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Cationic-Initiated Ring-Opening Polymerization of Cyclopropenone Ketals. II. Novel Polymers via Bromine as Polymerization Initiator

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Cationic-Initiated Ring-Opening Polymerization of Cyclopropenone Ketals. II. Novel Polymers via Bromine as Polymerization Initiator

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ABSTRACT

Cyclopropenone ketals are functionally capable of undergoing both vinyl and ring-opening polymerization. In a previous paper we reported ring-opening polymerization via boron trifluoride etherate initiation to yield a polymer of complicated structure. However, this previous study showed that conventional cationic initiators yield an exceptionally stable carbocation intermediate which is essentially incapable of further propagation. This paper reports the effective use of the unconventional cationic initiator, elemental bromine, to yield polymer, proposed to be formed by a sequence of steps which involve initial addition of bromine to the cyclopropene double bond, followed by electrophilic ring opening of the brominated cyclopropane ring and propagation via the carbocation intermediate formed. At least three different and simultaneous pathways are believed to be involved. The resulting polymers have $\overline{M}_n$ values in the range of 10,000.

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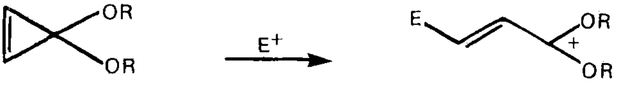
INTRODUCTION

Cyclopropenone ketals (I) are functionally capable of undergoing both vinyl polymerization and ring-opening polymerization. In a previous paper from these laboratories [1] it was shown that representative members of this series of compounds did not undergo polymerization in the presence of a variety of conventional cationic initiators under normal conditions. This reluctance on the part of these highly reactive monomers to undergo the normal cationic propagation step was shown to be the result of the inability of a highly resonance stabilized cationic intermediate (II) to open the ring of (I) in the chain-carrying step:



I II (1)

However, when cyclic cyclopropenone ketal (III) [6,6-dimethyl-4,8-dioxospiro(2.5)oct-1-ene] was subjected to a large excess of the conventional cationic initiator, $BF_3O(C_2H_5)_2$, polymerization did occur. The structure of the polymer was determined, and a mechanism for its formation was proposed [1].

We would now like to report the effective use of the unconventional cationic initiator, bromine, to yield polymer. The proposed mechanism of polymerization (Eq. 2) involves a sequence of steps which include initial addition of bromine to the double bond followed by electrophilic ring-opening of the highly strained brominated cyclopropane ring and propagation via a carbocation intermediate. This intermediate is believed to be formed by at least three different and simultaneous pathways. Evidence in support of the proposed mechanism is presented. Polymers having number-average molecular weights in the range of 10,000 were obtained.

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 were obtained using a Varian A-60 spectrometer. All chemical shifts are reported in parts per million (ppm) relative to the internal reference tetramethylsilane (TMS). Instrument conditions are stated for each analysis.

Infrared analysis was carried out on a Perkin-Elmer 281 spectrophotometer. Spectra of solid samples were obtained from a KBr disk, while those of liquids were obtained from a film. The ultraviolet spectral investigations of charge-transfer complexes were completed using a Beckman Acta V spectrophotometer. Quartz cells with 1 cm path length were used.

Number-average molecular weights of polymers were determined using a Mechrolab Model 302 or a Wescan Model 233 vapor pressure osmometer. Measurements were carried out in spectral grade acetone at 37°C. Benzil was used as the calibration standard.

Anhydrous solvents were obtained using the methods described by Gordon and Ford [2]. 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.

Polymerization

Synthesis of 6,6-Dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III)

This cyclopropenone ketal was synthesized according to the procedure given in the first paper of this series [1].

Polymerization of III with Bromine. In a typical reaction, 10 mmol of III and 5-10 mL of anhydrous solvent were introduced into a 25-mL round-bottomed flask under a brisk N_2 flow. The mixture was cooled in an ice-water bath to 0°C, and purified bromine (0.52 mL, 10 mmol) was added dropwise at such a rate as to maintain the pot temperature at 0 ± 2°C. After completion of the bromine addition, the mixture was stirred an additional 30 min at 0-25°C. Unreacted bromine was removed by washing the reaction mixture with 10% $NaHSO_3$ and water. The organic layer was separated, dried, and dripped into methanol to precipitate the polymer. The polymer was then dissolved in CH_2Cl_2 and reprecipitated in MeOH twice to give an off-white solid in 7-33% conversions.

The solvent and conditions of the polymerization experiments were subject to numerous variations and are listed in Table 1.

