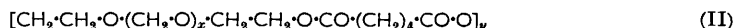**274. *Acetals and Oligoacetals. Part III.*[1] *Glycol Poly(oligo-formals).***

By A. J. DUKE.

Various glycol poly(oligoformals) and di-(2-hydroxyethyl) oligoformal polyadipates have been prepared. The applicability of the previously established spectral correlations to oligoformal groupings in polymeric systems is examined. The polymerisation product of 1,3,5-trioxepan is not the pure poly(diformal) (III; $x = 2$). 4-Methyl-1,3-dioxolan and 6-methyl-1,3,5-trioxepan are shown to be polymerisable.

POLYFORMALS formed from glycols with more than a molar quantity of formaldehyde are one of the classes of compound for which structures containing " oligoformal " * groups (I; $x > 1$) have been assumed.[2,3] The specific spectral absorptions recently found [2] for oligoformal groups with different values of x should permit determinations of the detailed structure of such polymers.

$$\cdot O \cdot [CH_2 \cdot O]_x \cdot \qquad (I)$$

$$[CH_2 \cdot CH_2 \cdot O \cdot (CH_2 \cdot O)_x \cdot CH_2 \cdot CH_2 \cdot O \cdot CO \cdot (CH_2)_4 \cdot CO \cdot O]_y \qquad (II)$$

The validity of the infrared correlation [2] for oligoformal groupings forming part of a polymer chain is shown, *inter alia*, from the spectra of the di-(2-hydroxyethyl) oligoformal polyadipates (II; $x = 1$—3), which have been obtained from the oligoformal diols by base-catalysed transesterification. The characteristic maxima are found at 1026, 989, and 968 cm.$^{-1}$, respectively, for $x = 1$, 2, and 3. Diethylene glycol polyadipate (II; $x = 0$) also fits well into this sequence, having only one strong absorption maximum in the 1150—900 cm.$^{-1}$ region, at 1129 cm.$^{-1}$. The maximum at 1110—1130 cm.$^{-1}$ in the spectra of long-chain ethers, $(R \cdot CH_2 \cdot CH_2)_2 O$,[4] is of course a logical limit to both of the two series of characteristic oligoformal absorptions.[2] The range of log (frequency — limit

* See Part I (ref. 2) for a note on the nomenclature used for groups of type (I).
[1] Part II, Webb and Duke, *J.*, 1962, 4320.
[2] Webb, Duke, and Smith, *J.*, 1962, 4307.
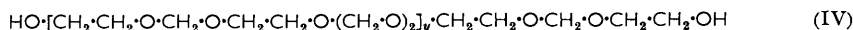[3] (a) Gresham, U.S.P. 2,350,350; (b) Gresham and Bell, U.S.P. 2,475,610 (Both to du Pont).
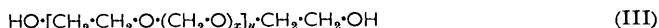[4] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958; and see Experimental of this paper.

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frequency),[5] for known monomeric and polymeric oligoformals, varies linearly with x for $x = 0$—6 (see Figure).

Ethylene glycol poly(monoformal) (III; $x = 1$), poly(diformal) (III, $x = 2$), and the alternating di-(2-hydroxyethyl) monoformal poly(diformal) (IV) have been prepared by

$$HO\cdot[CH_2\cdot CH_2\cdot O\cdot(CH_2\cdot O)_x]_y\cdot CH_2\cdot CH_2\cdot OH \qquad (III)$$

$$HO\cdot[CH_2\cdot CH_2\cdot O\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot O\cdot(CH_2\cdot O)_2]_y\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot OH \qquad (IV)$$

unequivocal procedures (see Experimental). Their nuclear magnetic resonance (n.m.r.) spectra showed at least 90% of the oligoformal units present to be as expected (Table 1 and ref. 2). They show infrared absorptions in the expected positions. However, the

Variation, with x, of range of log (frequency — limit frequency) for oligoformals.
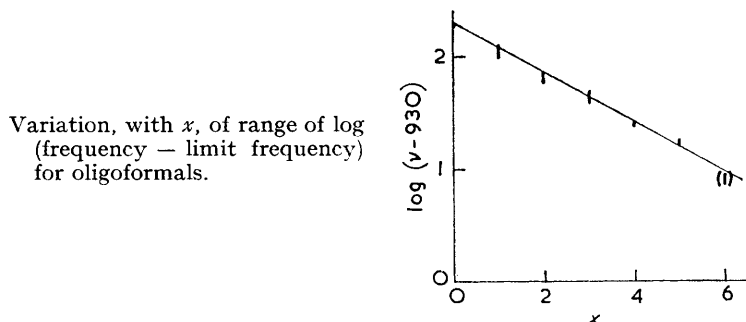
poly(diformal) also shows a weaker peak, at 1020 cm.$^{-1}$. The frequencies (and approximate peak widths) of the maxima near 1030 cm.$^{-1}$ (see Table 2) suggest that such an absorption may be general, at least for the ethylene glycol poly(oligoformals), although it is of lower

TABLE 1.

