The Polymerization Reaction of Sodium Phosphate

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The amorphous polymer of sodium phosphate is called by several names, such as Graham's salt, glassy phosphate, sodium metaphosphate glass, sodium polymetaphosphate, and sodium hexametaphosphate[1]. Although the chemical formula of this substance is the same as that of a metaphosphate $(NaPO_3)_n$, it is not a ring-phosphate but a kind of chain polymer[2-4] and so may be called a sodium polyphosphate. The polyphosphate usually prepared is, however, a branched polymer, and it is partly depolymerized within several hours after dissolution in water or in an aqueous sodium bromide solution[5-7]. It has been concluded that the depolymerization is mainly due to the hydrolysis at the point of branching[5,6]. Therefore, it is interesting to polymer chemists[5] that the solution obtained at the end of the hydrolysis contains unbranched molecules only, and that the distribution function of the molecular weight has been determined both theoretically and experimentally[8].

In the present paper, polymerization reaction of sodium phosphate will be studied. Generally speaking, polymerization reactions are classified into two types: (1) condensation polymerization, and (2) addition polymerization, the latter including ring-opening polymerization. In the case of the preparation of amorphous sodium polyphosphate, a reaction starting from sodium hydrogen orthophosphate:

$$n\mathrm{NaH_2PO_4} = (\mathrm{NaPO_3})_n + n\mathrm{H_2O} \qquad (1)$$

is a kind of condensation polymerization, while a reaction starting from sodium trimetaphosphate (a ring-phosphate):

$$(n/3)(\mathrm{NaPO_3})_3 = (\mathrm{NaPO_3})_n \qquad (2)$$

is a kind of ring-opening (addition) polymerization. In this paper, these two reactions will be compared on the basis of viscometry of the products.

Experimental

Material. — The sodium dihydrogen orthophosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) used was the same specimen as was used in a previous study[7]. The dihydrate was changed into an anhydrate by heating it at 110°C under a reduced pressure for about 15 hr.; thus it reached a constant weight and could be used for further experiments.

Sodium trimetaphosphate $(NaPO_3)_3$ was prepared by heating the above-described sodium dihydrogen orthophosphate anhydrate in a platinum crucible at 530°C for 5 hr.[1,3] and was then kept in a desiccator.

Polymerization Reaction. — The polymerization reaction was effected by heating about 7 g. of the starting material in a platinum crucible about 35 mm. in diameter, 37 mm. in height and about 30 ml. in capacity. For the heating, a Siliconit electric furnace BH-1020, equipped with a thermoelectric automatic regulator P-400 with a platinum platinum-rhodium thermocouple, was used. It took the furnace about 1.2, 1.8 and 3.5 hr. to reach 530, 700 and 900°C respectively from room temperature. At the end of the polymerization reaction, the content of the crucible was poured on a copper plate and pressed with another copper plate in order to cool the product rapidly.

Viscometry.—The product of the polymerization reaction was dissolved in a 0.07 N sodium bromide solution at the polymer concentration of 1 g./100 ml. It took about 1 hr. to dissolve. Solutions of other concentrations were prepared by the dilution of the above-prepared solution. Viscosity was measured by an Ostwald viscometer, while density was measured by an Ostwald pycnometer in a thermostat at 25.5°C.

Results and Discussion

Polymerization Equilibrium.—As the theory of reorganization[9] suggests, the polymerization reaction of phosphate will reach an equilibrium state if the reaction time is sufficiently long. The state of the equilibrium, however, may depend on the temperature. For a relatively long reaction time, therefore, the average molecular weight of the reaction product will

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depend more on the temperature than on the reaction time[10].

Setting the reaction time at 5 hr., the polymerization reaction was effected at various temperatures, and the average degree of polymerization, $\bar{n}$, of the product was determined by end-group titration. On the basis of the results shown in Fig. 1, it may be concluded that the degree of polymerization increases with the reaction temperature, and that the degrees of polymerization are equal for the products both by condensation polymerization and by ring-opening polymerization[11].

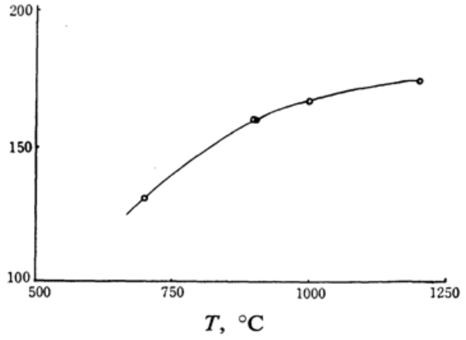

Fig. 1. Relation between polymerization temperature and average degree of polymerization for heating time of 5 hr.
- ○ Condensation polymerization of orthophosphate
- ● Ring opening polymerization of trimetaphosphate

