160. *The Stability of Polyvinyl Acetate in Technical Mustard Gas Solution.*

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Solutions of vinyl acetate polymers in a technical grade of mustard gas were unstable on storage. At first the viscosity was reduced, but later it increased, the process culminating in gelation. The cause of this instability has been traced to constitutional changes in the polymer brought about by interaction with the solvent. The first phase is associated with the rupture of weak linkages in the polymer chain. Later, cross-linking with the solvent takes place, yielding an insoluble polymer. McDowell and Kenyon's evidence for the existence of weak linkages in polyvinyl acetate has been re-examined and it has been shown that when the acetate groups of the polymer are removed by hydrolysis and subsequently restored by acetylation the initial and final polymers behave differently in mustard gas solution.

VISCOSITY changes in solutions of high polymers on ageing have been frequently reported. These changes may arise from different causes, such as variations in the degree of solvation of the polymer, or in the orientation or configuration of the macromolecules in solution. Again they may be due to changes in the chemical nature of the polymer or in its molecular weight.

An investigation of the behaviour of various high polymers in mustard gas solution revealed marked differences in stability on storage (Ministry of Supply, unpublished information). Thus, polymethyl methacrylate and polystyrene solutions remained stable for prolonged periods whereas, in the cases of cellulose esters and ethers, methylated starches, and chlorinated rubber, significant changes in viscosity occurred quite rapidly. With vinyl acetate polymers an initial reduction in viscosity was observed; later the viscosity increased and this trend continued to the point of gelation. Storage in contact with metallic iron accentuated the changes. Blaikie and Crozier (*Ind. Eng. Chem.*, 1936, **28**, 1155) aged solutions of polvinyl acetate in glacial acetic acid in glass bombs at 160° and observed an initial decrease in the viscosity followed by an increase at the end of four weeks; when air was excluded the changes were not so pronounced. Morrison, Holmes, and McIntosh (*Canad. J. Res.*, 1946, **24**, *B*, 179) reported on the instability of solutions of three polymers, polyvinyl acetate, polystyrene, and polymethyl methacrylate in each of three solvents, 2 : 2′-dichlorodiethyl ether, nitrobenzene, and 2 : 2′-dichlorodiethyl sulphide;

observed variations in viscosity were traced to changes in the molecular weight of the dissolved polymers caused by the presence of small amounts of impurities; in particular, oxygen appeared to give rise to degradation reactions, whereas iron salts caused the formation of gel structures. The production of insoluble cross-linked materials from solutions of various polymers by the agency of metallic halides active in Friedel–Crafts reactions has been demonstrated by Bevington and Norrish (*J.*, 1948, 771). In the case of polystyrene in ethylene dichloride the solvent participates in the reaction, leading to a cross-linked structure with elimination of hydrogen chloride.

The present investigation was undertaken with the object of elucidating the underlying cause of instability in the polyvinyl acetate–mustard gas system. By noting changes in viscosity the stability of solutions of commercial grades of polyvinyl acetate (manufactured by the Shawinigan Chemical Co., Canada, and marketed under the trade name " Gelva ") in mustard gas at 25°, 60°, and 100° was investigated. The mustard gas used was a commercial mixture of 60% of 2 : 2′-dichlorodiethyl sulphide and 40% of 2 : 2′-di-(2-chloroethylthio)diethyl ether by weight. A modified form of viscometer (Fig. 1) designed for dealing with vesicant liquids functioned very successfully; it was an adaptation of that used by Kuenen and Visser (Barr, " A Monograph of Viscometry," p. 123) for determining the viscosity of liquid butane. The progress of the stability tests for " Gelva 15 " is shown graphically in Fig. 2. At 25° a small but steady decrease in viscosity was observed for a period of 90 days. Likewise, at 60°, the viscosity decreased, but much faster. At 100°, however, the first reading, taken after 4 days, showed a definite increase and the viscosity continued to rise sharply until, after 6 days 19 hours, the solution set to a gel. It is possible that, in the last case, a reading taken at an earlier stage might have revealed an initial phase of viscosity depression.

FIG. 1.

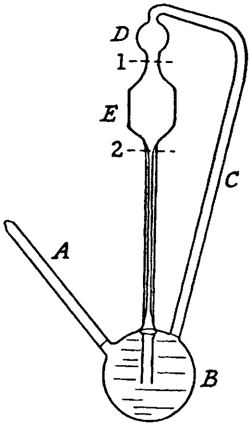
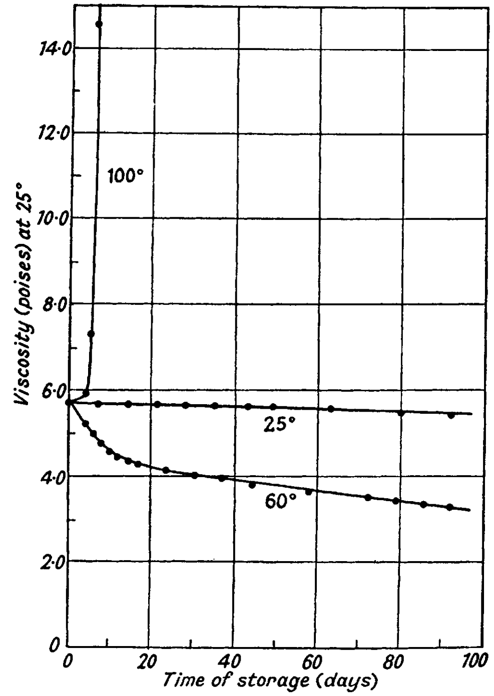


FIG. 2. *Viscosity changes of Gelva* 15 *solution on storage at* 25°, 60°, *and* 100°.



