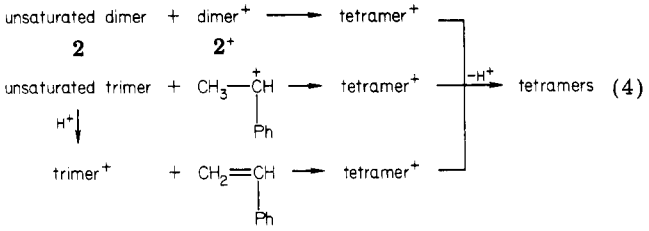
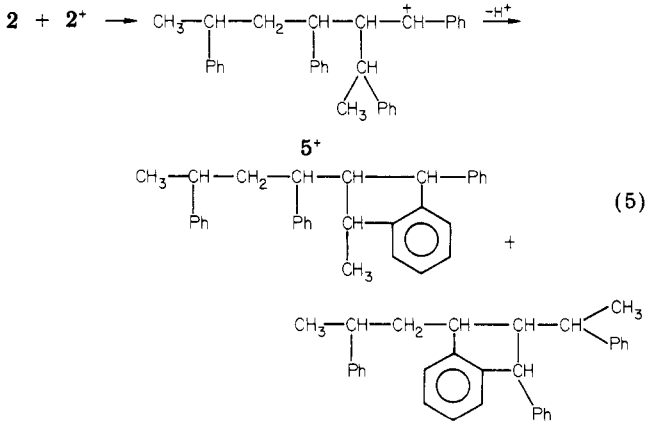
and/or to higher oligomers in the later stages of the reaction.

Figure 6 depicts $^1$H NMR spectra of the tetramer fractions produced under the same conditions as for the trimers. No important changes were observed in the $^1$H NMR spectra with conversion or reaction temperature. The spectra are characterized by the signals in the $Ar_2CH$ region ($\delta \sim 4$) and the virtual absence of olefinic protons ($\delta$ 6.2–6.3). These features indicate that the tetramers are predominantly of cyclic end groups (see below). The rather complicated spectra in Figure 6 also indicate the presence of many isomers in the tetramer fractions (an attempt to separate these isomeric tetramers by recycling GPC results in ill-resolved fractions containing two components even after recycling 54 times). The presence of isomeric tetramers seems reasonable in view of the multiple pathways for possible tetramer formation illustrated in eq 4.




Although the difficulty in separation of each tetramer hampered the detailed determination of its structure, the clear $Ar_2CH$ signals around $\delta$ 4 (Figure 6) are similar to that for the cyclic trimer **3C** and hence the major part of the tetramers may have cyclic end groups as in **3C**. Equation 5 shows examples of such cyclic tetramers, which




(5)

may be formed from **2** and $2^+$ via intramolecular Friedel–Crafts reaction of intermediate $5^+$. Similarly, the other pathways given in eq 4 may also yield cyclic tetramers.

A sample obtained from pMeSt dimer (1) (no. 2, Table III; Figure 3b) was also fractionated into dimer to tetramer portions. The dimer fraction consisted mainly of the cyclic isomer. Analysis by $^1$H NMR spectroscopy showed that the pMeSt trimers and tetramers are similar in structure to the corresponding styrene oligomers, indicating predominant formation of cyclic end groups.

To summarize, the present work has presented evidence for the depolymerization of the propagating dimer cations in the oligomerization of dimers **1** and **2**. The major products were trimers and tetramers with cyclic terminals.

**Acknowledgment.** We thank Mr. H. Hasegawa of our laboratory for helpful assistance in the NMR measurements.

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# Free Radical Copolymerization and Cationic Oligomerization of 4,7-Dihydro-1,3-dioxepin. Preparation of Poly[(hydroxymethyl)methylene]

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ABSTRACT: Free radical copolymerization of 4,7-dihydro-1,3-dioxepin with maleic anhydride gave 1:1 alternating copolymers possessing modest number-average molecular weights. Reduction with lithium aluminum hydride and hydrolysis of the copolymer gave water-soluble poly[(hydroxymethyl)methylene] with degree of polymerization 10.4–11.2. Cationic homopolymerization of 4,7-dihydro-1,3-dioxepin gave oligomers via ring-opening reaction.

