what unreliable evidence of the Eötvös equation as applied to surface tension of the sodium phosphate melts indicates an average size of *ca.* 9 phosphorus atoms per reorganization unit,[2] the flow unit of 8 phosphorus atoms could well be identical to the average-sized fragment in the reorganization process.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

Chain Branching in Glassy Polyphosphates: Dependence on the Na/P Ratio and Rate of Degradation at 25°[1]

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RECEIVED SEPTEMBER 1, 1954

The previously observed occurrence of an initial decrease of both viscosity and *p*H in freshly prepared aqueous solutions of glassy sodium polyphosphate was investigated with samples whose Na/P ratios ranged from 0.968 to 1.055. The phenomenon was observed at Na/P ratios up to 1.01. That the effect was due to the hydrolysis of weak bonds in the polymer molecules was confirmed by showing that the first-order rate constants of both the reduced viscosity decrease and the increase in the number of titratable hydrogen ions were equal. This rate constant was found to be $8(\pm 4) \times 10^{-3}$ min.$^{-1}$ at 25° and was apparently unaffected by the Na/P ratio and the molecular weight of the samples as well as by the *p*H and the NaBr concentration of the solutions. Evidence that these weak bonds occur at branch points in the polymer chains is presented, and by extrapolation of the data obtained in the rate studies the number of branches originally present in the samples is estimated. For glasses with Na/P ratios greater than unity this number is of the order of one branch for every 1000 P atoms.

In a recent paper[2] it was shown that both the viscosity and the *p*H of freshly prepared aqueous solutions of Graham's salts decreased for several hours before attaining constancy. These effects were ascribed to the hydrolytic degradation of the weak P–O bonds at branch points in the polymer chains. However, since Van Wazer's first-order approximation theory did not predict the existence of such branch points in polyphosphate glasses with Na/P ratios equal to or greater than unity,[3] an experimental study was undertaken aimed at correlating the presence and if possible the degree of chain branching of the glasses with their Na/P ratios. Na/P ratios investigated extended from 0.96 to 1.06 with by far the greatest number of samples covering the range from 0.990 to 1.010.

The presence of chain branching in a given sample was detected by the initial viscosity and *p*H changes. In order to confirm the soundness of this procedure, experiments aimed at obtaining further evidence that these changes reflect the degradation of branch points were performed with several of the samples. These experiments included measurement of the increase in titratable hydrogen ion content accompanying the viscosity decrease to prove the chemical nature of the process. The rates of these changes were compared to determine whether the same process was measured by both titration and viscosity methods. From these rate studies an estimate of the order of magnitude of the number of weak bonds (branches) initially present in a glass was obtained. The possibility of impurities being the cause of the weak bonds was also explored.

Since the dependence of the molecular weight of the polymers on their Na/P ratio has apparently not previously been determined for the range of Na/P ratios here under study, and since most samples of Graham's salt described in the literature fall within this range, this dependence is included in this paper as a possibly useful by-product of this research.

Experimental Materials and Methods

Preparation of Polymers.—Monomer samples with known Na/P ratios[4] were prepared as follows. A nearly saturated aqueous stock solution of $NaH_2PO_4 \cdot H_2O$ (Baker, reagent grade) was filtered, and an aliquot of this solution titrated to the first equivalence point of phosphoric acid with either 0.1 *N* NaOH or 0.1 *N* HCl depending on which side of the equivalence point the original sample was.[5] The same aliquot was then titrated to the second equivalence point in order to determine the total amount of phosphate present. From these data the Na/P ratio in the original stock solution was calculated. Varying amounts of NaOH or H_3PO_4 were added to different portions of the stock solution in order to bring each of these portions close to a desired Na/P ratio. The solutions were then evaporated to dryness, and the exact Na/P ratios of the anhydrous monomer samples were determined by titrating weighed aliquots with NaOH or HCl to the first equivalence point.

The polymers were then prepared by fusing the monomer samples in a platinum dish at a constant temperature between 920 and 960° for 12 hours[6] followed by rapid chilling of the melt between cold steel plates.[7]

Characterization of Polymers.—Although there is no reason to believe that the Na/P ratio changes under our mild fusion conditions, the Na/P ratios of most of the polymers were determined nonetheless. This determination depends on the assumption (whose validity is quite well established[2]) that 24 hours after dissolution all the polymer molecules are linear. If this is the case, a Na/P ratio of unity corresponds to the state where there is one hydrogen ion for each chain

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(1) This investigation was supported by a grant from the United States Atomic Energy Commission under contract AT(30-1)1018. These results will be contained in a thesis to be submitted by T. L. Treitler to the Graduate School of Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) U. P. Strauss, E. H. Smith and P. L. Wineman, THIS JOURNAL, **75**, 3935 (1953).

