (IX) was reactive under the new conditions prescribed for polymerization, or 2) addition of the initiating species at the double bond may have occurred to some extent to produce a reactive propagating species. The latter explanation is more consistent with the spectral properties of the polymer and with several observations concerning the reactivities of the proposed intermediates involved, and is elaborated on in the paragraphs that follow.

The low reactivity of the cyclopropenylium ion (IX) was illustrated by treating V with 5 mol% IX at 25°C. Following a 3-h reaction period, the monomer remained unreacted while some decomposition of the cation occurred to produce a brown-colored reaction mixture. Apparently IX is too stable to initiate the polymerization of V under the reaction conditions established for polymerization. Likewise, intermediate XII did not initiate the polymerization of V under similar conditions.

The IR spectral data provided evidence for the involvement of a vinyl dialkoxycarbocation intermediate (VIII) or (XII) in the polymerization of V. The spectrum exhibited an ester carbonyl band at 1730-1710 cm^{-1} and a double bond stretch at 1620-1600 cm^{-1}. Other major peaks observed were a methyl C–H stretch at 2960 cm^{-1}, a methylene C–H stretch at 2870 cm^{-1}, and a C–H bend at 1470 cm^{-1}. Also, broad bands at 1260, 1170, 1090, and 1030 cm^{-1} were present and were ascribed to an ester C–O–C stretch (Fig. 3). (An ether C–O–C stretch may also have been present.)

The presence of an ester carbonyl unit in the polymer (C=O stretch at 1720 cm^{-1}) could be rationalized through a mechanism involving ring-opening of a cyclic dialkoxycarbocation intermediate. This mechanism has been well documented in the case of dioxolenium ions which exclusively gave ester products in the presence of a variety of weak nucleophiles (Eq. 12) [28]. In addition, cyclic cyclopropanone

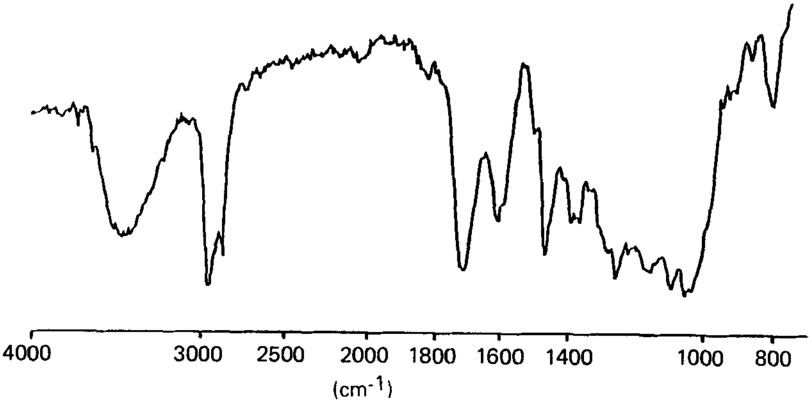
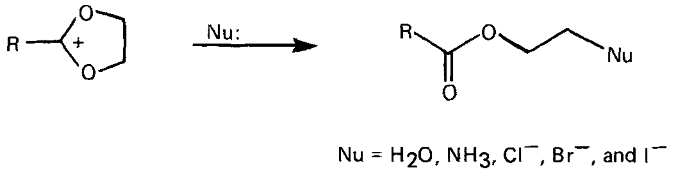


FIG. 3. IR spectrum of polymer obtained from 6,6-dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (V) and $BF_3 \cdot OEt_2$.

ketals gave esters in high yield in the presence of acid (Eq. 13) [29]. Ester formation was attributed to a dialkoxycarbocation intermediate generated by ring-opening of the cyclopropane moiety.



