

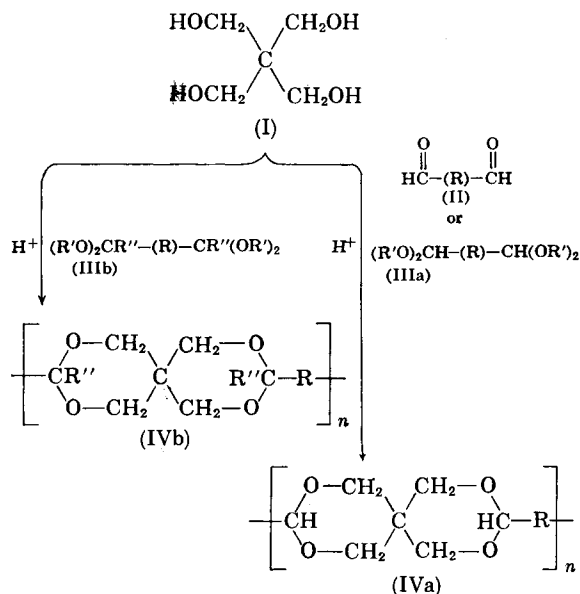
## Polyspiroacetal Resins. Part I. Initial Preparation and Characterization

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### INTRODUCTION

In the course of a search for new resins with useful properties, polyspiroacetals with the structures of formulas IVa and IVb were investigated. Prepared by the reaction of pentaerythritol (I) with a dialdehyde (II; R = alkyl, aryl), a diacetal (IIIa; R = alkyl, aryl; R' = alkyl), or a diketal (IIIb);



R, R', R'' = alkyl), these condensation polymers, with repeating neopentyl carbon atoms, were of interest because of their possible oxidative stability at elevated temperatures.

At the time this work was started, only three pertinent literature references had been uncovered. Read,<sup>1</sup> in 1912, reported obtaining an apparently high molecular weight solid by the strongly acid-catalyzed reaction of pentaerythritol and glyoxal. Much later, in 1951, Orth<sup>2</sup> mentioned two polyspiroacetals, prepared by a reaction of 2,6-dioxaspiro[3,3]heptane with terephthalaldehyde and with 1,4-cyclohexanedione, respectively. However, except for structural formulas, no details about their preparation or properties were fur-

nished. Two years later, Kropa and Thomas<sup>3</sup> described the preparation of some polyspiroacetal resins from various pentaerythritols and glyoxal. Like Orth, they also recognized that spirane units probably had formed, but they described, in addition, some of the properties of their baked films.

Since the present work has been completed, however, further references to these polymers have appeared in patents. Thus, Abbott and co-workers,<sup>4</sup> using substituted dialdehydes, also have prepared some polyspiroacetal resins, which reportedly are useful as plasticizers for cellulose acetate. In a different approach, Kress<sup>5</sup> used large excesses of various dialdehyde monomers to prepare apparently low molecular weight versions of some of these resins. The Kress products, with a probability of mainly terminal aldehyde groups, have been claimed as *in situ* curing agents for textiles.

More recently, in two patents,<sup>6,7</sup> some of these polymers have been described with properties reflecting higher molecular weights than previously reported. Prepared by a transacetalation reaction, they are described as forming useful films<sup>6</sup> and fibers.<sup>6,7</sup> A high degree of crystallinity is reported to be one of the significant properties found in some of the fiber-forming resins.<sup>7</sup>

In this paper, the synthesis and initial characterization of a variety of polyspiroacetals are reported.

### EXPERIMENTAL

Polymerization by direct condensation was carried out in an aqueous solution of equimolar quantities of pentaerythritol and a dialdehyde.<sup>8</sup> To the stirred solution at reflux was added a small amount of acid catalyst, usually about 0.5 wt.-% based on the total system. The most frequent catalyst used was *p*-toluenesulfonic acid. If polymerization occurred, the clear solution became opaque within a few minutes. At this point, either solid particles or oil droplets were visible on the flask walls. Where oil droplets originally formed, they became solid as

