viscosity of the products increases with a decrease in the cathodic current density. Variation of temperature over the studied range from 0° to 40° has no substantial effect on the degree of polymerization of methyl methacrylate.

(2) Stirring of the reaction mixture during polymerization retards polymerization and reduces the degree of polymerization considerably. It is suggested that this is due to acceleration of the termination reaction as a result of the entrapping of the polymer radicals in emulsified monomer droplets, and of the coalescence of the dispersed particles.

(3) Polymerization continues for a long time after the current is switched off (almost to the complete disappearance of monomer). The yield of polymer from this "after" polymerization is dependent on the length of time during which the current is passed.

Translated by E. O. PHILLIPS

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STUDIES IN CYCLIC POLYMERIZATION AND COPOLYMERIZATION —III. THE SYNTHESIS AND CYCLIC POLYMERIZATION OF ALIPHATIC DIVINYL ACETALS. A NEW METHOD OF PREPARATION OF POLYVINYL ACETALS*

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POLYVINYLACETALS are well known as very valuable plastics that are widely used in the production of paints, films, coatings for electrical insulation, adhesives etc. On the basis of views on the mechanism of the cyclic, or intermolecular–intramolecular polymerization of unconjugated dienes [1, 2] it would be expected that for polyvinylacetals, containing 1,3-dioxane units, the corresponding

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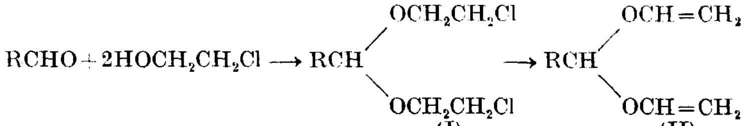
* Vysokomol. soedin. **3**: No. 4, 562–569, 1961.

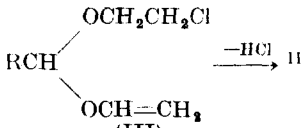
monomers—divinyl acetals—should exist. We have shown previously that polyvinylacetals† are in fact formed by the polymerization of divinyl acetals in the presence of radical initiators [3, 4].

In this paper a detailed account is given of a study of the synthesis and cyclic polymerization of three aliphatic divinyl acetals: divinyl formal (DVF), divinyl ethanal (EVE) and divinyl butyral (DVB). In the patent literature [5] there is an incomplete account of the preparation of DVF and DVB by dehydrohalogenation of the corresponding β,β'-dihalodiethyl acetal. We have developed a method of preparation of divinyl acetals from ethylene chlorohydrin according to the following scheme:



$$\mathrm{RCHO + 2HOCH_2CH_2Cl \longrightarrow \underset{(I)}{RCH{<}^{OCH_2CH_2Cl}_{OCH_2CH_2Cl}} \longrightarrow \underset{(II)}{RCH{<}^{OCH{=}CH_2}_{OCH{=}CH_2}}}$$

The dichloro-acetals (I) were obtained by reacting paraform, paraldehyde and butyraldehyde with ethylene chlorohydrin in the presence of acid (HCl) with removal of water by azeotropic distillation with benzene. Dichloro-acetal (I, $R=CH_3$) was also prepared by the addition of ethylene chlorohydrin to acetylene in the presence of mercuric sulphate. The dichloro-acetals (I) were dehydrochlorinated by heating with potassium or sodium hydroxide at 180–220° with simultaneous removal of the divinyl acetals (II) and water by distillation. The reaction was carried out in a copper vessel fitted with a stirrer, dropping funnel and fractionating column. The yield of divinyl acetal increases with increasing molecular weight of the aldehyde radical. If the dichloro-acetals (I) are run rapidly into the reactor, in addition to the divinyl acetals (II) products of incomplete dehydrochlorination—vinyl-β-chloroethyl acetals (III) are also formed. The latter readily split off hydrogen chloride on heating with alkali, forming the divinyl acetal (II).



$$\mathrm{\underset{(III)}{RCH{<}^{OCH_2CH_2Cl}_{OCH{=}CH_2}} \xrightarrow{-HCl} II}$$

The structure of the divinyl acetals formed was proved by hydrogenation and hydrolysis. As would be expected, on hydrogenation in the presence of a Pt catalyst 2 moles of hydrogen are absorbed with the formation of the diethyl acetals. The hydrolysis of 1 mole of the divinyl acetal by dilute sulphuric acid leads to the formation of 2 moles of acetaldehyde and 1 mole of the parent aldehyde. The divinyl acetals are colourless, mobile liquids with an ethereal odour. They can be distilled at atmospheric pressure or *in vacuo* without decomposition and without noticeable polymerization.

