EtOH (30 ml) was heated for 20 hr under reflux. The solution was concentrated by partial evaporation and then chromatographed on silica gel. Development with benzene–AcOEt (1: 1) gave colorless prisms (0.15 g, 12%) melting at 79—80° after recrystallization from dil. EtOH. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3250, 1640 (CONH). Mass Spectrum *m/e*: 261 (M$^+$). *Anal.* Calcd. for $C_{12}H_{23}ONS_2$: C, 55.17; H, 8.81; N, 5.36. Found: C, 55.41; H, 8.58; N, 5.04.

β-Cyclohexylcarbamoylethyl *n*-Butyl Disulfide (IIIb)——A solution of bis(β-cyclohexylcarbamoylethyl) disulfide (1.80 g, 5 mmole), cyclohexylamine (0.99 g, 10 mmole) and *n*-butanethiol (0.45 g, 5 mmole) in EtOH (30 ml) was heated for 20 hr under reflux. The solution was concentrated by partial evaporation and the residue was chromatographed on silica gel. Development with benzene–AcOEt (1: 1) gave colorless prisms (0.11 g, 8%). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3250, 1630 (CONH). *Anal.* Calcd. for $C_{13}H_{25}ONS_2$: C, 56.70; H, 9.15; N, 5.09. Found: C, 56.51; H, 8.92; N, 5.14.

Bis(β-cyclohexylcarbamoylethyl) Trisulfide (IIa) from Sodium β-Cyclohexylcarbamoylethylthiosulfate (IVa)——Sulfur (0.16 g, 5 m atom) was suspended to a solution of sodium β-cyclohexylcarbamoylethylthiosulfate (1.45 g, 5 mmole) and morpholine (0.87 g, 10 mmole) in H_2O (30 ml), and the mixture was heated for 20 hr under reflux. After cooling, the precipitates deposited were collected by filtration and recrystallized from EtOH to give colorless prisms (0.20 g, 20%) melting at 188—189°. *Anal.* Calcd. for $C_{18}H_{32}O_2N_2S_3$: C, 53.42; H, 7.97; N, 6.92. Found: C, 53.93; H, 8.01; N, 6.55. This compound was identified with an authentic sample prepared from bis(β-cyclohexylcarbamoylethyl) disulfide by mixed melting point determination and by comparison of the IR spectra.

Bis[β-(*p*-chlorophenylcarbamoyl)ethyl] Trisulfide (IIb) from Sodium β-(*p*-Chlorophenylcarbamoyl)ethylthiosulfate (IVb)——Sulfur (0.16 g, 5 m atom) was suspended to a solution of sodium β-(*p*-chlorophenylcarbamoyl)ethylthiosulfate (1.58 g, 5 mmole) and cyclohexylamine (0.99 g, 10 mmole) in H_2O (30 ml) and the mixture was heated for 20 hr under reflux. The precipitates deposited upon cooling were collected by filtration and recrystallized from EtOH to give colorless prisms (0.20 g, 19%) melting at 197—199°. This was identified with an authentic sample obtained from bis[β-(*p*-chlorophenylcarbamoyl)ethyl] disulfide by mixed melting point determination and by comparison of the IR spectra.

Bis(β-benzylcarbamoylethyl) Trisulfide (IIc) from Sodium β-Benzylcarbamoylethylthiosulfate (IVc)——Sulfur (0.16 g, 5 m atom) was suspended to a solution of sodium β-benzylcarbamoylethylthiosulfate (1.485 g, 5 mmole) and cyclohexylamine (0.99 g, 10 mmole) in H_2O (30 ml) and the mixture was heated for 20 hr under reflux. The precipitates deposited on cooling were collected by filtration and recrystallized from EtOH to give colorless prisms (0.65 g, 67%) of bis(β-benzylcarbamoylethyl) disulfide melting at 168—169°. Isolation of bis(β-benzylcarbamoylethyl) trisulfide from the filtrate was unsuccessful, but it was confirmed by thin-layer chromatograph.

Acknowledgement We are grateful to Mrs. K. Shiraki for microanalytical data. We also thank Mr. K. Takeda and Miss M. Sato for spectral data.

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Interaction between Iodine and Polyvinylpyrrolidone or α-Pyrrolidone

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Polyvinylpyrrolidone (PVP)-iodine-ethanol solutions keep germicidal action of iodine and have toxicity weaker than that of iodine.[2] Detailed mechanism of interaction of PVP with iodine has not been clarified yet. Therefore, in this work, interaction of PVP or α-pyrrolidone with iodine was investigated.

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[1] Location: *Hatanodai, 1-5-8, Shinagawa-ku, Tokyo.*

[2] G. Oster and E.H. Immergut, *J. Am. Chem. Soc.*, **76**, 1393 (1954); S. Siggia, *J. Am. Pharm. Assoc.*, **46**, 201 (1957).

