

Spontaneous Polymerization of Acetaldehyde to Polyacetaldehyde at Close to Dry-Ice Temperature

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Synopsis

Polyacetaldehyde has been prepared in the liquid and vapor phases without the addition of a catalyst by storing undiluted acetaldehyde in the dark at a temperature of -68°C . for 3-6 months. When acetaldehyde was stored in an untreated Pyrex flask, 20% high polymer, 55% paraldehyde, and less than 1% metaldehyde were obtained. The polymer was an elastomeric solid with a low to moderate degree of crystallinity and an intrinsic viscosity of 0.63 dl./g. When the sample was stored in a Pyrex flask which had been pretreated with alcoholic potassium hydroxide followed by a water wash, 16-17% high polymer and 6% paraldehyde were obtained. Some polymer formed on the unwetted glass above the liquid. It was slightly elastic, at least moderately crystalline, and had an intrinsic viscosity of 1.6 dl./g. It is suggested that the formation of this polymer was initiated by basic active sites on the Pyrex surface which acted by an anionic mechanism. Also some polymer was formed in the liquid phase. This material was an amorphous, highly viscous oil with an intrinsic viscosity of 0.28 dl./g. It was probably formed by a cationic mechanism. It is also suggested that a relatively small amount of paraldehyde was formed in the alkali-treated flask in the liquid phase due to neutralization of the Brønsted acid sites and possibly some of the Lewis acid sites on the surface of the flask.

The polymerization of acetaldehyde to polyacetaldehyde without the deliberate addition of a catalyst has been reported by Letort,¹⁻¹³ Travers,¹⁴ Rigby et al.,¹⁵ Bevington et al.,¹⁶ and Vogl.¹⁷ In all previous investigations in which no catalyst was added, polymerization was effected by freezing the acetaldehyde (-123.5°C .). No polymer was obtained at temperatures above the freezing point without the addition of a catalyst. Letort and Duval³ reported that in freeze (crystallization) polymerization neither the deposition of various substances (i.e., sodium carbonate, hydroquinone, or mercury) on the surface of the Pyrex or soft glass container for the acetaldehyde nor the pretreatment of the glass with chromic acid, followed by a water wash, affected the polymerization. Bevington and Norrish¹⁶ found that coating the glass receiver with paraffin also made no difference. However, Vogl¹⁷ noted that pretreating the flask with aqueous alkali reduced the yield of polymer to 1-2% in the freeze polymerization, while treatment with acid increased the yield slightly. It has now been found that the polymerization of acetaldehyde to high polymer will take place in the liquid and vapor phases without the deliberate addition of a

TABLE I. Properties of Polyacetaldehyde Formed at -68°C . in Pyrex Flasks

Flask no. ^a	Description of polymer	Time sample stored, months	Time polymer soln. stored at 25°C ., days	Intrinsic viscosity, dl./g.		Conversion of AcH, %		Sample degraded at 110°C ., %		Method of purifying polyacetaldehyde
				By extrapolation to zero concn.	By Sakurada equation	To high polymer	To para	Ratio para I para II	30 min.	
I	Rubbery solid	5.0	0		0.63				94	Washed with water and evacuated at 25°C . for 3 hr. with oil vacuum pump
I	Rubbery solid	5.0	0		0.55	19.4			96	Evacuated with Hg diffusion pump; sample temp. = -78°C . to 25°C . for 11-12 hr. and 25°C . for 5 hr.
I	Rubbery solid	5.0	3		0.507					"
I	Resembled silicon grease	5.8	0		0.297	14	57	12:1	99	"
II	Vapor-phase polymer: tacky, white solid, slightly elastic	5.95	0		1.59				79	"
II	Liquid phase polymer: very viscous transparent oil	6.0	0		0.277	17.5	6.4	7:1	88	"

^a Flask I was not treated with alkali while Flask II was treated with alcoholic KOH for a few minutes and then rinsed with water.