As shown in Schuerch's review on biomedical uses of polysaccharides,[1,2] synthetic water-soluble polymers of well-defined structure will be useful for biomedical applications such as blood volume expanders, neoplastic

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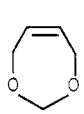
growth regulators, blood clotting control agents, interferon-producing agents, and so on.

For the preparation of water-soluble polymers, polymerization of 2-butene-1,4-diol (1) should lead to water-soluble poly[(hydroxymethyl)methylene] (2), but there are no reports on its polymerization behavior.

Generally, 1,2-disubstituted ethylene monomers undergo radical homopolymerization to form low molecular weight polymers due to steric hindrance. However, vinylene carbonate,[3-6] maleic anhydride,[7-9] N-substituted maleimide,[10-13] and dialkyl fumarates[14] homopolymerize to high molecular weight. Electron-poor maleic anhydride copolymerizes with electron-rich monomers such as styrene[15,16] and divinyl ether.[17-20]

Tying the hydroxy groups of 1 into a planar structure might decrease steric hindrance and enhance reactivity. The cyclic formal 4,7-dihydro-1,3-dioxepin (3) is readily prepared.[21,22] Although there are no reports on the polymerization of 3, Sterling[23] reported that 2-substituted 1,3-dioxepins homopolymerize and copolymerize with vinyl monomers such as vinylidene chloride, butadiene, methyl isopropyl ketone, and their mixtures.

Accordingly, it was the objective of this work to polymerize the cyclic derivative 3 and hydrolyze the polymer to water-soluble polymer 2. As a second objective, we hoped to subject 3 to ring-opening polymerization and to hydrate or hydroxylate to an alternating water-soluble polymer.



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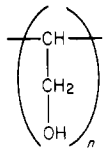

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## Experimental Section

**Measurements.** $^1$H NMR spectra were obtained with a Model EM 360L Varian NMR spectrometer. Infrared spectra were recorded with a Perkin-Elmer 337 spectrophotometer. Number-average molecular weight was determined by using a Hewlett-Packard Model 302B vapor pressure osmometer, with 1,2-dichloroethane or dimethylformamide as solvent at 37 °C. Viscosity of the polymers was determined at 30 °C, using 50 mg/10 mL of dimethyl sulfoxide solution in a Cannon-Fenske viscometer. Elemental analyses were performed by the University of Arizona Analytical Center (Tucson, Arizona).

**Preparation of 4,7-Dihydro-1,3-dioxepin (3).** Paraformaldehyde (6.01 g, 0.2 mol) was suspended in equimolar 2-butene-1,4-diol (1). A trace of *p*-toluenesulfonic acid was added and the mixture was heated to 140 °C. The reaction products, 3 and water, were distilled into a flask containing potassium carbonate to eliminate water. Redistillation over potassium carbonate gave 18.1 g of pure 3: bp 122–123 °C (760 mmHg) [lit.: 127 °C (760 mmHg),[21] 124 °C (760 mmHg)[22]]; yield 90.3%; the NMR and IR spectra agreed with those reported in the literature.[21,22]

**Purification of Solvents, Initiators, and Comonomers.** Benzene and tetrahydrofuran were dried over metallic sodium and distilled. Acetone was refluxed over sufficient potassium permanganate to retain its violet color, distilled, dried over anhydrous calcium sulfate, decanted, and distilled just before use. Dimethyl sulfoxide was stirred with calcium hydride overnight and fractionated from calcium hydride in vacuo. Tetramethylene sulfone (sulfolane) was dried over calcium hydride and distilled. $\alpha,\alpha'$-Azobis(isobutyronitrile) (AIBN) and benzoyl peroxide were purified by recrystallization. Boron trifluoride etherate was purified by distillation. Commercial tin tetrachloride, tungsten hexachloride, vanadium acetylacetonate, and 1.6 M *n*-butyllithium solution in *n*-hexane were used without purification. Methyl acrylate, diethyl fumarate, and diethyl maleate were dried over sodium sulfate and distilled. Maleic anhydride was purified by sublimation.