Intensities of n.m.r. peaks due to formal methylene protons, relative to the strongest peak of this group. (Chloroform solutions; the corresponding chemical shifts, τ, for definite maxima are given in parentheses.)

Poly(oligoformal)	Peak assignment (see text)		
	Monoformal	" Outer " methylene	" Inner " methylene
(III; $x = 1$)	1·0 (5·20)	⩽0·1	Nil
(IV)	0·4 (5·23)	1·0 (5·16)	⩽0·1
(III; $x = 2$)	⩽0·1 (5·22)	1·0 (5·16)	Nil
(III; x random, 1 to *ca.* 5)	0·4$_5$ (5·23)	1·0 (5·15)	0·8$_5$ (5·08)

TABLE 2.

Infrared absorption maxima of poly(oligoformals) in methylene chloride solution in the 1100—900 cm.$^{-1}$ region. (Strongest peaks are printed in bold type, and weak ones are in parentheses. sh = shoulder.)

Poly(oligoformal)	Peak positions (cm.$^{-1}$)	Approx. width of the maximum near 1030 cm.$^{-1}$
(III; $x = 1$)	**1036**, 1020sh	1020—1040
(IV)	**1020, 985**	1015—1030
(III; $x = 2$)	**1021, 984**	1015—1030
(III; x random, 1 to *ca.* 5)	**1027, 988, 970**, 957sh, 953—938sh	1020—1035
Polymerised (V; R = H).........................	**1026, 985**, 970sh, 955—938sh	1015—1030
Propylene glycol poly(monoformal)	**1037**, (985, 968)	1030—1045
Propylene glycol poly(oligoformal)............	**1033, 990—930**	1025—1040
Polymerised (V; R = Me)	**1028, 986**, 969sh, 958—935sh	1015—1035

⁵ Novak and Whalley, *Trans. Faraday Soc.*, 1959, **55**, 1484; Tadokoro, Yasumoto, Morimoto, and Murahashi, *Kobunshi Kagaku*, 1960, **17**, 95; Tadokoro, Kobayashi, Kawaguchi, Sobajima, Murahashi, and Matsui, *J. Chem. Phys.*, 1961, **35**, 369.

intensity than the characteristic monoformal peak. Absence of monoformal groupings cannot therefore be determined from infrared spectra alone.

An ethylene glycol poly(oligoformal) prepared by direct polycondensation of glycol with a three-molar excess of paraformaldehyde shows infrared absorptions corresponding to mono- and di-formal groups, and also at even lower frequencies (see Table 2), indicating the presence of at least tri-, tetra-, and penta-formal groups. Its n.m.r. spectrum shows that groups at least as high as pentaformal must be present. The intensity of the peak at $\tau = 5.08$, due to " inner " formal protons ($\cdot O \cdot CH_2 \cdot O \cdot CH_2 \cdot O \cdot CH_2 \cdot O \cdot$), is almost equal to that at $\tau = 5.15$, due to " outer " formal protons ($\cdot O \cdot CH_2 \cdot O \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2$) (Table 1). Since some diformal and triformal are present, and contribute more to the intensity of the latter peak than to that of the former, oligoformal groups with a numerical superiority of " inner " formal methylenes (*i.e.*, with $x \geqslant 5$) must also be present. The various groups are presumably randomly distributed.

