

Further Study of Unperturbed Chain Dimensions of Stereoregular Polyacrylonitrile in Solutions

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Synopsis : *An attempt was made to evaluate the unperturbed chain dimensions A of polyacrylonitrile with a wide range of stereoregularity, and of copolymers of acrylonitrile (AN) and methacrylonitrile (MA) or vinylidene chloride (VDC). For this purpose, the fraction, separated from four PAN samples with meso-meso triad content $mm = 26, 51, 71$ and 75% and together with those of copolymers from AN/MA (AN weight% : 92) and AN/VDC (AN weight % : 59) were utilized. The light scattering and viscosity data obtained for the above fractions were analyzed by the methods 2A ~ 2G, proposed previously.*

1 Introduction

In the preceding paper¹ the reliable database of polyacrylonitrile (PAN) and acrylonitrile (AN) copolymer solutions, particularly in aq nitric acid, was constructed and based on the above database the followings were derived : (a) the molecular weight dependence of the limiting viscosity number, $[\eta]$ (i.e., the Mark-Houwink-Sakurada equation), (b) the molecular weight dependence of the z-average mean-square radius of gyration $\langle S^2 \rangle_z^{1/2}$, (c) Flory theta composition of the mixture, determined by the second virial coefficient A_2 method, (d) Flory's viscosity parameter Φ_0 at unperturbed state, and (e) the unperturbed chain dimensions (UCD) A , directly measured for solutions by light scattering (LS) at the unperturbed state. This article is an extension of the preceding paper, attempting to evaluate the unperturbed chain dimensions A of PAN with a wide variety of stereoregularity (expressed in terms of meso-meso triad content(%) mm) and its related copolymers dissolved in various solvents including non-Flory's theta solvents. Direct LS measurements in Flory's theta solvent are, from theoretical point of view, the most reliable method to determine A , if the LS experiments can be carried out accurately even in poor solvent. However, in the case where A is dependent of solvent nature, A should be determined in non theta solvent. Reversely, the solvent dependence of A can only be concluded after successful determination of A in non theta solvents. For this purpose, the experimental data in the previous papers²⁻¹¹ were analyzed by thermo dynamic and hydrodynamic approaches (methods 2A ~ 2D and method 2E ~ 2G, respectively in section 2) in very systematic manner. First, applicability limit of the

above methods were examined for the systems and secondly, the most probable A values of PAN were evaluated as functions of the polymer stereoregularity and solvent nature (in this case, the concentration of aq nitric acid w_n).

2 Theoretical Background ¹²

The unperturbed chain dimensions can be expressed in terms of a short-range interaction parameter A given by eq(1) :

$$A = (\langle R^2 \rangle_{0,w} / M_w)^{1/2} \quad (1)$$

$\langle R^2 \rangle_{0,w}^{1/2}$ is the weight-average unperturbed end-to-end distance of a polymer chain, M_w , the weight-average molecular weight.

The conformation parameter σ and characteristic ratio C_∞ are defined by eq (2) and (3), respectively.

$$\sigma = (\langle R^2 \rangle_{w,0} / \langle R^2 \rangle_{0f})^{1/2} = A/A_f \quad (2)$$

$$C_\infty = A_\infty^2 M_b / \alpha \quad (3)$$

where $\langle R^2 \rangle_{0f} (= A_f M^{1/2})$ and A_f are the root mean-square end-to-end distance and the short-range interaction parameter of a hypothetical chain with free internal rotation ($A_f = 0.423 \times 10^{-8}$ cm for PAN), A_∞ , the asymptotic value of A at infinite molecular weight (in the case of $\alpha_2 \neq 0$, A value at $M_w = 1 \times 10^5$ is utilized as A_∞), M_b , the mean molecular weight per skeletal bond (=26.5 for PAN) and α , the mean bond length (= 1.54×10^{-8} cm for PAN). The methods of estimating A are summarized below.

2.1 Thermodynamic approach

Method 2A¹³

When the unperturbed radius of gyration $\langle S^2 \rangle_0^{1/2}$ can be measured in a Flory's theta solvent, where the second virial coefficient $A_2 = 0$, the excluded volume effect parameter $z = 0$ and the linear expansion factor $\alpha_s = 1$, A is directly evaluated by use of eq (1).

Method 2B¹³

When the linear expansion factor α_s is determined from the penetration function Ψ the unperturbed radius of gyration, $\langle S^2 \rangle_0^{1/2}$, accordingly A , can be evaluated from the

experimental data of $\langle S^2 \rangle^{1/2}$ in non-ideal solvents using eq (4).

$$\alpha_s = \langle S^2 \rangle^{1/2} / \langle S^2 \rangle_0^{1/2} \quad (4)$$

Note that only in the range $\alpha_s^3 < 2$, the value of α_s , does not depend significantly on the theory of A_2 adopted. $\langle S^2 \rangle_0$ can be transformed to $\langle R^2 \rangle_0$ by use of eq(5)¹⁴ :

$$\langle R^2 \rangle_0 = 6 \langle S^2 \rangle_0 \quad (5)$$

Then, we obtain from eq(1) and eq(5) the relation :

$$A = 6^{1/2} (\langle S^2 \rangle_{0,w} / M_w)^{1/2} \quad (1)'$$

where $\langle S^2 \rangle_{0,w}^{1/2}$ is the w-average radius of gyration.

In this section, eq (5) is applied even in the case where the unperturbed chain is non-Gaussian chain ; $\alpha_2 \neq 0$.

$$\alpha_2 = d \ln (\langle S^2 \rangle_0 / M) / d \ln M \quad (6)$$

Method 2C¹³

If the factor 1.78 in eq (7)

$$\alpha_s^3 - 1 = 1.78 z \quad (7)$$

is replaced by 2.0, which is widely used in practical cases, we obtain¹⁵

$$\alpha_s^3 - 1 \approx 2.0 z \quad (8)$$

Here,

$$z = (1/8 \pi^{3/2}) B A^{-3} M^{1/2} \quad (9)$$

and B is a long-range interaction parameter.

