

Light Scattering and Viscometric Study on Polyacrylonitrile in Dimethylformamide, Ethylene Carbonate/Water Mixture, and Aqueous Nitric Acid

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(Received September 12, 1984)

ABSTRACT: An attempt was made to determine the Flory theta solvents and the unperturbed chain dimension A of polyacrylonitrile (PAN). A sample of PAN, polymerized using redox catalyst and having isotactic triad of 26% and syndiotactic triad of 24%, was fractionated by successive solution fractionation method to give a series of fractions with the ratio of weight- to number-average molecular weight M_w/M_n of 1.15—1.41. A mixture of ethylene carbonate (EC) and water containing 85 wt% EC and aq. 55 wt% nitric acid was identified by the light scattering method to be Flory theta solvents at 25°C whose second virial coefficients were zero. The Mark-Houwink-Sakurada (MHS) equations were determined in various solvents. In the theta solvents, the radius of gyration $\langle S^2 \rangle_z^{1/2}$ was proportional to $M_w^{1/2}$ and the exponent a in MHS equations was always 0.5. The Flory viscosity parameter Φ was 2.3×10^{23} in DMF and 2.8×10^{23} in theta solvents, independent of M_w . The unperturbed chain dimension parameter A , the conformation parameter σ and the characteristic ratio C_∞ were determined by thermodynamic and hydrodynamic methods. Both methods gave consistent results. The solvent dependence of these parameters was demonstrated.

KEY WORDS Flory Solvent / Unperturbed Chain Dimension / Polyacrylonitrile / Second Virial Coefficient / Mark-Houwink-Sakurada Equation / Flory viscosity Parameter / Conformation Parameter / Characteristic Ratio /

In a previous paper,¹ we investigated the dilute solution properties of a random acrylonitrile (AN)/methyl acrylate (MA) copolymer with 92 wt% AN and found, using the light scattering method, ethylene carbonate (EC) and water containing 82.5 wt% EC and a 51 wt% aqueous nitric acid as a mixture, both to be Flory theta solvents at 25°C. The effect of polar solvent on molecular properties of the AN/MA copolymer was clarified.

In the past 30 years a number of investigators, including Cleland and Stockmayer,² Krigbaum and Kotliar,³ Onyon,⁴ Fujisaki and Kobayashi,⁵ Peebles,⁶ Kamide *et al.*,⁷ and Shibukawa and his coworkers,⁸ have studied the dilute solution properties of polyacrylo-

nitrile (PAN) in dimethylformamide (DMF) using light scattering and viscometric methods. These studies on PAN in DMF were clearly prompted by the industrial importance of PAN. Nevertheless, no theta solvent for PAN has been found by thermodynamic methods because of the experimental difficulty in eliminating the fluorescence usually contaminating the scattered light and low solubility of PAN.

Kamide and his collaborators^{9,10} identified some solvents as the theta solvent, though indirectly from the exponent value $a=0.5$ in the Mark-Houwink-Sakurada (MHS) equation:

$$[\eta] = K_m M^a \quad (1)$$

where $[\eta]$ is the limiting viscosity number, M , molecular weight, and K_m and a constants independent of M . It is a well established fact a becomes 0.5 in theta solvents. Based on this fact, Kamide *et al.* found an aqueous EC with 85 wt% to be a theta solvent at 25°C for a PAN prepared by conventional redox polymerization and EC itself to be also a theta solvent at 60°C for another PAN prepared by gamma-ray irradiation of urea–canal complex of AN (γ -PAN). However, they did not perform direct light scattering measurements of the unperturbed chain dimension of PAN in theta solvents and estimated it indirectly from thermodynamic and hydrodynamic data in non-theta solvents or from hydrodynamic data in an approximately theta solvent.

In this article, we determine theta solvents by light scattering and evaluated the thermodynamic and hydrodynamic properties of PAN in various solvents including the theta solvents thus obtained.