Polymerization of III with Bromine in High Vacuum. A breaksealed ampule containing 1.25 mL (24 mmol) of bromine in 5 mL of CH_2Cl_2 was attached to a polymer tube. The reaction vessel was charged with 20 mL of anhydrous CH_2Cl_2, and the contents were degassed 3 times. Pure III (3.4 g, 24 mmol) was introduced into the polymer tube via two trap-to-trap distillations, and the contents were sealed in vacuo. The solution of monomer and solvent was warmed to 0°C, and bromine was added in small portions from the ampule. Following a 2-h reac-

TABLE 1. Polymerization of III with Bromine

Experiment no.	(V) (mmol)	Br_2 (mmol)	Solvent	Conversion (%)	Additional conditions
1	6.0	10	CCl_4	10	a
2	5.0	5.1	CCl_4	7.3	a
3	5.0	0.10	CCl_4	0	a
4	5.0	1.0	CCl_4	0	a
5	5.0	5.1	CH_2Cl_2	15	0.10 mmol hydroquinone present
6	6.0	5.1	CH_2Cl_2	10	In vacuo (10^{-6} torr)
7	5.0	5.1	Et_2O	22	-78°C
8	5.0	5.1	CH_3COCH_3	0	5.0 mmol LiBr present
9	5.0	5.1	CH_2Cl_2	0	5.0 mmol pyridine present

10	5.0	10.1	CCl_4	30	a
11	5.0	10.1	C_6H_{12}	33	a
12	24	24	CH_2Cl_2	7.6[b]	10^{-6} torr
13	5.0	5.1	CH_3NO_2	0	a
14	18	16	CCl_4	7.0	25°C, N_2 atmosphere
15	5.0	5.5	$(HOCH_2 \rightarrow)_2$	0	a
16	7.7	5.0	ϕH	3.5	a
17	20	20	CCl_4	23	a
18	6.0	6.0	DMSO	0	a

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[a] Polymerization carried out at 0 ± 5°C in air by dropwise addition of Br_2.

[b] $\overline{M}_n$ = 10,400 by VPO.

TABLE 2. Reaction[a] of III with Other Halogenating Reagents

Experiment no.	III (mmol)	Reagent (mmol)	Solvent	Temperature (°C)
19	5.0	NBS, 5.0	CH_3COCH_3	25
20	5.0	HBr, XS	CH_2Cl_2	0
21	5.0	Cl_2, XS	CCl_4	0
22	5.0	$PyrBr_2$, 1.3	CH_2Cl_2	25
23	5.0	I_2, 5.0	CH_2Cl_2	25

[a] No polymer was obtained in these experiments.

tion period, the reaction mixture was worked-up in the usual manner. An off-white solid weighing 0.26 g was recovered.

Reaction of III with Other Halogenating Reagents. In a typical reaction, a 10-mL round-bottomed flask was charged with 5 mmol of III and 2-3 mL of solvent, and the contents were cooled to the prescribed reaction temperature (see Table 2). An appropriate quantity of reagent was added in small portions to the reaction mixture, followed by a 1-2 h reaction period. In the case of iodine, a large volume of solvent (25 mL) was required to completely dissolve the halogen. Pyridine perbromide ($PyrBr_2$) was prepared prior to use by the method of McElvain and Morris [3].

When the reaction mixture was added dropwise to a variety of nonsolvents, no solid precipitate was formed. Evaporation of solvent left a liquid residue which was predominantly starting material in all cases.

Model Compound Synthesis and Reactions

Synthesis of 2-(1',2',2'-Tribromoethyl)-5,5-dimethyl-1,3-dioxenium Bromide (IV)

This carbocation salt was synthesized by reaction of III with bromine (Eq. 2).

Preparation of 6,6-Dimethyl-4,8-dioxaspiro(2.5)octane (V)

A 1000-mL three-necked flask fitted with a N_2 inlet, condenser, drying tube, and addition funnel was charged with 41 g (1.6 mol) of HCl-etched magnesium turnings, and the assembled apparatus was flame-dried. The reaction vessel was cooled under a brisk stream of N_2, and several crystals of purified iodine were added, followed by a solution of 19 g (0.07 mol) of 2,2-bis(bromomethyl)-5,5-dimethyl-1,3-dioxane (X) (Eq. 8) in 100 mL of anhydrous THF.

Heat was applied to the stirred reaction mixture until an exothermic reaction began. The heating mantel was removed, and a solution of 71 g (0.33 mol) of X in 400 mL of anhydrous THF was added at such a rate as to maintain a vigorous reflux. Upon completion of the addition (0.5 h), the dark-gray mixture was heated an additional 2 h.

After cooling overnight, the solution was decanted from unreacted magnesium into 1000 mL of H_2O. The organic layer was separated, and the aqueous layer was extracted twice with 200 mL of diethyl ether. The combined organic layer and extracts were dried over $MgSO_4$, and the solvents were removed in vacuo, leaving a brown liquid. The residue was fractionally distilled at 40-41°C/5 mmHg to give 30 g of product or 53% of theory.