Experimental

The materials used were α-pyrrolidone, PVP K15, PVP K30 and PVP K90. Mean molecular weight of PVP K15, PVP K30 and PVP K90 by viscometry were 7.5×10^3, 4.0×10^4 and 9.6×10^5, respectively.[3] PVP K90 and PVP K15 were ball-milled in nitrogen, air or oxygen. Molecular weight of PVP was not changed by ball-milling. Molecular weight of PVP K90 ball-milled in nitrogen, air or oxygen for 420 hours were approximately 2.0×10^4 by viscometry.[3] The molecular weight distribution curves of these materials, obtained by the method described in the previous paper,[4] are shown in Fig. 1 and 2. Iodine, potassium iodide, ethanol, chloroform and carbon tetrachloride were of guaranteed grade.

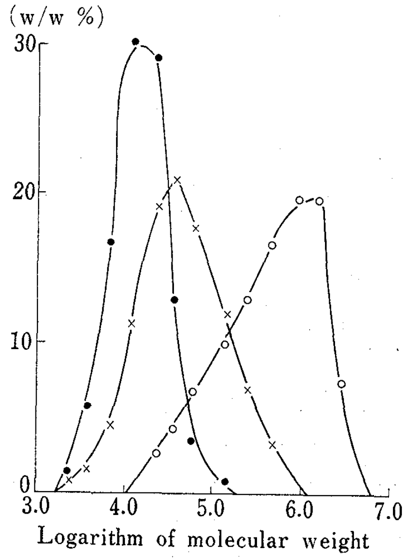

Fig. 1. Molecular Weight Distribution Curves of PVP K90, PVP K30 and PVP K15

—○—: PVP K90 —×—: PVP K30
—●—: PVP K15

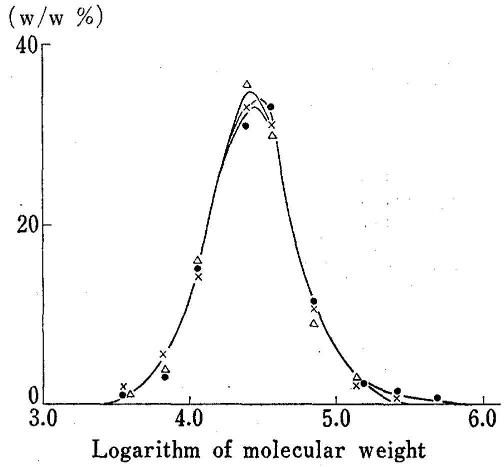

Fig. 2. Molecular Weight Distribution of PVP K90 Ball-Milled in Nitrogen, Air or Oxygen for 420 Hours

—●—: ball-milled in nitrogen
—×—: ball-milled in air
—△—: ball-milled in oxygen

Various amounts of iodine and PVP or α-pyrrolidone were dissolved in 50 v/v % aqueous ethanol solution, ethanol, chloroform or carbon tetrachloride, and after keeping the test solutions at 30° for various hours, absorption spectra were measured with a Hitachi recording spectrophotometer (Model EPS-2) and absorbance of the absorption maximum around 360 nm and 450 nm was measured with a Hitachi-Perkin Elmer spectrophotometer (Model 139). The nuclear magnetic resonance (NMR) spectra were measured with a Hitachi high resolution NMR spectrometer (Model R-20) and infrared (IR) spectra were measured with a Hitachi IR spectrometer (Model EPI-2). In this paper, the test solutions were kept at 30° for 24 hours after the preparation, when no description was given.

Results and Discussion

Interaction of iodine with PVP or α-pyrrolidone was investigated by the spectroscopic method. As shown in Fig. 3, absorbance at 292 nm and 360 nm increased remarkably by the addition of PVP to the ethanol solution of iodine immediately after the mixing, but the two peaks disappeared by keeping the test solution at 30° for 48 hours. The two peaks reappeared again by the addition of iodine to those colorless solutions.

The absorption spectra of chloroform solutions and carbon tetrachloride solutions of iodine were similar to those of iodine in a gaseous state,[5] and only one peak was observed around 520 nm. A new peak was observed at 370 nm in the absorption spectra of the chloroform solution of iodine by adding PVP whose molar concentration (monomer unit) was larger

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[3] N. Kaneniwa and A. Ikekawa, *Yakuzaigaku*, **31**, 201 (1971); *idem, Zairyo*, **20**, 720 (1971).

[4] N. Kaneniwa and A. Ikekawa, *Chem. Pharm. Bull.* (Tokyo), **20**, 1536 (1972); *idem, Zairyo*, **21**, 516 (1972).

[5] C.F. Hiskey and F.F. Cantwell, *J. Pharm. Sci.*, **55**, 166 (1966).

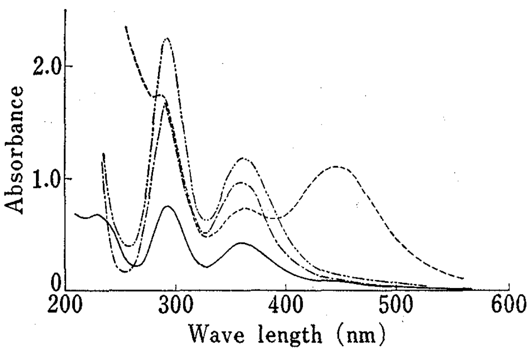

Fig. 3. Influence of Addition of Potassium Iodide or PVP on Absorption Spectra of Iodine–Ethanol Solutions

