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Cyclic and Polymeric Formals[1]

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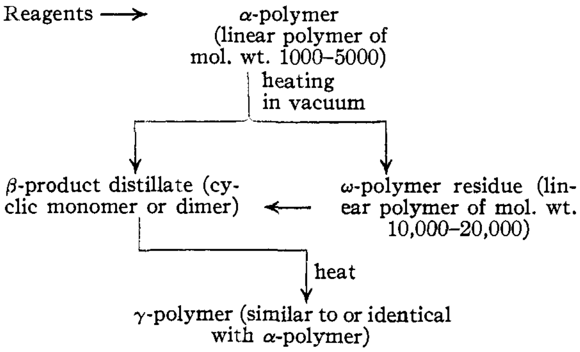
Macrocyclic esters and anhydrides can be obtained by depolymerizing the corresponding linear polymers.[2] The various relations involved are shown in the following diagram.



Heating the α-polymer causes (a) formation of traces of cyclic monomer and dimer derived from one and two structural units of the molecular chain and (b) coupling of the α-polymer chains to form the still longer chains of ω-polymer. Linear polyesters and polyanhydrides result from reversible bifunctional condensations. In the ideal case, it would be possible to establish an equilibrium among all the species of α-, β- and ω-forms, and constant removal of the β-forms by distillation should result in a complete transformation of the sample into cyclic monomer and/or dimer. This ideal is closely approached in some cases, the chief critical factors involved being inherent mobility of the link, catalysis, temperature and speed with which possible volatile products are withdrawn.

The fact that acetal interchanges are smoothly reversible reactions suggests that it should be possible to realize all these transformations among the acetals derived from glycols. For formals this is indeed true, and the compounds now reported constitute a new family of linear polymers and large rings. Here also, as with the esters and anhydrides, a single member may be obtained in the form of a macrocrystalline solid, an odorous (*e. g.*, musk-like) liquid, or a tough microcrystalline mass capable of being drawn into strong, pliable, highly oriented, silk-like filaments.

Preparation and Behavior of Formals.—Heating of a glycol with dibutyl formal and an acidic catalyst at about 150° results in acetal interchange with the distillation of butanol

$$\mathrm{HO(CH_2)_nOH + BuOCH_2OBu \longrightarrow \ldots\text{—}CH_2O(CH_2)_nO\text{—}\ldots + 2BuOH}$$

Trimethylene or tetramethylene glycol thus yields a mobile liquid easily distilled *in vacuo*, and the major primary product is, therefore, presumably the cyclic monomer. When the glycol is pentamethylene, or a higher one, the residue remaining from the removal of the alcohol is a viscous liquid. To ensure complete removal of volatile products, it is heated to 200–220° at low pressure. The remaining non-volatile product is then the α-polyacetal. That derived from decamethylene glycol, for example, is a waxy solid which crystallizes as a powder from hot ethyl acetate and then melts at 56.5–57°. Its observed apparent molecular weight was 2190. Similar α-polyformals were obtained from pentamethylene, hexamethylene, tetradecamethylene, and octadecamethylene glycols as well as from triethylene glycol. The last gave a sirupy product which showed no tendency to crystallize; the others were all solids.

When the α-polyformals were heated to 230–250° at low pressure in a still provided with a condenser placed close to the evaporating surface,[3] conversion to the β and ω forms occurred. Compared with the polyesters derived from carbonic acid, the rate of distillation was quite slow; in this respect, the polyformals resembled the previously described[3] polyesters derived from the higher dibasic acids such as sebacic; the tendency toward ω-polymer was greater than toward the β forms, and as the viscosity of the residue increased, the rate of distillation became less. The ultimate yield of distillate was, therefore, relatively small, and, as in the case of those polyesters that manifested a similar behavior, the distillates were largely the cyclic dimers which were without exception definitely crystalline solids of sharp melting points. The presence of cyclic monomer in the distillate could be inferred from the characteristic odor, and the monomer from

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[1] Paper XXIV on Polymerization and Ring Formation; Paper XXIII, THIS JOURNAL, **56**, 455 (1934).

