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Free Radical Ring-Opening Polymerization of 4-n-Hexyl- and 4-n-Decyl-2-methylene-1,3-dioxolanes

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ABSTRACT

Two alkyl-substituted cyclic ketene acetals, 4-n-hexyl-2-methylene-1,3-dioxolane (4) and 4-n-decyl-2-methylene-1,3-dioxolane (6), were shown to undergo free radical ring-opening polymerization with the introduction of an ester group into the backbone of an addition polymer. The spontaneous polymerization of 4 (presumable by an ionic mechanism) produced a polymer containing no ring-opened units; furthermore 4 and 6 could be stabilized with respect to spontaneous polymerization by the addition of small amounts of pyridine. On the other hand, the polymerization of 4 in a 50% (by weight) benzene solution at 110°C with di-tert-butyl peroxide as the catalyst gave quantitative ring opening to give a polyester containing both possible isomeric ring-opened units. Bulk polymerization of 4 at 60°C at 53% conversion gave 50% ring opening which was divided 31% to 19% between cleavage to give the intermediate secondary free radical and the intermediate primary radical. Copolymerization of 4 with equimolar quantities of styrene at 110°C gave at 56% conversion a copolymer consisting of 67% styrene units, 22% ester-containing units

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resulting from cleavage to form a secondary radical, 7% of the isomeric ester-containing units, and 4% nonring-opened units. Polymerization studies with monomer 6 gave results very similar to those obtained with 4.

INTRODUCTION

In a general research program designed to investigate free radical ring-opening polymerization, it was discovered that although there were very few examples [1-3] recorded in the literature, a wide variety of cyclic monomers would indeed undergo free radical ring-opening polymerization [4-7]. For example, in these laboratories it has been found recently that several cyclic ketene acetals, the isomeric structures of lactones, had undergone quantitative ring opening during the free radical polymerization [8-10]. The success of this method makes it possible to prepare polyesters or to introduce the ester linkage into the backbone of various addition copolymers by a free radical mechanism. For example, when the seven-membered cyclic ketene acetal, 2-methylene-1,3-dioxepane, was polymerized with di-tert-butyl peroxide, essentially pure poly-ε-caprolactone was isolated [8]. Similarly, the analogues 4,7-dimethyl-2-methylene-1,3-dioxepane and 5,6-benzo-2-methylene-1,3-dioxepane under the same conditions polymerized to form poly[ε-(β,ε-dimethyl)-caprolactone] and poly[ε-(γ,δ-benzo)caprolactone], respectively [9]. The isolation of these pure polyesters clearly indicated that these monomers have undergone quantitative ring opening during polymerization.

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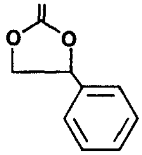

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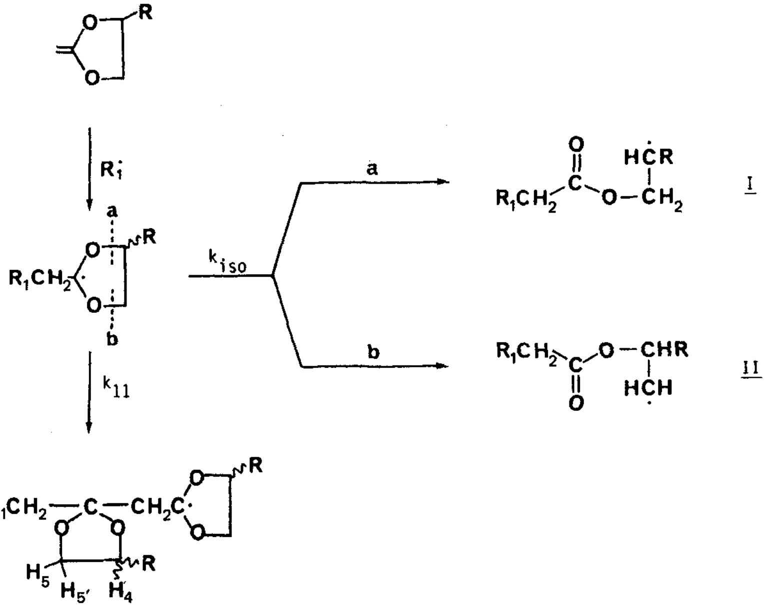
On the other hand, the five-membered cyclic ketene acetal, 2-methylene-1,3-dioxolane (1), polymerized with 50% ring opening at 60°C and 83% ring opening at 125°C [6]. Interestingly, the aryl substituted 4-phenyl-2-methylene-1,3-dioxolane (2) was shown to polymerize with quantitative ring opening and regioselectively to form the poly[γ-(β-phenyl)butyrolactone] [10]. The phenyl substituent on the

