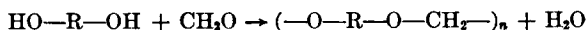


Properties of Polyformals of Alicyclic Diols*

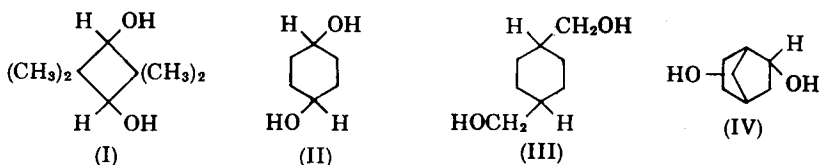
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Introduction

Polyformals were first prepared by Hill and Carothers,^{1,2} who heated aliphatic diols and dibutyl formal in the presence of acidic catalysts. These polymers had very low melting points (below 75°C.) and, apparently, no higher melting points have been reported for polyformals. Attempts were made to obtain higher-melting polyformals by this method with several alicyclic diols, but polymers of high molecular weight were not obtained and the products were highly colored.³ A new process for preparing these polymers with high molecular weights and substantially no color was then developed.^{3,4} In this process a diol, paraformaldehyde, and an acidic catalyst are heated in a water-immiscible solvent, and water is azeotropically removed. Depending upon the type of diol, the polymer is built up in this solution or in the solid phase. The reaction may be represented as follows:



The following alicyclic diols were used: *cis*-, *trans*-, and 1:1 *cis/trans* mixture of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (I), *trans*-1,4-cyclohexanediol (II), *trans*-1,4-cyclohexanedimethanol (III), and 2,5 (or 2,6)-norbornanediol (IV).



Details concerning the preparations of these polyformals are given in a recent publication.³ The properties of the polyformals are presented in this paper. Most of the properties of the 2,2,4,4-tetramethyl-1,3-cyclobutanediol polyformal were determined from the commercially available 1:1 *cis/trans* mixture; wherever polymers of the individual *cis* and *trans* isomers were used they are specifically indicated.

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Physical Testing Methods

Inherent viscosities were measured in 60:40 phenol/tetrachloroethane. Unless otherwise indicated, the softening ranges were determined under polarized light. The lower figure of each range was the temperature at which the polymer began to soften; the upper figure was the temperature at which the polymer began to flow. The differential thermal analysis (DTA) measurements were made under nitrogen with a heating rate of 5°C./min.

The relative hydrolytic stabilities of the polyformals were determined by heating equal amounts of the polymers (with substantially the same particle size) with excess 10% hydrochloric acid at 100°C. Since the alicyclic diols were soluble in hot water, hydrolysis was complete when solution was attained. Hydrolysis was also carried out with 10% hydrochloric acid, 10 and 20% sulfuric acid, and 10% sodium hydroxide on amorphous films of the tetramethylcyclobutanediol polyformal. These films were obtained by pressing and then quenching.

The tetramethylcyclobutanediol polymer was injection-molded in a Watson-Stillman 1 oz. injection-molding press to give $\frac{1}{8}$ in. buttons, $\frac{1}{16}$ in. tensile bars, and $\frac{1}{8}$ in. flexure bars. Standard ASTM procedures were used for measuring tensile properties,⁵ Izod impact strength,⁶ Rockwell hardness,⁷ and electrical properties.^{8,9} The heat-distortion temperatures (2% deflection) were measured in a forced-convection oven with a $\frac{1}{8}$ in. \times $\frac{7}{8}$ in. flexure bar.¹⁰ The button impact strength, which meas-

