Unperturbed Dimension and Conformation of Polyvinyl Chloride Chain in Solution

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The unperturbed chain dimension of polyvinyl chloride (PVC) prepared using the usual suspension polymerization is studied. The conversion of monomer to polymer is kept below 4% in order to prevent the branching reaction. By employing the Archibald ultracentrifugal procedure the molecular weight determination is made for fractionated PVC samples in tetrahydrofuran (THF). In a molecular weight range between 2.1×10^4 and 1.28×10^5 the Mark-Houwink-Sakurada equations for different solvents are: $[\eta](\mathrm{dl./g.})$ $=1.27 \times 10^{-4} M_w^{0.82}$ in THF (30°C), $1.41 \times 10^{-4} M_w^{0.82}$ in cyclohexanone (30°C), $6.94 \times 10^{-4} M_w^{0.61}$ in chlorobenzene (30°C), and $1.57 \times 10^{-4} M_w^{0.52}$ in chlorobenzene (15°C). The data reported by other authors and ours are analysed with the aid of the recent viscosity theory of Stockmayer and Fixman to estimate the unperturbed dimension in THF and cyclohexanone. It is found that the unperturbed dimensions obtained on the basis of the different sources fall on a nearly same value, even if the data of $[\eta]$ and M are quite different from each other. The conformational factor, σ, defined as the ratio of unperturbed dimension to that corresponding to the free rotation around the C—C bond, is evaluated to be about 2.1.

INTRODUCTION

Dilute solution viscosities of polyvinyl chloride (PVC) often change spontaneously, depending on the history of dissolution of polymer (temperature and duration of heating)[1~7] and also on the polymerization condition under which the polymer was prepared (temperature and monomer conversion)[1,8~10]. Such an unstable nature of the solution has made it difficult to determine the weight-averaged molecular weight, M_w, of PVC by light scattering. Thus the $[\eta] - M_w$ relationships ($[\eta]$ the intrinsic viscosity) which are available to date are characterized by a surprising lack of agreement[7,11~16]. In attempting to explain these discrepancies, Krotochvil notes that PVC molecules in dispersed state often exist partly in various forms of microgel particles[1].

In view that reliable weight-averaged molecular weights are essential to the study of the unperturbed chain dimension, the present work deals with the molecular weight determination using the Archibald ultracentrifugation method[17], which has been proved to make it possible to evaluate M_w without any serious disturbance due to microgel particles[18]. The data of $[\eta]$ and M_w thus obtained are analysed in accordance with the Stockmayer-Fixman equation to estimate the unperturbed dimension[19], and the chain conformation is discussed in comparison with the knowledge obtained for the solid state.

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EXPERIMENTAL

Sample Preparation Vinyl chloride monomer was polymerized using usual suspension method with lauroyl peroxide at 40°C. The conversion of monomer to polymer was kept below 4% in order to prevent the branching reaction*. To remove some impurities in the polymer sample, precipitation from tetrahydrofuran (THF) solution into water was made repeatedly, in advance of fractionation. To attain a successful fractionation of PVC, it is known that a mixed system of THF and water has been found to be the best[20]. Using this system, the whole polymer was fractionated into seven fractions at 30°C. Further fractionation into two fractions was carried out for the fractions F2, F3 and F4. In the case of the fractions having higher molecular weights, the precipitated phase was often in a form of gelatinous powder, being attached to the glass vessel.

Solvents Solvents used in this investigation were of reagent grades and distilled just before use. Distillates in following temperature ranges relevant to each solvent were collected; b.p. 65.9–66° for THF, b.p. 155.0–155.5° for cyclohexanone, and b.p. 131.7–132.0° for chlorobenzene.

