

Dissolution and Chain Dimensions of Nylon 6 in Metal Halide—Alcohol Systems

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ABSTRACT: The dissolution mechanism of Nylon 6 was investigated in connection with the chain conformations of the polymer in some complex solvents, such as the metal halide—alcohol systems. Infrared studies on both the polymer solutions and the metal halide—alcohol mixtures revealed that Nylon 6 forms a complex with the metal halide—alcohol complex solvent. The characteristic ratio ($\langle R_0^2 \rangle / nl^2 = 9.41$) of Nylon 6 was determined in a 15-g CaCl_2 /100-ml CH_3OH mixture at 35°C, a theta solution, and is considerably larger than Flory's value, 6.08, in which the specific solvent effects were not taken into account. It is pointed out how the solvent interactions affect the short-range interferences in the chain conformations in the complex solvent used in this work.

KEY WORDS Nylon 6 / Metal Halide—Alcohol Complex / Solubility / IR Spectra / Characteristic Ratio / Unperturbed Chain Dimension /

Though Nylon 66 is not soluble in alcohols at room temperature, it dissolves¹ in mixtures such as alkali halide—alcohol, alkaline earth metal—alcohol, and rhodanate—alcohol; in particular, this polymer easily dissolves in alcohol containing lithium chloride, calcium chloride, or zinc chloride. However, little has been reported on the dissolution mechanism of Nylon in these solvent systems or on the properties of these solutions.

Ford and Marshall² have performed analyses of the infrared and ultraviolet spectra of Nylon 66 in the LiCl —methanol, TiCl_4 —methanol, and SnCl_4 —amyl alcohol systems, and have pointed out that a coordination complex is formed between the metallic halide and the alcohol, with a coordinate bond between this complex and the amide oxygen atom of Nylon 66.

Aoki³ investigated the dissolution of Nylon 6 in CaCl_2 —methanol, and pointed out that when one of the methanol molecules coordinated to a Ca^{++} is removed, simultaneously the unpaired electron of the O atom in the amide group of Nylon 6 coordinates to the Ca^{++} . Thus, intermolecular hydrogen bonds, $>\text{C}=\text{O} \cdots \text{H}-\text{N}<$,

between the amide groups of Nylon 6 are destroyed and Nylon 6 dissolves in the solvent (see Figure 1). When water is added to such a Nylon solution (II), water molecules may be replaced by the CH_3OH molecules coordinated to Ca^{++} because of the considerable electronegativity of the water molecules. At the same time, the coordinate bond force between the O atom of the Nylon and the Ca-complex is diminished. Thus the insolubility of the polymer in alcohol is due to the formation of intermolecular hydrogen bounds.

For the chain conformations of Nylon, Saunders⁴ investigated the relation between the

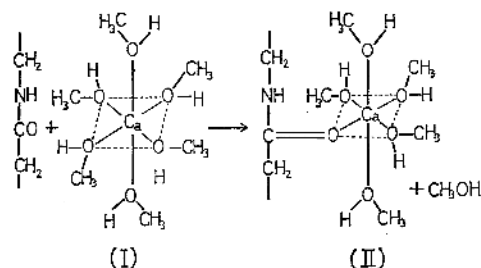


Figure 1. Dissolution mechanism of Nylon 6 in CaCl_2 —methanol system, as proposed by Aoki.³

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unperturbed mean-square end-to-end distance $\langle R_0^2 \rangle$ of the chain and the molecular weight M , using the viscosity data of Nylon 66 in a 90-% formic acid aqueous solution containing 2.3-mol/l KCl. He obtained a result of $[\langle R_0^2 \rangle / M]^{1/2} = 96 \times 10^{-10} \text{ cm mol}^{1/2} \text{ g}^{-1/2}$. Kurata and Stockmayer⁵ also reported $[\langle R_0^2 \rangle / M]^{1/2} = 89 \times 10^{-10}$ for Nylon 66 from viscosity data in *m*-cresol. On the other hand, Flory and Williams⁶ carried out theoretical calculations on $\langle R_0^2 \rangle$ for Nylon 66 and Nylon 6, and pointed out that the relation between $\langle R_0^2 \rangle$ and M obtained for both polymers is quite similar. We used the relationship between the molecular weight of Nylon 6 and the limiting viscosity number $[\eta]$ in a 90-% formic acid aqueous solution or in *m*-cresol, as reported by Watanabe,⁷ to determine the molecular weight of the polymer.