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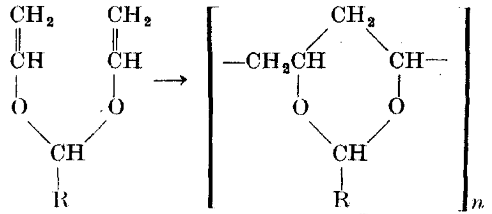
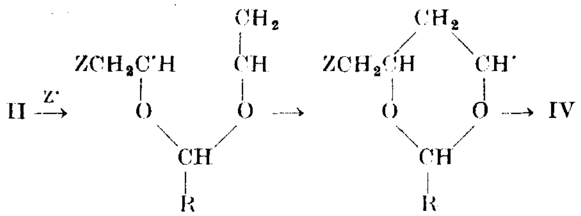
† In view of the name of the monomer the name "polyvinylacetal" should be replaced by "polydivinylacetal".

The divinyl acetals, being compounds with two isolated double bonds, can polymerize to form either linear–cyclic polymers or branched–crosslinked polymers. In fact, in a study of the polymerization of divinyl acetals in the presence of radical initiators and ionic polymerization catalysts we obtained both cyclic, soluble polymers and crosslinked, insoluble polymers. The bulk polymerization of the divinyl acetals in the presence of catalysts ($SnCl_4$, $FeCl_3$, $AlCl_3$) proceeds rapidly with the formation of crosslinked polymer which is insoluble in the usual organic solvents. In the presence of radical initiators cyclic polymerization occurs exclusively with the formation of acetals of polyvinylalcohol, i.e. polyvinylacetals (IV).



(IV)

The mechanism of activation of the original divinyl acetal monomers could be as follows: the addition of the initiator to one of the vinyl groups with the formation of an unsaturated radical which stabilizes itself by intramolecular cyclization thus forming a cyclic radical. Thus propagation takes place by alternate inter- and intramolecular reactions:



The optimal conditions for the cyclic polymerization of divinyl acetals in the presence of benzoyl peroxide (BPO) and azo*bis*isobutyronitrile (ADIB) were investigated. The effect of initiator concentration on yield of polymer was studied, taking DVB as an example. It was found that the cyclic polymerization rate, like that of vinyl polymerization, is proportional to the square root of the initiator concentration (Fig. 1). The dependence of the yield of polydivinylbutyral (PDVB) on polymerization temperature was also studied. It was found that in the presence of 1 mole % of ADIB the yield of polymer reaches 82% at 80° after which it falls with increasing temperature, whereas with BPO the yield of PDVB slowly increases with increasing temperature (Fig. 2).

In order to examine the effect of time of polymerization of DVF, DVE and DVB on polymer yield a series of experiments were carried out in which the temperature was 80° and the initiator concentration 1 mole % of the monomers (Fig. 3). It is seen from the diagram that the yield of the polydivinylacetals increases with increasing polymerization time over the first 5 hours, after which it remains practically constant.

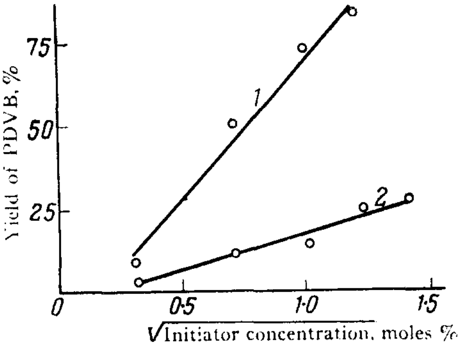


FIG. 1. The dependence of the yield of PDVB on initiator concentration at 80°. Polymerization time 40 hours: *1* - azo*bis*isobutyronitrile; *2* - benzoyl peroxide.