EXPERIMENTAL

Sample

A sample of PAN was prepared in water by the conventional free radical polymerization of acrylonitrile at 55°C using ammonium persulfate and ammonium hydrogen sulfite as initiators. The limiting viscosity number $[\eta]$ of this polymer was 210 ml g⁻¹ in DMF at 25°C and the viscosity-average molecular weight M_v was 1.68×10^5 as calculated from the MHS equation established here (see Table III).

Figure 1 shows a ¹³C NMR spectrum of the PAN sample in deuterated dimethyl sulfoxide (DMSO-*d*₆). The spectrum was obtained from a JOEL FX 270 Pulse-Fourier Transform NMR spectrometer (67.80 MHz) at 37°C. The triad tacticity was evaluated according to Inoue and Nishioka's procedure¹¹ from methine and cyano carbons, and both gave the same results: isotactic triad 26%; syndiotactic triad, 24%; heterotactic triad 50%. The PAN prepared in this study was isotactic diad of

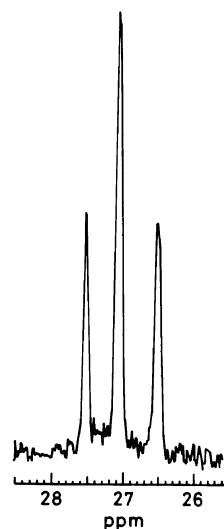


Figure 1. ¹³C NMR spectrum of the methine carbon of PAN in deuterated dimethyl sulfoxide (DMSO-*d*₆).

51%. This value is similar to those reported previously for PANs prepared by redox polymerization.¹²

Solvents

Reagent grade dimethylformamide (DMF), ethylene carbonate (EC) and analytical chemical grade 70 wt% aqueous nitric acid, dimethyl sulfoxide (DMSO) and toluene were utilized as received. The polymer, prepared by redox polymerization, contained a catalyst residue, such as -SO₃H, easily ionized in solvent, at the chain ends. The addition of LiCl reduced both $[\eta]$ and k' . 0.1-wt% LiCl was sufficient to suppress the ionic behavior of PAN solution and bring about a 2% decrease in $[\eta]$. We added 0.1 wt% of LiCl to DMF, in which PAN was dissolved. EC/water mixtures containing 85 and 87.5 wt% EC (*i.e.*, $w_e = 85$ and 87.5 wt%) were prepared by adding distilled water to EC, and, 55, 60, and 67 wt% aqueous nitric acid were prepared by adding distilled water to 70 wt% aqueous nitric acid. To these aqueous nitric acid 500 ppm of urea was added to accelerate the decomposition reaction of nitrous acid and nitrogen oxide (NO) remaining in the nitric acid and prevent

the decomposition reaction of nitric acid.

Fractionation

The successive solution fractionation (SSF) was employed using DMSO as solvent and toluene as non-solvent.¹ A complete liquid-liquid phase separation always occurred in PAN solutions of these solvents, and the polymer-lean phase at each step was separated as a fraction. Thus, a 1.0 wt% solution of PAN sample in DMSO was separated into 18 fractions at 45°C. Among them, these seven fractions each having a weight-average molecular weight M_w from 5.2×10^4 to 5.2×10^5 were used.

Solution Viscosity

Solution viscosity was measured in DMF (0.1 wt% LiCl), EC/water mixture ($w_e = 85$ wt%), and aqueous nitric acid (nitric acid content $w_n = 55$ and 67 wt%) with a modified Ubbelohde suspension type viscometer at $25 \pm 0.01^\circ\text{C}$. The polymer was dissolved in DMF, EC/water mixture and 55 wt% aqueous nitric acid at 50°C and in 67 wt% aqueous nitric acid at 20°C. The polymer in EC/water mixture was stored at 30°C.

Light Scattering

Light scattering measurements were made in DMF, EC/water mixture and aqueous nitric acid. Aqueous nitric acid is a very successful and widely used inorganic solvent for PAN. A light scattering photometer, Union Giken LS-601, and FICA photogoniometer, 42000 were used for the first solvent and the last two solvents, respectively.

(a) DMF

The basic procedure for preparing the solution was similar to that in the previous study.¹ But some improvement were made, such as using a polytetrafluoroethylene membrane filter FP-010 (pore diameter 0.10 μm), manufactured by Sumitomo Denko Co.