If the reduction in viscosity at 25° and 60° results from degradation of the polymeric molecules in contact with mustard gas, then this necessarily entails rupture of carbon–carbon bonds if, as is generally believed, the molecules of polyvinyl acetate consist of linear chains of such carbon-to-carbon linkages. Such a rupture seems very unlikely. A more plausible explanation is to be found in McDowell and Kenyon's suggestion (*J. Amer. Chem. Soc.*, 1940, **62**, 415) that a limited number of unstable linkages are present in the polyvinyl acetate chain. These, they suggest, may be due to oxygen from peroxide catalyst, or to acetaldehyde from the vinyl acetate monomer, entering into the polymer to produce a small number of such linkages. This concept of the inclusion of oxygen in the polymer structure has also been advanced by Staudinger and Schwalbach (*Annalen*, 1931, **488**, 8). The role of oxygen in vinyl polymerisation has been discussed by Barnes (*J. Amer. Chem. Soc.*, 1945, **67**, 217); and Bovey and Kolthoff (*ibid.*, 1947, **69**, 2143) have shown that, in the case of styrene, copolymerisation with oxygen to give a 1 : 1 copolymer is possible.

FIG. 3. *Viscosity changes of reacetylated Gelva* 15 *solution on storage at* 25°, 60°, *and* 100°.

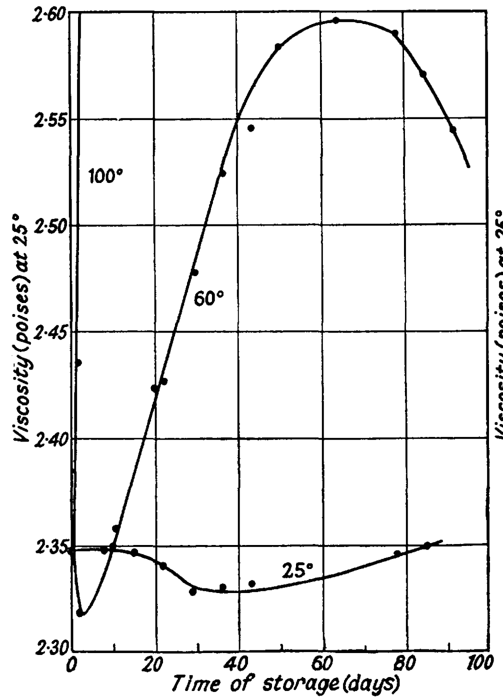
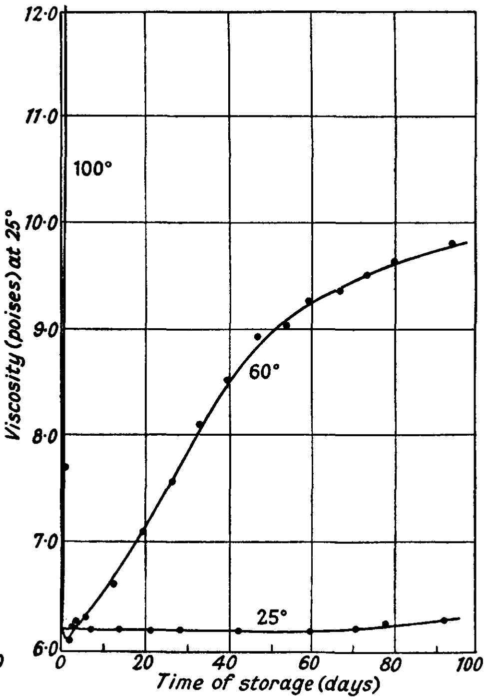


FIG. 4. *Viscosity changes of reacetylated Gelva* 45 *solution on storage at* 25°, 60°, *and* 100°.



If a limited number of such less stable linkages are present in polyvinyl acetate molecules, then the fission of these bonds would account for the observed behaviour of the polymer on the assumption that these bonds were vulnerable to mustard gas. Another reaction must be postulated to account for the marked increase in viscosity which follows the first phase of viscosity reduction.