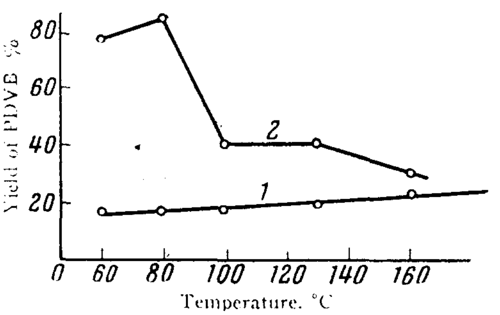


FIG. 2. The dependence of the yield of PDVB on polymerization temperature. Initiator concentration 1 mole %, polymerization time 40 hours: *1*—benzoyl peroxide; *2*—azo*bis*isobutyronitrile.

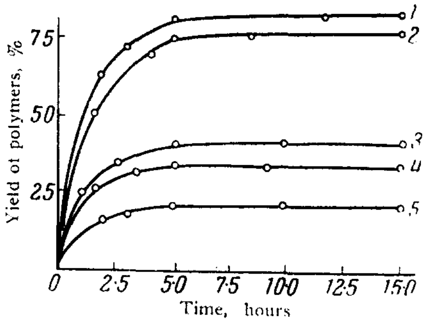


FIG. 3. The dependence of the yield of polydivinylacetals on polymerization time: *1*—DVB with ADIB; *2*—DVE with ADIB; *3*—DVF with BPO; *4*—DVE with BPO; *5*—DVB with BPO.

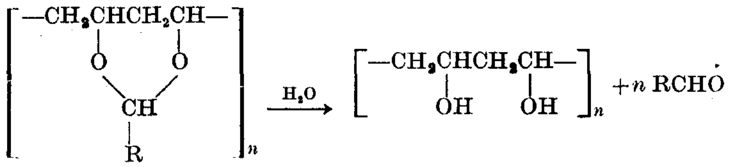
The polydivinylformal (PDVF) and polydivinylethanol (PDVE) that we obtained are white powders and the polydivinylbutral (PDVB) is a rubber-like mass. They are readily soluble in most organic solvents (aromatic hydrocarbons, chlorinated solvents etc.) but are difficultly soluble or completely insoluble in the lower alcohols. The degree of acetalation of the polydivinylacetals, in contrast to the commercial polyvinylacetals, is 100% (see Table).

ANALYSIS OF POLYDIVINYLACETALS

Polymer	Content of divinyl acetal groups in polymer	C, %		H, %	
		Found	Calculated	Found	Calculated
Polydivinylformal	99·3	60·17	60·05	8·08	8·06
	99·4	60·20		7·98	
Polydivinylethanal	99·4	63·10	63·13	8·34	8·83
	99·1	63·42		8·59	
Polydivinylbutyral	99·6	67·70	67·57	9·76	9·92
	99·8	67·82		9·75	
Commercial polyvinylbutyral	76·5	—	—	—	—
	76·2				

We studied also the chemical properties of the polydivinylacetals with the object of determining their structures. They show practically no capability of hydrogenation or addition of bromine, which indicates the absence of double bonds in the polymer.

The structure of the products from the cyclic polymerization of the divinyl acetals was proved conclusively by hydrolysis with an aqueous-alcohol solution of hydroxylamine hydrochloride. As expected this reaction brings about the formation of polyvinylalcohol in quantitative yield.



The polyvinylalcohol obtained is converted to polyvinylacetate by acetylation with acetic anhydride and on acetalation with aliphatic aldehydes forms technical polyvinylacetals with free OH groups. The presence of six-membered 1,3-dioxan rings in the polydivinylacetals is confirmed by the β-glycol structure of the polyvinylalcohol obtained, which in turn was proved by oxidation by the conventional method [6] to oxalic acid. The structure of the polydivinylacetals was also confirmed by spectrographic analysis. In the infra-red spectra* of DVE monomer there is an intense band, characteristic of the valency vibration of the double bond (vinyl group) at 1630–1640 cm^{-1}, whereas for the polymer (PDVE) this double-bond frequency is absent (Fig. 4). As is seen from Fig. 5 there is also practically no indication of unsaturation in the absorption spectra of PDVF and

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*The infra-red spectra were recorded by A. V. Mushegyan, to whom the authors are deeply grateful.

