Molecular Characterization of Nylon 6,6 and Its Dissolved State in Mixture of Calcium Chloride and Methanol

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ABSTRACT: An attempt was made to evaluate molecular parameters of poly(hexa-methyleneadipamide) (nylon 6,6) in mixture of calcium chloride and methanol with various calcium chloride concentrations (weight fraction W_{ca} against weight of the solvent mixture) using light scattering method. Dissolved state of the polymer was discussed in connection with the chain conformation based on data of viscosity, adiabatic compressibility, infrared (IR) spectra and ^1H and ^{13}C NMR spectra. The second virial coefficient A_2, obtained by the light scattering method, remarkably decreases with a decrease of W_{ca} below 0.15 and is expected to become zero at W_{ca} of ca. 0.115 (i.e., Flory's Θ solvent). From values of conformation parameter and characteristic ratio of the polymer, evaluated from radius of gyration at the Θ state, the nylon 6,6 molecule is judged to be very flexible in the unperturbed state. The viscosity of the polymer solution showed specific W_{ca} dependence, around $W_{ca} = 0.15$. The results of the viscosity, adiabatic compressibility, IR and NMR measurements on the solvent mixtures revealed that the above $W_{ca} = ca.$ 0.05, mole ratio of the undissociated $CaCl_2$ monotonically increases with W_{ca} and methanol molecules strongly interact with calcium chloride probably forming organometallic complex. The results of ^1H and ^{13}C NMR and IR measurements on the polymer solutions suggested that dissolution of nylon 6,6 in calcium chloride-methanol mixture with $W_{ca} \geq 0.1$ is realized at least by interaction of methanol and chlorine parts in the complex with amide carbonyl and amine: In the range of $0.1 \leq W_{ca} < 0.15$, selective absorption of weakly bound methanol molecules with the complex to nylon 6,6 plays an important role to determine the very compact chain conformation of the nylon 6,6 chain. Above $W_{ca} = 0.15$ dissolution of nylon 6,6 takes place by direct interaction of the very bulky and meta-stable associate form of solvent to polymer, which brings about large expansion of the nylon 6,6 chain in the solution.

KEY WORDS   Nylon 6,6 / Calcium Chloride and Methanol Mixture /
Viscosity / Light Scattering / Unperturbed Chain Dimension / Adiabatic
Compressibility / NMR / Metallic Halide Complex / Polymer-Solvent
Complex Interaction /

An industrial importance of poly(hexa-methyleneadipamide) (nylon 6,6) as a base material of fibers and engineering plastics has promoted its molecular characterization studies since 1960s. The pioneering studies were carried out by Saunders[1,2] and Elias and Schumacher[3] mainly using viscometric method. From reanalysis on the viscosity data reported by Elias and Schumacher, Kamide et al.[4] found that the unperturbed chain dimension A of nylon 6,6 in organic and acid solvents notably differs from solvent to solvent, ranging from 0.083 to 0.114 nm. Regarding the dissolved state of the nylon 6,6 in the solvent, Saunders[2,5-7] found that the nylon 6,6 molecular chains show a polyelectrolyte nature in aqueous acid solutions, such as aq 90 wt% formic acid soln and aq concd sulfuric acid

soln, owing to protonation of the polymer amide groups. Holms et al.[8,9] carried out ^{1}H, ^{13}C, and ^{15}N NMR measurements on the nylon 6,6 with the number-average molecular weight M_n of about 1.5×10^4 in trifluoroacetic acid (TFA), indicating that TFA molecules strongly interact with amide groups of the polymer chains. Ford and Marshall[10] studied on the dissolved state of nylon 6,6 in the mixture of alcohol and inorganic salt, such as methanol/LiCl, n-amylalcohol/SnCl$_4$ and methanol/TiCl$_4$, using infrared and ultraviolet spectroscopies. They reported that some kind of coordination complex is formed between the metallic halide and the alcohol molecules and the complex interacts selectively with amide groups of the nylon 6,6. From these results in the literature, we can readily expect that the chain conformation of the nylon 6,6 polymer in the solvent is primarily determined by the interaction between polar groups of nylon 6,6 and the solvent molecules. One of the typical mixture containing inorganic halide, calcium chloride-methanol system is also a solvent for aliphatic polyamides. Using this solvent with fixed calcium chloride concentration, Nakajima and Tanaami[11] discussed the chain flexibility of nylon 6 in view of the formation of polymer–metal halide complex based on infrared and viscosity data, concluding that methanol molecules associate with dissociated calcium and chloride ions leading to coordination complex, and this complex affects the short-range interference in the nylon 6 chain conformation. However, they did not investigate the detailed structure of the solvent complex as a function of the component of the mixture, accordingly the chain conformation of the polyamide. In addition, the difference in hydrogen bonding nature between nylon 6 and nylon 6,6 may influence on their solution properties, especially in such complex forming mixed solvent system.

In this study, an attempt was made to disclose chain conformation of the nylon 6,6 in the mixtures of calcium chloride–methanol using light scattering method, which has never been applied to this polymer solution successfully except for determination of the molecular weight,[1-3] and to elucidate the dissolved state of the nylon 6,6 in terms of the interaction between polymer and calcium chloride–methanol complex.

EXPERIMENTAL

Materials

Nylon 6,6 (Asahi Chemical Industry Co., Tokyo), polymerized by polycondensation method from hexamethylenediamine and adipic acid, was used as a starting sample (code PC1). The sample PC1 was subjected to solid phase polymerization at $220 \pm 10°C$ under purging of nitrogen gas with a flow rate of $400\,cm^3\,min^{-1}$ for 1 h. The limiting viscosity number $[\eta]$ of the sample obtained thus (code SP1) and the sample PC1 was determined from Huggins plots using aq 98% sulfuric acid soln as solvent at 25°C. The viscosity–average molecular weight M_v was estimated through the following Mark–Houwink–Sakurada[4] equation to be 1.55×10^5 for the sample SP1 and 3.6×10^4 for the sample PC1.

$$[\eta] = 6.3 \times 10^{-2} M_w{}^{0.73} \quad (cm^3\,g^{-1},\ 25°C) \tag{1}$$

where M_w is the weight-average molecular weight.