Equation (9) can be recast with the aid of eq (8) as

$$\langle S^2 \rangle_w^{3/2} / M_w^{3/2} = A^3 / 6^{3/2} + (1/4 \pi^{3/2}) B M_w^{1/2} \quad (10)$$

Plots of $\langle S^2 \rangle^{3/2} / M_w^{3/2}$ against $M_w^{1/2}$ (the Baumann plot)¹⁶ enables us to evaluate A from the intercept at $M_w^{1/2} = 0$. In this case, the unperturbed chain is assumed to be a Gaussian chain. The experimental data of the z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ were converted to the weight-average radius of gyration $\langle S^2 \rangle_w^{1/2}$.

Method 2D¹³

In the case of $\alpha_2 \neq 0$ (see eq(6)), the Baumann plot is not applicable and the following equation can be used in place of eq(10) :

$$\langle S^2 \rangle^{3/2} / M_w^{3(1+\alpha_2)/2} = K_0^{3/2} + (1/4 \pi^{3/2}) B M_w^{(1-3\alpha_2)/2} \quad (11)$$

where

$$K_0 = (\langle S^2 \rangle_0 / M_w) / M_w^{\alpha_2} \quad (12)$$

By use of eq (11) the plots of $\langle S^2 \rangle^{3/2} / M_w^{3(1+\alpha_2)/2}$ against $M_w^{(1-3\alpha_2)/2}$ (Baumann -Kamide -Miyazaki (BKM) plot) for a given solvent should result in a straight line and its extrapolation to $M_w^{1/2} = 0$ should give the $K_0^{3/2}$ value and accordingly K_0 .

2.2 Hydrodynamic approach

Method 2E

According to the Kurata-Yamakawa (KY) theory,¹⁷ the limiting viscosity number $[\eta]$ is given by eq (13) :

$$[\eta] = \pi^{3/2} N_A X F_0(X) \langle S^2 \rangle_0^{3/2} / M (1 + p(X) Z \cdot \cdot \cdot) \quad (13)$$

where N_A is the Avogadro number, $F_0(X)$ and $p(X)$ are functions of the draining parameter X . When $\alpha_2 = 0$, eq (13) can be rewritten on the basis of the Kawai-Kamide treatment¹⁸ as

$$[\eta] / f(X) M_w^{1/2} = K + (\Phi_0(X) p(X) (3/2 \pi)^{3/2} B M_w^{1/2} \quad (14)$$

where

$$K = \Phi_0(X_0) A^3 \quad (15)$$

and

$$f(X) = X F_0(X) / X_0 F_0(X_0) \quad (16)$$

The value of X_0 in eq (16) is determined by the equation :

$$\nu(X_0) = \epsilon (3 - n(X_0)) \quad (17)$$

The value of K (accordingly, A) can be determined as an intercept at $M_w^{1/2} \rightarrow 0$ of the plot of $[\eta]/f(X)M_w^{1/2}$ against $M_w^{1/2}$. The well-known Stockmayer-Fixman(SF) (or Kurata-Stockmayer-Fixman-Burchard(KSFB)) equation¹⁹ :

$$[\eta]/M_w^{1/2} = K + 2(3/2\pi)^{3/2} \Phi_0(\infty) B M_w^{1/2} \quad (18)$$

is derived from eq (13) by putting $X = \infty$ and neglecting terms higher than $M_w^{1/2}$. It should be noticed here that eq(18) does not hold when $\alpha_2 \neq 0$ and/or when X is finite or at least $X < X_0$. In the latter case, $\alpha\Phi$ in eq(19)

$$\Phi = K_\Phi M_w^{\alpha\Phi} \quad (19)$$

no longer becomes zero. Here Φ is the Flory's viscosity parameter (see, eq (25)). In eq(19) K_Φ and $\alpha\Phi$ are parameters characteristic of a polymer-solvent system and the molecular weight range, in which eq(19) holds. The above mentioned limitations to eq (18) have not been carefully taken into consideration when this equation was applied to cellulose and its derivative solutions. In the case $\alpha_2 = 0$ and $\alpha\Phi = 0$, the plot of $[\eta]/M_w^{1/2}$ vs. $M_w^{1/2}$ (SF plot), obtained from experimental data for a given polymer, should give a straight line and its intercept at $M_w^{1/2} \rightarrow 0$ and its slope should give K and B , respectively. Here, after the correction of molecular weight distribution of the sample was applied to K (see, eq(38)), A was evaluated from K value using eq (15) ($X_0 = \infty$). Here, $\Phi_0(\infty) = 2.87 \times 10^{23}$ was adopted.

Method 2F¹³

The following relation

$$\log K_m + \log [1 + 2(\alpha - 0.5 - \Delta - 1.5\alpha_2)^{-1} - 2^{-1}] = \log Kf(X) + (\alpha - 0.5 - \Delta - 1.5\alpha_2) \log M_0 \quad (20)$$

holds among parameters K_m , α of Mark-Houwink-Sakurada (MHS) equation (eq(21)), α_2 and X .

$$[\eta] = K_m M^\alpha \quad (21)$$

Here, Δ is the contribution of draining effect to the exponent α .

Equation (20) and similar equations were derived by Kamide, Kawai, and their coworkers.²⁰⁻²³ Δ in eq (20) is defined by eq (22).¹⁸

$$\Delta = \nu(X) - \nu(X_0) = \nu(X) - \epsilon (3 - n(X_0)) \quad (22)$$

$$\epsilon = d \ln \alpha_s / d \ln M \quad (23)$$

M_0 is a parameter depending on the molecular weight range, $M_1 \sim M_2$, to which eq(21) applies. In a case where the draining effect is negligible, the geometric mean, $(M_1 M_2)^{1/2}$, can be regarded, to a fairly good approximation, as M_0 .²³ K can be determined from K_m , α , X (accordingly, Δ) and α_2 . However, the accuracy of estimation of X by eq(20) is not so good.