McDowell and Kenyon's evidence for the possible existence of these unstable linkages was based on their experimental study of the molecular-weight relations in the system polyvinyl acetate ⟶ polyvinyl alcohol ⟶ polyvinyl acetate. Vinyl acetate polymers of various degrees of polymerisation were hydrolysed to polyvinyl alcohols and the latter acetylated to give polyvinyl acetates. It was found that the reacetylated polymers possessed degrees of polymerisation, as calculated from specific-viscosity measurements, which were less than those of the parent acetate polymers. This decrease of average chain length is attributed to the rupture of the less stable linkages in the macromolecules during the cycle of operations involving hydrolysis and acetylation. Certain unexplained differences in behaviour were observed between vinyl acetate polymers prepared in the laboratory and commercial polymers of unspecified origin. It is significant that no change in chain length was observed when one sample of reacetylated polyvinyl acetate was taken round a second cycle of hydrolysis and acetylation. Blaikie and Crozier (*loc. cit.*) had made a similar observation earlier; they also observed that a certain degree of apparent breakdown of polyvinyl acetate occurs when it is milled, heated with acetic acid, or treated with hydrochloric acid.

Employing the osmotic method Staudinger and Warth (*J. pr. Chem.*, 1940, **155**, 278) have also studied the molecular-weight relations in this cycle for polyvinyl acetate fractions obtained by precipitation of a laboratory-made sample as well as for commercial preparations. With the former little change was observed, whereas a significant reduction in chain length occurred with the commercial polymers of high molecular weight. Some experiments on the hydrolysis of polyvinyl acetate samples and acid treatment of various polyvinyl alcohols have been reported by Marvel and Inskeep (*J. Amer. Chem. Soc.*, 1943, **65**, 1710) in which the chain lengths measured by viscosity methods showed marked changes. These changes were in either direction depending on experimental conditions and were very irregular and unpredictable in amount. On spectroscopic evidence these authors suggested that polyvinyl alcohol contains a terminal aldehyde group. The presence of this end-group, with its ability to undergo acetal formation with the hydroxyl groups of neighbouring molecules under acid conditions and to participate in aldol or reverse aldol reactions under alkaline conditions, is believed to be responsible for the observed changes in molecular size of polyvinyl alcohol under the conditions described. Further, it is suggested that the same aldehyde group may be present at the end of the polyvinyl acetate chain. While these suggestions explain how it is possible to prepare polymers of higher molecular weight from polyvinyl acetate by hydrolysis and reacetylation they cannot account for the reduction in chain length observed under certain conditions.

Clarke and Blout (*J. Polymer Sci.*, 1946, **1**, 419) have shown that the viscosity of polyvinyl alcohol of high molecular weight is reduced in aqueous 0·02N-hydrochloric acid and is constant only after 24 hours' heating at 90—100°. Examination of the ultra-violet absorption spectra of the polyvinyl alcohol revealed an increase in intensity of a carbonyl band as a result of this treatment. However, these carbonyl groups appeared to be ketonic; they appear to be distributed at random along the polymer chain and independently of chain length.

Thompson and Torkington (*Trans. Faraday Soc.*, 1945, **41**, 246) have examined the infra-red spectra of polyvinyl alcohol but nothing emerged from their studies that would help to throw light on the degradation of the acetate. Ellis *et al.* (*J. Chem. Physics*, 1950, **18**, 413) have also investigated the infra-red spectrum of polyvinyl alcohol.

The evidence for degradation in the sequence of reactions involving alcoholysis and acetylation has been re-examined, using commercial polyvinyl acetates. The same polymers have been used in the stability tests in mustard gas solution. If the above reactions serve to rupture the weak bonds in the polymer chain, then the reacetylated polymers would be expected to behave differently in solution in mustard gas. Fig. 3 shows the viscosity changes of mustard gas solutions of reacetylated " Gelva 15 " on ageing at 25°, 60°, and 100°. Comparison with the data presented in Fig. 2 reveals a striking difference between the behaviour of original and reacetylated polymer. Fig. 4 shows the stability of reacetylated " Gelva 45 " (a polymer of higher molecular weight) in mustard gas solution under the same conditions. The significance of these results is discussed below (p. 892).

EXPERIMENTAL

Three commercial polyvinyl acetates—Gelva 7, Gelva 15, and Gelva 45—manufactured by the Shawinigan Chemical Co., Canada, were used. Found, for Gelva 7, 15, and 45 respectively : C, 55·5, 55·8, 55·6; H, 7·0, 7·0, 7·0; Ac, 50·0, 49·5, 49·0. Calc. for $(C_4H_6O_2)_n$: C, 55·8; H, 7·0; Ac, 50·0%.

Hydrolysis.—Several methods have been proposed for the hydrolysis of polyvinyl acetate to polyvinyl alcohol, utilising alkaline or acid conditions. The following methods were examined and compared :

(i) *Methyl-alcoholic sodium methoxide* (Staudinger, Frey, and Starck, *Ber.*, 1927, **60**, 1782). The polyvinyl alcohol from Gelva 15 was obtained in quantitative yield as a rather yellowish powder with ash content 1·82% and entirely free from acetate groups. A nitrogen atmosphere was maintained during the reaction. Dialysis was recommended by the authors for removal of the mineral matter present in the product. In this experiment ice-cold water (500 ml.) was used to wash the product. In a second preparation, with the same proportion of reactants but with 1 litre of ice-cold water used for washing of the polyvinyl alcohol the ash content was reduced to 1·20%; again, hydrolysis was complete. There is a possibility, both on dialysis and on washing with water, that some of the more soluble species of lower molecular weight might be removed with consequent increase in apparent molecular weight. However, as will be seen later, molecular-weight determinations by viscosity negative this.