The specific refractive index increment $d\bar{n}/dC$ for the PAN in DMF was determined to

be $0.078 \text{ cm}^3 \text{ g}^{-1}$ by a Shimadzu differential refractometer model DR-4 at 25°C at a wave length λ_0 of 633 nm. This value is comparable to $0.087 \text{ cm}^3 \text{ g}^{-1}$ ($\lambda_0 = 436 \text{ nm}$), determined for a redox PAN in DMF without LiCl.⁷

Polarized He-Ne laser light of wave length $\lambda_0 = 633 \text{ nm}$ was used as incident beam and the unpolarized scattering intensity was measured at various angles θ from 20 to 135°. A spectroscopic analysis of the scattering light from PAN/DMF solution when $\lambda_0 = 633 \text{ nm}$ showed no contamination by fluorescence and no correction of measured intensity for fluorescence, proposed before by Kamide *et al.*,⁷ was made. Calibration of the apparatus was made using benzene (the Rayleigh ratio at $\theta = 90^\circ$, $R_{90} = 11.84 \times 10^{-6}$ at $\lambda_0 = 633 \text{ nm}^{13}$). The data obtained were analyzed according to Zimm's procedure to evaluate the weight-average molecular weight M_w , z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ and second virial coefficient $A_{2,L}$.

(b) EC/Water Mixture

The PAN sample was dissolved at 50°C in two EC/water mixtures of EC content $w_e = 85$ and 87.5 wt%. The preparative procedure for the solution was the same as previously described.¹ No precipitation was observed in PAN solutions in the EC/water mixture during measurements at 25°C.

Detailed procedures for the light scattering measurements and analysis of data were the same as those described in the previous paper¹ for the AN/MA copolymer solution. The approximate value of M_w , determined in DMF, was assumed for the EC/water mixture, and $\langle S^2 \rangle_z^{1/2}$ and $A_{2,L}$ were calculated.

(c) Aqueous Nitric Acid

$\langle S^2 \rangle_z^{1/2}$ of the PAN in aqueous nitric acid ($w_n = 55, 60, \text{ and } 67 \text{ wt}\%$) was determined, assuming the M_w values measured in DMF to be obtainable even in nitric acid. This assumption was partly varied by confirming the constancy of M_w of PAN sample before and after dissolving in nitric acid for 3 h. Light scattering in the polymer/inorganic acid system was

first used by us in study of AN/MA copolymers¹ and was applied to PAN polymers without serious modification. Great care was taken to ensure that nitric acid in the solution did not decompose and the solution was kept colorless and transparent.

Osmotic Pressure

The number-average molecular weight M_n and second virial coefficient $A_{2,0}$ of the PAN/DMF system were determined by membrane osmometry by the same manner used for the AN/MA copolymer in DMF.

Adiabatic Compressibility

The adiabatic compressibility β of the solution was calculated by the equation of Laplace.

$$\beta = 1/(\rho v^2) \quad (2)$$

Here, ρ and v are the density and sound velocity of the solution, respectively. The ultrasonic velocity was measured with a Pierce type ultrasonic interferometer, employed by Kamide and Saito,¹⁴ operating at 4.99985 MHz. The temperature of the solution was controlled to $\pm 0.005^\circ\text{C}$ or less. ρ of the solution was measured with an Ostwald type pycnometer. Solutions of different concentrations (x : g-polymer/100 g-solvent) were prepared independently.

The weight of the solvated solvent per gram of polymer n was calculated by the equation of Passynsky.¹⁵

$$n = (1 - \beta/\beta_s)(100 - x)/x \quad (3)$$

β_s denotes the adiabatic compressibility of the solvent. Equation 3 was derived assuming the polymer and solvent in the solvating region to be incompressible.