Preparation of Solution For the reason mentioned in the "Introduction", we payed the most careful attention to the preparation of solutions. First we gathered experiences made by other authors from several literatures. One of them is that the viscosities of THF and cyclohexanone solutions of PVC are practically independent of dissolution temperature, if the solutions are prepared by heating for two hours at any temperature between 60 and 140°C[5]. Under the same condition as above, it has been experienced that dilute solution viscosities of ordinarily polymerized PVC remain stable for several days[6,7]. In order to reexamine these experiences, solutions of an unfractionated PVC sample prepared by heating at different temperatures, were tested by measuring their viscosities. Table 1 lists viscosity data of THF solutions prepared at 60, 80, 100 and 140°C for three hours, respectively. Moreover, we have investigated the change of viscosity with time. From this experiment, it was found that $[\eta]$ values of the solutions prepared by heating for three hours at 100°C showed no change with time for over five days. Thus this condition for preparing solutions was employed throughout this work. However, in preparing chlorobenzene solutions the heating was continued for a longer time than three hours.

Table 1. Viscosity data on THF solution of unfractionated PVC sample prepared at different temperatures.

Temp. (°C)	$[\eta]$ (dl./g.)	k'
60	1.38	0.37
80	1.38	0.37
100	1.38	0.38
140	1.38	0.40

* This polymer was kindly prepared in the Tokyo Research Institute of the Kureha Chem. Ind. Co., Ltd..

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Ultracentrifugation   All solution measurements were made in THF.   The Archibald centrifugal procedure[17,21] was applied for the molecular weight determination of the PVC fractions.   A PHYWE analytical ultracentrifuge was used. Rotor speeds employed were 13,000–23,000 r.p.m. with fluctuations less than 0.5%. The rotor temperature was kept to within ±0.3° at 30°C.   The other procedures of the centrifugation and the estimate of molecular weight have been described previously[17].   The apparent molecular weights, which are first obtained with data of centrifugation and defined by

$$M_{app}(t) = RT(dn_c/dr)/\omega^2 r(1-\bar{v}\rho_0)n_c, \tag{1}$$

are a function of time t and the initial concentration c_0.   Fig. 1 shows plots of M_{app} against t.   The time dependent nature of M_{app} has been already discussed
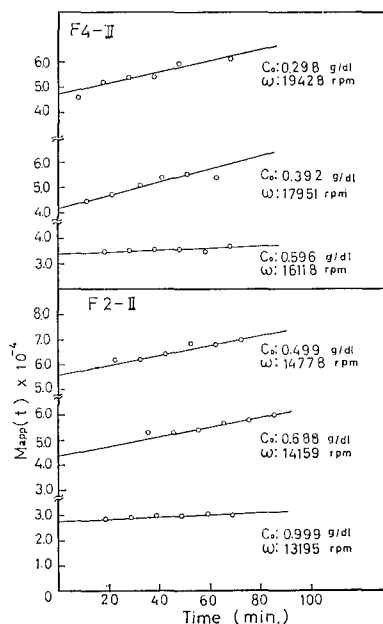

Fig. 1.   Time dependence of apparent molecular weights at the meniscus, $M_{app}(t)$, for the fractions F2–II and F4–II at 30°C.

theoretically as well as experimentally and it has been concluded that this trend could be interpreted in terms of both the thermodynamic non-ideality of the solution and the fractionation effect in the case of polydisperse solutes[17,21~23].   The time dependency observed here is in agreement with our theoretical prediction. It has been shown that the quantity M_{app}^{-1} can be expanded in terms of c_0 as

$$1/M_{app} = 1/M_w + 2A_2'c_0 + 0(c_0^2), \tag{2}$$

where M_w is the weight-average molecular weight of the solute, and A_2' is the light scattering second virial coefficient[17].   According to Eq. (2), the values of M_w and A_2' may be obtained from the intercept and initial slope of plot for M_{app}^{-1} vs. c_0.   In many previous studies of dilute polymer solutions, this sedimentation plots have been found always to exhibit upward curvatures, which make it dif-

ficult to estimate the molecular weight by extrapolating the plot to $c_0 = 0$[17,21~26]. The present theory does not provide the essential reason why the curvatures in the sedimentation plot appear. However, it has been found that the curvatures could be due to the polymolecularity of sample used[22,27]. In this measurement on the system PVC and THF, the curvatures in the plot of M_{app}^{-1} vs. c_0 have been found again. Therefore, M_{app} data obtained as a function of initial concentration c_0 were analysed according to the following semiempirical equation for estimating the weight-averaged molecular weight M_w and A_2' [28,29] ;