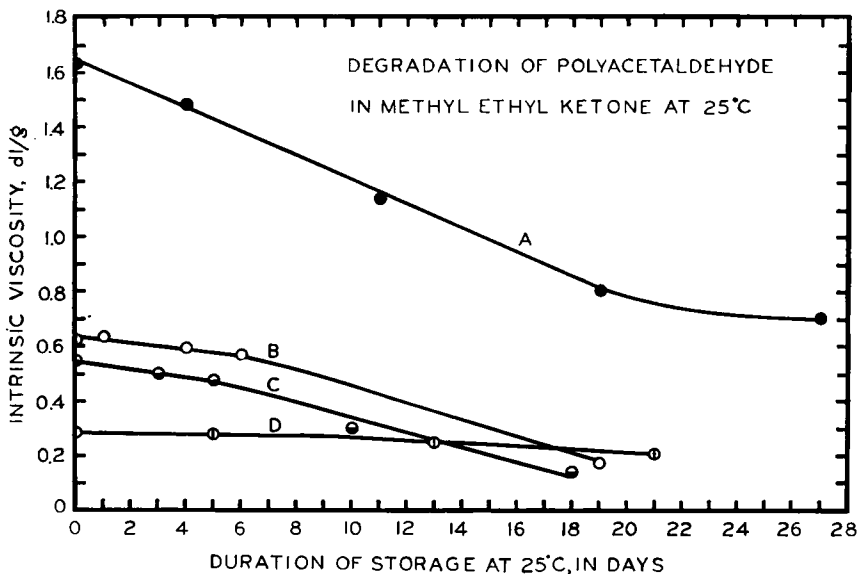


Fig. 1. Intrinsic viscosity of polyacetaldehyde vs. time: (A) polyacetaldehyde formed in vapor phase in alkali-treated flask; (B, C) polyacetaldehyde formed in untreated flask; (D) polyacetaldehyde formed in liquid phase in alkali-treated flask.

catalyst at a temperature of -68°C . over a period of several months and that the physical properties of the surface of the container greatly affect the course of the polymerization. One sample was stored in an untreated Pyrex Erlenmeyer flask at -68°C . and a second one in a Pyrex flask which had been rinsed first with alcoholic potassium hydroxide and then with water. After standing for 5–6 months in a freezer in the dark, the samples were examined and their properties are reported in Table I and Figure 1.

Experimental

In all experiments except one, Shawinigan Chemicals Ltd. acetaldehyde produced by the oxidation of ethylene in the presence of a palladium catalyst was used. Typically, this acetaldehyde contains about 100 ppm of acetic acid, 30 ppm peracetic acid, 10–20 ppm paraldehyde, <30 ppm water, <30 ppm crotonaldehyde, 10 ppb hydrogen chloride, and 1–3 ppm of organically bound chlorine. Two 1-liter, glass-stoppered (ungreased), Pyrex Erlenmeyer flasks were preconditioned by storing acetaldehyde in them at -12°C . for several months. Flask I was rinsed with acetaldehyde about a dozen times before being filled. After stoppering, the top of the flask was covered tightly with aluminum foil. Flask II was rinsed first with a nearly saturated solution of potassium hydroxide in isopropanol for several minutes, then with deionized water and finally with acetaldehyde. Both flasks were filled with 800–900 ml. of acetaldehyde and were stored in complete darkness at -68°C . Most of the air was flushed out of the

flasks with acetaldehyde vapor, but it is reasonable to suppose that air was slowly sucked into the flasks over a period of 1–2 weeks.

The contents of flask I (not treated with alkali) set to a hard mass in 3–4 months. In order to scrape off a sample for study, it was necessary to allow the sample to stand at ambient temperature for 20–30 min. One portion of the sample was washed with water to remove some of the acetaldehyde and then it was evacuated for 3 hr. at ambient temperature with a vacuum pump capable of evacuating down to 0.2 mm. Hg (absolute). The other portion of this same sample, as well as all other samples, was not washed but was evacuated with a mercury diffusion pump for periods ranging from 3.5 to 17 hr. The temperature of the sample was gradually raised from -78 to 25°C ., and ambient temperature was maintained for about 5 hr.