The purpose of this work is to investigate the complex formation and polymer chain conformations in metal halide—alcohol systems: in particular, in CaCl_2 —methanol for Nylon 6. The results will be compared with those for Nylon 66 reported by Ford², and for Nylon 6 proposed by Aoki.³

EXPERIMENTAL

Materials

Nylon 6 samples with different molecular weights were supplied through the courtesy of the Unitica Co. According to the purposes of the experiment these samples were fractionated. When fractionation was not necessary, the samples were purified twice in a formic acid—methanol system before use. If necessary, fractionations were carried out in a phenol—water system at 70°C. Alcohols and metal chlorides used were of Reagent Grade from Nakarai Chemical Co.

Solubility

A given amount of metal chloride was dissolved in alcohol under agitation in test tube at 30°C. Solubility of Nylon 6 in the solvent thus prepared was estimated by the content of the polymer dissolved after an agitation of 24 hr at 30°C while adding the polymer to the solvent.

Infrared Spectra

Infrared absorption spectra were measured

with a Nihon Kogaku Model DS-402G spectrophotometer at 30°C. Measurements were carried out using methanol solutions saturated with metal halide, and 10-g/dl-Nylon 6 solutions in these methanol solutions saturated with metal halide. For each case, a rock salt plate was used. The methanol used was Merk's Infrared Reagent Grade. Metal chloride were used after dehydrating with a vacuum pump under heating.

Viscosity Measurements

An Ostwald-type or Ubbelohde-type viscometer was used separately according to the purpose to obtain the limiting viscosity number $[\eta]$ from viscosity measurements. A characteristic feature in viscosity measurements for Nylon solutions in metal halide—alcohol systems is that the viscosity of the solvent (*i. e.*, metal halide—alcohol mixture) is high. Such behavior is attributed to the fact that these complex solvents (I in Figure 1) form hydrogen bonds with each other or with the alcohol molecules. The viscosity of the solvent is reduced by increasing the amount of water added.

RESULTS AND DISCUSSION

Solubility of Metal Chlorides in Alcohols

Table I shows the experimental results for the solubility (g metal halide in dl alcohol) of metal halides in several aliphatic alcohols at 30°C.

Table I. Solubility of metal halides, anhydrides, and hydrides in aliphatic alcohols at 30°C

Metal halide	Solubility, g halide/dl alcohol			
	Methanol	Ethanol	<i>n</i> -Butanol	<i>i</i> -Propanol
LiCl	40	20	10	Very small
CaCl ₂	30	25	7	Very small
CaCl ₂ ·H ₂ O	50	40	—	—
CaCl ₂ ·2H ₂ O	75	65	—	—
CaCl ₂ ·4H ₂ O	100	90	—	—
CaCl ₂ ·6H ₂ O	150	125	—	—
ZnCl ₂	120	100	20	Very small
MgCl ₂ ·6H ₂ O	Very large	Very large	—	Very small

Solubility of Nylon 6 in Metal Chloride—Alcohol Mixtures

The solvent compositions in which 0.2-g Nylon 6 can be dissolved to form an alcohol—metal

Table II. Composition range of metal chloride—alcohol mixtures in which Nylon 6 can be dissolved at 30°C

Metal halide	Solvent composition (g halide/dl alcohol)		
	Methanol	Ethanol	<i>n</i> -Butanol
LiCl	15—40	10—20	Insoluble
CaCl ₂	7—30 (50—12) ^a	5—25 (48—10) ^a	Insoluble
CaCl ₂ ·H ₂ O	10—50 (40—8) ^a	10—40 (28—7) ^a	Insoluble
CaCl ₂ ·2H ₂ O	15—75 (31—5) ^a	10—65 (32—5) ^a	Insoluble
CaCl ₂ ·4H ₂ O	30—100 (19—6) ^a	15—90 (27—4) ^a	Insoluble
CaCl ₂ ·6H ₂ O	50—150 (14—5) ^a	50—125 (10—4) ^a	Insoluble
ZnCl ₂	25—120	20—100	Insoluble

^a Numbers in parentheses denote the mol ratio of alcohol to Ca in the solvent systems in which Nylon 6 is dissolved.

chloride mixture at 30°C are shown in Table II.

