Cationic Polymerisation of 2 : 3-Dihydrofurans.

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The cationic polymerisation of three 2 : 3-dihydrofurans to polymers of high molecular weight is described. An investigation of the structures of the polymers is reported, and the softening-points of the polymers, which are considerably higher than those of aliphatic polyvinyl ethers, discussed in terms of their structures.

It is known (Hamann, *Angew. Chem.*, 1951, 231) that certain linear polyethers can be obtained by polymerisation of the corresponding cyclic ethers, for instance, a polymer having the repeat unit $\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot O\cdot$ is obtained by the cationic polymerisation of tetrahydrofuran (*idem, loc. cit.*). An attempt has been made to extend this method to the preparation of polyethers, having double bonds in the chain, by the cationic polymerisation of dihydrofurans. It was found that, although 2 : 5-dihydrofurans would not polymerise, 2 : 3-dihydrofurans polymerised readily in the presence of Friedel–Crafts catalysts.

2 : 3-Dihydro-5-methylfuran polymerised on addition of catalytic quantities of boron trifluoride, the experimental method being such that water was excluded as far as possible from the system. Polymerisation took place readily at −80° to give a glass-like polymer of high molecular weight. The molecular weight of the polymer (as indicated by its intrinsic viscosity) prepared in this manner showed no regular variation with the concentration of catalyst used, but was decreased considerably by the addition of small quantities of water. These effects are illustrated in the annexed table. It appears

Bulk polymerisation of 2 : 3-*dihydro-5-methylfuran* at −80°.

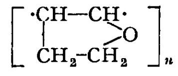
$[BF_3]$, mole l.$^{-1}$	0·01	0·01	0·033	0·10	0·01	0·01
[Added water], mole l.$^{-1}$	None	None	None	None	0·005	0·025
$[\eta]$, decilitre g.$^{-1}$	5·8	7·2	7·0	5·0	0·92	0·38

that water is an effective chain-termination or transfer agent and, if polymerisation is assumed to proceed *via* carbonium ions, this behaviour is consistent with reaction of the growing chain with water either by an elimination process to give a terminal double bond or by substitution to give a terminal hydroxyl group. The addition of relatively large quantities of water to the polymerisation mixture inactivated the catalyst. Thus, when the concentration of added water was increased to 0·1 mole l.$^{-1}$ polymerisation did not take place at —80°, but set in when the polymerisation mixture was warmed to 0°. When the concentration of water was increased to 0·2 mole l.$^{-1}$ polymerisation would not take place at all. Polymerisations at —40° and at 0° gave deeply coloured products from which polymers of low molecular weight were isolated.

Polymers of high molecular weight of 2 : 3-dihydro- and of 2 : 3-dihydro-2 : 2-dimethyl-furan were prepared by polymerisation of the dry monomers at —80°, 0·01M-boron trifluoride being used as catalyst. Polymers of low molecular weight were formed when polymerisation was at room temperature or when the monomers were not carefully dried. It therefore appears that the conditions principally necessary for the preparation of polymers of high molecular weight from 2 : 3-dihydrofurans are dry monomers and low temperatures of polymerisation.

There are two types of structure possible each corresponding to one of the two modes of cationic polymerisation that appear possible for 2 : 3-dihydrofurans :

(I) $[CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}O{\cdot}]_n$


$$\left[\begin{array}{l}\cdot CH—CH\cdot \\ | \qquad\; >O \\ CH_2-CH_2\end{array}\right]_n$$
(II)

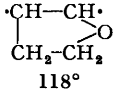
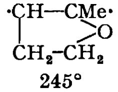
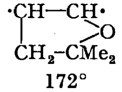
Results of an examination of the infra-red absorption spectra of the monomers and their polymers, carried out by Mr. R. G. J. Miller, are summarised in the following Table :

Frequencies (*cm.*$^{-1}$) *of bands in infra-red absorption spectra of* 2 : 3-*dihydrofurans and their polymers.*

	2 : 3-Dihydro-		2 : 3-Dihydro-5-methyl-		2 : 3-Dihydro-2 : 2-dimethyl-	
Furan :	monomer	polymer	monomer	polymer	monomer	polymer
C–O–C stretching	915	925	890	—	885	895
	1055	1060	1010	1060	1060	1048
cis-C=C hydrogen deformation ...	710	—	720	—	707	—
C=C stretching	1610	—	1670	—	1615	—