The NMR spectrum showed a four-proton singlet at 0.87 ppm, a six-proton singlet at 1.01 ppm, and a four-proton singlet at 3.53 ppm.

The infrared spectrum gave absorbances at 3095 (w), 3005 (m), 2950 (s), 2900 (s), 2860 (s), 2700 (w), 1470 (s), 1450 (s), 1402 (m), 1392 (m), 1355 (s), 1325 (s), 1310 (s), 1242 (s), 1195 (s), 1080 (s), 1045 (s), 1000 (s), 915 (s), 865 (s), 790 (m), 712 (m), and 635 (s). Analysis: Calculated for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.61; H, 9.95.

Reaction of V with Bromine. To a 25-mL round-bottomed flask was introduced 6 mmol of monomer and 4 mL of anhydrous CH_2Cl_2, and the contents were sealed with a rubber septum under N_2. A solution of 0.3 mL (6 mmol) of Br_2 in 5 mL of CH_2Cl_2 was added dropwise via a syringe to the reaction mixture while cooling in a water bath at 20°C. An exothermic reaction was noted during the addition. After the bromine had been added, stirring was continued for 1 h before pouring the contents into 50 mL of 10% $NaHSO_3$. The organic layer was separated, and the aqueous layer was extracted with 15 mL CH_2Cl_2. The combined organic layer and extract were washed with water, dried over $MgSO_4$, and solvent was removed in vacuo. The residue was identified by NMR as a mixture of starting material and VI (see Eq. 3).

The NMR spectrum of ester VI showed a six-proton singlet at 1.09 ppm, a two-proton triplet at 2.98 ppm, a two-proton singlet at 3.37 ppm, a two-proton singlet at 3.62 ppm, and a two-proton triplet at 4.04 ppm. Analysis: Calculated for $C_8H_{14}O_2Br_2$: C, 31.81; H, 4.67; Br, 52.92. Found: C, 31.76; H, 4.66; Br, 52.99.

Preparation of 2-(1'Propenyl)-5,5-dimethyl-1,3-dioxane (VII)

A 1000-mL round-bottomed flask was charged with 52.6 g (0.75 mol) of crotonaldehyde, 70.8 g (0.68 mol) of 2,2-dimethyl-1,3-propanediol, 400 mL of benzene, and 50 mg of p-TsOH. The contents were refluxed for 2 h while approximately 14 mL of H_2O was collected in a Dean-Starke trap. After cooling the contents, the solvent was removed in vacuo, and 5 g of CaO was added to destroy the acid catalyst. Following filtration, the product was stirred over CaH_2 for 24 h and fractionally distilled at 53-55°C/4 mmHg to give 66 g of product VII (63% of theory).

The proton NMR spectrum showed two three-proton singlets at 0.72 and 1.19 ppm, a three-proton doublet at 1.70 ppm, a four-proton multiplet at 3.53 ppm, a one-proton doublet at 4.78 ppm, and a two-proton multiplet at 5.3-6.1 ppm.

The infrared spectrum gave signals at 3030 (m), 2960 (s), 2870 (s), 2750 (w), 2700 (w), 1680 (m), 1460 (s), 1385 (s), 1370 (s), 1307 (m), 1230 (m), 1215 (m), 1170-1070 (s), 1040-920 (s), 790 (m), 665 (w), and 633 (w). Analysis: Calculated for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.28; H, 1032.

Preparation of 2(1',2'-Dibromopropyl)-5,5-dimethyl-1,3-dioxane (VIII)

Bromination was carried out by treating 1.6 g (0.010 mol) of VII in 20 mL of CCl_4 with a solution of 0.52 mL (0.010 mol) Br_2 in 5 mL CCl_4 at 25°C. The bromine was added in small portions while allowing time for each portion to decolorize prior to addition of the next. Solvent was removed in vacuo, leaving a liquid residue which was identified as the pure bromine-addition product. The yield of product VIII was 3.0 g (95% of theory).

Assignment of signals in the NMR spectrum were two three-proton singlets at 0.73 and 1.22 ppm, a three-proton doublet at 1.87 ppm, a four-proton doublet at 2.57 ppm, a two-proton multiplet at 4.2-4.7 ppm, and a one-proton doublet at 4.78 ppm.

Analysis: Calculated for $C_9H_{16}Br_2O_2$: C, 34.20; H, 5.10; Br, 50.57. Found: C, 34.32; H, 5.08; Br, 50.38.

Preparation of β,β-Dimethyl-γ-bromopropyl-2,3,3-tribromopropanoate (IX)

To a 25 mL round-bottomed flask was added 2.1 mL (40 mmol) of Br_2 and 10 mL of anhydrous CCl_4. The contents were cooled to 10-15°C in an ice-water bath, and a solution of 1.4 g (10 mmol) of III in 3 mL of CCl_4 was added in small portions over a 20-min period. The reaction mixture was allowed to stir at 25°C for 30 min and then poured into 100 mL of 10% $NaHSO_3$ solution. The organic layer was separated, and the aqueous phase was extracted once with 20 mL of $CHCl_3$. The combined organic layer and extract was dried over $MgSO_4$, filtered, and reduced in vacuo. The residue was distilled at 109-110°C/0.05 mmHg to afford pure ester IX in 81% yield.