Viscosity measurements were made with an Ostwald viscometer at 25°C . with methyl ethyl ketone as solvent. The percentage of paraldehyde in the crude polymerizate was determined by gas chromatography (column: 6 ft. \times $\frac{1}{4}$ in. copper tubing, packed with 20% LB 550-X Ucon Oil on Chromosorb P; temperature: 100 – 180°C . programmed at a rate of $5^{\circ}\text{C}/\text{min}$.; gas flow: 60 ml. helium/min.; detector: hot wire, 210 ma.) Infrared spectra of pelletized polyacetaldehyde samples were obtained with a Beckman IR4 spectrophotometer. The pellets (0.5 mm. thick) were prepared by mulling a mixture of about 0.38% polymer in potassium bromide, placing the mixture in a pellet die, evacuating, and applying a pressure of 10,000 psi in a Carver press for 2–3 min. The x-ray diffraction patterns were obtained with a North American Philips Co. instrument, type no. 12033.

Results

After 5 months' storage, the contents of Pyrex flask I (not treated with alkali) were found to consist of about 20% high polymer, about 55% paraldehyde (ratio paraldehyde I to paraldehyde II = 12:1¹⁸), less than 1% metaldehyde, and the rest acetaldehyde. The crude polymer was a gummy solid at room temperature. After a water wash and an evacuation for 3 hr., its intrinsic viscosity was found to be 0.63 dl./g. When a portion of the same original polymer (unwashed) was evacuated for 16 hr. with a mercury diffusion pump, while the temperature of the sample was gradually raised from -78 to 25°C ., its intrinsic viscosity was 0.55 dl./g. It was thus apparent that a little degradation of the polymer had taken place due to increase in the duration of evacuation. This was further confirmed by the observation that the vapor pressure in the evacuation line, after practically all the paraldehyde had distilled out of the polymer, was much higher than that which would have been expected from paraldehyde. An attempt to shorten the period of evacuation to 3.5 hr., without washing the polymer with water, was unsuccessful. Some paraldehyde and metaldehyde was left in the polymer, as shown by infrared and other analyses. On resampling flask I, after it had been stored for 5.8 months, it was found

that the intrinsic viscosity of the polymer had decreased by about 50% and the percentage of high polymer in the crude polymerizate had decreased substantially. The reason for this degradation can only be surmised. While the sample was heated three times to temperatures of the order of 0°C. for 20–30 min., the degradation of the polymer due to this would not ordinarily be expected to be great. Opening the flask undoubtedly introduced fresh oxygen which would be expected to react slowly with acetaldehyde, forming some fresh acetic acid and peracetic acid. Acetic acid is known to catalyze the depolymerization of polyacetaldehyde at 25–35°C.,¹⁶ but the sample was at about 0°C. for substantially less than 1 hr. Consequently, it is difficult to see how this could have had a great effect. There was also an appreciable loss of monomeric acetaldehyde during sampling. This may have caused a shift in the monomer–polymer equilibrium.

In flask II (alkali-treated) some polymer formed in the vapor phase on the unwetted glass after 3–4 months. Later some grew from or to the surface of the liquid in the vapor phase, forming one mass with the polymer already on the glass. A small portion of the total vapor-phase polymer was taken for study. However, most of the sample (80–90% of the total) was still a slightly viscous liquid at –68°C. after 6 months. The average composition of the flask was 16–17% high polymer, 6% paraldehyde (ratio of paraldehyde I to paraldehyde II = 7:1), negligible metaldehyde, and the rest acetaldehyde. The total conversion to high polymer was thus only moderately lower than that in flask I (untreated). The vapor-phase polymer was a white, slightly elastic solid with an intrinsic viscosity of 1.59 dl./g. while the polymer obtained on evaporating the liquid phase was a very viscous, colorless oil with an intrinsic viscosity of 0.28 dl./g. Thus the vapor-phase polymer had a much higher intrinsic viscosity than either the liquid-phase polymer or that obtained in the flask which had not been treated with alkali. Furthermore, it was substantially more stable thermally at 25–110°C. than the two latter samples (cf. Table I). In some experiments in which the preconditioning of the Pyrex flask was done with little care, the formation of polymer was observed to take place on untreated Pyrex. Thus it was apparent that the past history of the glass surface could sometimes affect the course of the polymerization.