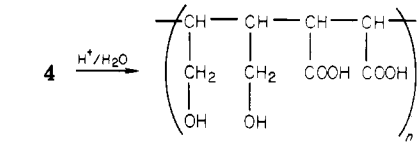
**Copolymerization.** Appropriate amounts of 3, comonomer, solvent, and initiator were weighed into a small glass ampule. The ampule was cooled at liquid nitrogen temperature, evacuated, and sealed off. Copolymerization was terminated by cooling at liquid nitrogen temperature. The copolymer was precipitated with *n*-pentane, purified by reprecipitation with chloroform as a solvent and *n*-pentane as a precipitant, and dried in vacuo. When sulfolane was used as the copolymerization solvent, the copolymer was precipitated by adding to 100 mL of diethyl ether.

**Preparation of Poly[(hydroxymethyl)methylene] (2).** Copolymer of 3 with maleic anhydride, 4 (0.387 g, $1.95 \times 10^{-3}$ mol of maleic anhydride units), was allowed to react with 0.171 g of lithium aluminum hydride ($4.51 \times 10^{-3}$ mol) in 20 mL of tetrahydrofuran at room temperature for 2 h. The reaction mixture was refluxed for 1 h, and 50 mL of 0.1 N aqueous hydrogen chloride solution was added. Tetrahydrofuran and water were evaporated off and the residue was dissolved in 50 mL of tetrahydrofuran. The solution was passed through cation and anion exchange resins (Dowex resins 1X8-100 and 50X100, dry mesh 70–100 for both resins). The tetrahydrofuran was evaporated and the polymer was precipitated into 100 mL of *n*-pentane. The polymer was purified by dissolution in acetone and reprecipitating into *n*-pentane and drying in vacuo. The new polymer was a white powder: yield 0.336 g (98%); $^1$H NMR ($Me_2SO$-$d_6$ + 1 drop of $D_2O$) $\delta$ 3.4 (CH, $CH_2$), 3.77 (free OH, S), 4.6 (hydrogen-bonded OH, br); $^1$H NMR (1:1 $Me_2SO$-$d_6$–$D_2O$) $\delta$ 3.38 ($CH_2$), 3.4 (CH), 4.37 (OH, S); IR (KBr) 3350 ($\nu_{O-H}$, s br), 2880, 2930 ($\nu_{C-H}$, m), 1460, 1410, 1330, 1220, 1110 ($\nu_{C-O}$, s), 1045 ($\nu_{C-O}$, s), 995, 865, 650 cm$^{-1}$.

The number-average molecular weight of the original copolymer 4 in dimethylformamide indicated that the degree of polymerization of 2 was 10.4–11.2.

Anal. Calcd for $(C_2H_4O)_n$: C, 54.5; H, 9.2. Found: C, 54.0; H, 8.9.

**Preparation of 5 (Hydrolysis of Copolymer of 4,7-Dihydro-1,3-dioxepin and Maleic Anhydride (Eq 1)).** Co-



(1)

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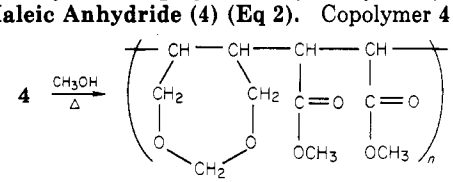
polymer 4 (0.224 g, $1.13 \times 10^{-3}$ mol of maleic anhydride units) was suspended in 30 mL of water and 1 drop of 37.1% aqueous hydrochloric acid was added. The suspension was refluxed for 2 h. The suspension changed to a clear solution. Water was evaporated and the residue was dissolved in a small amount of $Me_2SO$. The polymer was precipitated into 100 mL of ether, purified by reprecipitation, and dried in vacuo: yield 0.219 g (95%); $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 7.8 (COOH, OH, br), 2–5 (CH, $CH_2$, three kinds of CH and $CH_2$ are overlapped); IR (KBr) 3650–3300 ($\nu_{O-H}$ of $CH_2OH$, s br), 2980–2900 ($\nu_{C-H}$, m), 3000–2300 ($\nu_{O-H}$ of COOH, m br), 1730 ($\nu_{C=O}$, s), 1390 (s), 1190 (m) (coupling between in-plane O–H bending and C–O stretching of dimeric COOH), 1135 (m), 1040 (m) ($\nu_{C-O}$), 965 (w), 845 (w) (O–H bending) cm$^{-1}$.