TABLE I
Properties of Polyformals of Alicyclic Diols

Diol	Softening range, °C. ^a	DTA measurements		
		Transform. temp., °C. ^b	M. p., °C.	Hydrolysis time, min. ^c
1:1 <i>cis/trans</i> -2,2,4,4-Tetramethyl-1,3-cyclobutanediol	283-291	177	262	>360
<i>cis</i> -2,2,4,4-Tetramethyl-1,3-cyclobutanediol	284-289	213	285	—
<i>trans</i> -2,2,4,4-Tetramethyl-1,3-cyclobutanediol	275-280	197	260	—
<i>trans</i> -1,4-Cyclohexanediol	206-210	None	209	20
<i>trans</i> -1,4-Cyclohexanedi-methanol	83-86	—	78	70
2,5 (or 2,6)-Norbornanediol	83-98	—	—	20

^a The softening ranges of the tetramethylcyclobutanediol polyformals were determined under nitrogen in sealed capillaries. In air these polymers melted at 200-210°C. unless an antioxidant was present. The softening ranges of the other polymers were determined in air with polarized light; they melted at approximately the same temperatures under nitrogen.

^b The temperature at which one crystalline form changes to another.

^c Time for solution in 10% hydrochloric acid at 100°C.

ures the shatter resistance of the buttons ($1\frac{1}{8}$ in. diameter), was determined on a Tinius Olsen Impact Tester.

The tetramethylcyclobutanediol polyformal was cast into a film from chloroform and pressed into films at 310°C. by conventional techniques. The tensile properties were measured in an Instron Tensile Tester in accordance with standard ASTM procedures.¹¹ The heat-distortion temperatures (2% deflection) were measured in a forced-convection oven.¹⁰

The tetramethylcyclobutanediol polymer was also melt-spun into fibers at 300°C. The tenacity-elongation data were obtained on a constant-rate-of-elongation tester which is similar to an Instron Tester. The elastic modulus was obtained from the stress-strain diagram by measurement of the slope of the initial straight portion of the diagram. The bar sticking temperature was obtained by determining the minimum temperature at which yarn, under very light tension, stuck to a heated, polished, stainless-steel bar. Flow points were obtained by measuring the temperature of this bar at the point where the yarn showed a tendency to pull apart under a given load. The fabric stiffening temperature was obtained by determining the minimum temperature at which the fabric became stiff after being heated by an iron for 2 min.

Results and Discussion

Softening and Melting Points

The softening and melting points of the polyformals are given in Table I. These values are referred to as softening points when they were determined in the conventional manner and melting points when they were determined by DTA. Very unusual are the high values of the tetramethylcyclobutanediol polymers. As stated above, no melting points of polyformals above 75°C. have been reported, apparently.

Because of oxidative degradation, the tetramethylcyclobutanediol polyformals melted appreciably lower in the presence of air. These polymers could be protected, however, by the addition of conventional antioxidants. This was accomplished simply by stirring a suspension of the polymer particles (20 to 40 mesh) in an acetone solution of the antioxidant while the acetone was evaporated.

The use of DTA curves was convenient in determining the effectiveness of various types and amounts of antioxidants. The samples were heated in an oxygen atmosphere at 5°C./min., and the temperature at which oxidation took place was indicated by a large exothermic peak. Under these conditions oxidation of the untreated tetramethylcyclobutanediol polymer started at 140–150°C. and the exothermic peak occurred at 175–185°C. One of the most effective antioxidants was found to be *N*-phenyl-2-naphthylamine. When it was present in a concentration of 1%, oxidation of the polymer did not begin until 257°C.

The crystalline melting points of the polyformals were determined under nitrogen by DTA. Surprisingly, the curves also showed that changes took

place in the tetramethylcyclobutanediol polymers below their melting points. Apparently these changes are the same as those observed by x-ray diffractometric analysis, which showed that one crystalline form was transformed to another. According to the DTA and x-ray curves, these transformations are reversible, and the polymers revert to their initial crystalline forms on cooling. This phenomenon will be discussed in more detail in a separate paper.¹²

Solubility

All of the polymers were soluble in hot tetrachloroethane but, unexpectedly, the polyformal of the tetramethylcyclobutanediol isomer mixture was also soluble in chloroform and in hot toluene. The polyformals of cyclohexanedimethanol and norbornanediol were also soluble in chloroform and toluene, but the polyformal of cyclohexanediol was insoluble. All of the polymers were insoluble in methanol, ethyl acetate, and naphtha.

