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Influence of Ball-Milling Atmosphere on Decrease of Molecular Weight of Polyvinylpyrrolidone Powders

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The rate of a decrease of mean molecular weight and molecular weight distribution of polyvinylpyrrolidone (PVP) powders changed by ball-milling in nitrogen, air or oxygen were investigated, and influence of a ball-milling atmosphere on the probability in which a PVP molecule was broken in a unit time and molecular size distribution of the polymers formed by the break of a PVP molecule in a unit time was discussed.

If the function representing the probability in which a PVP molecule was cut off in a unit time, $S(M)$, was proportional to $(M-M_{\infty})^{a}$, a was considered to be between 1.0 and 1.5, and to be 1.0 for the case of ball-milling in nitrogen or air and to be larger than 1.0 for the case of ball-milling in oxygen.

It was considered to be much probable that a PVP molecule with molecular weight of 1.6×10^{6} was broken both at the center and at the molecular weight between 6×10^{3} and 1.1×10^{4} from the end of a main chain by ball-milling in nitrogen, and at the molecular weight of 3.6×10^{4} from the end by ball-milling in air or oxygen. It seemed to be possible that a PVP molecule with molecular weight of 1.6×10^{6} was broken at the molecular weight between 5.0×10^{4} and 3.7×10^{5} from the end by ball-milling in oxygen.

It was reported in the previous paper that the rate of a decrease of molecular weight of polyvinylpyrrolidone (PVP) powders by ball-milling was influenced by the atmosphere.[2] The rate of a decrease of molecular weight of PVP by ball-milling is controlled by the probability in which a PVP molecule is cut off by impact stress of balls in a unit time and by molecular weight distribution of the polymers formed by the break of a main chain of a PVP molecule under ball-milling in a unit time.

In this work, influence of a ball-milling atmosphere on these two factors controlling the rate of a decrease of molecular weight of PVP was investigated.

Experimental

The material used in this work was PVP K90 purchased from Wako Junyaku Kogyo Co. Monobasic potassium phosphate (KH_2PO_4) and dibasic sodium phosphate (Na_2HPO_4) were of special grade.

The method of ball-milling PVP K90 was the same as reported in the previous paper, with the exception of the revolving velocity of the mill of 120 r.p.m.[2] A viscosity of the KH_2PO_4–Na_2HPO_4 buffer solution (PH: 6.3, ionic intensity: 0.05) of the material was measured by the method reported in the previous paper.[2] Molecular weight distribution of the sample was also investigated according to the same method as reffered to the previous paper, by eluting with the KH_2PO_4–Na_2HPO_4 buffer solution.[2]

Result

1) Rate of a Decrease of mean Molecular Weight

In our another experiment, it was suggested that conformation of a PVP molecule in an aqueous solution was influenced by molecular weight and the chemical structure partially changed by ball-milling, and that of a molecule in an acidic solution was hardly influenced by them. Then, a viscosity of the KH_2PO_4–Na_2HPO_4 buffer solution of ball-milled PVP K90 was measured and molecular weight of the sample, M, was obtained by equation (1), which was wade

1) Location, *Hatanodai, 1-5-8, Shinagawa-ku, Tokyo.*
2) N. Kaneniwa and A. Ikekawa, *Yakuzaigaku*, **31**, 201 (1971); *idem, Zairyo*, **20**, 720 (1971).

from our results on molecular weigbt of PVP obtained by appli cation of Frank's equation.[2,3]

$$[\mu] = K_i M^{\alpha i} \tag{1}$$

$K_i = 5.5 \times 10^{-4}$ (100 ml/g), $\alpha i = 0.58$

$[\mu]$: Intrinsic viscosity of the KH_2PO_4–Na_2HPO_4 buffer solution of PVP

In Fig. 1, molecular weight of ball-milled PVP K90 was plotted versus ball-milling time. At the first stage of ball-milling, the rate of a decrease of molecular weight of PVP was the largest in oxygen and the smallest in nitrogen, which was the same results obtained by the measurement of a viscosity of the aqueous solution of the sample in the previous paper.[2] The relation between the tangent of the "molecular weight–ball-milling time" curve, $-dM/dt$, and molecular weight of ball-milled PVP, M, was investigated. Then, Eqs. (2), (3) and (4) were found to be applicable to a decrease of molecular weight of PVP under ball-milling in nitrogen, air and oxygen, respectively, as shown in Fig. 2, 3 and 4.