———: 1.1×10^{-4}M of iodine
-------: 9.9×10^{-4}M of iodine
—·—·—: 3.6×10^{-5}M of iodine and 2.6×10^{-4}M of potassium iodide
--------: 1.1×10^{-4}M of iodine and 1.1×10^{-2}M of PVP K15 (monomer unit) immediately after the mixing

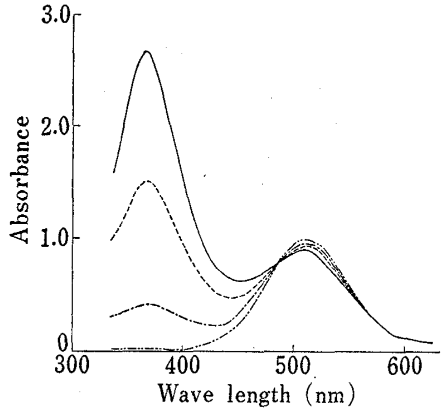

Fig. 4. Influence of the Addition of Various Amounts of PVP K15 on Absorption Spectra of the Chloroform Solutions of Iodine

concentration of iodine: 1.1×10^{-3}M
concentration of PVP K15 (monomer unit)
--------: 0M -------: 1.1×10^{-2}M
—·—·—: 5.7×10^{-3}M ———: 1.7×10^{-2}M

than that of iodine. (Fig. 4). When the molar concentration of PVP (monomer unit) was smaller than that of iodine, slight red shift of the peak at 515 nm was observed, but the peak at 370 nm was not observed. When 1.6×10^{-3}M—1.6×10^{-2}M of PVP K15 (monomer unit) was added to 1.6×10^{-3}M of iodine–chloroform solution, absorbance at 370 nm increased in proportion to the 1.5th power of the concentration of PVP K15. Absorbance at 370 nm was larger for the case of the addition of 2.1×10^{-4}M of iodine to 2.0×10^{-2}M of the chloroform solution of PVP K15 than for the case of the addition of 1.6×10^{-3}M of iodine. As shown in Fig. 4, an isosbestic point was observed at 490 nm in the absorption spectra of the chloroform solutions of PVP and iodine. But, absorbance around 360 nm decreased with an increase of the ratio

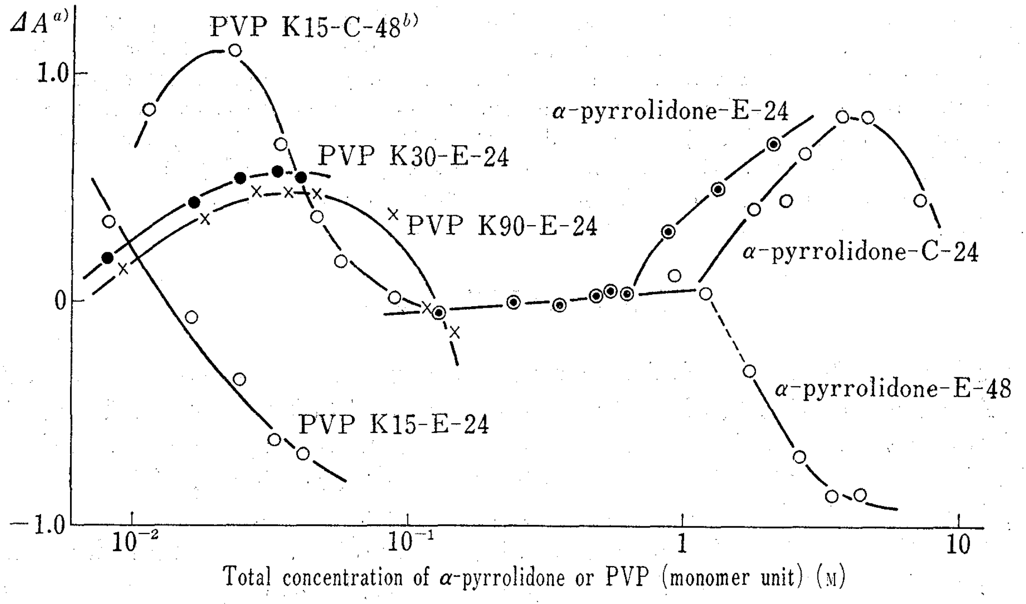

Fig. 5. Influence of the Total Concentration of α-Pyrrolidone or PVP on Absorbance of the Solutions of Iodine around 360 nm

concentration of iodine; 1.3×10^{-4}M in 50 v/v% aqueous ethanol solution (E, at 358 nm)
8.5×10^{-5}M in chloroform (C, at 370 nm)

a) ΔA; The difference of the absorption intensity of a solution of iodine around 360 nm in the presence of PVP or α-pyrrolidone to the intensity in the absence of PVP or α-pyrrolidone

b) for example; The results for chloroform solutions of PVP K15 and iodine kept at 30° for 48 hours after the mixing of the reagents.

of the concentration of PVP or α-pyrrolidone to the concentration of iodine, when the ratio was very large (Fig. 5 and 6).