(ii) *Cold alcoholic sodium hydroxide and a dioxan solution of polyvinyl acetate* (*Gelva* 15) (Staudinger and Warth, *J. pr. Chem.*, 1940, **155**, 278). Despite the careful exclusion of air the product, obtained after washing with ice-cold water (to remove sodium acetate and excess of sodium hydroxide), was slightly yellow; its ash content was 1·10 and its residual acetyl content 1·9%.

(iii) *Alcoholic hydrogen chloride.* Dry gaseous hydrogen chloride was slowly bubbled through a boiling solution of Gelva 15 in methyl alcohol. The solution darkened considerably and the precipitated polyvinyl alcohol was of a brownish colour. Polyvinyl alcohol is known to be very susceptible to hydrochloric acid, giving a water-insoluble black modification. This method does not appear to be satisfactory.

(iv) *Absolute alcohol containing* 1% *of sulphuric acid* (U.S.P. 2 109 883). A 20% solution (100 g.) of Gelva 15 in ethyl alcohol containing 1 g. of sulphuric acid was refluxed for 16 hours. The polyvinyl alcohol precipitated was pure white and granular. It was filtered off and washed with alcohol. When dried at 100° before analysis it darkened, owing to charring by sulphuric acid retained in it. The product was taken up in water and precipitated in a large volume of alcohol. This gave a purer material but it still appeared to retain some sulphuric acid. Its acetyl content was 1·94%. It is known that the last traces of acid are difficult to remove from polyvinyl alcohol. Hermann and Haehnel (*Ber.*, 1927, **60**, 1658) distinguish between " acid " polyvinyl alcohols and " alkali " polyvinyl alcohols. Polymers obtained by hydrolysis with dilute alcoholic acid cannot be completely reacetylated (Staudinger, Frey, and Starck, *loc. cit.*). This may be due to the loss of some hydroxyl groups by removal of water. Whether this dehydration occurs during the hydrolysis or on drying has not been ascertained but there are indications that the change is accelerated by residual traces of acid (Hermann and Haehnel, G.P. 480 866/1929).

(v) *Alcoholysis with an alkaline catalyst* (Blaikie and Crozier, *loc. cit.*). Polyvinyl acetate (100 g.) in dry methanol (600 ml.) was treated with potassium hydroxide (4 g.) in dry methanol. Alcoholysis occurred and, after 24 hours at room temperature, the polymeric alcohol separated as an opaque gel. The product was isolated by dissolving the gel in hot water, cooling, and pouring the solution into acetone (4 l.) which was vigorously stirred. The alcohol separated as a pure white fibrous material. When prepared by this method polyvinyl alcohol has a low ash content and contains but little residual hydrolysable matter. It can be easily and completely reacetylated. These considerations coupled with the apparent purity of the product led to the choice of this method for the present investigations. On analysis the polyvinyl alcohols from Gelva 7, 15, and 45 respectively gave the following results. Found, after drying at 105° for 1 hour in a vacuum: Ac, 1·2, 0·9, 1·0; ash, 1·31, 1·25, 2·20%.

Reacetylation.—The polyvinyl alcohol samples were reacetylated by heating them with acetic anhydride and pyridine. The polymer (1 part) was heated on the steam-bath with a 2 : 1-mixture by volume (10 parts) of pyridine and acetic anhydride both of " AnalaR " quality. Acetylation was complete in 8 hours, the resulting acetate dissolving in the reaction mixture to form a homogeneous dope. The ester was precipitated in distilled water, washed several times with large volumes of hot water, and ultimately dried in a vacuum at 105°. The reacetylated materials possessed acetyl contents equal to those of the parent acetates [Found: Ac (for Gelva 7) 50·0, (for Gelva 15) 49·8, (for Gelva 45) 50·4%].

By the same methods of hydrolysis and esterification the three samples of reacetylated polyvinyl acetates were taken round a second cycle. Again the final polyvinyl acetates possessed acetyl contents equal to those of the original acetate.

A sample of commercial polyvinyl alcohol (RH.349; completely hydrolysed polymer, of a medium viscosity, manufactured by E.I. du Pont de Nemours & Co.) was also taken round the cycle alcohol $\longrightarrow$ acetate $\longrightarrow$ alcohol by the same procedure.