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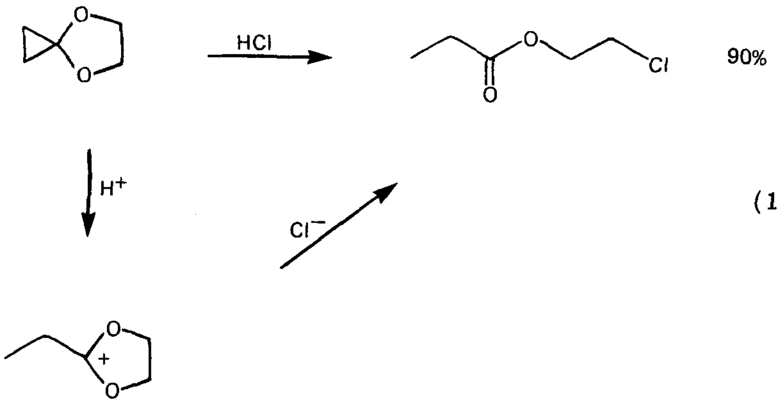

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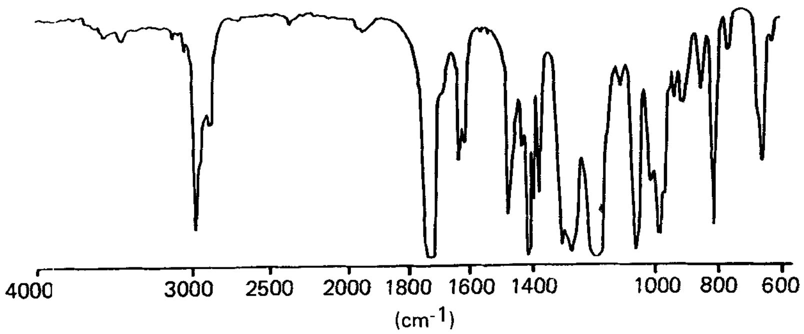


FIG. 4. IR spectrum of β,β-dimethyl-γ-bromopropylacrylate (XI).

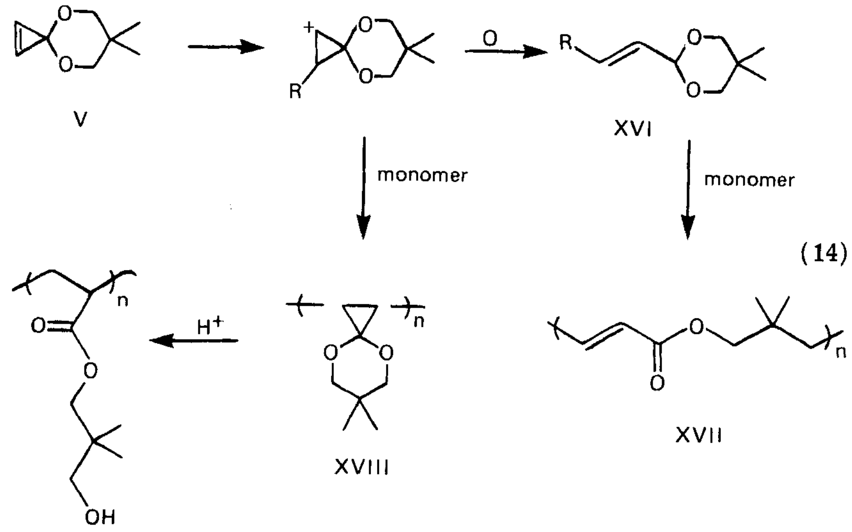
Formation of an α,β-unsaturated ester repeating unit in the polymer was explained by a mechanism involving a vinyl dialkoxycarbocation intermediate (VIII) identical to that proposed in Eq. (7). Nucleophilic ring-opening in an analogous fashion to that described earlier [28, 29] gave the proposed ester unit (XVII) (Eq. 14). Compound (XI) served as a good model compound for the repeating unit (XVII), and their IR spectra closely resembled one another (Figs. 3 and 4).

The same ester unit (XVII) could not be derived from the cyclopropenylium intermediate (IX) isolated earlier. In addition, unsaturation present in the polymer (C=C stretch at 1610 cm^{-1}) could not be justified by a mechanism involving ring-opening of the cyclopropanone ketal repeating unit (XVIII) (Eq. 14).