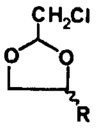
α-position of a cyclic ketene acetal certainly makes it more prone to undergo free radical ring opening and determines the direction of ring opening.

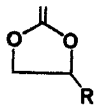
From elementary kinetics it is obvious that the extent of ring opening during the polymerization is determined by the ratio of the rate of ring opening (k_{iso}) to the rate of direct vinyl propagation without ring opening (k_{11}) which in turn is dependent on a number of factors including the temperature and the concentration of monomer. It is expected that there will be a greater extent of ring opening at higher temperatures or in the more dilute solutions.



Furthermore, when the parent 2-methylene-1,3-dioxolane (1) is unsymmetrically substituted, there are two possibilities for the opening of the ring which is determined by the relative stability of the isomerized (ring-opened) radical intermediates I and II. This substitution effect has been demonstrated by the exclusive isolation of essentially pure poly[γ-(β-phenyl)butyrolactone] from the 4-phenyl derivative 2, essentially free of γ-(γ-phenyl)butyrolactone units since the secondary benzyl radical I (R = $-\phi$) formed by ring opening at bond a is considerably more stable than the primary radical II (R = $-\phi$) theoretically formed by ring opening at bond b [10].

It was therefore of interest to see the effect of alkyl substituents on the polymerization of 2-methylene-1,3-dioxolanes. It was reasoned





R = -n-C_6H_{13} 3 4

R = -n-$C_{10}H_{21}$ 5 6

that the substituted analogues of 1 might be less hydrophilic because of the presence of a hydrocarbon side chain and that might make them easier to handle. Furthermore, if the monomers with a long side chain could undergo free radical polymerization with quantitative ring opening, the resulting polyesters would have long side chains attached to the polymers which would greatly influence their physical properties. This methodology should also be useful in the solution of the depolymerization problem of many addition polymers and the brittleness problem associated with some conventional polymers. For example, copolymerization of vinyl chloride with monomer 4 or 6 could introduce the ester group into the backbone of the addition polymer which would increase the thermal stability and, at the same time, the long side chains attached to the main polymer chain could serve as an internal plasticizer to reduce the brittleness of the copolymer compared to the pure polyvinyl chloride.

EXPERIMENTAL

cis- and trans-2-Chloromethyl-4-n-hexyl-1,3-dioxolane (3)

A mixture of 50 g (0.4 mol) of chloroacetaldehyde dimethyl acetal and 59.7 g (0.4 mol) of 1,2-octanediol was heated at 120°C with 0.5 g of Dowex (H^+) resin in a 200-mL flask equipped with a 10-cm Vigreaux column. After about the calculated amount of methanol had been collected by distillation over a period of 12 h, the resin was removed by filtration. The crude product was then purified by simple distillation to give 77 g (93%) of a mixture of cis- and trans- 3: bp 102°C (0.2 mm); IR (neat) 2960, 2920, 2860, 1140, 1045, 1010, 765 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.63-1.83 (broad, 13H, -n-C_6H_{13}), 3.33-3.76 (m, 3H, $-CH_2Cl$ and H_5 of $-OCH_2-$), 3.86-4.33 (m, 2H, $H_{5'}$ of $-OCH_2-$ and H_4 of $-OCH-$), 5.03-5.34 (m, 1H, $-OCHO-$).