[2] Hill and Carothers, *ibid.*, **54**, 1569 (1932); **55**, 5023, 5031 (1933).

[3] *Ibid.*, **55**, 5035 (1933).

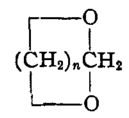
pentamethylene formal was obtained in sufficient quantity to permit isolation and purification. The α-polyformal from triethylene glycol differed from the other formals of similar unit length. It was a viscous liquid and when heated in vacuum at 200–250° it depolymerized very rapidly. The product apparently consisted essentially of monomer, which was isolated in a state of purity and in considerable quantity by fractional crystallization of the distillate.

Polymerization of Cyclic Formals.—The possible polymerization of cyclic acetals has occupied an important place in speculations concerning cellulose, starch, etc.,[4] but no clear example of a polymerization originating in an acetal linkage *per se* has been adduced. Among cyclic esters, rings of more than 5 atoms generally polymerize on being heated with catalysts and those of 6 atoms occupy a peculiar position because this transformation occurs with especial facility and is easily reversible.[5] It is of interest in this connection that trimethylene formal (6-ring) could not be induced to polymerize. The monomeric tetramethylene, pentamethylene and triethylene glycol formals, however, quickly became more viscous when heated (*e. g.*, at 150°) in the presence of a trace of sulfonic acid. Dimeric decamethylene formal (26-ring) when treated in this manner was converted to a microcrystalline solid having approximately the same melting point and molecular weight (2500) as the α-polymer from which the dimer was originally derived. Results obtained with monomers are indicated in the table.

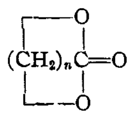
VISCOSITY CHANGE (IN ARBITRARY UNITS) OF MONOMERIC FORMALS HEATED WITH A TRACE OF CAMPHOR SULFONIC ACID

Formal	Ring size	Successive heating intervals	Time of flow, sec.
Trimethylene	6	Initial	4.5
		+2 hrs. at 100°	4.5
		+1.5 hrs. at 150°	4.5
Tetramethylene	7	Initial	4.5
		+2 hrs. at 100°	4.5
		+0.5 hr. at 150°	35
		+1.0 hr. at 150°	∞
Pentamethylene	8	Initial	4.5
		+2 hrs. at 100°	13
		+0.5 hr. at 150°	16

Odors.—The remarkable parallelism between the odors of macrocyclic ketones, lactones, carbonates, malonates, oxalates, sebacates, etc., of similar ring size previously reported[6] suggested that for musk-like odor the only requirement is a C=O group in a ring of suitable size. Meanwhile, Ruzicka[7] has extended his own researches and observed that the cyclic imine $\underline{-(CH_2)_{16}-NH-}$ has a musk-like odor, thus demonstrating that the presence of the carbonyl group is not necessary. The odors of the cyclic formals indicated in Table I now point to the same conclusion. Only the compounds marked * were actually isolated, but there is no doubt that the characteristic odor of the crude distillate was in each case due to cyclic monomer. The odors of the formals I were so strikingly similar to those of the corresponding carbonates II as to be almost indistinguishable from them.



(I)



(II)

TABLE I

ODORS OF MONOMERIC FORMALS

Glycol from which formal is derived	Ring size	Odor
*Tetramethylene	7	Sweet and penetrating
*Pentamethylene	8	Minty, camphoraceous
Hexamethylene	9	Minty
Nonamethylene	12	Earthy, camphoraceous
Decamethylene	13	Cedar, camphoraceous
Tetradecamethylene	17	Musk-like
Octadecamethylene	21	No odor
*Triethylene glycol	11	Faint, flowery