RESULTS AND DISCUSSION

Figure 2a, b, and c shows some typical Zimm plots of a PAN fraction (PAN-4, $M_w = 15.8 \times 10^4$) in DMF, 67 wt% aqueous nitric acid and EC/water mixture ($w_e = 85 \text{ wt}\%$). No

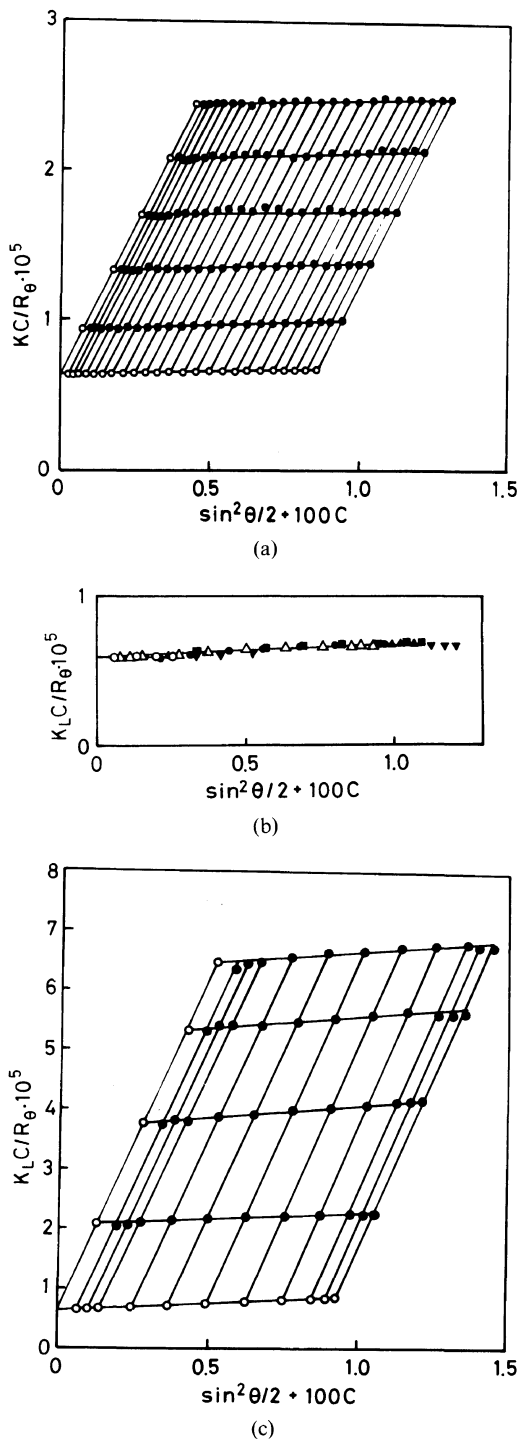


Figure 2. A typical Zimm plot for PAN-4 at 25°C: (a) in DMF; (b) in the EC/water mixture ($w_e = 85 \text{ wt}\%$); (c) in aqueous nitric acid ($w_n = 67 \text{ wt}\%$).

Dilute Solution Properties of Polyacrylonitrile

Table I. Results of light scattering and osmometry on polyacrylonitrile fractions in DMF, 67 wt% HNO₃, 85 wt% EC, and 55 wt% HNO₃ at 25°C

Sample	Light scattering						Osmometry	
	DMF			67 wt% HNO ₃	85 wt% EC	55 wt% HNO ₃	DMF	
	$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2} \times 10^8$ ^a	$A_2 \times 10^3$ ^b	$\langle S^2 \rangle_z^{1/2} \times 10^8$	$\langle S^2 \rangle_z^{1/2} \times 10^8$	$\langle S^2 \rangle_z^{1/2} \times 10^8$	$M_n \times 10^{-4}$	$A_2 \times 10^3$
PAN-1	5.2	128	2.65	142	98	112	3.9	1.87
PAN-2	7.5	153	2.45	176	117	135	6.2	1.64
PAN-3	10.7	183	2.59	218	140	161	—	—
PAN-4	15.8	236	2.55	262	170	196	11.2	1.83
PAN-5	21.5	276	2.20	310	198	229	16.0	1.64
PAN-6	31.2	333	2.00	395	239	276	27.0	1.49
PAN-7	52.0	453	1.80	505	309	356	—	—

^a cm. ^b mol·cm³·g⁻².

