

### 59. *The Spontaneous Low-temperature Polymerisation of Acetaldehyde.*

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The spontaneous low-temperature polymerisation of acetaldehyde is shown by quantitative measurements at various temperatures to occur only in the act of crystallisation, and to yield a product containing a small number of long chains. The reaction whereby these grow is strongly inhibited by the addition of other organic liquids to the aldehyde. The polymer appears to be a polyoxymethylene of variable character, some samples of which depolymerise rather readily at room temperature.

THE fact that acetaldehyde polymerises on cooling to low temperatures has been familiar for many years, but only qualitative experiments on the reaction have been reported. Travers (*Trans. Faraday Soc.*, 1936, **32**, 246) found that the reaction occurred more readily after successive vacuum distillations of the aldehyde, and concluded that it was inhibited by oxygen. Letort (*Compt. rend.*, 1936, **202**, 767; Letort and Duval, *ibid.*, 1943, **216**, 58, 606) obtained the polymer by condensation of the vapour at low pressures in a vessel cooled in liquid air. Under these conditions the reaction did not appear to be sensitive, at least qualitatively, to the purity of the material or to the presence of oxygen. By distilling off the unchanged aldehyde under reduced pressure the polymer was obtained as a colourless rubber-like material.\* Both Travers and Letort found that depolymerisation took place readily, particularly above room temperature.

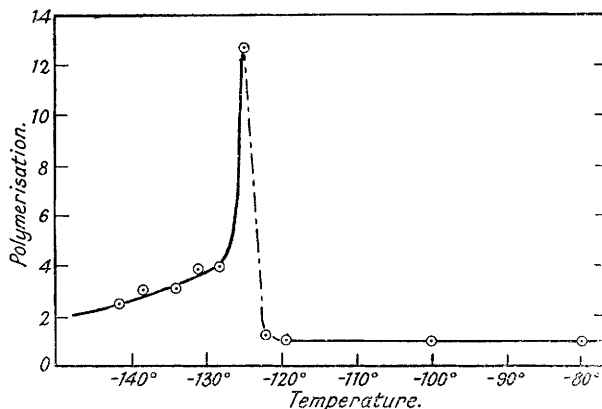
This polymerisation seemed to be a reaction of unusual interest in that it appeared to occur at a greater rate at a lower temperature. In the reaction of propylene with hydrogen chloride a similar behaviour has been attributed to an orientation effect (Sutherland and Maass, *Canadian J. Res.*, 1931, **5**, 48).

The present paper describes experiments on the kinetics of the low-temperature polymerisation of acetaldehyde which were carried out in order to throw light on the mechanism of the reaction. Experiments were also made to determine the probable nature of the polymer.

\* *Added in Proof.*—Since this paper was written we have received the communication of Letort, Duval, and Rollin (*Compt. rend.*, 1947, **224**, 50) reporting the non-occurrence of the polymerisation above the freezing point.

*Experimental Methods.*—Acetaldehyde was carefully fractionated through a long column. Experiments were made on 10 c.c. samples contained in stoppered "Pyrex" test tubes. Cooling was effected by three different methods, (a) direct immersion in liquid nitrogen, (b) immersion in liquid oxygen (with a thin copper sleeve around the test-tube as a safety precaution), and (c) immersion in a simple cryostat. The cryostat consisted of a cylindrical Dewar vessel containing light petroleum which was stirred and maintained at the required temperature by means of liquid air syphoned at the appropriate rate from a storage vessel into a metal tube closed at the bottom and dipping into the cryostat. In this way temperatures between  $-80^{\circ}$  and  $-140^{\circ}$  could be maintained within about  $1^{\circ}$  for considerable periods. They were measured by a pentane thermometer calibrated against a copper-constantan thermocouple and potentiometer.

The relative extent of polymerisation in different experiments was estimated by measurements of viscosity at  $0^{\circ}$  in Ostwald viscometers, calibrated by the use of suitable glycerol-water mixtures. Polymer samples which were too viscous to flow in an ordinary viscometer were compared by measuring the viscosity of acetone solutions. A few experiments were made on very viscous specimens by determining the rate of fall of small steel balls in the liquid.



*Effect of temperature on the polymerisation of acetaldehyde.* (The degree of polymerisation is given in terms of the viscosity of a standard acetone solution of the polymerised material relative to that of a corresponding solution of pure acetaldehyde.)