The similar phenomena were also observed by the addition of α-pyrrolidone to the solutions of iodine. By the addition of less than 0.6 M of α-pyrrolidone, a new peak was observed at 450 nm in the carbon tetrachloride solution of iodine, though only a slight red shift of the peak at 515 nm was observed in the chloroform solution. In addition to this band, the other band appeared at 372 nm by adding more than 0.6 M of α-pyrrolidone to 8.4×10^{-4} M of a carbon tetrachloride solution of iodine. (Fig. 7). In contrast with this finding, the peak at 372 nm was not observed by adding more than 0.6 M of α-pyrrolidone to 8.4×10^{-5} M of a carbon tetrachloride solution of iodine and absorbance at 450 nm decreased with an increase of the concentration of α-pyrrolidone. (Fig. 8). Absorbance of iodine in polar solvents around 360 nm increased remarkably by the addition of α-pyrrolidone immediately after the mixing. But the absorbance decreased gradually with the lapse of the time after the preparation. As shown in Fig. 5, an increase or a decrease of absorbance around 360 nm was observed only by adding more than 0.6 M of α-pyrrolidone to iodine. The value of the critical concentration, 0.6 M, was influenced little by the concentration of iodine.

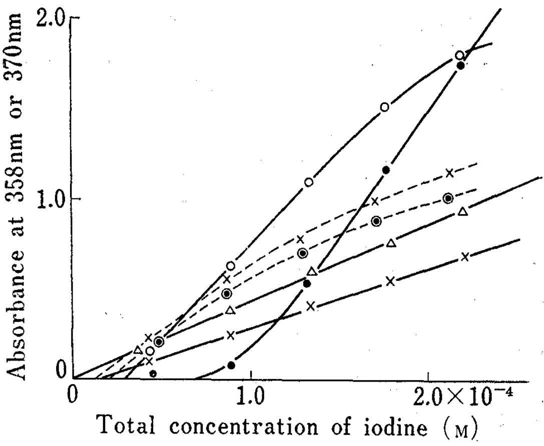

Fig. 6. Influence of the Total Concentration of Iodine on Absorbance of the 50 v/v% Aqueous Ethanol Solutions of PVP or α-Pyrrolidone at 358 nm and the Chloroform Solutions at 370 nm

———— : 50 v/v% aqueous ethanol solution
------ : chloroform solution
—●—: 1.9×10^{-2} M of PVP K15 (monomer unit)
—○—: 1.9×10^{-2} M of PVP K90 (monomer unit)
---×---: 1.8×10^{-2} M of PVP K15 (monomer unit)
---⊙---: 2.3 M of α-ryrrolidone
—△—: absence of PVP and α-pyrrolidone
—×—: 2.0×10^{-2} M of PVP K90 ball-milled in oxygen for 420 hours (monomer unit)

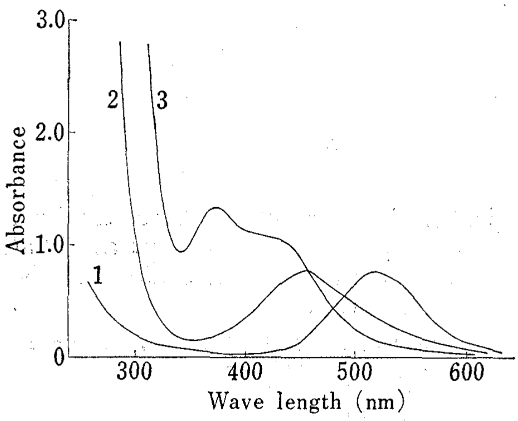

Fig. 7. Influence of the Addition of α-Pyrrolidone on an Absorption Spectrum of the Carbon Tetrachloride Solution of Iodine

1 8.4×10^{-4} M of iodine
2 4.4×10^{-1} M of α-pyrrolidone and 8.4×10^{-4} M of iodine
3 3.6 M of α-pyrrolidone and 8.4×10^{-4} M of iodine

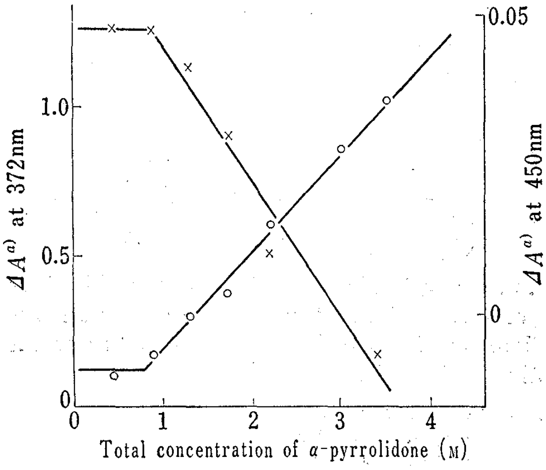

Fig. 8. Influence of Total Concentration of α-Pyrrolidone on Interaction with Iodine in Carbon Tetrachloride

total concentration of iodine	wave length for measurement
—○—: 8.4×10^{-4} M	372 nm
—×—: 8.4×10^{-5} M	450 nm

a) ΔA; The difference between absorbance of the iodine solution containing α-pyrrolidone and that of the iodine solution without α-pyrrolidone

It has been known that absorption maximum is observed around 450 nm in the absorption spectra of the alcohol solutions and the ether solutions of iodine,⁵⁾ and Mulliken, Hildebrand, *et al.* showed that the peak was due to iodine binding to oxygen.⁶⁾ Probably, absorbance around 450 nm for iodine in the carbon tetrachloride solutions of α-pyrrolidone is also due to iodine binding to oxygen of α-pyrrolidone molecules.