Time Dependence of Solution Viscosity.—The viscosity of solutions of the polymerization products decreases with time because of the depolymerization of the polyphosphate, and it has already been shown in a previous paper[7] that the reaction is of the first order. As the examples in Fig. 2 show, the viscosity, η, of the solution relative to that of the solvent (a 0.07 N sodium bromide solution) changes with time, τ, according to the following empirical equation:

$$\log(\eta-\eta_\infty)=\log(\eta_0-\eta_\infty)-K\tau \qquad (3)$$

where the constants, η_0, η_∞ and K, are the relative viscosities at $\tau=0$, $\tau=\infty$, and the rate constant respectively. As for the value of η_∞, the relative viscosity at $\tau=24$ hr. was used,

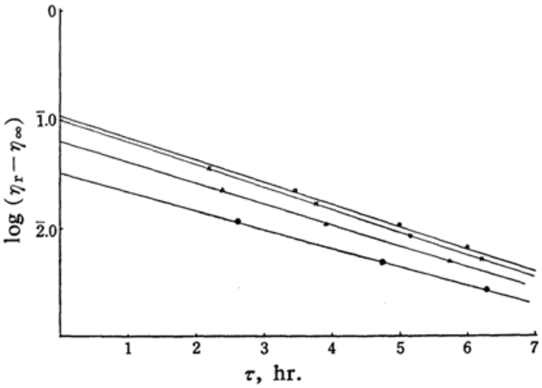

Fig. 2. Examples of decrease of solution viscosity with time in 0.07 N NaBr solution at 25.5°C for the product polymerized by heating of orthophosphate at 900°C for 6 hr. Concentration of solution: (○) 1, (×) 0.8, (△) 0.4 and (◎) 0.2 (g./100 ml.)

and the value of η_0 was determined on the basis of Eq. 3.

It was widely been known that the intrinsic viscosity of a solution is directly related to the average polymerization degree of the solute. In the case of solutions of sodium polyphosphate in the solvent 0.07 N sodium bromide, the relation between the intrinsic viscosity and the average molecular weight derived in the previous paper[7] can be rewritten as:

$$\bar{n}=877\,[\eta]-30.5 \qquad (4)$$

where $\bar{n}$ is the average polymerization degree.

The values of $[\eta_0]$ and $[\eta_\infty]$ were obtained on the basis of the values of η_0 and η_∞ respectively, measured at polymer concentrations of 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 g./100 ml. For the extrapolation to the infinite dilution, two equations,

$$\left.\begin{aligned}(\eta-1)/c&=[\eta]+k\,[\eta]^2c\\(\ln\eta)/c&=[\eta]-k'\,[\eta]^2c\end{aligned}\right\} \qquad (5)$$

together with the equation,

$$k+k'=0.5 \qquad (6)$$

were used to confirm the extrapolation[12,13].

As has already been stated in earlier in this paper, it has been concluded that the depolymerization is mainly due to the hydrolysis at the point of branching[5,6]. Therefore, $[\eta_0]$ should be related to the average polymerization degree of the whole molecule before the hydrolysis, that is, the branched molecule formed by the polymerization reaction. On the other hand, $[\eta_\infty]$ should be related to the average polymerization degree of hydrolyzed

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[11] The data shown in Fig. 1 were obtained by one of the authors (S. O.) at Kyushu University. The end group titration was made about 24h. after dissolution, and the P-O-H end group generated by the hydrolysis of a branching point was believed to be titrated as an end-group[6]. The values of $\bar{n}$ in Fig. 1, therefore, correspond to $\bar{n}_\infty$ of Figs. 3 and 4. The inexact agreement between the numerical values in these figures is probably due to the difference in the methods of $\bar{n}$ determination and also to a minor difference in the experimental techniques of the polymerization.

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molecules, that is, the average length of each branch.

The Condensation Polymerization of Sodium Dihydrogen Orthophosphate.—Sodium dihydrogen orthophosphate anhydrate (NaH_2PO_4) was put in a platinum crucible and heated in an electric furnace. After the furnace reached the polymerization temperature, the heating was further continued for 1/2, 3 and 6 hr. at that temperature (700°C or 900°C). The intrinsic viscosities, $[\eta_0]$ and $[\eta_\infty]$, of the polymerization products were measured. The results are shown in Table I. The $[\eta_0]$ and $[\eta_\infty]$ values of the products polymerized at 900°C were greater than those polymerized at 700°C. The $[\eta_0]$ value for 900°C reaches a maximum value (0.298) at about 3 hr. and then decreases, but the $[\eta_\infty]$ value for 900°C and the $[\eta_0]$ and $[\eta_\infty]$ values for 700°C are the greater, the longer the polymerization time. The $[\eta_\infty]$ value approaches 0.198 for 900°C and 0.140 for 700°C.