As is obvious from Tables I and II, the upper concentration limit of the metal halide in alcohol corresponds to the saturation concentration for each system. Generally, the solubility of Nylon 6 is reduced with decreasing concentration of metal halide from its saturation concentration and ultimately becomes zero. The lower limit concentration denotes the solvent composition at which the solubility of Nylon 6 becomes zero. The effect of hydrated water is as follows: the solubility of Nylon 6 in mono- and dihydride is not so different from that in the anhydride, but is reduced considerably in the tetrahydride. In the hexahydride, the Nylon 6 swells but cannot be dissolved.

The decrease in solubility seems to be more noticeable with methanol than with ethanol. The solubility of Nylon 6 is extremely low in butanol for each system. If we assume the coordination number of Ca to be 6, as shown in Figure 1, the numbers (mol alcohol/mol Ca) appearing in parentheses in Table II are quite reasonable.

We point out that a CaCl₂—methanol or CaCl₂—ethanol mixture containing a comparatively small amount of CaCl₂ can dissolve Nylon 6, and the addition of water reduces the

solubility of Nylon 6. Aoki³ has reported that Nylon 6 is not soluble in a MgCl₂—methanol mixture, but our result shows that methanol solutions saturated (at room temperature) with MgCl₂ can dissolve more than 5 g/dl of Nylon 6 at 40°C.

Solubility of Nylon 6 in HCl—Alcohol Mixtures

Additional investigation were performed with HCl in place of the metal chlorides. The alcohols used were methanol, ethanol, plus benzyl alcohol, and ethylene glycol. These alcohols were saturated with HCl gas at 0°C. The concentrations of HCl in methanol and ethanol were 1.9 and 3.0 mol%, respectively.

Table III. Solubility of Nylon 6 in HCl—alcohol saturation solutions at room temperature

HCl—Alcohol	Solubility of Nylon 6
HCl—Methanol	very large
HCl—Ethanol	very large
HCl—Benzyl alcohol	large
HCl—Ethylene glycol	large

A methanol solution saturated with HCl (1.9 mol%) dissolved more than 10 g/dl of Nylon 6 at room temperature. Moreover, the precipitation temperature of this solution was observed to be slightly below room temperature.

Infrared Spectra of Metal Chloride—Methanol, and of Nylon 6 in Metal Chloride—Methanol Mixtures

The OH stretching frequency ν_{OH} of the OH of methanol in the metal chloride—methanol mixtures (Table IV) decreases in the order of Cs > Li > H, Ba > Sr > Ca > Mg > Ti. The polarizability of an ion is proportional to z/r^2 , in which z and r are the valency of the ion and the ion radius, respectively; it reflects the strength of the electrostatic field of the ion. In Table V are the polarizabilities of metal ions, calculated by using Goldschmit's⁸ values for the ion radii.

As is obvious from Table V, z/r^2 decreases in the order of Ti > Mg > Ca > Li > Sr > Ba > Cs. This result is in accord with that obtained for ν_{OH} except that the order of Li and Sr is inverted. $\Delta\nu_{OH}$ in Table IV gives the shift of the OH stretching frequency of the alcohol due to complex formation with the metal halide

Table IV. Infrared absorption spectra of metal chloride-methanol mixtures and of Nylon 6 dissolved in these mixed solvents (30°C)