Solution Preparation

The mixture of calcium chloride and methanol was prepared by putting 0.22—0.25 g of anhydrous calcium chloride (guaranteed grade; the minimum CaCl$_2$ assay 95%; the maximum content of metals, such as iron, aluminum and barium, ca. 0.008%; Kishida Chemical Co., Osaka) into 0.78—0.75 g of distilled methanol. Hereafter, weight fraction of CaCl$_2$ in the mixture is termed as W_{ca} (w/w). The sample PC1 was swollen for one day in the mixture with W_{ca} ranging from 0.22 to 0.25 at room temperature and then dissolved at

632

80°C. In order to determine the lower limit of W_{ca} to be capable of dissolving the nylon 6,6, the methanol was added dropwise to the sample PC1 solution with $W_{ca} = 0.20$ until the solution started to reveal turbidity. W_{ca} determined thus was about 0.10.

Light Scattering

Refractive index n_0 of the solvent mixture with $W_{ca} = 0.125—0.20$ was measured by Abbe refractometer with an incident beam wave length λ_0 of 633 nm at 40°C.

The sample PC1 was dissolved in the mixture of $W_{ca} = 0.125—0.20$ at polymer concentration c (g cm^{-3}) of $(1—5) \times 10^{-3}$. The solution with $c = 4.8 \times 10^{-3}$ and $W_{ca} = 0.20$ was dialyzed using a commercially available cellulose membrane (Union Carbide Co., U.S.A.). Donnan membrane equilibrium was attained after 7 days dialysis. The specific refractive index increment at constant W_{ca} [$(dn/dc)_{W_{ca}}$] for the undialyzed solutions and at constant chemical potential of CaCl$_2$ [$(dn/dc)_\mu$] for the dialyzed solution was measured using differential refractometer type DR4 (Shimadzu, Kyoto) at 40°C with λ_0 of 633 nm. The solutions for the light scattering measurements were filtered through membrane made of polytetrafluoroethylene (Sumitomo Denko Co., Tokyo) with pore size of 0.1—0.45 μm, followed by direct pouring into the measurement cell. The intensity of scattered light was recorded on the light scattering apparatus, DLS-700 manufactured by Otsuka Electronics (Osaka) with λ_0 of 633 nm at 40 ± 0.1°C. The data were analyzed according to Zimm's procedure.

Viscosity Measurement

The viscosity of the solvent mixture with W_{ca} of 0—0.225 and the sample SP1 solution with $W_{ca} = 0.10—0.20$ was measured using Ubbelohde type viscometer at 40 ± 0.05°C. [η] and Huggins constant k' for the polymer solution were estimated from Huggins plot as an intercept at $c = 0$ and from a slope near $c = 0$, respectively.

Adiabatic Compressibility

Sonic velocity V of the solvent mixture with $W_{ca} = 0.001—0.20$ was measured using Nunisonics model 6080 Concentration Analyzer (MAPCO Inc., U.S.A.). The solution cell was immersed in water bath thermostatted at 40 ± 0.002°C. Adiabatic compressibility β of the mixture was evaluated through the relation:

$$\beta = \frac{1}{\rho V^2} \qquad (2)$$

where ρ is the density of the solvent mixture. The number of solvated solvent molecules to a solute molecule s was estimated according to Passynsky's equation[12,13]:

$$s = \frac{M}{m_s}\left(1 - \frac{\beta}{\beta_0}\right)\frac{(100 - W_{ca})}{W_{ca}} \qquad (3)$$

Here M and m_s are molecular weight of solute and solvent molecules, respectively. β_0 is β of the solvent. s of the methanol was estimated in the range from $W_{ca} = 0.001$ to 0.20 through eq 3.
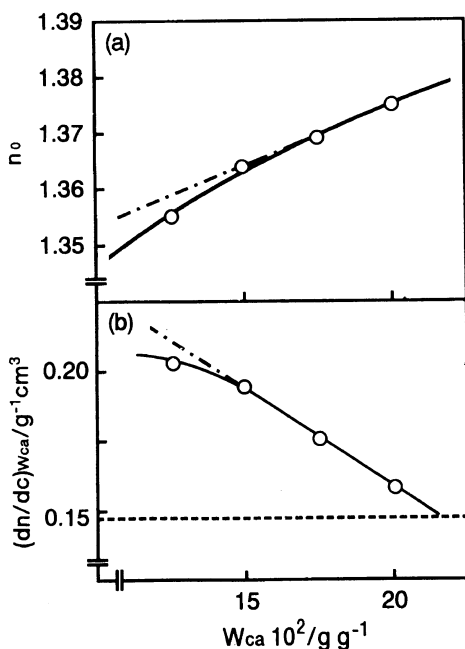
Nuclear Magnetic Resonance (NMR)

CaCl$_2$ and deuterated methanol (CD$_3$OD, Aldrich Chemical Co., Japan) mixture with CaCl$_2$ weight fraction of 0.087—0.184, corresponding to $W_{ca} = 0.10—0.20$, was prepared. Following the procedure described before, 0.02 g of the sample PC1 was dissolved in 1 cm^3 of each mixture except for one with $W_{ca} = 0.1$. Each mixture and the solution prepared were put into a sample probe with 5 mm diameter, together with tetramethylsilane as internal standard. ^{1}H and ^{13}C NMR spectra were recorded on NMR-FX200 (JEOL, Tokyo) at 40°C under the following conditions: Spectrum width, 2 kHz for ^{1}H NMR, 10 kHz for ^{13}C NMR; Pulse interval, 5, 4.6 s; flip angle, 7 μs = 45°, 6.5 μs = 45°; Number of accumulation, 8300—700 times.

CP/MAS ^{13}C NMR measurement on the sample PC1 was performed in the solid state using NMR-FX200 at 120°C under the fol-

lowing pulse conditions: spectrum width, 20 kHz; pulse interval, 5 s; flip angle, $5.5\,\mu s = 90°$; cross-polarization contact time, 2 ms; number of accumulation, 512 times.

Infrared Spectroscopy (IR)

Nylon 6,6 film was prepared from formic acid solution of the sample PC1 by solvent cast method followed by air drying. The air-dried film, the sample PC1 solution with $c = 0.01$ and $W_{ca} = 0.125$—0.2, and the solvent mixture with $W_{ca} = 0.125$—0.2 were sandwiched between two transparent plates made of KRS. IR spectra were recorded on a spectrometer model JIS-3505 FT-IR (JEOL, Japan). Differential spectra of nylon 6,6 solution and solvent mixture were obtained by subtracting IR spectrum of the solvent-mixture using absorbance at $1954.5\,cm^{-1}$ as standard.
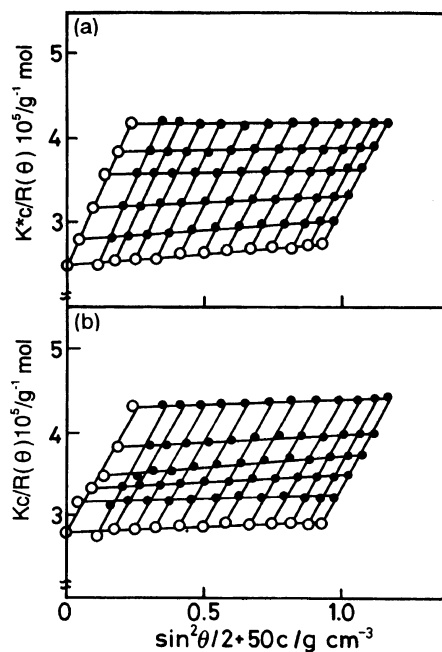
RESULTS AND DISCUSSION