Molecular-weight Determinations by the Viscosity Method.—McDowell and Kenyon (*loc. cit.*)

used the Staudinger viscosity relationship to measure chain lengths of original and regenerated polyvinyl acetates. The same value was assumed for the constant for both acetate and alcohol polymers ($K_{\mathrm{m}} = 2{\cdot}6 \times 10^{-4}$). In recent years Staudinger's original relationship has been largely discredited. Proved cases of disagreement with the " rule " now far outnumber the instances of agreement and various modifications have been proposed. There is evidence to show that K_{m} decreases as the molecular weight increases (Meyer, *Kolloid Z.*, **1941**, **95**, 70) and indeed Staudinger himself has adduced evidence indicating that this is so in the case of polyvinyl acetate and polyvinyl alcohol (Staudinger and Warth, *loc. cit.*) Further, there is no valid reason for assigning the same value to the constant for both polyvinyl acetate and alcohol.

The molecular weight of these two polymers cannot be compared in the same solvent since the alcohol is insoluble in the usual solvents for the ester and *vice versa*. Water and aqueous fatty acids are the only media in which polyvinyl alcohol can be dispersed for viscosity measurements. Formamide has been reported as a solvent for the alcohol but at ordinary temperatures the solution is too viscous for use in a viscometer. Ethylenediamine gave viscosity values which were inconsistent and irregular (Clarke and Blout, *loc. cit.*). In some cases, McDowell and Kenyon used formic acid as a solvent for the alcohol, again using the same value for K_{m}. Doubt is cast on the suitability of formic acid as a solvent for polyvinyl alcohol in viscosity determinations by Hermann's finding (U.S.P. 2 278 783) that esterification of the alcohol occurs readily therein at room temperature and in the absence of a catalyst. Water itself does not appear to be a perfect solvent for polyvinyl alcohol : in the cold, a clear solution is not always obtained, heat being sometimes necessary to disperse the substance completely. Marked differences in viscosity of polymeric substances have been observed in " good " and " poor " solvents (Kemp and Peters, *Ind. Eng. Chem.*, **1942**, **34**, 1192). For these reasons the validity of molecular-weight determinations of polyvinyl alcohol by the viscosity method are open to considerable doubt.

However, the viscosity method adequately served the purpose of the present investigation which was to compare the chain lengths of polyvinyl acetate samples before and after treatment and retreatment and, similarly, of polyvinyl alcohol samples derived from the foregoing esters. To conform with McDowell and Kenyon's data the Staudinger relationship, despite its inaccuracy, has been applied and for convenience the same value for K_{m} has been adopted for both polyvinyl alcohol and polyvinyl acetate. The molecular-weight and chain-length values quoted have no absolute significance but they serve to reflect changes.

Specific-viscosity determinations were carried out in B.S.S. Ostwald-type viscometers at 25° ± 0·02°. Molecular weights and average degrees of polymerisation were derived from the Staudinger relationship $M = \eta_{\mathrm{sp.}}/CK_{\mathrm{m}}$, with a value of $2{\cdot}6 \times 10^{-4}$ for K_{m}. Throughout, acetone was used as the solvent for the acetates and water for the alcohols and the concentration was of the order of 0·10 g. in 100 ml. of solution. All samples were dried at 105° for 1 hour under vacuum before weighing. Viscosity measurements were carried out in duplicate and the mean values used. The calculated values of the average degree of polymerisation (D.P.) and molecular weight (*M*) are presented in Table 1.

TABLE 1.

	I. Original polyvinyl acetate		I*a*. Polyvinyl alcohol by hydrolysis of I		II. Polyvinyl acetate by re-acetylation of I*a*		II*a*. Polyvinyl alcohol by hydrolysis of II		III. Polyvinyl acetate by re-acetylation of II*a*	
Grade	D.P.	*M*	D.P.	*M*	D.P.	*M*	D.P.	*M*	D.P.	*M*
Gelva 7	145	12 450	184	8 100	147	12 600	165	7 260	151	13 000
Gelva 15	205	17 700	205	9 000	178	15 300	209	9 200	177	15 200
Gelva 45	373	32 000	305	13 400	250	21 500	297	13 100	254	21 850

The molecular weight of the polyvinyl alcohol obtained from Gelva 15 by hydrolysis according to Staudinger, Frey, and Starck's method with methyl alcoholic sodium methoxide was also determined : Average D.P. of first preparation, 253; *M*, 11 100; average D.P. of second preparation, 245; *M*, 10 800.

The cycle starting with the commercial polyvinyl alcohol RH.349 gave the following results :

I. Polyvinyl alcohol, RH. 349		II. Polyvinyl acetate from I		III. Polyvinyl alcohol from II	
D.P.	*M*	D.P.	*M*	D.P.	*M*
344	15 100	295	25 400	293	12 900