Analysis. Calculated for $C_{10}H_{19}ClO_2$: C, 58.10; H, 9.27; Cl, 17.15. Found: C, 57.98; H, 9.50; Cl, 16.80.

4-n-Hexyl-2-methylene-1,3-dioxolane (4)

A mixture of 15 g (0.072 mol) of cis- and trans-2-chloromethyl-4-n-hexyl-1,3-dioxolane (3) in 20 mL of dry THF was added dropwise to a mixture of 12.22 g (0.15 mol) of KO-tert-Bu in 40 mL of dry THF at 60°C under a nitrogen atmosphere. After the addition was completed, the oil bath temperature was raised to 80°C to maintain a gentle reflux for 12 h. After the reaction mixture was cooled, 150 mL of petroleum ether was added, and the resulting precipitate was removed by filtration. After the solvents were removed by distillation under reduced pressure, the residue was vacuum distilled through a 10-cm Vigreaux column to give 10.5 g (85%) of monomer 4: bp 70-71°C (0.15 mm); IR (neat) 2950, 2930, 2860, 1680(s), 1215, 1045, 715 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.66-1.90 (broad, 13H, -n-C_6H_{13}), 3.20 (s, 2H, $CH_2{=}C$), 3.50-4.60 (m, 3H, $-OCH_2-$ and $-OCH-$).

Analysis. Calculated for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.71; H, 10.75.

cis- and trans-2-Chloromethyl-4-n-decyl-1,3-dioxolane (5)

A solution of 25 g (0.2 mol) of chloroacetaldehyde dimethyl acetal and 40.5 g (0.2 mol) of 1,2-dodecanediol was heated at 120°C with 0.5 g of Dowex (H^+) resin in a 200-mL flask equipped with a 10-cm Vigreaux column. After the calculated amount of methanol had been collected by distillation, the resin was removed by filtration. The crude product was then purified by simple distillation to give 46 g (88%) of a mixture of cis- and trans- 5: bp 117°C (0.01 mm); IR (neat) 2950, 2910, 2840, 1140, 1045, 1008, 760 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.60-1.80 (broad, 21H, -n-$C_{10}H_{21}$), 3.35-3.70 (m, 3H, $-CH_2Cl$ and H_5 of $-OCH_2-$), 3.85-4.25 (m, 2H, $H_{5'}$ of $-OCH_2-$ and H_4 of $-OCH-$), 5.03-5.30 (m, 1H, $-OCHO-$).

Analysis. Calculated for $C_{14}H_{27}ClO_2$: C, 63.98; H, 10.36; Cl, 13.49. Found: C, 64.25; H, 10.60; Cl, 13.24.

4-n-Decyl-2-methylene-1,3-dioxolane (6)

A mixture of 11.22 g (0.1 mol) of KO-tert-Bu in 40 mL of dry THF was kept at 60°C while a solution of 13.14 g (0.058 mol) of cis- and trans-2-chloromethyl-4-n-decyl-1,3-dioxolane (5) in 20 mL of dry THF was added dropwise under a nitrogen atmosphere. After the addition was completed, the oil bath temperature was raised to 85°C to maintain a gentle reflux for 12 h. After the reaction mixture was cooled, 150 mL of petroleum ether was added, and the resulting precipitate was removed by filtration. The volatile solvents were removed by distillation under reduced pressure, and the residue was vacuum distilled through a 10-cm Vigreaux column to give 8.5 g (75%) of monomer 6: bp 90-91°C (0.1 mm); IR (neat) 2955, 2920, 2850, 1683(s), 1210, 1046, 715 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.66-1.86 (broad, 21H, -n-$C_{10}H_{21}$), 3.18 (s, 2H, $CH_2{=}C$), 3.50-4.55 (m, 3H, –OCH_2– and –OCH–).

Analysis. Calculated for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.37; H, 11.64.