The proton NMR spectrum showed a six-proton singlet at 1.14 ppm, a two-proton singlet at 3.38 ppm, a two-proton singlet at 4.11 ppm, a one-proton multiplet at 4.4-4.7 ppm, and a one-proton doublet at 6.46 and 6.53 ppm.

The infrared spectrum exhibited major peaks at 2965 (s), 2870 (m), 1745 (s), 1605 (w), 1470 (m), 1395 (m), 1375 (m), 1260 (s), 1180 (s), 1140 (s), 1093 (s), 1023 (s), 980 (m), 785 (w), 765 (w), and 660 (w). Analysis: Calculated for $C_8H_{12}Br_4O_2$: C, 20.90; H, 2.63; Br, 69.52. Found: C, 20.93; H, 2.58; Br, 69.59.

Preparation of 2,2-Bis(bromomethyl-5,5-dimethyl-1,3-dioxane (X)

A 200-mL round-bottomed flask was charged with 34 mL (0.44 mol) of 2,2-dimethoxypropane, 42 g (0.40 mol) of 2,2-dimethyl-1,3-propanediol, and 4 drops of concentrated H_2SO_4. The reaction vessel was fitted with a condenser set downward for distillation, and methanol byproduct was distilled at 60-65°C over a 2-h period. The product was distilled directly from the reaction vessel at 51-52°C/25 mmHg to give a 65% yield of 2,2,5,5-tetramethyl-1,3-dioxane (XII); Ref. 4, bp 143°C/760 mmHg.

A 250-mL three-necked flask equipped with a stir bar, condenser, drying tube, and addition funnel was charged with 23 g (0.16 mol) of XII, 100 mL of $CHCl_3$, and 33 g (0.33 mol) of $CaCO_3$. The reaction mixture was warmed to a gentle reflux, and the addition of 18 mL (0.33 mol) of Br_2 was begun. The heating mantel was removed, and bromine was added at such a rate as to maintain a gentle reflux (total addition required 1 h). The reaction mixture was then allowed to cool and was poured into 250 mL of H_2O. After filtering, the organic layer was separated, washed with 15% $NaHSO_3$ and H_2O, and dried over Na_2SO_4. Solvent was removed in vacuo, and the residue was distilled at 79-81°C/0.01 mmHg to give 33 g of X (69% of theory).

NMR analysis showed a six-proton singlet at 1.01 ppm and two four-proton singlets at 3.54 and 3.71 ppm. Absorbances in the infrared spectrum were observed at 2995 (s), 2900 (s), 1475 (s), 1440 (s), 1400 (s), 1380 (m), 1365 (m), 1270 (s), 1190-1010 (5 strong bands), 690 (s), and 670 (s). Analysis: Calculated for $C_8H_{14}Br_2O_2$: C, 31.81; H, 4.67; Br, 52.92. Found: C, 31.95; H, 4.70; Br, 52.76.

Preparation of β,β-Dimethyl-γ-bromopropyl-2,3-dibromo-1-butanoate (XI)

Ring opening of the dioxane moiety was achieved by refluxing 3.2 g (0.020 mol) crotonaldehyde acetal (VII) with 2.1 mL (0.040 mol) of Br_2 in 100 mL of CCl_4 for 2 h. Upon cooling the reaction mixture, solvent was removed in vacuo to give a residue which was a mixture of the desired ester XI and the brominated acetal. Fractional distillation at 120-125°C/0.04 mmHg afforded pure ester XI in 42% yield.

The proton NMR spectrum showed a six-proton singlet at 1.15 Hz, a three-proton singlet at 2.05 ppm, a two-proton singlet at 3.42 ppm, a two-proton singlet at 4.17 ppm, a one-proton doublet at 4.3-4.5 ppm, and a one-proton quartet at 4.6-5.0 ppm. Side bands were observed for each signal and were attributed to stereoisomers, i.e., RR, RS, SR, and SS.

The infrared spectrum showed major peaks at 2960 (s), 2930 (s), 2870 (s), 1730 (s), 1465 (s), 1440 (s), 1390 (m), 1370 (m), 1300-1190 (s), 1150 (m), 1080 (m), 1020 (m), 985 (m), 790 (m), and 650 (m). Analysis: Calculated for $C_9H_{15}Br_3O_2$: C, 27.37; H, 3.83; Br, 60.70. Found: C, 27.31; H, 3.86; Br, 60.88.