n_0 of the solvent mixture and $(dn/dc)_{W_{ca}}$ of the undialyzed polymer solution is plotted against W_{ca} in Figure 1a and b, respectively. n_0 and $(dn/dc)_{W_{ca}}$ (solid line) monotonically change with an increase of W_{ca}, while a downward deviation at $W_{ca} = ca.$ 0.15 was observed for both plots. $(dn/dc)_{\mu}$ of the dialyzed solution is shown by a broken line in Figure 1b, for convenience.

Figure 2a and b representatively depict Zimm plots of the sample PC1 solutions with $W_{ca} = 0.20$ before and after dialysis. Both plots show little distortion even at low scattering angle θ, indicating that the solutions prepared were almost free from any contamination of dust and/or gel-like materials. From the plots of the undialyzed solutions, we estimated the apparent weight-average molecular weight $M_w{}^*$, the apparent second virial coefficient $A_2{}^*$ and z-average radius of gyration $\langle S^2 \rangle_z{}^{1/2}$,

Figure 1. Refractive index n_0 of the mixture of calcium chloride and methanol (a) and specific refractive index increment at constant W_{ca} [$(dn/dc)_{W_{ca}}$] for the undialyzed solutions (solid line) and at constant chemical potential of CaCl$_2$ [$(dn/dc)_{\mu}$] for the dialyzed nylon 6,6 solution (broken line) against CaCl$_2$ soln. with $W_{ca} = 0.2$ (b) at 40°C plotted against calcium chloride concentration W_{ca}.

Figure 2. Zimm plots of nylon 6,6 (sample code PC1) solutions with $W_{ca} = 20\%$ at 40°C. Undialyzed (a) and dialyzed (b).

Table I. Results on the light scattering measurements on undialyzed and dialyzed nylon 6,6
(the sample code PC1) in mixture of calcium chloride and methanol with calcium
concentration W_{ca} ranging from 12.5 to 20% at 40°C and expansion factor α_s[a]

W_{ca}	$M_w^* \times 10^{-4}$	$M_w \times 10^{-4}$	$A_2^* \times 10^3$	$A_2 \times 10^3$	$\langle S^2 \rangle_z^{1/2} \times 10^6$	α_s
%	$g\,mol^{-1}$	$g\,mol^{-1}$	$mol\,cm^3\,g^{-2}$	$mol\,cm^3\,g^{-2}$	cm	
12.5	2.54	—	1.00	0.56	0.69	1.08
15.0	2.86	—	1.47	9.53	0.91	1.42
17.5	3.33	—	1.57	1.19	1.16	1.81
20.0	3.76	—	1.59	1.36	1.29	2.01
Dialyzed	—	4.41	—	1.20	1.19	1.86

[a] M_w^*, M_w, the apparent and true weight-average molecular weight; A_2^*, A_2, the apparent and true second virial coefficient; $\langle S^2 \rangle_z^{1/2}$, the z-average radius of gyration.

which are summarized in Table I.

M_w^* and M_w relate to the reduced scattering intensity $R(\theta)$ as follows[14]:

$$\left[\frac{K^*c}{R(\theta)} \right]_{c=0} = [M_w^* P(\theta)]^{-1} \qquad (4\text{-}1)$$

$$\left[\frac{Kc}{R(\theta)} \right]_{c=0} = [M_w P(\theta)]^{-1} \qquad (4\text{-}2)$$

where $P(\theta)$ is a scattering function and K^* and K are optical constants given as follows:

$$K^* = \frac{2\pi^2 n_0^2}{\lambda_0^4 N_A} \left(\frac{dn}{dc} \right)_{W_{ca}}^2 \qquad (5\text{-}1)$$

$$K = K^* \left[\frac{\left(\frac{dn}{dc} \right)_\mu}{\left(\frac{dn}{dc} \right)_{W_{ca}}} \right]^2 \qquad (5\text{-}2)$$

Here N_A is the Avogadro's number.

The second virial coefficient A_2 is described in terms of M_w^*, M_w and A_2^* as follows[14]:

$$A_2 = \frac{M_w^*}{M_w} A_2^* \qquad (6)$$

Substitution of M_w^*, M_w and A_2^* obtained experimentally into eq 6 gives us A_2.

Selective adsorption parameter ξ_a is defined as follows[14]:

$$\xi_a = \left(\sqrt{\frac{M_w^*}{M_w}} - 1 \right) \frac{\rho_{soln} \left(\frac{dn}{dc} \right)_{W_{ca}}}{\rho_{ca} \left(\frac{dn_0}{dW_{ca}} \right)} \qquad (7)$$

where ρ_{soln} and ρ_{ca} are the density of the polymer solution and calcium chloride in the mixture, respectively. In this study, the density of the solvent mixture ρ determined using picnometer at 40°C was used as the value of ρ_{soln}, because the polymer solutions prepared here were sufficiently dilute and ρ_{ca} was assumed to be unity.