$$\ln(1/M_{app}) = \ln(1/M_w) + 2A'_2 M_w c_0.$$

The corresponding plots for M_{app} vs. c_0 are seen in Fig. 2.
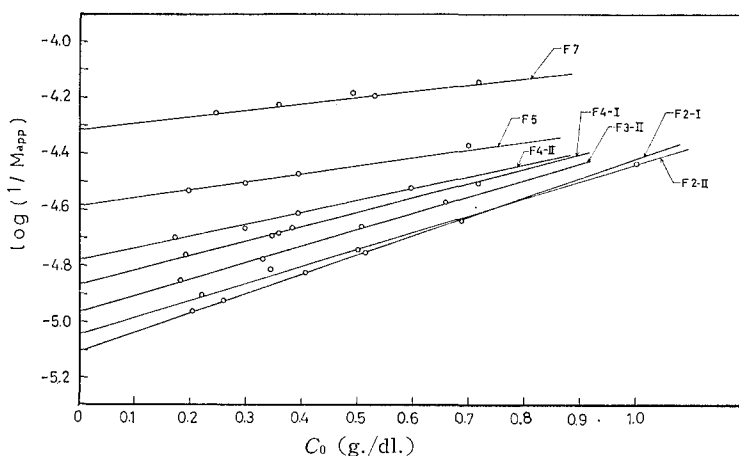

Fig. 2. Plots of $\log(1/M_{app})$ as a function of initial concentration c_0 at 30°C.

Bouyancy Factor The partial specific volume, $\bar{v}$, of PVC in THF and the density, ρ_0, of THF reported by Kegeles *et al.*[24] are 0.742_9 ml./g. at 25° and 0.8826 g./ml. at 25°, respectively. We have again measured densities for this system at 30°C, using a 25-ml pycnometer in a concentration range of 0.15–0.85 g./dl.. Fig.
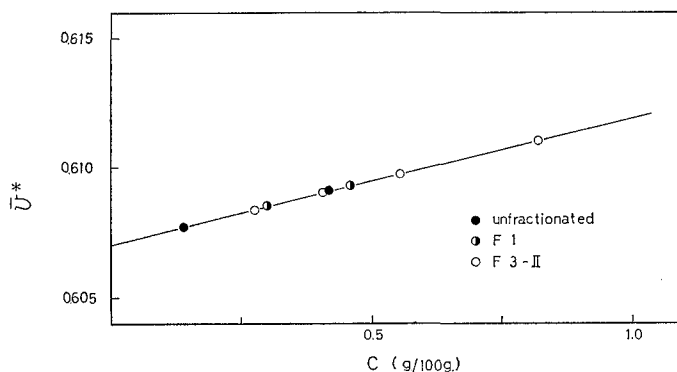

Fig. 3. Plots of apparent specific volume, $\bar{v}^*$, as a function of concentration for the whole polymer, the fractions F1 and F3–II in THF at 30°C.

3 shows the apparent specific volume, $\bar{v}^*$, as a function of concentration c at 30°C. From this plot it is seen that the value of $\bar{v}^*$ for the unfractionated sample and the fractions of F1 and F3-II fall on a straight line over the whole range of c_0 studied, and that a good reproducibility of the determination was confirmed. The values thus determined were $\bar{v}=0.607_1$ and $\rho_0=0.8761$. It should be noted here that the $\bar{v}$ value obtained is remarkably lower than the values reported by Kegeles *et al.*[24]. As will be described later, however, it may be attributed to a difference in the stereochemical nature or degree of crystallinity between these two samples. In any event, we used the value 0.468 for the bouyancy factor $(1-\bar{v}\rho_0)$.

