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Changes in Degree of Polymerization and Weight of Cellulose Untreated and Treated with Inorganic Salts during Pyrolysis

By

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Summary : Studies on pyrolysis of cellulose which is a main component of wood were carried out with the purpose of yielding information basic for the development of fire-retardant wood and wood-based materials.

The used cellulose is fibrous linter. The treated samples were prepared by immersing the cellulose in aqueous solution of diammonium monohydrogen phosphate, sodium tetraborate decahydrate, ammonium bromide, or sodium chloride. These samples were heated *in vacuo*, and their degree of the polymerization (DP) and weight losses were obtained by the viscosimetry and by means of a thermal balance, respectively. The thermal analyses of differential thermal analysis (DTA), thermogravimetry (TG), and differential scanning calorimetry (DSC) were carried out for these samples. Furthermore, the elementary analysis was made for the charred residues which were yielded with the isothermal heatings.

A chain reaction mechanism is proposed, which is composed of random-scission initiation, propagation, and grafting termination. The changes in the DP and the weight by the pyrolysis are generally explained by this model. According to the model, the leveling off of the DP with the pyrolysis is regarded as indicating a stationary state between the initiation and the termination. On the other hand, the weight loss with the pyrolysis is regarded as being caused by volatile levoglucosan produced with the propagation, and is expressed in an apparent first-order reaction at the late stage, agreeing with the chain mechanism. The behaviors of the TG, the DTA, and the DSC of the untreated and treated celluloses are explained with the model, and the results of the elementary analysis support the model.

The obtained activation energies of the initiation of the untreated, phosphate-treated, borate-treated, bromide-treated, and chloride-treated celluloses are 38.0, 35.4, 29.6, 26.8, and 32.6 kcal/mole, respectively. The corresponding pre-exponential factors are 1.4×10^{10}, 6.9×10^{12}, 1.6×10^{7}, 7.4×10^{8}, and 9.3×10^{7} sec^{-1}, respectively. For the phosphate-treated cellulose, however, different values of 25.8 kcal/mole and 1.2×10^{7} sec^{-1} as the Arrhenius parameters of this reaction are derived from the DP at the early stage. The corresponding Arrhenius parameters of the termination of the above samples are determined to be 31.4, 25.0, 23.0, and 19.3 kcal/mole, and 2.9×10^{9}, 1.5×10^{10}, 2.5×10^{5}, 1.7×10^{9}, and 9.9×10^{4} sec^{-1}, respectively.

On the other hand, the determined activation energies of the first-order weight losses of the untreated, phosphate-treated, borate-treated, and chloride-treated celluloses are 44.7, 40.7, 49.9, and 44.3 kcal/mole, respectively. And the corresponding pre-exponential factors are 3.9×10^{13}, 6.9×10^{13}, 2.0×10^{16}, and 3.5×10^{14} sec^{-1}, respectively. The Arrhenius parameters of the weight loss in an apparent first-order reaction of the bromide-treated cellulose could not be obtained, probably because of the complexity caused by the effect of the fine structures.

I. Introduction

Wood flames with the heating. The process to the flaming may be qualitatively described as follows : At the beginning heated wood is decomdosed to produce gas, tar, and char. Furthermore, the tar is pyrolyzed to yield inflammable gaseous products which diffuse into the ambient atmosphere. When the pyrolysis rate of the wood increases, in spite of the diffusion

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the ambient inflammable gas mixed with air is concentrated over the critical point for the ignition, and then flashes over with inductive energy given from spark discharge, a pilot flame, or others. The wood is stronger heated with the additional heat from the flame, and then the combustion is accelerated.

The rate of the pyrolysis of wood prior to the combustion has been shown to be the sum of the pyrolysis rate of each wood component[1)]. In the thermogravimetries (TG) of wood components[2)~9)], it has been found that hemicellulose and lignin begin to lose weight at lower temperature than for cellulose, but cellulose which has the highest threshold temperature of the weight loss shows the highest rate of the weight loss of three components. Since the cellulose content of wood is generally above 50%, the above increase in the concentration of the inflammable mixed gas around the heated wood which continuously diffuses into the surroundings is reasonably supposed to be supported by the pyrolysis of the cellulose. Therefore, investigations on the pyrolysis of the cellulose which passes through a simpler course than for the wood is expected to give excellent results for the development of flame-retardant wood.

Many kinetic results have been reported on pyrolyses of celluloses. They, for the most part, were obtained by various weight loss methods. Otherwise, some results by differential thermal analysis (DTA) or differential scanning calorimetry (DSC) have been presented with or without thermogravimetry (TG). Since in these analyses changes in mass or energy which are accompanied by the volatilization of pyrolysis products with low molecular weight are directly or indirectly measured, it is difficult to obtain any information about molecular changes of cellulose itself.

In the early stage of the pyrolysis of cellulose, the rapid shortening of the chain, which is expressed in the change in the degree of polymerization (DP), is observed, The reductions in the DP of celluloses with heating have been mostly measured by viscosimetry[10)~16)]. The kinetic analysis for the decreases in the DP has been made on the basis of the well-known rate equation

$$\frac{1}{p}-\frac{1}{p_0}=k_i t \qquad (1)$$

where p and p_0 are the number average DP at the time t and 0, and k_i the rate constant. The above equation, which was used at first in the field of cellulose hydrolysis[17)18)], was derived from the expression for linear polymers which were subjected to random scission[19)]

$$L=L_0\exp(-k_i t) \qquad (2)$$

where L and L_0 were the numbers of chain linkages at the time t and 0, respectively. However, the change in the DP of cellulose during pyrolysis could not sufficiently be explained by means of the above equation alone, because of the observed leveling off of the DP[10)11)15)]. It seems necessary to re-examine the assumption of the random scission or to take any simultaneous reactions into consideration for a more satisfactory kinetic study of the pyrolysis.

II. Theory

In addition to the random scission reaction, chain propagation and chain termination may be taken as the possible reactions which affect the DP of cellulose during pyrolysis. The propagation reaction reduces the DP, while the termination reaction increases or does not affect it.

It may be assumed that the propagation which depolymerizes a cellulose molecule and

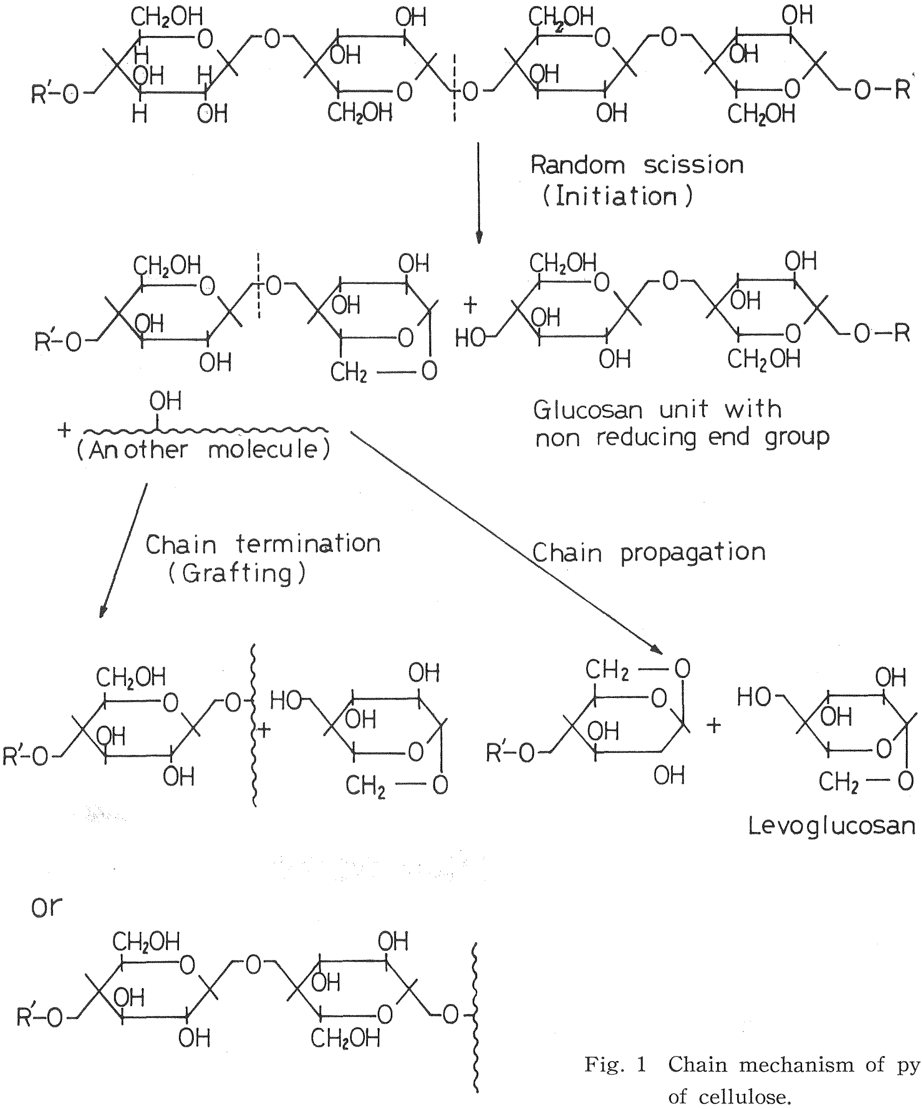

Fig. 1 Chain mechanism of pyrolysis of cellulose.

produces volatile levoglucosan begins at the end glucosidic bond of one of two fragment chains produced by the random-scission initiation, as disscussed by many authors20)~24), and the termination is chiefly caused by the combination of the active end unit with a hydroxyl group of another chain, as illustrated in Fig. 1. Then, ignoring the loss in the number of the cellulose chains at the last step of the propagation, the rate equation for the change in the number of the chains is expressed as

$$\frac{dn_r}{dt}=k_iL-k_t[\mathrm{OH}]n_r \tag{3}$$

where k_t is the rate constant of the termination, n_r the increment in the number of the molecules, and [OH] the number of the hydroxyl groups. If both fragment chains which are produced with a random scission process are assumed to undergo the termination as well as the propagation25), k_t should be replaced by $2k_t$.

When the DP of the heated cellulose levels off and then is not low, the linkage number may be expressed as

$$L \fallingdotseq np \qquad (4)$$

where n is the number of the molecular chains. Moreover, if the weight loss with the heating is small in comparison to the original weight, so np may be assumed to be nearly constant. The value of 〔OH〕 also must be nearly constant in the same sense. Then the expression

$$n_r - n_{r0} = \left(\frac{k_i L}{k_t'} - n_{r0}\right)[1 - \exp(-k_t' t)] \qquad (5)$$

is given by integrating the eq. (3) assuming $n_r = n_{r0}$ at $t = 0$, because of the decomposition before the sample attains the desired reaction temperature, and by making the substitution $k_t' = k_t$ 〔OH〕.

On the other hand, the separated expression of n_r and n_{r0}

$$n_r = L\left(\frac{1}{p} - \frac{1}{p_u}\right) \text{ and } n_{r0} = L\left(\frac{1}{p_0} - \frac{1}{p_u}\right) \qquad (6)$$

are directly obtained from eq. (4). In the above equations p_u is the DP befor the heating. Eqs. (5) and (6) make the following expression

$$\frac{1}{p} - \frac{1}{p_0} = \left[\frac{k_i}{k_t'} - \left(\frac{1}{p_0} - \frac{1}{p_u}\right)\right][1 - \exp(-k_t' t)] \qquad (7)$$

At $t = \infty$, the above equation is reduced to

$$\frac{1}{p_\infty} = \frac{k_i}{k_t'} + \frac{1}{p_u} \qquad (8)$$

where p_∞ is the leveling off DP. Eliminating $1/p_u$ from eqs. (7) and (8), the expressions

$$\frac{1}{p_\infty} - \frac{1}{p} = \left(\frac{1}{p_\infty} - \frac{1}{p_0}\right)\exp(-k_t' t) \qquad (9)$$

and

$$\frac{dt}{d}\left(\frac{1}{p}\right) = k_t'\left(\frac{1}{p_\infty} - \frac{1}{p}\right) \qquad (10)$$

are obtained. Eq. (9) takes the same form as an expression for scission of weak glucocidic bonds with hydrolysis by ELEMA[26], though it expresses a different reaction from the termination. His equation inevitably means leveling off DP that must be caused by lattice defects.

Since according to eq. (10) the extrapolation of the straight-line plot of $d(1/p)/dt$ vs. $1/p$ should give $1/p_\infty$ at $d(1/p)/dt = 0$, a mean by which the leveling off DP may be estimated is provided for the cases of the experimentally undetermined leveling off DP. The value of k_t' is obtained from a slope of a straight part which is formed by the semi-logarithmic plots of $\ln(1/p_\infty - 1/p)$ vs. t according to eq. (9). Then, the value of k_i is given by applying the obtained value of k_t' and the measured or estimated value of p_∞ to eq. (8) as well as to eq. (9). By the way, the value of k_t' should be obtained also from the plots according to eq. (10) which was used to estimate the leveling off DP, but this way is not adopted, because of introducing large errors.

Although the weight loss of cellulose with the heating would be contributed by various factors, such as dehydration, splitting of side groups, and so on, if it depends upon the above-mentioned propagation reaction alone, then the rate of weight loss can be expressed by

$$-\frac{dw}{dt} = k_p n_r \qquad (11)$$

where w is the number of the structral unit and k_p the rate constant of the propagation. At the leveling off of the DP, the number of the molecules is seen to be constant in eq. (6). Then, the stationary valuse n_{rs} of the increment in the molecular number is derived as

$$n_{rs} = \frac{k_i L}{k_t'} \qquad (12)$$

from eq. (3). Substituting n_{rs} into the right-hand side of eq. (11), the expression of the rate of the weight loss at the late stage

$$-\frac{dw}{dt} = \frac{k_i k_p}{k_t'} L \qquad (13)$$

is obtained. In the above equation, which is the same expression as has been derived by Boyd[27] and modified by Okamoto[23], the weight loss is seen to be a first-order reaction, because the linkage number may be assumed to be lost with the propagation alone and to be nearly equal to the number of the structural unit at this stage[*1].

III. Experimental

The cellulose sample used for this study was purified fibrous cotton linter which was supplied by Hercules Inco. (Wilmington, Delaware, U. S. A.) via Daicel Lts. (Osaka, Japan). Its weight average DP was found to be 2971. The sample was held in a vacuum desiccator at room temperature before the treatment with chemicals and heating it.

Inorganic salts used for the treatment of the cellulose are diammonium monohydrogen phosphate $(NH_4)_2HPO_4$, sodium tetraborate decahydrate $Na_2B_4O_7 \cdot 10\,H_2O$, ammonium bromide NH_4Br, and sodium chloride NaCl in CP grade. The cellulose sample was dipped in each aqueous solution of the 0.5% salts except sodium borate and of 1% sodium borate for about 90 min at room temperature, and then the solutions were filtered through a fused glass funnel (No. 3) with an aspirator. The cellulose residues on the fused glass were freeze-dried and then held in the vacuum desiccator before the heating. The take-ups of ammonium phosphate, sodium borate, ammonium bromide, and sodium chloride are about 4.4, 7.5, 4.5, and 5.5% of the original weight of each cellulose sample, respectively.

For the viscosimetry the untreated cellulose in the weight range of 100～110 or 200～210 mg which was contained in a platinic crucible was heated *in vacuo* (10^{-2}～10^{-3} mm Hg) with the heating rate of 5°C/min from room temperature to desired constant temperature, and then at the constant temperature by means of the apparatus schematically shown in Fig. 2. The heating duration was measured from the origin at which temperature just attained to a constant value. On the other hand, the salt-treated samples of 50～55 mg were heated at constant temperature over the whole heating periods using the same apparatus. After the heating, the system was first restored to atmospheric pressure with nitrogen gas, then the sample was weighed, and dissolved in cadoxen. The runs for the untreated sample were carried out at the four constant temperatures of 235.9°±2.8°, 257.0°±1.5°, 277.8°±1.7°, and 298.4°±1.4°C. The isothermal heatings for the treated samples were conducted within ±1°C of the desired constant temperatures.

The used cadoxen of the cellulose solvent was prepared according to the method modified by Kayama and Higgins[29] on the basis of Smith and co-workers'[30]. Namely, cadmium oxide

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[*1] Prof. Okamoto, Faculty of Agriculture, Kyoto University, has shown the same result of the first-order weight loss. His rate equation was rigorously derived from a linear differential equation which was made of eqs. (3) and (11)[28].

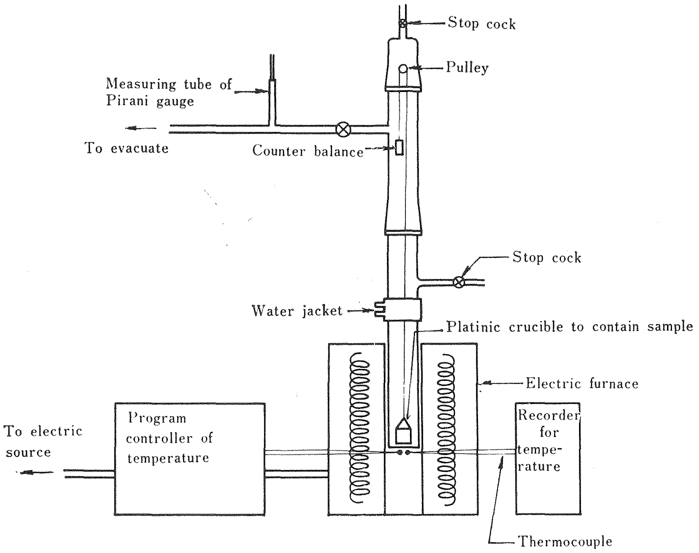

Fig. 2 Heating apparatus.

was dissolved in strong stirred, cold aqueous solution of ethylenediamine at about −5°C, and then the obtained raw solution was purified with a centrifuge. The cadoxen was held in a refrigerator. The concentration of cadmium oxide and ethylenediamine are about 26.3 and 6.2%, respectively.

The intrinsic viscosity $[\eta]$ of the cadoxen solutions of the cellulose samples, which were dissolved enough to measure the correct viscosity, was determined by the ordinary plots of the reduced viscosity vs. the concentration. The DP was calculated according to the equation[31],

$$[\eta]=1.84\times10^{-2}\times p_W^{0.76} \qquad (14)$$

ignoring effects of the used salts on the relation and the DP distribution. In eq. (14) p_W is the weight average DP.

