

Polyspiroacetal Resins. Part II. Structure and Properties of Polyspiroacetals from Pentaerythritol-Glutaraldehyde and from (Pentaerythritol-Dipentaerythritol)-Glutaraldehyde

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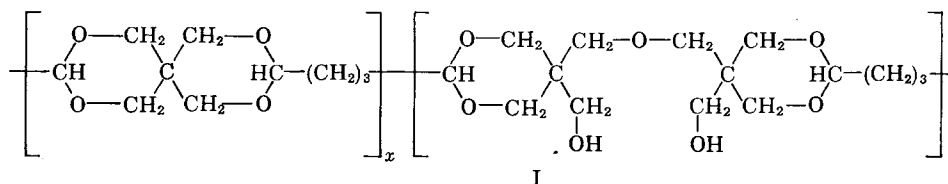
INTRODUCTION

Of the various polyspiroacetal resins described in the preceding paper,¹ those prepared from pentaerythritol-dipentaerythritol mixtures and glutaraldehyde exhibited especially interesting properties (I).

at 20°C. in cresylic acid (Barrett cresylic acid R-7B).

A. Structural Evidence

Evidence supporting the indicated structure of these polymers falls into three categories.



Crosslinked films were flexible, tough, and resistant to solvents and to air oxidation. As a result, a more detailed investigation was carried out on this resin.

EXPERIMENTAL RESULTS

The resins investigated here were prepared by direct condensation as described previously.^{1,2} The four representative polymers examined are listed in Table I. They cover three different polyol ratios and two different levels of molecular weight. As mentioned in the previous article,¹ melting ranges were determined by a Kofler hot stage-polarizing microscope combination, and molecular weights were calculated from hydroxyl end-group analyses. The molecular weights in Table I should be considered mainly as orders of magnitude, since most of these resins swelled slightly but did not dissolve in the pyridine-acetic anhydride reagent. The molecular weight calculated for resin (d) is the least accurate, since the titration values for its endgroups showed the largest per cent standard deviation. For comparison, the intrinsic viscosities also are included. These were obtained

First, these polyspiroacetals have been obtained regularly in nearly theoretical yields. Such evidence, however, is supporting more than definitive.

Secondly, an elemental analysis of copolymer type (b) has furnished good agreement with calculated values.

Calc'd. for $C_{85}H_{148}O_{37}$: C, 58.2%; H, 8.2%. Found: C, 58.4%; H, 8.2%.

The empirical formula is based on the experimental molecular weight, with proper allowance for endgroups.

Finally, the strongest evidence for the structure is based on infrared analysis of these resins. Spectra were obtained with a Beckman IR-5 double-beam infrared spectrophotometer. For these solid samples, a potassium bromide pressed disk technique was used. A spectrum for polymer (b) of Table I is presented in Figure 1a.

This spectrum shows identifiable bands at 2.90 μ (OH), 3.40 and 3.52 μ (aliphatic C-H), 5.76 μ (carbonyl), 6.7-6.8 μ (CH_2 bending), 7.08 μ (tertiary C-H), and 8.21, 8.50, 8.65, 9.02, 9.32, and 9.52 μ (C-O stretching).

Interestingly, the spectra for polymers (a)

TABLE I

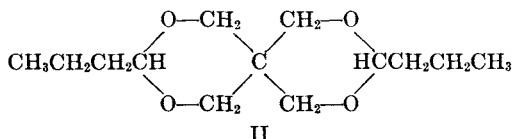
Polyspiroacetals Derived from Pentaerythritol-Glutaraldehyde and (Pentaerythritol-Dipentaerythritol)-Glutaraldehyde

Polymer	Composition		Emulsifier	Yield, %	Kofler melting range, °C.	Molecular weight	[η]
	Pentaerythritol, wt.-%	Dipentaerythritol, wt.-%					
(a)	100	0	None	97	200-202 ^a	1,300	0.16
(b)	88	12	"	94	201-205 ^a	1,750	0.17
(c)	76	24	"	93	181-186 ^a	1,200	0.18
(d)	88	12	Sodium lauryl sulfate, 1%	99	233-238 ^a	~10,000 (?)	0.28

^a Crystallites melted without appearance of liquid.

through (d) in Table I were very similar, except for moderate variations in the relative intensities of some absorption peaks. Apparently infrared analysis, within the monomer limits examined, does not differentiate here between the spiroacetal rings contributed by pentaerythritol and the individual dioxane rings contributed by dipentaerythritol.

For structural evidence, the polymer spectrum in Figure 1a can be compared with the spectrum (Fig. 1b) of pentaerythritol dibutylal (II).



The general similarity in wavelength for many of the major peaks should be good supporting evidence for a similarity in structure.