Putting $\alpha_2 = 0$ and $\Delta = 0$ in eq(20), we obtain :

$$-\log K_m + \log [1 + 2\{(\alpha - 0.5)^{-1} - 2\}^{-1}] = -\log K + (\alpha - 0.5) \log M_0 \quad (24)$$

Equation(24) is, in principle, equivalent to eq(18). By use of eq (20) , K (accordingly, A) can be evaluated from experimental data of K_m , α , and M_0 , provided that $\alpha_2 = 0$ and $\alpha_\phi = 0$ (i. e., $X \approx \infty$). It has been ascertained that eq(21) is quite useful for estimating the K value of vinyl-type polymers.²⁴

Method 2G¹³

The limiting viscosity number $[\eta]$ is expressed by

$$[\eta] = 6^{3/2} \Phi (\langle S^2 \rangle_{w,0} / M_w)^{3/2} M_w^{1/2} \alpha_s^3 \quad (25)$$

The molecular weight dependence of Φ , α_ϕ , given by eq (19) can be interpreted as another indication of the draining effect. Note that eq(19) is an empirically approximated equation.

α_ϕ is given by

$$\alpha_\phi = [\nu(X) - \epsilon (3 - n(X))]_{AV} \quad (26)$$

It is clear that for X_0 α_ϕ becomes essentially zero and $\alpha_\phi \approx \Delta$ (see, eq (22)). The right

hand side term in eq(26) is a kind of average value of $(v(X) - e(3 - n(X)))$ over the molecular weight range concerned.

Combination of eq(12),(19) and(25) leads to the equation of $[\eta]$ for the polymer solution in which $\alpha_2 \neq 0$ and $\alpha_\Phi \neq 0$ hold, as is the case of cellulose, amylose and their derivatives, given by eq (27) :

$$[\eta]/M^{0.5+\alpha_\Phi+1.5\alpha_2} = 6^{3/2}K_\Phi K_0^{3/2} + 0.66K_\Phi BM^{(1-3\alpha_2)/2} \quad (27)$$

Equation(27) is a straightforward generalization of eq(18) in the most versatile form.

According to eq(27), a graph of $[\eta]/M_w^{0.5+\alpha_\Phi+1.5\alpha_2}$ as a function of $M^{(1-3\alpha_2)/2}$ (Kamide-Miyazaki (KM) I plot) should be linear, having $6^{3/2}K_\Phi K_0$ (accordingly, K_0) as the intercept. From eq (25), the MHS exponent α ($\equiv \text{dln}[\eta]/\text{dln} M$) can be written as follows

$$\alpha = 0.5 + \alpha_\Phi + \alpha_1 + 1.5\alpha_2 \quad (28)$$

where

$$\alpha_1 = 3e \quad (29)$$

α_1 is the contribution of the volume effect to the MHS exponent α and can be roughly estimated from α , α_Φ , and α_2 , through use of eq (28).

In the case of $\alpha_2 = 0$ and $\alpha_\Phi = 0$, method 2D is equal to method 2C, and method 2G reduces to method 2E. In good solvents where the penetration function Ψ exceeds 0.2, we could not determine α_s because the theoretical limiting upper value of Ψ is 1/5.047. Thus, method 2B is limited in its applicability to the small α_s region. This is the case for cellulose and its derivatives.¹²

3 Results and Discussion

Table 1 summarizes the Flory theta solvents and solvent mixtures of polyacrylonitrile (PAN) and its copolymers (See, also Table 13 of ref. 1). All the Flory's solvents were experimentally determined by the light scattering method as the solvent, in which the second virial coefficient A_2 becomes zero.

If the LS measurements in theta solvents are possible method 2A can be straightforwardly applicable, giving the most reliable information on A . LS measurements were possible for AN/MA copolymer (92wt% AN) in ethylene carbonate (EC)/water (82.5/7.5 wt/wt) at 25°C(8 samples) and in 51wt% aq nitric acid (6 samples) and for PAN with mm

=26% in EC/water (85/15, wt/wt)(7 samples) and in 55 wt% nitric acid (7 samples), respectively. The results for all the samples are collected in Table 17 of ref 1. LS measurements on stereoregular PAN in aq nitric acid with Flory's theta composition were often unsuccessful due to experimental difficulty encountered in exclusion procedure of gel-like materials during filtration. This was the case of highly isotactic PANs (mm = 53 and 75 %) in theta solvents.

Table 1 Flory's theta solvent and solvent mixtures of polyacrylonitrile and acrylonitrile copolymer

Polymer	Flory solvent at 25°C	Method	Sample No.	Ref.	
AN/MA* ^a	82.5wt% EC* ^b /water	$A_2=0$	2	Fig.3 ⁵	
	51wt% aq nitric acid	$A_2=0 (B=0)$	1	Fig.4 ⁵	
PAN	mm=26%	85wt% EC/water	Zimm plot(slope)	1	Fig.4 ⁶
		55wt% aq nitric acid	Zimm plot(slope)	1	Fig.3 ⁶
	=53%	56.5wt% aq nitric acid	$A_2=0$	1	Fig.3 ⁸
	=71%	57.5wt% aq nitric acid	$A_2=0$	1	Fig.7 ⁹
	=75%	57wt% aq nitric acid	$A_2=0$	5	Fig.4 ¹⁰

*a acrylonitrile/methyl acrylate copolymer (AN : 92wt%)

*b ethylene carbonate

The z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ and the limiting viscosity number $[\eta]$, determined by light scattering method and viscometry, respectively, for Flory's theta solution are empirically related to the weight-average molecular weight M_w through the relations :

$$\langle S^2 \rangle_z^{1/2} = K_{\gamma\theta} M_w^{\gamma\theta} \quad (30)$$

$$[\eta]_\theta = K_{m\theta} M_w^{\alpha\theta} \quad (31)$$

where $\langle S^2 \rangle_z^{1/2}$ and $[\eta]_\theta$ mean the $\langle S^2 \rangle_z^{1/2}$ and $[\eta]$ in the theta solutions.