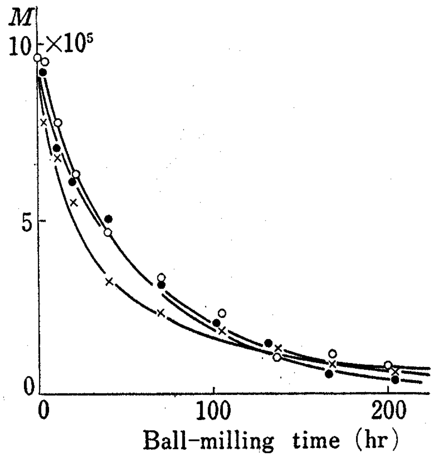

Fig. 1. Decrease of Molecular Weight, M, of PVP Powders by Ball-Milling

atmosphere ○: in nitrogen
●: in air
×: in oxygen

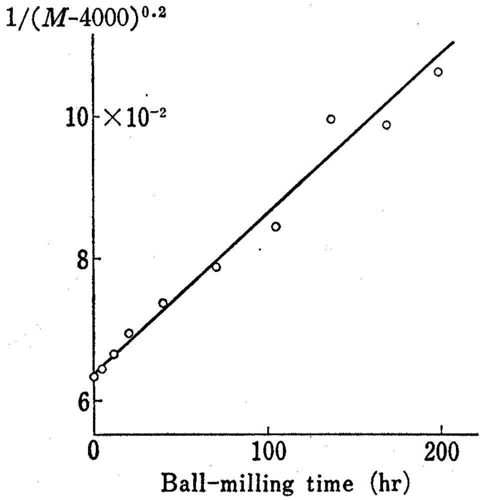

Fig. 2. Rate of Decrease of Molecular Weight of PVP Powders under Ball-Milling in Nitrogen

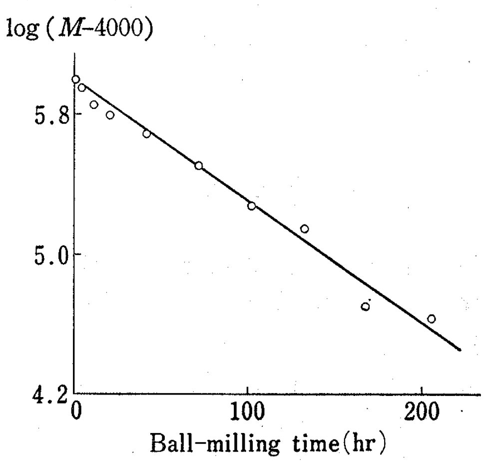

Fig. 3. Rate of Decrease of Molecular Weight of PVP Powders under Ball-Milling in Air

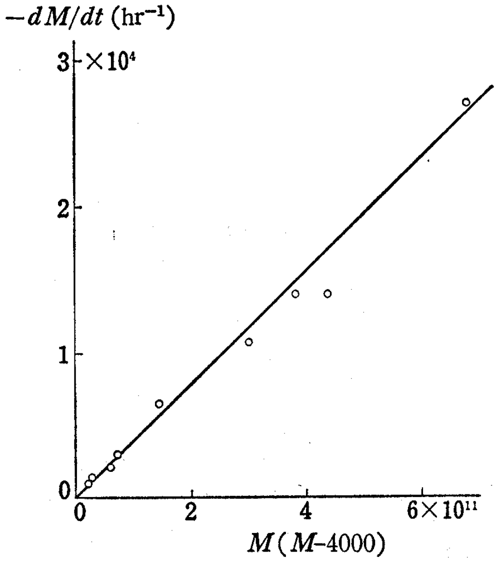

Fig. 4. Rate of Decrease of Molecular Weight of PVP Powders under Ball-Milling in Oxygen

3) H. Frank and G. Levy, *J. Polymer Sci.*, **10, 371 (1953).**

$$-dM/dt = k_n(M-4000)^{1.2} \quad (2)$$

$$-dM/dt = k_a(M-4000) \quad (3)$$

$$-dM/dt = k_oM(M-4000) \quad (4)$$

k_n, k_a, k_o: constants

2) Molecular Weight Distribution of PVP changed by Ball-Milling

Fig. 5, 6 and 7 show molecular weight distribution of PVP changed by ball-milling in nitrogen, air and oxygen, respectively. In these cases, two peaks were observed in molecular weight distribution curves of the samples, and the peak at the molecular weight of approximately 10^6 decreased and the peak at the molecular weight between 2×10^4 and 4×10^4 increased with an increase of ball-milling time.