*Effect of Temperature.*—A series of identical samples of aldehyde were cooled in the cryostat for periods of 10 minutes at different temperatures between  $-80^{\circ}$  and  $-140^{\circ}$ . The products were warmed rapidly to room temperature and dissolved in a standard volume of acetone, and the viscosity was measured. The results are given in the figure, where the viscosity of the solution (in terms of the time of flow relative to that of a corresponding solution of pure acetaldehyde) is plotted against temperature.

It will be seen that above the freezing point of acetaldehyde ( $-123.5^{\circ}$ ) there is no polymerisation. Acetaldehyde cooled just to its freezing point polymerises to a considerable extent. Samples placed in a bath at still lower temperatures suffer progressively less polymerisation. Other experiments showed that samples which had been cooled to the freezing point but which did not solidify owing to super-cooling did not polymerise. From this it would appear that polymerisation takes place only when the acetaldehyde is in the act of crystallising at its freezing point. The polymerisation evidently decreases at lower temperature because the increasing rate of solidification leaves less time for polymerisation. This is confirmed by experiments in which the samples were cooled directly in a bath of liquid nitrogen. This gave very rapid freezing of the aldehyde and very little polymerisation was observed. Erratic results obtained with samples cooled in liquid oxygen and having a metal sleeve round the container are due to the irreproducible rates of cooling, as was shown by experiments in which the actual rate of fall in temperature was observed by a thermocouple placed in the tube.

*Effect of Time of Cooling.*—To investigate whether, at a fixed temperature, the reaction was progressive, or whether, as concluded above, it occurred only during the actual act of freezing, the following experiment was carried out. A series of identical samples of aldehyde were immersed simultaneously in the low-temperature bath and removed after different periods of time. Each sample of polymer was dissolved in fixed volumes of acetone, and the extent of polymerisation determined as explained above. The results are given in Table I, in which  $t$  is the time of cooling in minutes and  $\eta$  is the viscosity of the acetone solution relative to the standard. It will be seen that the reaction is not progressive, but appears only to occur during the initial act of freezing.

TABLE I.

*Variation of the extent of polymerisation with time at a fixed temperature.*

Temp.	<i>t.</i>	$\eta$ .	Temp.	<i>t.</i>	$\eta$ .	Temp.	<i>t.</i>	$\eta$ .
-125°	10	7.07	-127°	10	2.09 *	-132°	10	3.27
	20	5.37		20	6.68		20	2.40
	30	5.56		30	6.79		30	2.37
	40	5.68		40	7.62		40	2.51

\* Probably supercooled.

In a similar experiment the sample of aldehyde was cooled for a short time, allowed to warm to room temperature, tested, and then cooled again. All the increase in viscosity took place during the first period of cooling. No further reaction was observed during subsequent freezings.

*Effect of Added Substances on the Polymerisation.*—A series of experiments were made with aldehyde containing known small amounts of foreign substances, namely acetone, propaldehyde, and chloroform. Samples containing from 1.0% to 10% of these substances were prepared, and the relative times of flow after cooling for a fixed time under standard conditions were measured. The results are given in Table II, in which *M* is the molar fraction of added substance, and  $\eta$  is the viscosity relative to pure acetaldehyde.

TABLE II.

*Effect of added substances on the polymerisation.*

Time of cooling, 10 minutes. Temperature, -130°.

Subs. added.	<i>M.</i>	$\eta$ .	Subs. added.	<i>M.</i>	$\eta$ .	Subs. added.	<i>M.</i>	$\eta$ .
Acetone	0.0076	46.25	Propaldehyde	0.0077	very large	Chloroform	0.0207	very large
	0.0151	5.20		0.0154	346.9		0.0340	205.3
	0.0225	2.78		0.0229	31.1		0.0470	15.9
	0.0298	4.68		0.0376	4.17		0.0596	6.3
	0.0365	1.50		0.0518	5.74		0.0779	2.4
0.0440	1.49	0.0724	4.39					

It will be seen that quite small amounts of added substances reduce the extent of polymerisation to a marked extent. (The greatly reduced polymerisation observed with samples of acetaldehyde which had been stored after distillation may be attributed to traces of paraldehyde and acetic acid formed by slow polymerisation or oxidation. The different rates of polymerisation observed on different occasions and with different samples of aldehyde are to be attributed similarly to the presence of small amounts of impurity.)