(3) J. R. Van Wazer, *ibid.*, **72**, 644 (1950).

(4) Strictly speaking, if the samples contain other metallic cations as impurities, what we call the Na/P ratio is really the ratio of total equivalents of metallic cation to total equivalents of phosphorus.

(5) If the Na/P ratio of the $NaH_2PO_4 \cdot H_2O$ was exactly unity, *i.e.*, if the $NaH_2PO_4 \cdot H_2O$ was perfectly pure, the solution would be at the equivalence point without the addition of acid or base. By the analytical method described in the text it was found that the Na/P ratios of our commercially obtained reagent grade $NaH_2PO_4 \cdot H_2O$ samples varied from 0.995 to 1.007.

(6) A few tests showed that prolonging the fusion time to 24 hours did not affect the properties of the product.

(7) L. F. Audrieth and R. N. Bell, in "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 105.

end and where the solution is exactly at the strong acid inflection point[8,9] on the pH against Na/P ratio curve.[10] Therefore, by titrating a weighed aliquot of the polymer after it has been in solution for 24 hours with HCl or NaOH to this inflection point, one can determine how much the Na/P ratio is below or above unity.

The titration curve has a second inflection point at a pH value close to 9. This weak acid inflection point[8,9] corresponds to the state where all the hydrogen ions at the chain ends have been neutralized and replaced by sodium ions. By titrating an aliquot of a polymer sample with NaOH to this second inflection point, one obtains the total number of hydrogen ions in the dissolved sample at the time of the titration.[11,12] These hydrogen ions may originate in two ways: first, they may already be present in the glass before dissolution if under the conditions of fusion employed the condensation polymerization did not go to completion ("water of constitution")[13]; second, during and after dissolution each hydrolytic P–O bond rupture will result in two hydrogen ions.

By titrating from the first to the second inflection point, the number of end-groups present can be determined. End-group molecular weights were calculated with the assumption that twenty-four hours after dissolution there are two end-groups for each polymer molecule.[12,14]

All the titrations were carried out under CO_2-free conditions with a model G Beckman pH meter using from 5 to 10 g. of sample.

Weight average molecular weights of the polymers were calculated from intrinsic viscosity values, obtained in 0.035 N NaBr, by the relation[15]

$$M_w = 6.25 \times 10^4 ([\eta] - 0.028) \qquad (1)$$

Viscosities were measured at 25.00° in a Bingham viscometer[16] operating at driving pressures ranging from 40 to 180 g./cm.^{2}. The viscometer constant $(pt)_0$ for water was 8,120 g. sec./cm.^{2}.

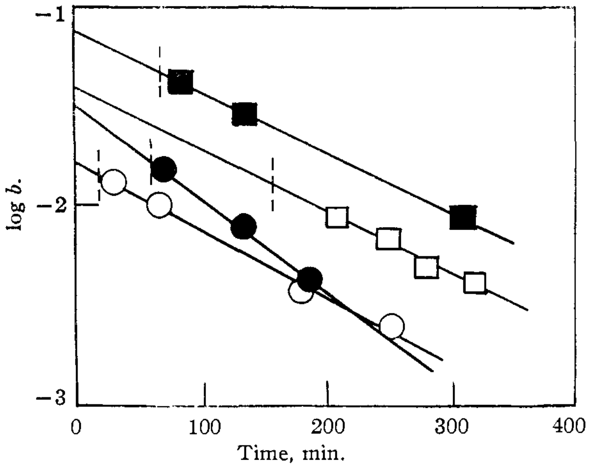

Fig. 1.—Rates of hydrolytic degradation of P–O bonds at branch points in glassy sodium polyphosphates. Circles refer to sample T182A (Na/P = 1.001), squares to sample T196A (Na/P = 0.996). Open circles or squares refer to titration for hydrogen ions ($b = [h_\infty - h]/2$), shaded symbols to viscosimetry ($b = 2000/M_{w\infty} - 2000/M_w$). Time is measured from beginning of dissolution, vertical dashed lines indicate times when samples were first observed to be completely in solution.