TABLE I. CONDENSATION POLYMERIZATION OF SODIUM DIHYDROGEN ORTHOPHOSPHATE

Preheating time* hr.	Polymerization condition Temp. °C	Time hr.	Intrinsic viscosity $[\eta_0]$	$[\eta_\infty]$
1.9	700	1/2	0.164	0.132
1.7	700	3	0.184	0.134
1.7	700	6	0.182	0.140
3.6	900	1/2	0.253	0.168
3.4	900	3	0.298	0.188
3.5	900	6	0.283	0.198
0	—	0	0.0313**	0.0313**

* The time required to reach the polymerization temperature.

** Sodium dihydrogen orthophosphate itself.

The Ring-opening Polymerization of Sodium Trimetaphosphate. — Sodium trimetaphosphate kept in a platinum crucible at room temperature was put in an electric furnace. The furnace had been heated, in advance, to the polymerization temperature. When the heating of 5 min.~2 hr. for the polymerization was over, the product was taken out and the $[\eta_0]$ and $[\eta_\infty]$ values were measured. The results are shown in Table II. The relation between the intrinsic viscosities and the polymerization time is entirely different from the case of condensation polymerization. The maximum points of $[\eta_0]$ and $[\eta_\infty]$ are located at the reaction time shorter than 5 min. for 900°C and 11 min. for 700°C. Five or eleven minutes is required to melt the contents of the crucible. In the case of ring-opening polymerization, therefore, the polymerization is finished almost immediately after the material is melted. The $[\eta_0]$ value is greater for 700°C than for 900°C, and decreases rapidly when the polymerization time becomes longer. The $[\eta_\infty]$ value decreases gradually and approaches 0.166 for 900°C and 0.145 for 700°C.

TABLE II. RING-OPENING POLYMERIZATION OF SODIUM TRIMETAPHOSPHATE

Polymerization condition Temp. °C	Time min.	Intrinsic viscosity $[\eta_0]$	$[\eta_\infty]$
700	11	0.878	0.318
700	15	0.832	0.332
700	30	0.724	0.314
700	60	0.311	0.181
700	120	0.198	0.145
900	5	0.729	0.356
900	15	0.509	0.273
900	30	0.384	0.235
900	60	0.289	0.190
900	120	0.211	0.166
—	0	0.016*	0.016*

* Sodium trimetaphosphate itself

A Comparison of Condensation Polymerization and Ring-opening Polymerization.—The intrinsic viscosities, $[\eta_0]$ and $[\eta_\infty]$, were recalculated to the average degrees of polymerization, $\bar{n}_0$ and $\bar{n}_\infty$ respectively, according to Eq. 4, where $\bar{n}_0$ is the polymerization degree of the whole molecule[14] and $\bar{n}_\infty$ is the average polymerization degree of each branch in the molecule. Therefore, the apparent number of branches in one molecule, B, may be obtained by;

$$B=\bar{n}_0/\bar{n}_\infty \qquad (7)$$

The results of the calculation are shown in Figs. 3, 4 and 5.

On the basis of these results, the following points may be emphasized. In the case of the condensation polymerization, both $\bar{n}_0$ and $\bar{n}_\infty$ are the greater, the higher the temperature. This would mean that the polymerization due to the separation of water proceeds the further, the higher the temperature. When the reaction time is longer than 3 hr., the thermal separation of branches occurs simultaneously, so that B and $\bar{n}_0$ decrease to some extent, especially at a high temperature (900°C). The length of each branch, $\bar{n}_\infty$, however, shows no appreciable decrease. In the case of the ring-opening polymerization, on the contrary, the

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[14] In this case, the molecules are branched. The relation between $[\eta]$ and $\bar{n}$ for branched polymer should be different from that for unbranched polymer. The correction factor for the branching is not known in the case of a sodium polyphosphate solution, but it is not large in the case of an organic polymer. Therefore, Eq. 4 was used to obtain an apparent value of $\bar{n}$. The value thus obtained may be expected to be correct in its order of magnitude.