TABLE II
X-Ray Analysis of Polyspiroacetal Resins

Location of x-ray reflections, A.				Intensity	Remarks
Resin (a)	Resin (b)	Resin (c)	Resin (d)		
7.55	8.03	7.71	8.03	High	Outer edge of diffuse inner ring
5.36	5.42	5.28	5.48	High	—
4.59	4.56	4.60	4.59	Very high	Very broad; may be more than one reflection
3.55	3.54	3.48	3.55	Medium	—
3.15	—	3.18	—	Very low	—
2.71	2.76	2.72	2.71	Medium high	—
2.38	—	2.37	2.37	Very low	—
2.18	—	2.17	2.18	Very low	—

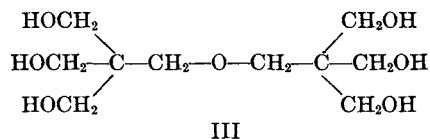
Since the high melting points and relative insolubility of these resins suggested possible crystallinity, x-ray analyses also were obtained. Diffraction pictures for polymers (a) through (d) are shown in Figure 2.

The analyses of these pictures, indicated by the intensities of the x-ray reflections, their diffuseness, and the interplanar spacings, are presented in Table II. In this table, the reflections are listed in order outward from the center of the diffraction pattern.

On the basis of these results, the polymers appear to be about 20-40% crystalline. Significantly, however, a higher molecular weight sample of polymer (a) has been reported to be as much as 72% crystalline.³

B. Properties

1. Influence of Dipentaerythritol Content. For the ultimate combination of film properties sought, dipentaerythritol (III) proved to be a useful co-



monomer. In amounts of up to 25 wt.-% of the polyol mixture, it produced in the original thermoplastic resin a wider solubility range. In the final crosslinked films, it produced a wider curing range for optimum flexibility. The topic of solubility behavior will be discussed in more detail later in this article. However, the effect of dipentaerythritol content on the optimum curing range can be observed by two representative examples in Table III. Films with an optimum amount of cross linking agent were applied from solution as 1.5 mil coatings on AWG #18 copper wire. A wide range of coating speeds—and, hence,

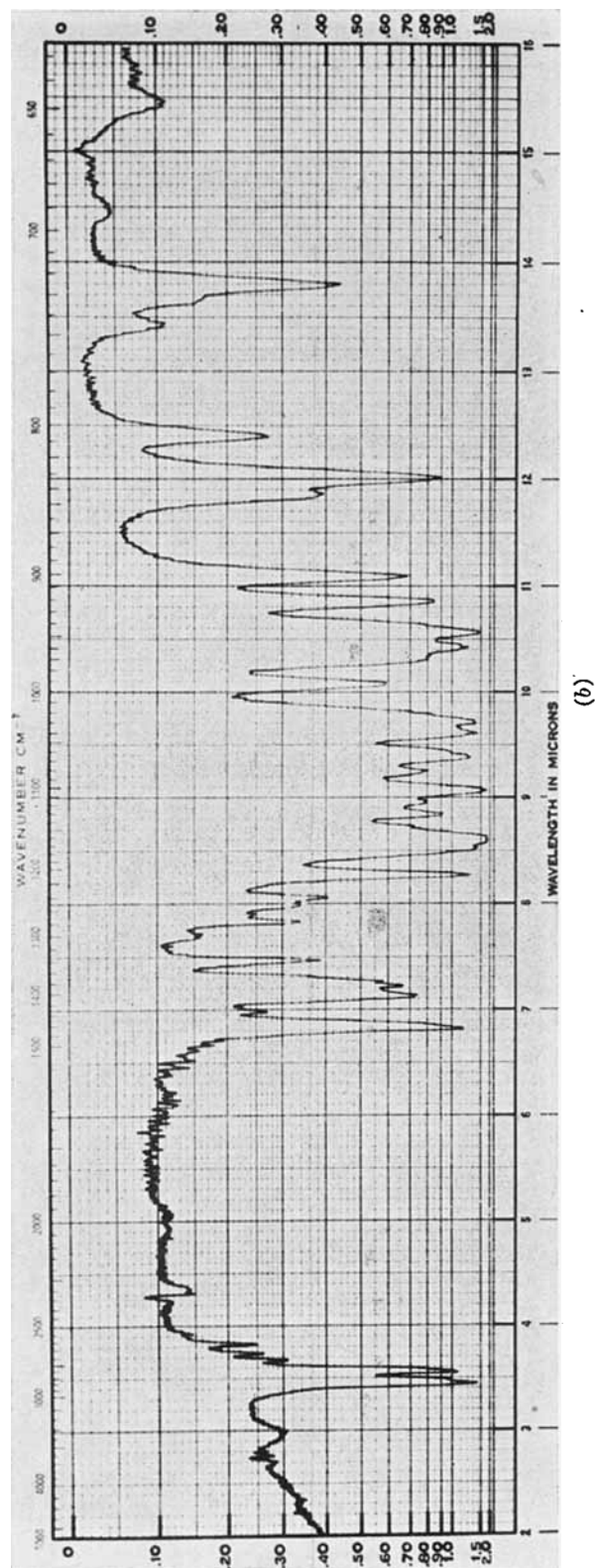
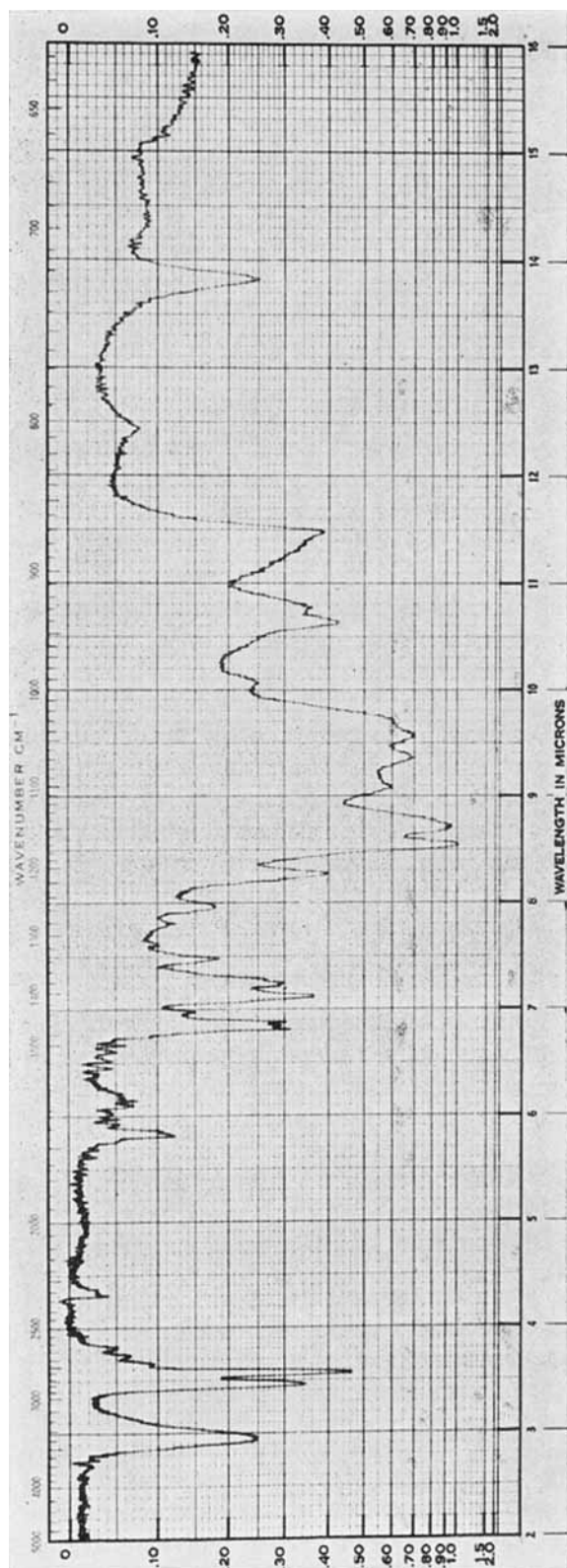