Viscosity Measurements A dilution viscometer of the Ubbelohde type with flow time of 190.3 sec. for THF was used. The measurement was carried out in three solvents, *i.e.* in THF at 30°, in cyclohexanone at 30°, in chlorobenzene at 15° and 30°C. The kinetic energy correction for $[\eta]$ was determined to be less than 0.1%. The intrinsic viscosity was determined by making extrapolation in two types of plots, *i.e.* η_{sp}/c *vs.* c, and $\ln\eta_{rel}/c$ *vs.* c. Here, the concentration c is expressed in terms of g./dl..

Infrared Spectra A Hitachi model EPI-2 infrared spectrophotometer with a KBr prism was used for the range between 750 and 550 cm^{-1}. Infrared spectra of films were taken at 25°C and the optical density for absorption was determined by the base-line method.

RESULT AND DISCUSSION

Relationship between $[\eta]$ and M_w In Table 2 are summarized the values of $[\eta]$, the Huggins constant k', M_w, A_2', and $A_2'M_w/[\eta]$ obtained in this study. Double-Logarithmic plots of $[\eta]$ *vs.* M_w are shown in Fig. 4. By making use of the least square method, the Mark-Houwink-Sakurada equations, $[\eta]=K'M_w{}^a$, for the present data are obtained for each solvent used within a range of molecular weights from 2.06×10^4 to 1.28×10^5. They are:

$$[\eta]_{30°}(\text{dl./g.})=1.27\times10^{-4}M^{0.82} \quad \text{(in THF)}$$
$$[\eta]_{30°}(\text{dl./g.})=1.41\times10^{-4}M^{0.82} \quad \text{(in cyclohexanone)}$$
$$[\eta]_{30°}(\text{dl./g.})=6.94\times10^{-4}M^{0.61} \quad \text{(in chlorobenzene)}$$

Table 2. Archibald ultracentrifugation and viscosity data for PVC in various solvents.

| Frac-tion	$M_w \cdot 10^{-4}$	$A'_2 \cdot 10^3$ (c.g.s)	$[\eta]$ (dl./g.) and k'				$M_w \cdot A'_2/[\eta]$*
			THF 30°	Cyclohexa-none 30°	Chloro-benzene 30°	Chloro-benzene 15°	
F1	—	—	1.83 (0.38)	—	—	—	—
F2-I	12.80	0.62	1.90 (0.41)	—	0.93 (0.61)	—	42.1
F2-II	11.10	0.63	1.82 (0.43)	1.88 (0.35)	0.84 (0.77)	0.67 (0.54)	38.6
F3-II	9.22	0.74	—	1.77 (0.34)	0.71 (0.78)	0.62 (0.55)	—
F4-I	7.34	0.81	1.29 (0.43)	1.31 (0.31)	0.60 (0.74)	—	46.2
F4-II	6.02	0.81	1.00 (0.39)	1.10 (0.26)	0.55 (0.62)	0.50 (0.54)	48.6
F5	3.85	0.86	0.70 (0.41)	0.74 (0.27)	0.43 (0.43)	0.39 (0.37)	47.0
F7	2.06	1.28	0.45 (0.37)	0.48 (0.30)	0.31 (0.81)	—	58.4

* The values are those in THF, 30°C.
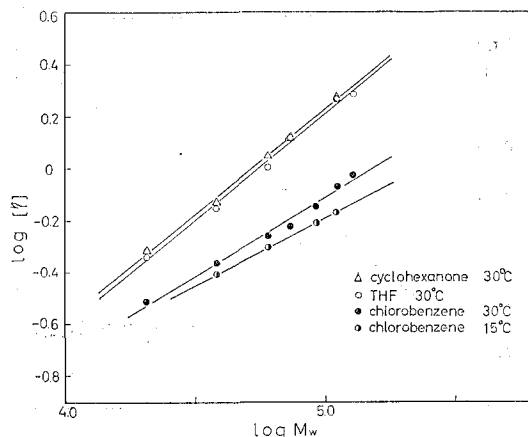
Fig. 4. Intrinsic viscosity *vs.* weight-average molecular weight for PVC fractions in different solvents.

$$[\eta]_{15^\circ}(\text{dl./g.}) = 1.57 \times 10^{-4} M_w^{0.52} \qquad (\text{in chlorobenzene}).$$

It is seen that in agreement with the earlier finding reported by Staudinger, the $[\eta]$-M_w relationship for THF is almost identical with that for cyclohexanone[30]. To compare our own results with those reported by other authors[7,11~16,31~33], the parameters involved in the Mark-Houwink-Sakurada equation, K' and α, are listed in Table 3 after recalculated in the unit of g./dl.. Fig. 5 is a graphical representation of the comparison made in Table 3.