Homopolymerization of 4-n-Hexyl-2-methylene-1,3-dioxolane (4)

A. In Bulk

In a 10-mL sealed polymerization tube, 1.0 g of 4 was heated with 17 mg (2 mol%) of di-tert-butyl peroxide at 110°C for 48 h. After the tube was cooled and opened, the mixture was dissolved in $CHCl_3$. This solution was then added dropwise into a vigorously stirred methanol solution to give a viscous liquid precipitate. After the liquid precipitate was isolated and dried in vacuo at 100°C overnight, 0.54 g (54%) of a viscous polymer was obtained: $[\eta]$ = 0.01 at 30°C in benzene; IR (neat) 2950, 2920, 2855, 1730(s), 1160 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.66-1.95 (broad, -n-C_6H_{13}), 2.05-2.65 [broad, –CH_2CO_2– and nonring-opened –$CH_2C(O–)_2$–], 3.25-3.70 (broad, H_5 of nonring-opened –OCH_2–), 3.80-4.35 (broad, –CO_2CH_2–, $H_{5'}$ and H_4 of nonring-opened –OCH_2– and –OCH–), 4.70-5.10 (broad, –CO_2CH–); ^{13}C NMR (25.2 MHz, $CDCl_3$) δ 14.05-44.66 [m, -n-C_6H_{13}, –CH_2CO_2– and nonring-opened –$CH_2C(O–)_2$–], 64.17-76.35 (m, –CO_2CH_2–, –CO_2CH– and nonring-opened –OCH_2– and –OCH–), 109.19 (nonring-opened ketal carbon –OCO–), 169.15 (–CO_2CH–), 172.15 (–CO_2CH_2–).

Analysis. Calculated for $(C_{10}H_{18}O_2)_n$: C, 70.55; H, 10.66. Found: C, 70.70; H, 10.90.

Similar procedures were applied to the syntheses of other polymers at other temperatures and identification of their structures.

B. In Solution

In a 10-mL sealed polymerization tube, 0.5 g of 4 and 0.5 g of dry benzene were heated with 34 mg (8 mol%) of di-tert-butyl peroxide at 110°C for 48 h. After the tube was opened, the mixture was dissolved in $CHCl_3$. This solution was added dropwise to a vigorously stirred methanol solution, and the resulting liquid precipitate was isolated and dried in vacuo overnight at 100°C to give 0.34 g (68%) of a viscous polymer: $[\eta]$ = 0.007 at 30°C in benzene; IR (neat) 2950, 2920, 2855, 1733(s), 1250, 1160 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.66-1.90 (broad, -n-C_6H_{13}), 2.00-2.70(broad, –CH_2CO_2–), 3.90-4.25 (broad, –CO_2CH_2–), 4.70-5.10 (broad, –CO_2CH–); ^{13}C NMR (25.2 MHz, $CDCl_3$) δ 14.04-43.63 (m, -n-C_6H_{13} and –CH_2CO_2–), 64.48, 66.42, 70.99, 73.33 (–CO_2CH_2– and –CO_2CH–), 170.01-174.71 (broad, –CO_2–).

Analysis. Calculated for $(C_{10}H_{18}O_2)_n$: C, 70.55; H, 10.66. Found: C, 69.97; H, 11.06.

C. Spontaneous Polymerization

The freshly distilled monomer 4, which was not stabilized by the addition of a trace of dry pyridine, would polymerize to form a viscous liquid if exposed to the air. This spontaneously formed polymer was further purified by washing with methanol and dried in vacuo at 100°C overnight: $[\eta] = 0.19$ at 30°C in benzene; IR (neat) 2950, 2920, 2845, 1170, 1050 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.55-1.85 (broad, 13H, -n-C_6H_{13}), 1.90-2.50 [broad, 2H, $-CH_2C(O-)_2-$], 3.20-3.73 (broad, 1H, H_5 of $-OCH_2-$), 3.73-4.30 (broad, 2H, $H_{5'}$ of $-OCH_2-$ and H_4 of $-OCH-$); ^{13}C NMR (25.2 MHz, $CDCl_3$) δ 14.06, 22.63, 26.29, 29.48, 31.85, 33.45 ($-C_6H_{13}$), 45.17 [broad, $-\underline{C}H_2C(O-)_2-$], 69.26, 75.38,($-OCH_2-$ and $-OCH-$), 109.04 ($-\underline{O}C\underline{O}-$).