Figure 3a, b and c show W_{ca} dependence of M_w^*, ξ_a (a), A_2^*, A_2 (b) and $\langle S^2 \rangle_z^{1/2}$ (c) for the sample PC1. In the whole range of W_{ca} investigated, ξ_a is negative due to the relation of $M_w^* < M_w$ (broken line) and increases linearly with W_{ca}, indicating that methanol molecules selectively solvate to the polymer chain and amount of the solvated molecules decreases with an increase of W_{ca}. Details of interaction between polymer and solvent molecules are discussed latter. A_2^* and A_2 remarkably increase with W_{ca} in the range $W_{ca} < 0.15$ and A_2^* seems to approach an asymptotic value at $W_{ca} \geqq 0.175$. These W_{ca} dependence of ξ_a, A_2^* and A_2 suggest at least that adsorption behavior of the solvent mixture onto nylon 6,6 is different below and above $W_{ca} = 0.15$—0.175. $A_2 = 0$ is realized at $W_{ca} =$
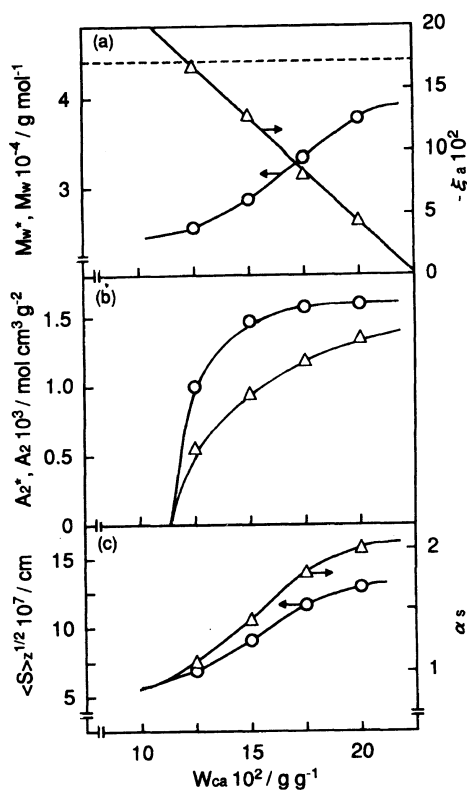
Figure 3. The apparent and true weight-average molecular weight M_w^*, M_w (dotted line), adsorption parameter ξ_a (broken line) (a), the apparent and true second virial coefficient A_2 (b) and z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ (c) plotted against calcium chloride concentration W_{ca}.

ca. 0.115, indicating that the calcium chloride-methanol mixture with W_{ca} of about 0.115 is expected to be the Flory's Θ solvent for nylon 6,6 at 40°C. $\langle S^2 \rangle_z^{1/2}$ at $A_2 = 0$, i.e., the radius of gyration at unperturbed state $\langle S^2 \rangle_{z,0}^{1/2}$, is 6.4 nm for this sample. From $\langle S^2 \rangle_{z,0}^{1/2}$ value, the linear expansion factor α_s, defined as $\alpha_s = \langle S^2 \rangle_z^{1/2} / \langle S^2 \rangle_{z,0}^{1/2}$, is estimated (triangle in Figure 3c). Owing to the increase of the interaction between polymer and solvent molecules as discussed later, the nylon 6,6 chains expand with W_{ca}, approaching to an asymptotic value near $W_{ca} = 0.2$.

The unperturbed chain dimension A of the Gaussian chain is written as a function of the radius of gyration as follows:

$$A = \sqrt{\frac{6 \langle S^2 \rangle_{w,0}}{M_w}} \qquad (8)$$

Here, $\langle S^2 \rangle_{w,0}^{1/2}$ is the weight-average radius of gyration of the polymer chain at the unperturbed state and relates to $\langle S^2 \rangle_{z,0}^{1/2}$, when molecular weight distribution function (MWDF) of the polymer is Schultz–Zimm type through the following equation:

$$\langle S^2 \rangle_{w,0}^{1/2} = \sqrt{\frac{h+1}{h+2}} \langle S^2 \rangle_{z,0}^{1/2} \qquad (9)$$

where

$$h = \left(\frac{M_w}{M_n} - 1 \right)^{-1} \qquad (10)$$

M_n is the number-average molecular weight. Hattori et al.[15] carried out successive precipitation fractionation of the sample PC1, using a mixture of phenol/tetrachloroethane (4/6 w/w) as a solvent and n-heptane as a coagulant, finding that MWDF estimated by the cumulative method can be approximated to be Schultz–Zimm type with $M_w/M_n = 2$ with high accuracy.

Substitution of M_w and $\langle S^2 \rangle_{w,0}^{1/2}$, which is estimated from eq 9 and 10, into eq 8 gives us A of the nylon 6,6 to be 0.061 nm. This value is appreciably smaller than the reported values of A in various good solvents (0.083—0.114 nm)[4] and in aq 90% formic acid with 0.23M KCl (0.096 nm). The latter solvent is also an another Flory's Θ solvent for the nylon 6,6 according to Saunders.[1,2] Note here that all of these A are determined by the viscosity methods, such as Stockmayer–Fixman[2,3] and Kamide methods.[4] However, both methods include two essential problems; one is uncertainty of the value of the Flory's viscosity parameter, which reportedly ranges from 2.2×10^{23} to 2.87×10^{23} (cm³ g⁻¹) in the literature; the other is that both methods are only applicable to the system where draining effect can be completely neglected.[16] Unfortunately, for the nylon 6,6 solutions, it has never been

Table II. Comparison of conformation parameter σ and characteristic ratio C_∞ of various synthetic and derivatized natural polymers determined by light scattering method in Θ solvent[17] except for the nylon 6,6

Polymer	Solvent	Temp/°C	σ	C_∞
Polyethylene	Bis-2-ethylhexil adipate	145	2.27	10.3
a-Polypropylene	Diphenyl ether	145	1.44	4.15
a-Poly(methyl methacrylate)	Butylchloride	35.4	1.74	6.05
Poly(vinyl acetate)	Heptane/3-methyl-2-butanone	25	2.24	10.0
a-Polystyrene	Cyclohexane	34	2.28	10.4
Amylose tricarbanilate	Dioxan/methanol	20	11.7	—
Cellulose triacetate	Cyclohedxanol	73	2.52	—
Nylon 6,6	Calcium chloride/methanol[a]	40	1.12	4.29

[a] Weight ratio of calcium chloride to total weight of mixture $W_{ca} = 11.5\%$.

proved whether the effect is negligible or not. From these reasons, the A values of the nylon 6,6 evaluated hitherto is considered not to be reliable.

Conformation parameter σ and characteristic ratio of the polymer chain with infinite molecular weight C_∞, defined in eq 11 and 12 respectively, are able to be evaluated from A.

$$\sigma = \frac{A}{A_f} \quad (11)$$

$$C_\infty = \frac{A_\infty^2 M_b}{l^2} \quad (12)$$

Here, A_f is A of freely rotating chain to be 0.0545 nm for the nylon 6,6; A_∞, A at infinite molecular weight; M_b, the molecular weight of skeletal bond; l, root mean square length of a bond constituting a polymer chain. If we assume that the unperturbed chain dimension of nylon 6,6 polymeric chain is independent of molecular weight in the region of M_w more than 4×10^4, we can obtain σ and C_∞ to be 1.12 and 4.29, respectively. In Table II, σ and C_∞ of the various polymers estimated from the data of light scattering in Θ solvent picked up from ref 17 are listed. Inspection of the table shows that the polymers with small σ and C_∞, for example less than 2 and 10, respectively are a few and the nylon 6,6 is categorized as very flexible polymer.