Anal. Calcd for $(C_8H_{12}O_6)_n$: C, 47.1; H, 5.9. Found: C, 47.0; H, 5.7.

**Methanolysis of Copolymer of 4,7-Dihydro-1,3-dioxepin with Maleic Anhydride (4) (Eq 2).** Copolymer 4 is not hy-



(2)

6

drolytically stable under atmospheric conditions. Conversion of 4 to relatively stable 6 was accomplished by the following reaction.

Copolymer 4 (0.500 g, $2.52 \times 10^{-3}$ mol) was dissolved in 20 mL of tetrahydrofuran, and 20 mL of absolute methanol was added. The solution was refluxed overnight. After removal of methanol and tetrahydrofuran, the polymer was precipitated by adding to 100 mL of *n*-pentane. The polymer was purified by reprecipitation and dried in vacuo: yield 0.573 g (94%); $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 3.53 (s, br), 3.9 (br) (both signals are overlapped, 14 H), 4.67

Table I
Copolymerization of 4,7-Dihydro-1,3-dioxepin (3, $M_1$)[a]

| no. | comonomer $M_2$ | total of monomers, g | solvent, (mL) | [AIBN], mol % | [$M_1$] in feed, mol % | % yield | [$M_1$] in copolymer,[b] mol % | $[\eta]_{inh}$,[c] dL/g |
|---|---|---|---|---|---|---|---|---|
| 1 | none | 0.9856 | none | 1.03 | 100 | 0 | | |
| 2 | methyl acrylate | 1.1375 | none | 0.79 | 72.3 | 19 | 9 | 0.05 |
| 3 | methyl acrylate | 1.0195 | none | 1.03 | 49.8 | 36 | 6 | 0.06 |
| 4 | methyl acrylate | 1.0760 | none | 0.82 | 17.1 | 68 | 3 | 0.13 |
| 5 | methyl acrylate | 0.8166 | none | 0.63 | 0 | 100 | | |
| 6 | diethyl fumarate | 1.4325 | none | 1.20 | 52.3 | 0 | | |
| 7 | diethyl fumarate | 1.4769 | none | 1.10 | 35.8 | 12 | 15 | 0.03 |
| 8 | diethyl fumarate | 1.7182 | none | 0.94 | 14.2 | 14 | 13 | |
| 9 | diethyl fumarate | 1.7123 | none | 0.88 | 0 | 39 | | 0.11 |
| 10 | diethyl maleate | 1.3624 | none | 1.02 | 49.9 | 0 | | |
| 11 | diethyl maleate | 1.0072 | none | 1.48 | 37.0 | 3 | 35 | |
| 12 | diethyl maleate | 1.7609 | none | 1.02 | 0 | 2 | 0 | |
| 13 | maleic anhydride | 0.5047 | benzene (0.5) | 0.38 | 100.0 | 0 | | |
| 14 | maleic anhydride | 0.9989 | benzene (1.0) | 1.08 | 76.2 | 44 | 48 | 0.05 |
| 15 | maleic anhydride | 1.0393 | benzene (1.0) | 0.94 | 50.0 | 38 | 50 | 0.07 |
| 16 | maleic anhydride | 0.9978 | benzene (1.0) | 0.97 | 26.5 | 46 | 52 | 0.06 (560)[d] |
| 17 | maleic anhydride | 0.5033 | benzene (0.5) | 1.08 | 0 | 0 | | |
| 18 | maleic anhydride | 1.1760 | acetone (1.0) | 0.70 | 49.6 | 48 | 50 | 0.05 (510)[d] |
| 19 | maleic anhydride | 1.1468 | THF (1.0) | 1.11 | 49.8 | 55 | 50 | 0.05 |
| 20 | maleic anhydride | 1.2163 | sulfolane (1.0) | 1.03 | 49.9 | 49 | 50 | 0.06 (530)[d] |

[a] Time, 12 h; temperature, 70 °C. [b] Calculated from $^1$H NMR spectrum. [c] In dimethyl sulfoxide at 30 °C. [d] Number-average molecular weight (VPO, 37 °C, DMF).