It is to be noted in the figure that our relationships obtained in THF and cyclohexanone deviate considerably from those of the other authors. This fact will be interpreted in terms of the following three different points of view. The first one may be based on the chain branching. Bovey *et al.* have found that the

Table 3. List of the Mark-Houwink-Sakurada constants, $[\eta] = K'M^\alpha$.

Author	Solvent	Temp. (°C)	$K' \cdot 10^4$	α	Range $M \cdot 10^{-4}$	Method	Reference
Breitenbach	Cyclo-	20	1.16	0.85	3 – 10	O S	31)
Danusso	hexanone	25	2.40	0.77	2 – 14	O S	32)
Ciampa		25	1.23	0.83	2 – 17	O S	13)
Mead and Fuoss		25	11.2	1.0	— —	L S	16)
Ciampa		25	11.0	1.0	2 – 14	L S	13)
This work		30	1.41	0.82	2 – 13	A U	
Batzer	THF	20	36.3	0.92	3 – 17	G S	33)
Takahashi		25	4.98	0.69	4 – 18	L S	12)
Asahina		30	6.38	0.65	3.5–32	L S	14)
Kobayashi		30	2.19	0.54	3.5–32	L S	7)
Freeman		25	1.63	0.77	2.5–17	L S	11)
This work		30	1.27	0.82	2 – 13	A U	

O S: Osmotic Pressure
L S: Light Scattering
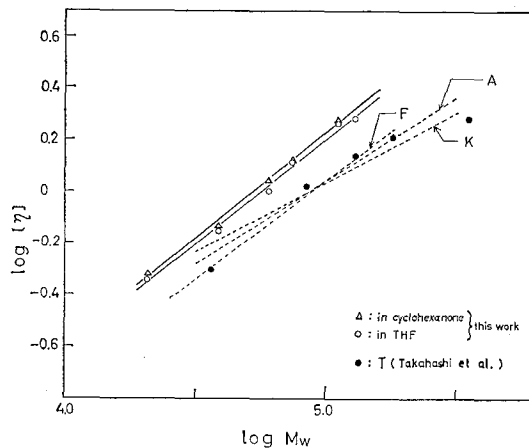A U: Archibald Ultracentrifugation

Fig. 5. Intrinsic viscosity and weight-average molecular weight relationships reported by various authors for PVC fractions: (A) Asahina; (F) Freeman and Manning; (K) Kobayashi; (●) Takahashi; (△) and (○) indicate our data in cyclohexanone and THF, respectively. For details, see Table 3.

PVC samples obtained by polymerization at higher temperatures ($\sim 50°C$) exhibited lower crystallinities than those obtained at the lower temperatures[36]. This observation has been interpreted in terms of chain branchings that would occur during polymerization at the higher temperatures. However, the chain branching will play not so serious role for interpreting the disagreement found between $[\eta]$-M relationships in this work. As has been pointed out by Freeman and Manning[11], the effect of branching upon $[\eta]$ is not prominent in the lower molecular weight range studied just in the present work.