In order to clarify the characteristic features of the nylon 6,6 solutions, such as remarkable decrease of the second virial coefficient below $W_{ca} = 0.15$, Θ solvent at $W_{ca} = ca.$ 0.11, and very high chain flexibility of nylon 6,6 in the unperturbed state, structure of the solvent mixture and polymer-solvent interaction in the solution were investigated in detail, at least judging from the values of chain conformation parameters at Θ state.

For the methanol–CaCl$_2$ system at 40°C, a ratio of the specific viscosity η_{sp} to root of the concentration of CaCl$_2$ (c_{CA}; g cm^{-3}) is plotted against $c_{CA}^{1/2}$ in Figure 4. Regarding an electrolyte solution in dilute resume, where perfectly dissociated ions and solvent interact together only through electrostatic Coulomb force, the specific viscosity η_{sp} of the solution is expressed as a function of the concentration of solute molecules c (g cm^{-3}) as follows[18]:
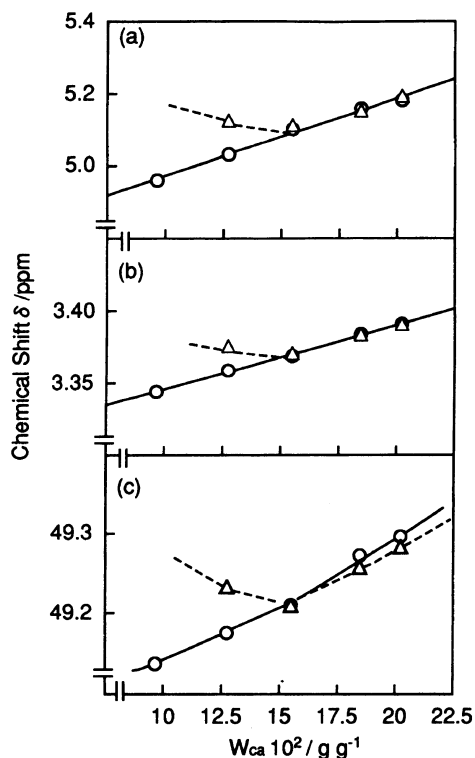
$$\frac{\eta_{sp}}{\sqrt{c}} = a + b\sqrt{c} \quad (13)$$

where coefficients a and b are the parameters representing specific interaction, such as ion–ion and ion–solvent molecule, respectively. In the region of $c_{CA}^{1/2}$ lower than 0.2 ($c_{CA} = 0.040$, $W_{ca} = 0.048$) (indicated by filled arrow), in the Figure 4, the relationship between the ratio $\eta_{sp}/c_{CA}^{1/2}$ of the methanol–CaCl$_2$ system and $c^{1/2}$ is simply expressed by a linear line with $a = 0$ and positive b, indicating that interaction
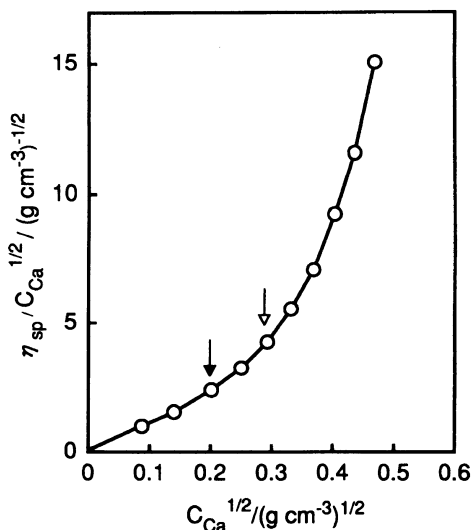
Figure 4. Ratio of specific viscosity η_{sp} to root of calcium concentration C_{CA}, $\eta_{sp}/C_{CA}^{1/2}$, of the mixture of methanol and calcium chloride at 40°C plotted against $C_{CA}^{1/2}$.

Figure 5. Calcium chloride concentration W_{ca} dependence of chemical shift of hydroxy proton δ_{OH} (a), methyl proton δ_{CH_3} (b) and methyl carbon δ_C (c) of methanol molecule in solvent mixture (circle) and in nylon 6,6 solution (triangle).

between solute molecules is almost negligible, and the ions of calcium and chloride strongly interact to methanol molecules. Above $c_{CA}^{1/2} = 0.2$, data of $\eta_{sp}/c_{CA}^{1/2}$ reveal remarkable upward departure from the line as observed for other salts of class in methanol[19] and sodium and potassium chlorides and bromides in N-methylformamide.[20] That type of derivation from Jones and Dole's equation for the various salts in aqueous and non aqueous solvents was reasonably explained by occurrence of ion association.[21] So in the present mixed solvent system, association between Ca^{2+}, Cl^{-} ions and methanol seems to occur above $c_{CA} = 0.04$ ($W_{ca} = 0.047$) and mole ratio of the associating ions to dissociating one monotonically increases with an increase of content of $CaCl_2$ in the mixture. In fact, at very high $CaCl_2$ concentration ($W_{ca} > 0.40$), coordination complex in the form of $[Ca(CH_3OH)_4]^{2+}(Cl^{-})_2$[22], is isolated as solid and has been industrially utilized as a starting material for purification of methanol.[23] It should be pointed out that W_{ca} value of onset of the deviation is far lower than the minimum W_{ca} of the mixed solvent capable to dissolve the nylon 6,6 (indicated by

unfilled arrow). From these facts the complex of methanol associated with $CaCl_2$ is considered to play an important role to dissolution of the solid nylon 6,6 into the mixture.

Figure 5a, b, c show W_{ca} dependence of chemical shift, determined by ^1H and ^{13}C NMR spectrum, of hydroxy proton δ_{OH} (a), methyl proton δ_{CH_3} (b) and methyl carbon δ_C (c) of undeuterated methanol molecules in the solvent mixture (circle) with W_{ca} ranging from 0.095 to 0.20. The hydrogen and carbon atoms of the methanol molecules become magnetically deshielded by an increase of the concentration of $CaCl_2$. Note here that effect of metal atoms included in the $CaCl_2$ reagent as impurity on the chemical shift can be ignored, because the assay of the metal atoms is

negligibly small. Considering strong electron acceptor nature of calcium ions, the concurrent deshielding trend of three kinds of atoms for methanol molecule with increasing W_{ca} seems to be reasoned only when calcium atom coordinates with oxygen in methanol molecules, thus indicating a selective association of methanol molecules with undissociated Ca ions, rather than chloride ions.