Analysis. Calculated for $(C_{10}H_{18}O_2)_n$: C, 70.55; H, 10.66. Found: C, 70.26; H, 10.88.

Homopolymerization of 4-n-Decyl-2-methylene-1,3-dioxolane (6)

In a 10-mL sealed polymerization tube, 1.2 g of 6 was polymerized with 16 mg (2 mol%) of di-tert-butyl peroxide at 110°C for 65 h. After the reaction mixture was dissolved in $CHCl_3$, this solution was added dropwise to a vigorously stirred methanol solution. The resulting viscous precipitate was isolated and dried in vacuo at 100°C overnight to give 0.816 g (68%) of a liquid polymer: $[\eta] = 0.01$ at 30°C in benzene; IR (neat) 2960, 2920, 2850, 1735(s), 1160 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.65-1.70 (broad, -n-$C_{10}H_{21}$), 2.10-2.70 [broad, $-CH_2CO_2-$ and nonring-opened $-CH_2C(O-)_2-$], 3.30-3.90 (broad, H_5 of nonring-opened $-OCH_2-$), 3.90-4.25 (broad, $-CO_2CH_2-$, $H_{5'}$ and H_4 of nonring-opened $-OCH_2-$ and $-OCH-$), 4.70-5.10 (broad, $-CO_2CH-$).

Analysis. Calculated for $(C_{14}H_{26}O_2)_n$: C, 74.28; H, 11.58. Found: C, 74.46; H, 11.86.

The same procedures were used for the polymerizations at other temperatures and identification of their structures.

Copolymerization of 4-n-Decyl-2-methylene-1,3-dioxolane (6) with Styrene

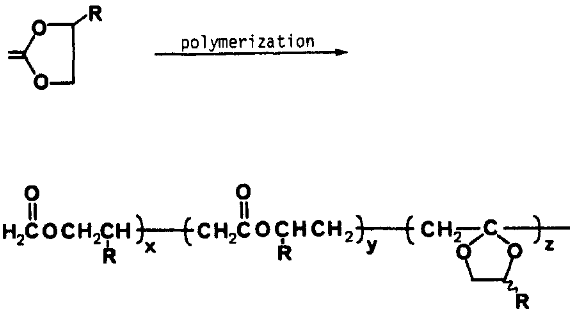
In a 10-mL sealed polymerization tube, a mixture of 800 mg (3.53 mmol) of 6, 368 mg (3.53 mmol) of styrene, and 21 mg (2 mol%) of di-tert-butyl peroxide was heated at 110°C for 65 h. After the reaction mixture was dissolved in $CHCl_3$, the solution was added to methanol to precipitate the copolymer. The collected solid was dried in vacuo at 45°C overnight to give 654 mg (56%) of a somewhat waxy white solid copolymer: $[\eta] = 0.15$ at 30°C in benzene; IR (film) 3060, 3020, 2920, 2850, 1735, 1600, 1490, 1450, 1170, 755, 695 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.65-2.10 (-n-$C_{10}H_{21}$ and $-C\underline{H}\emptyset C\underline{H}_2-$), 2.10-2.55 [$-CH_2CO_2-$ and nonring-opened $-CH_2C(O-)_2-$], 3.35-3.60 (H_5 of nonring-opened $-OCH_2-$), 3.83-4.33 ($-CO_2CH_2-$, $H_{5'}$ and H_4 of nonring-opened $-OCH_2-$ and $-OCH-$), 4.67-5.06 ($-CO_2CH-$), 6.30-7.35 (aromatic H's); ^{13}C NMR (25.2 MHz, $CDCl_3$) δ 14.09-48.95 [m, $-\underline{C}H\phi\underline{C}H_2-$, $-n-C_{10}H_{21}$, $-\underline{C}H_2CO_2-$ and nonring-opened $-\underline{C}H_2C(O-)_2-$], 64.50-73.28 (m, $-CO_2\underline{C}H-$, $-CO_2\underline{C}H_2-$ and nonring-opened $-OCH_2-$ and $-OCH-$), 108.72 (nonring-opened ketal carbon $-OCO-$), 125.47, 127.80, 145.12 (aromatic C's), 172.10 ($-CO_2-$).