Metal halide	Mixed solvent		Nylon 6 in mixed solvent		
	OH stretching		Amide I (C=O stretching)		Amide II
	ν_{OH} , cm ⁻¹	$\Delta\nu_{\text{OH}}$, cm ⁻¹	ν_{CO} , cm ⁻¹	$\Delta\nu_{\text{CO}}$, cm ⁻¹	ν , cm ⁻¹
TiCl ₄	3200 ^a	450 ^a	1607 ^a	80 ^a	
TiCl ₄			1610	77	1555
MgCl ₂	3260	400	1635	52	1560
CaCl ₂	3290	360	1635	52	1565
SrCl ₂	3310	340	1635	52	1550
BaCl ₂	3320	330			
HCl	3320	330	1655	32	1540
LiCl	3325 ^a				
LiCl	3320	330	1655	32	1555
CsCl	3330	320			
CaCl ₂ -N-Methyl acetamide			1640	47	1580

^a Data of Ford and Marshall.²

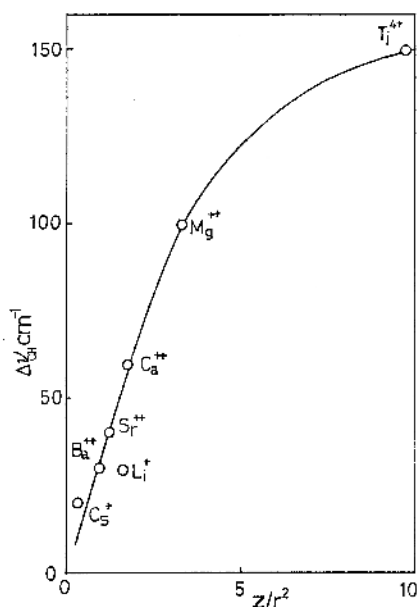
$\Delta\nu_{\text{OH}}$: Shift of the alcohol OH stretching frequency on complexing with metal chloride (free OH frequency, 3650 cm⁻¹).

$\Delta\nu_{\text{CO}}$: Shift of the amide CO stretching frequency from the nonassociated frequency at 1687 cm⁻¹.

Table V. Radius and polarizability of metal ions

Metal cation	Ion radius, (Å)	z/r^2
Li ⁺	0.78	1.6
Cs ⁺	1.65	0.4
Mg ⁺⁺	0.78	3.3
Ca ⁺⁺	1.06	1.8
Sr ⁺⁺	1.27	1.2
Ba ⁺⁺	1.43	1.0
Ti ⁺⁺	0.64	9.8

relative to the frequency² 3650 cm⁻¹ for free OH. Alternatively, the reference frequency may be taken as 3350 cm⁻¹ by taking into account the shift (300 cm⁻¹) due to the hydrogen bonding between methanol molecules. Thus, $\Delta\nu$ ($=\Delta\nu_{\text{OH}}-300$) was plotted against z/r^2 in Figure 2. $\Delta\nu$ increases with increasing strength of the electrostatic field of the ion. Such a result suggests that some of the methanol molecules contact directly with a metal ion at a distance corresponding to the ion radius.

**Figure 2.** Shift $\Delta\nu$ of the OH-stretching frequency for metal cation-methanol systems, plotted against the polarizability of metal cations (30°C).

ν_{CO} , $\Delta\nu_{\text{CO}}$, and ν in Table IV concern Nylon 6 dissolved in methanol-metal chloride mixtures. The amide I band is assigned to the C=O stretching frequency of the amide group. In accordance with the valency of the coexisting metal cation, ν_{CO} takes three different values, i. e., 1655 cm⁻¹, 1635 cm⁻¹, and 1610 cm⁻¹, respectively, for uni-, di-, and tetravalent cations. By assuming the CO stretching frequency of the nonassociated amide² to be 1687 cm⁻¹, the frequency shift from there was designated as $\Delta\nu_{\text{CO}}$. The fact that the values of $\Delta\nu_{\text{CO}}$ for three divalent cations, Mg, Ca, and Sr, are identical, in spite of the difference in their ionic radii, suggests that the coordinate bond strength between the cation and the carbonyl oxygen atom is independent of the ionic radii of the divalent cations. The model (II) in Figure 1, in which the metal cation and the carbonyl oxygen atom are assumed to contact each other at the ion radius and the van der Waals radius, respectively, may not be the decisive one. For the distance between the metal cation and the carbonyl oxygen atom may be somewhat larger than the sum of the ion radius and van der Waals radius, because of