Fig. 1. Infrared spectra of (a) polyspiroacetal (b); (b) pentaerythritol dibutylal.

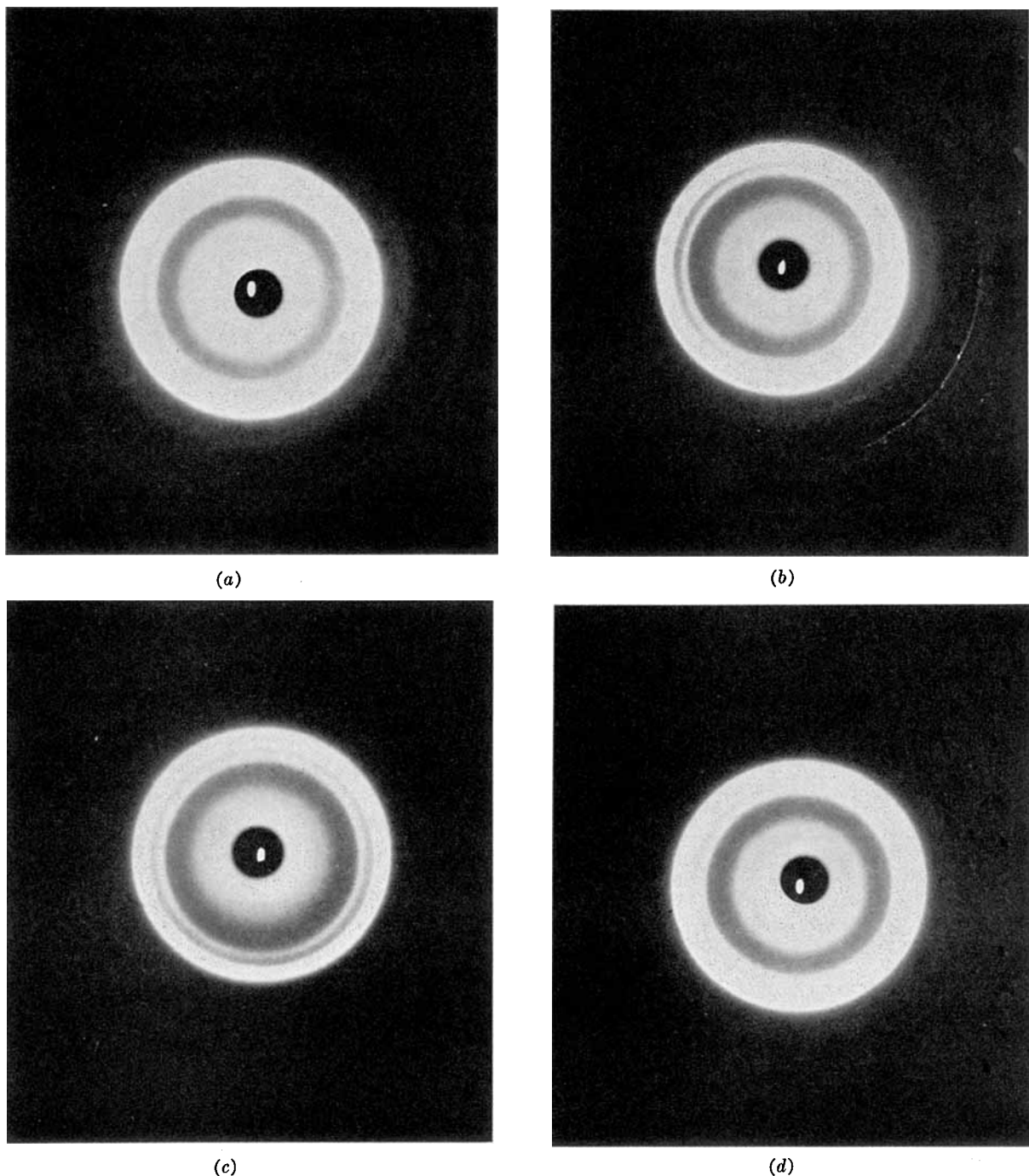


Fig. 2. X-ray diffraction pictures of polyspiroacetals: (a) polymer (a), (b) polymer (b), (c) polymer (c), and (d) polymer (d) of Table I. Analyses taken on the powdered resin.

varying degrees of exposure to heat—was examined under otherwise identical coating conditions (oven temperature, 350°C.). Flexibility of the final coating was measured by a slightly modified A.S.A. procedure.⁴ This involved, after an initial elongation of 25%, wrapping the coated wire ten times

consecutively around a mandrel of its own diameter. Where no cracks could be observed in the stretched coating on the ten twists, the coating was assigned an optimum flexibility value of one diameter. Table III illustrates the influence of dipentaerythritol content on the optimum curing

range for maximum film flexibility. The accumulated results of a large number of such experiments indicate that the variations in Table III are statistically significant.

Both the resin solubility and the film flexibility improvements just mentioned can be explained by an accompanying decrease in crystallinity. Even a visual comparison between the polyspirane and polydioxane units in formula I illustrates the much greater flexibility to be expected in the latter structure.

All attempts to incorporate more than 25% of dipentaerythritol into the polyol mixture produced only increasingly insoluble polymers. In support of these results, the homopolymer of dipentaerythritol and glutaraldehyde could be obtained only as an amorphous, hard, totally insoluble solid. Cross-linking appears to have occurred, but the chemical reactions involved are not certain.

TABLE III

Influence of Dipentaerythritol Comonomer Content on Optimum Film Flexibility Curing Range

Amount dipentaerythritol, wt.-%	Crosslinking agent		Range of coating speeds to obtain one diameter flexibility, ft./min.
	Agent	Amount, wt.-%	
0	Pyromellitic dianhydride	5	1
24	Pyromellitic dianhydride	5	5

2. Molecular Weight. As has been mentioned, molecular weights were determined by hydroxyl endgroup analysis. In a polymerization system which is homogeneous initially and heterogeneous finally, the molecular weight was found to be influenced significantly both by reaction temperature and by some surfactant additives.

In general, the higher the polymerization temperature, the higher was the polymer molecular weight. This is illustrated in Table IV.

So far this behavior is best explained on the basis of solubility. Thus, the higher the polymerization temperature, the longer do the growing polymer chains apparently remain dissolved in the aqueous medium before precipitating.

Similarly, the effect of adding a surfactant like sodium lauryl sulfate agrees with this hypothesis of

TABLE IV
Influence of Polymerization Temperature on Polyspiroacetal Molecular Weight

Polymerization temp., °C.	Polyol composition		Polymer molecular weight
	Pentaerythritol, wt.-%	Dipentaerythritol, wt.-%	
70	88	12	800
100	88	12	1300-1600
70	76	24	1030
100	76	24	2500

improving the solvency of the aqueous reaction medium for the polymer molecules. In Table I, polymers (b) and (d) illustrate clearly the effect of even a small amount of sodium lauryl sulfate on the final polymer molecular weight. In support of this explanation, some recent pertinent work has been reported,^{5,6} in which such high polymers as poly(vinyl acetate), poly(vinyl formal), and poly(vinyl butyral) have been dissolved successfully in aqueous anionic surfactant solutions. In all these reported examples, the solutions were prepared from the bulk polymers and not via an emulsion polymerization.

Some support for the concept of polyspiroacetal polymer growth mainly in solution can be observed by comparing the curves in Figure 3. These curves indicate yields that were obtained by removing from an aqueous polymerization at specified times all of the polymer which had accumulated by precipitation. This system contained 12 wt.-% of dipentaerythritol in its polyol composition. In addition, no surfactant was present. In Figure 3, curve *B* indicates that a moderate increase in the molecular weight takes place during the course of the reaction. Simultaneously, however, the rate of conversion (curve *A*) is so rapid that most of the polymer is formed within 30 min. Within this initial period, the molecular weight of the precipitated polymer for all practical purposes has remained constant at approximately 750. Since the usual overall molecular weight of most runs with this charge has been about 1200-1300, these results point to most of the polymer growth in solution but also a certain amount of post precipitation chain growth in or on the solid phase.