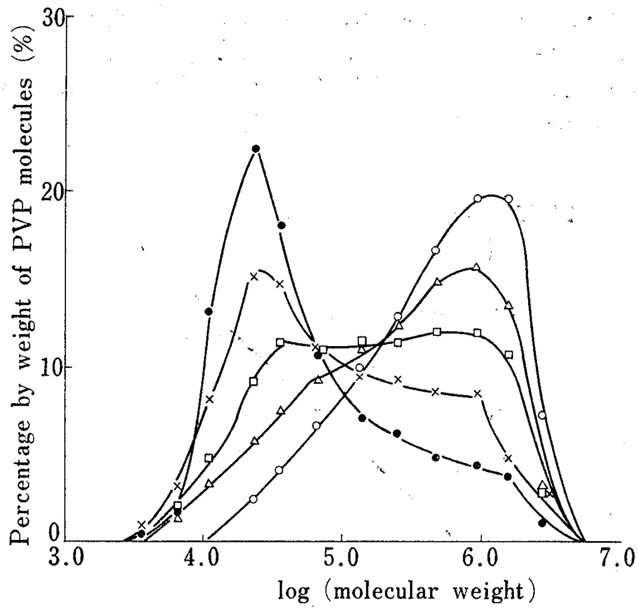

Fig. 5. Molecular Weight Distribution of PVP Powders Changed by Ball-Milling in Nitrogen

ball-milling time (hr)
○: 0 △: 30 □: 67 ×: 124 ●: 200

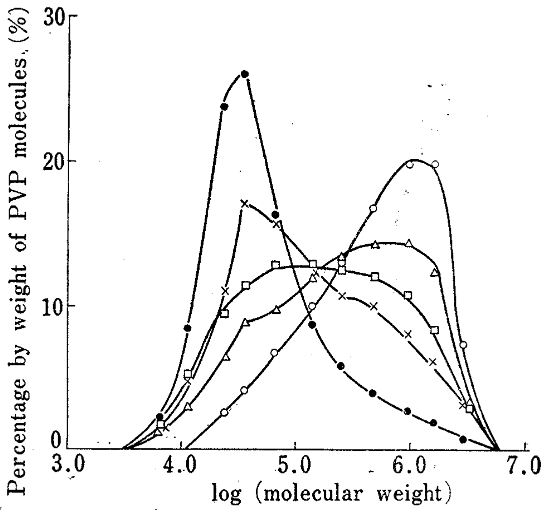

Fig. 6. Molecular Weight Distribution of PVP Powders Changed by Ball-Milling in Air

ball-milling time (hr)
○: 0 △: 21 □: 54 ×: 103 ●: 205

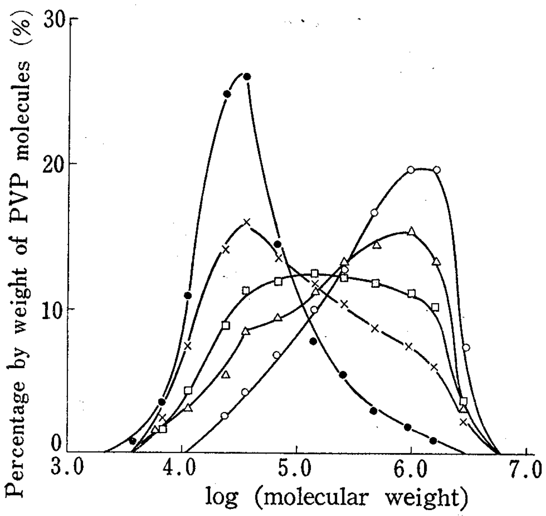

Fig. 7. Molecular Weight Distribution of PVP Powders Changed by Ball-Milling in Oxygen

ball-milling time (hr)
○: 0 △: 21 □: 54 ×: 104 ●: 204

Discussion

1) Molecular Size Distribution of the Polymers formed by the Break of a PVP Molecule