The product obtained on polymerisation of 1,3,5-trioxepan (V; R = H) by boron trifluoride has been assumed [3b] to be the poly(diformal) (III; $x = 2$), and it was indicated that the trioxepan was regenerated on depolymerisation. This assumption appeared plausible. Oligoformals are more susceptible to acid catalysis than are the corresponding

$$\text{(V)} \qquad\qquad \text{(VI)}$$
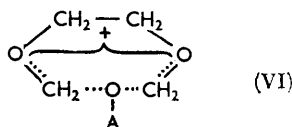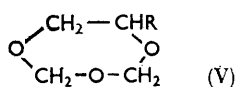
monoformals,[2] and co-ordination of compound (V; R = H) as in (VI; A = H, BF_3^-, or a further VI) would give greater charge delocalisation than is possible without disruption of the molecule, if co-ordination were to occur at a terminal oxygen. However, the spectra of polymer isolated from polymerisations of 1,3,5-trioxepan (V; R = H), or of 6-methyl-1,3,5-trioxepan (V; R = Me), show no evidence for selective formation of poly(diformal). Comparable amounts of mono- and di-formal groups, and also some triformal and higher oligoformal groups, are present even after short reaction times (Table 2 and Experimental). Depolymerisation of poly-(1,3,5-trioxepan) gives a mixture of 1,3-dioxolan, 1,3,5-trioxepan, and formaldehyde polymers.

Since 6-methyl-1,3,5-trioxepan has now been found to be polymerisable, it is worthy of note that the corresponding dioxolan, 4-methyl-1,3-dioxolan, is also polymerised by boron trifluoride, albeit in low yield, in contrast to literature findings.[6] The characteristic bands in the spectra of propylene glycol poly(oligoformals) are similar to those in the ethylene series (see Table 2).

Because of the close proximity of the successive oligoformal group in glycol poly-(oligoformals), some coupling of the vibrations responsible for the characteristic absorptions

TABLE 3.

Infrared absorption maxima of *ca.* 25% solutions of poly(oligoformals) in chloroform, in the 2200—1800 cm.$^{-1}$ region (strongest peaks in bold type).

Poly(oligoformal)	Peak positions (cm.$^{-1}$)
(III; $x = 1$)	2140, 2040, **1960**, 1880
(IV)	2140, **2030**, 1975
(III; $x = 2$)	2120, 2050, **1960**, 1900sh
(III; x random, 1 to *ca.* 5	2110sh, **2035**, **1950**, 1880
Polymerised (V; R = H)	2120sh, **2040**, **1960**, 1880

is to be expected, since the latter are assigned [2,7] to modes which involve predominantly C–O stretching. The occurrence (see above) of a band near 1020 cm.$^{-1}$ may perhaps be due to such coupling. Moreover, the spectra in the " first overtone " region (Table 3)

[6] Okada, *Kogyo Kagaku Zasshi*, 1962, **65**, 691, A47.

[7] Philpotts, Evans, and Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1051; Miyazawa, *J. Chem. Phys.*, 1961, **35**, 693; see also ref 5.

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permit the tentative suggestion that adjacent like and unlike oligoformal groups may perhaps be distinguished spectroscopically. The " homopolymers " (III; $x = 1$ or 2) have their strongest band between 2200 and 1800 cm.$^{-1}$, near 1950 cm.$^{-1}$, whereas the " alternating copolymer " (IV) has its strongest band at 2030 cm.$^{-1}$. Random ethylene glycol poly(oligoformal), which presumably contains adjacent pairs both of like and of unlike groups, shows peaks of comparable intensity at both positions, that of the latter decreasing with decreasing molecular weight (decreasing opportunity for strict alternation).

EXPERIMENTAL

Di-(2-hydroxyethyl) Oligoformal Polyadipates.—Equimolar amounts (*ca.* 0·01 mole) of di-(2-hydroxyethyl) oligoformal (or diethylene glycol) and diethyl adipate were mixed in a little methanol, sodium (*ca.* 5 mg.) was added, and the mixture was heated (i) at room temperature, increasing to 100° during 26 hr. under 15 mm. pressure, with addition of a further portion of sodium after 20 hr., and (ii) at 150°, increasing to 210° during 25 hr. under 0·1—0·2 mm. pressure. The polyadipates were thus obtained as dark brown viscous liquids which crystallised to waxes on cooling. More forcing reaction conditions did not further decrease the slight residual hydroxyl intensity observable in their infrared spectra. The spectra indicated that negligible interconversion of oligoformal groups had occurred during reaction.

Since few infrared spectra of ethers of the type $(R \cdot CH_2 \cdot CH_2)_2O$ appear to have been published, the range of values for the C–O stretching frequency used in the Figure was based on those for diethyl (1110), di-n-butyl (1122), and di-(2-chloroethyl) ether (1126), 2-ethoxyethanol (1119), and diethylene glycol (1129) and its polyadipate (1129 cm.$^{-1}$).