Analysis. Calculated for $(C_{14}H_{26}O_2)_{0.334}(C_8H_8)_{0.666}$: C, 82.88; H, 9.74. Found C, 82.92; H, 9.91.

RESULTS AND DISCUSSION

For the reasons discussed above, 4-n-hexyl-2-methylene-1,3-dioxolane (4) and 4-n-decyl-2-methylene-1,3-dioxolane (6) were synthesized by acetal exchange reactions of chloroacetaldehyde dimethyl acetal with 1,2-octanediol and 1,2-dodecanediol, respectively, followed by dehydrochlorinations of the resulting cis- and trans- mixtures of 3 and 5. The substituted monomers 4 and 6 were much more stable and easier to handle than the parent compound 1, and they could be stored unchanged for a period of time in the presence of a trace of dry pyridine. The unstabilized solutions of 4 and 6 showed no indication of the presence of any ring-opening units in their structures. These pyridine stabilized solutions were used for the subsequent radical polymerization studies.

When 4-n-hexyl monomer 4 was polymerized at 110°C over a period of 48 h with 2 mol% of di-tert-butyl peroxide as the initiator, a viscous liquid polymer was isolated after purification. The ^{13}C NMR spectrum (Fig. 1) of this polymer showed two ester signals at δ 172.14 ppm and δ 169.16 ppm and a signal at δ 109.19 ppm corresponding to a ketal carbon. These signals indicated that the unsymmetrically substituted 1,3-dioxolane ring did open in two possible directions to form two different kinds of ester linkages, as well as producing some nonring-opened units in the polymer chain. This



$$\xrightarrow{\text{polymerization}} -(CH_2\overset{O}{\overset{\|}{C}}OCH_2\underset{R}{CH})_x-(CH_2\overset{O}{\overset{\|}{C}}O\underset{R}{CH}CH_2)_y-(CH_2-C-)_z-$$

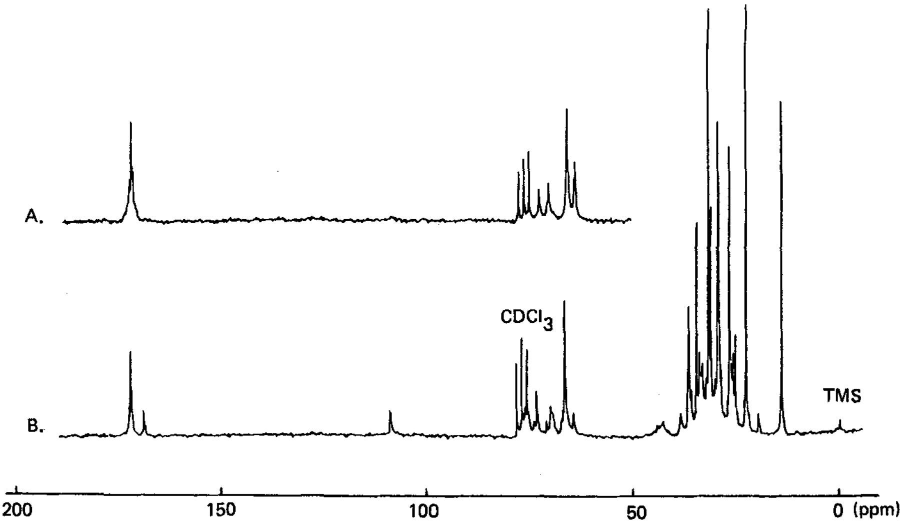


FIG. 1. ^{13}C NMR spectra of the polymers made from 4-n-hexyl-2-methylene-1,3-dioxolane (4). A: At 110°C in benzene (1:1 by wt). B: At 110°C in bulk.