3. Solubility. Of many possible solvents examined, only phenol and some liquid homologs produced solutions which were fluid at room temperature. Another small group of liquids produced polymer solutions which were fluid

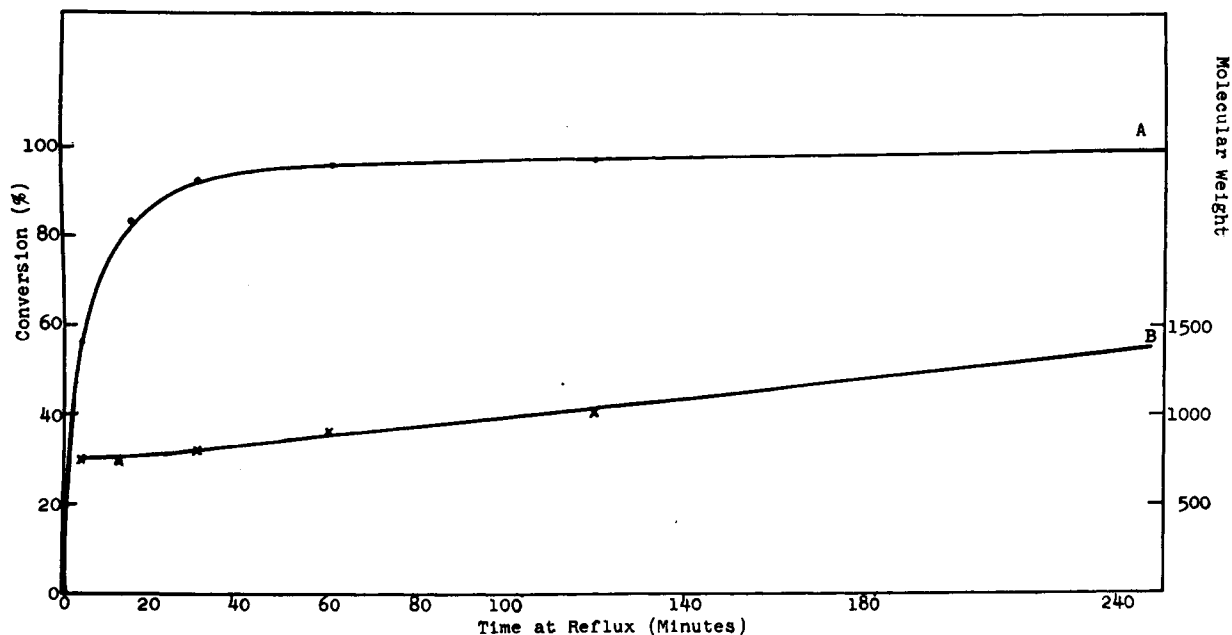


Fig. 3. (A) rate of conversion of polyspiroacetal; (B) molecular weight variation with time.

at elevated temperatures only. The overwhelming majority of liquids either swelled the resins slightly or else did not affect them at all. Table V summarizes these results for resin (b) of Table I.

TABLE V

Classification of Liquids as Solvents for (Pentaerythritol-Dipentaerythritol)-Glutaraldehyde Polyspiroacetals^a

Solvents at room temp.	Solvents at elevated temps.	Nonsolvents	
		Swelling agents	Totally ineffective
Phenol	Furfuryl alcohol	Furfural	Common alcohols
Cresylic acid	Benzyl alcohol	Chlorobenzene	esters
	Dimethyl sulfoxide	Ethylene chloride	
Some liquid phenolic resins	2-Pyrrolidone	Cyclohexanone	ketones
	Tricresyl phosphate		hydrocarbons
	Tricresyl phosphate		chlorinated liquids
	Dimethylformamide		nitromethane
	Dimethylacetamide		
	Pyridine		
	Some liquid epoxy resins		

^a Solution concentration approximately 10%. Resin (b) of Table I used here.

A limited investigation indicates that the solubility behavior is essentially the same for the pentaerythritol - glutaraldehyde homopolymer. However, with 24% dipentaerythritol content, the copolymer displayed a noticeably wider solubility range, both with respect to number of solvents and with respect to tolerance of nonsolvents by cresylic acid solutions.

In addition, these resins exhibited solution and film compatibility with epoxy, phenolic, melamine, and poly(vinyl formal) resins, as well as with blocked polyisocyanates. However, film compatibility in many instances required that the solutions be cast and the films cured at elevated temperatures to prevent formation of a two-phase system before crosslinking.

4. Gelation. One of the properties of the polyspiroacetals observed early was their often rapid conversion to gel in cresylic acid solution. For a better understanding of the phenomenon, some viscosity experiments were carried out.

First, the influence of time, of concentration and of temperature on solution viscosity were examined. The results are presented in Figure 4. All of the samples were prepared by dissolving the resin in cresylic acid at 60°C. and then cooling quickly to 25°C.