PDVB in the double-bond frequency region. The glass temperatures of PDVF, PDVE and PDVB, found by extrapolation of the straight line section of the thermomechanical curve (with a load of 0·8 kg/cm^2) to the abscissa, are 74°,

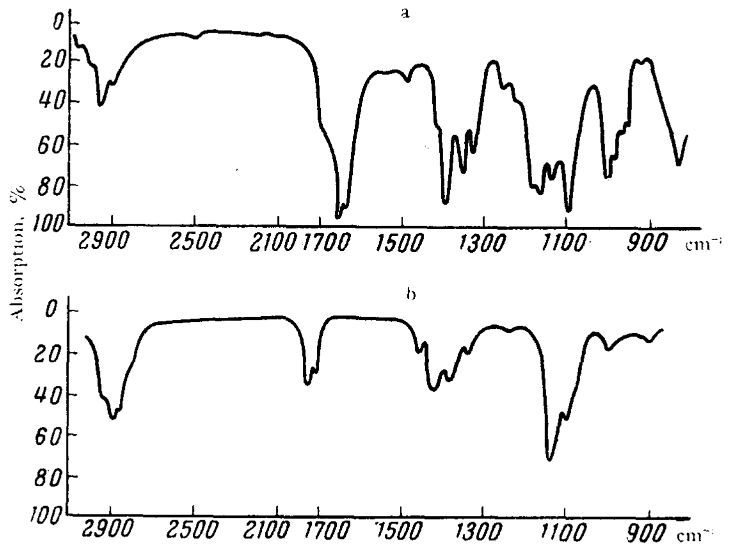

FIG. 4. Infra-red absorption spectra: *a*—DVE; *b*—PDVE.

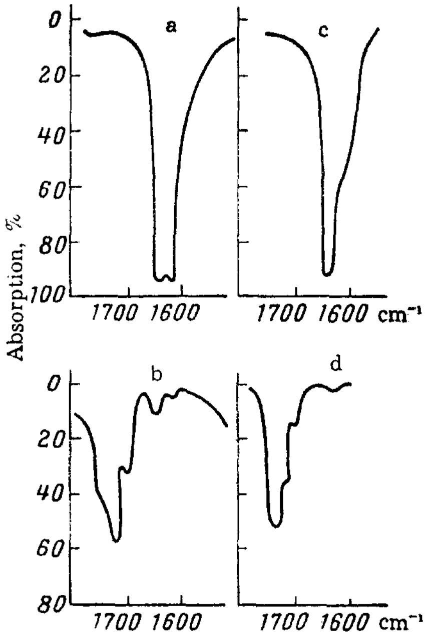

FIG. 5. Infra-red spectra in the double-bond valency vibration region: *a*—DVF; *b*—PDVF; *c*—DVB; *d*—PDVB.

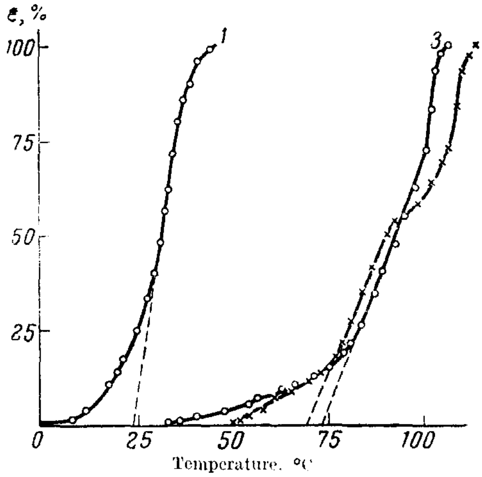

FIG. 6. Thermomechanical properties of the polydivinylacetals: *1*—PDVB; *2*—PDVE; *3*—PDVF.

69° and 24° respectively (Fig. 6). As in the case of the commercial polyvinylacetals the glass temperature falls with increasing length of the aldehyde radical.

The molecular weight of the polydivinylacetals was found to be ~10,000 (ebullioscopically in benzene), which is in agreement with viscometric measurements of the degree of polymerization of the polyvinylalcohol obtained by hydrolysis of the polydivinylacetals. The intrinsic viscosity in benzene of the three polydivinylacetals prepared varied between 0·1 and 0·15 (20°). It is interesting to note that the polydivinylacetals prepared by simultaneous initiation with ADIB and ultra-violet light (SVDSH-250 lamp) have a higher intrinsic viscosity.