δ_{OH}, δ_{CH_3}, and δ_C of undeuterated methanol molecules in the nylon 6,6 solution are represented by triangle in Figure 5. An addition of nylon 6,6 polymer to the mixture brings about the lower magnetic field shift of the hydrogen and carbon atoms of methanol in the lower W_{ca} region than 0.15, while the effect of the polymer to the methanol molecules is almost ignored in higher W_{ca} region. This again strongly suggests the different dissolved state or dissolving mechanism of nylon 6,6 in methanol–$CaCl_2$ below and above $W_{ca} = ca.$ 0.15. Seeing from solvent mixture side, the dissolved state of methanol in the nylon 6,6 solution with low W_{ca} should become equal to that in the solution with $W_{ca} > 0.15$.

Figure 6 shows number of solvated methanol s in $CaCl_2$–methanol mixture as a function of W_{ca}. s decreases almost linearly with an increase in W_{ca} except for near $W_{ca} = 0$, showing no W_{ca} specificity. At $W_{ca} = ca.$ 0.10 which is almost Θ solvent composition and also minimum value for dissolution of nylon 6,6, one mol of $CaCl_2$ is solvated with 7—8 mol of methanol. s is almost $6 \, mol \, mol^{-1}$ at $W_{ca} = $ 0.15—0.175 giving an asymptotic value of A_2*. Interestingly, if we extrapolate the plot to $W_{ca} = 0.4$ we can estimates $s = 4$ $(mol \, mol^{-1})$, which can be referred to the complex from $[Ca(CH_3OH)_4]^{2+}(Cl^-)_2$ (hereafter referred to as associate form I), as described before. Of course, the residual methanol molecules are exchanging with the solvated ones. Taking this fact and the possible octa-valent coordination of Ca ion[24,25] into consideration, 6 mol of methanol may coordinate with one mol of Ca ion in the form, for example, [Ca(CH_3-
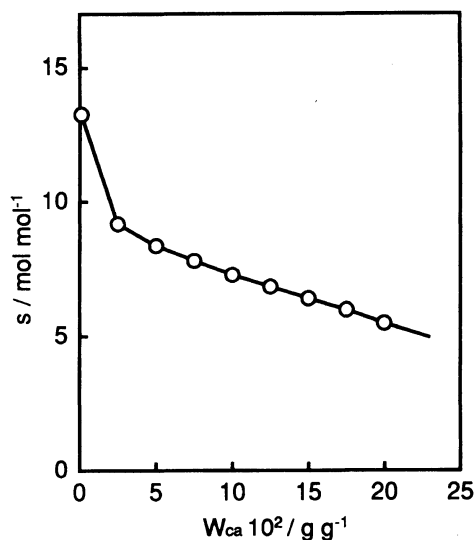

Figure 6. Calcium chloride concentration W_{ca} dependence of solvating solute molecules number s of the mixture of methanol and calcium chloride at 40°C.

OH)$_6$]$^{2+}$(Cl$^-$)$_2$ at $W_{ca} = 0.15$—0.175. Tentative structures of solvent mixture at $W_{ca} = ca.$ 0.10, 0.15—0.175, and 0.4 are illustrated as representatives in Figure 7. Note that the structure for the mixture at $W_{ca} = ca.$ 0.10 can explain the NMR results obtained when nylon 6,6 is added to the mixture if we consider that extra-solvated methanol first interacts with nylon 6,6, being into the transition state, $[Ca(CH_3OH)_6]^{2+}(Cl^-)_2$.

Figure 8a, b show W_{ca} dependence of $[\eta]$ and k' obtained by the Huggins plots for the polymer (sample SP1) solutions. In the region of $W_{ca} < 0.13$, $[\eta]$ increases almost linearly with W_{ca} and shows a plateau near $W_{ca} = 0.13$—0.175, where the data points rather scatter, and again increases from the point of $W_{ca} = 0.175$. Just at the W_{ca} region where the line of $[\eta]$ shows plateau, k' becomes maximum. These facts certify that the dissolution state of polymer is quite different below and above $W_{ca} = ca.$ 0.15—0.175, especially the nylon 6,6 dissolves in the mixture with $W_{ca} = ca.$ 0.15—0.175 in quite specific manner.
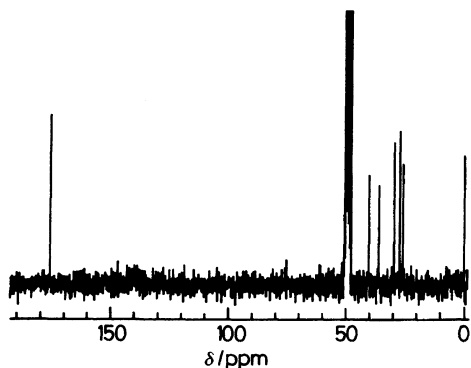
In Figure 9, ^{13}C NMR spectrum of the nylon

(a)   (b)   (c)
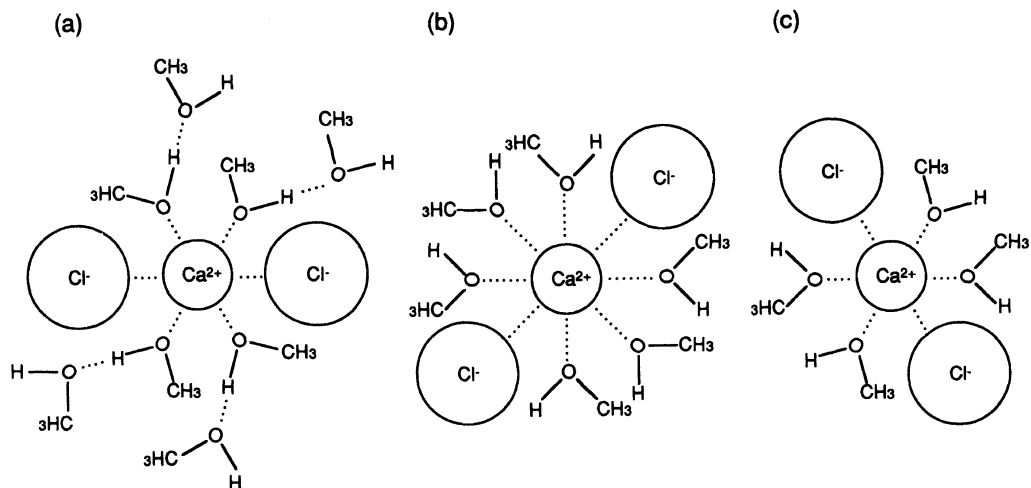
Figure 7. Schematic representation of $CaCl_2$–methanol complex in the solvent mixture at 40°C, (a) $0.1 \leqq W_{ca} \leqq 0.15$; (b) $0.15 < W_{ca} \leqq 0.175$; (c) $W_{ca} = 0.4$.
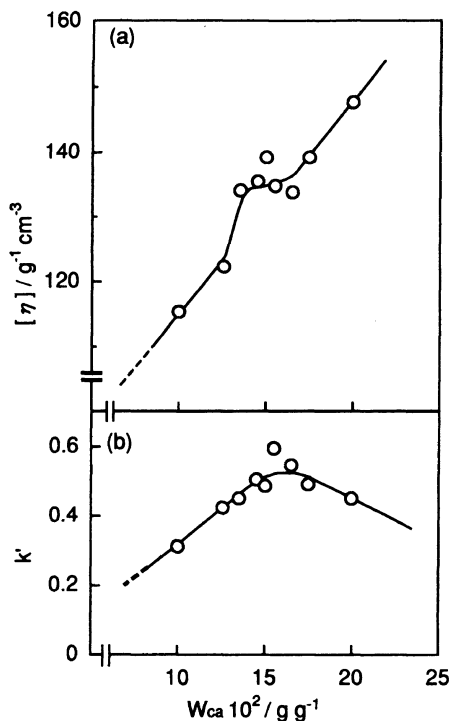