observation is consistent with its ^{1}H NMR spectrum; a signal at δ 4.90 ppm corresponding to the methine proton attached to an ester oxygen formed by ring opening at bond b, a signal at δ 4.05 ppm corresponding to the methylene protons next to the ester oxygen formed by ring opening at bond a, and a signal at δ 3.43 ppm corresponding to the nonring-opened units. The signal at δ 4.05 ppm was actually overlapped with part of the nonring-opened signals which will be discussed later.

In order to determine the effect of concentration on the extent of ring opening, monomer 4 was polymerized at 110°C in benzene (1:1 by weight) with 8 mol% of di-tert-butyl peroxide as the initiator for 48 h. A viscous liquid polymer was isolated after purification. Interestingly, this polymer showed different structure from the one made at the same temperature in bulk. The absence of the signal at δ 3.43 ppm in its ^{1}H NMR spectrum and the lack of a peak around 109 ppm in its ^{13}C NMR spectrum clearly indicated that monomer 4 had undergone essentially quantitative ring opening in this solution polymerization. The signals at δ 4.90 ppm and δ 4.05 ppm in its ^{1}H NMR spectrum showed that the ring opening still occurred in both directions.

It was of interest to calculate the amounts of ring opening at bond a or bond b and the nonring-opened units. Since the spontaneously formed polymer from monomer 4 involved no ring opening during polymerization as indicated by the absence of carbonyl absorption in

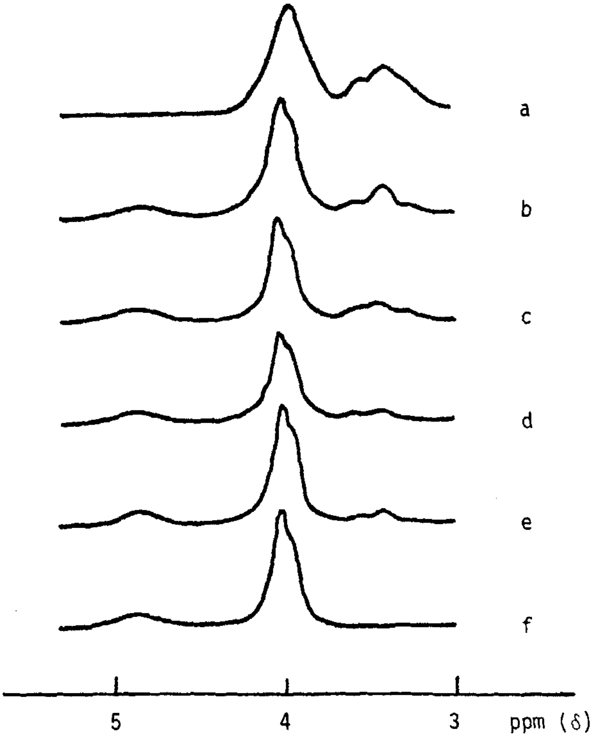


FIG. 2. Partial 60 MHz ^{1}H NMR spectra of polymers made from 4-n-hexyl-2-methylene-1,3-dioxolane (4) under various conditions. a: Spontaneous polymerization with 0% ring opening. b: At 60°C in bulk. c: At 80°C in bulk. d: At 90°C in bulk. e: At 110°C in bulk. f: At 110°C in benzene (1:1 by wt) with 100% ring opening.