EXPERIMENTAL

β,β′-Dichlorodiethyl formal. 161 g of anhydrous ethylene chlorohydrin containing 3 g of hydrogen chloride, 35 g of paraform and 250 g of benzene were placed in a round-bottomed flask fitted with a reflux condenser connected to a Dean and Stark water separator. The reaction mixture was heated in a metal bath at 100–110° until the evolution of water ceased. A total quantity of 17·9 ml of water was collected as compared with 18 ml required by theory. After removal of the benzene by distillation the residue was redistilled *in vacuo*. 164 g (yield 94·8% of theory) of the dichloro-formal (I, R=H) was obtained in the form of a colourless liquid of b.p. 94–96°/10 mm, n_D^{20} 1·4550. According to the literature, b.p. 218–219, $d^{10\cdot5}$ 1·2406 [7].

Divinyl formal. 85 g of granular potassium hydroxide was placed in a copper reactor fitted with a copper stirrer, a dropping funnel and a fractionating column connected to a take-off condenser. The reactor was heated to 180–220° in a metal bath and 53·3 g of β,β′-dichlorodiethyl formal was added dropwise over a period of 6 hours at a rate sufficient to maintain the vapour temperature in the range 70–85°. The reaction product distilled off with the water formed by the reaction between HCl and KOH in the dehydrochlorination of the dichlorodiethyl formal. Toward the end of the reaction dry air was passed through the reaction mixture for complete removal of the dehydrochlorination products. The distillate was saturated with potassium carbonate, extracted with ether and the ethereal extract dried over magnesium sulphate. After removal of the ether the residue was redistilled at atmospheric pressure. 12·6 g of divinyl formal (II, R=H) (yield 41% of theory) was obtained in the form of a colourless, mobile liquid with an ethereal odour. B.p. 87–89°/680 mm, n_D^{20} 1·4215, d_4^{20} 0·9077.

Found %: C 60·40; 60·27; H 8·40; 8·21; MR_D 27·96.
$C_5H_8O_2$. Calculated %: C 60·05; H 8·06; MR_D 27·64.

In addition 4·0 g (yield 9·6% of theory) of β-chloroethylvinyl formal (III, R=H) of b.p. 149–151°/680 mm, n_D^{20} 1·4385, d_4^{20} 1·0903.

Found %: Cl 25·87; MR_D 32·90.
$C_5H_9O_2Cl$. Calculated %: Cl 25·99; MR_D 32·97.

ββ′-Dichlorodiethyl ethanal

(a) *From paraldehyde.* The synthesis is similar to that of dichloro-formal. From 900 g of ethylene chlorohydrin containing 10 g of hydrogen chloride, 216 g of paraldehyde and 700 ml of benzene, 570 g of dichloro-ethanol (I, R=CH_3) was obtained (yield 62% of theory). B.p. 100–102°/10·5 mm, n_D^{20} 1·4535. According to the literature, b.p. 116·5–117°/25 mm, n_D^{20} 1·4529 [8].

(b) *From acetaldehyde.* 75 g of cooled acetaldehyde was added to 161 g of ethylene chlorohydrin containing 5 g of hydrogen chloride. The reaction mixture was allowed to stand for 3 days and was then treated with anhydrous potassium carbonate and distilled. 60 g of the dichloro-ethanal (I, R=CH_3) (yield 35% of theory) was obtained. B.p. 100–101°/11 mm n_D^{20} 1·4530.

(c) *From acetylene.* 40·2 g of dry ethylene chlorohydrin, 2 g of mercuric sulphate and 1 g of trichloroacetic acid were placed in a three-necked flask fitted with a mechanical stirrer, a reflux condenser and an inlet tube for acetylene. The reaction mixture was heated on a water bath at 60–90° and dry acetylene was passed through over a period of 5 hours. The product was treated with potassium carbonate, extracted with ether and distilled *in vacuo*. 11·7 g of the dichloro-ethanal (I, R=CH_3) (yield 25% of theory) was obtained. B.p. 99–102°/10 mm, n_D^{20} 1·4530.

Divinyl ethanal. The synthesis is similar to that of divinyl formal. 284 g of the dichloro-ethanal (I, R=CH_3) was added dropwise to 400 g of potassium hydroxide at 200° with vigorous stirring over 12 hours at a rate adjusted to keep the vapour temperature within the range of 75–90°. On distillation of the product 87 g of divinyl ethanal (yield 52% of theory) was obtained. B.p. 100–102°/680 mm, n_D^{20} 1·4180, d_4^{20} 0·8960.