In the previous paper, it was considered from the spectroscopic investigation that the peak around 360 nm for the solutions of iodine was attributed not only to triiodide anions but to the iodine which was in the diatomic state and the interatomic distance of which was a little prolonged by the interaction with the molecules of the solvent and so on. It was also found in the previous paper that absorbance of the solutions of iodine around 360 nm increased by the addition of polyethylene glycol. And it was considered that the absorption of the ethanol solution of iodine around 360 nm was attributed to the iodine in the diatomic state and whose interatomic distance was a little prolonged by the interaction with ethanol molecules. It was also considered that formation of the iodine in the diatomic state and with a little prolonged interatomic distance became remarkable by the addition of polyethylene glycol.⁷⁾ Colorless solutions were not obtained even by adding extremely large amount of polyethylene glycol to the solution of iodine.⁷⁾ On the contrary, colorless solutions were obtained by adding large amount of PVP or α-pyrrolidone to the solution of iodine immediately after the mixing. The brown solution recovered again, by the addition of iodine to these colorless solutions. These facts show that iodine molecules are dissociated into triiodide anions or monoiodide anions by the addition of PVP or α-pyrrolidone.

Fig. 9 and 10 show the variation of absorbance of the solution of iodine and PVP or α-pyrrolidone around 360 nm with the lapse of the time kept at 30° after the mixing. When the ratio of the molar concentration of PVP (monomer unit) to that of iodine was 1.9×10,

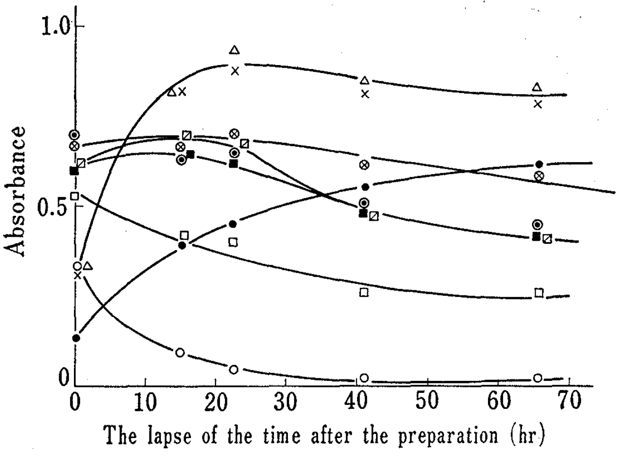

Fig. 9. Relation between Absorbance of Iodine–PVP–Ethanol Solutions at 360 nm and the Time for the Solutions Kept at 30° after the Mixing of the Reagents

1.1×10^{-4}M of iodine and 2.1×10^{-2}M of PVP (monomer unit)
—●—: absent of PVP
—×—: PVP K90
—△—: PVP K30
—○—: PVP K15
—▨—: PVP K90 ball-milled in nitrogen
—■—: PVP K90 ball-milled in air
—□—: PVP K90 ball-milled in oxygen
—⊙—: PVP K15 ball-milled in nitrogen
—⊗—: PVP K15 ball-milled in oxygen

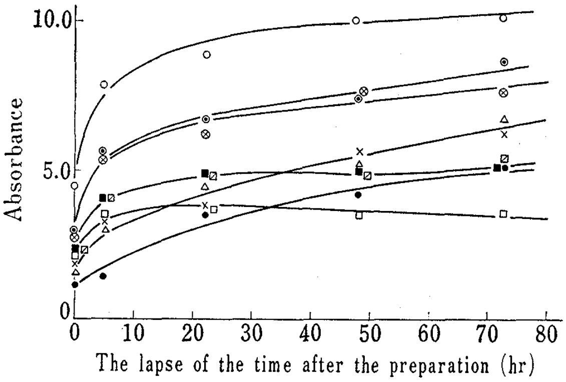

Fig. 10. Influence of the Time for Iodine–PVP–Ethanol Solutions Kept at 30° after the Preparation on Absorbance of the Solutions at 360 nm

1.1×10^{-2}M of iodine and 2.1×10^{-2}M of PVP (monomer unit)
—●—: absent of PVP
—×—: PVP K90
—△—: PVP K30
—○—: PVP K15
—▨—: PVP K90 ball-milled in nitrogen
—■—: PVP K90 ball-milled in air
—□—: PVP K90 ball-milled in oxygen
—⊙—: PVP K15 ball-milled in nitrogen
—⊗—: PVP K15 ball-milled in oxygen