Initial Degradation Rates.—The initial degradation of several of the polymers was followed at 25° in the absence of CO_2 both by titration for hydrogen ions and by viscosity measurements. The titrations were performed on 100–150 ml. aliquots which were withdrawn at various intervals from the thermostated 10% polymer solution in which the degradation took place. Each titration was completed in less than ten minutes. The viscosity method consumed much less polymer. The degradation of the 1% polymer solutions took place in the viscometer, and each viscosity determination was finished in less than five minutes.

If the degradation follows first-order kinetics, the results can be expressed by the relation

$$\log b = -0.434kt + \log b_0 \qquad (2)$$

where b is the number of meq. of branches per g. of polymer, t is the time in min. and k is the rate constant in min.$^{-1}$. The symbol b_0 refers to b at $t = 0$, and with the proper choice of zero time it should be a rough measure of the initial number of branches in the sample. If one extrapolates a log b against t plot back to the time when the dissolution was complete, one obtains too small a value for the initial number of branches since some degradation undoubtedly takes place during dissolution. If, on the other hand, one extrapolates back to the time when the sample first came in contact with the solvent, one obtains too high an estimate since during the dissolution not all branch points are immediately accessible to the solvent.[17]

The value of b is related to h, the number of meq. of titratable hydrogen ions per g. of polymer, by the expression

$$b = (h_\infty - h)/2 \qquad (3)$$

The quantity h_∞ is the value of h after the initial degradation is finished. Its value was usually determined 24 hours after the completion of dissolution. If equation 2 is satisfied, a plot of log $[(h_\infty - h)/2]$ against t should give a straight line. Such test plots for two of the samples, one with Na/P = 1.001 the other with Na/P = 0.997, are shown in Fig. 1 (open circles and squares, respectively) to be in agreement with our hypothesis.

The value of b can be related to the number average molecular weight, M_n, by the expression

$$b = \frac{1000}{M_{n\infty}} - \frac{1000}{M_n} \qquad (4)$$

where the subscript ∞ has the same significance as before. Since most of the viscosity rate studies were performed with 1% aqueous polymer solutions, a relationship between the reduced viscosity in such solutions and the molecular weight was necessary. A surprisingly simple empirical relation which was satisfied by more than twenty samples ranging in molecular weight from 3,000 to 20,000 (after having been in solution for 24 hours) is the expression

$$M_w = 33{,}100(\eta_{sp}/C)_{1\%\ \text{in}\ H_2O} - 300 \qquad (5)$$

One half this weight average molecular weight is assumed to be equal to M_n[18] from which b is calculated by equation 4.[19] In Fig. 1 a test plot is shown to be linear (shaded squares) and quite close to the line obtained for the same polymer by the titration method. In the case of one sample the changes in the reduced viscosity were followed in 0.035 N NaBr solution. Since the reduced viscosity against concentration lines are horizontal in this solvent,[2] it is possible to obtain M_w from equation 1 if one substitutes the reduced for the intrinsic viscosity. In Fig. 1 it is shown that equation 2 is also satisfied for this case (shaded circles), and that again there is close agreement with the results obtained with the same sample by the titration method.

From the slopes and intercepts of the log b against t plots the values of k and b_0 are determined according to equation 2. If, as in Fig. 1, the time is measured from the beginning of

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(8) H. Rudy and H. Schlosser, *Ber.*, **73B**, 484 (1940).

(9) J. R. Van Wazer and K. A. Holst, THIS JOURNAL, **72**, 639 (1950).

(10) In a 1% polymer solution the pH at this inflection point is 5.6.

(11) O. T. Quimby, *Chem. Revs.*, **40**, 141 (1947).

(12) J. R. Van Wazer, THIS JOURNAL, **72**, 647 (1950).

(13) B. Topley, *Quart. Revs.*, **3**, 345 (1949).

(14) O. Samuelson, *Svensk. Kem. Tid.*, **56**, 343 (1944).

(15) This relation is based on light scattering results in the molecular weight range from 7000 to 20,000.[2] The equation originally given has been adjusted to be satisfied also by the appropriate values of C.P. sodium tripolyphosphate. Equation 1 should therefore apply to the molecular weight range from 300 to 20,000.

(16) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y., 1922.

(17) This argument rests on the assumption that the degradation rate is not unduly accelerated during dissolution.