Each sample was fractionated into eleven fractions by Sepharose 6B. Molecular weight distribution of the sample can be represented by a vector obtained by arranging the numerical values of the percentage by weight of PVP in each fraction in order of high molecular weight. When $(x_1, x_2, \cdots, x_{11})$ is the vector of molecular weight distribution of the original PVP and $(x_1', x_2', \cdots, x_{11}')$ is that of the ball-milled PVP, Eq. (5) is applied.

$$\sum_{i=1}^{11} x_i = \sum_{i=1}^{11} x_i' = 1 \tag{5}$$

Here, A_{ij} is defined as Eq. (6), where SF_{ij} is the weight of PVP removed from the j th fraction to the i th fraction by ball-milling and SD_j is the weight of PVP in the j th fraction before ball-milling.

$$A_{ij} = SF_{ij}/SD_j \quad (1 \leqq i,\ j \leqq 11) \tag{6}$$

If it is assumed that ball-milling causes only a decrease of molecular weight of PVP, Eqs. (7) and (8-i) (i=1—11) are applied.

$$i < j \quad A_{ij} = 0, \quad i \geqq j \quad 0 \leqq A_{ij} \leqq 1, \quad \sum_{i=1}^{11} A_{ij} = 1 \tag{7}$$

$$x_1' = A_{11} x_1 \tag{8-1}$$

$$x_2' = A_{21} x_1 + A_{22} x_2 \tag{8-2}$$

$$\vdots$$

$$x_{11}' = A_{11\,1} x_1 + A_{11\,2} x_2 + \cdots + A_{11\,11} x_{11} \tag{8-11}$$

Equation (8-i) (i=1—11) is represented by Eq. (9).

$$\begin{vmatrix} A_{11} & 0 & 0 & 0 \\ A_{21} & A_{22} & 0 \cdots\cdots & 0 \\ \vdots & \vdots & & \vdots \\ A_{11\,1} & A_{11\,2} & \cdots\cdots\cdots & A_{11\,11} \end{vmatrix} \begin{vmatrix} x_1 \\ x_2 \\ \vdots \\ x_{11} \end{vmatrix} = \begin{vmatrix} x_1' \\ x_2' \\ \vdots \\ x_{11}' \end{vmatrix} \tag{9}$$

In this work, the matrix in Eq. (9) with the element of A_{ij} is called a degradation matrix.

Probability in which a PVP molecule is cut off under ball-milling in a unit time is considered to be represented by a function of molecular weight, $S(M)$. Baramboim reported that the rate of a decrease of molecular weight of some polymers by ball-milling was proportional to $(M/M_\infty - 1)$, that is, to the number of the sections broken by the impact stress of balls, where M_∞ was the lowest molecular weight obtained by ball-milling.[4] Therefore, in this work, $S(M)$ was assumed to be represented by Eq. (10).

$$S(M) = (K'/M_\infty{}^{\alpha})(M - M_\infty{}^{\alpha}) = K(M - M_\infty)^{\alpha} \tag{10}$$

$K = K'/M_\infty$, K, K': constants

α: A parameter dependent on a ball-milling atmosphere and so on

The element of the degradation matrix, A_{jj}, is equal to the percentage by weight of PVP which was not broken by ball-milling in the j th fraction. Accordingly, $(1\text{-}A_{jj})$ is equal to the percentage by weight of PVP which was broken by ball-milling in the j th fraction. Equation (11) is applicable, if probability in which PVP molecules in the j th fraction are cut off is proportional to the number of the molecules in the fraction.

$$1 - A_{jj} = K''(M_j - M_\infty)^{\alpha}/M_j \tag{11}$$

M_j: Mean molecular weight of PVP in the jth fraction

K'': A parameter dependent on a ball-milling time and so on

The numerical value of A_{11} can be obtained from Eq. (8-1). Therefore, all the values of A_{jj} can be obtained by Eq. (11). Then, the numerical value of A_{21} can also be obtained by

4) N.K. Baramboim, *Zh. Fiz. Khim.*, **32**, 432 (1958); *idem, Dokl. Akad. Nauk SSSR*, **114**, 568 (1957).