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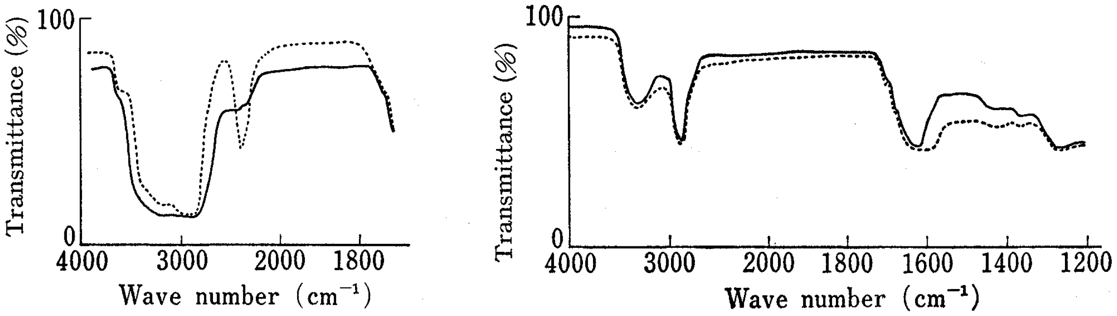
6) R.S. Mulliken, *J. Am. Chem. Soc.*, 72, 600 (1950); J.H. Hildebrand and B.H. Glascock, *ibid.*, 31, 26 (1909).
7) N. Kaneniwa, A. Ikekawa, and H. Hayase, *Chem. Pharm, Bull.* (Tokyo), 22, 2635 (1974).

absorbance of the solutions of original PVP increased with the lapse of the time, and the rate of an increase of absorbance at the initial stage was the largest in case of the solution of PVP K15. When the ratio was 1.9×10^2, absorbance of the solutions of original PVP increased at the initial stage and reached maximum, then decreased gradually with the lapse of the time. This tendency was remarkable in case of the solution of PVP K15. It was considered that interaction of PVP with iodine was influenced by the molecular weight of PVP. On the other hand, in case of the solutions of ball-milled PVP, variation of absorbance with the lapse of the time was small in both cases. It seems to be probable that dissociation of iodine in the solution of ball-milled PVP is not so remarkable as in the solution of original PVP.

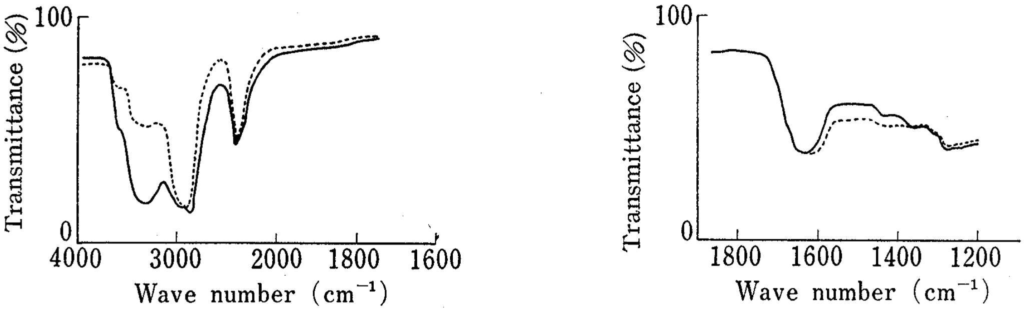
Ogata reported that, for cyclic amides in equimolar concentration of hydrochloric acid, the N-H absorption in the 3400—3500 cm^{-1} region was replaced by a broard absorption in the 2000—2400 cm^{-1} region. He reported the absorption at 2000—2400 cm^{-1} region to be due to the N^+H_2 stretching motion.[8] Kusakawa reported that the N-H absorption of aniline shifted from 3360 cm^{-1} to 2880 cm^{-1} by interacting with iodine just as with hydrochloric acid, accompanied by an increase of the absorption intensity, and considered this shift to be due to the binding of $-N^+H_2—I_2^-$.[9] As shown in Fig. 11, a new band appeared at 2400 cm^{-1} region by the addition of iodine to a chloroform solution of α-pyrrolidone. Probably, N^+ is formed in α-pyrrolidone molecules by the interaction with iodine. The new band at 2400 cm^{-1} region was also observed in the IR spectra of the chloroform solutions of PVP K90 ball-milled



———: 5.3×10^{-1}M of α-pyrrolidone
-------: 5.3×10^{-1}M of α-pyrrolidone and 1.9×10^{-2}M of iodine

———: 3.1×10^{-1}M of PVP K30 (monomer unit)
-------: 3.1×10^{-1}M of PVP K30 (monomer unit) and 1.9×10^{-2}M of iodine

Fig. 11. Influence of Addition of iodine on IR Spectra of Chloroform Solutions of α-Pyrrolidone and PVP



3.2×10^{-1}M of PVP K90 ball-milled in nitrogen (monomer unit)
———: without iodine
-------: with 1.9×10^{-2}M of iodine

2.8×10^{-1}M of PVP K90 ball-milled in oxygen (monomer unit)
———: without iodine
-------: with 1.9×10^{-2}M of iodine

Fig. 12. Influence of Addition of Iodine on IR Spectra of Chloroform Solutions of Ball-Milled PVP

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[8] N. Ogata, *Bull. Chem. Soc. Japan*, **34**, 248 (1961).