(18) J. R. Van Wazer, THIS JOURNAL, **72**, 906 (1950).

(19) Since both eq. 1 and 5 were obtained for the polymers in their unbranched state and having molecular weights up to 20,000, the use of these equations to follow the decrease of the molecular weight of the polymers in their branched state when the initially measured values may be as high as 35,000 introduces a slight error which we shall neglect here.

TABLE I

VARIOUS PROPERTIES OF GLASSY SODIUM POLYPHOSPHATES AS A FUNCTION OF THE Na/P RATIO

Sample	Na/P ratio Monomer	Na/P ratio Polymer	M_w	End gp. Mol. wt.	$(\eta sp/C)_1$ in 1% aq. soln.[a]	$(\eta sp/C)_\infty$ in 1% aq. soln.[b]	pH_1 in 1% aq. soln.[a]	pH_∞ in 1% aq. soln.[b]	$h_1 \times 10^2$ (meq./g.)[a]	$h_\infty \times 10^2$ (meq./g.)[b]	$k \times 10^3$ (min.$^{-1}$) Titn.	$k \times 10^3$ (min.$^{-1}$) Visc.	$b_0 \times 10^2$ (meq./g.) Titn.	$b_0 \times 10^2$ (meq./g.) Visc.
T436	0.968	...	6,800	....	0.470	0.195	3.63	3.43	...	...	...	9.3	.....	23.4–59.0
T130C	.984	0.985	9,700	....	0.770	.304	4.08	3.75	...	...	...	7.2	.....	12.9–20.9
T130B	.991	...	13,100	....	0.780	.400	4.38	4.02	...	...	...	6.7	.....	7.9–11.5
T196A	.996	.997	20,100	18,000	1.060	.604	5.04	4.47	12.43	14.23	8.3	7.4	1.4–5.3	4.9– 8.0
T1272	.998	...	17,900	....	0.753	.556	5.28	4.82	...	...	...	6.0	.....	3.1– 4.1
T1271	.999	.998	17,200	15,500	0.718	.525	5.54	4.96	...	14.10	...	5.8	.....	3.4– 4.5
T194B	1.000	.999	20,000	18,100	1.055	.634	6.16	5.03	9.59	11.79	8.7	7.5	1.8–2.7	4.4– 5.3
T182A	1.000	1.001	20,500	18,600	0.420[c]	.352[c]	6.06	5.70	6.95	9.55	7.5	10.9[c]	1.4–1.6	1.9–2.9[c]
T187B	1.000	1.001	18,300	16,600	.752	.565	6.33	5.88	10.62	11.17	9.9	10.0	0.6–0.9	2.6–3.8
T 92B	1.001	1.002	19,200	17,900	.660	.588	6.55	6.40	...	...	...	12.0	.....	1.4–3.9
T143B	1.002	1.002	17,300	16,000	.602	.533	6.64	6.45	10.06	10.50	12.0	7.7	0.5–1.4	0.7–2.0
T 95A	1.003	...	17,500	....	.635	.545	6.62	6.47	9.30	9.60	7.0	7.6	0.2–0.6	2.0–2.4
T 94B	1.003	1.003	18,600	17,200	.621	.545	6.67	6.50	8.80	9.51	8.0	7.7	0.4–1.0	1.5–1.9
T 93C	1.002	1.003	17,700	16,600	.620	.556	6.71	6.62	...	8.87	...	6.9	.....	1.0–1.5
T421	1.007	...	12,600	....	.395	.375	7.32	7.12	...	...	...	...	.....	....
T412	1.010	...	10,900	....	.350	.340	7.32	7.27	...	...	...	...	.....	....
T424	1.015	...	8,200	....	.260	.255	7.47	7.40	...	...	...	...	.....	....
T435	1.040	...	4,300	....	.137	.137	7.98	7.95	...	...	...	...	.....	....
T437	1.055	...	3,200	....	.105	.105	8.12	8.12	...	...	...	...	.....	....
										Av.	8.8 ± 3	8.0 ± 4		

[a] The subscript 1 refers to the first measurement after completion of dissolution. [b] The subscript ∞ refers to the measurement made approximately 24 hours after completion of dissolution. [c] Measured in 0.035 N NaBr solution.

the dissolution, the intercepts give an upper limit to the possible value of b_0, as has been discussed before.[17] The vertical dashed lines indicate the times when dissolution was complete and therefore give the lower limits to the possible values of b_0.