Stability of Solutions of Polyvinyl Acetate in Technical Mustard Gas.—The viscosities of solutions of the original and reacetylated polymers in mustard gas were investigated at 25°, 60°, and 100° in the viscometer shown in Fig. 1. Owing to the difficulty of introducing a constant volume of viscous liquid the original viscosity of the mustard gas solution was determined first in either a No. 3 or a No. 4 B.S.S. Ostwald-type viscometer with the standard attachment for closing the top of the U-tubes and for raising the liquid into the upper bulb. The small bulbs normally packed with cotton wool were filled with granulated active carbon. The No. 4 viscometer was calibrated with castor oil of known viscosity as determined in a No. 3 viscometer standardised with 60% sucrose solution. The viscosity of the freshly prepared mustard gas solutions having been determined, the solutions were introduced into the modified viscometer through the side-arm *A* without wetting the sides of the glass. The side arm was then sealed off. The lower bulb *B* was filled until the level of the liquid was just below the point of entry of the side-arm *C*. The diameter and length of the capillary and the dimensions of the viscometer were such as to correspond roughly to a No. 3 or No. 4 B.S.S. viscometer according to the viscosity range to be covered. For an observation the instrument was inverted so that the contents of the lower bulb *B* ran through the wide side-arm *C* and filled the bulbs *D* and *E* giving a continuous thread of liquid in the capillary. When the viscometer was returned to the normal position the excess of liquid ran back through *C* and the contents of *D* and *E* passed through the capillary. The meniscus was timed from mark 1 to mark 2 and in this manner determinations were repeated as often as desired, without opening the apparatus and without fear of contamination. Bulb *D* served to give the operator more time in which to make the necessary adjustments to the vertical and allowed the excess of viscous fluid in *C* to return to *B*. To avoid drainage errors the side-arm *C* was joined to bulb *D* at an acute angle. A most important constructional feature was the length of the tube leading from the capillary to the liquid in bulb *B* : this must be such that when the viscometer is inverted and the liquid has come to rest no part of the tube should extend above the liquid level, otherwise when the instrument is returned to the normal position an air bubble is trapped in the tube and passes into the capillary. Further, when in the normal position, the end of the tube must be below the liquid level so as to ensure even flow through the capillary.

All viscosity determinations were carried out at 25° ± 0·02°. The mustard gas solutions were stored in the sealed modified viscometers at 100° ± 0·25°, 60° ± 0·25°, or 25° + 0·2°; those at the higher temperatures were removed at intervals, inverted, allowed to cool at room temperature for ½ hour and thereafter for sufficient time to attain the temperature of the 25° thermostat before measurement of the viscosity. In the storage baths the whole of the viscometer was submerged while a ball-and-socket fitting permitted easy inversion and adjustment to the vertical in the 25° thermostat.

The mustard gas solutions of the acetates were prepared at room temperature by stirring the pulverised resin with the mustard gas in a round-bottomed flask fitted with a glycerol-vapour seal. Complete dissolution was effected in about 18 hours. The polymer solutions were filtered and used directly for density and viscosity measurements in the B.S.S. viscometers. Part of the same solutions was introduced into the modified viscometers which were then sealed. From the time of flow in this instrument at 25° the constant of the viscometer was calculated; this was then used in all subsequent viscosity determinations. The viscosity–time of storage data for Gelva 15 (13% solution), reacetylated Gelva 15 (10% solution), and reacetylated Gelva 45 (10% solution) at 25°, 60°, and 100° are presented in Figs. 2, 3, and 4 respectively.

The polymer solutions darkened very considerably on storage at the three temperatures. It is also clear from the results that taking the polyvinyl acetate through the cycle acetate ⟶ alcohol ⟶ acetate produces a marked effect as shown by the different forms of the viscosity–time of storage curves for the original and reacetylated materials. There is no certainty that the use of the highest temperature (100°) served to accelerate the changes taking place at lower temperatures, 25° and 60°—other reactions may have complicated the issue. At 100° the viscosity of the Gelva 15, reacetylated Gelva 15, and reacetylated Gelva 45 solutions increased rapidly and progressively and in a comparatively short time gel formation ensued. With the reacetylated Gelva 45 gel formation was more rapid than with either of the Gelvas 15. It is possible that had the first reading been taken after a shorter time the early portion of the curve might have been different : an initial phase of viscosity reduction similar to that observed at the lower temperatures might have been missed on this account.

The results of the storage tests at 60° revealed some interesting differences between original and reacetylated polyvinyl acetates. At this temperature the mustard gas solution of Gelva 15 showed a progressive decrease in viscosity during 106 days covered by the experiments, during which time the viscosity was reduced by almost a half. In marked contrast a solution of the corresponding reacetylated material showed only an initial and very slight depression in viscosity followed by a steady increase for a long period, but in the later stages there appeared a tendency for the viscosity to fall off again. Similarly, in the concluding stages of the tests on reacetylated Gelva 45 a falling-off in viscosity was also observed. The incidence of this phase marked by departure from the rising part of the curve coincided with the first observation of the deposition from solution in progressively increasing amount of some insoluble finely divided material.

At 25° the viscosity changes during the period of test were small but the trend was the same as at 60°. The interesting point was that whereas the original polymer solution progressively decreased in viscosity the reacetylated polymer solutions showed only a slight initial reduction in viscosity, the curve passed through a minimum, and then continued to rise steadily.