[9] H. Kusakawa, *Nippon Kagaku Zasshi*, **85**, 244 (1964).

in nitrogen. (Fig. 12). It is considered that N^+ is formed in the pyrrolidone rings of PVP ball-milled in nitrogen by the interaction with chloroform molecules. It seems to be probable that the chemical structure of PVP is partially changed by ball-milling in nitrogen. In these cases, a decrease of the transmittance around 1600 cm^{-1} region by the addition of iodine was not observed. In contrast with this finding, transmittance of the chloroform solutions of the other materials around 1600 cm^{-1} region decreased by the addition of iodine, but the new band at 2400 cm^{-1} did not appear in these cases. Kurosaki reported that the absorption of free C=O of α-pyrrolidone appeared at 1707 cm^{-1} and that the band shifted to a lower frequency by hydrogen-bonding.[10] It is suggested from this fact that a decrease of transmittance of the solution of PVP around 1600 cm^{-1} region by the addition of iodine is attributed to the interaction of iodine with oxygen of carbonyl groups of PVP. Figs. 9 and 10 show that the addition of ball-milled PVP K90 is not so effective for dissociation of iodine as the addition of original PVP. Furthermore, absorption around 370 nm was not observed in the chloroform solution of iodine and α-pyrrolidone under the experimental condition in Fig. 11. On the basis of these findings, it is considered as follows. It is necessary for iodine molecules to interact with oxygen of carbonyl groups of PVP in order to dissociate into triiodide anions and monoiodide anions. Formation of N^+ in PVP molecules or α-pyrrolidone molecules prevents iodine molecules from dissociation.

As shown in Figs. 13 and 14, broad signals were obtained around 2.2, 3.2 and 3.7 ppm of δ in the NMR spectra of deuterochloroform solutions of original PVP or ball-milled PVP. The signals were observed around 2.8 ppm of δ for the solutions of PVP K90 or PVP K30 and around 4.2 and 6.8 ppm of δ for the solutions containing large amount of PVP K15 or containing iodine. Three signals were obtained around 2.2, 3.2 and 7.7 ppm of δ in the NMR spectra of the deuterochloroform solutions of α-pyrrolidone. The number of protons to which each of the signals was attributed was calculated from the data of the area of the signlas. (Tables

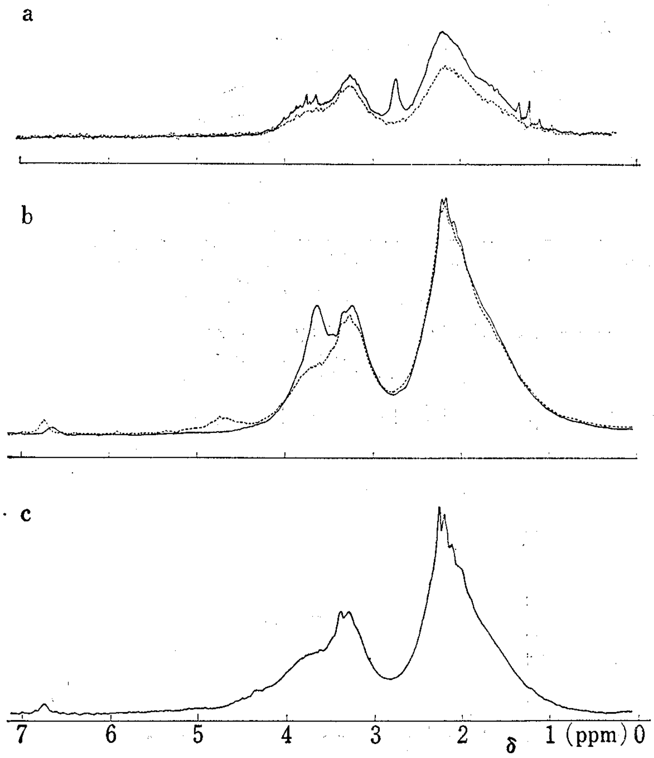

Fig. 13. Influence of Addition of Iodine on NMR Spectra of the Deuterochloroform Solutions of Original PVP

a 4.2×10^{-1}M of PVP K90 (monomer unit)
———: without iodine
-------: with 1.9×10^{-2}M of iodine
b 1.2M of PVP K15 (monomer unit)
———: without iodine
-------: with 1.8×10^{-2}M of iodine
c 2.3M of PVP K15

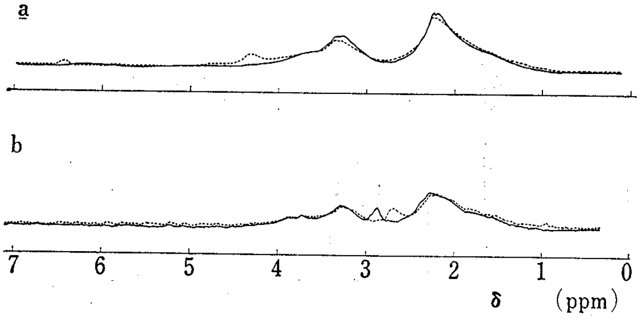

Fig. 14. Influence of Addition of Iodine on NMR Spectra of the Deuterochloroform Solutions of PVP K15 Ball-Milled in Oxygen

a 6.7×10^{-1}M of PVP K15 ball-milled in oxygen (monomer unit)
———: without iodine
-------: with 1.9×10^{-2}M of iodine
b 1.8×10^{-1}M of PVP K15 ball-milled in oxygen (monomer unit)
———: without iodine
-------: with 2.1×10^{-2}M of iodine