RESULTS AND DISCUSSION

The polymerization of 6,6-dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III) with bromine occurred in a variety of solvents at -78 to 25°C in air or inert atmosphere (Table 1). The reaction conditions for optimum conversion to polymer required the following: 1) 1-2 equivalents of bromine, 2) reaction temperatures in the range of -5 to 5°C, and 3) a nonpolar to moderately-polar solvent. No polymer was produced when polar solvents such as DMSO, CH_3NO_2, and ethylene glycol were used or when less than 0.2 equivalents of bromine were added.

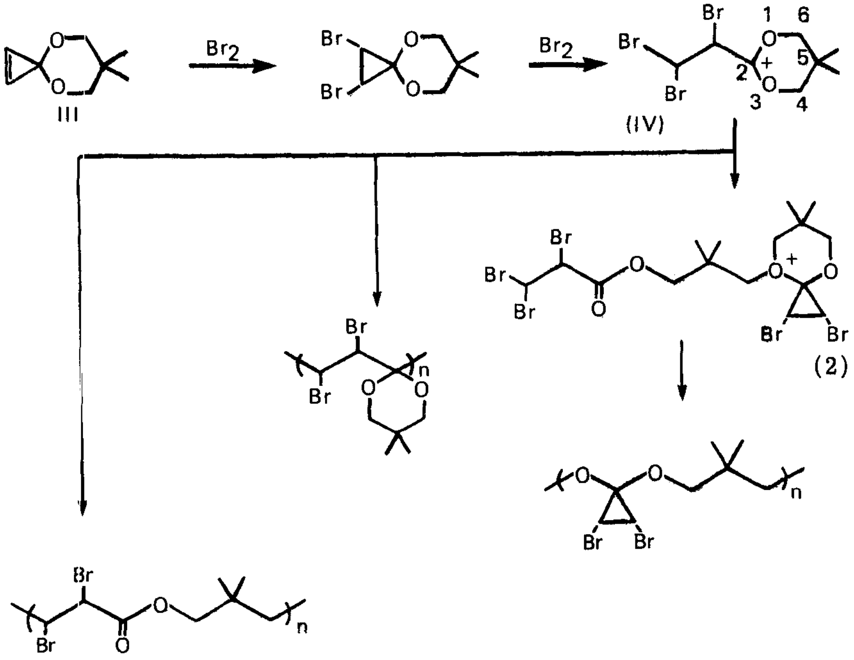
Bromine proved to be a unique polymerization initiator for III, since other halogens and various brominating agents produced no polymer under similar conditions (Table 2). The inability of these reagents to polymerize monomer III was attributed to their low electrophilicity relative to bromine. As a result, these reagents were not capable of electrophilic ring-opening of the cyclopropane moiety in the monomer.

A mechanistic study of the bromination-polymerization reaction was undertaken, and a complex sequence of steps involving several propagation pathways was postulated. Radical initiation was initially considered, but was ruled out on the basis of a lack of any inhibitory effect on the polymerization by hydroquinone and oxygen. Hydroquinone and oxygen are efficient radical scavengers capable of prohibiting radical-initiated polymerizations [5]. On the other hand, the presence of organic bases, such as pyridine and DMSO, did prohibit polymerization; thus, cationic-initiated polymerization was suspected. The following mechanism (Eq. 2) was consistent with several observations pertaining to the influence of reaction conditions on the polymerization and with the structural units identified from spectral data.

The first step involved bromination of the cyclopropene double bond which released the enormous strain on the sp^2 carbons of the cyclopropene ring. Subsequent electrophilic ring-opening of the cyclopropane ring did not occur until bromine addition had occurred to a large extent. Apparently, at high concentrations of unreacted monomer, the cyclopropene double bond acted as a scavenger for bromine. Thus, no significant polymerization occurred in the presence of small quantities of bromine, i.e., Experiments 3 and 4 in Table 1.

Electrophilic ring-opening of the cyclopropane ring produced the dialkoxycarbocation intermediate (IV) which presumably initiated propagation by three simultaneous pathways. Other similar cationic intermediates have been synthesized [5-8] and used as initiators in a variety of cationic polymerizations [9, 10]. Also, the formation of a dialkoxycarbocation intermediate during the polymerization of acrolein acetals was suggested [11-13].