All the polyacetaldehyde samples were examined by infrared spectrometry and x-ray diffraction. These spectra were compared with those obtained with a sample of polyacetaldehyde prepared by the freeze method of Letort^{1–13} and Travers.¹⁴ The freeze polymer is generally considered to be amorphous, although Letort and Richard^{13,19} suggested that a part of the polymer chain may consist of a succession of syndiotactic units. The infrared spectrum of the polymer formed in the liquid phase in the alkali-treated flask (II) was found to be almost identical to that of the amorphous polymer, as reported by Furukawa.¹⁹ The doublet at 10.39 and 10.81 μ was slightly more resolved than that of the freeze polymer, and the x-ray diffraction pattern was perhaps very slightly sharper. Thus the liquid-phase polymer was essentially amorphous, although there were sug-

gestions of a very low degree of crystallinity. The polymer which formed in the vapor phase in the alkali-treated flask had an infrared spectrum very similar to that of the crystalline polymer of Furukawa,¹⁹ except that the doublet at 10.39 and 10.81 μ was not quite so well resolved, and a partially resolved doublet at 8.90 and 9.05 μ was noted instead of a single band at 8.91 μ . Two small bands at 8.63 and 12.0 μ , which are apparently characteristic of crystalline polymer, were present. The x-ray diffraction pattern of the vapor-phase polymer was somewhat sharper than those of the other samples, thus confirming that this sample was the most crystalline one prepared in this investigation and that it possessed at least a moderate degree of crystallinity. The polyacetaldehyde which formed in the untreated flask was found to have an infrared spectrum intermediate between those of the liquid and vapor-phase polymers described above. Consequently, it is reasonable to suppose that it possessed an intermediate degree of crystallinity.

Discussion

The polymer which formed in the vapor phase in the alkali-treated flask had a much higher molecular weight and thermal stability than the liquid-phase polymer. It also appeared to possess a substantial degree of crystallinity, while the liquid-phase polymer was essentially amorphous. Firstly, these observations would suggest that the alkali treatment had introduced some basic active sites on the Pyrex surface which acted in the vapor phase by an anionic mechanism. Secondly they would suggest that the liquid-phase polymer had formed by a cationic mechanism, undoubtedly catalyzed in part by the acetic and peracetic acids present in the original acetaldehyde. It seems improbable that the concentrations of these acids were greatly reduced by the alkali treatment of the flask, since the alkali was thoroughly washed off beforehand. From infrared studies several investigators²⁰⁻²⁴ have found evidence that certain borosilicate and other glass surfaces contain Brønsted and/or Lewis acid sites. Lewis acid sites appear to have been identified more often than the Brønsted. Vogl¹⁷ has shown that at -65°C . certain Brønsted and Lewis acids initiate the formation of polyacetaldehyde and/or paraldehyde in various solvents. The relative proportion of the products appears to depend on the activity as well as the concentration of the initiator. Highly active initiators, which at relatively high concentrations give rise to only paraldehyde, produce polyacetaldehyde at much lower concentrations. The alkali treatment of the Pyrex surface in the present investigation reduced the conversion of acetaldehyde to paraldehyde by about 90% but reduced that to high polymer by only about 15%. This would suggest that most of the highly active centers, which catalyzed the formation of paraldehyde, were neutralized while most of the less active centers which (together with acetic acid) catalyzed the formation of high polymer, were left unchanged. Since Brønsted acids are relatively strong and the Lewis acids relatively weak, it is reasonable to suppose that the alkali treatment would neutralize,

for the most, the Brønsted acid sites but would probably leave most of the Lewis acid sites unaffected. Work in this laboratory by D. Willermet has shown that certain Brønsted acids (e.g., hydrogen chloride) will initiate the formation of paraldehyde and/or polyacetaldehyde at -78°C . The neutralization of the Brønsted acid sites would therefore be expected to reduce the conversions of acetaldehyde to paraldehyde and high polymer. Since the chief initiator for high polymer formation in the liquid phase was probably acetic acid and not the Brønsted or Lewis acid sites, the reduction in the amount of polymer formed would not have been expected to be very great. The great reduction in the molecular weight of the polymer was probably due to the neutralization of the Brønsted acid and possibly some of the Lewis acid sites.