interactions between the methylene group of Nylon and the methanol molecules coordinating to the metal cations. When this distance becomes sufficiently large, the effect of the ion radius of the metal cation may disappear. In the case of divalent cations, $\Delta\nu_{\text{OH}}$ varies from 400 cm^{-1} for Mg to 330 cm^{-1} for Ba, but $\Delta\nu_{\text{CO}}$ does not vary for either cations and remains at 52 cm^{-1} . The difference in the infrared absorption spectra between univalent and tetravalent cations may be understood from electrostatic interactions. The amide II band has been assigned⁹ to the coupling of $\delta(\text{NH})$ with $\nu(\text{C}-\text{N})$, and is known to appear at 1560 cm^{-1} for Nylon 6 itself. Numerical values of ν listed in Table IV are approximately constant within $\pm 5\text{ cm}^{-1}$, except the one for the H^+ system. This result may mean that the conformation of this atomic group is not largely affected by the presence of a solvent. On the last line of Table IV, numerical values for *N*-methyl acetamide— CaCl_2 system are shown for comparison.

Later, we will refer further to the interaction of these complex solvents with Nylon 6, in relation to the chain dimensions of Nylon in these solvents.

Relation between $[\eta]$ and M in CaCl_2 —Methanol Systems

The molecular weight M of Nylon 6 was estimated from $[\eta]$ in dl/g at 25°C by using eq 1, which was obtained by rearranging the result reported by Watanabe.⁷

$$[\eta] = 1.10 \times 10^{-3} M^{0.72}, \quad \text{in 90-\% formic acid aq solution} \quad (1)$$

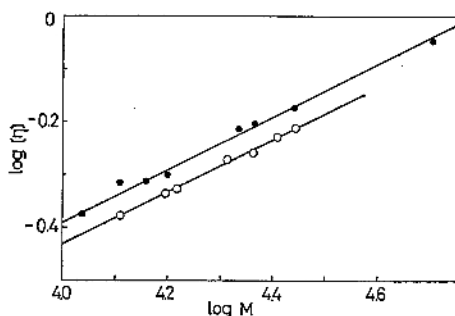


Figure 3. Relation between M of Nylon 6 and $[\eta]$ in CaCl_2 —methanol systems at 35°C . Solvent composition: (O) 15-g CaCl_2 /dl methanol; (●) 20-g CaCl_2 /dl methanol.

Figure 3 shows the relations between the molecular weight M and the $[\eta]$ at 35°C in 15-g CaCl_2 /dl methanol and in 20-g CaCl_2 /dl methanol systems for fractionated Nylon 6 samples. Two straight lines in Figure 3 lead to the following equations:

$$[\eta] = 3.68 \times 10^{-3} M^{0.50}, \quad \text{in 15-g } \text{CaCl}_2/\text{dl } \text{CH}_3\text{OH} \quad (2)$$

$$[\eta] = 3.86 \times 10^{-3} M^{0.506}, \quad \text{in 20-g } \text{CaCl}_2/\text{dl } \text{CH}_3\text{OH} \quad (3)$$

The exponents of M in 15-g/dl- and 20-g/dl- CaCl_2 solutions are 0.500 and 0.506, respectively. This fact means that the former solution just satisfies the theta condition and the latter one is very close to the theta solution. The experimental results were plotted according to Fixman's equation¹⁰ in Figure 4. From the intercept on the ordinate, we obtain K_θ in the equation $[\eta] = K_\theta M^{0.5}$ as $K_\theta = 3.68 \times 10^{-3}$. Further, we estimate the ratio of the unperturbed mean-square end-to-end distance $\langle R_0^2 \rangle$ to the molecular weight M , from the equation $K_\theta = \Phi_0 [\langle R_0^2 \rangle / M]^{3/2}$, by using the value $\Phi_0 = 2.5 \times 10^{21}$:

$$[\langle R_0^2 \rangle / M]^{3/2} = 1.14 \times 10^{-8} \text{ cm mol}^{1/2} \text{ g}^{-1/2} \quad (4)$$