In order to measure the weight loss with the isothermal heating, the cellulose samples of about 50 mg were heated *in vacuo* ($2-3\times10^{-1}$ mm Hg) with the rate of 5°C/min from room temperature up to desired constant temperature, and then at the constant temperature. The weight in the isothermal heating was measured after attaining to the constant temperature. These heating were carried out within ±3°C of the constant temperature by means of a Sinku Riko (Yokohama, Japan) TGD-1500 Differential Thermal Balance, which was formerly reported by HIRATA and ABE[24].

After the isothermal heatings, elementary analyses of residual samples obtained at two different temperatures for each treatment were carried out in Wako Pure Chemical Industry Ltd. (Osaka, Japan). In the elementary analyses the amounts of carbon, hydrogen, nitogen, and ash were measured three times for each sample. The ash contents were obtained with the heating for 5 min at 800°C.

Thermal analyses of thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) were carried out for the untreated and treated samples. The TG and the DTA were simultaneously conducted *in vacuo* ($2-3\times10^{-1}$ mm Hg) with the heating rate of 5°C/min, applying the samples of the original weight of about 50 mg to the above Differential Thermal Balance. The DSC was carried out with the heating rate of 8°C/min, by means of Perkin-Elmer DSC-1B. The amounts of the used samples are in the range of 4.5～9.0 mg.

IV. **Results**

IV. 1 **Viscosimetry**

The lenght of the polymer chains of the cellulose untreated and treated with the inorganic salts was found to be rapidly reduced with the heating at first, as shown by the changes in the DP in Figs. 3～7. However, the rate of the reductions in the DP decreased with time, and

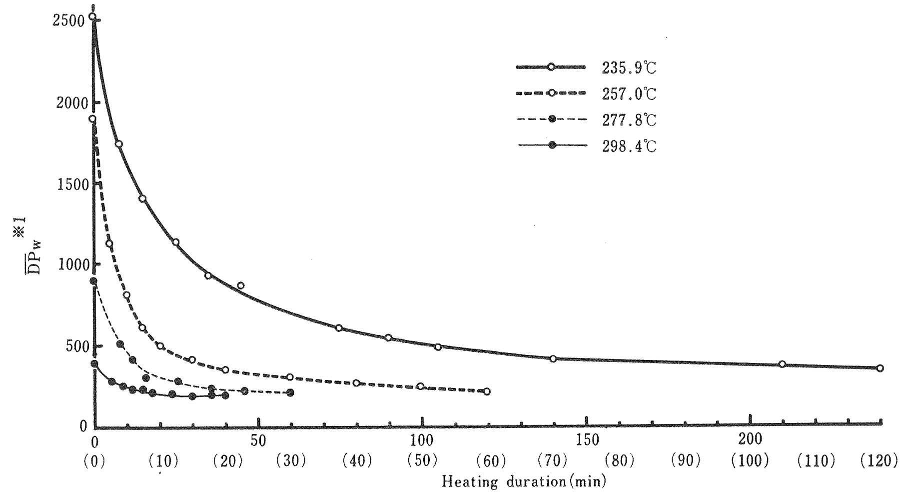

Fig. 3 Decreases in DP of untreated cellulose during pyrolysis. Both the heating durations at 277.8° and 298.4°C are shown by the parenthesized values.

*1 $\overline{DP}_W$ is the weight average DP.

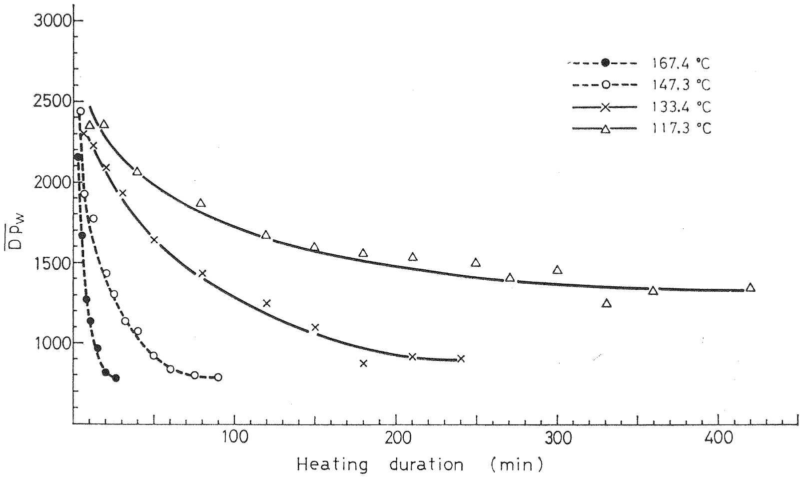

Fig. 4 Decreases in DP of cellulose treated with ammonium phosphate during pyrolysis.

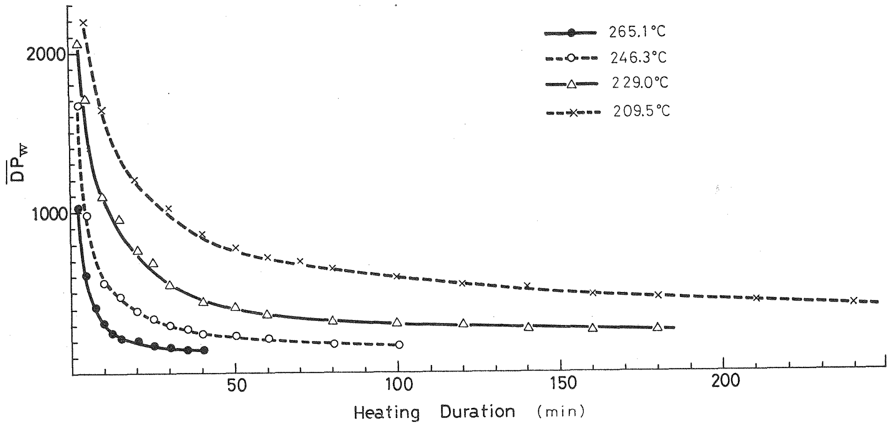

Fig. 5 Decreases in DP of cellulose treated with sodium borate during pyrolysis.

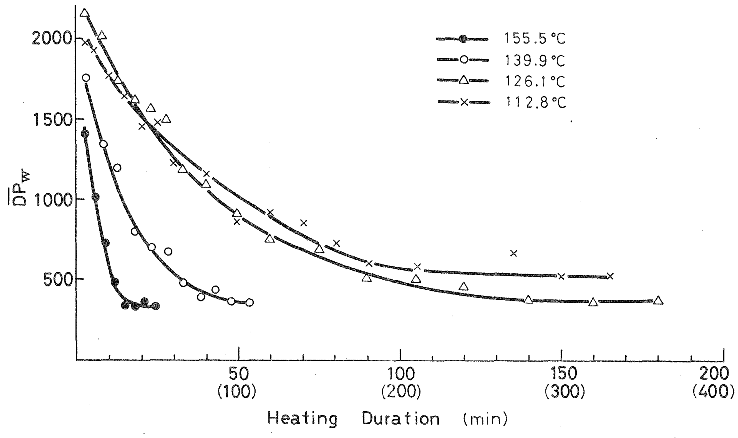

Fig. 6 Decreases in DP of cellulose treated with ammonium bromide during pyrolysis.

The heating duration at 112.8°C is shown by the parenthesized values.

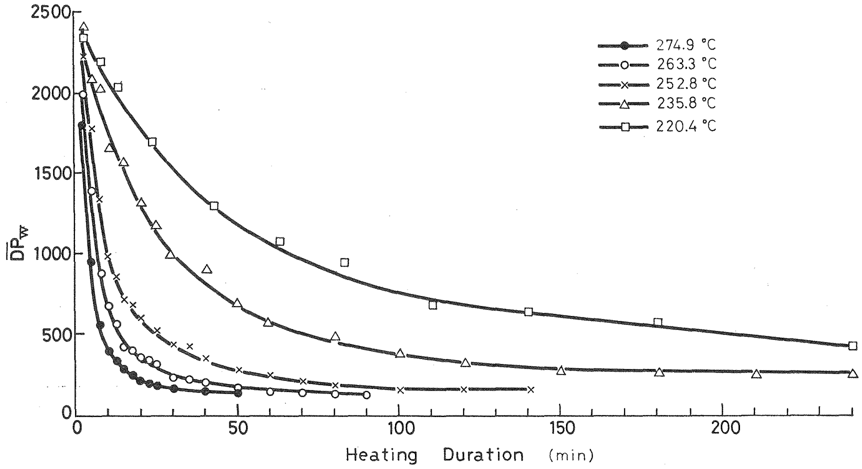

Fig. 7 Decreases in DP of cellulose treated with sodium chloride during pyrolysis.

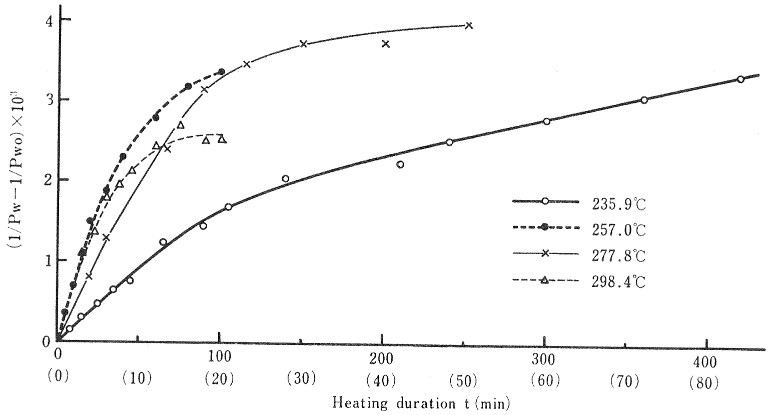

Fig. 8 Differences of reciprocals of DP of untreated cellulose between heating durations of 0 and *t*.

Both the heating durations at 277.8° and 298.4°C are shown by the parenthesized values.

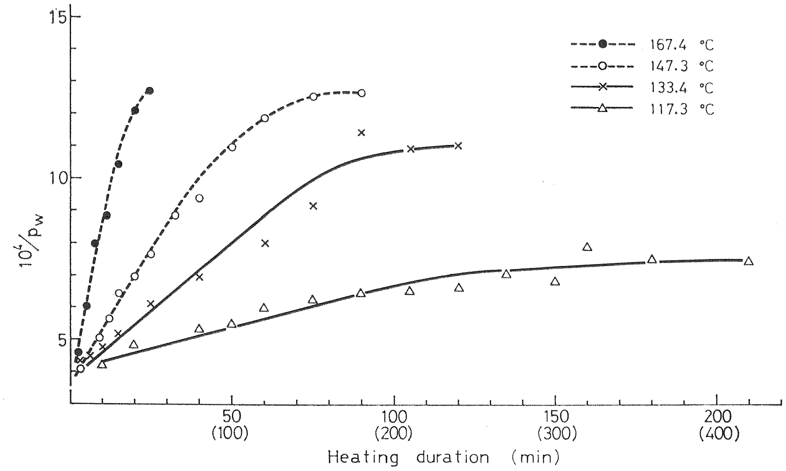

Fig. 9 Reciprocals of DP of phosphate-treated cellulose. The heating durations at 133.4° and 117.3°C are expressed by the parenthesized values.

the DP levelled off at last. The leveling off DP of each sample is seen to depend upon the temperature from the above figures.

For the untreated cellulose the different values of the DP at the time 0 were obtained depending upon the temperatures, because the heating time to elevate the temperature up to the constant value with the rate of 5°C/min was different. The leveling off DP of about 195 observed at 298.4°C surprisingly approaches to the value of 200 for cotton cellulose at 300°C *in vacuo* by GOLOVA and KRYILOVA[10], but is somewhat higher than for slash pine pulp by MILLETT and GOEDKEN[12].

The salt-treated samples, especially, the phosphate- and bromide-treated samples had to be heated at far lower temperature than for the untreated sample, because of the insolubility of both the samples heated at high temperature. The leveling off DP of the phosphate-treated sample could not be determined at the highest temperature due to the insolubility. Further-

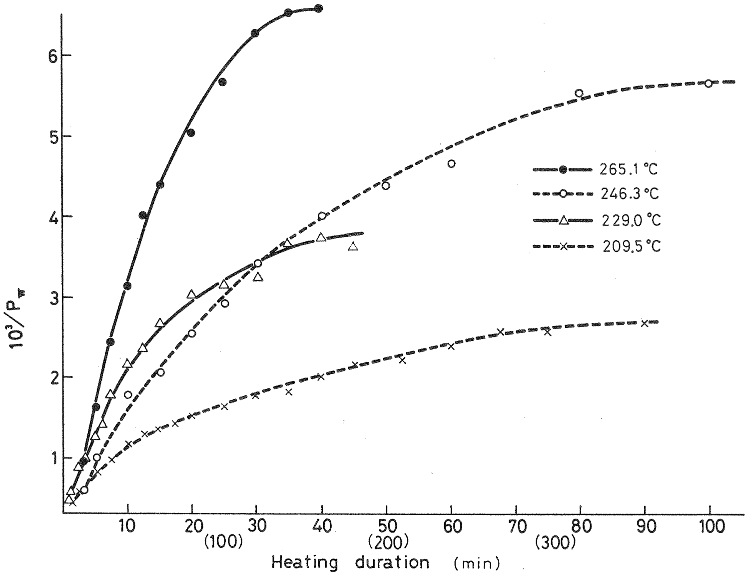

Fig. 10 Reciprocals of DP of borate-treated cellulose. Both the heating durations at 229.0° and 209.5°C are shown by the parenthesized values

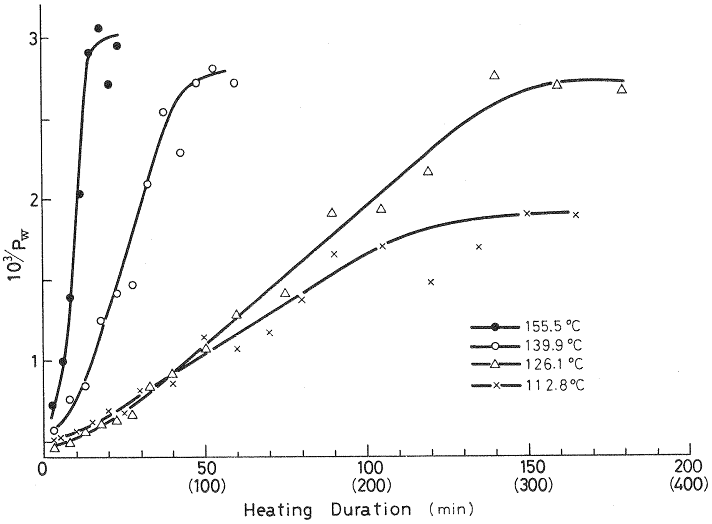

Fig. 11 Reciprocals of DP of bromide-treated cellulose. The heating duration at 112.8°C is shown by the parenthesized values.

more, that of the chloride-treated sample could not be given at the lowest and highest temperatures, because of the insufficient quantity of the sample.

For the determination of the kinetic parameters for the random scission of the chains from the viscosity measurements, eq. (1) is transformed into

$$\frac{1}{p_W} - \frac{1}{p_{W0}} = \frac{k_i}{2}t \qquad (15)$$

on the basis of the relation between number and weight average DP of a polymer with the

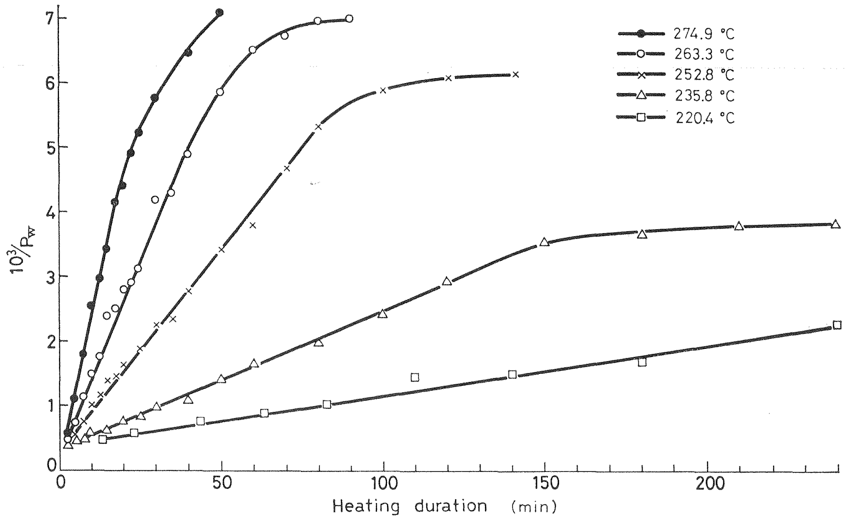

Fig. 12 Reciprocals of DP of chloride-treated cellulose.

Table 1. Kinetic parameters for random scission

Salts for treatment	$T^{a)}$ (°C)	$k_i{}^{b)}$ (sec^{-1})	$E^{c)}$ (kcal/mole)	$A^{d)}$ (sec^{-1})	$\bar{p}_{W\infty}{}^{e)}$
Untreated	298.4	1.23×10^{-5}	32.2	4.3×10^{7}	186
	277.8	7.25×10^{-6}			190
	257.0	2.38×10^{-6}			228
	235.9	6.53×10^{-7}			252
$(NH_4)_2HPO_4$	167.4	1.76×10^{-6}	25.8	1.2×10^{7}	
	147.3	5.43×10^{-7}			790
	133.4	1.43×10^{-7}			905
	117.3	4.50×10^{-8}			1,340
$Na_2B_4O_7\cdot10\,H_2O$	265.1	1.43×10^{-5}	27.4	1.8×10^{6}	152
	246.3	5.53×10^{-6}			179
	229.0	1.69×10^{-6}			267
	209.5	7.42×10^{-7}			364
NH_4Br	155.5	7.93×10^{-6}			339
		5.44×10^{-6}			
	139.9	2.13×10^{-6}	30.2	2.2×10^{10}	356
		1.63×10^{-6}			
	126.1	5.73×10^{-7}	27.0	3.3×10^{8}	374
		5.14×10^{-7}			
	112.8	2.87×10^{-7}			524
		2.02×10^{-7}			

Note : a) T is the temperature, b) k_i the rate constant (for the bromide-treated sample, the values in the upper and lower lines are respectively obtained from the straight part and the average slope between the reciprocals of the DP at the time 0 and at the end of the straight part in Fig. 11), c) E the activation energy of, d) A the pre-exponential factor of Arrhenius, and e) $\bar{p}_{W\infty}$ the leveling off DP in the weight average (the values of the untreated sample were obtained by the estimation according to eq. (10)).