One sample of polyacetaldehyde was prepared from acetaldehyde manufactured from acetylene by storing it in an untreated Pyrex flask at -68°C . for 3 months. The intrinsic viscosity of the polymer was 0.71 dl./g. (25°C . in acetone), which was very close to the value obtained with acetaldehyde manufactured from ethylene. The effect on polymerization of those impurities, which were not present in both acetaldehyde from acetylene and that from ethylene, was therefore not great.

The solutions of the various polymer samples in methyl ethyl ketone were stored in the dark at about 25°C . for periods up to 27 days. The intrinsic viscosities were determined from time to time and some of the preliminary results are plotted in Figure 1. In many instances, the intrinsic viscosity was obtained by using the Sakurada equation with one point rather than plotting several viscosity numbers against concentration and extrapolating to zero concentration. The difference in values obtained by these two methods varied from 1.4 to 4.4% (cf. Table I). From Figure 1, it will be noted that the intrinsic viscosities decreased linearly with time for periods varying from 5 to 19 days. During the first 6 days, the rate of degradation (expressed as the percentage decrease in intrinsic viscosity during that period) was 15–16% for the polymer formed in the vapor phase in the alkali-treated flask (A), 12–17% for the polymer formed in the untreated flask (B and C), and about 3% for the polymer formed in the liquid phase in the alkali-treated flask (D). After 6 days, the intrinsic viscosity of polymer A continued to decrease at the same rate as before, but between 19 and 27 days it began to level off. In contrast to this, the intrinsic viscosities of polymers B, C, and D decreased at accelerated rates. Since polymers capable of existing in the crystalline state are generally more stable than amorphous ones, the greater resistance of polymer A to degradation (except during the first 6 days) is consistent with the previous observation that it was more crystalline (in the solid state) than polymers B, C, and D. The leveling off in the rate of degradation of polymer A after 19–27 days might indicate that most of the atactic units in the polymer chain had already degraded and that essentially only tactic units remained.

Polymer C, after being degraded in the solid phase over a period of three weeks by being heated to 0°C . for 20–30 min. three times in the presence

of air, had an intrinsic viscosity almost the same as that of polymer D. In solution it degraded virtually identically to polymer D. These observations would suggest that degraded polymer C and polymer D (which was amorphous) were identical.

R. M. Kitchen of our Works Laboratory observed the formation of polyacetaldehyde in 1963 in plant samples of acetaldehyde which had been cooled with Dry Ice. These samples were examined by D. Willermet. A. Dupré and A. L. da Costa carried out the infrared studies, R. C. White the gas-liquid chromatographic analyses, and E. Moreau the viscosity measurements in this investigation.

References

1. M. Letort, *Compt. Rend.*, **202**, 767 (1936).
2. M. Letort and X. Duval, *Compt. Rend.*, **216**, 58 (1943).
3. M. Letort and X. Duval, *Compt. Rend.*, **216**, 608 (1943).
4. M. Letort, X. Duval, and Y. Rollin, *Compt. Rend.*, **224**, 50 (1947).
5. M. Letort and J. Petry, *Compt. Rend.*, **231**, 519 (1950).
6. M. Letort and J. Petry, *Compt. Rend.*, **231**, 545 (1950).
7. M. Letort and A. Richard, *Compt. Rend.*, **240**, 86 (1955).
8. M. Letort and J. Petry, *J. Chim. Phys.*, **48**, 594 (1951).
9. M. Letort and P. Mathis, *Compt. Rend.*, **241**, 651 (1955).
10. M. Letort and P. Mathis, *Compt. Rend.*, **241**, 1765 (1955).
11. M. Letort and P. Mathis, *Compt. Rend.*, **242**, 371 (1956).
12. M. Letort and P. Mathis, *Compt. Rend.*, **249**, 274 (1959).
13. M. Letort and A. J. Richard, *J. Chim. Phys.*, **57**, 752 (1960).
14. M. W. Travers, *Trans. Faraday Soc.*, **32**, 246 (1936).
15. H. A. Rigby, C. J. Danby, and C. N. Hinshelwood, *J. Chem. Soc.*, **1948**, 234.
16. J. C. Bevington and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A196**, 363 (1949).
17. O. Vogl, *J. Polymer Sci. A*, **2**, 4591 (1964).
18. E. C. Craven, H. Jowitt, and W. R. Ward, *J. Appl. Chem.*, **12**, 526 (1962).
19. J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Oxides*, Interscience, New York, 1963, pp. 88, 96.
20. I. D. Chapman and M. L. Hair, *Trans. Faraday Soc.*, **61**, 1507 (1965).
21. I. D. Chapman and M. L. Hair, *J. Catalysis*, **2**, 145 (1963).
22. T. H. Elmer, I. D. Chapman, and M. E. Nordberg, *J. Phys. Chem.*, **67**, 2219 (1963).
23. N. W. Cant and L. H. Little, *Can. J. Chem.*, **42**, 802 (1964).
24. M. Fulman, *Trans. Faraday Soc.*, **57**, 2000 (1961).