The factors responsible for the initial downward trend of the viscosity–time of storage curves having been elucidated to some degree, an attempt was made to find out the underlying cause of the subsequent increase in viscosity. Solutions of polyvinyl acetate (Gelva 15 and 45) in the same grade of technical mustard gas which had been stored at 60° in varnished-metal containers for 17 weeks were examined. The first was a solution of Gelva 15 of original viscosity 12·3 poises at 10°. After 17 weeks' storage the viscosity had been reduced to 5·2 poises. The second was a solution of Gelva 45 of original viscosity 11·65 poises at 10°; its viscosity had been reduced to 2·05 poises during the same period. Both solutions were very dark and contained an appreciable amount of sediment; this was removed by filtration and was not examined further. Viscosity determinations at 25° on the filtrates gave the following results : Gelva 15 solution, 2·90 poises; Gelva 45 solution, 1·43 poises. Samples of the polymers were recovered from the solutions by precipitation in a large volume of ether. This gave dark brown rubbery masses, which were washed with fresh volumes of ether and then heated with a large volume of water on the steam-bath. This hot-water treatment was repeated several times with fresh quantities of distilled water until all the occluded mustard gas had been hydrolysed and removed. The materials were then dried in a vacuum at 105°. When dry they were dark brown brittle resins, completely insoluble in all the usual solvents for polyvinyl acetate showing a marked tendency to swell to soft rubber-like masses. Owing to this insolubility no estimate of their molecular weights could be made. The materials had all the properties of highly cross-linked derivatives. Both contained sulphur and chlorine (Found, for recovered Gelva 15 and 45 respectively : Ac, 38·0, 32·7; Cl, 1·85, 2·55; S, 1·85, 2·6%). On hydrolysis the recovered polymers did not give water-soluble derivatives.

Constitutional changes in the polymer during storage in the mustard gas solution were also investigated. The bulk of the Gelva 15 solution made up for the viscosity determinations was introduced by suction into a flask which was immersed in the 60° thermostat. A sample of the polymer was recovered from this solution before the commencement of the storage tests. At intervals, some of the polymer solution was withdrawn by siphoning for examination of the polymer. The procedure already outlined, *viz.*, precipitation with ether, and repeated washing with hot water, was adopted for working-up the recovered polymer. The sample of polymer recovered from the mustard gas solution directly it had been made up, *i.e.*, before storage at 60°, had already suffered some slight change. There had been a noticeable darkening; it contained traces of chlorine but no sulphur. Hydrolysis showed only 45·5% of acetyl, against 50% for the original Gelva 15; boiling with N-alkali for this determination revealed a very small amount of brownish solid remaining undissolved. Under the same conditions polyvinyl acetate is completely hydrolysed to water-soluble polyvinyl alcohol. The material was not completely soluble in acetone, an exceedingly small fraction remained undissolved; this was filtered off; the average D.P. calculated from the specific viscosity was 211 compared with 205 for the original Gelva 15.

The polymer recovered after 7 days' storage at 60° showed even greater modification. It was darker and contained traces of both chlorine and sulphur. The acetyl content had been reduced to 46·7%. The material contained a higher proportion of alkali- and acetone-insoluble material. No specific-viscosity determination was carried out on this specimen for this reason. Instead, a portion of the material was exhaustively extracted with acetone in a Soxhlet apparatus and the soluble and the insoluble fraction were isolated separately. This procedure was followed in the examination of all subsequent samples of recovered polymer. Sulphur, chlorine, and acetyl determinations were carried out on both soluble and insoluble fractions and, in the case of the former, specific viscosity determinations in acetone solution (a value of $2{\cdot}6 \times 10^{-4}$ was assigned to K_{m}). The results are summarised in the following table.

TABLE 2. *Changes in composition of Gelva* 15 *stored in mustard gas solution at* 60°.

Soluble fraction.

Time of storage (days)	Acetone-soluble, %	D.P.	Ac, % *	S, % *	Cl, % *
0	~100	211	48·5	Nil	Trace
7	<100	310	42·4	0·37	0·71
16	82·9	300	43·7	0·07	0·83
28	47·5	176	47·0	0·69	0·67
54	76·7	229	41·7	1·27	0·83
83	62·6	169	54·7	1·13	1·24

Insoluble fraction.

Time of storage (days)	Acetone-insoluble, %	Ac, % *	S, % *	Cl, % *
7	—	54·6	0·45	1·05
16	16·6	42·9	0·26	1·60
28	52·0	51·1	0·08	0·63
54	24·2	44·5	0·63	1·18
83	38·0	43·9	0·92	1·23

* Microanalyses by Drs. Weiler and Strauss, Oxford.

The values quoted for acetyl content are based on the assumption that it was the only hydrolysable group present. It is highly probable that some hydrogen chloride was also removed in some cases and these results are therefore of doubtful value. Little reliance can also be placed on the values for the average degree of polymerisation of the acetone-soluble portions of the recovered polymer.