Hydrolytic Stability

Since formals are readily hydrolyzed by acids, polyformals can be expected to be unstable to acids. The polyformals of two secondary diols, cyclohexanediol and norbornanediol, were easily hydrolyzed by 10% hydrochloric acid at 100°C. (Table I). The tetramethylcyclobutanediol polyformal, on the other hand, was unusually resistant to hydrolysis. A film did not begin to disintegrate in 10% hydrochloric acid at 100°C. until after 4 hrs., and in 20% sulfuric acid until after 33 hrs. (Table II). The time for a film to begin to disintegrate in 10% aqueous sodium hydroxide at 100°C. is not known, but after 7 days a film was still tough. This outstanding resistance to alkaline hydrolysis is unusual for a condensation polymer.

TABLE II
Hydrolytic Stability of Tetramethylcyclobutanediol Polyformal Films^a

Hydrolysis medium	Temp., °C.	Time ^b
10% Hydrochloric acid	100	4 hr.
10% Sulfuric acid	100	6 hr.
20% Sulfuric acid	100	33 hr. ^c
10% Sodium hydroxide	100	>7 days ^d
Water ^e	110	>10 days ^f

^a Pressed at 280°C. and immediately quenched; thickness was 1 mil.

^b Time before disintegration of the film began.

^c Film was still tough after 24 hrs.

^d Film was still tough after 7 days.

^e Film was heated at 100% relative humidity in a sealed bottle.

^f Film was still tough after 10 days; during this period the inherent viscosity decreased only 16% (0.81 to 0.68).

*Molding, Film, and Fiber Properties of the
Tetramethylcyclobutanediol Polyformal*

The properties of the molding plastic, film, and fibers obtained from the polyformal of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (1:1 *cis/trans* mixture) are given in Tables III, IV, and V. These properties of the plastic were not appreciably affected by the presence or absence of an antioxidant,

TABLE III
Properties of Tetramethylcyclobutanediol Polyformal Plastic^a

Tensile properties	
Break strength, psi	4340
Yield strength, psi	—
Elongation, %	20
Modulus, psi	206,000
Heat-distortion temp., °C.	
At 66 psi	178
At 264 psi	119
Impact strength, button, in.-lb.	
At 25°C.	30
At -40°C.	23
Impact strength, Izod, ft.-lb./in. of notch	4.2
Rockwell hardness, <i>R</i>	51
Specific gravity	1.05
Electrical properties	
Dielectric constant at 0.1-100 kcycles and 25-150°C.	2.84-2.70
Dissipation factor at 0.1-100 kcycles and 25-150°C., %	0.14-0.04
Resistivity, ohm-cm.	6.6×10^{15}

^a Injection-molded at 560°F. (293°C.). Inherent viscosity 1.03 (1.16 before molding). polymer had been thermally stabilized by treating with refluxing acetic anhydride.

TABLE IV
Properties of Tetramethylcyclobutanediol Polyformal Films

	Cast film ^b	Pressed film ^a	
		Unstretched	Stretched ^c
Tensile properties			
Yield strength, psi	3800 ^d	2040	6700 ^d
Break strength, psi	2500	2160	12,400
Elongation, %	28	175	24
Modulus, psi	180,000	82,000	315,000
Heat-distortion temp., °C.			
At 5 psi	161	42	188
At 50 psi	145	35	185
Specific gravity	1.04	1.04	1.07
Refractive index at 27°C.	1.480	—	—

^a Polymer contains 1% *N*-phenyl-2-naphthylamine; pressed at 310°C. and immediately quenched; inherent viscosity 1.08 (1.36 before pressing).

^b Cast from chloroform; inherent viscosity 1.2.