In Figure 4, the influence of concentration at room temperature and at 50°C. can be examined. At room temperature, a difference of only 3.6%

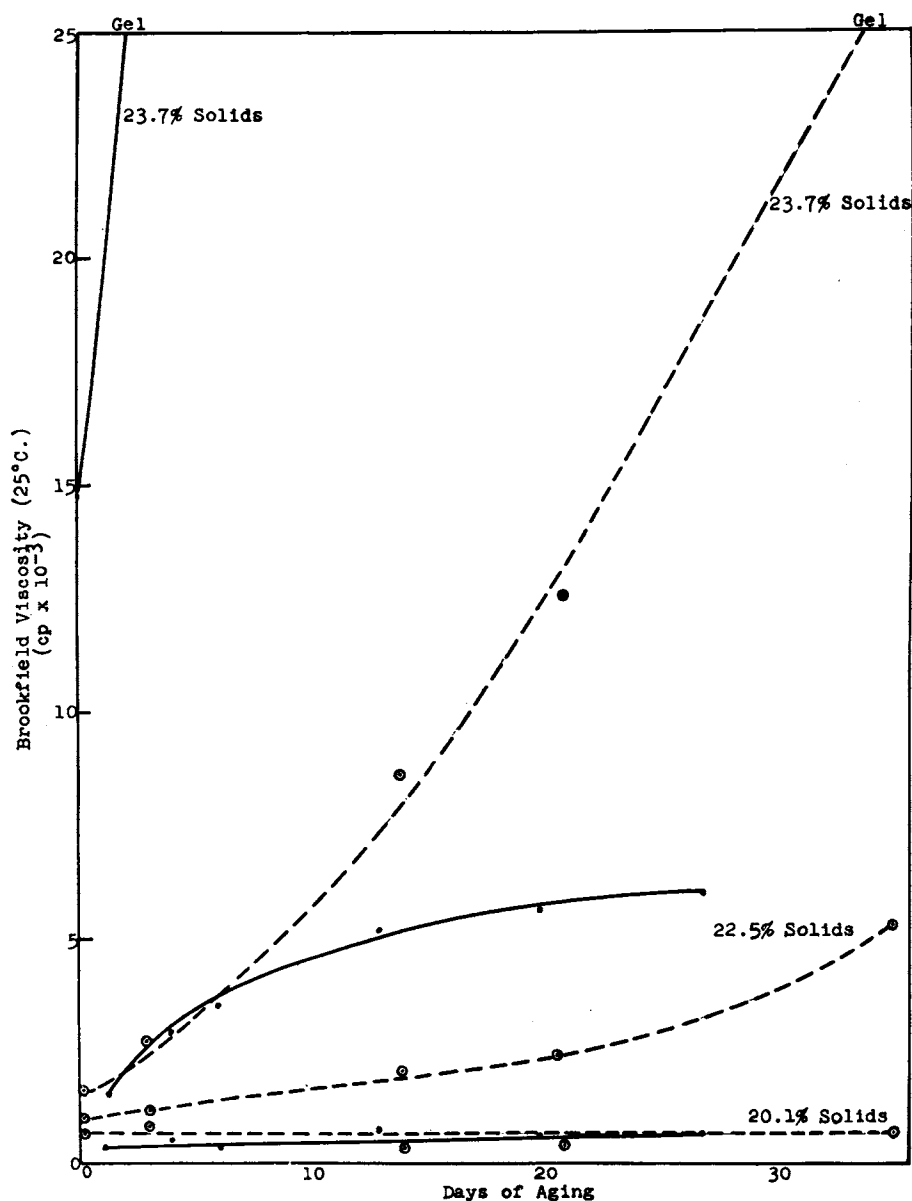


Fig. 4. Influence of concentration, temperature, and time on the solution viscosities of poly-spiroacetal (b), containing 12% dipentaerythritol, in cresylic acid: (—) aged at room temperature; (---) aged at 50°C.

solids could produce solution stability or rapid gelation. Aging the solutions at 50°C. instead of room temperature did improve the solution stability at the higher concentration (23.7%), but the rate of gelation still was relatively rapid. Concentration in the range of 20–23% solids obviously marks a critical border range for solution stability.

At lower concentrations, however, the rate of gelation appears negligible or nonexistent. This is indicated by the viscosities in Table VI. Why the viscosities decreased slightly over the indicated time

period is not understood. However, the data in Table VI do indicate viscosity stability in solutions of lower concentration.

Next, the influence of resin molecular weight on the rate of change in viscosity was examined. Two examples are presented in Figure 5. As can be observed, the higher molecular weight produced a greater rate of viscosity increase. Still other molecular weights produced correlating slopes consistent with the curves in Figure 5.