Evidence for the formation of the dialkoxycarbocation intermediate IV was obtained by treating the saturated analog of III, V, with

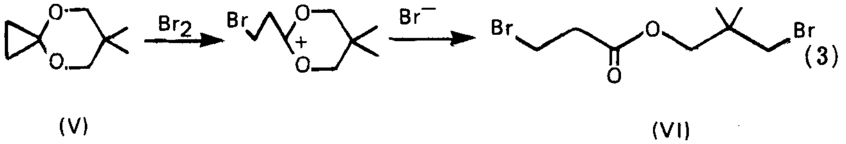


III

(IV)

(2)

one equivalent of bromine at 25°C. The major product was VI, accompanied by the formation of some oligomeric products:

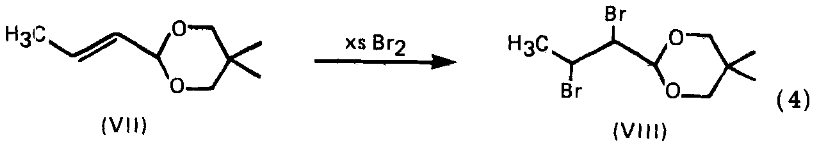


(V)

(VI)

(3)

Formation of the ester VI could only be rationalized through a dialkoxycarbocation intermediate, since the dioxane moiety showed no tendency to undergo electrophilic ring-opening in the presence of bromine, i.e., the reaction of VII with excess bromine resulted in bromine addition to the double bond exclusively:

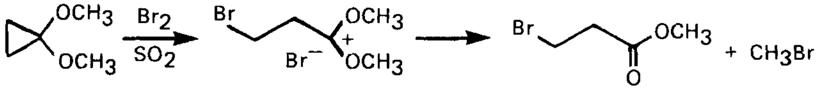


(VII)

(VIII)

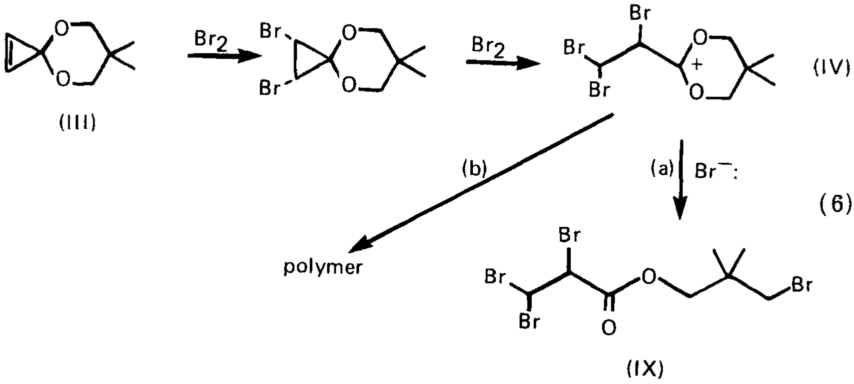
(4)

A similar dialkoxycarbonium ion created by electrophilic ring-opening of 1,1-dimethoxycyclopropane with bromine was reported by Dusseau et al. [14]. The intermediate was sufficiently stable at -60°C in sulfur dioxide to permit detection and characterization by NMR. Upon increasing the temperature to -30°C, dealkylation by bromide ion gave methyl 3-bromopropanoate:



(5)

When the cyclopropenone ketal (III) was added to excess bromine, a near quantitative yield of IX was produced (Eq. 6). Formation of the ester (IX) proceeded by a mechanism similar to that proposed for the formation of ester (VI), i.e., electrophilic ring-opening of the cyclopropane ring followed by nucleophilic ring-opening of the dioxane moiety. Nucleophilic attack by bromide ion (pathway a) occurred exclusively in the presence of excess bromine. However, in excess monomer, propagation (pathway b) apparently occurred to a small extent (7-33%) in addition to attack by bromide ion.



(6)

Several structural units were identified in the polymer obtained from III and bromine on the basis of spectral data comparisons with model compounds. The infrared and proton NMR data for appropriate model compounds are compiled in Table 3 and are matched with major absorptions observed in the infrared and NMR spectra of the polymer (Figs. 1 and 2).

Assignment of the complex signals in the ^{1}H-NMR spectrum of the polymer was based mostly on the spectral data reported for 2-(1',2'-dibromopropyl)-5,5-dimethyl-1,3-dioxane (VIII), IX, X, and XI. The broad singlet at 1.07 ppm was ascribed to the gem-dimethyl protons of the ester unit and the dioxane unit from comparison with X and XI. Two weak signals at 0.77 and 1.25 ppm were attributed to the non-

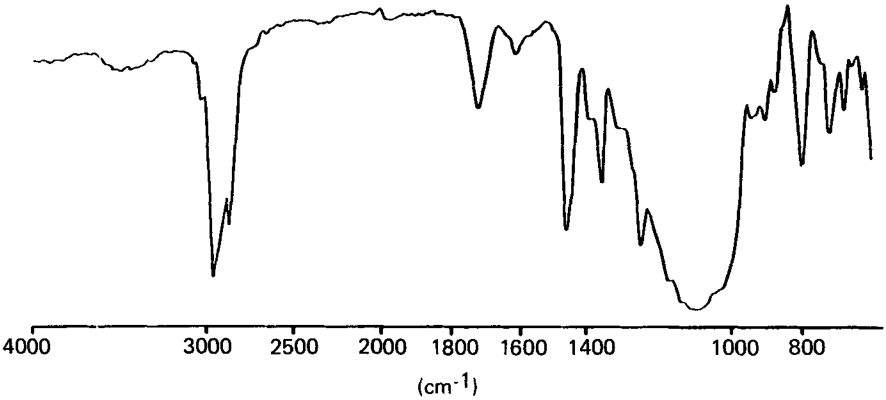


FIG. 1. IR spectrum of polymer obtained from 6,6-dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III) and bromine.