Found %: C 63·06; 63·41; H 9·06; 8·81; MR_D 32·09.
$C_6H_{10}O_2$. Calculated %: C 63·15; H 8·83; MR_D 32·26.

In addition, in this experiment 38 g of vinyl-β-chloroethyl ethanal (III, R=CH_3) (yield 17·2% of theory) was obtained. B.p. 55–56°/12 mm, n_D^{20} 1·4365, d_4^{20} 1·0470.

Found %: C 47·53; H 7·60; Cl 22·98; MR_D 37·65.
$C_6H_{11}O_2Cl$. Calculated %: C 47·18; H 7·36; Cl 23·54; MR_D 37·59.

β,β′-Dichlorodiethyl butyral. This was prepared by the same method as for the dichloro-formal (I, R=H). 180 g of the dichloro-butyral (I, R=n-C_3H_7) was obtained from 161 g of anhydrous ethylene chlorohydrin containing 3 g of hydrogen chloride, 90 g of butyraldehyde and 250 ml of benzene (yield 85% of theory). B.p. 84–85°/3 mm, 120–122°/11 mm, n_D^{20} 1·4525, d_4^{20} 1·1183.

Found %: C 44·9; H 8·00; Cl 33·06; MR_D 51·94.
$C_8H_{16}O_2Cl_2$. Calculated %: C 44·65; H 7·89; Cl 33·00; MR_D 52·16.

Divinyl butyral. The synthesis was similar to that of divinyl formal. 107·6 g of the dichloro-butyral (I, R=n-C_3H_7) was added dropwise over 5 hours to 84 g of potassium hydroxide at 200–220° at a rate adjusted to keep the vapour temperature within the range of 85–95°. 46·2 g of divinyl butyral (yield 65% of theory) was obtained, with b.p. 44–45°/13 mm, 138–139°/680 mm, n_D^{20} 1·4250, d_4^{20} 0·870.

Found %: C 67·79; 67·81; H 10·15; 10·30; MR_D 41·75.
$C_8H_{14}O_2$. Calculated %: C 67·57; H 9·92; MR_D 41·50.

In this experiment 14·8 g of vinyl-β-chloroethyl butyral (III, R=n-C_3H_7) was also obtained (yield 16·5% of theory). B.p. 80–82°/12 mm, n_D^{20} 1·4110, d_4^{20} 1·0020.

Found %: C 53·4; H 8·70; Cl 20·35; MR_D 47·04.
$C_8H_{15}O_2Cl$. Calculated %: C 53·76; H 8·45; Cl 19·84; MR_D 46·83.

The vinyl-β-chloroethyl butyral obtained splits off HCl comparatively readily on heating with potassium hydroxide.

Hydrogenation of divinyl butyral. A solution of 1·4 g of the material in 10 ml of alcohol was hydrogenated in the presence of a Pt catalyst. The theoretical quantity of hydrogen required for two double bonds was absorbed. The catalyst was filtered off and the filtrate was distilled at atmospheric pressure. 1·2 g of diethyl butyral was obtained, with b.p. 141–143°, n_D^{20} 1·3965. According to the literature, b.p. 143–145°, n_D^{20} 1·3958 [9].

Hydrolysis of divinyl butyral. 15 ml of 2% sulphuric acid and 4·3 g of divinyl butyral were placed in a three-necked flask fitted with a mechanical stirrer, a 40 cm fractionating column and a take-off condenser leading to a receiver thoroughly cooled in an ice–salt mixture. The reaction mixture was stirred vigorously at 50–75° for 1 hour. 2·4 g of acetaldehyde (yield 90% of theory), of b.p. 20–22°, was collected. The 2,4-dinitrophenyl hydrazone of the product melted at 145–147° and did not depress the melting point of an authentic sample. 6 g of 2,4-dinitrophenylhydrazine, dissolved in 15 ml of alcohol and 10 ml of 50% sulphuric acid, was added to an aqueous solution of the hydrolysis products. 5·2 g of the 2,4-dinitrophenylhydrazone of butyraldehyde was obtained, melting at 125–126° and giving no melting-point depression with an authentic sample.