Table 2 collects γ_θ and α_θ values for PAN and AN/MA copolymers. The parameter α_2 defined by in eq(6) is related to γ_θ through the relation :

$$\alpha_2 = \gamma_\theta - 0.5 \quad (32)$$

and are included also in the table. It is evident from Table 2 that except PAN(mm=75%), PAN and AN copolymers can be regarded as Gaussian chain at their unperturbed state ($\alpha_2 = 0$) and the ratio $\langle S^2 \rangle^{1/2} / M_w^{1/2}$ at unperturbed state is a characteristic parameter of a chain and method 2D reduces to method 2C.

 Table 2 γ and α in theta solvents; γ_θ and α_θ

Polymer	Flory's theta solvent					
	EC/water			aq nitric acid		
	γ_θ	α_2	α_θ	γ_θ	α_2	α_θ
AN/MA	0.50	0	0.50 ₂	0.50	0	0.50 ₂
PAN						
mm=26%	0.50	0	0.49 ₀	0.50 ₂	0	0.50 ₁
53%	—	—	—	0.51	0.01	0.50 ₁
75%	—	—	—	0.49 ₈	-0.01	0.50 ₇

Table 3 lists the average values of the ratio of the weight-average unperturbed radius of gyration $\langle S^2 \rangle_{0,w}^{1/2}$ to $M_w^{1/2}$, for AN/MA and PAN, evaluated directly by LS method. Here, $\langle S^2 \rangle_z^{1/2}$ is converted to $\langle S^2 \rangle_w^{1/2}$ by the relation,

$$\langle S^2 \rangle_w^{1/2} = q_s \langle S^2 \rangle_z^{1/2} \quad (33)$$

with

$$q_s = (1 + h) / (2\gamma + 1 + h) \quad (34)^{25}$$

$$\gamma = d \ln \langle S^2 \rangle_w^{1/2} / d \ln M_w \quad (30)'$$

$$h = \{ (M_w / M_n) - 1 \}^{-1} \quad (35)$$

(M_n : the number-average molecular weight)

In deriving eq(33) the polymer fractions are assumed to have the Schulz-Zimm type distribution. For the samples utilized in this study the polymolecularity was 1.3 ~ 1.5.

For PAN with mm=53% a 57wt% aq nitric acid is the solution of minimum acid concentration, in which LS measurements can be carried out. This composition is in very vicinity to that of the Flory's theta solution (56.5wt% aq nitric acid). Then, $\langle S^2 \rangle_{0,w}^{1/2} / M_w^{1/2}$ (and accordingly, A) was extrapolated using the plot of $\langle S^2 \rangle_z^{1/2}$ vs. the nitric acid concentration w_n (Fig.6 of ref.8). The $\langle S^2 \rangle_{0,w}^{1/2} / M_w^{1/2}$ value thus estimated is shown in Table 3 in parenthesis.

Table 3 The radius of gyration $\langle S^2 \rangle_{0,w}^{1/2} / M_w^{1/2}$ of polyacrylonitrile, directly measured by light scattering method, in Flory's theta solutions

Solvent	$\langle S^2 \rangle_{0,w}^{1/2} / M_w^{1/2} \times 10^8 \text{cm}$				
	AN/MA* ^a	PAN			
		mm=26%	mm=53%	mm=71%	mm=75%
EC/water* ^b	0.36	0.39	—	—	—
aq nitric acid					
51wt%	0.41 ₀	—	—	—	—
55wt%	—	0.43 ₂	—	—	—
56wt%	—	—	(0.42 ₆)* ^c	—	—
57wt%	—	—	—	—	0.80
57.5wt%	—	—	—	0.75	—

*a acrylonitrile/methyl acrylate copolymer (AN : 92wt%)

*b ethylene carbonate

*c extrapolated value

For PAN with mm=71% the difference between the Flory composition (57.5%) and the minimum concentration (60wt%) of the solutions, in which LS measurements can be carried out accurately, was 2.5wt%. The value of $\langle S^2 \rangle_{0,w}^{1/2} / M_w^{1/2}$ for the polymer (mm=71%) was indirectly evaluated⁹ : $\langle S^2 \rangle_z^{1/2}$ value for a sample $\gamma \cdot 2 \cdot 3$ ($M_w = 17.4 \times 10^4$ from Table III of ref.9) was extrapolated linearly at 57.5wt% aq nitric acid (Fig.7 of ref.9) to be 38.5nm (Fig.9 of ref.9), which was converted using eq(33) to $\langle S^2 \rangle_w^{1/2}$. Note that the A value for mm = 71% is estimated from a single sample with relatively large uncertainty.

But, as far as PAN with mm=75% is concerned, LS measurements were possible down to 56wt% nitric acid and the $\langle S^2 \rangle_{0,w}^{1/2} / M_w^{1/2}$ value (accordingly, A value) was determined by the interpolation method (theta composition = 57%). The result is shown with bracket in Table 3.

Note that the above LS measurements had been performed over long spun (1967 ~ 1998) and meanwhile the light scattering technology advanced remarkably to allow the accurate measurements on highly stereoregular PAN in aq nitric acid.

The unperturbed chain dimensions A was evaluated from $\langle S^2 \rangle_{0,w}^{1/2} / M_w^{1/2}$ data using eq(1) and eq(5). The results of averaged A values are summarized in Table 4. Method 2A could be applied to the AN/MA copolymer and PAN (mm=26%) in the two theta solvents, respectively. The A values in the EC/water mixture is about 11 ~ 13%

smaller than those in aq nitric acid. This significant difference suggests strongly that the dissolved state of the polymer in these two mixtures should not be the same, probably as a result of a specific interaction of nitric acid on the polymer chain.