Eq. (8-2). If probability in which a PVP molecule with the molecular weight of M_i is broken at the molecular weight of M_x from the end of a main chain is assumed to depend on $(M_x - M_\infty)/M_i$ and to be independent of M_j, Eq. (12) is applicable between A_{ij} ($i \neq j$, $i > 1$) and A_{i1}, where k′ is the largest of the integers which are equal to or smaller than $(n-i)(i-j)/(n-j)$ and k″ is the largest of the integers which are equal to or smaller than $(n-i)(i-j-1)/(n-j)$.

$$A_{ij} = S(M_j)/S(M_1)\Big[\sum_{k=2}^{k'} A_{k1} + \{(n-i)(i-j)/(n-j) - k'\}A_{k'+1} - \sum_{k=2}^{k''} A_{k1} - \{(n-i)(i-j-1)/(n-j) - k''\}A_{k''+1}\Big] \quad (12)$$

Under the assumptions mentioned above, the values of A_{ij} were calculated in five cases that α is equal to 0, 0.5, 1.0, 1.5, and 2.0. Abnormally large values of $\sum_{i=1}^{11} A_{ij}$ were obtained in cases that α is equal to 0, 0.5, and 2.0, respectively. Reasonable values were obtained for all the elements in a degradation matrix, when α is assumed to be between 1.0 and 1.5. Negative values larger than -1.0 were obtained for some of the elements. These negative values were considered to be due to the experimental errors included in x_i and x_i', and these elements were regarded as zero. The obtained values of $\sum_{i=1}^{11} A_{ij}$ were between 0.9 and 1.1, and each of the elements was corrected by proportional calculation so that the values of $\sum_{i=1}^{11} A_{ij}$ were 1.0. In Table I is tabullated an example of a degradation matrix with the corrected values of A_{ij}.

Table I. Degradation Matrix for Ball-Milling PVP Powders in Nitrogen for 11 hours ($\alpha = 1.0$)

0.510	0	0	0	0	0	0	0	0	0	0
0.317	0.565	0	0	0	0	0	0	0	0	0
0	0.280	0.606	0	0	0	0	0	0	0	0
0.070	0.014	0.254	0.658	0	0	0	0	0	0	0
0	0.048	0.028	0.221	0.695	0	0	0	0	0	0
0.007	0.003	0.028	0.042	0.195	0.730	0	0	0	0	0
0.064	0.034	0.006	0.008	0.043	0.174	0.765	0	0	0	0
0	0.025	0.051	0.036	0.005	0.039	0.166	0.795	0	0	0
0	0	0	0.013	0.040	0.039	0.020	0.162	0.810	0	0
0.031	0.025	0.019	0.013	0.007	0	0.031	0.030	0.152	0.842	0
0.003	0.006	0.009	0.011	0.015	0.020	0.017	0.014	0.038	0.158	1.000

Molecular size distribution of the polymers formed by the break of a PVP molecule with molecular weight of 1.6×10^6 was calculated from the values of A_{i2}. As shown in Fig. 8, three peaks were observed in molecular size distribution curves, the first peak at the molecular weight between 6.3×10^3 and 1.1×10^4, the second peak at molecular weight of 3.6×10^4 and the third peak at molecular weight between 10^6 and 2.5×10^5. It is considered to be much probable that a PVP molecule with molecular weight of 1.6×10^6 is cut off at the molecular weight of 6.3×10^3—1.1×10^4 and 3.6×10^4 from the end, and at the center of a main chain.

Molecular size distribution of the polymers formed by the break of a PVP molecule with molecular weight of 1.6×10^6 by ball-milling for infinitely short time was obtained by extrapolating the "percentage by number of the polymers in each fraction formed by the break of a PVP molecule with molecular weight of 1.6×10^6–ball-milling time" curve (See Fig. 9).

The polymers formed by a break of a PVP molecule with molecular weight of 1.6×10^6 were fractionated into four fractions, as shown in Table II. Table II shows the numerical values of the percentage by number of the molecules in each fraction formed by ball-milling

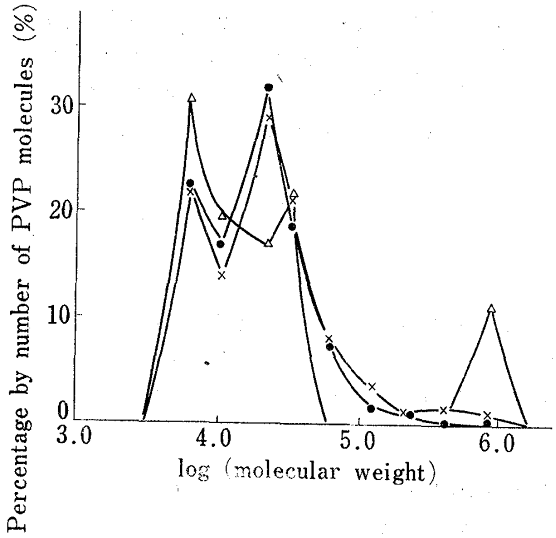

Fig. 8. Molecular Size Distribution of the Polymers Formed by the Break of a PVP Molecule with Molecular Wieght of 1.6×10^6 by Ball-Milling in Nitrogen