Résumé

Le polyacétaldéhyde a été préparé en phases liquide et vapeur sans addition d'un catalyseur en gardant l'acétaldéhyde non-dilué à l'obscurité à température de -68°C pendant 4 à 6 mois. Si l'acétaldéhyde est maintenu dans un bouteille de pyrex non-traité, 20% de haut polymère, 55% de paraldéhyde et moins de 1% de métaldéhyde sont obtenus. Le polymère est un solide élastomère avec un degré de cristallinité faible à modéré et une viscosité intrinsèque de 0.63 dl/g. Si l'échantillon a été gardé dans une bouteille en pyrex qui a été prétraité avec l'hydroxyde de potassium alcoolique, suivi d'un lavage à l'eau, 16-17% de haut polymère et 6% de paraldéhyde sont obtenus. Une certaine quantité de polymère est formé sur le verre non-humidifié au-dessus du liquide. Il était faiblement élastique au moins modérément cristallin et avait une viscosité intrinsèque de 1.6 dl/g. On suggère que la formation de ce polymère était initiée par des sites actifs basiques à la surface du pyrex qui réagissent par mécanisme anionique.

Également quelque polymère était formé dans la phase liquide. Ce matériau était amorphe, hautement visqueux avec une viscosité intrinsèque de 0.28 dl/g. Il est probablement formé par un mécanisme cationique. Il est également suggéré qu'une quantité relativement faible de paraldehyde était formé dans la bouteille traitée par les alcalis en phase liquide par suite de la neutralisation des sites acides de Brønsted et peut-être de certains sites acides de Lewis à la surface de la bouteille.

Zusammenfassung

Polyacetaldehyd wurde in flüssiger und gasförmiger Phase ohne Zusatz eines Katalysators durch Lagerung von unverdünntem Acetaldehyd im Dunkeln bei einer Temperatur von -68°C während 4 bis 6 Monaten dargestellt. Beim Aufbewahren von Acetaldehyd in einer nicht vorbehandelten Pyrexflasche wurden 20% Hochpolymeres, 55% Paraldehyd und weniger als 1% Metaldehyd erhalten. Das Polymere war ein elastischer Festkörper mit mässigem Kristallinitätsgrad und einer Viskositätszahl von 0,63 dl/g. Beim Aufbewahren der Probe in einer mit alkoholischem Kaliumhydroxyd vorbehandelten und dann mit Wasser ausgewaschenen Pyrexflasche wurden 16–17% Hochpolymeres und 6% Paraldehyd erhalten. Etwas Polymeres bildete sich am unbenetzten Glas oberhalb der Flüssigkeit. Es war schwach elastisch, zumindest mässig kristallin und besass eine Viskositätszahl von 1,6 dl/g. Es wird angenommen, dass die Bildung dieses Polymeren von basischen aktiven Stellen an der Pyrexoberfläche ausgeht, und über einen anionischen Mechanismus verläuft. Etwas Polymeres bildete sich auch in der flüssigen Phase. Dieses Material bildete ein amorphes, hochviskoses Öl mit einer Viskositätszahl von 0,28 dl/g. Es wurde wahrscheinlich über einen kationischen Mechanismus gebildet. Schliesslich wird angenommen, dass in der Alkalibehandelten Flasche eine verhältnismässig kleine Paraldehydmenge wegen der Neutralisation der Brønsted-Säure-Stellen und möglicherweise einiger Lewis-Säure-Stellen an der Oberfläche der Flasche in flüssiger Phase gebildet wurde.

Received April 14, 1966

Prod. No. 1385