Figure 1 shows the plot of A , evaluated in theta solvent, versus stereoregularity, expressed by mm content. It is clear from the figure that A value of PAN has a tendency to take larger value with increasing its tacticity.

Table 4 The unperturbed chain dimensions A determined by method 2A of polyacrylonitrile

Solvent	A				
	AN/MA ^{*a}	PAN			
		mm=26%	mm=53%	mm=71%	mm=75%
EC/water	0.74[8] ^{*b}	0.85[7]	—	—	—
aq nitric acid					
51wt%	0.93[6]	—	—	—	—
55wt%	—	1.09[7]	—	—	—
56wt%	—	—	(0.94)	—	—
57wt%	—	—	—	—	1.65[9]
57.5wt%	—	—	—	1.83[1]	—

*a acrylonitrile/methyl acrylate copolymer (AN : 92wt%)

*b []; number of fractions

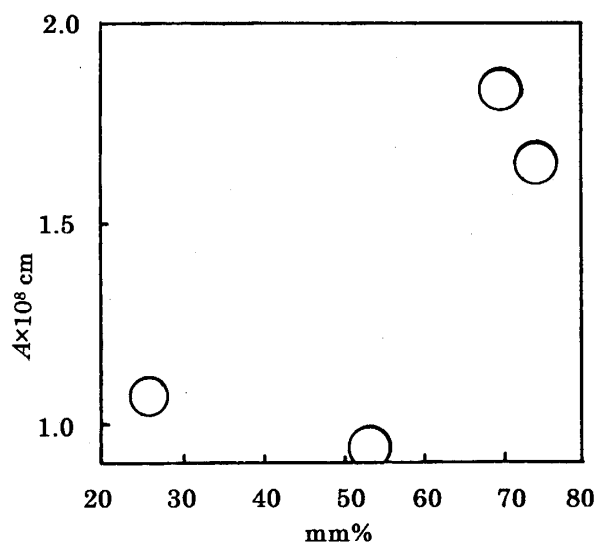


Figure 1 Plots of the unperturbed chain dimensions A in Flory's theta solvents as function of mm triad content of polyacrylonitrile at 25°C

The molecular weight dependence of Flory's viscosity parameter Φ (α_Φ in eq(19)) was determined using the experimental data. α_Φ was found to be approximately zero except PAN (mm= 75%), for which α_Φ values are listed in Table 5. The table indicates that only for PAN (mm= 75%) method 2G is applicable.

Table 5 α_Φ (eq (19)) of PAN (mm=75%) in aq nitric acid

Aq nitric acid(wt%)	α_Φ
57.4	0.078
60	0.085
65	0.048
70	0.030

Tables 6 ~ 11 summarize the unperturbed chain dimensions A , estimated by methods 2A~2G, of AN/MA and AN/VDC copolymers and PAN with mm = 26, 53, 71 and 75% in various solvents. Here, $K_{m\theta}$, defined as K_m evaluated in theta solvent by eq(18) or eq(24), corresponds to fractions with some polydispersity (even if small) and then, the polymolecularity correction q_η should be applied to $K_{m\theta}$ to obtain the value for mono-disperse samples $K_{m\theta(m)}$ through use of the relations :

$$K \equiv K_{m\theta(m)} = q_\eta K_{m\theta} \quad (37)$$

with

$$q_\eta = (h+1/2) \Gamma(h+1/2) / \{(h+1)^{1/2} \Gamma(h+1/2)\} \quad (38)^{26}$$

where Γ is Gamma function and q_η is, for example, 0.971 for $M_w/M_n = 1.3$.

Table 6 Unperturbed chain dimensions A of AN/MA copolymer in various solvents at 25°C

Method	$A \times 10^8 / \text{cm}$					
	DMF	EC/water ($w_e = 82.5\%$)	aq nitric acid			
			51wt%	55wt%	67wt%	80wt%
2A	—	0.74	0.93	—	—	—
2B	0.86	—	—	1.12	1.30	1.55
2C	0.93	—	—	1.11	1.29	1.42
2E	—	0.81	0.89	0.89	1.04	1.07
2F	0.89	0.82	0.91	0.92	1.00	1.06
most probable	0.90	0.74	0.93	1.12	1.30	1.49

Further Study of Unperturbed Chain Dimensions of ...

Table 7 Unperturbed chain dimensions A of AN/VDC copolymer (AN : 59wt%) in various solvents at 25°C

Method	$A \times 10^8 / \text{cm}$				
	DMAc ^{*a}	DMF ^{*b}	γ -BL ^{*c}	n-MP ^{*d}	70wt%HNO ₃
2C	1.11	—	—	—	—
2E	0.98	0.95	0.95	1.00	0.88
2F	0.98	0.95	0.95	1.00	0.85
most probable	0.98	0.95	0.94	1.00	0.86

*a, dimethyl acetamide *b, dimethyl formamide *c, γ -butyrolactone
*d, N-methyl-2-pyrrolidone

Table 8a Unperturbed chain dimensions A of PAN (mm=26%) in various solvents at 25°C

Method	$A \times 10^8 / \text{cm}$		
	DMF	DMSO	EC/water ($w_e=85\text{wt}\%$)
T ^{*a} { 2A	—	—	0.85
2C	1.03	1.12	0.85
H ^{*b} { 2E	0.99	1.07	0.90
2F	1.05	1.10	0.90
most probable	1.03	1.10	0.85

*a, Thermodynamic approach *b, Hydrodynamic approach

Table 8b Unperturbed chain dimensions A of PAN(mm= 26%) in various solvents at 25°C

Method	$A \times 10^8 / \text{cm}$				
	aq nitric acid				
	55wt%	60wt%	65wt%	67wt%	70wt%
T ^{*a} { 2A	0.98	—	—	—	—
2C	0.97	1.26	1.45	1.18	1.56
H ^{*b} { 2E	1.03	1.09	1.08	1.07	1.09
2F	1.03	1.09	1.08	1.08	1.08
most probable	0.98	1.26	1.45	1.18	1.56