Finally we calculate the characteristic ratio, defined by $\langle R_0^2 \rangle / n\bar{l}^2$, where n is the number of chemical bonds in a Nylon chain and \bar{l} is the average length of the bond, $\bar{l} = 2.22\text{ \AA}$:

$$\langle R_0^2 \rangle / n\bar{l}^2 = 9.41 \quad (5)$$

In Table VI, the characteristic ratios experimentally obtained for Nylon 66 by Saunders⁴ and theoretically calculated for Nylon 6, Nylon 66, and a model polymer by Flory and Williams⁶, were compared with our result.

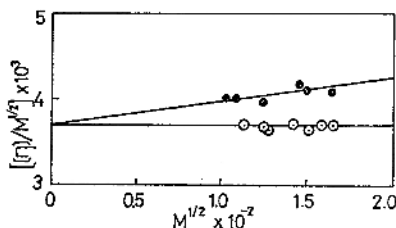


Figure 4. Fixman's plots for Nylon 6 in CaCl_2 —methanol systems. Solvent composition: (O) 15-g CaCl_2 /dl methanol; (●) 20-g CaCl_2 /dl methanol.

Table VI. Comparison of characteristic ratios of Nylon

Author	Polymer	K_θ	$\langle R_0^2 \rangle / nl^2$	°C	Solvent
this work	Nylon 6	3.68×10^{-3}	9.41	35	CaCl ₂ —CH ₃ OH
Saunders ⁴	Nylon 66	1.92×10^{-3}	6.10	25	2.3-M KCL/90-% formic acid
Flory ⁶	Nylon 6		6.08	25	calculation
Flory ⁶	Nylon 66		6.10	25	calculation
Flory ⁶	Model polymer including <i>trans</i> -CH ₂ —CH ₂ in place of CO—NH of Nylon 6.		8.93	25	calculation

Saunders⁴ reported that an aqueous solution of 90-% formic acid including 2.3-mol/l KCl acts as a theta solvent for Nylon 66 at 25°C, and obtained $K_\theta = 1.92 \times 10^{-3}$. This value, using $\Phi_0 = 2.5 \times 10^{21}$, leads to $\langle R_0^2 \rangle / nl^2 = 6.10$, as shown in Table VI. Flory and Williams,⁶ on the other hand, have theoretically estimated the characteristic ratio as $\langle R_0^2 \rangle / nl^2 = 6.08$ by using the statistical weights σ 's and ω 's for the three-bond and four-bond interactions, respectively. They assigned $\sigma = 0.43$, $\sigma_\alpha = \sigma_\beta = \sigma_\gamma = \sigma_\delta = 1$, $\omega = 0.034$, and $\omega_\alpha = \omega_\beta = \omega_\gamma = \omega_\delta = 0.10$, and derived $\langle R_0^2 \rangle / nl^2 = 6.08$ for Nylon 6. Saunders' experimental characteristic ratio coincides with Flory's theoretical one. Our experimental value is larger than Flory's value by more than 50%, and also larger than the value 8.0 for polyethylene. Flory⁶ also calculated the characteristic ratio for a virtual polymer which replaces the CO—NH of Nylon 66 by a *trans*-CH₂—CH₂; using $\sigma = 0.43$ and $\omega = 0.034$, he obtained $\langle R_0^2 \rangle / nl^2 = 8.93$. This value is rather close to our experimental value 9.41.