DISCUSSION

The interpretation of these results is complicated by the fact that the mustard gas used was a technical mixture of two compounds. In both compounds the main reactivity resides in the ω-chlorine atoms and in general their reactions are very similar. The reduction of acetyl content of the recovered polymer, the presence in the polymer of both sulphur and chlorine, and the peculiar solubility relations in acetone point to reaction between polymer and solvent leading to a cross-linked structure. Polyvinyl alcohol is known to form cross-linked derivatives with terminally substituted dichloro-compounds such as glycerol, 1 : 3-dichlorohydrin, dichlorodimethyl and dichlorodiethyl ether (Jones, *Brit. Plastics*, 1944, **16**, 81) and presumably mustard gas will react similarly. It seems likely that some of the acetate groups in the polyvinyl acetate have undergone hydrolysis under the catalytic influence of hydrogen chloride from the mustard gas mixture. The vinyl alcohol units thus introduced into the chain are then attacked by mustard gas to give

$$\begin{array}{l} -CH_2-CH- \\ \qquad\ | \\ \qquad O\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2Cl \end{array}$$

and

$$\begin{array}{l} -CH_2-CH- \\ \qquad\ | \\ \qquad O\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2Cl \end{array}$$

Some of these units react further to give cross-linked structures. It is also possible that some of the vinyl alcohol units react directly with the hydrogen chloride to give vinyl chloride units. The existence of cross-bonds would explain the insolubility of the recovered polymer and its marked swelling under the influence of solvents. All these reactions are dependent on the presence of water in the system : considerable support for this theory of the reaction mechanism is forthcoming from the work of Morrison, Mungen, *et al.* (unpublished Canadian Reports, Ministry of Supply) who showed that gelation does not appear in pure mustard gas or in technical mustard gas to which 5% of acetic anhydride has been added.

The observed viscosity changes on storage are clearly the net result of two opposing tendencies—a chain-breaking mechanism and a cross-linking process, the former predominating in the early stages. It appears from Table 1 that in the case of Gelva 7, the polymer of lowest molecular weight, there is no change in average degree of polymerisation when the acetate groups are removed by alkaline hydrolysis and subsequently restored by acetylation. However, with the polymers of higher molecular weight, Gelva 15 and Gelva 45, there is a definite reduction in chain length in this cycle of operations and the higher the molecular weight the greater the reduction. Reduction below 50% has never been observed. All the reacetylated polymers suffer no further change when subjected a second time to hydrolysis and reacetylation. The good agreement between the degree of polymerisation values for polyvinyl alcohols I*a* and II*a* suggests that chain rupture takes place during the original hydrolysis and not during reacetylation.

The results for the commercial polyvinyl alcohol RH.349 (Table 2) appear somewhat anomalous in that degradation seems to have occurred in the reacetylation stage. It may be significant that the acetylation reaction here appeared to be more difficult to complete. The reacetylated material contained only 48·74% of acetyl, against 50% for complete esterification. (The author has no information about the method of hydrolysis used in the commercial preparation of RH.349.) The value for the average degree of polymerisation of the polyvinyl alcohol obtained from Gelva 15 by methyl-alcoholic sodium methoxide is appreciably higher than the value quoted in Table 1; this suggests that the amount of degradation varies with the method of hydrolysis.

All the evidence points to the occurrence in polyvinyl acetate of high molecular weight of some weak links which are vulnerable under the conditions of alkaline hydrolysis. Reference has been made to the suggestion that these may be oxygen bonds. It is of interest that Kornblum and De La Mare (*J. Amer. Chem. Soc.*, 1951, **73**, 880) recently demonstrated the ready decomposition of *tert.*-butyl 1-phenylethyl peroxide by bases such as potassium hydroxide, sodium ethoxide, or piperidine. The mechanism advanced to explain this decomposition presupposes the existence of a hydrogen atom on the carbon attached to the peroxide linkage and consequently only those dialkyl peroxides where this condition is fulfilled will undergo this base-catalysed decomposition. A peroxide linkage in polyvinyl acetate might conceivably be ruptured in this manner on alkaline hydrolysis and so would yield a polyvinyl alcohol with a terminal aldehydic group. Further evidence is clearly needed before the true nature of these weak linkages in polyvinyl acetate can be truly established.*

Figs. 2 and 3 reveal a striking difference in behaviour between parent polyvinyl acetate and the same polymer after alkaline hydrolysis and acetylation. The first phase of viscosity reduction is much less evident in the latter but it is significant that it has not altogether disappeared. It would therefore seem that some of the weak bonds have survived the mild hydrolytic treatment but these are ruptured on contact with the mustard gas mixture.

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* Wheeler, Ernst, Kennedy, and Crozier (Amer. Chem. Soc. Spring 1951 Meeting, Abstracts) have recently presented evidence indicating that the reduction in molecular weight of polyvinyl acetate on hydrolysis and reacetylation is due to the removal of polymer branches attached to the parent polymer through acetate groups. It is suggested that these side branches result from transfer reactions with the C–H bonds of the acetate groups of both monomer and polymer. Other vinyl esters are shown to undergo a similar degradation. Also it is shown that polyvinyl alcohol molecules can unite with each other under certain conditions and hence mask this degradation.