Table 1. (Continued)

Salts for treatment	$T^{a)}$ (℃)	$k_i^{b)}$ (sec^{-1})	$E^{c)}$ (kcal/mole)	$A^{d)}$ (sec^{-1})	$p_{W\infty}^{e)}$
Nacl	274.9	7.77×10^{-6}	33.0	1.1×10^{8}	
	263.3	3.95×10^{-6}			143
	252.8	2.12×10^{-6}			163
	235.8	2.27×10^{-7}			263
	220.4	2.70×10^{-7}			

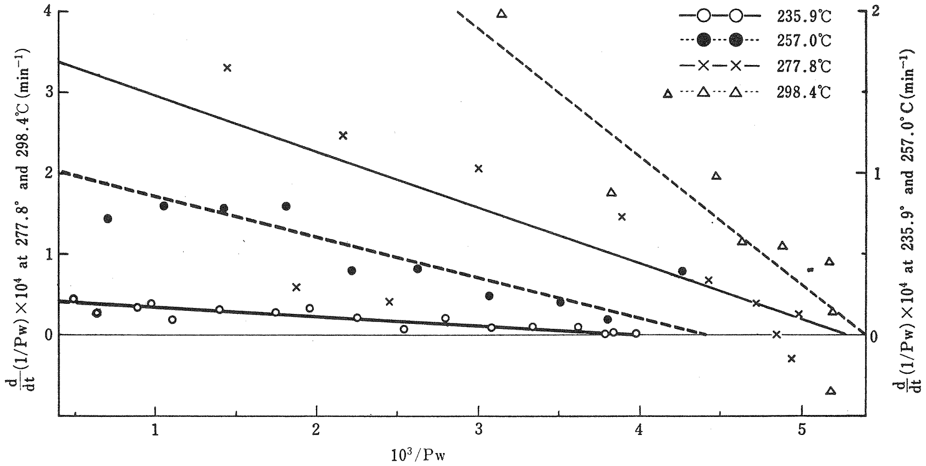

Fig. 13 Estimationt of leveling off DP of untreated cellulose.

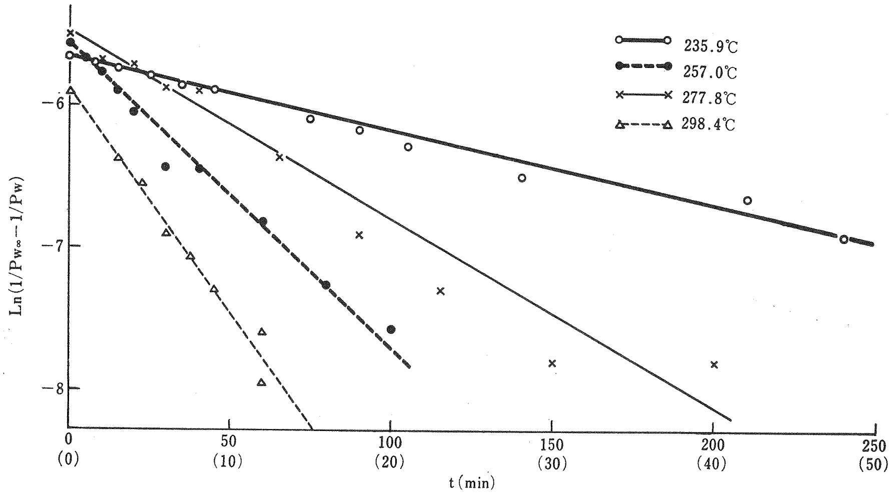

Fig. 14 Determination of rate constants of termination for untreated cellulose.

Both the heating durations at 277.8° and 298.4℃ are shown by the parenthesized values.

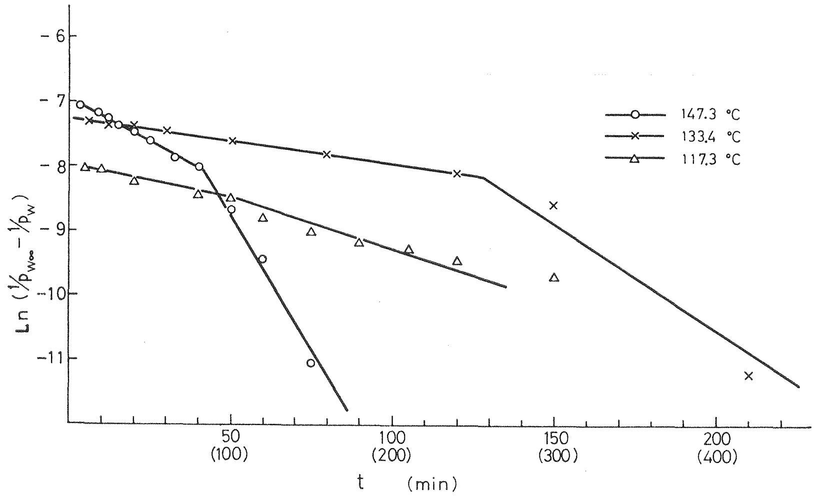

Fig. 15 Determination of rate constants of termination for phosphate-treated cellulose.
The parenthesized values on the abscissa express t at 117.3°C.

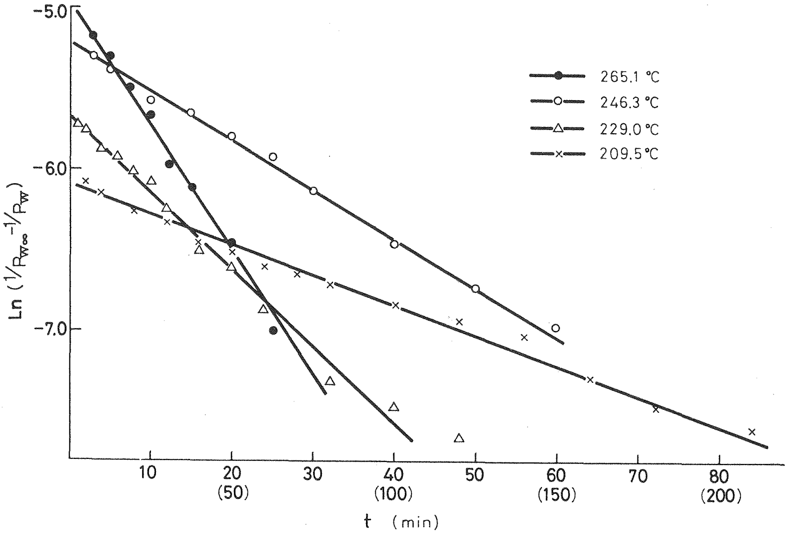

Fig. 16 Determination of rate constants of termination for borate-treated cellulose.
Both the heating durations at 229.0° and 209.5°C are shown by the parenthesized values.

most probable molecular weight distribution[32]. In eq. (15) p_{W0} denotes p_W at $t=0$. The plots of $1/p_W$ vs. t according to the above equation, which were given in Figs. 8~12, should form straight lines, if the random scission of the chains alone took place as a principal pyrolytic reaction. These plots for all the samples, however, form curves, which have straight parts at the early stages of the pyrolyses, as shown in the figures. Especially, the plots for the phosphate- and chloride-treated samples give the straight parts for the considerably wide ranges of the time. The reciprocals of the DP of all the samples in the above figures seem

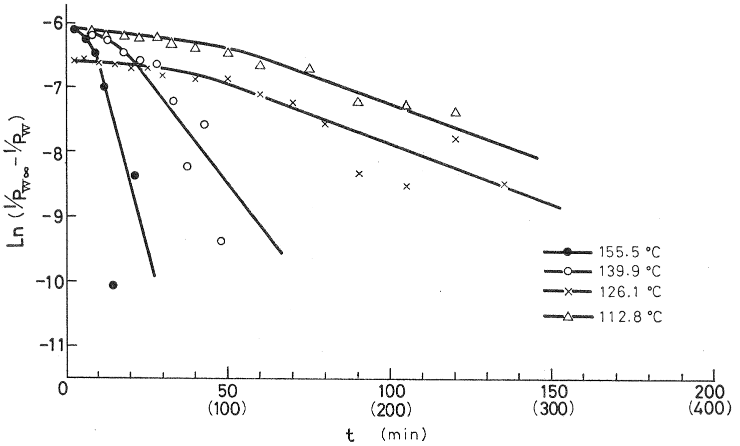

Fig. 17 Determination of rate constants of termination bromide-treated cellulose.
The parenthesized values of *t* show those at 112.8°C.

Table 2. Kinetic parameters for termination through chain mechanism

Salts for treatment	*T* (°C)	k_t' (sec^{-1})	*E* (kcal/mole)	$A^{a)}$ (sec^{-1})
Untreated	298.4	2.65×10^{-3}	31.4	2.9×10^{9}
	277.8	1.11×10^{-3}		
	257.0	3.62×10^{-4}		
	235.9	8.55×10^{-5}		
$(NH_4)_2HPO_4$	147.3	1.39×10^{-3}	25.0	1.5×10^{10}
	133.4	5.50×10^{-4}		
	117.3	1.35×10^{-4}		
$Na_2B_4O_7\cdot10\,H_2O$	265.1	1.25×10^{-3}	20.5	2.5×10^{5}
	246.3	5.03×10^{-4}		
	229.0	3.03×10^{-4}		
	209, 5	1.33×10^{-4}		
NH_4Br	155.5	3.02×10^{-3}	23.0	1.7×10^{9}
	139.9	1.07×10^{-3}		
	126.1	2.93×10^{-4}		
	112.8	1.50×10^{-4}		
NaCl	263.3	1.43×10^{-3}	19.3	9.9×10^{4}
	252.8	9.60×10^{-4}		
	235.8	5.55×10^{-4}		

Note : a) The values are expressed as the product of the pre-exponential factor and the concentration of the hydroxyl group.

to level off at last. For the bromide-treated sample, the changes in the reciprocals are distinguished into three stages, as seen in Fig. 11. The reciprocals relatively slowly increase at the first stage, and then linearly and rapidly increase at the second stage, but finally level off at the third stage.

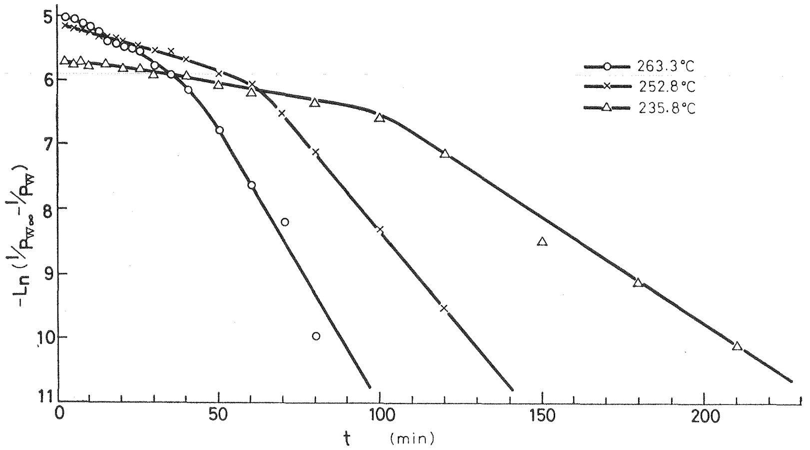

Fig. 18 Determination of rate constants of termination for chloride-treated cellulose.

Table 3. Kinetic parameters for random-scission initiation through chain mechanism

Salts for treatment	T (°C)	k_i (sec^{-1})	E (kcal/mole)	A (sec^{-1})
Untreated	298.4	2.69×10^{-5}	38.0	1.4×10^{10}
	277.8	1.09×10^{-5}		
	257.0	2.95×10^{-6}		
	235.9	6.18×10^{-7}		
$(NH_4)_2HPO_4$	147.3	2.48×10^{-6}	35.4	6.9×10^{12}
	133.4	8.02×10^{-7}		
	117.3	1.00×10^{-7}		
$Na_2B_4O_7\cdot10\,H_2O$	265.1	1.56×10^{-5}	29.6	1.6×10^{7}
	246.3	5.26×10^{-6}		
	229.0	2.05×10^{-6}		
	209.5	6.32×10^{-7}		
NH_4Br	115.5	1.58×10^{-5}	26.8	7.4×10^{8}
	139.9	5.29×10^{-6}		
	126.1	1.37×10^{-6}		
	112.8	4.72×10^{-7}		
NaCl	263.3	4.75×10^{-6}	32.6	9.3×10^{7}
	252.8	2.78×10^{-6}		
	235.8	9.62×10^{-7}		

The rate constants of the random scission were determined from the slopes of the above initial straight parts, assuming the constant amounts of the salts during the pyrolyses. For the bromide-treated sample, a pair of the rate constant was obtained at each temperature. One was derived from the straight part at the above second stage, and another was obtained from an average slope between the reciprocals at the time 0 and at the end of the straight part. These four pairs of the rate constants are given together with the rate constants for other samples and the leveling off DP in Table 1.

Since for all the samples the plots according to eq. (15) did not make satisfactory straight lines over the whole ranges, the attempts to apply the chain mechanism to the changes in the DP were made. In advance of the determinations of the rate constants of the termination reaction, the leveling off DP of the untreated cellulose was estimated with the plots of $d(1/p_W)/dt$ vs. $1/p_W$ according to eq. (10) shown in Fig. 13, because of the uncertain measurements. The estimated values of it are listed in Table 1. In order to determine the rate constants of the termination, the plots of $\ln(1/p_{W\infty}-1/p_W)$ vs. t according to eq. (9) are carried out in Figs. 14～18. The slopes of the straight lines made of the plots should give the rate constants of the termination. These plots for the untreated and borate-treated samples make straight lines over the studied range, but the plots for the phosphate-, bromide-, and chloride-treated samples form lines with gentle slopes at the early stage and with steep slopes at the late stage of the pyrolyses, as shown in the above figures. For the latter samples, the plots for the random scission according to eq. (15) make the considerably long straight lines at the early stage, while those plots for the former samples are little considered to form the corresponding straight parts, as shown in Figs. 8～12. Therefore, it is supposed for the phosphate-, bromide-, and chloride-treated samples that only the random scission substantially occurred at the initial stage of the pyrolyses, and that two reactions of the random-scission initiation and the termination generated at the late stage. Although the plotted dots for the bromide-treated sample are somewhat scattered, the rate constants of the termination for the above three samples including the bromide-treated cellulose are determined from the slopes of the straight plots at the late stage. The obtained values are given with those for the untreated and borate-treated samples in Table 2.

The rate constants of the random-scission initiation were computed by means of eq. (8), for which the values of the DP before the heating and of the leveling off, and the rate constants of the termination were substituted. The obtained rate constants are listed in Table 3.

Temperature dependence of rate of a reaction has been expressed by Arrhenius' equation

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{16}$$

where k is the rate constant, A the pre-exponential factor, R the gas constant, E the activation energy, and T the absolute temperature. In order to obtain the pre-exponential factors and the activation energies of the random scission, the initiation, and the termination, the plots of $\ln k$ vs. $1/T$ according to eq. (16), which were called Arrhenius plots, were made for all the samples. These Arrhenius plots are shown in Figs. 19～26. The obtained activation energies and pre-exponential factors of the random scission, the termination, and the random-scission initiation are listed in Tables 1, 2 and 3, respectively.

IV. 2 **Weight measurements**

The weight losses of the untreated and salt-treated samples with the isothermal heatings are observed at the higher temperature than the random scission, as seen in Figs. 27～31. It is seen from these figures that the weight loss is less for the treated samples than for the untreated sample, as reported by many workers. The treated samples except the chloride-treated sample left the stable residues over 40% of the original weight, but the untreated sample produced the stable residue below 20%.

The bromide-treated cellulose of the salt-treated samples shows remarkable weight losses, as seen in Fig. 30. The weight was readily reduced at the lower temperature than 200°C, and

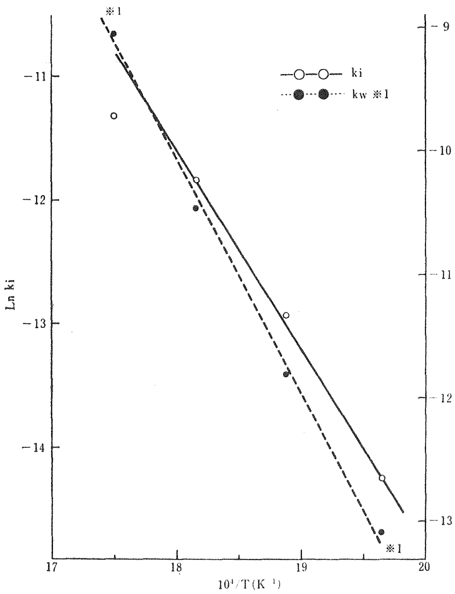

Fig. 19 Arrhenius plots of rate constants of random scission determined from reciprocals of DP for untreated cellulose.

*1 The previously reported rate constants of the apparent zeroth-order weight loss[33] are not taken into consideration in this paper.

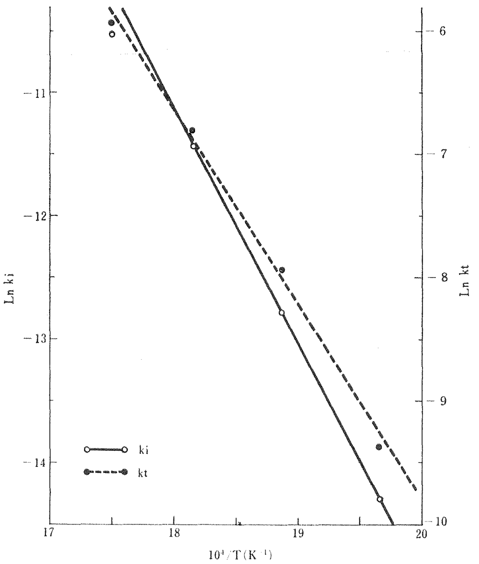

Fig. 20 Arrhenius plots of rate constants of initiation and termination determined through chain mechanism for untreated cellulose.