Di-(2-hydroxyethyl) Monoformal Poly(diformal), and Ethylene Glycol Poly(diformal).—Di-(2-hydroxyethyl) monoformal (13·6 g., 0·1 mole) was refluxed in dry dioxan (100 ml.) with magnetic stirring, and sodium (4·6 g.) and di(chloromethyl) ether (11·3 g.) were added during 30 hr. in alternate small and approximately equivalent portions. Each addition of sodium was allowed to dissolve completely before the ether portion was introduced, and a slight excess of alkoxide was maintained in the solution throughout.* After a final 1 hr. under reflux, methanol (5 ml.) and then 40% potassium hydroxide (20 ml.) were run in slowly with continued reflux, the mixture was filtered, and the organic layer separated and evaporated, leaving *di-(2-hydroxy-ethyl) monoformal poly(diformal)* (15·7 g.) as a light brown wax.

A similar reaction on the 1/40 mole scale, using di-(2-hydroxyethyl) diformal instead of the monoformal, and extracting the relatively insoluble product from the final filtered solid with hot dioxan (100 ml.), gave *ethylene glycol poly(diformal)* (5·0 g.), also a light brown wax. Ethylene glycol was not a satisfactory starting material for the production of the poly(diformal).

Analytical data on these and other ethylene glycol poly(oligoformals) are given in Table 4. Mean values of x and y [formula (III)] were calculated either from the fractional content of carbon (c) and hydrogen (h), or from that of formaldehyde (f) and the molecular weight by hydroxyl analysis (M). The two methods agree well except when $Me \cdot O \cdot CH_2 \cdot O \cdot CH_2 \cdot O \cdot$ end-groups are present [compound (IV)]. The relationships are:

$$x = (433h + 15 \cdot 8c - 48 \cdot 2)/(24 \cdot 2 - 56 \cdot 7c - 24h)$$

$$y = (62 \cdot 07c - 24 \cdot 02)/[x(12 \cdot 01 - 30 \cdot 03c) + (24 \cdot 02 - 44 \cdot 05c)]$$

or

$$x = 1 \cdot 467Mf/[M(1 - f) - 62]$$

$$y = (M - 62)/(30x + 44)$$

Ethylene Glycol Poly(oligoformal) and 1,3,5-Trioxepan.—Ethylene glycol (62 g.), para-formaldehyde (90 g.), toluene-*p*-sulphonic acid (1 g.), and benzene (40 ml.) were refluxed into a water-entrainer for 2 hr., evolving 33 ml. of aqueous phase. Formaldehyde polymers then began to be deposited in the head; 50% aqueous sodium hydroxide (160 g.) was run in slowly with continued reflux, and reflux was continued overnight. The organic layer was then filtered,

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* This technique was superior to the first method of Reiche and Gross,[8] in which complete dissolution of the sodium powder in the diol solution could not be effected before addition of the di(chloromethyl) ether. Some interconversion of oligoformal groups occurred as a result.

[8] Reiche and Gross, *Chem. Ber.*, 1960, **93**, 259.

using a filter aid, and washed with benzene. Solvent, 1,3-dioxolan, and 1,3,5-trioxepan were distilled, heating to 165°/1 atm., and subsequently at 100° while reducing the pressure to 0·05 mm. *Ethylene glycol poly(oligoformal)* was left as a light brown viscous oil which subsequently partly crystallised (61·7 g.). It could be decolourised by passage over alumina (Brockmann grade III) in 25% solution in benzene (see Table 4).

TABLE 4.

Analytical data on ethylene glycol poly(oligoformals).

Nominal value of x	Found				Calculated *			
					From C and H		From CH_2O and M	
	C (%)	H (%)	CH_2O (%)	M by hydroxyl analysis	x	y	x	y
1	—	—	42·5	2500	—	—	†	—
			43·8	2600				
1 and 2*	45·78	7·76	48·0	820	1·8	9	1·6	8·5
	46·03	7·92	48·5	850				
2*	44·55	8·01	52·0	1850	2·2	2·5	1·7	18
			51·5	2050				
Random ‡	46·45	7·83	53·5	1100	1·8	>10	1·9	11
	46·6	7·66		1170				
Random...............	45·66	7·94	—	840	1·9	6·5	—	—
	45·52	7·84		850				
Random...............	—	—	48·0	430	—	—	1·9	3·5
			48·5	440				

* No allowance made for $Me \cdot O \cdot CH_2 \cdot O \cdot CH_2 \cdot O \cdot$ end-groups. † Theoretical CH_2O content for infinite M, 40·6%. ‡ As described in full (see Experimental).