Figure 8. Limiting viscosity number $[\eta]$ (a) and Huggins constant k' (b) of nylon 6,6 in mixture of calcium chloride and methanol at 40°C plotted against calcium chloride concentration W_{ca}.

Figure 9. NMR spectra of nylon 6,6 solution with $W_{ca} = 20\%$ at 40°C.

6,6 solutions with $W_{ca} = 0.20$ is representatively shown. By referring to assignment in the literature,[8,9] each peak in ^{13}C NMR spectrum of the nylon 6,6 solutions with $W_{ca} = 0.20$ was ascribed as follows: Methylene carbons at α and β position from amide carbonyl, α-C=O, 36.184 ppm, β-C=O, 25.953 ppm; methylene carbons at α and β and γ position from amide amine, α-NH, 40.583 ppm, β-NH, 29.744 ppm, γ-NH, 27.411 ppm; amide carbonyl carbon, 176.062 ppm. Note that ^{13}C NMR peaks for α-NH carbon and amide carbonyl carbon for nylon 6,6 solid at 120°C were found at 40.678
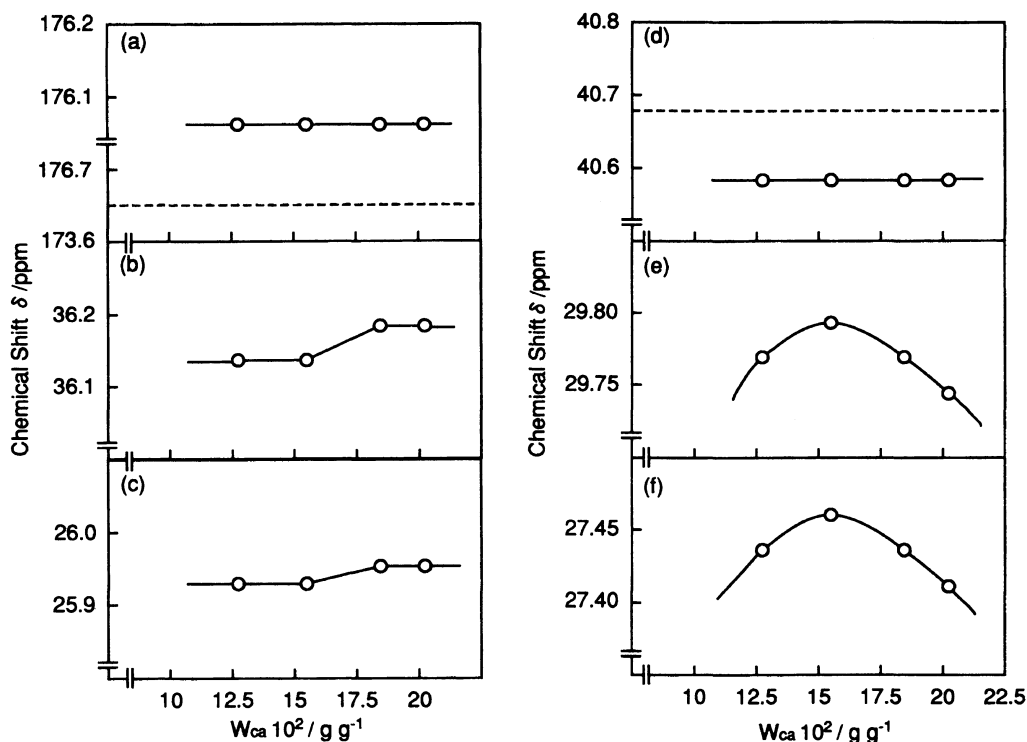
Figure 10. Calcium chloride concentration W_{ca} dependence of chemical shift δ of (a) amide carbonyl carbon; (b) α-C=O; (c) β-C=O; (d) α-NH; (e) β-NH; (f) γ-NH (solid line) of nylon 6,6 in solution at 40°C. Broken line, amide carbonyl carbon (a) and α-NH (d) of nylon 6,6 in solid state at 120°C.

and 173.65 ppm, respectively.

The W_{ca} dependence of chemical shift of these carbons is shown in Figure 10. The chemical shift of both carbonyl carbon and α-NH is almost independent of W_{ca} (Figure 10a, d). Since carbonyl carbon peak of nylon 6,6 solid at 120°C shifted to considerably lower magnetic field after nylon 6,6 dissolved in the solvent mixture, electron density on carbonyl carbon is diminished by direct interaction of solvent mixture (probably hydroxyl hydrogen of methanol) on carbonyl oxygen. This prediction is supported by the results reported by Ford and Marshall,[10] and Nakajima and Tanaami[11] who showed by infrared spectroscopy for nylon 6,6 and nylon 6 in the calcium chloride–methanol system, that stretching frequency of the amide carbonyl group of the both polyamides obviously shifts to higher

wave number side, comparing to the frequency of the nonassociated amide. Likewise, the lower magnetic field shift (*ca.* 0.1 ppm) of α-NH methylene carbon from its solid to solution is significant (Figure 10d). In order to elucidate this fact we need to take some interaction of amide NH site of nylon 6,6 with solvent mixture into consideration. The independency of chemical shifts for carbonyl carbon and a-NH methylene carbon on W_{ca} clearly indicates that in the dissolved state both carbonyl and amine sites in amide group of polymer should be strongly interacted with components in some associated form of solvent mixture, irrespective of the W_{ca} concentration investigated here. On the other hand, chemical shifts of β- and γ-NH methylene carbons (Figure 10e, f) reconfirmed that dissolved state of polymer in $CaCl_2$–methanol mixture with $W_{ca} = ca.$ 0.15 is specific