Polymerization of the divinyl acetals. In all cases polymerization was carried out in thoroughly washed, glass ampoules. After placing the freshly distilled monomer and initiator in the ampoule the latter was cooled, swept out with pure nitrogen and evacuated. The sealed ampoule was placed in a thermostat with accurate temperature control (±0·5%) and a well-stirred liquid. At the end of the polymerization process the ampoule was cooled rapidly and opened. The polymer was freed from unreacted monomer by steam-distillation and reprecipitated by alcohol from benzene solution. The polymer obtained was dried *in vacuo* (10–12 mm) at 54° to constant weight.

The acetal-group content of the polyvinylacetals was determined by the hydrolytic oximation method. For control a parallel analysis of a commercial sample of polyvinylbutyral was carried out. The results of these analyses and the elementary analyses are given in the Table.

Hydrolysis of polydivinylethanal. A mixture of 4 g of PDVE, 80 ml of alcohol and a solution of 2·44 g of hydroxylamine hydrochloride in 4 ml of water was refluxed on the water bath. After an hour a fine, flocculent precipitate of polyvinylalcohol separated from the homogeneous solution. The mixture was centrifuged and the residue was dissolved in water and reprecipitated with methanol. The product was separated and dried to constant weight *in vacuo* (11 mm) at 45°. 1·45 g (yield 95% of theory) of polyvinylalcohol was obtained in the form of a white powder, readily soluble in water and in hot glycerol. The ethanal-group content of the polymer was 1·5%. The molecular weight, determined viscometrically ($\eta = 0{\cdot}166$) was 4530.

Hydrolysis of polydivinylbutyral. A solution of 1 g of hydroxylamine hydrochloride in 20 g of 90% alcohol was added to a solution of 2 g of PDVB in 60 g of dioxan. The mixture was heated on a boiling water bath for 2 hours. The product was isolated as above. 0·8 g of polyvinylalcohol was obtained.

Found %: C 54·10; H 9·62.
$(C_2H_4O)_n$. Calculated %: C 54·54; H 9·09.

Acetalation of polyvinylalcohol. (a) 0·65 g of butyraldehyde and 8 g of a 5% solution of the polyvinylalcohol, containing one drop of hydrochloric acid, was placed in a three-necked flask fitted with a mechanical stirrer and a reflux condenser. The mixture was heated slowly (over a period of 6 hours) to 55°. The polymer that separated was washed with hot water and dried to constant weight *in vacuo* (10 mm) at 54°. The softening range of the polyvinylbutyral obtained was 109–130° (capillary). The quantity of divinylbutyral units in the polymer, determined by the oxime method, was 62·7%. (b) The polyvinylalcohol was acetalated with paraldehyde in the same way. The polyvinyethanal obtained had a softening range of 105–140° (capillary) and contained 33·1% of ethanal groups, corresponding to 63·04 g of divinylethanal units.

Acetylation of polyvinylalcohol. A mixture of 1 g of polyvinylalcohol, obtained by the hydrolysis of the polydivinylacetals, 8 g of acetic anhydride and 1 g of anhydrous sodium acetate was heated slowly (over a period of 1 hour) to boiling point. The homogeneous solution obtained was poured into hot water, the reaction product was separated, dissolved in alcohol and again precipitated by water. The polyvinylacetate obtained was dried to constant weight *in vacuo* (12 mm) at 54°. The acetate-group content, found by alkaline saponification, was 66·4%, corresponding to 96·7% vinyl acetate units.

Oxidation of polyvinylalcohol. A solution of 0·7 g of the polyvinylalcohol in 120 ml of 20% nitric acid was evaporated to dryness on a boiling water bath and the residue was thoroughly extracted with ether. After removal of the ether by distillation the product was recrystallized from water and its melting point was determined. The melting point found was 101–103° and a mixed melting point with oxalic acid was not depressed.

CONCLUSIONS

(1) Divinyl formal, divinyl ethanal and divinyl butyral have been synthesized by acetalation of the corresponding aldehydes with ethylene chlorohydrin and subsequent dehydrochlorination of the β,β'-dichlorodiethyl acetals.

(2) It is shown that the two vinyl groups in the divinyl acetals join up in "head-to-tail" fashion in the presence of radical initiators to form cyclic, 1,3-dioxan units from which acetal derivatives of polyvinylalcohol (polyvinylacetals) are formed by intermolecular addition.

(3) The optimal conditions for the cyclic polymerization of the divinyl acetals and the properties of the polydivinylacetals formed have been studied.

Translated by E. O. PHILLIPS

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