Table II. Limiting viscosity number $[\eta]$ and Flory viscosity parameter Φ for polyacrylonitrile fractions in various solvents at 25°C

Sample	$M_w \times 10^4$	DMF		67 wt% HNO ₃		85 wt% EC/W		55 wt% HNO ₃	
		$[\eta]$ ^a	Φ ^b	$[\eta]$	Φ	$[\eta]$	Φ	$[\eta]$	Φ
PAN-1	5.2	90	2.13	105	1.48	52	2.74	82	2.90
PAN-2	7.5	117	2.32	135	1.59	62	2.76	92	2.66
PAN-3	10.7	143	2.38	165	1.62	77	2.89	115	2.80
PAN-4	15.8	192	2.20	205	1.40	89	2.73	132	2.64
PAN-5	21.5	235	2.28	256	1.52	101	2.66	163	2.77
PAN-6	31.2	298	2.40	304	1.41	130	2.83	192	2.72
PAN-7	52.0	445	2.38	460	1.49	160	2.69	256	2.81

^a cm³·g⁻¹. ^b 10²³·g⁻¹.

downward distortion is observed for these plots, suggesting the correction of fluorescence, unavoidably necessary for a PAN/DMF solution without LiCl at incident light λ_0 436 nm and 546 nm, not to be needed.

Table I lists M_w , M_n , $\langle S^2 \rangle_z^{1/2}$, $A_{2,L}$ and $A_{2,0}$ for seven PAN fractions in DMF. The table also contains the data for $\langle S^2 \rangle_z^{1/2}$ for the same fractions in 67 and 55 wt% aqueous nitric acid and EC/water mixture with $w_e = 85$ wt%, all at 25°C. From Table I, it is apparent that the polymolecularity of the fraction covering $M_w \times 10^{-4}$ from 5.2 to 52.0 is almost constant, ($M_w/M_n = 1.15$ — 1.41 (average, 1.29)). Separation of a series of fractions of constant polymolecularity is an advantage of

SSF as predicted by theory.¹⁶ Note that all the polymer samples utilized hitherto in the literature were all prepared by successive precipitation fractionation (SPF) and the polymolecularity of the fractions obtained by SPF depends significantly on M_w .

Table II shows the limiting viscosity numbers $[\eta]$ in DMF, 67 and 55 wt% aqueous nitric acid, and EC/water mixture with $w_e = 85$ wt%.

Figure 3 shows a plot of $(K_L C/R_\theta)_{\theta \rightarrow 0}$ against the polymer concentration C for fraction PAN-4 with $M_w = 15.8 \times 10^4$ in aqueous nitric acid at various w_n . Here,

$$K_L = ((2\pi^2 \tilde{n}_0^2)/(\lambda_0^4 N_A)) (d\tilde{n}/dC)_{w_e}^2 (1 + \xi_a (d\tilde{n}_0/dw_e)/(d\tilde{n}/dC)_{w_e})^2;$$

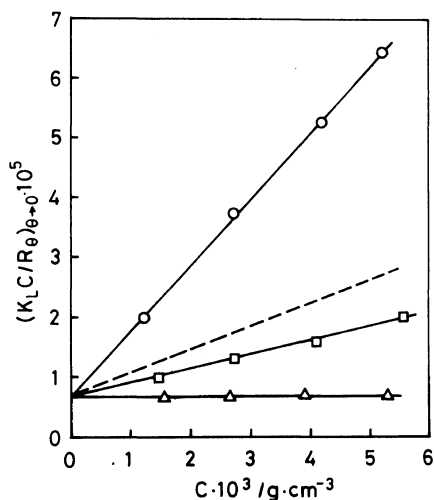


Figure 3. Plot of $(K_L C/R_\theta)_{\theta \rightarrow 0}$ versus polymer concentration C for PAN-4 in aqueous nitric acid at 25°C: \circ , $w_n = 67$ wt%; \square , $w_n = 60$ wt%; \triangle , $w_n = 55$ wt%; broken line, in DMF at 25°C.