*a, Thermodynamic approach *b, Hydrodynamic approach

Table 9 Unperturbed chain dimensions A of PAN (mm = 53%) in various solvents at 25°C

Method	DMSO	$A \times 10^8 / \text{cm}$		
		aq nitric acid		
		56.5wt%	57wt%	67wt%
T ^{*a} {	2A	—	(1.06) ^{*a}	—
	2B	1.19	—	—
	2C	1.10	—	1.05
H ^{*b} {	2E	1.03	0.95	0.96
	2F	1.09	1.01	1.01
most probable		1.15	1.06	1.05

*a, Thermodynamic approach : $A = \langle S^2 \rangle_{0,Z}^{1/2} \times q_s \times 6^{1/2} \times M_w^{-1/2} = 218 \times 10^{-8} \times 0.812 \times 6^{1/2} \times (1.68 \times 10^5)^{-1/2} = 1.057 \times 10^{-8} \text{ cm}$

*b, Hydrodynamic approach

Table 10 Unperturbed chain dimensions A of PAN (mm = 71%) in various solvents at 25°C

Method	$A \times 10^8 / \text{cm}$
	aq nitric acid 55%
	2A
	1.83 ^{*a}

*a $A = \langle S^2 \rangle_{0,Z}^{1/2} \times q_s \times 6^{1/2} \times M_w^{-1/2} = 385 \times 10^{-8} \times 0.812 \times 6^{1/2} \times (1.74 \times 10^5)^{-1/2} = 1.83 \times 10^{-8} \text{ cm}$

Table 11 Unperturbed chain dimensions A of PAN (mm = 75%) in various solvents at 25°C

Method	$A \times 10^8 / \text{cm}$					
	aq nitric acid					60wt%
	56wt%	57wt%	60wt%	65wt%	70wt%	NaSCN
T ^{*a} {	2A	—	1.60 ^{*c}	—	—	—
	2C	1.57	1.58	1.80	2.09	2.33
	2D	—	1.60	1.80	2.07	2.30
H ^{*b} {	2E	—	1.08	1.12	1.17	1.19
	2F	1.06	1.08	1.11	1.17	1.19
	2G	—	1.56	1.88	2.08	2.26
most probable		1.57	1.60	1.80	2.08	2.30

*a, Thermodynamic approach

*b, Hydrodynamic approach

*c, Interpolated values

Then, A can be calculated from eq(15)' :

$$A = \{K/\Phi_0(X_0)\}^{1/3} = \{q_n K_{m\theta}/\Phi_0(X_0)\}^{1/3} \quad (15)'$$

Inspection of the above tables leads us to the following conclusions :

AN/MA copolymer : Except for aq nitric acid with acid content $w_n \geq 55\%$ all methods give almost the same A value ; the relation

$$A_{(2A)} \approx A_{(2B)} \approx A_{(2C)} \approx A_{(2E)} \approx A_{(2F)} \quad (39)$$

($A_{(2A)}$, $A_{(2B)}$, $A_{(2C)}$, $A_{(2E)}$, $A_{(2F)}$ are A values evaluated by method 2A, method 2B, method 2C, method 2E, method 2F).

holds for the solutions, except aq nitric acid with $w_n > 51\text{wt}\%$.

AN/VDC copolymer : the relation $A_{(2C)} \geq A_{(2E)} \approx A_{(2F)}$ (40)

holds its validity : $A_{(2C)}$ is slightly larger than $A_{(2E)}$ and $A_{(2F)}$, although the difference seems insignificant.

PAN (mm=26%) : In theta solvents, eq(39) holds also⁷. In non-theta organic solvents $A_{(2C)}$ is some several % larger than $A_{(2E)} (\approx A_{(2F)})$:

$$A_{(2C)} > A_{(2E)} \approx A_{(2F)} \quad (41)$$

In non-theta aq nitric acid the difference of A between thermodynamic and hydrodynamic approaches becomes noticeable ;

$$A_{(2C)} \gg A_{(2E)} \approx A_{(2F)} \quad (42)$$

Note that the thermodynamic approach is theoretically preferable to the hydrodynamic approach.

PAN (mm=53%) : In theta solution (aq nitric acid with $w_n = 56.5\text{wt}\%$) methods 2A, 2E and 2F yield approximately the same A values (i.e., eq(39) is expected to hold). In non-theta solvents PAN (mm = 53%) obeyed eq(41).

PAN (mm=75%) : Validity of eq(42) is confirmed over a whole range of concentration investigated. When the non-Gaussian nature of polymeric chain in theta solvent α_2

(from eq(33)) ($\alpha_2 = \gamma_\theta - 0.5 = 0.494 - 0.5 = -0.006 \approx -0.01$) and the molecular weight dependence of Φ , α_Φ (from Table 5 $\alpha_\Phi \approx 0.085$ at 57.0wt% nitric acid) are reasonably considered, the relation

$$A_{(2A)} \approx A_{(2C)} \approx A_{(2D)} \approx A_{(2G)} \gg A_{(2E)} \approx A_{(2F)} \quad (43)$$

was confirmed to be valid. The above relation was first obtained for numerous cellulose and cellulose derivative solutions.

Table 12 summarizes the most probable A values ($A_{(m)}$), deduced from Table 6 ~ 11, of PAN molecules with a wide variety of the microtacticity in various solvents or solvent mixtures. In the table, the extrapolated values are shown in parenthesis and asterics mean theta solvents.