Fibers from ω-Polyformals.—ω-Polyesters and polyanhydrides can be drawn out into continuous filaments which readily accept permanently a high degree of orientation along the fiber axis and have very good strength and pliability.[8] These materials are in fact the only truly synthetic fibers for which any measured strengths have been reported although it appears that continuous oriented filaments can also be drawn from polyoxymethylene and polyethylene oxide[9] when their molecular weights are sufficiently high. In all these classes of compounds as in cellulose itself,

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[4] See, for example, Hibbert and Timm, THIS JOURNAL, **45**, 2433 (1923); Hill and Hibbert, *ibid.*, 3108, 3124; Helferich and Sparmberg, *Ber.*, **64**, 104 (1931); Bergmann and Miekeley, *ibid.*, **62**, 2297 (1929).

[5] Carothers and Van Natta, THIS JOURNAL, **52**, 314 (1930); Hill and Carothers, *ibid.*, **55**, 5037 (1933).

[6] *Ibid.*, **55**, 5039 (1933).

[7] Ruzicka, Salomon and Meyer, *Helv. Chim. Acta*, **17**, 882 (1934).

[8] THIS JOURNAL, **54**, 1579 (1932).

[9] Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932, p. 262; Sauter, *Z. physik. Chem.*, **21B**, 161 (1933).

very long molecules are made up of units joined through C–O bonds. In the ω-polyformals as in cellulose, this linkage is actually an acetal linkage. It is not surprising then that the ω-polyformals can also be drawn into oriented filaments. x-Ray diagrams for unoriented and oriented ω-polydecamethylene formal are shown in Figs. 1 and 2.

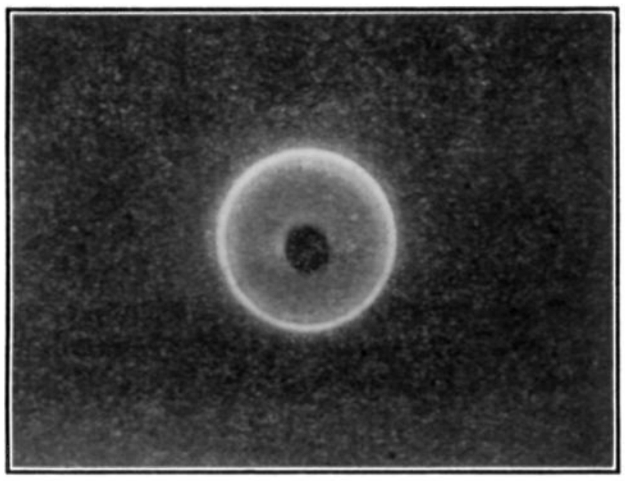

Fig. 1.—x-Ray diffraction pattern of ω-decamethylene formal.

Ease of Depolymerization.—The most obvious factor influencing ease of depolymerization is the reactivity characteristic of the type of linkage involved. Polyanhydrides are depolymerized much more readily than polyesters. The relative ease of hydrolysis of the ethylene acetals derived from formaldehyde, acetaldehyde and acetone is approximately 1:4000:44,000.[10] That the alkylene formals depolymerize with difficulty is therefore not surprising. One might expect that it would be very much easier to form macrocyclic acetals from other aldehydes and ketones; unfortunately, various other complications arise in these cases.

Rings of 9 to 12 atoms are especially difficult to form and in some cases exceptionally unstable. This may be attributed to repulsions arising from methylene hydrogens whose external radii are forced by the shape of the molecule into a space too small to receive them.[11] As we have already pointed out,[12] oxygens in a chain may relieve strains of this type since they carry no hydrogens and their valences are probably more flexible than those of carbon.[13] Further presumed illustrations of the oxygen effect: polyformals (III) are definitely more difficult to depolymerize than are polycarbonates (IV), and triethylene glycol formal (V) is very much more easily depolymerized than alkylene formals of similar unit length.

$$\cdots\text{—}(\mathrm{O{-}R{-}O{-}CH_2})_x\text{—}\cdots \qquad \cdots\text{—}(\mathrm{O{-}R{-}O{-}CO})_x\text{—}\cdots$$