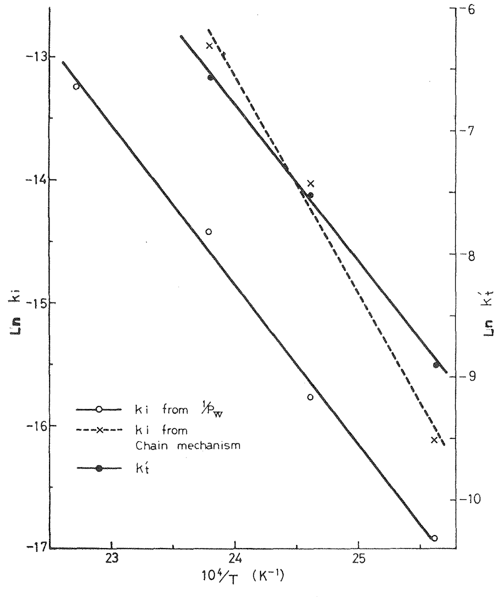

Fig. 21 Arrhenius plots of rate constants of random scission and termination for phosphate-treated cellulose.

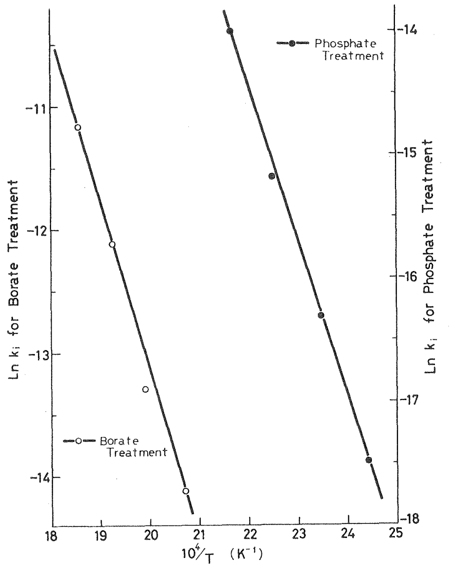

Fig. 22 Arrhenius plots of rate constants of random scission from reciprocals of DP for phosphate-*1 and borate-treated celluloses.

*1 Cited from the previous paper by HIRATA, OKAMOTO, and NAITO[42].

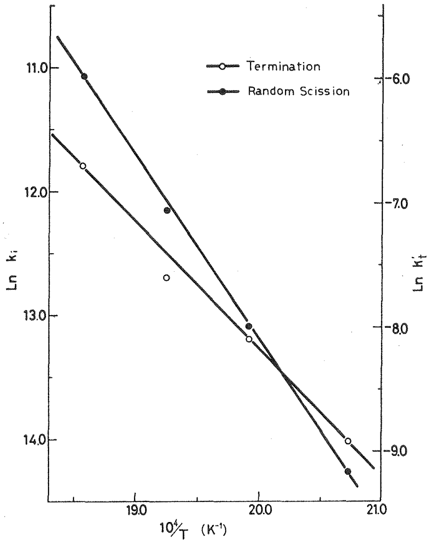

Fig. 23 Arrhenius plots of rate constants of initiation and termination through chain mechanism for borate-treated cellulose.

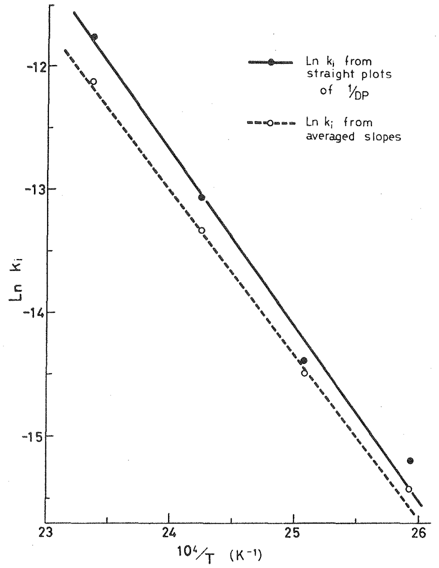

Fig. 24 Arrhenius plots of rate constants of random scission from reciprocals of DP for bromide-treated cellulose.

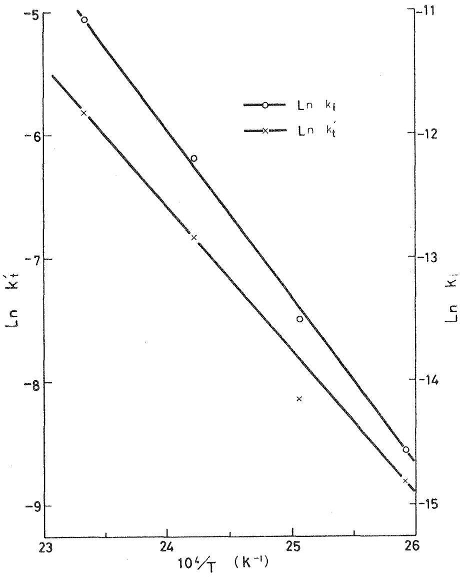

Fig. 25 Arrhenius plots of rate constants of initiation and termination through chain mechanism for bromide-treated cellulose.

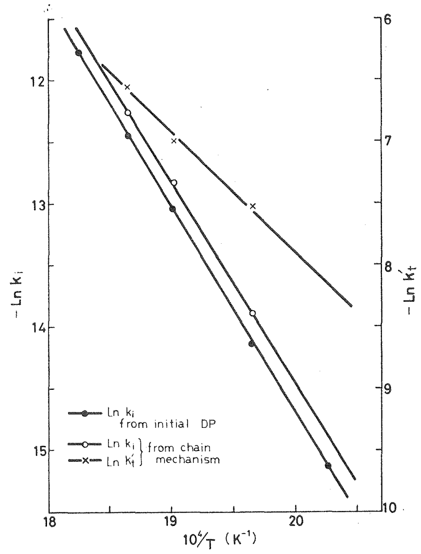

Fig. 26 Arrhenius plots of rate constants of random scission and termination for chloride-treated cellulose.

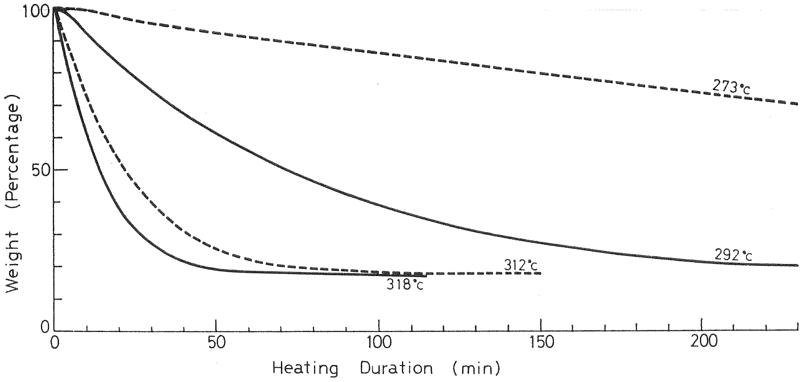

Fig. 27 Decrease in weight of untreated cellulose with heating.

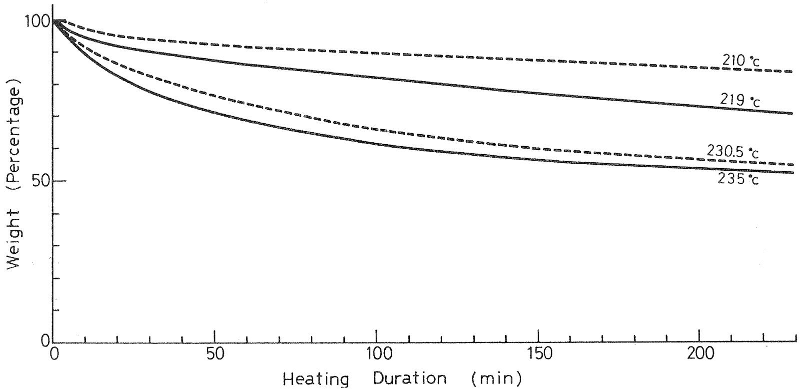

Fig. 28 Decrease in weight of phosphate-treated cellulose with heating.

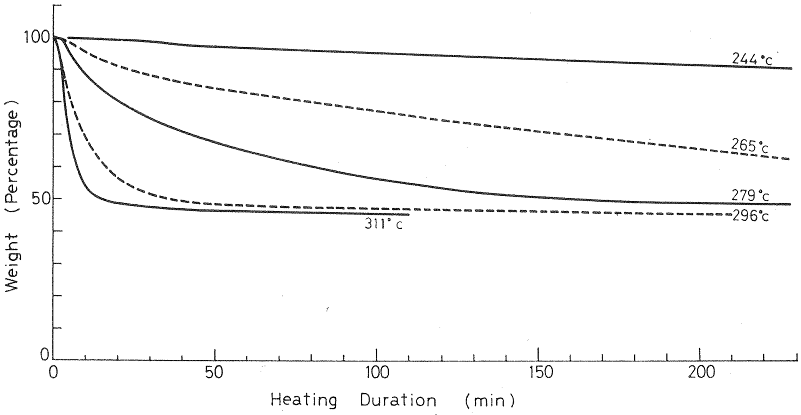

Fig. 29 Decrease in weight of borate-treated cellulose with heating.

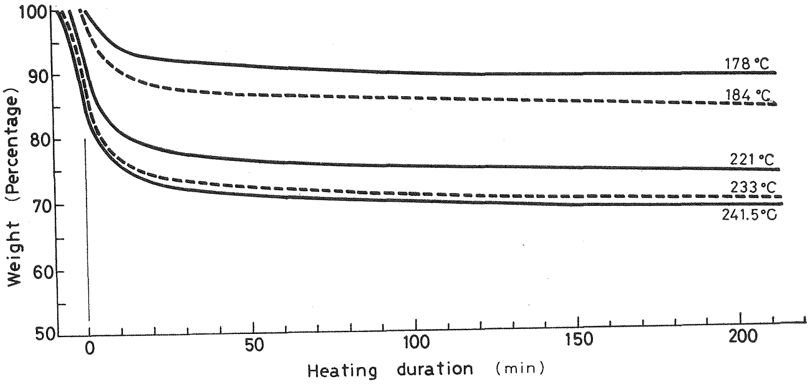

Fig. 30 Decrease in weight of bromide-treated cellulose with heating.

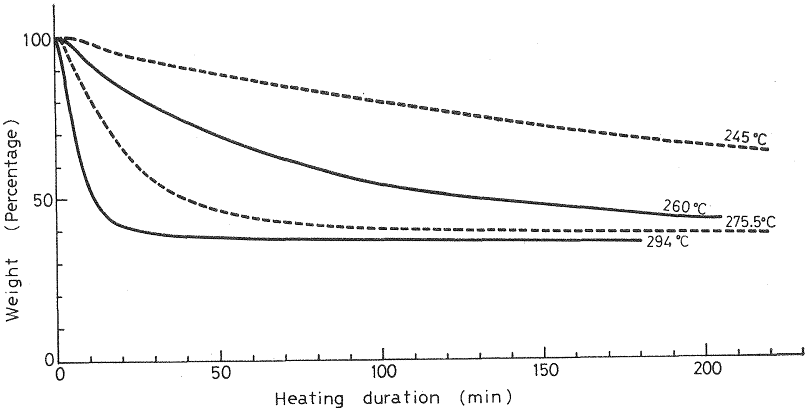

Fig. 31 Decrease in weight of chloride-treated cellulose with heating.

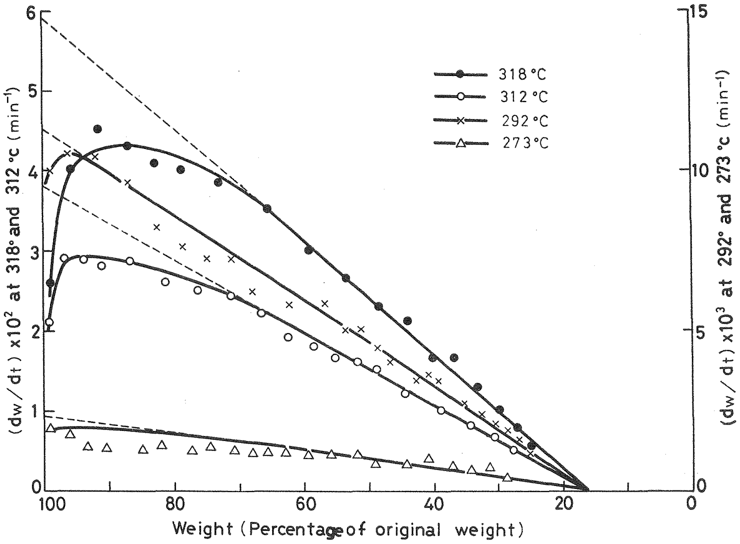

Fig. 32 Plots of weight loss rate vs. residual weight for untreated cellulose.

considerable quantities of the weight were lost before elevating the temperature up to the desired constant values higher than 200°C with the heating rate of 5°C/min. These amounts are found as the weight losses at the time 0 in Fig. 30. In spite of the observed unstable part of the weight, the solid residues were produced in large quantities.

While weight loss with pyrolysis of cellulose has not perfectly been expressed as a first-oder reaction, the greater part of the reported kinetic parameters has been determined by means of rate equations in first-oder law. For the determination of the rate constant of the first-order weight loss in eq. (13), the plots of the weight loss rate vs. the weight are carried out for the untreated and salt-treated samples except the bromide-treated one in Figs. 32~35. These plots, made after the manner by MADORSKY and coworkers[20], form straight lines at the late stage of the heating in agreement with the results by them. For the bromide-treated sample, however, the attempts to make kinetic analysis on the weight losses did not give significant results, probably because the observed amounts of the weight loss at the constant temperature were too small to make kinetic calculations and further its process was complex, as later suggested.

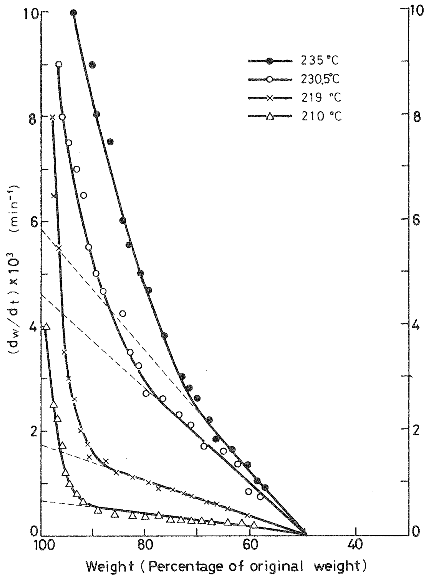

Fig. 33 Plots of weight loss rate vs. residual weight for phosphate-treated cellulose.

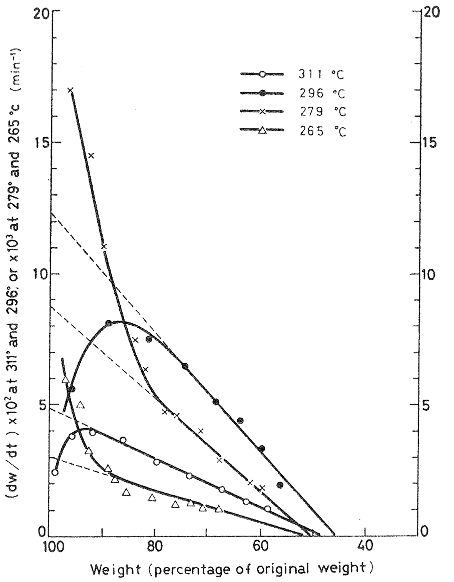

Fig. 34 Plots of weight loss rate vs. residual weight for borate-treated cellulose.

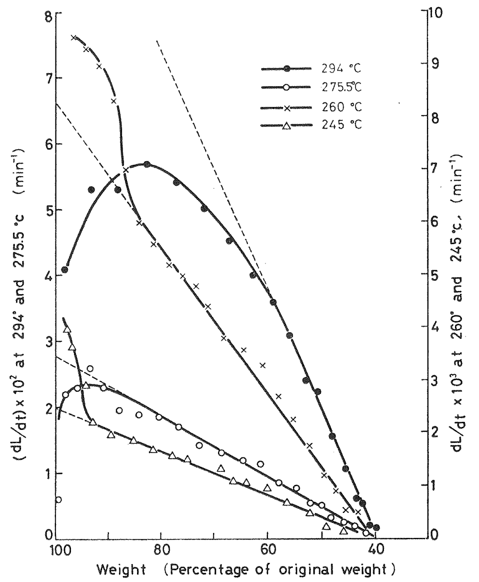

Fig. 35 Plots of weight loss rate vs. residual weight for chloride-treated cellulose.

The slopes of the straight lines in the above figures give the rate constants of the weight loss, as seen from the relation

$$\left(\frac{dw}{dt}\right)_1-\left(\frac{dw}{dt}\right)_2=k_w(w_2-w_1) \qquad (17)$$

where $(dw/dt)_1$ and $(dw/dt)_2$ are the weight loss rates at the residual weights or structural unit numbers w_1 and w_2, and k_w the rate constant of the weight loss, and the subscript w denotes the weight loss. The obtained rate constants are given in Table 4. The Arrhenius

Table 4. Kinetic parameters for first-order weight loss

Salts for treatment	T (℃)	k_w (sec^{-1})	E (kcal/mole)	A (sec^{-1})
Untreated	318	1.17×10^{-3}	44.7	3.9×10^{13}
	312	7.54×10^{-4}		
	292	2.24×10^{-4}		
	273	4.76×10^{-5}		
$(NH_4)_2HPO_4$	235	1.92×10^{-4}	40.7	6.9×10^{13}
	230.5	1.52×10^{-4}		
	219	5.87×10^{-5}		
	210	2.29×10^{-5}		
$Na_2B_4O_7\cdot10\,H_2O$	311	3.80×10^{-3}	49.9	2.0×10^{16}
	296	1.55×10^{-3}		
	279	2.96×10^{-4}		
	265	1.08×10^{-4}		
NaCl	294	3.04×10^{-3}	44.3	3.5×10^{14}
	275.5	7.67×10^{-4}		
	260	2.32×10^{-4}		
	245	7.08×10^{-5}		

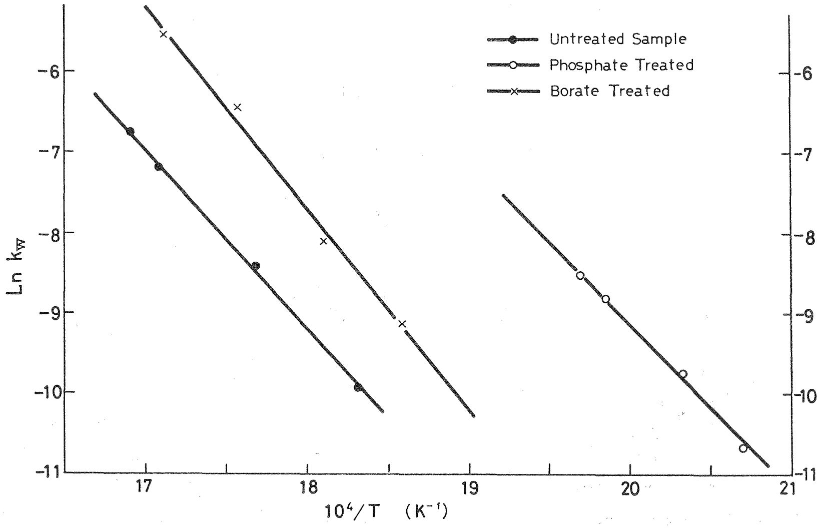

Fig. 36 Arrhenius plots of rate constants for weight losses of celluloses with heating.