^c Stretched 150% at 75°C. and heat-set at 208°C. for 30 sec.

^d 2% offset yield.

but the thermal properties of the fiber (bar sticking temperature, etc.) were substantially lower when an antioxidant was not present.

The dielectric constant and dissipation factor (Table III) were remarkably constant over the range of 0.1–100 kcycles and 25–150°C. In this respect the polymer is perhaps superior to all known polyesters.

There was a dramatic improvement in the properties of the pressed film when the film was stretched and heat-set (Table IV). As would be expected, these properties were superior to those of the cast film. Possibly appreciably better properties can be obtained by extruding the film and studying the stretching and heat-setting conditions.

The properties of melt-spun fibers obtained in a preliminary experiment are given in Table V. It is somewhat surprising that the bar sticking temperature is higher than the flow point. The fabric stiffening temperature, which is a truer indication of the maximum-use temperature, is also higher.

TABLE V
Properties of Tetramethylcyclobutanediol Polyformal Fiber^a

Tensile properties	
Tenacity, g./denier	2.4
Elongation, %	9
Elastic modulus, g./denier	43
Bar sticking temp., °C.	235–242
Flow point at 0.2 g./denier, °C.	185
Fabric stiffening temp., °C.	225
Shrinkage, %	
In boiling water	0
In air at 175°C.	1.5

^a Polymer contains 1% *N*-phenyl-2-naphthylamine; melt-spun at 300°C.; inherent viscosity 1.1 (1.2 before spinning); drafted in air at 180°C. with draft ratio of 4.3 and then heated for 5 min. at constant length at 175°C.

The structure of the tetramethylcyclobutanediol polyformal makes the polymer very unusual. Because of its many unusual and unexpected properties, this polymer will be the subject of further study.

We would like to acknowledge the assistance and suggestions of Russell Gilkey, of these laboratories.

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Synopsis

The properties of the polyformals of several alicyclic diols were determined. Particularly unusual were the properties of the polyformal of 2,2,4,4-tetramethyl-1,3-cyclobutanediol. The polymer of the 1:1 *cis/trans* diol mixture had a reversible transition in crystalline phase at about 177°C. and a crystalline melting point of 262°C. The polymer was soluble in chloroform and in hot toluene. It was resistant to hydrolysis, particularly alkaline hydrolysis. Physical properties were determined on molded specimens obtained by injection-molding, on films obtained by casting and pressing, and on fibers obtained by melt-spinning.

Résumé

On a déterminé les propriétés des polyformals de plusieurs diols alicycliques. Des particularités inhabituelles se présentent dans les propriétés des polyformals de 2,2,4,4-tétraméthyl-cyclobutanediol. Le polymère du mélange de diol 1/1 *cis/trans* montre une transition réversible en phase cristalline à environ 177°C. et un point de fusion cristallin à 262°C. Le polymère est soluble dans le chloroforme et le toluène à chaud. Il est résistant à l'hydrolyse, particulièrement à l'hydrolyse alcaline. On a déterminé des propriétés physiques sur des spécimens moulés obtenus par moulage par injection, sur des films obtenus par coulée et pression, et sur des fils obtenus par filage à l'état fondu.

Zusammenfassung

Die Eigenschaften der Polyformale einiger alicyclischer Diole wurden bestimmt. Besonders ungewöhnliche Eigenschaften zeigte das Polyformal von 2,2,4,4-Tetramethyl-1,3-cyclobutandiol. Das Polymere aus der 1:1 *cis-trans*-Diolmischung besass eine reversible Umwandlung in der kristallinen Phase bei etwa 177°C. und einen Schmelzpunkt von 262°C. Das Polymere war in Chloroform und heissem Toluol löslich. Es war gegen Hydrolyse, besonders gegen alkalische Hydrolyse, beständig. Physikalische Eigenschaften wurden an Spritzgussproben, an gegossenen und gepressten Folien und an schmelzgesponnenen Fasern bestimmt.

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