$(d\tilde{n}/dC)_{w_e}$ is the refractive index increment of the polymer solution at constant composition ($0.114 \text{ cm}^3 \text{ g}^{-1}$ at $w_e = 85$ wt%), $d\tilde{n}_0/dw_e$, the refractive index increment of the binary mixture ($0.087 \text{ cm}^3/\text{g}$), ξ_a , the preferential adsorption parameter ($\equiv -dw_e/dC$)¹⁷; \tilde{n}_0 , refractive index of the solvent, and N_A , Avogadro's constant. The value of K_L was evaluated by substituting the experimental values of $(C/R_\theta)_{\theta \rightarrow 0}^{-1}$ for aqueous nitric acid and M_w obtained in DMF into the relation $K_L = (1/M_w)(C/R_\theta)_{\theta \rightarrow 0}^{-1}$. $K_L \times 10^{17}$ was 1.21 and 1.14 for $w_n = 55$ and 67 wt%, respectively.

The slope of the plot, equal to $2A_{2,L}$, becomes zero at $w_n = 55$ wt% with an estimated uncertainty of ± 1 wt% for w_n . That is, 55 wt% aqueous nitric acid can be regarded as a Flory theta solvent for PAN. Comparable results have been obtained for AN/MA copolymer¹ a 51 wt% nitric acid is a Flory theta solvent.

Figure 4 shows a plot of $(K_L C/R_\theta)_{\theta \rightarrow 0}$ against C for fraction PAN-4 with $M_w = 15.8 \times 10^4$ in various EC/water mixtures. Here, K_L was evaluated from the experimental values of $(C/R_\theta)_{c \rightarrow 0}$ for the EC/water mix-

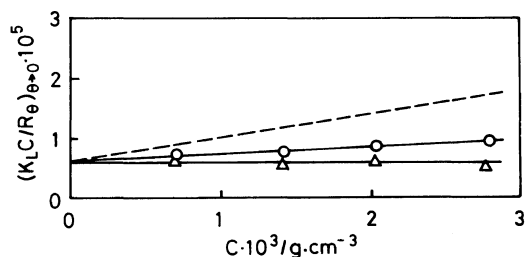


Figure 4. Plot of $(K_L C/R_\theta)_{\theta \rightarrow 0}$ versus polymer concentration C for PAN-4 in EC/water mixture at 25°C: \circ , $w_e = 87.5$ wt%; \triangle , $w_e = 85$ wt%; broken line, in DMF at 25°C.

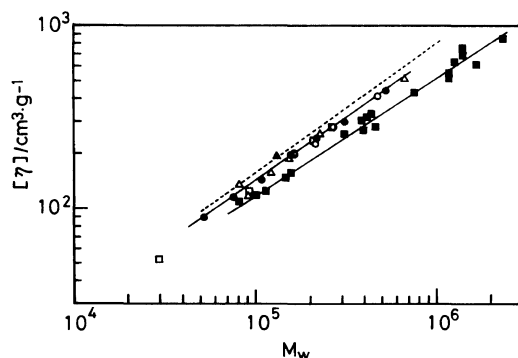


Figure 5. Log-log plots of limiting viscosity number $[\eta]$ versus weight-average molecular weight M_w for PAN in DMF at 25°C: \square , Cleand and Stockmayer²; \blacktriangle , Krigbaum and Kotliar³; \triangle , Onyon⁴; \blacksquare , Peebles⁶; \circ , Shibukawa *et al.*⁸; dotted line, eq (e-1); \bullet , this work.

ture and M_w value obtained in DMF. The value of K_L so determined was (1.03×10^{-7}) for EC/water mixtures with $w_e = 85$ –87.5 wt%. The slope of the plot reduced to zero in $w_e = 85$ wt% at 25°C, which is another theta solvent for PAN. It was confirmed that the solutions of PAN in 55 wt% aqueous nitric acid and EC/water mixture ($w_e = 85$ wt%) were very stable and no indication of aggregation or crystallization was detected at 25°C within 6×10^3 min. The reliability of the Kamide *et al.* estimation of the theta solvent (EC/water with $w_e = 85$ wt% at 26°C) for redox PAN by the hydrodynamic approach is definitely confirmed. In Figures 3 and 4 the $(K_L C/R_\theta)_{\theta \rightarrow 0}$ vs. C plot for the same fraction in DMF is shown by the broken line.