Table 5. Arrhenius parameters for propagation

Salts for treatment	$E_p$$^{a)}$ (kcal/mole)	$A_p$$^{a)}$ (sec^{-1})	$E_p-E_t$$^{b)}$ (kcal/mole)	A_p/A_t'
Untreated	38.1	8.1×10^{12}	6.7	2.8×10^{3}
$(NH_4)_2HPO_4$	30.3	1.5×10^{11}	5.3	10
$Na_2B_4O_7\cdot10\,H_2O$	40.8	5.0×10^{14}	20.3	2.0×10^{9}
NaCl	31.0	3.8×10^{10}	11.7	3.8×10^{5}

Note : a) The subscript p and b) t designate the propagation and the termination, respectively.

plots of those rate constants are performed in Figs. 36 and 37. Also the Arrhenius parameters obtained from the plots are listed in the same table.

If the weight losses are assumed to be caused by the volatilization of levoglucosan produced with the chain propagation reaction, from eqs. (13) and (17) the rate constant of the first-order weight loss may be given as

$$k_w=\frac{k_i k_p}{k_t'} \qquad (18)$$

where the subscript p denotes the propagation. Applying the Arrhenius equation, eq. (18) gives

$$\ln k_w=\ln\frac{k_i k_p}{k_t'}=\ln\frac{A_i A_p}{A_t'}-\frac{E_i+E_p-E_t}{RT} \qquad (19)$$

where the subscripts i and t denote the initiation and the termination, and A_t' denotes A_t [OH]. Since the pre-exponential factors and the activation energies of the weight losses in Table 4 may be regarded as the values of A_iA_p/A_t' and $E_i+E_p-E_t$, as shown by eq. (19), the Arrhenius parameters of the propagation can be derived from those of the initiation, the termination, and the weight loss. The obtained parameters are listed in Table 5.

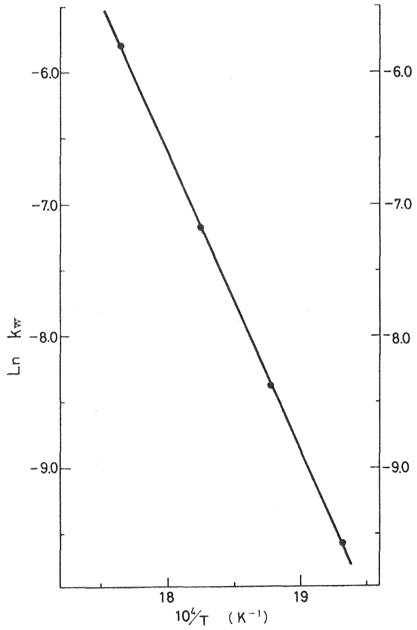

Fig. 37 Arrhenius plots of rate constant of weight loss of chloride-treated cellulose.

IV. 3 **Elementary analyses**

The carbon, hydrogen, oxygen, and ash contents of the isothermally heated samples were obtained from the results of the elementary analyses, and are given together with the heating durations, the temperatures, and the yields of the residues in Table 6. In addition, the ratios of the carbon and hydrogen atoms to oxygen atoms contained in the residues are listed in the last column of the same table. Nitrogen was not found in any of the samples. It is found in Table 6 that the content of the carbon reasonably increased with the progress of the pyrolysis, while those of the hydrogen and the oxygen decreased with the pyrolysis.

On the other hand, the reductions in the percentages of the original amounts of these elements by the pyrolysis are shown with the yields of the residues in Fig. 38. The decrease of fhe carbon was slow at first but accelerated with the progress of the pyrolysis, while those of the hydrogen and the oxygen were rapid at first but graduated into retardation, as seen

Table 6. Contents of elements in residue

Treatment	T (°C)	t (min)	Residual weight (%)	Contents, weight (%)				Rational formula
				C[a]	H[a]	O[b]	Ash[c]	
Untreated	318	115	16.9	78.01	4.22	17.06	0.71	$C_{62}H_{40}O_{10}$
	292	263	19.1	75.10	4.26	20.59	0.05	$C_{49}H_{33}O_{10}$
$(NH_4)_2HPO_4$	235	503	47.2	62.20	3.99	27.11	5.7	$C_{31}H_{24}O_{10}$
	210	1,180	55.5	54.67	4.71	35.72	4.9	$C_{21}H_{21}O_{10}$
$Na_2B_4O_7 \cdot$ 10 H_2O	311	110	45.1	62.12	3.89	25.09	8.9	$C_{33}H_{25}O_{10}$
	265	1,000	46.3	62.86	4.18	24.36	8.6	$C_{35}H_{28}O_{10}$
NH_4Br	221	799	71.6	55.28	5.06	39.54	0.12	$C_{19}H_{20}O_{10}$
	178	1,060	79.0	49.06	5.52	45.17	0.25	$C_{15}H_{20}O_{10}$
NaCl	294	180	35.6	62.91	4.09	17.60	15.4	$C_{47}H_{37}O_{10}$
	245	610	45.9	61.69	4.40	21.91	12.0	$C_{38}H_{32}O_{10}$

Not : a) The contents of carbon and hydrogen were given by averaging three values measured for each sample. All the differences between maxima and minima of these three values for each content are within 1%. b) The oxygen contents were given as 100% minus the contents of carbon, hydrogen, and ash. c) The ash contents of the untreated and bromide-treated samples were measured actually. Those of the phosphate- and borate-treated samples were given on the basis of assumptions that diammonium hydrogen phosphate was modified to yield metaphosphoric acid[34] and sodium tetraborate decahydrate lost the water of crystalization with the heatings, respectively. Those of the chloride-treated samples were calculated samples were calculated with an assumption that the complete amounts of the salt were left in the residues.

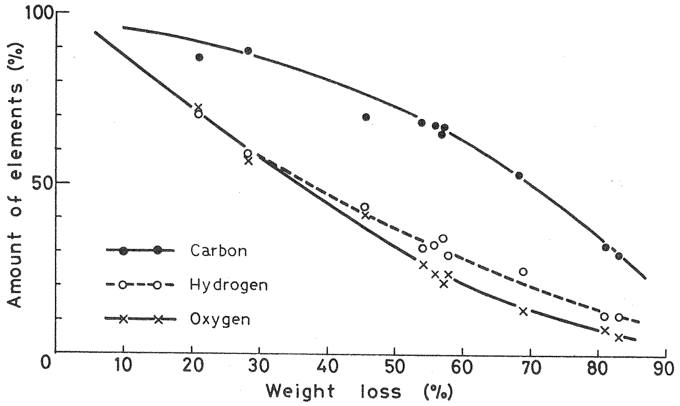

Fig. 38 Decreases in amounsts of elements in residue.
The values used for the plots were corrected with the amounts of residue minus those of the salts and the ash.

in Fig. 38, though the figure was made on the basis of the residues from the differently treated samples. These suggest that the weight losses were caused not only by the propagation reaction but also by the dehydration and other reactions. Furthermore, it is noted that the charred residue from the untreated sample heated even at 318°C of the temperature still retains the hydrogen and the oxygen of about 11.6 and 6.0% of the original amounts, respectively.

IV. 4 **Thermal analyses**

The thermogravimetry (TG), the differential thermal analysis (DTA), and the differential scanning calorimetry (DSC) were performed for all the samples. The TG and DTA curves of the untreated, phosphate-, and borate-treated samples are shown in Fig. 39, and those of the untreated, bromide-, and chloride-treated samples are shown in Fig. 40. The DSC curves of the untreated, phosphate-, and borate-treated samples are given in Fig. 41, and those of the untreated, bromide-, and chloride-treated samples are given in Fig. 42. The thermal analysis curves of the untreated cellulose are described in all these figures, because of the comparison between the untreated and salt-treated samples.

The weight loss was prompted with the salt treatment, in agreement with many TG results. The threshold temperatures for the active weight loss were lowered by about 49° and 147°C with the phosphate and bromide treatments, respectively, while those for the borate- and chloride-treated sample are only about 12° and 25°C, as seen from the data given in Table 7. On the other hand, the amounts of the stable residues increased with the treatments, as shown in the same table.

The bromide-treated cellulose shows complicated TG behaviors, as found in Fig. 40. The

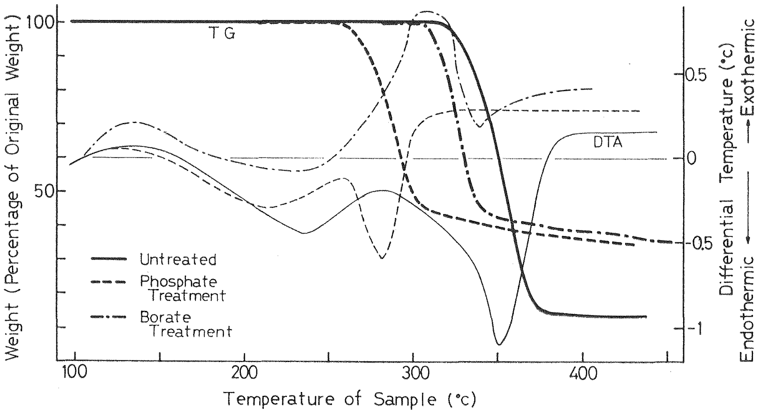

Fig. 39 Thermogravimetric and differential thermal analysis curves of celluloses untreated, treated with ammonium phosphate, and with sodium borate.

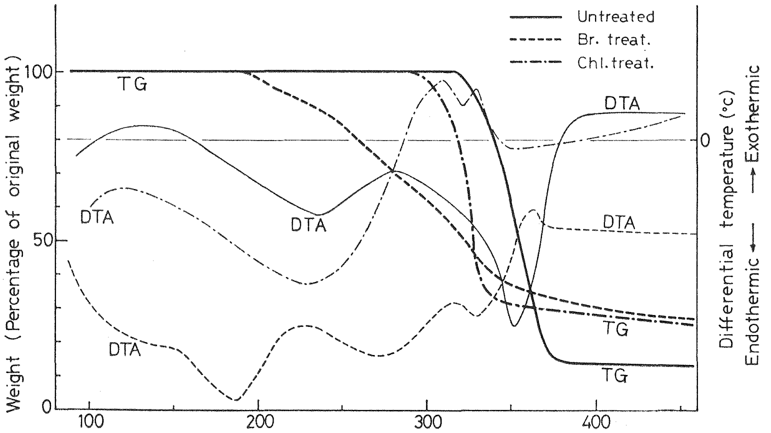

Fig. 40 Thermogravimetric and differential thermal analysis curves of celluloses untreated, treated with ammonium bromide, and with sodium chloride.

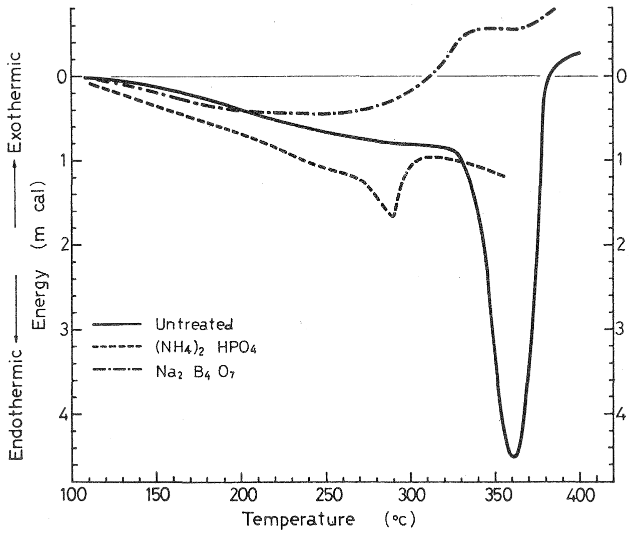

Fig. 41 Differential scanning calorimetric curves of untreated, phosphate-, and borate-treated celluloses.

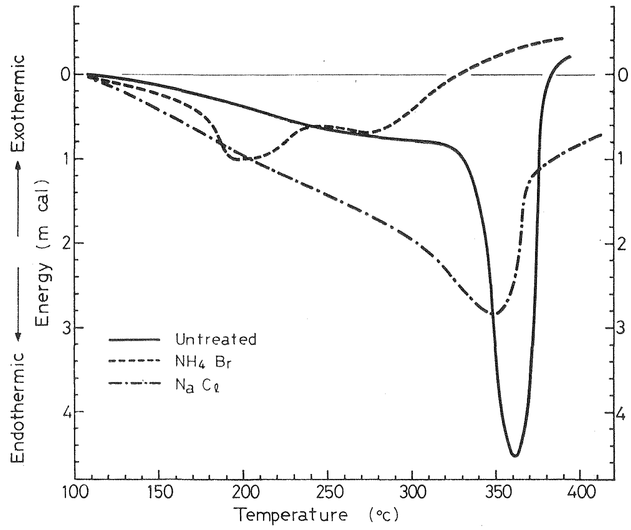

Fig. 42 Differential scanning calorimetric curves of untreated, bromide-, and chloride-treated celluloses.

Table 7. Summary of TG behaviors

Salts for treatment	*Threshold* and *termination* temperatures for active weight loss (°C)		Residue at termination temperature (%)
Untreated	317	380	14
$(NH_4)_2HPO_4$	258	318	45
$Na_2B_4O_7 \cdot 10\,H_2O$	305	350	43
NH_4Br	190	360	35
NaCl	292	350	31

TG and DTA curves in the figure indicate at least three stages of the weight loss, which are represented by the DTA endothermic peaks at about 190°, 270°, and 330°C. Similar complications to these have been reprorted on cellulose powder treated with ammonium bromide35). The reason why the attempts to obtain kinetic data on the weight loss in the former section resulted in failure may partly be given by the above complications.

The DTA curves of the untreated and treated samples are similar to those of the DSC. The observed endothermic and exothermic peaks are summarized in Table 8. Since the heating rate for the DSC (8°C/min) is higher than for the DTA (5°C/min), the peaks on the DSC curves shifted towards the higher temperature side.

The broad endothermic peak at the lower temperature for the untreated sample has not been observed in DTA of cellulose powder by HIRATA and ABE24). The second sharp peak, which has been found for the cellulose powder, may be due to the heat of the volatilization of the pyrolysis products (the tar). The first endothermic peak for the phosphate-treated sample may agree with DTA endothermic range composed of some peaks for ash-free filter paper treated with ammonium phosphate by AKITA and KASE36), and for the cellulose powder treated with ammonium phosphate by HIRATA and ABE35). The second peak may be caused by the volatilization of the pyrolysis products.

Three endothermic peaks of the DTA for the bromide-treated sample observed in the present study have been found in the DTA of the cellulose powder treated with ammonium bromide35). But the last endothermic peak of the present DTA is not found on the present DSC curve. The broad endothermic peaks of the DTA and the DSC at the lower temperatures for the borate- and chloride-treated samples have been observed in the DTA for the chloride-treated cellulose powder, but have not been found for the borate-treated cellulose powder37). The apparent exothermic peaks of the DTA and the DSC for the borate-treated sample have been found also on the DTA curve of the borate-treated cellulose powder37).

Table 8. Summary of DTA and DSC behaviors

Salts for treatment	Temperature of endothermic peaks (°C)	Temperature of exothermic peaks (°C)
Untreated		
DTA	235, 350	
DSC	200—300, 360	
$(NH_4)_2HPO_4$		
DTA	215, 280	
DSC	220—260, 290	
$Na_2B_4O_7 \cdot 10\,H_2O$		
DTA	(230), 340	(305)
DSC	(260), 360	(330)
NH_4Br		
DTA	190, 270, 330	(360)
DSC	200, 280	
NaCl		
DTA	230, 320	(310), (330)
DSC	(180—250), 350	

V. Discussion

This chapter of the discussion is composed of five sections denoted by each treatment, for the evaluations of effects of the salts on the pyrolytic reactions.

V. 1 **Untreated cellulose**

Although the estimated values of the leveling off DP are used to determine the rate constants, the changes in the DP whith the pyrolysis are satisfactorily expressed by eq. (9) derived from the chain mechanism, as shown in Fig. 14. Therefore, the leveling off of the DP observed in the present pyrolysis is reasonably interpreted to show the stationary state between the random-scission initiation and the grafting termination. On the leveling off of DP of heated cellulose, another interpretation has been presented. Namely, the leveling off DP by pyrolysis as well as hydrolysis may correspond to the crystallite length in cellulose11)15). This interpretation based on the physical structure is supported with the reports10)11)15)38) in which cellulose was considered to be pyrolyzed in the amorphous region at first. However, it is difficult to explain the temperature dependence of the leveling off DP not with the chemical reactions but with the physical structure.

The more the heating temperature is elevated, the more the difference between k_i derived from eqs. (8) and (1) increases. In other words, the present chain mechanism makes the temperature effect of the random scission more pronounced than the apparent results by eq. (1), as shown by the somewhat higher activation energy and pre-exponential factor from eq. (8) than from eq. (1). The former activation energy is considerably lower than by Chatterjee and Conrad22), and by Chatterjee39) from the data by Lipska and Parker40), but higher than the value by Millett and co-workers13). It approximates to the values reported by Fung14), Okamoto23), and Hirata and Abe24).

The value of E_p is somewhat higher than the previous values from apparent zeroth-order weight loss of the same material and for the above cellulose powder24), but approximately agrees with those for absorbent cotton and ball-milled cellulose by Chatterjee and Conrad22), for α-cellulose by Chatterjee39), and estimated by Okamoto23). The value of E_t is higher than that estimated by Okamoto23). The obtained activation energy of the first-oder weight loss is placed in the range of 35～50 kcal/mole which has been reported on isothermal heatings of celluloses1)20)22)38)39)40).

The propagation reaction has the value of A_p in agreement with the normal value of about 10^{13} sec^{-1} for unimolecular decomposition. On the other hand, since that for the initiation is considerably lower than the above normal value, the reactant is expected to lose a considerable degreee of freedom in the transition state. The pre-exponential factor for the termination can not be compared with the above normal value, because of the value of A_t' determined as A_t [OH].