TABLE I  
 Structure and Initial Properties of Some Polyspiroacetal Resins

Dialdehyde or diketone	Polymer <sup>a</sup>				Method of preparation	Yield, %	Melting range, °C.		$\overline{DP}$	Mol. wt.	Vis- cosity, c'poise (20°C., 7½% cresylic acid solution)
	R	R''	x	y			Fisher- Johns	Kofler			
a. Glyoxal	—	H	1.4	0.1	Trans- acetal- ation	64	>310	191–209 <sup>b</sup>	1.5	252	40.0
b. Malon- aldehyde	—CH <sub>2</sub> —	H	21.6	0	“	70	>300	°	21.6	3720	62.8
c. Glutar- aldehyde	—(CH <sub>2</sub> ) <sub>3</sub> —	H	21.7	1.6	Aqueous conden- sation	92	260–270	247–257 <sup>b</sup>	23.3	4850	111
d. 3-Methyl- glutar- aldehyde	$\begin{array}{c} \text{CH}_3 \\   \\ \text{—CH}_2\text{CHCH}_2\text{—} \end{array}$	H	35	2.6	“	98	205–208	148–160 <sup>b</sup>	37.5	8350	65.8
e. Tereph- thalal- dehyde	—C <sub>6</sub> H <sub>4</sub> —	H	7.7	0.6	“	55	>300	°	8.3	2000	<sup>d</sup>
f. 2,5-Hex- anedione	—(CH <sub>2</sub> ) <sub>2</sub> —	CH <sub>3</sub>	38.5	0	Trans- acetal- ation	27	225–238	216–221	38.5	8250	51.8

<sup>a</sup> Refers to structure (VI).

<sup>b</sup> Crystallites melted without appearance of liquid.

<sup>c</sup> Degradation obscured an accurate melting range.

<sup>d</sup> Small amount of gel present in solution.

the reaction progressed. The final reaction mixture usually was a slurry of solid particles in the aqueous medium. (An exception to this was the 3-methylglutaraldehyde polymer, which was isolated as a solid lump and which had to be crushed.) Termination of the reaction was effected by the addition of a slight excess of aqueous potassium hydroxide. The reaction mixture then was filtered. The collected resin was washed several times with excess water followed by methanol. The final polymer generally was dried under vacuum at 55°C.

For polymerization by transacetalation,<sup>8</sup> equimolar quantities of pentaerythritol and diacetal monomer were added to benzene. To the slurry, maintained at 80–83°C., was added *p*-toluenesulfonic acid catalyst, usually in a concentration of about 0.3 wt.-% of the entire system. (For the glyoxal polymer, however, about three times the standard amount of catalyst was required.) Shortly thereafter, an alcohol-benzene azeotrope began to distill. The reaction was allowed to continue until no more azeotrope was produced. Next the benzene solution of low molecular weight polymer was

diluted with about four times its volume of cresylic acid (essentially a mixture of *m*- and *p*-cresols plus xylenols), and a further 0.6 wt.-% of catalyst was added. The cresylic acid solution was stirred at 85°C. for about 2 hr. Then all the alcohol formed by further polymerization plus all the remaining benzene were distilled under moderate vacuum. The residual polymer solution was allowed to cool to room temperature, at which time it was made alkaline with sufficient aqueous potassium hydroxide to convert all the cresylic acid to its water-soluble salt. This mixture then was diluted with water and filtered. The collected polymer, at this point in the form of swollen particles, was washed and dried as described previously in the aqueous process.

The melting range of these polymers was examined, both by a Fisher-Johns melting point apparatus and by a Kofler hot stage-polarizing microscope combination. Originally the standard slow increase in temperature on the Fisher-Johns apparatus was observed to produce no melting—only crosslinking and subsequently, degradation being noted. Therefore another method for de-

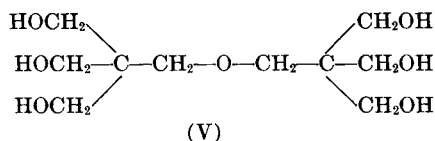
termining the melting range on the Fisher-Johns apparatus was evaluated. Small amounts of polymer were dropped on the hot stage at various temperatures. Either melting occurred almost immediately or it never occurred, for crosslinking usually resulted from continued heating somewhere above 200°C. The lowest detectable temperatures at which melting took place were designated the Fisher-Johns melting range. The minimum values were reproducible within several degrees. Where a comparison is possible, the Fisher-Johns values invariably are higher than the Kofler hot stage values, as indicated in Table I.

Both the average degree of polymerization and the molecular weight of these polymers were determined by hydroxyl endgroup analysis.<sup>9-11</sup> The hydroxyl content was analyzed by acetylation in pyridine-acetic anhydride solution, followed by titration with aqueous potassium hydroxide. Duplicate samples and blanks were used. One point of caution is that the calculated molecular weights are less reliable for lower yields of polymer.