Figure 5 shows the plots of $\log[\eta]$ against $\log M_w$ for PAN in DMF constructed from the present and literature data. The latter were obtained from the original data, with correction made from the temperature effect on $[\eta]$, when necessary. M_w values of these data were obtained by fluorescence correction in the light scattering experiment ($\lambda=436$ and 546 nm) except for those of Shibukawa *et al.*⁸ The data points of Cleland and Stockmayer,² Krigbaum and Kotliar,³ Onyon⁴ and Shibukawa *et al.*⁸ can be reasonably expressed by the MHS equation: $[\eta]=0.052 M_w^{0.69}$ established in this study. In contrast Peebles' data⁶ deviates to the higher M_w side for the same $[\eta]$. Peebles used 0.5% Cornell Standard Polystyrene in toluene for the instrument calibration, but we, Cleland and Stockmayer,² Onyon,⁴ Shibukawa *et al.*⁸ used benzene. The significant difference in log-log plot of $[\eta]$ and M_w between Peebles and others may thus be explained by the differences in the standard materials used for the instrumental calibration. Here, the only exception is the case of Krigbaum and Kotliar,³ who used the literature value of turbidity, $\lambda_0=436$ nm ($\tau=3.50 \times 10^{-3}$ cm⁻¹) for 0.5% Cornell Standard Polystyrene in toluene, although they actually measured at 546 nm.

Figure 6a and b shows log-log plots of $[\eta]$ vs. M_w for the PAN and AN/MA copolymer in DMF, EC/water mixtures and aqueous nitric acids. We carefully reexamined $d\tilde{n}/dC$ for AN/MA copolymer in DMF at 25°C and reached the conclusion that the value of $d\tilde{n}/dC$ (0.77 cm³ g⁻¹) in the previous paper¹ is some 3% underestimated (0.079 cm³ g⁻¹). Accordingly, the M_w values in the literature¹ are overestimated by 6% and the M_w values cited for AN/MA copolymer have been corrected in this paper. The EC/water mixture with $w_e=82.5$ wt% and aqueous nitric acid with $w_n=51$ wt% at 25°C was found to consist of theta solvents for the AN/MA copolymer (with 92 ± 0.5 wt% in AN) in the previous paper.¹ The parameter K_m and a in the MHS

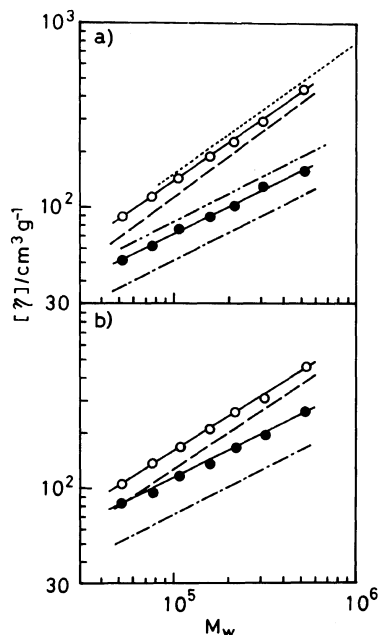


Figure 6. Log-log plots of limiting viscosity number $[\eta]$ versus weight-average molecular weight M_w for PAN at 25°C: a) \circ , in DMF; \bullet , in EC/water mixture ($w_e=85$ wt%); dotted line, PAN in DMF¹; broken line, the AN/MA copolymer in DMF¹; dot-dash line, the AN/MA copolymer in EC/water mixture ($w_e=82.5$ wt%);¹ dot-dot-dash line, PAN in EC/water mixture ($w_e=82.5$ wt%);⁹ b) \circ , in 67 wt% aqueous nitric acid; \bullet , in 55 wt% aqueous nitric acid; broken line, the AN/MA copolymer in 67 wt% aqueous nitric acid¹; dot-dash line, the AN/MA copolymer in 51 wt% aqueous nitric acid.¹