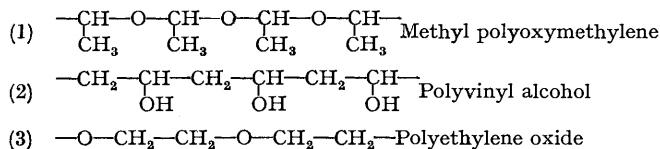
*The Depolymerisation.*—The product obtained by cooling aldehyde under the conditions described was a very viscous liquid, or even a gel. Large quantities of unchanged aldehyde could be removed under reduced pressure leaving a rubber-like spongy solid. When kept at room temperature this reverted fairly rapidly to a liquid of which a considerable proportion was aldehyde. The rate of this depolymerisation varied considerably with different samples of polymer; the most stable remained solid for about two weeks; others became liquid in a few days.

The polymer was readily soluble in acetone, giving a viscous solution. Depolymerisation, as measured by the decrease in viscosity, took place at least as readily in solution as in the solid. A series of experiments were made in which the change of viscosity of acetone solutions of the polymer with time at different temperatures was measured. Again a very marked difference in the behaviour of different samples was encountered. It was not found possible to obtain a satisfactory temperature coefficient from which the activation energy of the depolymerisation might have been calculated. All the samples investigated appeared to be stable below a given temperature, and to depolymerise at an increasing rate at higher temperatures. The temperature below which depolymerisation did not take place varied from sample to sample, some being stable below -9°, some only below -20°.

*The Nature of the Polymer.*—(a) *Molecular weight.* The number average molecular weight of samples of acetaldehyde which had been polymerised so as to have a high viscosity was measured cryoscopically in benzene. Values in the region of 55 were obtained. The solution therefore consisted of a relatively small number of rather large polymer molecules dissolved in unchanged aldehyde. The fact that the material obtained by the removal of the aldehyde was an elastic solid indicated that its molecular weight was probably in the region of several thousand. This solid dissolved in benzene only very slowly. The resulting solutions gave molecular weights of the order of 600. This low value was clearly due to partial depolymerisation, or incomplete removal of residual unchanged acetaldehyde.

(b) *X-Ray diffraction investigation.* Several X-ray diffraction photographs of thin films of the solid polymer were taken by Mr. H. M. Powell, who found two diffuse rings of diameters 3.16 cm. and 1.65 cm. (copper  $K\alpha$  radiation, film-specimen distance 3.8 cm.), corresponding to repeat distances of 3.9 Å. and 7.2 Å.

(c) *Chemical evidence.* Chemical analysis confirmed that the polymer had the same empirical formula as acetaldehyde, *i.e.*, it had a repeat unit of  $C_2H_4O$ . There are three possible structures for this polymer :



Polyvinyl alcohols are well known : they are soluble in water and insoluble in most organic solvents. Polyethylene oxides are also soluble in water. The polymer from acetaldehyde is insoluble in water though soluble in acetone and benzene. Methyl-substituted polyoxymethylenes corresponding to structure (1) do not appear to have been described. Of the three alternatives this structure requires the least reorganisation of the acetaldehyde molecule and on chemical evidence appears to be the most plausible.

One of the possible configurations of an alternating carbon-oxygen chain gives repeat distances of 3.86 Å. and 7.70 Å.

*Discussion.*—The experiments described above suggest that the uncatalysed low-temperature polymerisation of acetaldehyde is an entirely new type of reaction. Polymerisation to form what are probably long methyl polyoxymethylene chains appears to take place when the acetaldehyde is in the act of crystallising from the liquid. The slower this process the greater the extent of the polymerisation. The high viscosity and low number average molecular weight of the polymerised aldehyde suggest that a relatively small number of long chains are formed.

It would appear that as the acetaldehyde freezes chemical interaction can on rare occasion occur between successive molecules which attach themselves to the crystal lattice. (The necessary activation energy may probably be derived from the latent heat of fusion.) A free valency is thereby formed, and succeeding molecules as they orient themselves to join the lattice apparently form fresh chemical bonds with some ease and so build up the long chain. It is clear that the interposition of a molecule of another substance in place of acetaldehyde would break this chain. This would explain the sensitivity of the reaction to the presence of impurities, the polymerisation being strongly inhibited by the presence of small amounts of other substances, even of polymer formed in an earlier partial polymerisation.

The reason for the ease of depolymerisation is not clear, but it is probably significant that methyl polyoxymethylenes do not appear to have been previously described, this fact indicating their relative instability.