Another point of view may be related to the stereoregurality of PVC. A number of IR-studies on PVC has proved that the syndiotactic stereoregurality
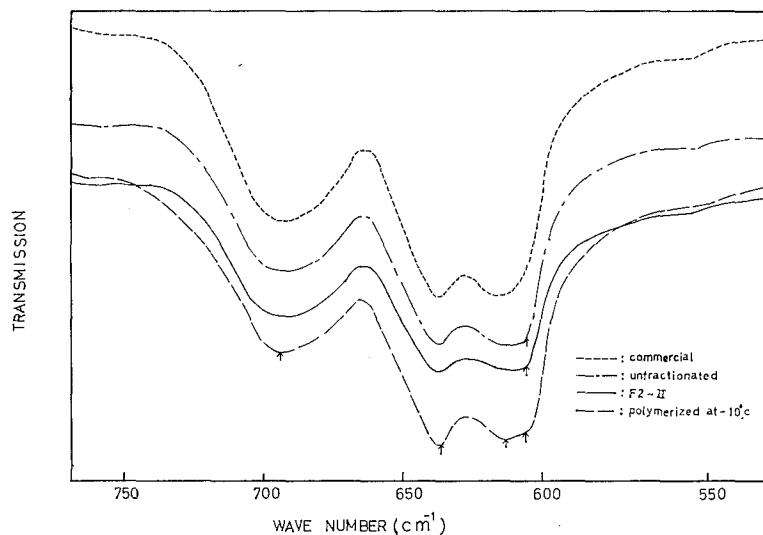

Fig. 6. IR-spectrum of PVC films.

increases with lowering the polymerization temperature, thus resulting in an increases of the crystallinity[37~42]. The branching reaction also will be suppressed at the same time[43,44]. Shimanouchi *et al.*[45] and Krimm[38] have given assignments to the ·C-Cl stretching vibrations due to possible changes in the molecular configurations. The assignments made by Shimanouchi *et al.* are as follows; the band at 690 cm^{-1} (here after designated as α band) is characteristic of the isotactic part of the chain, while the bands at 638, 615 and 603 cm^{-1} (β, γ and δ band, respectively) are characteristic of the syndiotactic part.

Fig. 6 illustrates IR-spectra of PVC films prepared with a commercial product, our whole polymer, the fraction F2–II and a sample polymerized at −10°C. The IR-spectra of the latter three samples exhibit the absorption band at 603 cm^{-1} even if they appear only as shoulders attached to the γ band. Differing from the above spectra, the commercial sample shows no δ band. In Table 4 are listed the absorption ratios, D_β/D_α and D_γ/D_α, which were evaluated from Fig. 6 by the base line method. This result suggests that the sample used in this work should have fairly a higher tacticity than those commercially available, and may afford a basis for explaining the disagreement among $[\eta]$-M relationships.

Table 4. Absorption ratio, D_{638}/D_{690} and D_{615}/D_{690} for PVC samples.

PVC sample	D_{638}/D_{690}	D_{615}/D_{690}
Commercial	1.36	1.35
Unfractionated	1.48	1.51
F2–II	1.42	1.40
Polymerized at −10°C	1.47	1.45

Another evidence for the fairly high tacticity of the present sample (probably for few branching of our sample, at the same time) may be drawn from the result of density of the sample. As was stated in a previous section, the partial (apparent) specific volumes, $\bar{v}$, of the present sample (0.607_1 ml./g.) is remarkably lower than that found by Kegeles (0.742_9 ml./g.)[24]. Such a large difference as found in $\bar{v}$ could not be observed by determing the density of these samples in solid state, however.
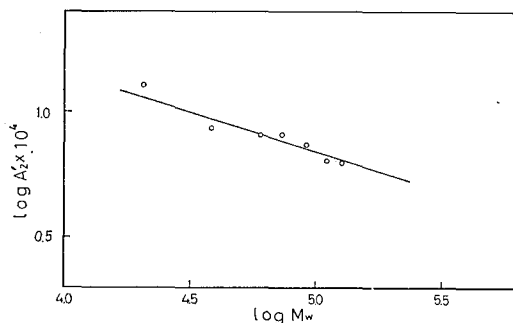

Fig. 7. Relationship between osmotic second virial coefficient and molecular weight in THF at 30°C.

Fig. 7 shows a plot for M_w-dependence of A_2'. The A_2' values decrease with increasing M_w, and the value -0.31 is obtained for ν, the exponent to M in the relation $A_2' \propto M^\nu$.