Table 12 The most probable unperturbed chain dimensions $A_{(m)}$ of polyacrylonitrile in various solvents

Solvent	$A_{(m)} \times 10^8$ (cm)					
	AN/MA	AN/VDC	PAN			
			mm=26%	mm=53%	mm=71%	mm=75%
DMF	0.90	0.95	1.03	—	—	—
DMSO	—	—	1.10	1.15	—	—
EC/water	0.74*	—	0.95*	—	—	—
HNO ₃						
51%	0.93*	—	—	—	—	—
55%	1.12	—	0.98*	—	—	—
56%	—	—	—	—	—	1.57
56.5%	—	—	—	(1.06)*	—	—
57%	—	—	—	1.05	—	1.60*
57.5%	—	—	—	—	(1.83)*	—
60%	—	—	1.26	—	—	1.80
65%	—	—	1.45	—	—	2.08
67%	1.30	—	1.18	1.10	—	—
70%	—	0.86	1.56	—	—	2.30
80%	1.49	—	—	—	—	—
60% aq NaSCN	—	—	—	—	—	2.00

* Flory's theta solvent

Further Study of Unperturbed Chain Dimensions of ...

PAN molecules have larger A in aq nitric acid than in organic solvents. Thermodynamic affinity of aq NaSCN solution against PAN molecule seems quite similar to aq nitric acid.

Figure 2 shows the dependence of the unperturbed chain dimensions A on the acid concentration w_n of aq nitric acid. The A value increases significantly with an increase in w_n : Polymer chain becomes rigid in concentrated acid solution. The plots can be roughly classified into two groups: AN/MA copolymer and PAN (mm=26 and 53%) belong to a group and PAN(mm= 75%) to the second group. The dependence of A on w_n , dA/dw_n , is larger for PAN with larger mm content.

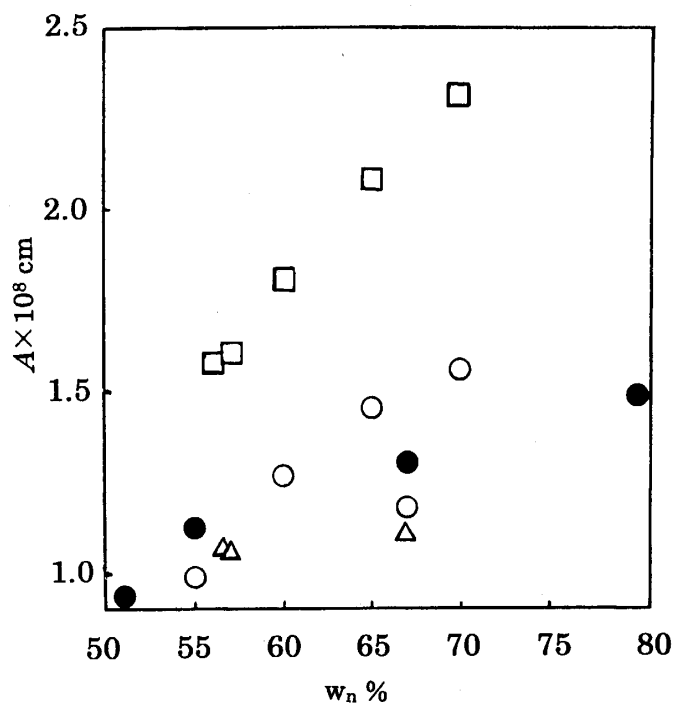


Figure 2 Plots of the unperturbed chain dimensions A of polyacrylonitrile versus nitric acid concentration w_n of aq nitric acid solutions: ●, AN/MA copolymer; ○, PAN (mm=26%); △, PAN (mm=53%); □, PAN (mm=75%)

Figure 3 shows the dependence of the unperturbed chain dimensions A on the isotacticity mm. Evidently A value in aq nitric acid is larger for PAN with higher tacticity. In organic solvent such as DMSO the dependence of A on mm content (i.e., dA/dmm) is quite small, even if significantly positive.

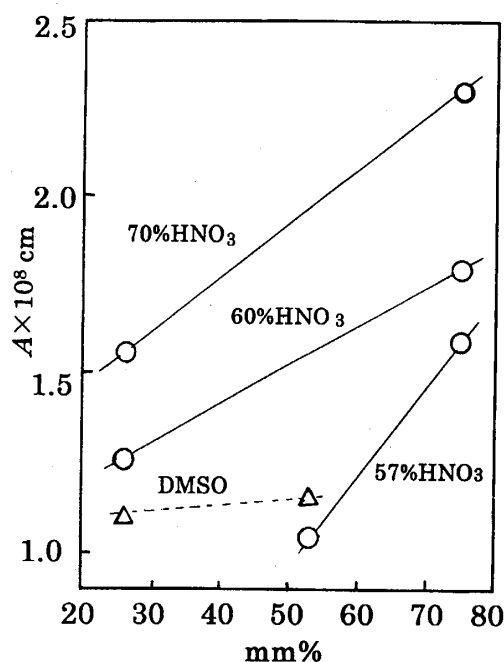


Figure 3 Effect of mm content on the unperturbed chain dimensions A of polyacrylonitrile dissolved in a given solvent (Δ) or solvent mixture (\circ)

Figure 4 shows the dependence of A on the solvation in PAN~aq nitric acid system. Here, $N_{s,0}$ is the weight of solvated solvent per gram of polymer at infinite dilution. In Figure 4, $N_{s,0}$ values are taken from Fig.19 of ref 10. The relations for PAN(mm= 26%) and PAN(mm= 53%) yield roughly a common curve, but the relation corresponding to PAN(mm= 75%) derivatives from the above curve, shifting to higher A axis. It was indicated in another study⁸ that the relation between A of PAN(mm= 26%), PAN (mm=53%) and AN/MA copolymer and $N_{s,0}$, in various organic solvents, including dimethylsulfoxide(DMSO), dimethylacetamide (DMAc) and dimethylformamide(DMF), builds a common curve. The rigidity of higher tactic PAN is larger than that simply expected from the solvation. In the previous paper¹⁰ it was shown that in aq nitric acid $N_{s,0}$ increases with acid concentration w_n , approaching an asymptotic value, whose magnitude depends on the tacticity of polymers. A polymer with low stereoregularity exhibits larger $N_{s,0}$ value than a polymer with higher isotacticity at the same acid concentration. This means that highly stereoregular PAN has less tendency to solvate with aq nitric acid.