These data show that the absorption bands characteristic of the C=C-bond, which are present in the spectra of the monomers, do not occur in the polymers. Further, in the spectra of the polymers the bands associated with the C–O–C-frequencies occur in positions similar to those in which the ether bands of the monomers were found, and are characteristic of cyclic ethers, *e.g.*, tetrahydrofuran, which has absorption bands at 905 and 1075 cm.$^{-1}$ (H. A. Willis, personal communication), rather than of linear ethers which absorb in the region of 1130 cm.$^{-1}$, *e.g.*, polytetrahydrofuran absorbs at 1130 cm.$^{-1}$ (H. A. Willis, *loc. cit.*). This evidence is therefore completely consistent with structure (II), but inconsistent with (I). It is perhaps noteworthy that 2 : 3-dihydrofurans do not contain the group $>C=CH_2$, which has been considered (Schildknecht, Zoss, and Grosser, *Ind. Eng. Chem.*, 1949, **41**, 2891) to be necessary if a vinyl monomer is to form homopolymers readily by ethenoid polymerisation.

Softening-point determinations, carried out on samples of each polymer by the " Vicat " method (see " Kunstharzpressstoffe," W Mehdorn, V.D.I., Forschungs-heft VDI-Verlag G.m.b.H., Berlin, 1934), gave the values listed below. These values are considerably higher than those of aliphatic polyvinyl ethers, which are rubbers at room temperature (Schildknecht *et al.*, *loc. cit.*). Frith and Tucket (" Linear Polymers," Longmans,

Polymer of	2 : 3-dihydrofuran	2 : 3-dihydro-5-methylfuran	2 : 3-dihydro-2 : 2-dimethylfuran
Repeat unit	 $\begin{array}{l}\cdot CH—CH\cdot \\ | \qquad\; >O \\ CH_2-CH_2\end{array}$	 $\begin{array}{l}\cdot CH—CMe\cdot \\ | \qquad\; >O \\ CH_2-CH_2\end{array}$	 $\begin{array}{l}\cdot CH—CH\cdot \\ | \qquad\; >O \\ CH_2-CMe_2\end{array}$
Softening point ...	118°	245°	172°

Green and Co., London, 1951, p. 328) have show that the " Vicat " softening point provides a measure of the elastic, rather than the viscous, properties of an amorphous polymer, and therefore a measure of its chain flexibility. Some explanation of the high softening point of poly-2 : 3-dihydrofuran is therefore possible on a structural basis, for in this polymer rotation about some chain bonds is prevented by their incorporation in a strained ring, while rotation about others is restricted by the steric hindrance afforded by the rings, so that the polymer chain must be less flexible than the chain in polyvinyl ethers. Construction of Stuart molecular models showed that methyl substitution on the poly-2 : 3-dihydrofuran chain increased its rigidity, while dimethyl substitution remote from the chain had a similar, though less marked, effect.

EXPERIMENTAL

Preparation of the Monomers.—2 : 3-Dihydrofuran was prepared by Normant's method (*Compt. rend.*, 1949, **228**, 102), and 2 : 3-dihydro-5-methylfuran according to Paul and Tchelitcheff (*Bull. Soc. chim.*, 1950, 520). A mixture of the two isomeric dihydro-2 : 2-dimethylfurans was prepared as described by Colonge and Garnier (*ibid.*, 1948, 432), and fractionated through a 3-ft. column filled with metal packing (Dixon, *J. Soc. Chem. Ind.*, 1949, **68**, 299), to give two main fractions; 2 : 3-dihydro-2 : 2-dimethylfuran, b. p. 78·0°/764 mm., n_D^{20} 1·4123 (Found : C, 73·3; H, 10·3. Calc. for $C_6H_{10}O$: C, 73·5; H, 10·3%), and 2 : 5-dihydro-2 : 2-dimethylfuran, b. p. 84·6°/764 mm., n_D^{20} 1·4158 (Found : C, 73·2; H, 10·5%). Normant (*Compt. rend.*, 1948, **227**, 283) records b. p. 77—78° for the 2 : 3-dihydrofuran, and b. p. 85—86° for its 2 : 5-isomer.