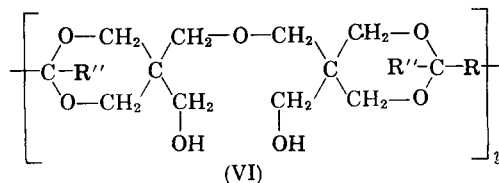
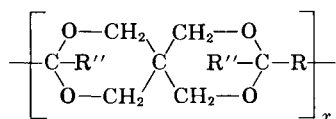
These polymers proved to be soluble in commercial cresylic acid (Barrett cresylic acid R-7B). Viscosities were obtained on 7½% cresylic acid solutions at 20°C. with a Fenske-Ostwald viscosimeter. For this phase of the work, intrinsic viscosities were not sought because the molecular weights could be calculated readily by the endgroup technique described above.

## RESULTS

Relatively early in this work, the strongly crystalline behavior of these polymers became apparent. For film applications, some means of controlling and decreasing this crystalline character became desirable. One means was by preparing copolymers containing dipentaerythritol (V) as a second polyol monomer.



The resulting copolymer structure (VI) then could be represented schematically as a mixture of the following units:



Both  $x$  and  $y$  refer merely to individual unit contents in the polymer molecules and do not signify any form of block polymer.

The resins described in this paper comprise both homopolymers with pentaerythritol and copolymers with pentaerythritol and dipentaerythritol. In this article, technical pentaerythritol, which contains approximately 12 wt.-% of dipentaerythritol, was used in preparing the copolymers. Because of this added composition variable, a strict comparison between all the polymers in Table I is not possible. However, the second paper in this series<sup>12</sup> will show that, in these polymers, 12 wt.-% of the dipentaerythritol monomer does not appear to influence greatly such properties as the melting point or intrinsic viscosity.

Some additional comments on the resins in Table I are appropriate.

### a. Poly { [3,9-(2,4,8,10-tetroxaspiro[5,5]undecane)] co [2,2'-bis[(5-hydroxymethyl-5-*m*-dioxanylene) methyl] oxide] }

Attempted preparation of this resin by direct condensation of technical pentaerythritol with glyoxal yielded only an oil. In contrast, transacetalation produced a solid. In addition to the significantly greater amount of catalyst required, the latter polymerization took about six times as long as the corresponding malonaldehyde transacetalation. Not surprisingly, an extremely low molecular weight product was obtained here. Very likely, steric hindrance is involved, for molecular models of this polymer are extremely compact and have a hindered freedom of rotation. As might be expected from the low molecular weight, the film properties of this polymer were poor.

### b. Poly[3-(methylene),9-(2,4,8,10-tetroxaspiro[5,5]undecane)]

This polymer was prepared by transacetalation from pentaerythritol and malonaldehyde diacetal to avoid the known instability of free malonaldehyde under acidic conditions. Except for the ease of polymerization, the details are similar to those of the preceding polymer. In spite of a higher molecular weight and greater chain flexibility, how-

ever, films of this resin were brittle, even when carefully crosslinked for still higher molecular weight.

**c. Poly{ [3-(1,3-trimethylene), 9-(2,4,8,10-tetroxaspiro[5,5]undecane)]co{2-(1,3-trimethylene), 2'-bis[(5-hydroxymethyl-5-*m*-dioxanylene)-methyl]oxide} }**

This resin was obtained repeatedly from technical pentaerythritol and glutaraldehyde in yields of between 90 and 100%. Interestingly, a variation in the molecular weight was found to occur if some emulsifier was present during the polymerization. One of the most effective emulsifiers was found to be sodium lauryl sulfate. With emulsifier present in the polymerization reaction, the elapsed time to initial precipitation of polymer was increased significantly, and the resulting polymer was found to have about twice the molecular weight of the resin prepared without emulsifier. The most acceptable explanation advanced so far for this behavior is that the emulsifier improves the solvency of the aqueous medium enough to permit greater chain growth before precipitation. The doubled molecular weight can be accounted for by the coupling of shorter polymer chains in solution followed immediately by precipitation. Thus far, experiments indicate that polymerization occurs mainly in the solution phase of the system.

In general, uncured films of this polymer were hard and transparent. In addition, their adhesion to glass and metals was good. Uncured they were brittle, but with an optimum amount of crosslinking by such materials as polyisocyanates, anhydrides, and other polyfunctional reactants for hydroxyl groups, they exhibited good flexibility. This polymer will be discussed in greater detail in the article following this one.<sup>12</sup>

**d. Poly{ [3-(1,3-isobutylene), 9-(2,4,8,10-tetroxaspiro[5,5]undecane)]co{2-(1,3-isobutylene), 2'-bis[(5-hydroxymethyl-5-*m*-dioxanylene)-methyl] oxide} }**

This polymer, prepared from technical pentaerythritol and 3-methylglutaraldehyde, possessed one of the highest molecular weights obtained by direct condensation, although the presence of emulsifier was a contributing factor. Unlike its unsubstituted homolog, it passed through an oil phase before precipitating as a solid. Excellent solubility of the intermediate oil stage in the aqueous medium is believed to be one main reason for the high molecular weight.