The presence of some cyclopropanone ketal units (XVIII) in the polymer was not ruled out by spectral data, and it is likely that these repeating units contributed to the formation of cross-links in the polymer. Cross-linking presumably occurred by electrophilic ring-opening of the enchained cyclopropane ring to generate a dialkoxycarbocation in a similar manner to that depicted in Eq. 14. The resulting pendant cationated species could then react with monomer to cause branching or could react with nucleophilic sites on a polymer chain to produce cross-links.

Evidently, formation of the cyclopropenylium ion (IX) did occur to some extent in addition to and separate from polymerization. In fact, polymerization was apparently a minor reaction (0-7%) relative to alkoxide abstraction. For this reason, large amounts of initiator (4-5 mol%) were required to achieve low conversions to polymer.

According to the data available, the structure shown in Eq. (15) for the polymer obtained from $BF_3 \cdot OEt_2$ and V is proposed. Repeating unit XVII was present in much larger quantity than XVIII.



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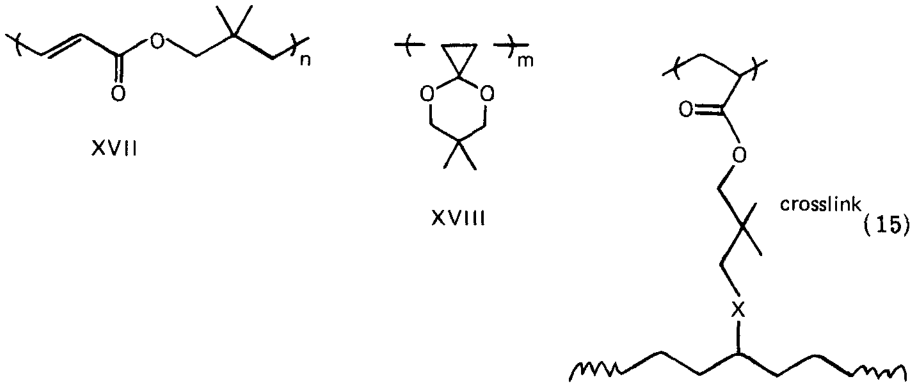

(15)

Radical Initiation

All attempts to homopolymerize cyclopropenone ketals by a radical chain-growth mechanism were unsuccessful. Radical initiators such as azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) in the temperature range of 25-80°C were investigated. In addition, photolysis in the presence of a variety of sensitizers was studied.

As in the case of cationic initiation, the formation of a stable intermediate is suggested to account for the nonpolymerizability of cyclopropenone ketals by a radical mechanism [30].

Steric inhibition of propagation may also have played a significant role in preventing the homopolymerization of cyclopropenone ketals. Generally, 1,2-disubstituted olefins do not polymerize under established conditions for radical-initiated polymerization [31]. An attempt to trap a radical intermediate generated from cyclopropenone ketal (V) with 2,2,6,6-tetramethylpiperidine-1-oxyl [32] as radical trapping agent was unsuccessful.

CONCLUSIONS

Cyclopropenone ketals did not polymerize in the presence of a variety of cationic initiators under normal conditions. In each case the formation of a stable carbocation intermediate was suggested to account for their sluggish reactivity. Synthesis and isolation of these intermediates was achieved by reacting equivalent amounts of monomer and $BF_3 \cdot OEt_2$ at -78°C. The resulting cationic intermediates were characterized by NMR, and their low reactivity toward monomer was demonstrated.

Polymerization of cyclopropenone ketals was accomplished in the presence of 4-5 mol% $BF_3 \cdot OEt_2$ at 25-50°C. Apparently the more demanding reaction conditions promoted a minor conversion to polymer involving an allyl dialkoxycarbonium ion intermediate. An α,β-unsaturated ester repeating unit was proposed, with minor cyclopropanone ketal units present as cross-linkable sites.

Attempts to polymerize cyclopropenone ketals with radical initiators were unsuccessful. Steric inhibition of propagation was suggested to account for their nonpolymerizability. Adverse interactions between the 1,2-olefinic substituents apparently rendered polymerization unfavorable.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation, Grant No. DMR-80-20206, and the Department of Chemistry at the University of Florida for financial support of this work. We are also grateful to Mr David Schechtman for his contributions to the synthetic program.

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Accepted by editor April 4, 1984
Received for publication May 7, 1984