Products of lower molecular weight but similar formaldehyde content (see Table 4) were obtained from reactions stopped after evolution of lesser amounts of aqueous phase.

Redistillation of the volatile by-product from a similar reaction on fifty times the scale gave 1,3,5-trioxepan (299 g., 5·8%),[3b] b. p. 128—130° (after re-fractionation), n_D^{25} 1·4258, d_{25}^{25} 1·149, spec. refraction 0·2226 (calc. 0·2248) (Found: C, 45·95; H, 7·75. Calc. for $C_4H_8O_3$: C, 46·1; H, 7·75%).

Ethylene Glycol Poly(monoformal).—Reaction as for the poly(oligoformal) (above), but using only 30 g. of paraformaldehyde, gave ethylene glycol poly(monoformal) (52·3 g.) as a very light yellow wax.

Alternatively, boron trifluoride etherate (5 g.) was added to 1,3-dioxolan (100 g.), and polymerisation was initiated by gentle warming. The evolution of heat was controlled at 50°. Benzene (100 ml.) and sodium carbonate (15 g.) were then added, and the mixture was refluxed overnight, filtered, and evaporated, finally heating to 100°/15 mm. The ethylene glycol poly(monoformal) thus obtained was a colourless wax. The infrared spectra of the two samples were identical.

Propylene Glycol Poly(oligoformal) and 6-Methyl-1,3,5-Trioxepan.—Propylene glycol (525 g.), paraformaldehyde (622 g.), benzene (450 ml.), and toluene-*p*-sulphonic acid (7 g.) were treated as above for ethylene glycol, but with stirring, and evolved 217 ml. of aqueous phase. 50% Sodium hydroxide solution (560 g.) was then run in cautiously at reflux, and the mixture was worked up as before, finally heating to 150°/0·2 mm., to leave propylene glycol poly(oligoformal) as a light brown wax (72·0 g.).

The combined distillates were fractionally redistilled, giving first benzene and 4-methyl-1,3-dioxolan, and then 6-*methyl*-1,3,5-*trioxepan*, b. p. 138—141° (70 g., 8·6%), n_D^{20} 1·4249, d_{25}^{25} 1·082, spec. refraction 0·2353 (calc. 0·2374) (Found: C, 50·85; H, 8·4. $C_5H_{10}O_3$ requires C, 50·9; H, 8·5%).

Polymerisation of Trioxepans.—Portions of boron trifluoride etherate (0·1 ml.) and 1,3,5-trioxepan (2 ml.) were mixed. After various periods from 2 min. to 24 hr., 40% sodium hydroxide (1 ml.) was added, the mixture was shaken overnight, and the aqueous phase was separated as far as possible. Tetrahydrofuran (5 ml.) was then added, and the organic phase

separated, dried (Na₂SO₄), filtered, and evaporated, giving white semi-solid polymer, in substantially quantitative yields after 10 min. or longer reaction. The various samples gave indistinguishable infrared spectra. Use of only 0·01 ml. of catalyst gave very little polymer after 30 min. A similar reaction using 6-methyl-1,3,5-trioxepan gave 0·9 g. of white semi-solid polymer.

Propylene Glycol Poly(monoformal).—(a) *By direct polycondensation.* Propylene glycol (76 g.), paraformaldehyde (30 g.), toluene-*p*-sulphonic acid (1 g.), and benzene (40 ml.) were treated as usual, and evolved 20 ml. of aqueous phase. Working up as above gave propylene glycol poly(monoformal) (3·9 g.) as a colourless fairly mobile oil (Found: CH₂O, 20·5%).

(b) *By polymerisation of 4-methyl-1,3-dioxolan.* Boron trifluoride etherate (2 ml.) was added to 4-methyl-1,3-dioxolan (50 g.), and the mixture was left overnight. 40% Aqueous sodium hydroxide (40 ml.) was then added cautiously, and, after the evolution of heat had subsided, the mixture was shaken vigorously, benzene (20 ml.) was aded, and the mixture was centrifuged. Evaporation of the supernatant liquid then left propylene glycol poly(monoformal) (9·2 g.) as an orange, fairly mobile oil (Found: CH₂O, 28·4%). The infrared spectrum of this product differed from that of the preceding product only in the relative intensities of some peaks; in particular it showed about 40% lower hydroxyl intensity.