Analysis for Impurities.—Several representative samples were analyzed for possible contamination by platinum using two colorimetric methods described by Sandell.[20] The iodoplatinate method gave as an upper limit 2×10^{-4} mmole/g. and the more sensitive stannous chloride method 4×10^{-5} mmole/g. Analysis for other trace elements was accomplished by carbon arc spectrography using the method described by Merritt, Willard and Dean.[21] The following values are upper limits for the elements listed, expressed in mmoles of metal per g. of sample: calcium, 0.025; magnesium, 0.01; zinc, 0.005; iron, 10^{-4}; arsenic, 10^{-4}; lead, 10^{-4}; silicon, 10^{-5}.

Results and Discussion

The results obtained with nineteen representative samples are summarized in Table I. In the second and third columns the Na/P ratios of the monomers and polymers are compared and found to be identical within the limits of experimental accuracy.[22] This result indicates that the Na/P ratio is not changed during the fusion process and also confirms the conclusion that all branches have disappeared 24 hours after dissolution[2] since the Na/P ratio determination of the polymers depends on the correctness of this conclusion. In the fourth column of Table I the weight average molecular weight, M_w, measured viscosimetrically after the completion of the initial degradation, is seen to increase as the Na/P ratio approaches unity from either above or below, but between the values of 0.997 and 1.003 changes in the Na/P ratio seem to have little effect on the molecular weight under the consistent conditions of preparation used here. In this narrow range the molecular weight is controlled by small amounts of "water of constitution" which overshadow the effect of the Na/P ratio (see Discussion below). The values of the end-group molecular weight in the next column run parallel to M_w, but the 2:1 relationship between M_w and the end-group molecular weight,[23] which might be anticipated from the expected molecular weight distribution,[12] is not observed. At least part of the discrepancy is due to the presence of simple metaphosphate rings.[12] Part may also be due to a departure from the ideal random distribution of the chain lengths. A quantitative investigation of this discrepancy is in progress.

In the next four columns the initial and the 24 hour readings of the reduced viscosity and of the pH of 1% aqueous polymer solutions are presented in order to show the total observed change of these quantities for each sample.[24] These changes are seen to be still quite pronounced at a Na/P ratio of 1.007, but they begin to approach the limits of experimental precision in the Na/P ratio range from 1.010 to 1.015, and they are no longer noticeable at 1.040. In the next two columns the values of the initial and the 24 hour measurements of the titratable hydrogen ion concentrations are compared. These results show clearly that the viscosity and pH decreases are accompanied by a measurable increase in the number of hydrogen ions, which indicates that a degradation of a chemical nature occurs.

In the next two columns the rate constants as defined by equation 2 and as determined by the titration and by the viscosity methods are given. Two important features stand out. First, the averages of all the rate constants measured by these two different experimental methods are equal within the limits of error, in agreement with the hypothesis that the two methods really measure the same degradation process. Second, while the rate constant

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(20) E. B. Sandell, "Colorimetric Analysis of Trace Metals," 2nd ed., Interscience Publishers, New York, N. Y., 1950, pp. 495–497.

(21) L. L. Merritt, H. H. Willard and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Co., New York, N. Y., 1951, pp. 95–97.

(22) The Na/P ratio of the monomers can be determined to ±0.001, that of the polymers somewhat more precisely (to ±0.0003) because the latter titration curve is much steeper at the inflection point.

(23) C. E. H. Bawn, "The Chemistry of High Polymers," Interscience Publishers, New York, N. Y., 1948, p. 35.

(24) Since the initial readings for the different samples were taken at different times after dissolution they are not comparable.

fluctuates irregularly about its mean from sample to sample, it seems to be unaffected by the concentration, by the molecular weight and by the Na/P ratio of the polymers as well as by the *p*H and the sodium bromide concentration of the solutions.

The lower and upper limits of b_0, the initial branch content of the samples, as determined by the titration and by the viscosity methods are shown in the last two columns. Here the agreement between the values obtained by the two experimental methods is not so good.[25] However, considering that these values are obtained by an extrapolation procedure which in some cases extends considerably beyond the range of experimental data and which for the upper limits includes the unknown dissolution process, the fact that the two methods give values of the same order of magnitude is all that can be expected. As anticipated, there is an over-all decrease of b_0 with increasing Na/P ratio.