The difference between our experimental value

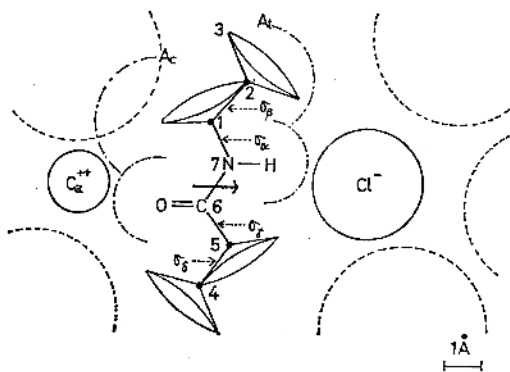


Figure 5. Dissolution of Nylon 6 in the CaCl₂—methanol system.

and Flory's theoretical value for the $\langle R_0^2 \rangle / nl^2$ of Nylon 6 can be explained by taking into account the specific solvent effect for the unperturbed chain dimension in a complex solvent such as those used in the present study.

We propose a model, indicated in Figure 5, for Nylon 6 dissolved in a CaCl₂—methanol mixture. In this figure, the symbols σ 's are the same as Flory's⁶. The filled circle denotes the methylene unit, and the arrow designates the dipole moment (3.7 Debye¹¹) of the amide group. Further, the broken circle (-----) denotes the van der Waals' radius for methanol, assumed to be 2.5 Å, and circles A_t and A_c represent the van der Waals' radii (2.0 Å) for the methylene groups C₍₂₎ which are located at the *trans* and *cis* conformations around the bond N₍₁₎—C₍₁₎. For Ca⁺⁺ and Cl⁻, circles were drawn with their ion radii.

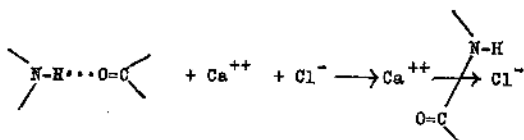
To stabilize the large dipole moment of the amide group, the cation Ca⁺⁺ and the anion Cl⁻ may locate approximately on the amide plane in the direction of the dipole. Either the cation or the anion forms a complex with the methanol; since the former is smaller than the latter in its ion radius, the cation is more strongly solvated than the anion. For example, the electric displacement e/r^2 at $r = 2$ Å from the center of a univalent ion is extremely large: $e/r^2 = 1.2 \times 10^6$ e. s. u. Thus, the nearest neighbor molecule may be strongly oriented toward the ion.

Flory and Williams⁶, in the calculation of the chain dimension, designated σ the statistical weight factor of the gauche (+) or gauche (-) conformation normalized to a weight of unity for the *trans* conformation, and assigned $\sigma_\alpha = \sigma_\beta = \sigma_\gamma = 1$ and $\sigma_\delta = 0.5-1$ for the four methylene units adjoining the amide group, *i. e.*, C₍₁₎, C₍₂₎, C₍₃₎ and C₍₄₎. For the other

methylene, $C_{(3)}$, they assigned $\sigma=0.43$ on the basis of a calculation for polyethylene. In other words, with respect to the four methylene units adjoining to the amide group, Flory's model is very close to the free rotation model. Such a model leads, as a matter of course, to a rather small characteristic ratio.

To explain the numerical value of the characteristic ratio of Nylon 6 obtained in this work from measurements in the CaCl_2 -methanol system, the statistical weight factors used by Flory seem to be inadequate. The methylene units in our solvent system may have some interactions with the nearest neighbor methanol molecules solvated to the ions, and thus the amide group may be sandwiched with these solvated ions. Such interactions would reduce σ_a , σ_β , σ_γ , and σ_δ from unity and make the characteristic ratio larger. Thus the numerical value, $\langle R_0^2 \rangle / nl^2 = 9.41$, obtained by us may be explained at least qualitatively. In our case, the solvent contributes to the short-range interference of the polymer chain. As mentioned above, the infrared spectra have indicated that the cation Ca^{++} does not contact directly with the $\text{C}=\text{O}$ (at a distance equal to the sum of the ion radius of Ca^{++} and the van der Waals' radius of $\text{C}=\text{O}$). This fact does not contradict our suggestion that some interactions exist between the methylene group and the methanol molecules.

Finally, we briefly mention the dissolution of Nylon 6 in the CaCl_2 -methanol system. For the amide portion, we have the following scheme:



If the decrease of the free energy in this process overcomes the change of the free energy for all other portions, then Nylon 6 will be dissolved in this solvent system.

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