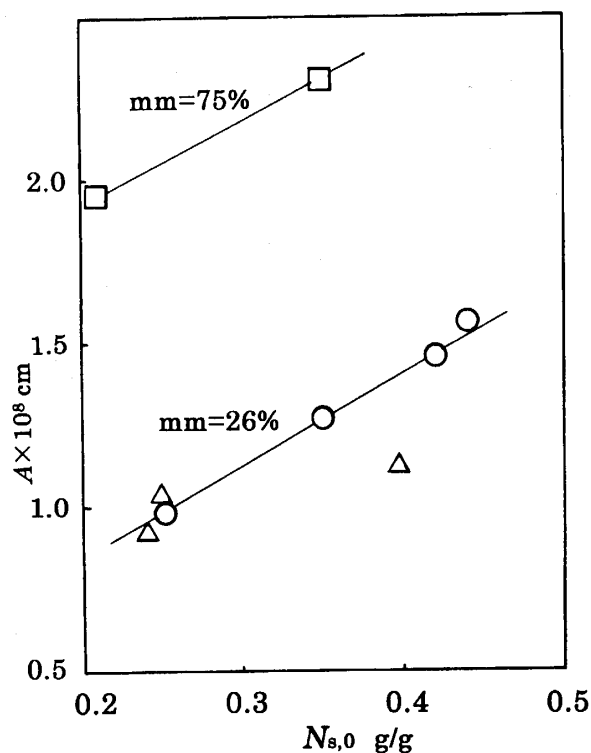


Figure 4 Correlations between the unperturbed chain dimensions A and the weight of solvated solvent molecule per unit weight of polymer $N_{s,0}$ of polyacrylonitrile ~ aq nitric acid system : ○, PAN (mm=26%); △, PAN (mm=53%); □, PAN (mm=75%)

Kamide and his coworkers³⁰ analyzed on the ^{13}C NMR spectra of PAN (mm=26%) and PAN (mm=53%) in DMSO-d_6 ³⁰, concluding that the meso part of PAN may have a trans-trans or almost trans-trans conformation (Figure 5) and the former conformation might stiffen the meso sequence in the solution. Thereafter, Kamide et al.⁸ proposed a hypothetical PAN chain, in which the meso sequence can be regarded as at least partly, a rigid rod and the racemo sequence is freely rotatable (Figure 5). As the meso-meso (mm) triad content becomes higher, the number of 'free' CN group per gram of PAN polymer (i.e., the racemo-racemo(rr) triad content) will decrease: For example, PAN (mm=26%), PAN (mm=53%), and AN (mm=71%) samples have rr=23%, 12%, and 0.07% (see, Table 3 of ref 1). The solvation of solvent molecules against a polymer chain may occur exclusively between solvent molecules and 'free' CN group (in other words CN group in racemo sequence) of a chain. Therefore, the experimental fact that an increase in mm content brings about a decrease in $N_{s,0}$ ¹⁰ can be explained by the above concept.

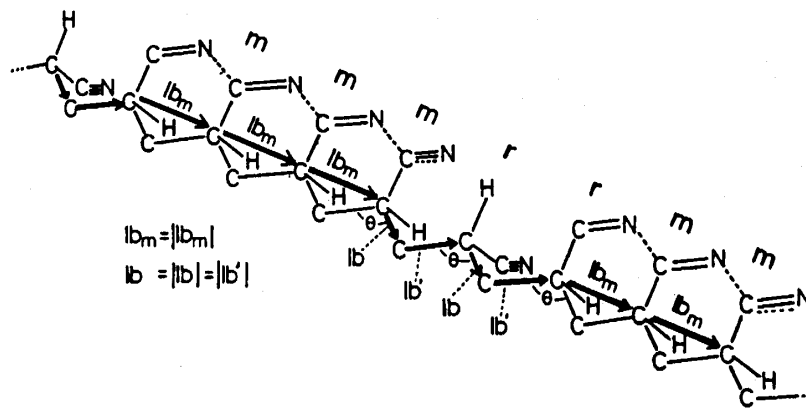


Fig.5 Polyacrylonitrile chain model

Even at $B=0$ (i.e., $\alpha_s = 1$) the radius of gyration of a solvated chain is regarded as unperturbed chain and this is larger than that of unsolvated chain. The solvent effect of A value, observed for PAN solutions (see, Table 12, Fig.1), can be explained in terms of solvation, which should be distinguished strictly from the excluded volume effect (i.e., the long-range interaction).

Decrease in number of free (racemo) CN group and increase in number (part) of rigid rod will compensate with each other. In the same solvent PAN having higher mm content show smaller $N_{s,0}$ (Fig.20 of ref 10), but larger A (Figure 2), suggesting strongly that the contribution of rod segment plays more important role to A than that of the solvation.

4 Conclusion

- 1 AN copolymer and relatively low stereoregular PAN can be analyzed by thermodynamic and hydrodynamic approaches to estimate the unperturbed chain dimensions A .
- 2 For highly isotactic PAN the molecular weight dependence of $\Phi(\alpha\Phi)$ and of the non-Gaussian nature of the unperturbed chain (α_2) should be taken into account in order to apply the hydrodynamic approach.
- 3 The most probable A values are collected as functions of mm content of PAN and acid concentration w_n , of nitric acid as solvents.
- 4 The A value, directly evaluated for a given PAN by the light scattering measurement in Floly's theta solutions, exhibited a notable solvent nature dependence. This can be explained by the solvation of the unperturbed chain.
- 5 The A value of given PAN increases in the acid concentration w_n .

- 6 The A value of PAN, dissolved in the same solvent, increases with the meso-meso triad content of the polymer.
- 7 PAN(mm= 26%) and PAN(mm= 53%) yield the same $A \sim N_{s,0}$ relations, but the relation for PAN(mm= 75%) differs significantly from the above relations.

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Kenji Kamide

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