(III) (IV)

$$\cdots\text{—}(\mathrm{OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2})_x\text{—}\cdots$$

(V)

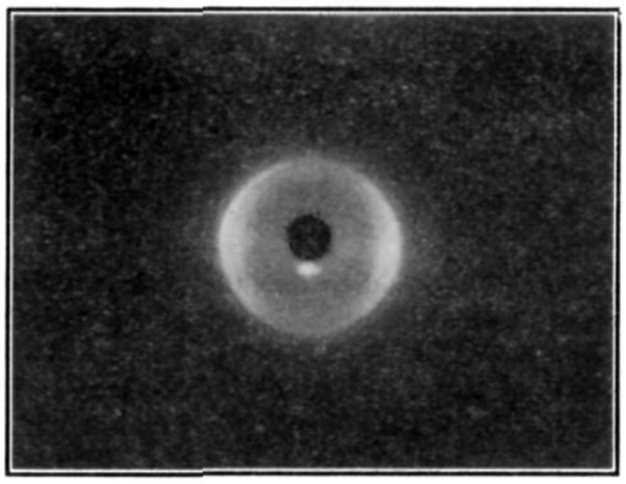

Fig. 2.—x-Ray diffraction pattern of cold-drawn ω-decamethylene formal.

Experimental Part

Tetramethylene Formal.—Difficultly separable mixtures were formed when the interchange method was applied to this compound. The most convenient method was to distil the glycol (30 g.) with trioxymethylene (10 g.) and a trace of camphor sulfonic acid (bath temperature, 210°). Fractionation of the distillate gave some tetrahydrofuran, and then a liquid boiling at 112–117° which was washed with strong caustic and redistilled at low pressure. It had d^{20}_{4} 1.0022; n^{20}_{D} 1.4310; M_D found, 26.34; M_D calcd., 26.38.

Decamethylene Formal.—Dibutyl formal (0.2 mole) with a 5% excess of decamethylene glycol and 0.1 g. of ferric chloride gave fairly rapid reaction at 165° (bath). The temperature was raised to 200° during two hours and heating continued for one and one-half hours in a good vacuum. The distillate was 98% of the theoretical calculated as butyl alcohol; the yield of residual *α-polymer* was 103%. When cold, it was a light brown rather hard wax. When dissolved in hot ethyl acetate (150 cc. for 17.5 g.), it separated in the form of a microcrystalline powder; soluble in chloroform, benzene, carbon tetrachloride and xylene; insoluble in alcohol, ether, petroleum, hydrocarbons and acetone.

β-Product.—Eight grams of the crude α-polymer was heated in a 250-cc. suction flask provided with a test-tube through which water could be circulated to act as an internal condenser;[14] temperature, 230–250° (bath); pressure, about 1 mm. After forty-eight hours 2 g. of distillate had collected. It was a pasty mixture of liquid and crystals having a pleasant camphoraceous odor. The solid portion after crystallization from alcohol was odorless and melted at 93–94°. It was the *cyclic dimer*.

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[10] Leutner, *Monatsh.*, **60**, 317 (1932).

[11] Stoll and Stoll-Comte, *Helv. Chim. Acta*, **13**, 1185 (1930); Hill and Carothers, THIS JOURNAL, **55**, 5023, 5031 (1933).

[12] THIS JOURNAL, **55**, 5050 (1933).

[13] *Cf.* Sidgwick, "Annual Reports of the Progress of Chemistry for 1932," p. 73.

[14] THIS JOURNAL, **55**, 5035 (1935).