as postulated in Figure 8. Lowest magnetic field shifts of these methylene carbons in the above mixture with $W_{ca} = ca.$ 0.15 could not be understood without considering direct interaction of solvent component to methylene hydrogen or long-distance deshielding effect, both brought about by the some specific coordination form of solvent mixture having a certain steric factor. In this sense, solvent mixture with $W_{ca} = 0.15$—0.175 should take a distinguished coordination form from those at $W_{ca} = ca.$ 0.10 and $W_{ca} > 0.175$. If the octavalent coordination form shown in Figure 7 is assumed for the mixture with $W_{ca} = 0.15$—0.175 and this form is meta-stable comparing to the stable hexa-valent calcium ion form (*i.e.*, at $W_{ca} = ca.$ 0.10 and $W_{ca} \gg 0.175$), two extra methanol molecules solvated directly to calcium ion may interact with β- and γ-NH methylene hydrogen not with α-NH methylene hydrogen. The latter reason will be discussed later. Lower magnetic field shifts of α-C=O and β-C=O methylene carbons (Figure 10b, c) in the $W_{ca} > 0.175$ is easily understood by the direct interaction of hydroxyl group of methanol cooperated in some coordination form of calcium ion to amide carbonyl oxygen, leading to a mesomery effect on α- and β-C=O methylene carbons.

The last problem left here is whether NH site of amide of polymer and Cl ions really take part in the dissolved state of polymer and this is clearly pictured in Figure 11. Infrared analysis on NH stretching vibration revealed that contact of the polymer with solvent mixture with $W_{ca} \geqq 0.125$ gives a new absorption band at $2760\,cm^{-1}$, which is characteristic band of cationized $NH(NH_2^+)$ stretching as pointed out by Saunders[6] and Schaefgen *et al.*[26] and is never observed for the polymer in the solid state (Figure 11a) and split of the deformation vibration band observed at 1550 cm^{-1} for polymer film (broken line)[27] into two peaks (Figure 11b). The latter fact denotes that at least two vibrational states of NH exist in the solvent mixture. Cationized form of
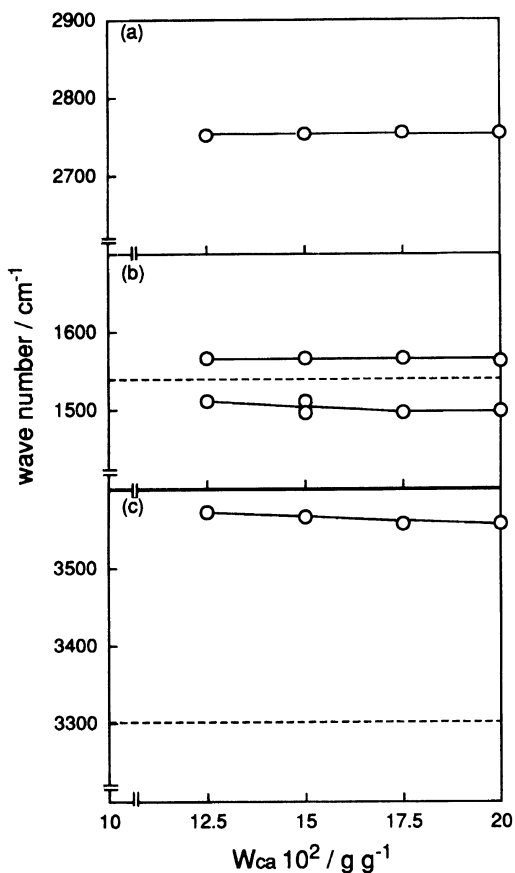
Figure 11. Calcium chloride concentration W_{ca} dependence of IR resonance absorption wave number of (a) NH stretching of nylon 6,6 solution; (b) cationized $NH(NH_2^+)$ stretching; (c) NH deformation (solid line). Broken line in the Figure denotes, NH stretching (b) and NH deformation (c) of nylon 6,6 solid film.

amide amine is only possible when Cl^- in the coordination form of solvent (associated form) or CH_3–O–H$\cdots Cl^-$ part in the associated form of solvent directly interacts with NH site. Furthermore, NH stretching at $3300\,cm^{-1}$ (broken line in Figure 11c)[28-30] is shifted to higher frequency side (above $3550\,cm^{-1}$) when contacted with solvent mixture with $W_{ca} \geqq$ 0.125. This means that hydrogen bond between amide groups of polymer in solid is completely destructed by solvent mixture, again suggesting strong affinity of Cl^- or the CH_3–O–H$\cdots Cl^-$ to amide NH site of polymer in the solvent

mixture. Introduction of such bulky complex to NH site may hinder the approaching of the other components to α-NH methylene site at any W_{ca}.

CONCLUSIONS

The following conclusions were drawn from the studies on mixture of calcium chloride and methanol and nylon 6,6 solution.

1. The second virial coefficient obtained by light scattering method remarkably decreases with a decrease of W_{ca} below 0.15 and was expected to be zero at $W_{ca} = ca.$ 0.115 (i.e., Flory's Θ solvent).

2. From value of conformation parameter and characteristic ratio, evaluated using a value of radius of gyration at the Θ state, the nylon 6,6 molecule is judged to be very flexible.

3. The viscosity of the nylon 6,6 in the mixture of calcium chloride and methanol reveals extraordinary W_{ca} dependence near $W_{ca} = 0.15$.

4. In the solvent mixture with W_{ca} above ca. 0.05, $CaCl_2$ molecules associate forming metal halide complex with methanol molecules. The structure of the complex changes depending on W_{ca}, approaching to stable form, $[Ca(CH_3OH)_4]^{2+}(Cl^-)_2$, with an increase of W_{ca} above 0.175.

5. Dissolution of nylon 6,6 in calcium chloride-methanol mixture with $W_{ca} \geqq 0.1$ is realized at least by interaction of methanol and chlorine parts in the associated form of solvent mixture with amide carbonyl and amine: In the range of $W_{ca} < 0.15$, selective absorption of extra solvated methanol molecules or weakly bound methanol molecules with the stable associate form of the complex to nylon 6,6 plays an important role to determine the very compact chain conformation of the nylon 6,6 chain. Dissolution of nylon 6,6 at $W_{ca} = 0.15$— 0.25 (upper limit of dissolution) takes place by direct interaction of the very bulky and meta-stable associate form of solvent to polymer, which brings about large expansion of the

nylon 6,6 chain in the solution.

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