Compared to the glutaraldehyde homolog, this polymer exhibited a lower melting point, solubility in a wider range of solvents, and softer films.

**e. Poly{ [3-(*p*-phenylene), 9-(2,4,8,10-tetroxaspiro[5,5]undecane)]co{2-(*p*-phenylene), 2'-bis[(5-hydroxymethyl-5-*m*-dioxanylene)methyl]oxide} }**

This resin, previously mentioned by Orth,<sup>2</sup> was obtained from technical pentaerythritol and terephthalaldehyde only when about four times the usual amount of catalyst was used. Along with polymerization, however, some crosslinking occurred. The standard 7½% cresylic acid solution revealed not only some gel particles but also a thixotropic behavior. Whether the latter is directly connected with the crosslinking remains to be determined.

**f. Poly[3-(ethylene), 9-(3,9-dimethyl-2,4,8,10-tetroxaspiro[5,5]undecane)]**

Attempts to prepare this polymer by direct condensation from pentaerythritol and 2,5-hexanedione were unsuccessful. However, the resin was prepared by transacetalation from the tetraethyl diketal (b.p. 76–77°C./35 mm.; m.p. 64–65°C.). The final product was a brittle powder which, nevertheless, produced a tough transparent film. The low yield perhaps can be correlated with the unexpectedly large amount of distillate collected. The unsaturation of ketals under the influence of heat and acid is a known reaction, and alcohol is one of the products.<sup>13</sup>

## DISCUSSION

No polymer was obtained from  $\alpha$ -hydroxyadipaldehyde and pentaerythritol, in agreement with Read's findings<sup>1</sup> that neither salicylaldehyde nor glucose reacts with pentaerythritol in the presence of acid catalyst. All these examples suggest that, under the conditions employed, various aldehyde intramolecular reactions—such as hydrogen bonding and hemiacetal formation—are favored over intermolecular acetal formation with pentaerythritol. By analogy with the structure of glucose,  $\alpha$ -hydroxyadipaldehyde may fit into this category because of a cyclic hemiacetal structure.

In general, the high melting point and low solubility of polyspiroacetal resins indicate strong interchain forces and a high degree of order. Although only a limited number of resins are presented in Table I, their melting ranges suggest that the spirane unit is the main contributor to crystallinity. Molecular models support this idea and indicate

also that flexibility is contributed by aliphatic portions of the polymer molecule derived from the dialdehyde and dipentaerythritol components. Undoubtedly, intermolecular hydrogen bonding by the hydroxyl groups also contributes to the strong interchain forces.

The effect of methyl substituents on the melting point and solubility behavior of these polymers is suggested by those properties of polymers (d) and (f) in Table I. As might be expected, in both instances the melting points decreased noticeably and the range of solvents increased compared to the unsubstituted polymer.

Detailed data on various properties of some polymers of type (c) (Table I) are presented in the accompanying article.<sup>12</sup>

We are indebted to Drs. R. N. Crozier and A. H. Markhart for their many helpful suggestions and comments during this work.

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### Synopsis

The reaction of various dialdehydes and one diketone with pentaerythritol or pentaerythritol-dipentaerythritol mixtures, has produced a series of thermoplastic, polyspiroacetal resins. These possess molecular weights up to 10,000, solubility in a limited range of solvents, and high melting points. Some of these, with an optimum amount of cross-linking, have produced transparent, tough, flexible films.

### Résumé

La réaction de différents dialdéhydes et d'une dicétone avec du pentaérythritol, ou avec des mélanges pentaérythritol-dipentaérythritol, donne lieu à la formation d'une série de résines polyspiroacétaliques thermoplastiques. Ces résines ont des poids moléculaires qui dépassent 10.000, une solubilité dans un nombre limité de solvants et des points de fusion élevés. Certaines d'entr'elles, qui ont un degré de pontage approprié, donnent lieu à la formation de films transparents, résistants et flexibles.

### Zusammenfassung

Die Reaktion verschiedener Dialdehyde und eines Diketons mit Pentaerythritol oder Pentaerythritol-Dipentaerythritol Mischungen ergab eine Reihe von Thermoplasten, Polyspiroacetalharze. Diese besitzen ein Molekulargewicht bis zu 10.000, Löslichkeit in einer beschränkten Anzahl von Lösungsmitteln und hohe Schmelzpunkte. Einige von ihnen ergaben bei geeigneter Vernetzung transparente, zähe, flexible Filme.

Received February 16, 1961

Revised May 12, 1961