Table II
Chemical Shifts (δ) of Copolymers of 4,7-Dihydro-1,3-dioxepin (3, $M_1$) and Comonomer ($M_2$)[a]

| | in monomer unit 5 ($M_1$) of copolymer | | | in monomer unit $M_2$ in copolymer | | | | |
|---|---|---|---|---|---|---|---|---|
| comonomer $M_2$ | CH | $CH_2O$ | $OCH_3$ | CH | $CH_2$ | $OCH_3$ | $OCH_2$ | $OCH_3$ |
| methyl acrylate | 1.3-2.6 | 3.7 | 4.67 and 4.73 | 1.3-2.6 | 1.3-2.6 | 3.68 | | |
| diethyl fumarate[b] | 3.2 | 4.2 | 4.7 | 3.2 | | | 4.2 | 1.26 |
| diethyl maleate[c] | 3-4 | 4.2 | 4.8 | 3-4 | | | 4.2 | 1.25 |
| maleic anhydride | 3-4 | 3-4 | 4.7 | 3-4 | | | | |

[a] Solvent, $CDCl_3$. [b] Homopolymer signals at δ 1.24 ($CCH_3$), 3.20 (CHCO), and 4.12 ($COOCH_2$). [c] Homopolymer signals at δ 1.27 ($CCH_3$), 3.22 (CHCO), and 4.14 ($COOCH_2$).

($OCH_2O$, 2 H, br); IR (KBr) 1730 ($\nu_{C=O}$ of ester group) cm$^{-1}$. The very strong absorption of 4 at 1780 cm$^{-1}$ had disappeared completely.

**Reduction and Hydrolysis of 6 to 2 (Eq 3).** Copolymer 6

$$6 \xrightarrow[2.\ H^+/H_2O]{1.\ LiAlH_4/THF} 2 \qquad (3)$$

(53 mg, $2.17 \times 10^{-4}$ mol of maleic anhydride units) was reacted with 16.9 mg of lithium aluminum hydride ($14.45 \times 10^{-4}$ mol) in 20 mL of tetrahydrofuran at room temperature for 1 h. After refluxing for 30 min, the reaction mixture was treated with 10 mL of 0.1 N aqueous hydrogen chloride solution. Water and tetrahydrofuran were evaporated and the residue was dissolved in 100 mL of tetrahydrofuran. The solution was passed through cation and anion exchange resins. Tetrahydrofuran was evaporated and the polymer was purified by precipitation in pentane. The NMR and IR spectra of the polymer were almost the same as those of 2 prepared from 4 by reduction and hydrolysis.

**Homopolymer of 4,7-Dihydro-1,3-dioxepin (3).** The required amount of monomer was weighed into a small glass ampule, and the ampule was cooled at −78 °C. Initiator or initiator solution in *n*-hexane was added and the ampule was evacuated and sealed off. Radical polymerization was terminated by cooling, and the reaction mixture was poured into large amounts of *n*-pentane. Cationic polymerization was terminated by adding a few milliliters of triethylamine–methanol mixture (volume ratio, 1:4) and polymer was precipitated by adding to *n*-pentane. Polymers were purified by reprecipitation from chloroform as a solvent and *n*-pentane as a precipitant and dried in vacuo.

## Results

**Free Radical Copolymerization of 3 with Methyl Acrylate, Diethyl Fumarate, and Diethyl Maleate.** The copolymerization results are shown in Table I. NMR results for the copolymers are listed in Table II.

The copolymers of 3 with methyl acrylate are colorless, sticky solids possessing inherent viscosities from 0.03 to 0.13 dL/g. Decreasing the mole percent of 3 in the feed increased the conversion and the inherent viscosity of the copolymers but decreased the mole percent of the unit of 3.

The copolymerization of 3 with diethyl fumarate and with diethyl maleate also gave copolymers. The homopolymer of diethyl fumarate was prepared with 39% conversion and 0.11 dL/g inherent viscosity.

No further work was done because the content of 3 was so low.