An obvious question during the work was

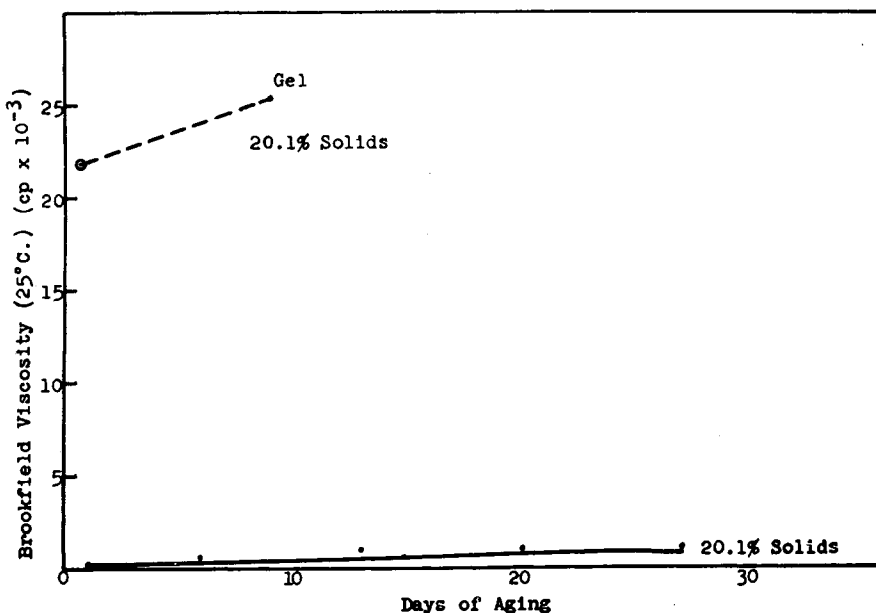


Fig. 5. Influence of molecular weight of polyspiroacetal (containing 12% dipentaerythritol) and time on solution viscosity in cresylic acid: (—) low molecular weight resin; (---) higher molecular weight resin. Solutions of both resins aged at room temperature.

TABLE VI
Effect of Room Temperature Aging on Viscosities of Low Concentration Polyspiroacetal Solutions

Polyspiroacetal (12% dipentaerythritol)	Viscosity (c'poise) in 7 ¹ / ₂ % cresylic acid solns. at 25°C. after aging period indicated		
	0 Days	35 Days	115 Days
1. Low molecular weight	64.5	63.7	63.6
2. Higher molecular weight	123.2	116.2	115.2

whether the gelation was physical, chemical, or a mixture of both. Chemical gelation was a definite possibility, since the polymer molecules have reactive end-and-side groups available for further reaction—both with themselves and the solvent—under existing conditions. The data of Figures 4 and 5 lend some support to the idea of physical gelation. Thus, aging at higher temperatures might be expected to accelerate chemical reactions producing gelation. Actually, aging at higher temperatures decelerated the rate of viscosity increase. In addition, higher molecular weight resins would be expected to have available potentially fewer reactive functional groups for chemical crosslinking. Yet, higher molecular weights underwent an accelerated rate of gelation here.

Additional evidence was sought by the following experiment. A sample of gel formed by the 23.7%

solution (Fig. 4) was heated to 100°C. with stirring. When the gel liquefied and remained fluid at room temperature, the likelihood of a physical phenomenon was further supported. This solution next was diluted to a 7¹/₂% cresylic acid solution, and the latter viscosity was measured. This value then was compared with that of a 7¹/₂% solution taken when the 23.7% solution was first prepared. The results are presented in Table VII. Reversibility in the gel system definitely supports a physical phenomenon, although the higher viscosity value in Table VII indicates that the gel structure may not have been completely broken down by the terminal heating.

TABLE VII
Comparison of Dilute Solution Viscosities Before and After Gelation

Gel sample history	Viscosity of diluted 7 ¹ / ₂ % cresylic acid soln. (20°C.), c'poise
1. Initial 23.7% soln.	64.5
2. Heated and reliquefied 23.7% gel	75.8

Thus far, attempts to inhibit the rate of gelation at higher resin concentrations have been unsuccess-

ful. The additives that were tried either had little effect or accelerated the phenomenon.

According to literature sources,^{7,8} such gelation behavior is dependent greatly upon factors such as polymer crystallinity and secondary valence forces like hydrogen bonding. Other properties described for the polyspiroacetals appear to be consistent with these requirements.

5. Films. Useful films of the polyspiroacetals could be prepared readily by building up the molecular weight through controlled crosslinking. One of the better crosslinking agents has been pyromellitic dianhydride (PMDA), used in amounts of about 5 wt.-% of the resin. For tensile strength measurements, a solution was prepared containing polyspiroacetal (c), 60 g.; pyromellitic dianhydride, 3 g.; Zinc Nuodex solution (solution of zinc naphthenate containing 10% zinc, Nuodex Products Co., Inc., Elizabeth, N. J.), 3 ml.; cresylic acid, 150 ml. Films were coated on tin panels and cured at 310–320°C. for 5 min. Amalgamating the tin interfaces with mercury then allowed the films to be removed. After being conditioned at 73°F. and 50% R.H., these films were tested for tensile strength and elongation at a crosshead speed of 0.2 in./min. The results are presented in Table VIII.

TABLE VIII
Tensile Strength and Elongation of Crosslinked Polyspiroacetal Films

Film thickness, mils	Number of specimens tested	Average tensile strength at break, psi	Average elongation, %
0.7	14	5544	1.7
1.7	13	5628	2.4
3.1	7	8974	6.6

As expected, the general stress-strain pattern of the films in Table VIII was similar to those of other crosslinked materials. They showed no yield point but instead failed at the point of greatest stress.