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[10] K. Kurosaki, *Nippon Kagaku Zasshi*, 82, 1691 (1961)

I and II). The NMR spectrum of 1-propyl-2-pyrrolidone was reported to be analysed as shown in Table III.[11] The NMR spectra of PVP and α-pyrrolidone were analysed as tabulated in Table IV on the basis of the analysis in Table III. In Table I, the signals of the solution of PVP K15 around 3.2 and 3.7 ppm partially shifted to higher values of δ by an increase of the concentration of PVP or by the addition of iodine. This tendency was also

Table I. Number of Protons to Which Each of the Signal in NMR Spectra of Deuterochloroform Solutions of PVP or α-Pyrrolidone is Attributed

	I[a]	II[b]	δ (ppm) 2.2	2.7—2.9	3.2	3.7	4.2—4.8	6.4—6.8	7.7
α-Pyrrolidone	6.5×10^{-1}		3.62		2.33				1.05
α-Pyrrolidone	6.5×10^{-1}	1.9×10^{-2}	3.86		2.24				0.91
PVP K15	4.6×10^{-1}		5.42		2.46	1.13			
PVP K15	2.3		5.45		2.24	0.80	0.43	0.08	
PVP K15	4.6×10^{-1}	1.8×10^{-2}	5.57		2.24	0.98	0.23		
PVP K30	3.4×10^{-1}		5.45	0.59	1.86	1.10			
PVP K30	1.0		5.43		2.17	1.40			
PVP K30	3.4×10^{-1}	1.8×10^{-2}	5.57		2.50	0.93			
PVP K90	4.2×10^{-1}		5.67	0.58	1.89	1.03			
PVP K90	4.2×10^{-1}	1.9×10^{-2}	5.61		2.42	0.97			

a) concentration of α-pyrrolidone or PVP (monomer unit) (M)
b) concentration of iodine (M)

Table II. Number of Protons to Which Each of the Signals in NMR Spectra of Deuterochloroform Solutions of Ball-Milled PVP is Attributed

	I[a]	II[b]	III[c]	δ (ppm) 2.2	2.7—2.9	3.3	3.7	4.3—4.8	6.4—6.8
PVP K15	Nitrogen	4.3×10^{-1}		5.62		2.29	1.09		
PVP K15	Nitrogen	4.3×10^{-1}	1.8×10^{-2}	5.28		2.09	1.44	0.19	
PVP K15	Oxygen	1.8×10^{-1}		5.20	0.84	1.85	1.12		
PVP K15	Oxygen	1.8×10^{-1}	2.1×10^{-2}	4.96	1.29	1.81	0.94		
PVP K15	Oxygen	6.7×10^{-1}		5.31		2.58	1.11		
PVP K15	Oxygen	6.7×10^{-1}	1.9×10^{-2}	5.29		1.98	0.87	0.70	0.17
PVP K90	Nitrogen	4.4×10^{-1}		6.02		1.95	1.03		
PVP K90	Nitrogen	4.4×10^{-1}	2.1×10^{-2}	5.83		1.90	1.27		
PVP K90	Air	2.4×10^{-1}		5.96		2.19	0.86		
PVP K90	Air	2.4×10^{-1}	2.1×10^{-2}	5.60		2.08	1.32		
PVP K90	Oxygen	4.7×10^{-1}		6.10		1.98	0.92		
PVP K90	Oxygen	4.7×10^{-1}	1.8×10^{-2}	5.03		2.66	1.30		

a) ball-milling atmosphere
b) concentration of PVP (monomer unit) (M)
c) concentration of iodine (M)

Table III. NMR Spectrum of 1-Propyl-2-pyrrolidinone

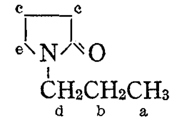
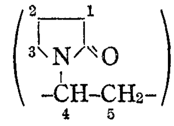
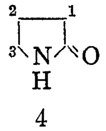
		δ
	a	0.96 ppm
	b	1.13—1.69
	c	1.85—2.42
	d	3.20 or 3.34
	e	3.34 or 3.20

Table IV. Analysis of the NMR spectra of PVP and α-Pyrrolidone

	A NMR spectrum of PVP Position	δ (ppm)		A NMR spectrum of α-pyrrolidone Position	δ (ppm)
	1, 2, 5	2.2		1, 2	2.2
	3	3.2		3	3.2
	4	3.7		4	7.7

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[11] The Sadtler standard spectra 7595M

observed in case of the addition of iodine to the solution of PVP K15 ball-milled in oxygen. The signal of the solution of PVP K30 and PVP K90 around 2.8 ppm shifted to higher values of δ by an increase of the concentration of PVP or by the addition of iodine. The similar phenomenon was also observed for the solution of PVP K15 ball-milled in oxygen when the concentration of PVP increased. But apparent variation was not observed in the spectra of the solutions of α-pyrrolidone by an increase of the concentration of α-pyrrolidone or by the addition of iodine.

It was shown in Tables I and II that, in case of PVP K15, the signals attributed to the protons around the carbon atoms adjacent to nitrogen atoms of pyrrolidone rings were influenced by the addition of iodine. It seems to be possible that iodine molecules interact with nitrogen atoms of pyrrolidone rings of PVP.

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