As has been discussed before, the values of h_∞ arose from the hydrolytic degradation of weak bonds and from the hydrogen ions originally present in the glass. By the use of equation 2, an estimate of the latter quantity which is also a measure of the incompleteness of the condensation polymerization process can be obtained. It is seen that, except for one sample, even the upper limits of b_0 do not completely account for the values of h_∞ and that therefore some hydrogen ions are probably present in most of the glasses. In terms of "water of constitution" the value was always less than 0.1% by weight; yet this small amount is sufficient to account for the observation that the molecular weights did not increase to much larger values than those observed as the Na/P ratio of the samples approached unity.

While it has been shown that the initial viscosity and *p*H drops are due to a hydrolytic degradation, some confirmation that this degradation is really caused by the hydrolysis of P–O bonds at branch points is needed. Since the hydrolysis at a branch point should result in two hydrogen ions but in only one end-group while the hydrolysis at any point in the linear portion of a chain should result in two end-groups, the most direct proof of our hypothesis should be obtained by comparing the change in the number of hydrogen ions with the change in the number of end-groups. This comparison was attempted, but the experimental error was so great in the end-group determination during the rapidly proceeding early phase of the hydrolysis[26] that the results were meaningless. Nevertheless, there are several reasons why one can exclude hydrolysis of linear portions of the chain as a cause for the initial hydrolysis. First, the linear hydrolysis rate under our conditions can be calculated from relevant measurements[27,28] to range from about 8×10^{-6} to 3×10^{-8} min.$^{-1}$ as the pH increases from 3 to 8, which is 3 to 5 orders of magnitude slower than the rate of the initial hydrolysis process with which we are concerned here. Moreover, unless there were a few especially weak bonds in the linear chain, a degradation involving linear chains would continue until only low molecular weight species are left, whereas the initial degradation comes to a halt when the molecular weight is still high. Such weak bonds are difficult to justify unless there are some elements other than phosphorus and oxygen in the polymer chain structure. Thilo has shown that an arsenic atom replacing a phosphorus atom in the chain will result in rapid hydrolysis of the As–O bond on dissolution.[29,30] However, since the amount of arsenic present is more than at least one order of magnitude smaller than the lowest possible value of b_0, this possibility can also be eliminated. Similar considerations hold for silicon. It is also impossible to visualize any process by which the cations Ca^{++}, Mg^{++} and Zn^{++}, whose concentration in the samples is of the same order of magnitude as b_0, could cause the observed increase in the amount of titrable hydrogen ion.

Thus, the hydrolysis of branch points in the chain is the only remaining possibility. That such branch points should be unstable in water has been deduced from theoretical considerations.[9] Moreover, their presence in samples whose Na/P ratio is less than unity is generally accepted.[3] Therefore, the observation that the rate constant *k* for the initial degradation is the same for Na/P ratios above and below unity is positive confirmatory evidence for the presence of chain branching in samples whose Na/P ratios are slightly larger than one. The number of branch points per 1000 phosphorus atoms is equal to $b_0 \times 102$ and is therefore closely approximated by the values appearing in Table I in the column headed by $b_0 \times 10^2$. This number is seen to be quite small in the composition range in which the glasses are commonly known as Graham's salts ($1 \leq \text{Na/P} \leq 1.01$), so small in fact that less than one out of every two polymer molecules in the glass can contain a branch. Yet the hydrolysis of this small number of branches accounts satisfactorily for the relatively large initial drop of the reduced viscosity.

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(25) The quantitics obtained by the viscosity method would be decreased by approximately $^1/_2$ their value and the agreement with the titration data thereby considerably improved if one uses the number average molecular weight obtained by dividing the viscosity weight average by the value of 1.1, which is the observed average ratio of the weight average to the end-group molecular weight; this contrasts with the theoretical value of 2 for this ratio which was used in the text.

(26) The end-group determination during hydrolysis is much less precise than the hydrogen ion determination because the former depends on titrating between two end-points.

(27) R. Pfanstiel and R. K. Iler, THIS JOURNAL, **74**, 6059 (1952).

(28) J. P. Crowther and A. E. R. Westman, *Can. J. Chem.*, **32**, 42 (1954).

(29) E. Thilo and I. Plaetschke, *Z. anorg. Chem.*, **260**, 297 (1949).

(30) E. Thilo, G. Schulz and E. Wichman, *ibid.*, **272**, 184 (1953).