The flexibility of these same films was good.

Finally, since oxidative thermal stability was one of the initial incentives for developing these resins, the thermal stability of polyspiroacetal magnet wire was examined. Thus, copper wires coated with 1.5 mil films of crosslinked polyspiroacetal (b) were compared with similar specimens coated with a crosslinked polyester based on poly(ethylene terephthalate).⁹

The method of testing is based on an electrical industry procedure.¹⁰ This measures the time to insulation failure of twisted pairs of coated wire aged at elevated temperatures and placed periodically under a 1-kv. load. Enough specimens for statistical significance are used. In Table IX, the lives of the two resin systems are compared at two

TABLE IX
Thermal Life to 1-kv. Failure of Crosslinked Polyspiroacetal and Polyester

Aging temp., °C.	Average 1-kv. dielectric life, Hr.	
	Polyspiroacetal (b), PMDA (5%)	Polyester
200	1100	1800
240	135	180

different aging temperatures. When the values in Table IX are plotted with others on logarithmic graph paper, their curves fall comparatively near each other. By this criterion, the thermal stability of this polyspiroacetal—a polyether—has achieved the order of magnitude of poly(ethylene terephthalate), a polyester.

DISCUSSION

The polyspiroacetals discussed in this paper illustrate the value for film properties of a balance between polymer structural components producing crystallinity and polymer components producing flexibility. As film formers, these polymers are consistent with general ideas already presented in the literature.¹¹ In addition, their oxidative thermal stability, as determined by dielectric resistance measurements, appears to be almost that of the poly(ethylene terephthalate) system. Because of the general oxidative instability of many aliphatic or alicyclic ethers at elevated temperatures,¹² the demonstrated improvement in thermal stability by these polyspiroacetals points in part to the contribution of the spirane neopentyl carbons. These totally substituted carbon atoms, by their probable early termination of progressive unsaturation in the polymer molecule, appear to aid retention of much of the original film flexibility as well as other properties.

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Synopsis

Polyspiroacetal polymers and copolymers derived from pentaerythritol, dipentaerythritol, and glutaraldehyde were prepared and examined for physical properties. Elemental and infrared analyses support the polyspiroacetal structure. X-ray analysis indicates a range of 20–40% crystallinity. Dipentaerythritol was observed to influence in varying degrees the crystallinity, the solubility, and the optimum range of film curing conditions. Resins with more than 25% dipentaerythritol always crosslinked during polymerization. In addition, the variables influencing such resin properties as molecular weight and gelation were examined. Films crosslinked with pyromellitic dianhydride exhibited good flexibility and tensile strength. Moreover,

their oxidative thermal stability was only slightly less than that of crosslinked poly(ethylene terephthalate).

Résumé

On prépare divers polymères polyspiroacétals et copolymères dérivés du pentaérythritol, du dipentaérythrytol et de l'aldéhyde glutarique et on les analyse du point de vue des propriétés physiques. Des analyses élémentaires et infra-rouges permettent de déterminer la structure du polyspiroacétal. L'analyse aux rayons-X indique une cristallinité de l'ordre de 20 à 40%. On observe que la présence de dipentaérythritol influence à divers degrés la cristallinité, la solubilité générale et les conditions optima de vulcanisation du film. Cependant, les résines contenant plus de 25% de dipentaérythritol forment toujours des ponts durant la polymérisation. De plus, on examine les variables influençant des propriétés telles que le poids moléculaire et la gélification de la solution. Les films formant des ponts avec le dianhydride pyromellitique, montrent une bonne flexibilité et une résistance à la tension. En outre, leur stabilité vis-à-vis de l'oxydation thermique est seulement un peu plus faible que celle des ponts de téréphthalates de polyéthylène, si on se base sur les mesures de la chute diélectrique.

Zusammenfassung

Es wurden verschiedene Polyspiroacetalpolymere und -copolymere aus Pentaerythritol und Glutaraldehyd hergestellt und ihre physikalischen Eigenschaften untersucht. Elementaranalyse und Infrarotuntersuchungen liefern eine Stütze für die Polyspiroacetalstruktur. Die Röntgenanalyse ergibt eine Kristallinität von 20–40%. Das Vorhandensein von Dipentaerythritol beeinflusst die Kristallinität, die allgemeine Löslichkeit und den Optimalbereich der Behandlungsbedingungen für Filme in verschiedenem Ausmass. Harze mit mehr als 25% Dipentaerythritol vernetzten während der Polymerisation. Weiters wurden die Variablen untersucht, die solche Eigenschaften des Harzes wie Molekulargewicht und Gelbildung in Lösung beeinflussen. Mit Pyromellithsäuredianhydrid geeignet vernetzte Filme zeigten eine gute Flexibilität und Zugfestigkeit. Auch war ihre thermisch-oxydative Beständigkeit, wie die Messung des dielektrischen Durchschlags zeigte, nur wenig schlechter als die von vernetztem Polyäthylenterephthalat.

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