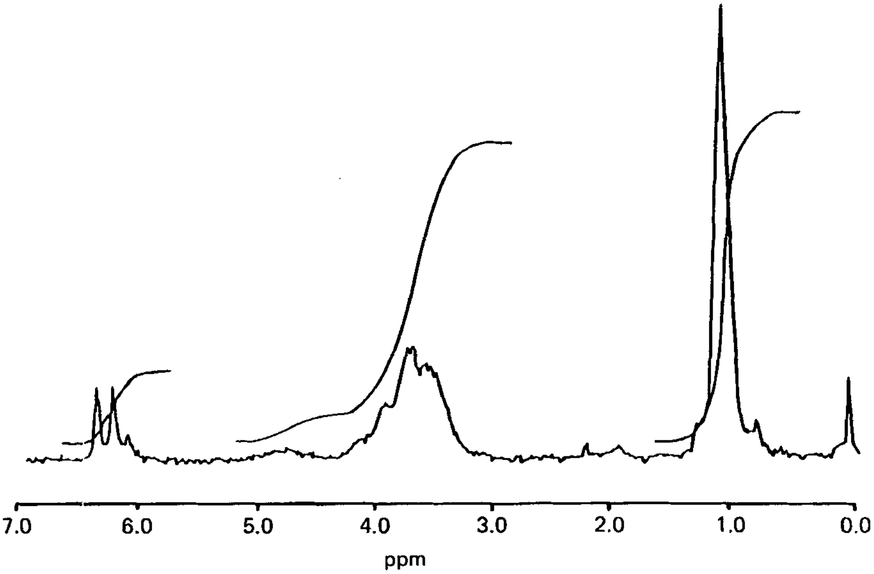
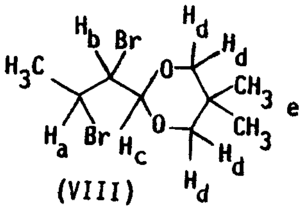
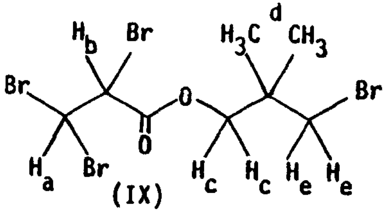
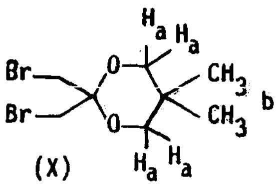
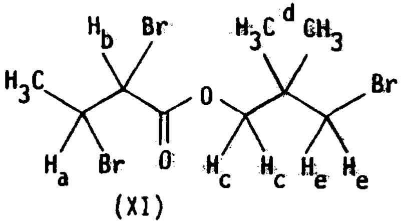


FIG. 2. ^{1}H-NMR spectrum of polymer obtained from 6,6-dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III) and bromine.

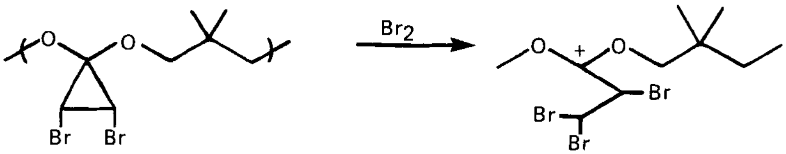
TABLE 3. Spectral Data of Model Compounds

	NMR	IR	
 (VIII)	a) 4.06-4.45 ppm, m	C–H Stretch	2960 cm^{-1}
	b) 4.06-4.45 ppm, m	C–H Stretch	2870 cm^{-1}
	c) 4.78 ppm, d	C–H Bend	1470 cm^{-1}
	d) 3.57 ppm, d	C–O–C Stretch	1180-980 cm^{-1}
	e) 0.73, 1.22 ppm, s		
 (IX)	a) 6.46, 6.53 ppm, d	C–H Stretch	2965 cm^{-1}
	b) 4.4-4.7 ppm, m	C–H Stretch	2870 cm^{-1}
	c) 4.11 ppm, s	C=O Stretch	1760-1735 cm^{-1}
	d) 1.14 ppm, s	C–H Bend	1470 cm^{-1}
	e) 3.38 ppm, s	C–O–C Stretch	1260, 1180, 1140, 1090, 1025 cm^{-1}