(calculated under the assumption that α is 1.0)
ball-milling time (hr)
△: 30 ×: 124 ●: 200

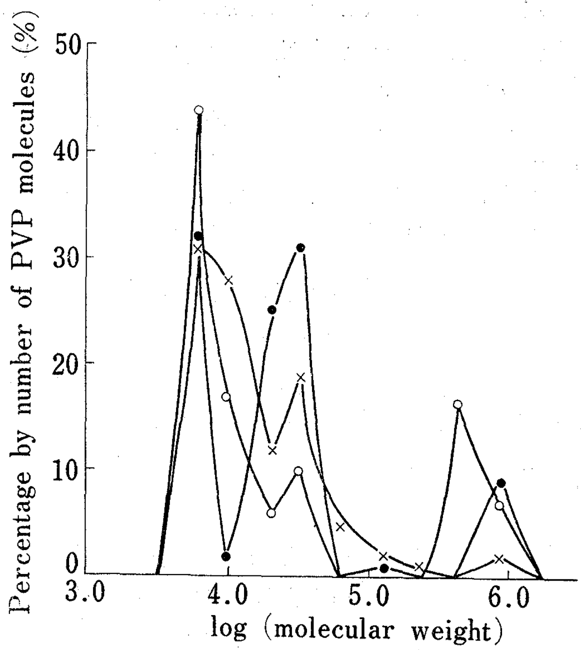

Fig. 9. Molecular Size Distribution of the Polymers formed by the Break of a PVP Molecule with Molecular Weight of 1.6×10^6 after Ball-Milling for Infinitely Short Time

atmosphere	assumption
○: in nitrogen	α=1.0
●: in air	α=1.0
×: in oxygen	α=1.5

a PVP molecule with molecular weight of 1.6×10^6 for infinitely short time, obtained by extrapolating the "percentage by number of the molecules in each fraction–ball-milling time" curve. From Fig. 9 and Table II, it seems to be confirmed as follows, without concern with the value of α. It is much probable that a PVP molecule is cut off at the molecular weight of 3.6×10^4 from the end of a main chain under ball-milling in an oxygen-containing atmosphere, and at the molecular weight of 6×10^3—1.1×10^4 from the end and at the center under ball-milling in nitrogen.

Table II. Molecular Size Distribution of the Polymers Formed by the Break of a PVP Molecule with Molecular Weight of 1.6×10^6 by Ball-Milling for an Infinitely Short Time

α	Molecular weight	Ball-milling atmosphere		
		Nitrogen	Air	Oxygen
1.0	1.6×10^6—3.7×10^5	23 n/n %	9 n/n %	10 n/n %
	3.7×10^5—5.0×10^4	0	1	0
	5.0×10^4—1.8×10^4	16	56	52
	1.8×10^4—4.0×10^3	61	34	38
1.2	1.6×10^6—3.7×10^5	8		
	3.7×10^5—5.0×10^4	14		
	5.0×10^4—1.8×10^4	12		
	1.8×10^4—4.0×10^3	66		
1.5	1.6×10^6—3.7×10^5	8	1	2
	3.7×10^5—5.0×10^4	5	14	8
	5.0×10^4—1.8×10^4	15	34	31
	1.8×10^4—4.0×10^3	72	51	59

2) Rate of a Decrease of Mean Molecular Weight

It is now assumed that only the polymers with molecular weight of M_j are selectively broken by ball-milling, though the original PVP has wide molecular weight distribution. Then, the rate of a decrease of molecular weight of PVP by ball-milling is expressed by Eq. (13), where ϕ_j is the percentage by weight of PVP in the fraction of molecular weight of M_j and $B(M_j)$ is weight mean molecular weight of the polymers formed by the break of a PVP molecule with molecular weight of M_j.