**Copolymerization of 4,7-Dihydro-1,3-dioxepin (3) with Maleic Anhydride.** The copolymerization of 3 and maleic anhydride gave a white powder. NMR results for the copolymers are shown in Table II. The copolymer composition was calculated from the relative intensity of acetal protons at δ 4.7 to other signals. The results are also shown in Table I, indicating that strictly 1:1 alternating copolymers are formed under various conditions. The inherent viscosity of the copolymers was very low. The number-average molecular weights are from 510 to 560.

**Reduction and Hydrolysis of 4 and 6.** Polymer 2 was prepared from 4 by reduction and from 6 by reduction and hydrolysis with good conversion. Polymer 2 is soluble in dimethyl sulfoxide, *N*,*N*-dimethylformamide, and water. NMR spectra are shown in Figure 1 with assignments for each signal. The hydroxyl groups of 2 showed one signal

Table III
Oligomerization of 4,7-Dihydro-1,3-dioxepin (3)[a]

| no. | monomer, g | initiator (mol %) | solvent (mL) | temp, °C | time, h | yield, wt % | MW[b] |
|---|---|---|---|---|---|---|---|
| 1 | 1.0281 | AIBN (1.97) | none | 70 | 60 | 0 | |
| 2 | 1.0347 | AIBN + $h\nu$ (2.36) | none | room temp | 60 | 0 | |
| 3 | 1.0126 | $(PhCOO)_2$ (2.13) | none | 70 | 60 | 0 | |
| 4 | 1.0043 | $(PhCOO)_2$ + $h\nu$ (2.19) | none | room temp | 60 | 0 | |
| 5 | 1.0174 | $BF_3OEt_2$ (1.0) | none | 25 | 60 | 3 | |
| 6 | 1.2285 | $BF_3OEt_2$ (1.0) | none | 70 | 24 | 20 | 660 |
| 7 | 0.8768 | $SnCl_4$ (1.0) | none | 25 | 60 | 0 | |
| 8 | 0.9749 | $SnCl_4$ (1.0) | none | 70 | 24 | 3 | |
| 9 | 1.0066 | $WCl_5$ (1.56) | none | 0 | 60 | 33 | 540 |
| 10 | 1.6614 | $WCl_5$ (1.49) | none | 70 | 60 | 23 | 980 |
| 11 | 1.0110 | $V(C_5H_7O_2)_3$ (1.10) | none | 0 | 60 | 0.3 | |
| 12 | 1.1856 | $V(C_5H_7O_2)_3$ (1.18) | none | 70 | 60 | 6 | 540 |
| 13 | 1.1775 | $WCl_5$-*n*-BuLi (1.32) ([*n*-BuLi]/[$WCl_5$] = 1.06) | *n*-hexane (0.5) | 25 | 60 | 5 | |
| 14 | 0.9349 | $WCl_5$-*n*-BuLi (1.73) ([*n*-BuLi]/[$WCl_5$] = 0.98) | *n*-hexane (0.5) | 70 | 60 | 11 | |

[a] Polymer structure, $-OCH_2CH{=}CHCH_2OCH_2-$, **7**. [b] VPO, 37 °C, 1,2-dichloroethane.

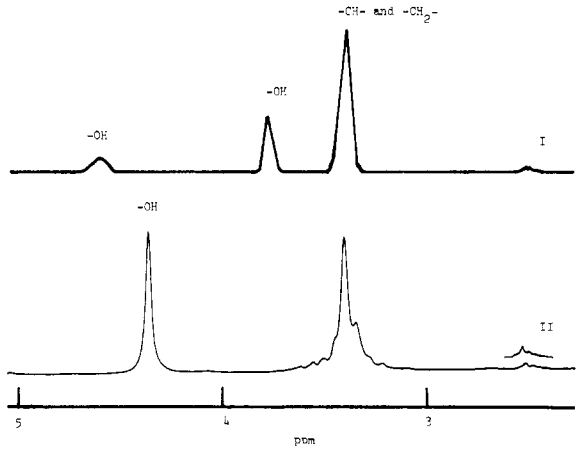



**Figure 1.** $^1H$ NMR spectra of poly[(hydroxymethyl)methylene]. Solvent: I, $Me_2SO$-$d_6$ + 1 drop of $D_2O$; II, 1:1 $Me_2SO$-$d_6$–$D_2O$.

in $Me_2SO$-$d_6$ and 1:1 $Me_2SO$-$d_6$–$D_2O$ solution. In $Me_2SO$-$d_6$ + 1 drop of the $D_2O$, two signals were observed (Figure 1, I), suggesting that strong intramolecular hydrogen bonding occurs in $Me_2SO$ and strong intermolecular hydrogen bonding between polymer and $D_2O$ occurs in 1:1 $Me_2SO$–$D_2O$. The IR spectrum (KBr) showed a strong absorption at 3380 $cm^{-1}$, which is assigned to the hydrogen-bonding hydroxyl stretching band.