 (X)	a) 3.55 ppm, s	C–H Stretch	2996 cm^{-1}
	b) 1.01 ppm, s	C–H Stretch	2900 cm^{-1}
		C–H Bend	1475 cm^{-1}
		C–H Bend	1440 cm^{-1}
		C–H Bend	1400 cm^{-1}
		C–O–C Stretch	1190-1010 cm^{-1}
 (XI)	a) 4.3-4.5 ppm, d	C–H Stretch	2960 cm^{-1}
	b) 4.6-5.0 ppm, q	C–H Stretch	2870 cm^{-1}
	c) 4.1-4.2 ppm, d	C=O Stretch	1770-1730 cm^{-1}
	d) 1.15 ppm, s	C–H Bend	1470 cm^{-1}
	e) 3.42 ppm, m	C–H Bend	1440 cm^{-1}
		C–O–C Stretch	1300-980 cm^{-1}

equivalent gem-dimethyl protons of the dioxane unit endgroup according to the spectrum of VIII. A broad signal in the region of 3.3-4.3 ppm was attributable to several protons: the methylene protons adjacent to the carboxy group (4.0-4.3 ppm), methylene protons adjacent to an ether oxygen atom (3.5-3.8 ppm), methylene protons adjacent to bromine (3.3-3.5 ppm), and methine protons adjacent to bromine (3.8-4.3 ppm). A weak, broad signal at 4.6-4.9 ppm was ascribed to the methine proton in the ester unit alpha to a bromine atom and a carbonyl group by comparison with XI.

The dibromomethine group created by electrophilic ring-opening of the cyclopropane moiety by bromine appeared at 6.35 and 6.21 ppm in the NMR spectrum of the polymer in accordance with the like protons of model compound IX. The relatively large amount of these protons in the spectrum indicated that the pendant cyclopropane moiety on the polymer had undergone ring opening with bromine (Eq. 7). No protons were observed at 3.1 ppm, ascribable to the protons on the pendant cyclopropane moiety.



(7)

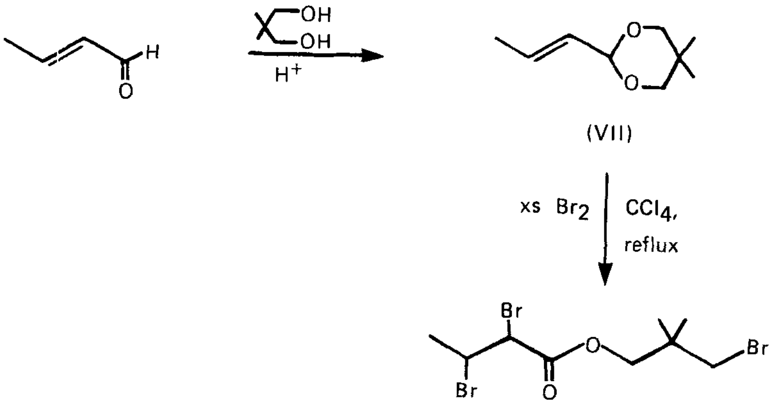
The infrared spectrum of the polymer was very similar to that exhibited by the polymer obtained with $BF_3 \cdot OEt_2$ initiator at 25°C [1]. Common absorptions observed in the spectra of both polymers were a methyl C–H stretch at 2970, a methylene C–H stretch at 2870 cm^{-1}, a C–H bend at 1470 cm^{-1}, and a broad C–O–C stretch in the region 1260-960 cm^{-1}. An ester carbonyl stretch at 1720 cm^{-1} was also present in the bromine polymers, but was less intense than that observed for the $BF_3 \cdot OEt_2$ initiated polymers. No double bond stretch at 1610 cm^{-1} was observed.

The syntheses of model compounds VIII and IX are depicted in Eqs. (4) and (6), respectively. Compound X was prepared by alpha-bromination of XII in the presence of $CaCO_3$ (Eq. 8). The inorganic base served as a scavenger for hydrogen bromide by-product.

(8)

(XII) (X)

Compound XI was obtained by treating VII with bromine under sufficiently rigorous conditions to achieve nucleophilic ring-opening of the dioxane moiety in addition to bromination of the double bond. Thus, when VII was refluxed for several hours in the presence of excess bromine, the desired ester (XI) was produced in moderate yield:



(XI)

(9)

SUMMARY AND CONCLUSIONS

Bromination of cyclopropenone ketals gave 7-33% conversions to polymer under a variety of conditions. A mechanism involving electrophilic ring-opening of the cyclopropane ring to generate a dialkoxycarbocation was proposed on the basis of spectral data and reactions of model compounds. The carbocation intermediate apparently reacted with brominated monomer by three distinct and simultaneous pathways to produce a terpolymer. Subsequent reactions at reactive sites on the polymer chain further complicated the structure. A series of model compounds was prepared to assist elucidation of the polymeric structure.

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