$$-dM/dt = k_m(\phi_j/M_j)S(M_j)\{M_j-B(M_j)\} \tag{13}$$

k_m: a constant

In case that α is equal to 1.0, $[M_j-B(M_j)]$ is considered approximately to be inversely proportional to M_j when a PVP molecule is broken at the end, and to be constant when a PVP molecule is broken at the center. For these cases, Eq. (13) is expressed by Eqs. (14) and (15), respectively.

$$-dM/dt = k_m'(\phi_j/M_j)(M_j-M_\infty)\{M_j-B(M_j)\} \approx k_m''\phi_j \tag{14}$$

$$-dM/dt = k_m'(\phi_j/M_j)(M_j-M_\infty)\{M_j-B(M_j)\} \approx k_m'''\phi_j(M_j-M_\infty) \tag{15}$$

k_m, k_m', k_m'', k_m''': constants

A molecular weight distribution curve is now assumed to bear a close resemblance to stairs where a percentage by weight of PVP, with molecular weight between M_j and $M_j+\Delta M_j$ is constant. In fact, all the molecules in a mill have probability to be broken by impact stress of balls. Therefore, the real rate of a decrease of molecular weight of PVP by ball-milling is expressed by Eq. (16) in case that a PVP molecule is broken at the end, and by Eq. (17) in case that a PVP molecule is broken at the center.

$$-dM/dt \approx k_m''\sum_j \phi_j \int_{M=M_j}^{M_j+\Delta M_j} dM / \sum_j \phi_j$$

$$\approx k_m''(\bar{M}-M_\infty) \tag{16}$$

$$-dM/dt \approx k_m'''\sum_j \phi_j \int_{M=M_j}^{M_j+\Delta M_j} (M-M_\infty)dM / \sum_j \phi_j$$

$$\approx k_m'''\bar{M}(\bar{M}-M_\infty) \tag{17}$$

$\bar{M}$: weight mean molecular weight of PVP

Equation (16) is identical with Eq. (3) for the case of ball-milling in air. Good applicability of Eq. (2) to bal-milling in nitrogen will be due to high probability in which a PVP molecule is broken both at the center and at the molecular weight of $6\times10^3-1.1\times10^4$ from the end.

It is not considered to be much probable, from Fig. 9 and Table II, that a PVP molecule is cut off at the center in oxygen, though Eq. (17) is identical with Eq. (4). This fact shows that α is larger than 1.0 for the case of ball-milling in oxygen. It seems to be possible from Table II that a PVP molecule is cut off at the molecular weight between 3.7×10^5 and 5.0×10^4 by ball-milling in oxygen. If α is 1.5 and $[M_j-B(M_j)]/M_j$ is inversely proportional to the square root of M_j, Eq. (18) is applicable under the same assumption as that for Eq. (13).

$$-dM/dt = k_m(\phi_j/M_j)(M_j-M_\infty)^{1.5}\{M_j-B(M_j)\}$$

$$\approx k_m''''\phi_j(M_j-M_\infty) \tag{18}$$

k_m'''': a constant

Accordingly, in this case, a real rate of a decrease of molecular weight of PVP with wide molecular weight distribution by ball-milling is expressed by Eq. (19), under the assumption that a molecular weight distribution curve has a strong resemblance to stairs.

$$-dM/dt \approx k_m'''' \sum_j \phi_j \int_{M=M_j}^{M_j+\Delta M_j} (M-M_\infty)dM / \sum_j \phi_j$$
$$\approx k_m'''' \bar{M}(\bar{M}-M_\infty) \tag{19}$$

Equation (19) is identical with Eq. (4).

From the above facts, it was clarified that a ball-milling atmosphere influenced both the probability in which a PVP molecule is broken and molecular size distribution of the polymers formed by the break of a PVP molecule in a unit time. The parameter α in Eq. (10) is considered to be between 1.0 and 1.5, and to be 1.0 for the case of ball-milling in nitrogen or air and to be larger than 1.0 for the case of ball-milling in oxygen. It is considered to be much probable that a PVP molecule is broken both at the center and at the molecular weight between 6×10^3 and 1.1×10^4 from the end by ball-milling in nitrogen, and at the molecular weight of 3.6×10^4 from the end by ball-milling in air or oxygen. It seems to be possible that a PVP molecule is broken at the molecular weight between 3.7×10^5 and 5.0×10^4 from the end by ball-milling in oxygen.