Purification of the Monomers.—2 : 3-Dihydrofurans are oxidised by air (Paul and Tchelitcheff. *loc. cit.*) to products which give characteristic infra-red absorption bands at 1728 and 1745 cm.$^{-1}$. These impurities were removed by refluxing the monomers with freshly fused potassium hydroxide, distilling then from the potash, and fractionating the distillate. To prevent further oxidation (the infra-red absorption bands rapidly reappeared if the monomers were exposed to air), the above operations were carried out under nitrogen. After fractionation, the monomers were dried *in vacuo* over sodium wire, and then distilled in a good vacuum into the storage section of the polymerisation apparatus. The purified monomers either did not absorb, or only absorbed very weakly at 1725 and 1745 cm.$^{-1}$, and had the following physical constants : 2 : 3-dihydrofuran, b. p. 54·6°/764 mm., n_D^{20} 1·4230 (Normant, *Compt. rend.*, 1949, **228**, 102, records b. p. 54·5°/760 mm., $n_D^{18 \cdot 5}$ 1·424) ; 2 : 3-dihydro-5-methylfuran, b. p. 79·6—79·7°/760 mm., n_D^{20} 1·4296 (Schniepp and Gellar, *J. Amer. Chem. Soc.*, 1947, **69**, 672, record b. p. 80°/760 mm., n_D^{25} 1·4290) ; and 2 : 3-dihydro-2 : 2-dimethylfuran, b. p. 78·0°/764 mm., n_D^{20} 1·4123.

Boron Trifluoride.—This was prepared by dropping redistilled fluorosulphonic acid on to a slight excess of boric acid, and the trifluoride purified by passing it through traps cooled to −80°. The purified gas was collected in a trap cooled in liquid nitrogen, and then distilled in a nitrogen atmosphere into a second trap forming part of the polymerisation apparatus. The second trap was evacuated and the boron trifluoride melted down, out-gassed, and distilled *in vacuo*, a middle fraction being collected in a storage bulb.

Polymerisation Technique.—To exclude moisture the monomer and the catalyst were handled *in vacuo*, according to the following procedure : (i) A measured quantity of monomer was distilled into a graduated tube, and from there into the reaction tube (about 15 ml. capacity), which was constricted just below its junction with the rest of the apparatus. The monomer was then frozen by liquid nitrogen. (ii) A quantity of boron trifluoride was measured into a constant-volume, variable-pressure gas-burette, and distilled from the burette bulb on to the frozen monomer. (iii) The reaction tube was sealed, and warmed to −80° by shaking in a solid carbon dioxide–methanol bath. When polymerisation was complete (after 48 hr. at −80°) the tube was cooled with liquid nitrogen, the polymer cracking away from the glass and bursting the tube. The polymer was kept cold with liquid nitrogen and broken up in a percussion mortar. The frozen fragments were dropped into chloroform (600 ml.)–methanol (30 ml.), cooled to −60°. Ammonia was passed in and the mixture allowed to warm gradually to room temperature. The viscous solution was filtered, and the polymer recovered by precipitation with methanol. After being washed twice with methanol, the precipitated polymer was dried in a vacuum desiccator. The above procedure was necessary since, when the polymer was allowed to warm from −80° before it had been treated to destroy the catalyst, a short exothermic reaction set in and the polymer became deeply coloured, and then decomposed at 100°.

Viscosity Measurements.—The intrinsic viscosities of the polymers in chloroform solution were measured at 20°, an Ostwald No. 1 viscometer being used. The plot of η_s/C against C, where η_s is the specific viscosity and C the concentration, gave straight lines in the concentration range 0·025—0·15 g. decilitre^{-1}.

Softening-point Measurements.—Samples of each polymer suitable for softening-point determination were prepared by moulding the powdered polymer at 200° for 30 min. at 1000 lb./sq. in., air being excluded. In this way slightly coloured sheets of polymer were obtained, the softening points of which were determined: The specimen was stressed by a circular penetrometer needle of 1 mm.^{2} cross-sectional area loaded with 1 kg. and was heated at 50°/hr. The Vicat and 1/10 Vicat softening points are the temperatures at which penetrations of 1 mm. and 0·1 mm., respectively, are obtained.

Softening-point data.

	[η] (decilitre g.$^{-1}$)			
Polymer of	Before moulding	After moulding	1/10 Vicat	Vicat
2 : 3-Dihydrofuran	3·5	2·1	108°	117°
„	2·2	1·4	107	118
2 : 3-Dihydro-5-methylfuran	6·8	4·5	238	245
„ „	4·2	2·5	231	245
„ „	0·92	1·0	>220 [a]	>220 [a]
2 : 3-Dihydro-2 : 2-dimethylfuran	8·0	3·3	162	172

[a] Determination prevented by breakdown of the apparatus at 220°.

The moulding process reduces the intrinsic viscosity of the polymer, but comparison of the data given for samples of the same polymer but of different molecular weight shows that the softening point is independent of the molecular weight, in the molecular-weight range investigated. Hence the softening points of the mouldings are a true measure of the softening points of the polymers, and are not distorted by the reduction in molecular weight caused by moulding.

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