**Preparation of Water-Soluble Polymer 5.** Copolymer **4** gave **5** by acid hydrolysis. Compound **5** is a white powder, soluble in dimethyl sulfoxide, *N*,*N*-dimethylformamide, methanol, and water and insoluble in acetone, tetrahydrofuran, ethers, and hydrocarbons. The IR spectrum showed that the OH and COOH participate in internal and/or intramolecular hydrogen bonding.

**Donor–Acceptor Complex between 4,7-Dihydro-1,3-dioxepin (3) and Maleic Anhydride.** $^1H$ NMR studies showed no strong interaction between **3** and maleic anhydride, suggesting that the interaction is very weak. The finding is supported by the fact that no copolymerization of **3** and maleic anhydride was observed in dimethyl sulfoxide.

**Ring-Opening Oligomerization.** The oligomerization results are shown in Table III. 4,7-Dihydro-1,3-dioxepin (**3**) did not homopolymerize under free radical conditions. Cationic and/or coordinated polymerization gave **7**. The

$$3 \xrightarrow[\text{ring opening}]{>O^+-} \underset{\mathbf{7}}{-OCH_2CH{=}CHCH_2OCH_2-} \qquad (4)$$

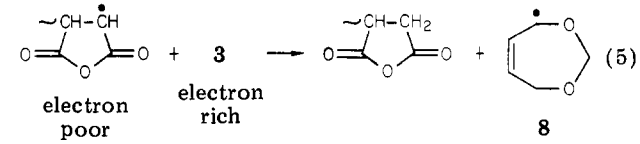
number-average molecular weights were from 540 to 980. NMR spectra of oligomers in $CDCl_3$ showed signals at $\delta$ 4.16 ($OCH_2$, 4 H, d, $J$ = 4.5 Hz), 4.69 ($OCH_2O$, 2 H, s), 5.73 (CH=CH, 2 H, t, $J$ = 4.5 Hz). The IR spectra of the oligomers showed very strong absorptions at 1030 and 865 $cm^{-1}$ ($\nu_{C\text{-}O\text{-}C}$).

## Discussion

The free radical copolymerizations of 4,7-dihydro-1,3-dioxepin (**3**) with methyl acrylate, diethyl fumarate, and diethyl maleate gave copolymers. As shown in Table I, the mole percent of **3** in copolymers is low.

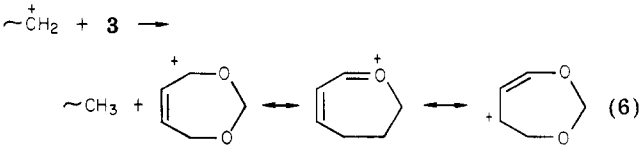
On the other hand, the free radical copolymerization of **3** with maleic anhydride gave strictly 1:1 alternating copolymers, **4**. The results suggest that some charge-transfer complex is formed and/or that some polar interaction (donor–acceptor complex) occurs prior to the copolymerization.

The low molecular weight of **4** is probably due to the transfer to monomer **3**. The resulting radical **8** is stable.




A similar transfer reaction was proposed by Pawloski and Sterling[25] from the fact that the viscosity of polystyrene prepared in the presence of 2,2′-methylenebis(4,7-dihydro-1,3-dioxepin) or 2,2′-*p*-phenylenebis(4,7-dihydro-1,3-dioxepin) with the use of benzoyl peroxide initiator is lower than that of polystyrene.

As shown in Table III, **3** does not homopolymerize under free radical conditions but does homopolymerize under cationic conditions to form oligomers via ring opening. The low number-average molecular weight and conversion suggest that some termination and/or transfer reactions occur from the propagating chain end to **3** (eq 6).