An average number of a structural unit produced for each initiation process is called kinetic chain length. The present kinetic chain length ν, which is given by the ratio of the rate of the propagation to that of the initiation, is expressed as

$$\nu = \frac{k_p n_r}{k_i L} = \frac{k_p}{k_t'} = \frac{A_p}{A_t'} \exp\left(-\frac{E_p - E_t}{RT}\right) \tag{20}$$

at the stationary state. The value of ν is readily calculated using the ratio A_p/A_t' and the difference $E_t - E_p$ given in Table 5. The average numbers of levoglucosan produced for each scission of the chain at 250°, 275°, and 300°C are estimated to be about 4 or 5, 6, and 8 with the calculations according to eq. (20). The result is different from a constant ν (about 3) which was calculated on the basis of roughly measured weight[33]. The present values coincide with that at 170°C estimated by OKAMOTO[23] from the data by MAJOR[11], but are lower than those at temperature above 260°C calculated by OKAMOTO[23] from the data by NUNOMURA and coworkers[16].

If the chain fragments produced by the random scission are more unstable than the original polymers and the polymers grafted or cross-linked by the termination are more stable than those given by the random scission, the random scission and the termination are considered to be endothermic and exothermic, respectively. Hence, the broad endothermic peaks on the DTA and DSC curves at the low temperature may be explained to be caused by the endothermic reaction of the random scission. The endothermic effect of the random scission may be reduced by the exothermic termination with the increase of the heating time. The effects of these reactions on the DTA and DSC curves are considered to be overcome by the heat of the volatilization of the levoglucosan and other pyrolysis products at the stage of the active weight loss, as suggested by the sharp peak at the high temperature in Figs. 39～42. The broad peak at the low temperature has not been found in previous DTA of cellulose powder[24]. The reason may be given by the low rate of the random scission, as shown in Fig. 43 in which the changes in the DP of the cellulose powder with the heating are shown.

The amount of the stable residue is determined to be about 14% from the TG, as shown in Table 6. The value approximately agrees with about 13% for the cellulose powder[24]. It, however, is suggested to be about 16% at any temperature by the weight loss rates in Fig. 32. The lower amount from the TG may refer to the determination at the higher temperature (380°C) than for the weight loss rates, as explained in the following section.

Since in cellulose pyrolysis the very slow diffusion of activated centers would make the termination between an adjacent pair of them negligible, it is reasonable to assume the present pseudo-first order termination. Furthermore, the above-mentioned grafting or cross-linking with the termination coincides with the reduction in the solubility in cuoxam[15], the initial losses in the weight and the accessibility[38], and the change in the mechanical properties[41] reported on heated celluloses. The present termination mechanism is supported also with the results of the elementary analyses that the residue charred even at 318°C contained oxygen of about 6% of the original amount. Grafted or cross-linked molecules, however, may

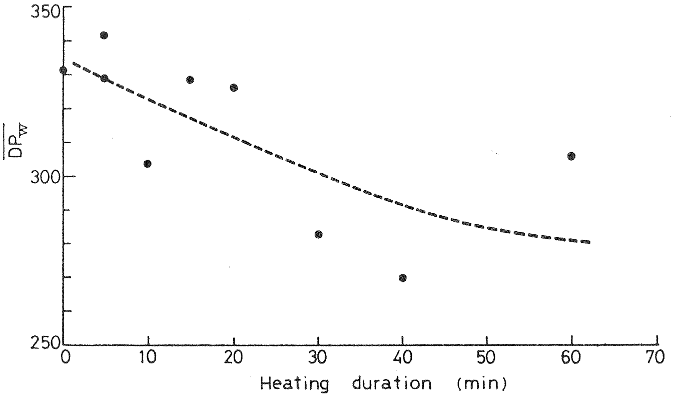

Fig. 43 Decrease in DP of cellulose powder during pyrolysis.

Heating conditions are the same as for the untreated linter cellulose. The temperature is 257.0°C.

affect the relation between the DP and 〔η〕. This possibility has not been taken into the present consideration.

V. 2 **Phosphate-treated cellulose**

The plots of the reciprocals of the DP according to eq. (15) make straight lines for a fair range of the time, as shown in Fig. 9. These plots suggest that the random scission alone occurred and then the termination may substantially be neglected at the early stage. The chain reaction with the random-scission initiation and the grafting termination is considered to be brought about at the late stage, at which the plots of the reciprocals form lines with curvatures. Therefore, it is reasonable to determine the rate constants of the termination from the steep slopes at the late stage in Fig. 15.

The phosphate-treated cellulose which was heated for long durations could not dissolve in the cadoxen. Since cellulose treated with ammonium phosphate has been reported to produce more water than for the cellulose untreated and treated with boric acid at the early stage of the pyrolysis[16)], the low solubility of the here heated sample is thought to be caused not by the grafted or cross-linked molecules but by the dehydrated molecules. Moreover, the modification of the hydroxyl group with the dehydration may be the cause for the result that the termination could not be appreciated at the early stage of the pyrolysis.

The Arrhenius parameters of the random scission, namely, E_i and A_i from the reciprocals of the DP according to eq. (15) approximately agree with previously reported values[42)], but are considerably lower than those determined by using eqs. (8) and (9) according to the chain mechanism. The similar relation to this was discussed on the untreated cellulose in the former section. Since the heating procedure to elevate the temperature up to the constant values with the rate of 5°C/min was used fo the untreated sample, but was not used in the present case, the degradation by the pre-heatings with the different durations before the time 0 did not take place. The difference between two pairs of the Arrhenius parameters are not considered to be explained with the same reason as for the untreated cellulose (in the former section, although the reason was not certainly described, the wrong values of k_i were assumed to be derived from using eq. (15)).

If two pairs of E_i and A_i obtained by using eqs. (15) and (8) are proper to the reactions at the early and late stages, respectively, the transition state may be different between the reactions at two stages. Since the value of E_i at the early stage is considerably lower than that at the late stage, the salt is understood to strongly accelerate the reaction at the former stage but not to retain the effect of the acceleration at the latter. In other words, the effect of the salt at the early stage, which accelerated the dehydration of the hydroxyl groups[16)] and the scission of the glucosidic bonds, is supposed to be lost probably with the thermal modification of the salt. Therefore, there is the possibility that the same group of the salt was involved in both the reactions of the dehydration and the scission. The above-mentioned differences between two pairs of E_i and A_i, however, may refer to experimental errors, such as, the wrong leveling off DP, as suggested by the somewhat scattered plots in Fig. 4.

Since the present E_i at the early stage is about 12 kcal/mole lower than that of the untreated sample, and on the other hand the corresponding A_i is 10^{-3} times as small as that of the untreated one, the temperature dependence decreased and the degsee of the freedom at the transition state seems to be somewhat lost with the treatment. Namely, the scission of the glucosidic bond seems to be accelerated with an activated complex formed with the salt and the glucosidic bond. It is noted that the value of E_i at the late stage approximately agrees with that for the untreated cellulose, though the corresponding value of A_i is somewhat higher than for the untreated sample.

The value of E_t for this sample is about 6.5 kcal/mole lower than for the untreated sample and A_t' for this sample is approximately equal to that for the untreated sample, as shown in Table 2. Then the termination reaction is seen to be furthered with the treatment.

The amounts of the stable residues seem to depend upon the temperature and to range from 49 to 51%, as shown in Fig. 33, while that at the completion of the active weight loss in the TG (at about 318°C) is about 45%, as shown in Fig. 39. These amounts increased over three times those for the untreated sample with the treatment. Similar results have been reported on celluloses treated with ammonium phosphate3)16)35)42)~46). Since the weight in the TG slowly decreased after the active weight loss, as shown in Fig. 39, then the above residues are supposed to contain relatively unstable moieties. The increases in the residues may be given not only by the carbonization with the dehydration but also by the cross-linking with the accelerated termination. The slow weight loss after the active weight loss in the TG is considered to be referred to the pyrolysis of the cross-linked structures. This supposition is supported with the results of the elementary analysis in Table 6, for the stable residues obtained with the isothermal heatings at 235° and 210°C still retained considerable amounts of oxygen and hydrogen. Furthermore, it agrees with the suggestion from Fig. 38 that the more the residue was yielded the more contents of oxygen and hydrogen were high.

Carbon content of cellulose is about 44% in the weight. Therefore, the complete dehydration can theoretically yield the maximum amount of the charred residue of about 44%. Since the carbon would be lost by the volatilization of the levoglucosan produced with the propagation, the yield of the stable residue should be lower than the above value. However, the plots of the weight loss rate in Fig. 33 suggest the higher yields than 44%, as above stated. The question of the present yields may be solved by the relatively stable structures of the molecules cross-linked or grafted with the termination.

The greater part of the weight loss was caused by the volatilization of the produced tar and water. From kinetic analyses, weight of celluloses treated with ammonium phosphate has been found to be lost through two or more different stages of the pyrolyses *in vacuo*3)16)36)43)44)46). The present activation energy of the weight loss is considerably lower than so far reported values on weight loss at the second or final stage except for sulphite pulp treated with ammonium phosphate by INAGAKI and KATSUURA44)46).

Since cellulose untreated10) and treated with ammonium phosphate16) have been reported to produce most water at the early stage of the pyrolysis, the weight loss at the late stage may be assumed to be chiefly caused by the propagation. Therefore, the Arrhenius parameters of the propagation were calculated according to eq. (19). The value of E_p was lowered by about 8 kcal/mole with the treatment. Although the obtained Arrhenius parameters are not fully believed, the values of ν obtained from the calculation by means of eq. (20) and the data in Table 5 lead us to suppose that the average numbers of the levoglucosan produced per one hundred scissions of the chains are about 6 at 250°, about 8 at 275°, and about 10 at 300°C. The kinetic chain length largely decreased with the treatment.

The broad endothermic peak observed at the low temperature in the present DTA and DSC may be referred to the random scission. The same region has been found to contain two or three peaks of the DTA35)36)45). These peaks were interpreted to be caused by other reactions than the random scission. In elevating temperature of thermal analysis, the random scission and the termination which have not been taken into consideration may be interpreted to occur over the wide range at the relatively low temperature, and then to form an inconspicuous broad peak. Other reported peaks which have been found within the region of the present broad peak can not be appreciated in the present DTA and DSC, probably because of the small effects of the heat.

V. 3 **Borate-treated cellulose**

For this sample the plots of the reciprocals of the DP vs. the heating time according to eq. (15) do not show substantially linear parts, as seen in Fig. 10. Therefore, the pyrolysis may be explained to be controlled by the chain mechanism over the range studied by the viscosimetry. This explanation is supported by the linear plots according to eq. (9) in Fig. 16. The values of E_i and A_i derived from the maximum slopes of the curved plots of the reciprocals of the DP vs. the the time in Fig. 10 almost agree with those through the chain mechanism. However, the latter values should be adopted, because of the linear relationship shown by the plots in Fig. 16.

Both the degree of freedom of the activated complex and the temperature dependence of the random scission decreased with the treatment, as seen by the reductions of about 10^3 times in the pre-exponential factor and of about 8 kcal/mole in the activation energy. Therefore, the random scission was accelerated in the studied temperature range.

On the other hand, also the values of E_t and A_t' decreased with the treatment. These decrements are larger than those for the random scission. Hence, it is supposed that at the low temperature the termination was more accelerated than the random scission with the treatment, but that at the high temperature the random scission was more accelerated than the termination.

The obtained leveling off DP is higher than that of the untreated sample at the low temperature due to the more accelerated termination, but is lower than of the untreated one at the high temperature because of the more accelerated random scission. This temperature dependence larger than of the untreated sample is explained also by comparing both the differences between E_i and E_t for two samples according to eq. (8). Similar dependency of leveling off DP on temperature is suggested from changes in DP of borax-treated filter paper, schematically drawn by FUNG, TSUCHIYA, and SUMI[47]. However, the leveling off DP supposed from the DP change at 200°C shown by them[47] is considerably lower than the present value at 209.5°C. This inconsistency may be derived from the different celluloses and salt contents.

The weight loss by the isothermal pyrolysis decreased with the treatment, as seen in Figs. 27 and 29. Furthermore, in the TG the charred residue at the termination of the active weight loss increased from 14 to 43% of the original weight with the treatment, as shown in Fig. 39 and Table 7. The yields of the stable residues in the isothermal heatings are predicted to be in the range of 46～52% and to depend upon the temperature, as seen in Fig. 34. The temperature dependence of the yield of the residue is shown also in the TG curve. Namely, in Fig. 39 the yield is seen to decrease from 43 to 36% with elevating the temperature from 350° to 450°C. From these temperature dependences, the charred residue is suggested to contain decomposable structures. The unstable moiety is considered to be formed by the crosslinking with the termination. This presumption is backed up by the results of the elementary analysis given in Table 6, where the residues are shown to include the considerable quantities of hydrogen and oxygen other than carbon.

The values of E_w and A_w increased by about 5 kcal/mole and 10^3 times with the treatment, as shown in Table 4. Also the values of E_p and A_p somewhat increased, as seen in Table 5. The values of ν are calculated to be about 6 at 250°, 15 at 275°, and 36 at 300°C, respectively. The calculated value at 250°C approximates that of the untreated rample, but the values at 275° and 300°C are over 4 and 5 times as large as those of the untreated sample, respectively. The temperature dependence of the kinetic chain length greatly increased with the treatment, as predicted in Table 5.

Although the activation energies of the weight loss and of the propagation were higher than those of the untreated sample, the active weight loss in the TG began at the somewhat lower temperature than for the untreated one. In addition, it seems that the weight loss rate increased more than for the untreated sample with the elevation of the temperature, as shown in Fig. 39. The lower threshold temperature of the active weight loss may be interpreted to be ascribed to the random scission accelerated with the treatment which initiates the weight loss. If the weight loss rate was exactly determined by eq. (11) derived from the chain mechanism, the effect of the apparent high barrier of the energy on the weight loss decreased with the elevation of the temperature and therefore in the high temperature range the larger pre-exponential factor should make the weight loss rate higher than that of the untreated sample.

The threshold temperature of the weight loss is the highest of the salt-treated samples, as shown in Table 7, probably because of the stable structure cross-linked by the termination most accelerated with the borate. The interpretation is supported with the reported retardation of beginning of weight loss of cellulose powder in TG with the increase of borate content[37)] and the activation energy increased of strength loss of fiber boards with borax treatment[13)].

In the DTA two endothermic and an apparent exothermic peaks were observed, as shown in Fig. 39. Similar peaks seem to be presented on the DSC curves in Fig. 40, as summarized in Table 8. Furthermore, similar exothermic peak was previously reported on cellulose powder treated with sodium borate[37)]. It may be explained for these peaks that the first broad endothermic peak formed by the random scission was lowered by the termination accelerated with the borate, and then the exothermic one was formed, but the exothermic effect was overcome by the evaporation heat of the levoglucosan shown as the third peak.

V. 4 **Bromide-treated cellulose**

The linkages in the amorphous regions have been assumed so far to have the same bond strength as in the crystallites. For the present sample, however, the scission of the linkages with the heating seems to be affected by the fine structures. The changes in the DP are suggested to be distinguished into three stages from the plots of the reciprocals of the DP vs. the time in Fig. 11. The reciprocals slowly increased at first and then rapidly increased, but levelled off at last, as shown in the figure. If the chain scissions preferentially occurred in the amorphous regions and then occurred in the crystallites, as formerly presented[10)11)15)38)], the average DP should slowly decrease at first and subsequently rapidly decrease, because, in addition to the chain scissions in the amorphous regions, those in the crystallite generated at the late stage. Therefore, the present initial slow reductions in the DP may be interpreted to reflect the preceding scission of the chains in the amorphous region. The second stage of the rapid reductions in the DP may be caused by the chain scission later generated in the crystalline and amorphous regions. The third stage of the leveling off in the DP may correspond to the stationary state between the initiation and the termination.

If the glucosidic bonds in the amorphous region were more weakened than those in the crystallite by effects of the salt, their breakdowns in the former should be appreciably preceded at the low temperature used in this study. The observed reduction in the DP with the bromide treatment at room temperature (2,971 to 2,200) is thought to be favorable evidence for the interpretation of effects of the salt. The intense actions of the bromide will be later discussed to support the interpretation.

The values of E_i and A_i derived from the straight parts of the reciprocals of the DP in Fig. 11 are somewhat higher than those from the average slopes between the reciprocals at the time 0 and at the end of the straight part. The latter values are almost identical with those of the initiation derived from the chain mechanism, as shown in Tables 1 and 3. The higher values obtained from the straight parts may refer to the later occurred scission of the chains in the crystallites, as above-mentioned. Hence, the higher values should not be regarded as the correct parameters.

The values of E_i and E_t decreased with the treatment, as compared with those for the untreated sample in Tables 2 and 3. The reductions in E_i and E_t amounts to about 11 and 8.5 kcal/mole, respectively. On the other hand, the value of A_i decreased with the treatment, but A_t' is close to the value for the untreated sample. The acceleration of the random scission by the bromide is seen to be greater than that of the termination. Therefore, the DP rapidly decreased even at the low temperature and the leveling off DP is relatively low, as shown in Fig. 6 and Table 1.

Since ammonium bromide has been reported to strongly promote carbonization of wood at the early stage of the heating$^{48)}$, the observed insolubility of the present samples which were heated for long durations may be attributed to dehydrated molecules, as conjectured for the phosphate-treated cellulose. Moreover, the effect of the present termination on the DP was not found at the early stage, as proven by the linear increases in the reciprocals of the DP in Fig. 11. Linear increases in these reciprocals are observed also on the phosphate-treated cellulose in Fig. 9. Since the hydroxyl groups are assumed to be largely modified by the dehydration accelerated by the bromide at the early stage of the pyrolysis, the termination reaction between the hydroxyl group and the chain fragment is interpreted not to generate at the stage.

The rate constants of the first-order weight loss could not be obtained, because of its complicated changes, as suggested in Fig. 30. It is supposed in the figure that the amounts of the solid residue yielded with the isothermal heating largely varied with the temperature. Furthermore, in the same figure this sample is seen to contained a considerable quantily of unstable structure which were decomposed at the temperature below 200°C.