Unperturbed Dimensions The properties of linear polymers in dilute solution are greatly influenced by the excluded volume effect. Thus one of the purposes for studying dilute solution properties is to evaluate the unperturbed dimension of polymer chain (the short-range interactions), A, and the interaction parameter between segments in a chain (the long-range interactions) B. These two parameters, A and B, may be estimated by applying the Stockmayer-Fixman equation to data of $[\eta]$ and M obtained in any solvent[19]. The equation is given by

$$[\eta]/M^{1/2} = K + 0.51\Phi_0 B M^{1/2} \qquad (3)$$

$$K = \Phi_0 A^3 = \Phi_0 (<L^2>_0/M)^{3/2} \qquad (4)$$

$$B = \beta/m_s^2 \qquad (5)$$

$$A = (<L^2>_0/M)^{1/2}, \qquad (6)$$

where $<L^2>_0^{1/2}$: the unperturbed end-to-end distance

  Φ_0 : the Flory viscosity constant at Theta point[46]

  β : the binary cluster integral between segments

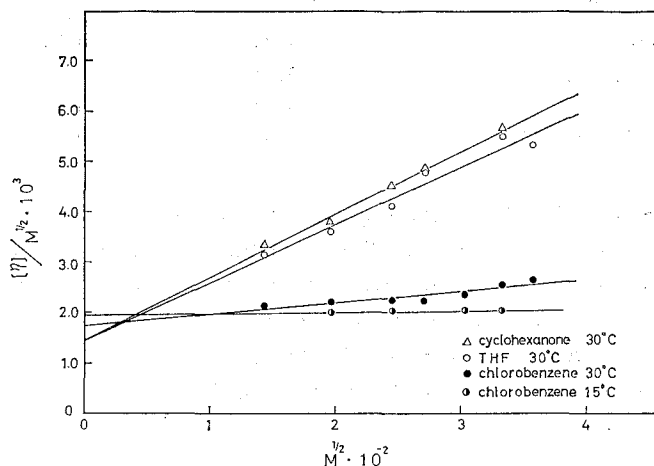 m_s : the molar weight of a segment.

Fig. 8. Stockmayer-Fixman's plots with $[\eta]$ and M_w data in different solvents.

Fig. 8 shows plots of Eq. (3) with $[\eta]$ values determined in THF, cyclohexanone at 30°C, and in chlorobenzene at 15° and 30°C and M_w values determined by the Archibald method. Table 5 involves the values of K, $B(T)$ and A obtained graphically with Fig. 8. Here, assuming $\Phi_0 = 2.87 \times 10^{21}$, we calculated the value of A. Now we evaluate the conformational factor σ which is defined by the ratio:

$$\sigma = <L^2>_0^{1/2}/<L^2>_{0f}^{1/2}. \qquad (7)$$

The quantity $<L^2>_{0f}$ is the mean square end-to-end distance when a chain is composed of atoms connected with a fixed valence angle θ but without any hindrance of internal rotations, that is, free internal rotation. This is expressed for

Table 5. Constants K, $B(T)$ and A in Tetrahydrofuran, Cyclohexanone and Chlorobenzene.

Author	Solvent	$K \cdot 10^3$ ($[\eta]$ in 100 ml/g)	$B(T) \cdot 10^5$	$A \cdot 10^9$	σ	$T°$C	Ref.
Freeman et al.	THF	1.32	0.66	7.72	1.98	25	11)
Takahashi et al.		1.60	0.59	8.23	2.11	25	12)
Kobayashi		3.07	0.12	10.23	2.62	30	7)
Asahina		2.24	0.40	9.21	2.36	30	14)
This work		1.44	1.14	7.95	2.04	30	
Ciampa et al.[a]	Cyclohexanone	1.94	0.47	8.78	2.25	25	13)
This work		1.46	1.24	7.98	2.05	30	
Sato	Benzyl alcohol	1.56	—	8.16	2.09	155.4	34)
Nakajima	THF+H$_2$O (mixed θ solvent)	2.11	—	9.03	2.31	30	35)
This work	Chlorobenzene	1.95	0.02	8.79	2.26	15	
This work		1.74	0.22	8.46	2.17	30	

a) From data of $M_w < 1 \cdot 10^5$.