its IR spectrum, this polymer was chosen as one of the reference materials. The ^{1}H NMR spectrum of this nonring-opened polymer showed a signal at δ 3.43 corresponding to one proton by integration which was assigned to H_5, one of the methylene protons next to the oxygen, and an other signal at δ 4.05 ppm corresponding to two protons by integration which was assigned to H_5, and the methine proton next to the oxygen. The chemical shifts of the H_5, $H_{5'}$ and H_4 in this polymer are very similar to those of the 2-chloromethyl-4-n-hexyl-1,3-dioxolane (3). By comparing this ^{1}H NMR spectrum of 0% ring-opened polymer with that of 100% ring-opened polymer made at 110°C in benzene, it was clearly indicated that the signal at δ 4.05 ppm actually corresponds to an overlap of the methylene protons next to the ester oxygen formed by ring opening at bond a as well as the two other protons from the nonring-opened units for the polymers containing some nonring-opened structures.

TABLE 1. Homopolymerization of 4-n-Hexyl-2-methylene-1,3-dioxolane (4) at Various Temperatures and the Structures of the Corresponding Polymers

Initiator (mol%)	T (°C)	Polymerization time (h)	Polymer yield (%)	Extent of ring opening[a] (mol%)		Extent of nonring opening[a] (mol%)
				At bond a	At bond b	
AIBN[b] 2.6	60	48	53	31	19	50
AIBN 2.0	80	48	45	39	24	37
AIBN 2.7	90	24	52	40	27	33
DTBP[c] 2.0	110	48	54	40	33	27
DTBP[d] 8.0	110	48	68	67	33	0

[a] From ^{1}H and ^{13}C NMR studies.

[b] AIBN, azobisisobutyronitrile.

[c] DTBP, di-tert-butyl peroxide.

[d] Solution polymerization in benzene (1:1 by wt).

TABLE 2. Homopolymerization of 4-n-Decyl-2-methylene-1,3-dioxolane (6) at Various Temperatures and the Structures of the Corresponding Polymers

Initiator (mol %)		T (°C)	Polymerization time (h)	Polymer yield (%)	Extent of ring opening[a] (mol%)		Extent of nonring opening[a] (mol%)
					At bond a	At bond b	
AIBN	2.8	60	48	53	35	20	45
AIBN	2.0	80	72	49	37	28	35
AIBN	3.3	90	24	55	43	31	26
DTBP	2.0	110	65	68	61	27	12
DTBP[b]	8.0	110	65	70	68	32	0

[a] From ^{1}H and ^{13}C NMR studies.
[b] Solution polymerization in benzene (1:1 by wt).

The gradual change of ^1H NMR spectra can be observed by obtaining the polymers at various temperatures (Fig. 2). The extent of ring opening at either bond a or bond b and the nonring-opened units can therefore be calculated from the ^1H NMR integrations (Table 1). This gradual change also indicated that higher temperatures or more dilute conditions favored ring opening.

Similar results were obtained for the polymerization of monomer 6 as shown in Table 2. The larger substituent, n-decyl group, made the ring opening more favorable apparently by slowing down the rate of direct vinyl propagation (k_{11}) because of steric hindrance. The extent of ring opening also increased with higher temperatures and more dilute concentrations.

In a copolymerization experiment, equal molar amounts of monomer 6 and styrene were polymerized at 110°C in the presence of 2 mol% of di-tert-butyl peroxide as the initiator for a period of 65 h. A solid polymer obtained in a 56% conversion was isolated after purification. From ^1H and ^{13}C NMR studies as well as elemental analysis, it was shown that this copolymer contained 67 mol% of styrene units, 22 mol% of ester linkages formed by ring opening of 6 at bond a, 7 mol% of the other ester linkages formed by ring opening of 6 at bond b, and 4 mol% of nonring-opened structures.

Thus it has been demonstrated that the cyclic ketene acetals are viable monomers for making polyesters by a free radical ring-opening mechanism. By varying the size of the ring and the type of substituent on the ring, various polyesters can be formed which are difficult to obtain by conventional condensation polymerizations. Furthermore, copolymerizations of vinyl monomers with these ketene acetals can make possible the introduction of the ester functionalities into the backbones of addition polymers, which has been shown to increase the thermal stability as well as to modify the chemical and physical properties of these copolymers.

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