The proceeding of the pyrolysis complicated by the action of the bromide are again shown with the thermal analyses of the TG, the DTA, and the DSC. The TG and DTA curves in Fig. 40 indicate at least three stages of the weight loss, which are represented by DTA endothermic peaks at about 190°, 270°, and 330°C, as summarized in Table 8. The first and second stages are confirmed also by endothermic peaks at 200° and 280°C in the DSC curve, as shown in Fig. 41. It is difficult to give an exact explanation of the complicated TG and DTA behaviors. In the present case, however, a simplified explanation may be of significance, that the first stage of the weight loss is mostly caused by the sublimation or the decomposition of the salt, and the second and third stages correspond to pyrolytic reactions in the amorphous and crystalline regions, respectively. This interpretation agrees with the above presumption from the DP changes that the pyrolysis of the amorphous region is more strongly promoted than of the crystallites by the salt. Furthermore, this is supported by similar behaviors and interpretations of TG and DTA reported on cellulose powder treated with ammonium bromide[35]. By the way, the apparent exothermic peak at 360°C may be given by the termination to decrease the evaporation heat of the pyrolysis products.

The yield of the residue at the termination temperature of the active weight loss is about 35% and increased by the treatment, as shown in Table 7. The yield, however, decreased with the increase of the temperature, as shown in Fig. 40. Since the residue still contained an unstable part at the termination temperature of the active weight loss, it may be composed of not only dehydrated structures but also cross-linked ones by the termination reaction.

V. 5 **Chloride-treated cellulose**

The reciprocals of the DP linearly increased at first with the time for a considerably wide range, as shown in Fig. 12. Hence, the termination mechanism is little considered to be brought about for those durations. The Arrhenius parameters of the random scission obtained from the above linear plots of the reciprocals vs. the time satisfactorily agree with those of the initiation from the plots according to the chain mechanism in Fig. 18. Therefore, although the task of an explanation of the reason why the termination did not generate at the early stage is left, the model of the pyrolysis with the chain mechanism is supported also by these results.

The obtained activation energies and pre-exponential factors of the random scission and of the termination are lower than those of the corresponding reactions for the untreated sample, as shown in Tables 2 and 3. Since the value of E_i decreased by about 5 kcal/mole with the treatment, while the corresponding reduction in E_t is about 12 kcal/mole, the temperature dependence of the leveling off DP is shown to decrease with the treatment by means of eq. (3). However, the ratio of A_i to A_t' increased by about 500 times with the treatment. Therefore, the leveling off DP at low temperature should be higher than that for the untreated sample, but at high temperature should be lower than for the untreated one. This expectation agrees with the comparison of the leveling off DP between these samples.

The value of E_w agrees with the value for the untreated sample, but is about 9 kcal/mole higher than for cotton impregnated with sodium chloride by MADORSKY and co-workers[20]. The value of A_w is somewhat greater than that for the untreated sample, as shown in Table 4. As shown in Fig. 40, the active weight loss of this sample in the TG began at the somewhat lower temperature than for the untreated one, in spite of the about equal activation energies here obtained for both the samples. Since the active weight loss is assumed to be caused by the chain mechanism which begins with the random-scission initiation, the present TG behavior may be reasonably explained with the reduction in E_i by the treatment.

The DP changes at the early stage show no indication of the present termination reaction. Since the threshold temperature of the active weight loss of this sample in the TG is far higher than of the bromide- and phosphate-treated ones, as shown in Table 7, and the good solubility was observed even after the prolonged heatings, probably the cause is different from that for both the latter ones. The reason why the termination did not occur is supposed that the salt either stablized the activated centers of the chain fragments or made the hydroxyl groups inert at the early stage.

The plots of the weight loss rate vs. the residual weight in Fig. 35 suggest the approximately constant amount of the stable residue, namely, about 40% to be yielded at any temperature in the studied range. This temperature dependence is similar to that for untreated cotton but different from that for the cotton impregnated with sodium chloride by MADORSKY and co-workers[20].

Although the constant amount of the residues were suggested in the isothermal heatings, the corrseponding amount after the active weight loss in the TG is seen to slowly decrease in Fig. 40. Therefore, the residue is considered to contain moiety of unstable structure which was probably formed with the termination, as also suggested from the results of the elementary analysis in Table 6. These amounts are larger than those from the untreated sample, agreeing with many reported results. These amounts seem to increase not only by the dehydration but also by the cross-linking with the termination accelerated by the salt, as indicated by the decrease in E_t in Table 2.

The kinetic chain length calculated according to eq. (20) and by using the data in Table 5 is about 5 at 250°, 8 at 275°, and 13 at 300°C. The values for this sample of the treated ones most approximate to the values for the untreated sample in the calculated range of the temperature. However, the temperature dependence of the kinetic chain length increased with the treatment.

A broad and deep endothermic peak before the active weight loss is formed on the DTA curve, as shown in Fig. 40. On the other hand, the corresponding thermal change is found as a shallow dent on the DSC curve in Fig. 41. These endothermic changes are supposed to be given with the random scission reaction. An endothermic change with the weight loss is certainly found on the DSC curve. Furthermore, an endothermic peak caused by the active weight loss on the DTA curve is recognized as a col between two apparent exothermic peaks. It may be interpreted that these two exothermic peaks were formed by an endothermic effect of the weight loss which occurred within the exothermic region given by the termination. It is noted that the exothermic peaks are observed for the borate- and chloride-treated samples with the low activation energies of the termination. In spite of the above effects, however, sodium chloride is an ineffective salt as a fire retardant, probably because the salt restrains the termination at the early stage of the pyrolysis and has the less effect of the dehydration than effective salts.

VI. Conclusions

1) The changes in the DP and the weight of untreated and salt-treated celluloses with the heatings *in vacuo* are generally explained by a persented model of a chain mechanism with random-scission initiation, with propagation in which levoglucosan is produced, and with grafting termination. According to the model, the leveling off of the DP is given by the stationary state between the initiation and the termination, and the weight loss at the late stage of the pyrolysis is regarded as an apparent first-order reaction.

The behaviors shown in the thermal analyses of the TG, the DTA, and the DSC of the untreated and treated celluloses can be interpreted by means of the chain mechanism. The results of the elementary analysis for the residues support the present model.

2) Since inorganic salts added to the cellulose accelerated both the reactions of the random scission and the termination, then the cross-linking as the result of the termination was promoted and thermally stable structures are considered to increase. The charred residues from the treated celluloses are supposed to increase not only with the accelerated dehydration

but also with the increased effect of the termination.

The threshold temperatures of the weight loss of the treated celluloses in the TG are interpreted to be lowered with the random scission accelerated by the salts which initiates the propagation. These temperatures, however, may be lowered with the effects of the dehydration of the salts.

3) The pyrolyses of the untreated and treated celluloses are characterized as follows: The pyrolyses of the untreated cellulose and the cellulose treated with sodium borate were shown to be controlled by the chain reaction with the random scission and the termination from the viscosimetries. On the other hand, the pyrolyses of the celluloses treated with ammonium phosphate, ammonium bromide, and sodium chloride proceeded with the random scission at the early stage and with the above chain mechanism at the late stage. The reaction mechanism of the random scission of the phosphate-treated cellulose at the early stage may be different from that at the late stage. It is considered that the random scission of the bromide-treated cellulose occurred at first in the amorphous region and then in the crystallite. The rate of the random scission of the chloride-treated cellulose at the early stage is equal to that derived from the chain mechanism.

The weight loss of the untreated and treated celluloses by the pyrolysis can be expressed to obey an apparent first-order reaction except for the bromide-treated cellulose. For the bromide-treated cellulose is supposed from the TG that the weight loss was brought about preferentially in the amorphous region and subsequently in the crystallite. Therefore, the kinetic parameters for the weight loss could not be determined.

4) The obtained activation energies of the initiation of the untreated, phosphate-treated, borate-treated, bromide-treated, and chloride-treated celluloses are 38.0, 35.4, 29.6, 28.6, and 32.6 kcal/mole, respectively. The corresponding pre-exponential factors are 1.4×10^{10}, 6.9×10^{12}, 1.6×10^{7}, 7.4×10^{8}, and 9.3×10^{7} sec^{-1}, respectively. For the phosphate-treated cellulose, however, different values of 25.8 kcal/mole and 1.2×10^{12} sec^{-1} are given to the Arrhenius parameters of the random scission from the DP at the early stage. The corresponding Arrhenius parameters of the termination for the above samples are 31.4, 25.0, 20.5, 23.0, and 19.3 kcal/mole, and 2.9×10^{9}, 1.5×10^{10}, 2.5×10^{5}, 1.7×10^{9}, and 9.9×10^{4} sec^{-1}, respectively.

On the other hand, the determined activation energies of the first-order weight losses of the untreated, phosphate-treated, borate-treated, and chloride-treated celluloses are 44.7, 40.7, 49.9, and 44.3 kcal/mole, respectively. And the corresponding pre-exponential factors are 3.9×10^{13}, 6.9×10^{13}, 2.0×10^{16}, and 3.5×10^{14} sec^{-1}, respectively.

5) Suppresion of flame by halogenous which are released from wood into gas phase with the heating, and decrease in inflammable products from wood by changing the course of the pyrolysis have generally been accepted as two sorts of important effects of flame-retardants of wood[49]. The latter effects have been considered to be given by the carbonization with the dehydration promoted by the retardants. In the present study on the pyrolysis of the cellulose, however, the weight loss with the heating which means the generation of inflammable products is suggested to be accompanied by changes of the polymer chains. It is particularly noted that the grafting-termination reaction not only terminates the depolymerization of the cellulose but also forms thermally stable structures. For the future, flame-retardants of wood must be re-examined from the viewpoint of effects on the changes of the polymer chains, which is believed to be useful for the development of flame-retardant wood and wood-based materials.

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無処理および無機塩で処理されたセルロースの熱分解による重合度および重量の変化

平田利美(1)

（概要）

1. 緒言

木材は加熱されると気体，タール，炭に分解される。タールはさらに分解されて，可燃性気体を生成する。この可燃性気体と空気が混合した雰囲気は，口火や火花等で発火する。この発炎によって木材はさらに強く加熱され，燃え広がって行く。このような現象を木材成分の熱重量測定(TG)による熱分解挙動2)~9)および含有量等からみると，セルロースが木材の燃焼をになう主要な成分であることが分る。防火木質材料を開発するためには，木材の燃焼に先行する熱分解およびこれにおよぼす防火薬剤の作用を明らかにすることが重要である。しかし，木材は複雑な多成分系の物質であるため，この研究では単純な構造のセルロースを対象に，各種の薬剤で処理し，それらの熱分解挙動を求めることにした。

セルロースの熱分解に関する今までの研究は重量減少の測定にもとづいたものが主である。その他，示差熱分析（DTA）や示差走査熱量測定（DSC）等の熱分析法による結果が報告されている。しかし，これらの方法ではセルロースの物理的性質の変化を知り得ても，これらの変化をもたらした内部構造の変化，たとえば化学構造の変性，高分子鎖構造の変化，結晶構造や配列の変化等々を知ることはむづかしい。ここでは，粘度法によって重合度を求め，高分子鎖としてのセルロースの熱分解挙動を分析すると共に，重量減少測定，および TG, DTA, DSC 等の熱分析を補足的に行うこととした。

一方，処理薬剤としては，防火薬剤としてよく使われているリン酸アンモニウム，臭化アンモニウム，およびホウ酸ナトリウムをとりあげた。さらに，熱分解に及ぼす効果を比較するため，防火効果のない塩化ナトリウムも選んだ。

2. 理論

加熱によるセルロースの重合度の減少は大部分，粘度法によって求められてきた10)~16)。それらの速度論はよく知られている次式に基づいて展開されてきた。

$$\frac{1}{p}-\frac{1}{p_0}=k_it \qquad (1)$$

ここで p および p_0 は加熱時間 t および 0 の時の数平均重合度，k_i はセルロース鎖のランダム切断反応の速度定数である。この式は直鎖高分子のランダム切断による結合の減少に対する速度式

$$L=L_0\exp(-k_it) \qquad (2)$$

から誘導される19)。上式において，L および L_0 は時間 t および 0 の時の結合数である。しかしなが

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ら，熱分解中のセルロースの重合度は，その平衡化現象[10][11][15]からも分るように，(1) 式では十分に表現され得ない。

そこで，Fig. 1 に示されている熱分解機構を提案した[33]。すなわち，ランダム切断を開始反応とし，開始反応で生成された2分子の一方がレボグルコサンを生成する生長反応あるいはセルロース水酸基と結合するグラフト化停止反応を経るという連鎖反応機構が仮定された。このモデルによる速度式は次のように示される。

$$\frac{dn_r}{dt}=k_iL-k_t[\mathrm{OH}]n_r \tag{3}$$

ここに n_r は増加分子数，k_t は停止反応の速度定数，〔OH〕は水酸基の数である。

加熱されたセルロースの重合度が低くない値でもって平衡化する時，結合数を

$$L\fallingdotseq np \tag{4}$$

と表わすことができる。ここに n は鎖分子の数である。加熱による重量減少が小さい時，np および停止反応を経る鎖の活性点周囲の〔OH〕がほぼ一定とみなされる得る。そこで，$t=0$ の時 $n_r=n_{r0}$ とし，$k_t'\equiv k_t[\mathrm{OH}]$ として，(3) 式を積分すれば

$$n_r-n_{r0}=\left(\frac{k_iL}{k_t'}-n_{r0}\right)[1-\exp(-k_t't)] \tag{5}$$

が得られる。一方，(4) 式から n_r と n_{r0} の別な表現式

$$n_r=L\left(\frac{1}{p}-\frac{1}{p_u}\right)\quad\text{および}\quad n_{r0}=L\left(\frac{1}{p_0}-\frac{1}{p_u}\right) \tag{6}$$

が得られる。ここに p_u は加熱前の重合度である。(5) および (6)式から

$$\frac{1}{p}-\frac{1}{p_0}=\left[\frac{k_i}{k_t'}-\left(\frac{1}{p_0}-\frac{1}{p_u}\right)\right][1-\exp(-k_t't)] \tag{7}$$

が導かれる。(7) 式は $t=\infty$ で次のように変形される。

$$\frac{1}{p_\infty}=\frac{k_i}{k_t'}+\frac{1}{p_u} \tag{8}$$

ここに p_∞ は平衡重合度である。(8) 式を (7) 式に代入して $1/p_u$ を消去すれば

$$\frac{1}{p_\infty}-\frac{1}{p}=\left(\frac{1}{p_\infty}-\frac{1}{p_0}\right)\exp(-k_t't) \tag{9}$$

が得られ，これを t について微分すれば

$$\frac{d}{dt}\left(\frac{1}{p}\right)=k_t'\left(\frac{1}{p_\infty}-\frac{1}{p}\right) \tag{10}$$

が得られる。

実験的に平衡重合度が求められない時，(10) 式にしたがって得られる $d(1/p)/dt$ 対 $1/p$ の直線プロットを $d(1/p)/dt=0$ に外挿すれば $1/p_\infty$ の値が求められ，平衡重合度の推定ができる。このプロットの勾配は k_t' に相当するが，精度が良くないので，この研究では (9) 式にしたがった $\ln(1/p_\infty-1/p)$ 対 t の半対数プロットの勾配から k_t' を求めた。得られた k_t' を (8) 式に代入すれば k_i が算出される。

加熱による重量減少には脱水等の寄与もあるが，生長反応によって生成されるレボグルコサンの揮化によって重量減少が起ると仮定すれば，その速度式は

$$-\frac{dw}{dt}=k_pn_r \tag{11}$$

の形をとる。ここに w は構造単位数，k_p は生長反応の速度定数である。重合度が平衡化すると分子数が一定になることが (6) 式で示される。そこで増加分子数の定常値 n_{rs} は (3) 式から

$$n_{rs}=\frac{k_iL}{k_t'} \tag{12}$$

として得られ，これを (11) 式に代入すれば，加熱の後期における重量減少速度式

$$-\frac{dw}{dt}=\frac{k_ik_p}{k_t'}L \tag{13}$$

が得られる。同じ形の式は Boyd[27] および 岡本[23]によって得られている。

3. 実験方法

使用されたセルーロス試料は精製されたリンター繊維で，その重量平均重合度は2971である。処理に用いられた塩はリン酸二アンモニウム $(NH_4)_2HPO_4$，四ホウ酸ナトリウム10水塩 $Na_2B_4O_7\cdot10H_2O$，臭化アンモニウム NH_4Br，および塩化ナトリウム NaCl で，すべて1級の純度を有している。

セルロース試料は各塩の水溶液に約90分間浸漬された後，凍結乾燥され，加熱前まで真空デシケーターに保存された。リン酸アンモニウム，ホウ酸ナトリウム，臭化アンモニウム，塩化ナトリウムの添加量は，それぞれ，4.4，7.5，4.5，5.5%である。

粘度測定用試料の加熱は，真空度 10^{-2}～10^{-3} mm Hg の雰囲気中で，Fig. 2 に示されている装置により行われた。無処理試料は室温から予定温度へ 5°C/min の速度で昇温させてから，一定温度を保って加熱された。処理試料は初めから一定温度で加熱された。温度が高すぎると加熱された試料が溶解しないので，加熱温度は各試料の溶解性に合せて選ばれた。粘度はカドキセン溶液として測定された。重合度は次式[31]によって算出された。

$$[\eta]=1.84\times10^{-2}\times p_W{}^{0.76} \tag{14}$$

ここに $[\eta]$ は極限粘度，p_W は重量平均重合度である。

等温加熱による重量減少は真空理工社の示差熱天秤 TGD-1500 M で測定された。試料は先ず室温から予定温度へ 5°C/min で昇温され，以後一定温度で加熱された。加熱温度は昇温段階での重量減少が大きくならないよう，各試料毎に4点選ばれた。雰囲気は $2\sim3\times10^{-1}$ mm Hg であった。

重量減少の測定で生じた各試料の炭化残渣から，それぞれ2個ずつ，合計10個選ばれ，和光純薬工業社（大阪）で元素分析された。この元素分析では，炭素，水素，窒素，および灰分の含有量が各炭化残渣について3回測定された。灰分の含有量は800°C で5分間加熱されて求められた。

TG および DTA は，同じ示差熱天秤 TGD-1500 M を用い，昇温速度 5°C/min，真空度 $2\sim3\times10^{-1}$ mm Hg の条件で同時測定された。DSC は Perkin-Elmer 社の DSC-1B により，8°C/min，窒素ガス流量15～30 cc/min の条件で行われた。

4. 結果

4.1 粘度測定

処理および無処理試料共に，初め鎖の長さが急激に短くなったが，やがて平衡化したことが Fig. 3～7 によって分る。鎖の長さが一定になった時の重合度，すなわち平衡重合度は Table 1 に示されている。