The biological activity of **4** will be investigated, since divinyl ether–maleic anhydride copolymer is a promising antitumor agent[26,27] and interferon inducer.[28,29]

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# Cationic Copolymers of Isobutylene. 5. Copolymerization of Isobutylene and *cis*-1,3-Pentadiene

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ABSTRACT: The structure of cationic isobutylene (I)–*cis*-1,3-pentadiene (cP) copolymer was investigated by means of $^{13}C$ NMR spectroscopy. The diene was present in the copolymer chains mainly as trans-1,4 units, but cis-1,2, trans-1,2, trans-4,1, and trans-4,3 units were also observed. The attack at position 4 of cP occurred by sterically unhindered carbenium ions arising from cP and not from I. The isomerization of cP to *trans*-1,3-pentadiene was ascertained to occur under mild conditions in the presence of $BF_3$·$OEt_2$. The evaluation of the fractions of triads centered on I was found to be in fair agreement with the calculated random distribution of the monomer units.

## Introduction

In previous work we studied the structure and the monomer distribution in isobutylene–*trans*-1,3-pentadiene (I–tP) copolymers by means of $^{13}C$ NMR spectroscopy.[1] *cis*-1,3-Pentadiene (cP) is less reactive than the trans isomer in both the cationic homopolymerization and copolymerization with isobutylene.[2,3] This minor reactivity is accompanied by a major complexity of the copolymerization and of the structural features of the resulting copolymer. These aspects are investigated in the present paper.

## Experimental Section

**Materials.** Reagents and solvents, i.e., isobutylene, $C_2H_5AlCl_2$, *n*-pentane, and $CH_2Cl_2$, were obtained and handled as described previously.[1a,3] $BF_3$·$OEt_2$ (Fluka AG) was distilled under vacuum before use and stored under a dry nitrogen atmosphere. *cis*-1,3-Pentadiene (Fluka AG) was purified by distillation under an inert atmosphere and stored at 0 °C (VPC purity >99%, the remaining main components being cyclopentene (0.5%) and *trans*-1,3-pentadiene (0.3%)).

**Procedure.** The copolymerization procedure previously described for I–tP copolymer[1a] was adopted. Typical copolymerizations were carried out under the following conditions: −70 °C, [I] = 1.5 mol/L, [cP]/[I] = 1.14 mole ratio, $[C_2H_5AlCl_2]$ = 0.050 mol/L, solvent 1:1 *n*-pentane–$CH_2Cl_2$ mixture (by volume), time 30 min, conversion 21%. The cP content of the resulting copolymer was 29 mol%; $[\eta]$ = 0.13 dL/g (in cyclohexane, 30 °C).

Some GPC experiments carried out as previously reported[4] yielded broad, symmetric monomodal distribution curves. Homopolymerizations and cis–trans isomerization experiments with cP were performed under conditions similar to those of the copolymerizations. The diene, dissolved in the *n*-pentane–$CH_2Cl_2$ mixture and kept at −70 °C, was contacted with catalyst for different time periods. Samples withdrawn from the reactor were treated with $CH_3OH$ and analyzed by VPC (column: 20% $\beta,\beta'$-oxobis(propionitrile), 5 m, $T$ = 50 °C, carrier He, 60 $cm^3$/min) for the relative concentration of cis and trans isomer. At the end of each experiment, the solution was poured into methanol to precipitate any formed polymer.

**Analyses.** $^1H$ and $^{13}C$ NMR spectra were obtained at 25 °C in $CDCl_3$ with a Varian XL-100 spectrometer as described previously.[1a] Selective-decoupling experiments were carried out as reported elsewhere.[1a] The copolymer composition was evaluated by $^1H$ NMR measurements. IR spectra were obtained with a Perkin-Elmer Model 225 instrument.

## Results and Discussion

**I–cP Copolymer and cP Homopolymer.** Figure 1 shows the $^{13}C$ NMR spectrum of I–cP copolymer containing 29 mol % cP. All the signals observed previously in the spectrum of I–tP copolymer are also present in Figure 1. They were assigned in previous work[1a] and comprise almost all the signals having stronger intensity.

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