TABLE III. TEMPERATURE DEPENDENCE OF THE AVERAGE DEGREE OF POLYMERIZATION OF EACH BRANCH AT RELATIVELY LONG POLYMERIZATION TIME

Ref.	Polymerization		Polymerization degree		
	Time, hr.	Starting material	700°	900°	Method
Fig. 1	5	Ortho	126	160	End group titration
Fig. 1	5	Trimeta	—	160	End group titration
Fig. 3	6	Ortho	92	143	Viscometry
Fig. 4	2	Trimeta	97	115	Viscometry

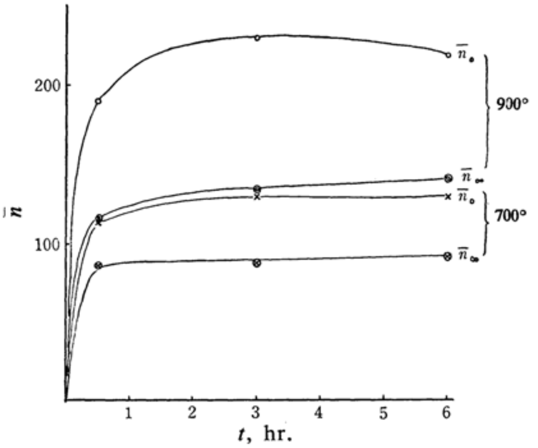

Fig. 3. Dependence of degree of polymerization on the time of polymerization of orthophosphate.

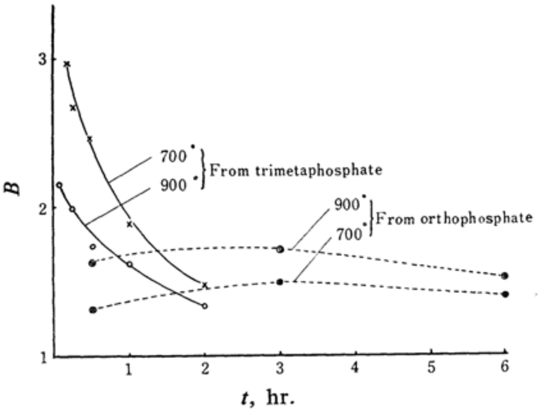

Fig. 5. Relation between the number of branching and the polymerization time.

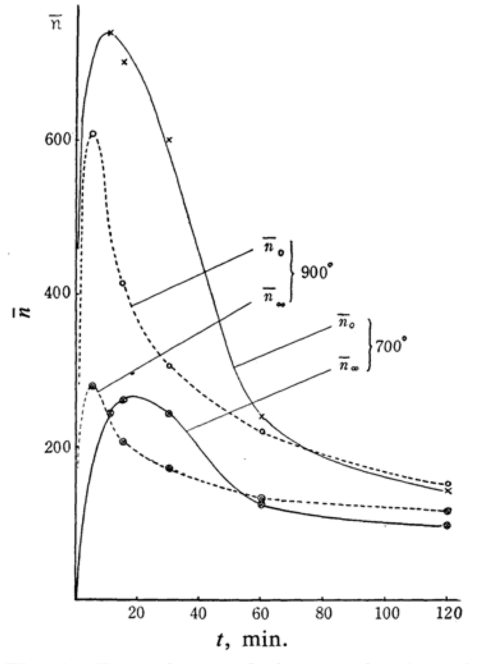

Fig. 4. Dependence of degree of polymerization on the time of polymerization of trimetaphosphate.

$\bar{n}_0$ and $\bar{n}_\infty$ values are the greater, the lower the temperature, if the reaction time is shorter than 1 hr., and they do not depend too much on the temperature if the reaction time is longer than 1 hr. This would mean that the polymerization is completed within 5∼11 min., so that the thermal depolymerization is more important in this case. The higher the temperature, the more the separation of the branches proceeds and the more the degree of polymerization, $\bar{n}_0$, decreases. In this case, the thermal break-up of each polymer chain occurs within at least 1 hr., in addition to the separation of the branches at the branching points. After 2 hr., the $\bar{n}_\infty$ value becomes the larger, the higher the temperature. As is shown in Table III, these findings tend to accord with the results of Figs. 1 and 3, although the numerical values do not exactly coincide with each other, probably because of the differences in experimental methods, as has already pointed out[11].

Thus, the remarkable difference between the condensation polymerization and the ring-opening polymerization can be explained by considering that both the polymerization and depolymerization occur during the heating, and that the process of polymerization is more important in the case of the condensation polymerization because the removal of water needs much heating, while the process of depolymerization is more important in the case of the ring-opening polymerization because in this case the polymerization is completed almost immediately after the material is melted.

Summary

Two kinds of polymerization reactions, the condensation polymerization of sodium dihydrogen orthophosphate anhydrate (NaH_2PO_4) and the ring-opening polymerization of sodium trimetaphosphate, have been compared by determining the average degree of polymerization of the whole molecule, $\bar{n}_0$, and of each branch, $\bar{n}_\infty$, and the average number of branches, B, per molecule.

As a result, it has been concluded that the remarkable difference between these two reactions can be explained by simultaneous polymerization and depolymerization during the heating. In the case of the condensation polymerization, the polymerization process is more important because the removal of water needs much heating, while, in the case of the ring-opening polymerization, the depolymerization process is more important because the polymerization is completed almost immediately after the material is melted.

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