先ず，従来の方法でランダム切断の速度定数を求めるため，(1) 式をセルロース分子が最も確からしい

分子量分布[32]を持つと仮定して，次のように変形した。

$$\frac{1}{p_W}-\frac{1}{p_{W0}}=\frac{k_i}{2}t \qquad (15)$$

ここに p_{W0} は $t=0$ の時の p_W である。この式にしたがった $1/p_W-1/p_{W0}$ 対 t または $1/p_W$ 対 t のプロットは Fig. 8〜12 に示されている。これらの図では満足な直線性が示されていない。これらのプロットの初期の直線部分の勾配から，ランダム切断の速度定数を算出して，Table 1 にのせた。なお，臭化アンモニウム処理試料について，$1/p_W$ が初め緩やかに，次いで急にしかも直線的に増加し，最後に平衡化したことが Fig. 11 から分る。そこで，直線部分からの速度定数以外に，$1/p_{W0}$ と直線部分の終りの $1/p_W$ との間の平均勾配からも速度定数を求め，Table 1 にのせた。

Fig. 8〜12 で示されるように，(1) 式に適合する重合度の範囲が初期に限定されている。そこで，提案した熱分解モデル[33]から得られた (9) 式にしたがってプロットが作られた。これらのプロットは Fig. 14〜18 に示されている。なお，これに先立ち，無処理試料の平衡重合度を，(10) 式にしたがって Fig. 13 に示されるプロットを作って推定した。これらのプロットは，無処理およびホウ酸ナトリウム処理試料については，実験の全範囲にわたって直線を形成しているが (Fig. 14 および 16)，リン酸アンモニウム (Fig. 15)，臭化アンモニウム (Fig. 17)，および塩化ナトリウム処理試料 (Fig. 18) では折れ曲った線になっている。後の3試料については，Fig. 9, 11, および 12 に示されているように，(15) 式にしたがった $1/p_W$ 対 t のプロットが前半で比較的長い直線部分を形成している。すなわち，その期間ではランダム切断反応しか起らなかったと思われる。したがって，その期間を過ぎた後半でランダム切断とグラフト化の連鎖反応が起ると仮定し，Fig. 15, 17, および 18 では後期における急な勾配の直線部分から k_t' を求めた。これらの値は Table 2 にのせられている。さらに，得られた k_t' を (8) 式に代入して k_i を求め，Table 3 にのせた。速度定数はアレニウスの式によって

$$k=A\exp\left(-\frac{E}{RT}\right) \qquad (16)$$

と表わされる。ここに k は速度定数，A は前置係数，R は気体定数，E は活性化エネルギー，T は絶対温度である。各試料のランダム切断および停止（グラフト化）反応の A と E を求めるため，今まで得られた速度定数の値を用い，(16) 式にしたがって $\ln k$ 対 $1/T$ のアレニウスプロットを行った。これらは Fig. 19〜26 に示されている。これらのプロットから得られたアレニウスパラメーターは，それぞれ，Table 2, 3 に示されている。

4. 2 重量減少

等温加熱による各セルロース試料の重量減少の進行情況が Fig. 27〜31 に示されている。塩処理によって生成された炭の量は，これらの図から推測されるように，大幅に増加した。

(13) 式で表わされた1次反応の重量減少の速度定数を求めるため，次式にしたがって，dw/dt 対 w のプロットを作った。

$$\left(\frac{dw}{dt}\right)_1-\left(\frac{dw}{dt}\right)_2=k_w(w_2-w_1) \qquad (17)$$

ここに $(dw/dt)_1$ および $(dw/dt)_2$ は残存重量あるいは残存構造単位数が w_1 および w_2 の時の重量減少速度で，k_w はみかけの1次反応速度定数である。これらのプロットは Fig. 32〜35 に示されている。臭化アンモニウム処理試料については，1次反応の速度定数を得ようとして行った幾つかの試みがすべて成

功しなかった。臭化アンモニウム処理試料を除いた他の試料に関するこれらのプロットは，加熱の後期で直線を形成しており，その勾配から k_w を求め，Table 4 にのせた。これらの速度定数のアレニウスプロットは Fig. 36 と 37 で作られ，得られたアレニウスパラメーターも同じ表に示している。

後期における重量減少がレボグルコサンの揮化によってひき起されるとすれば，(13) および (17) 式から

$$k_w = \frac{k_i k_p}{k_t'} \qquad (18)$$

が得られる。これをアレニウスの式にあてはめると次のような式が導かれる。

$$\ln k_w = \ln\frac{A_i A_p}{A_t'} - \frac{E_i+E_p-E_t}{RT} \qquad (19)$$

ここに脚符の i, p, t は開始，生長，停止の各反応を意味する。また，A_t' は At〔OH〕を表わす。(19) 式によって生長反応のアレニウスパラメーターが算出され，Table 5 にのせられた。

4. 3　元素分析

元素分析によって得られた炭化残渣の炭素，水素，酸素，および灰分の含有量は Table 6 に示されている。この表から，当然ながら，炭素の含有量が熱分解の進行と共に増加した一方，水素と酸素の含有量が減少したことが分る。他方，熱分解によるこれら元素の減少は Fig. 38 に示されている。炭素は残渣の多い段階ではゆっくりと減少したが，熱分解が進むと急に減少した。水素と酸素は熱分解の進行の程度が小さい段階でかなり急に減少し，進行度が大きくなると緩やかに減少したことが分る。なお，318°C で加熱された無処理試料から収量された炭化残渣でさえ，酸素および水素が初めの量の 6.0 および 11.6% も残っているのは注目に値する。

4. 4　熱分析

全試料について TG, DTA, および DSC が行われた。無処理，リン酸アンモニウム処理，およびホウ酸ナトリウム処理の各試料の TG および DTA 曲線は Fig. 39 に，無処理，臭化アンモニウム処理，および塩化ナトリウム処理の各試料の TG および DTA 曲線は Fig. 40 に示されている。無処理，リン酸アンモニウム処理，およびホウ酸ナトリウム処理の各試料の DSC 曲線は Fig. 41 に，無処理，臭化アンモニウム処理，および塩化ナトリウム処理の各試料の DSC 曲線は Fig. 42 にのせられている。

塩処理によって重量減少の開始が早められたが，炭の収量は増加したことが，TG 曲線から分る。これらの結果は Table 7 にまとめられている。

各試料の DTA 曲線は対応する DSC 曲線に似た特徴を示している。これらの曲線に見出されたピークは Table 8 に要約されている。DSC の昇温速度が DTA の場合より大きいのでピークが高温側に転移した。

5. 考察

5. 1　無処理セルロース

平衡重合度に推定値が用いられているとはいえ，Fig. 14 におけるプロットから，熱分解による重合度変化が (9) 式によってうまく表わされることが分る。したがって，平衡重合度はランダム切断の開始反応とグラフト化の停止反応との定常状態と示すと解釈されてよいと思われる。平衡重合度が物理的構造に基因するという解釈11)15)では，ここで見出された平衡重合度の温度依存性を説明することが困難である。

加熱温度が高ければ高い程，(8) 式と (1) 式から算出された k_i の差が大きくなっている。すなわち，連鎖機構におけるランダム切断の温度効果がより顕著になっている。

各開始反応過程ごとに生成される構造単位の平均数を意味する動力学鎖長 ν は，定常状態において次式によって与えられる。

$$\nu = \frac{k_p n_r}{k_i L} \fallingdotseq \frac{k_p}{k_t'} = \frac{A_p}{A_t'} \exp\left(-\frac{E_p - E_t}{RT}\right) \tag{20}$$

(20) 式に Table 5 のデータを応用することにより，鎖の切断ごとに生成されたレボグルコサンの平均数は，250° で 4 ないし 5，275° で約 6，300°C で約 8 であると推定される。

DTA および DSC 曲線の初期の幅広い吸熱領域はランダム切断によって生じたと考えられる。この吸熱領域は停止反応の発熱効果によってうち消され，300°C を越えると熱分解生成物の揮化による鋭い吸熱ピークが生じてくると考えられる。以前に報告されたセルロース粉の DTA 曲線[24]には，今回見出されたような低温側の幅広い吸熱領域が観測されなかったのは，Fig. 43 から示唆されるように，ランダム切断速度が小さかったためと考えられる。

TG において，急激な重量減少後も緩やかに重量が減少したが，これは炭化残渣に多少不安定な構造が含まれているためと考えられる。この構造は多分停止反応によって形成された架橋から成っている可能性がある。元素分析の結果はこの推定をうらづけている。

5. 2　リン酸アンモニウム処理セルロース

Fig. 9 に示されているように，重合度の逆数対加熱時間のプロットが，はじめかなりの間直線を形成するから，この間はランダム切断だけ起り，後半になって停止とランダム切断との連鎖反応が起ったと考えられる。

アレニウスの活性化エネルギーと前置係数を無処理試料のものと比較すると，処理によってランダム切断および停止反応が大幅に促進されたことが分る。停止反応による架橋の形成により，構造の安定化が起ると考えられる。したがって，この試料の炭化残渣が多いのは塩の脱水炭化作用によるだけでなく，停止反応の促進にもよると考えられる。この推定は元素分析の結果にも適合する。

(20) 式によって求められた動力学鎖長は，250° で約 6/100，275° で約 8/100，300°C で約 1 である。これらの値は計算に用いられたアレニウスのパラメーターが十分に信用できない点を考慮に入れても，無処理試料の場合に比べ非常に小さいといい得る。

5. 3　ホウ酸ナトリウム処理セルロース

この試料の重合度の逆数対加熱時間のプロットは，Fig. 10 に示されるように，実質的に直線部分がない。さらに，連鎖機構にもとづいて導かれた (9) 式にしたがったプロットは Fig. 16 に示されるように，加熱期間の全体にわたって直線を形成している。したがって，この試料の熱分解は初めから連鎖機構によってコントロールされたと考えられる。

アレニウスのパラメーターの比較により，処理によってランダム切断および停止の両反応が促進されたことが分る。この促進の程度は，低温ではランダム切断より停止の方が大きく，高温ではその逆である。したがって，平衡重合度は低温側では無処理試料のものより大きいが，高温になると無処理試料のものより小さい。炭化残渣は無処理試料の場合より大幅に増大している。これは塩による停止反応の促進に負うところが大きいと考えられる。停止反応による架橋構造の形成は，元素分析の結果からも推定される。

5. 4　臭化アンモニウム処理セルロース

この試料の加熱による重合度の変化には微細構造の影響があらわれているように思われる。すなわち，Fig. 11 における重合度の逆数の加熱時間による最初の緩やかな増加は非晶領域のセルロース鎖の切断を示し，続く急激な増加は非晶領域に加え結晶領域での鎖の切断が起ったことを示し，最後の重合度の平衡化はランダム切断と停止との間の定常状態を意味すると考えられる。この試料についてだけ微細構造の影響がみられたのは，臭化アンモニウムが非晶領域のグルコシド結合の切断をより強く促進し，しかも加熱温度が低かったため，非晶領域と結晶領域での鎖の切断速度の差がより大きくなったためであろう。

処理によってランダム切断と停止が共に促進されたことがアレニウスのパラメーターで示されるが，特に前者の反応の促進が大きかったので，重合度の低下が急激で，しかも平衡重合度が比較的低いという結果になった。

等温加熱による重量減少は1次反応として解析できなかった。これは多分反応が複雑なためであろう。TG および DTA の熱分析から，重量減少が3段階に分れたことが示唆される。すなわち，DTA の 190°, 270°, 300°C における吸熱ピークがこれらの段階を代表している。初めの重量減少は主に塩の分解または昇華，2番目の段階はセルロース非晶領域の分解，3番目の段階は主としてセルロースの微結晶の分解によってそれぞれ起されたと推定される。この推定は重合度の変化に関する前述の解釈とも一致する。

急激な重量減少の終了時点における炭化残渣は約35%であるが，これがさらに温度の上昇につれて緩やかに減少することが，Fig. 40 に示されている。炭化残渣に含まれるこの不安定部分は，多分，停止反応によって形成された架橋を含んでいると考えられる。

5. 5　塩化ナトリウム処理セルロース

重合度の測定から，この試料の熱分解は初めかなり長い期間，ランダム切断だけで進行したと考えられる。しかし，最終的には重合度が平衡化したので，停止とランダム切断の反応による連鎖機構が熱分解をコントロールしたと解釈される。活性化エネルギーおよび前置係数を無処理試料のものと比べることにより，平衡重合度が低温側では無処理試料のそれより高く，高温側では低いと予想される。この理論的予想は実際のデータとも適合する。

重量減少の活性化エネルギーが無処理試料のものとほぼ等しいにもかかわらず，TG における重量減少の開始が無処理試料より早いのは，重量減少もランダム切断を開始反応とする連鎖機構に支配されると仮定すれば矛盾しない。しかし，重量減少は生長反応だけでなく，脱水によって起る可能性をも考慮に入れて解釈しなければならない。

TG において，急激な重量減少後の残渣は無処理試料の残渣よりかなり多いが，その後の昇温により緩やかに減少したことが，Fig. 40 から分る。炭化残渣に含まれるこれらの比較的不安定な部分は，Table 6 の元素分析の結果からも推定されるように，多分，停止反応による架橋の形成によるものであろう。したがって，処理による炭化残渣の増加は停止反応の促進によるところが大きいと考えられる。(20) 式によって算出された動力学鎖長は 250° で約 5，275° で約 8，300°C で約 13 である。これらの値は処理試料の中，最も無処理試料のそれに近い。

DTA 曲線において，急激な重量減少の前に現われた幅広い吸熱ピークは，多分ランダム切断反応によって作られたのであろう。重量減少による DTA の吸熱ピークは，みかけ上二つの発熱ピークにはさまれた形になっているのが Fig. 40 に示されている。これは多分，停止反応によって生じた DTA の発熱領域

の中で重量減少の吸熱が生じたためであろう。

6. 結　　論

1) セルロースの熱分解に対して提案した連鎖機構，すなわち，鎖のランダム切断を開始反応とし，レボグルコサンの生成を生長反応とし，グラフト化を停止反応とする熱分解モデルが，無機塩の添加のいかんを問わず，一般的に成り立つことが，真空で加熱されたセルロース試料の粘度および重量測定によって示された。この研究では，熱分解による重合度の平衡化は開始反応との間に成立した定常状態によって与えられたと解釈される。一方，重量減少は生長反応によってひき起され，この定常状態ではみかけの1次反応にしたがうと解釈される。

TG, DTA, および DSC の熱分析で示された無処理および塩処理セルロースの挙動がこの連鎖機構によって説明された。さらに，元素分析の結果もこのモデルを支持している。

2) 塩の添加によって開始反応だけでなく，停止反応も促進されたので，結果的に架橋の形成が促進され，熱的に安定な構造が増加したと推定される。処理による炭化残渣の増加は塩による炭化作用の促進によるだけでなく，この停止反応の加速にもよると考えられる。

TG において処理試料の重量減少の開始が早められたのは，塩の脱水作用に依存しただけでなく，生長反応の開始反応であるランダム切断が塩の作用によって促進されたためと解釈される。

3) 無処理および各処理試料の熱分解は次のように特徴づけられる。重合度変化から，無処理およびホウ酸ナトリウム処理セルロースの熱分解は全期間にわたってランダム切断と停止との連鎖反応によってコントロールされていたことが分る。これに対して，リン酸アンモニウム，臭化アンモニウム，および塩化ナトリウムで処理された各セルロースの熱分解は，初期においてランダム切断だけで進行し，後期においてランダム切断と停止との連鎖反応によって進行したことが分る。リン酸アンモニウム処理試料のランダム切断の反応機構は前期と後期とでは異っている可能性がある。臭化アンモニウム処理試料のランダム切断反応は，初め非晶領域で優先的に起り，おくれて微結晶で起ると推定される。塩化ナトリウム処理試料の初期のランダム切断と後期における連鎖反応としてのランダム切断との速度は等しい。

熱分解による重量減少は，臭化アンモニウム処理試料を除いて，加熱の後期でみかけの1次反応として表わされる。臭化アンモニウム処理試料の重量減少は，初め非晶領域で起り，おくれて結晶領域で起ることが，TG の結果から推定される。このため，この試料の重量減少に関する速度論的解析が成功しなかったと考えられる。

4) 無処理，リン酸アンモニウム処理，ホウ酸ナトリウム処理，臭化アンモニウム処理，および塩化ナトリウム処理の各試料の開始反応の活性化エネルギーは，それぞれ，38.0，35.4，29.6，26.8，および32.6 kcal/mole で，その前置係数は，それぞれ，1.4×10^{10}，6.9×10^{12}，1.6×10^{7}，7.4×10^{8}，および $9.3\times10^{7}\ \mathrm{sec}^{-1}$ である。しかしながら，リン酸アンモニウム処理試料に関して，初期の重合度変化から求められたランダム切断の活性化エネルギーと前置係数が上記の値と異っており，それぞれ，25.8 kcal/mole および $1.2\times10^{7}\ \mathrm{sec}^{-1}$ である。前述の各試料の停止反応の対応するアレニウスパラメーターは，それぞれ，31.4，25.0，20.5，23.0，および 19.3 kcal/mole，および 2.9×10^{9}，15×10^{10}，2.5×10^{5}，1.7×10^{9}，および $9.9\times10^{4}\ \mathrm{sec}^{-1}$ である。

一方，無処理，リン酸アンモニウム処理，ホウ酸ナトリウム処理，および塩化ナトリウム処理の各試料

のみかけの1次反応の重量減少の活性化エネルギーは，それぞれ，44.7，40.7，49.9，および 44.3 kcal/mole で，対応する前置係数は，それぞれ，3.9×10^{13}，6.9×10^{13}，2.0×10^{16}，および 3.5×10^{14} sec^{-1} である。なお，前述のように，臭化アンモニウム処理試料の重量減少の速度論パラメーターは求められ得なかった。

5)　木材防火薬剤の一般的効果として，従来，加熱によって気相に放出されたハロゲン等による発炎阻止，および木材の熱分解コースの変更による可燃性成分の生成の削減[49]の二つが主に期待されてきた。後者の効果は主として脱水炭化によって達せられると考えられてきた。しかし，セルロースを対象としたこの研究では，可燃性成分の生成を意味する重量減少が高分子鎖の変化に直接結びついていることが示された。たとえば，グラフト化停止反応によってレボグルコサンの生成が停止されるだけでなく，熱的に安定な架橋構造が形成されるという防火効果が示された。今後，高分子鎖としての変化に及ぼす効果の面から防火薬剤の作用を見直し，開発する必要があろう。

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