vinyl polymers by

$$<L^2>_{or} = nl^2(1+\cos\theta)(1-\cos\theta)^{-1}, \tag{8}$$

where n and l are the number and the length of C–C bond, respectively. For a PVC chain $l = 1.54$Å, $\cos\theta = 0.333$, and $(<L^2>_{or}/M)^{1/2} = 3.89 \times 10^{-11}$ are obtained. Values of σ obtained in this study are: 2.04 in THF (30°C), 2.05 in cyclohexanone (30°C), 2.17 in chlorobenzene (30°C), and 2.26 in chlorobenzene (15°C), respectively. The higher σ value in chlorobenzene might be interpreted in terms of a solvent effect that would be observed for polymers possessing polar groups.

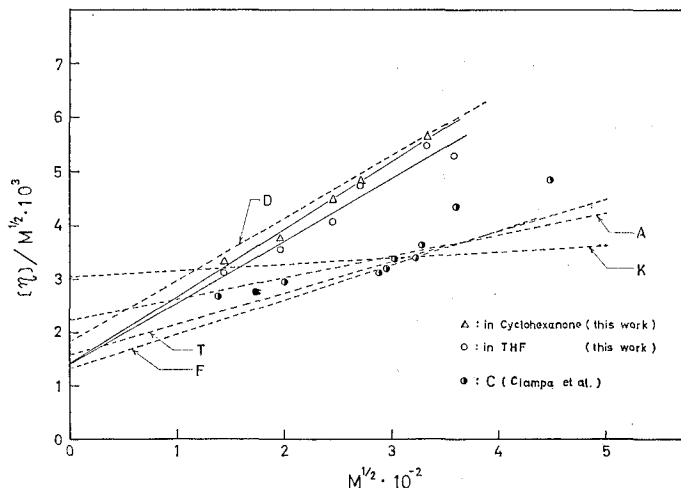Fig. 9 shows plots of Eq. (3) with the $[\eta]$-M_w relationships by the other

Fig. 9. Stockmayer-Fixman's plots with $[\eta]$ and M_w data reported by various authors for PVC fractions: (A) Asahina; (F) Freeman and Manning; (K) Kobayashi; (T) Takahashi; (◑) Ciampa; (D) Danusso (M_n); (△) and (○) indicate our data in cyclohexanone and THF, respectively. For details, see Tables 3 and 5.

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authors for PVC in THF and cyclohexanone. It is seen in the figure that those plots differ from each other but straight lines meet together at ca. 1.5×10^{-3} (which yields $\sigma = 2.1$) on the ordinate, except a few plots. Comparison of data summarized in Table 5 indicates that the conformational factor σ for ordinarily polymerized PVC may be represented by a value of 2.1. This value may be fairly large in comparison with those of other non-polar vinyl polymers. The σ value of polyethylene chain, which takes the same conformation as that of PVC[48], the planer zigzag, amounts to 1.8 at room temperature[47]. The difference in σ value between PVC and polyethylene may be understood not on the basis of the molar volume of substituent, which is often regarded as a measure of steric hindrance, but mainly by taking the dipole interactions of C—Cl bonds into consideration.

Nakajima *et al.* have pointed out that the unperturbed dimension of PVC increases as polymerization temperature is lowered; the sample prepared at lower temperatures should be more rich in the syndiotactic portion[35]. In connection with the above observation, a comment will be added here. As has been mentioned, the σ value obtained with our samples lies within the range on which the estimated σ values using the other data fell. When we recall that our sample has fairly a high tacticity so far as the IR-study indicates (see Fig. 6 and Table 4), we are not ready to support straight-forward the conclusion drawn by Nakajima *et al.*[35]. There exist still some unknown factors which govern the stereochemical structure of PVC.

ACKNOWLEDGMENT

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