TABLE II

DATA ON FORMALS

Name of formal	M. p., °C.	Formula	Analytical data					
			Calcd.			Found		
			C	H	Mol. wt.	C	H	Mol. wt. in freezing benzene
Tetramethylene, monomer	B. p. 112–117	$C_5H_{10}O_2$	58.8	9.9	102	59.6	10.0	103
Decamethylene, α-polymer	56–57	$(C_{11}H_{22}O_2)_x$	70.9	11.9	$(186)_x$	68.9	11.7	2190
Decamethylene, dimer	93–94	$(C_{11}H_{22}O_2)_2$	70.9	11.9	372	70.8	12.1	368
Pentamethylene, dimer	55–56	$(C_6H_{12}O_2)_2$	62.1	10.4	232	61.8	10.5	262[a]
Pentamethylene, monomer	B. p. 40–44 (11 mm.)	$C_6H_{12}O_2$	62.1	10.4	...	62.0	10.8	...
Hexamethylene, dimer	71–72	$(C_7H_{12}O_2)_2$	64.6	10.8	260	64.0	10.6	257
Nonamethylene, dimer	68–69	$(C_{10}H_{20}O_2)_2$	69.8	11.6	344	69.8	11.6	334[a]
Tetradecamethylene, α-polymer	68–69	$(C_{15}H_{30}O_2)_x$	74.4	12.4	$(242)_x$	73.1	12.1	2480
Tetradecamethylene, dimer	103.5–104	$(C_{15}H_{30}O_2)_2$	74.4	12.4	484	74.4	12.5	503
Triethylene glycol, monomer	18–20	$C_7H_{14}O_4$	51.9	8.6	162	51.6	8.4	161

[a] In boiling benzene.

ω-Polymer.—The residue from the above was a hard, very tough, opaque, leather-like mass. It melted (became transparent) at 58–63°, but at this temperature it was too stiff to flow and showed considerable resistance to deformation. At slightly higher temperatures, it could be drawn out into thin strips or filaments which could be stretched and cold-drawn.[15] The product then showed fiber orientation (Fig. 2) and also exhibited parallel extinction between crossed Nicols. The cold-drawn material was exceedingly strong, tough and pliable.

γ-Polymer.—The cyclic dimer (0.5 g.) with a trace of camphor sulfonic acid heated at 150° soon became very viscous and the characteristic odor of the cyclic monomer appeared. After an hour, the melt when cooled set to a hard wax, easily electrified when powdered. Purified out of benzene, it separated as a microcrystalline powder, m. p. 58–59°; molecular weight observed in freezing benzene, 2580.

Other Formals.—The other α-polyformals were for the most part brittle waxy solids, and the observed melting points were: pentamethylene 38–39°, hexamethylene 38°, nonamethylene 54–55°, tetradecamethylene 68–69°, octadecamethylene 71–72° and triethylene, sirup. The β-polymers were generally pasty solids having the odors indicated in Table I and, when purified by crystallization from alcohol, yielded the odorless crystalline dimers whose melting points are shown in Table II. Pentamethylene formal depolymerized more readily than its higher homologs, and the monomer was isolated from the β-product as a colorless liquid of camphoraceous odor; b. p. 40–44° at 11 mm. Triethylene glycol formal depolymerized more readily than any of the others and gave a 70% yield of β-product which apparently consisted largely of monomer melting at 18–20°.

Summary

A new class of linear polymers represented by the general formula $\cdots\text{—}[CH_2\text{—}O\text{—}R\text{—}O]_x\text{—}\cdots$ is obtained by the action of alkyl formals on the higher glycols (above tetramethylene). These α-polyformals can in part be depolymerized to the β-forms (cyclic monomer and dimer) and in part converted to the higher ω-polyformals. The latter can be drawn out into strong, pliable, highly oriented fibers. The β-forms constitute a new type of large rings; the monomers have odors scarcely distinguishable from the corresponding carbonates $\underline{\text{—O—R—O—CO—}}$ and in particular tetradecamethylene formal, the 17-membered ring, has a musk-like odor. The dimers are odorless crystalline solids. Trimethylene formal (6-membered ring) does not polymerize, and no polymeric form is known, but tetramethylene formal (7-membered ring) and the higher ones polymerize rapidly (*e. g.*, at 150°) when catalyzed by acid.

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[15] THIS JOURNAL, 54, 1580 (1932).