Table III. K_m and a in Mark-Houwink-Sakurada equations and K_γ and γ in relations between $\langle S^2 \rangle_z^{1/2}$ and M_w for PAN in various solvents at 25°C

Solvent	K_m	a	$K_\gamma \times 10^8$	γ
DMF	0.0520	0.69 ₀	0.317	0.55 ₁
85 wt% EC/W	0.256	0.49 ₀	0.431	0.50 ₀
55 wt% HNO ₃	0.342	0.50 ₁	0.480	0.50 ₂
67 wt% HNO ₃	0.122	0.62 ₂	0.359	0.55 ₂

equation (eq 1) were evaluated by the least-squares method and the results are summarized in Table III.

The MHS parameters in Table III can be corrected for the polydispersity of the PAN samples ($M_w/M_n=1.15-1.41$ (average, 1.29))

assuming the Schulz–Zimm distribution of molecular weight. The results are as follows:

$$[\eta] = 0.0533 M_w^{0.69} \quad \text{in DMF at } 25^\circ\text{C} \quad (\text{a})$$

$$[\eta] = 0.126 M_w^{0.62}$$

$$\text{in } 67 \text{ wt}\% \text{ nitric acid at } 25^\circ\text{C} \quad (\text{b})$$

$$[\eta] = 0.263 M_w^{0.49}$$

$$\text{in EC/water mixture } (w_e = 85 \text{ wt}\%) \text{ at } 25^\circ\text{C} \quad (\text{c})$$

and

$$[\eta] = 0.351 M_w^{0.50}$$

$$\text{in } 55 \text{ wt}\% \text{ nitric acid at } 25^\circ\text{C} \quad (\text{d})$$

Kamide *et al.*⁷ established the following MHS equations

$$[\eta] = 0.0466 M_w^{0.71}$$

$$(5 \times 10^4 < M_w < 1 \times 10^6, 36 \text{ samples}) \quad (\text{e-1})$$

for PAN, prepared by conventional redox polymerization, in DMF at 20°C and

$$[\eta] = 0.0429 M_w^{0.71}$$

$$(9.3 \times 10^4 < M_w < 1 \times 10^6, 11 \text{ samples}) \quad (\text{e-2})$$

for PAN, prepared by non-redox, precipitation polymerization, in DMF at 20°C .

Equation e-1 can be converted to the MHS equation in DMF with LiCl (0.1 wt%) at 25°C

$$[\eta] = 0.0444 M_w^{0.712} \quad (\text{e-1})'$$

and is shown in Figure 6a as the dotted line. Here, the effect of LiCl in DMF on $[\eta]$, as observed in this study, and temperature on K_m and a in eq 1, obtained by Fujisaki and Kobayashi¹⁸ for PAN/DMF system, was taken into consideration. K_m in eq (e-1)' is some 10% smaller and a in eq (e-1)' is 0.02 larger than those obtained in this study.

The values of the exponent a in the two solvent mixtures are as expected 0.5 ± 0.01 (see eq c and d). Hence, we can conclude from the light scattering and solution viscosity measurements that EC/water ($w_e = 85 \text{ wt}\%$) and 55 wt% aqueous nitric acid are Flory theta

solvents for redox PAN with isotactic triad 26%, syndiotactic triad 24%, and heterotactic triad 50%.

Kamide *et al.*⁹ showed that the following MHS equation

$$[\eta] = 0.282 M_r^{0.50} \quad (\text{f})$$

holds for redox PAN in EC/water mixture with $w_e = 85 \text{ wt}\%$ at 26°C , where M_v was calculated using e-1. Equation f is shown in Figure 6a as the dot-dot-dash line. The significant difference in K_m between eq f and that established here in EC/water ($w_e = 85 \text{ wt}\%$) can be attributed to the experimental uncertainty of correction for fluorescence used in determining M_w . Using the experimental data for the effects of LiCl and temperature on $[\eta]$ in DMF, we can reconstruct two MHS equations for PAN in EC/water ($w_e = 85 \text{ wt}\%$) at 30°C and 35°C in ref 9 and estimate the MHS equation by extrapolating the above two eq to $a = 0.50$ in the form,

$$[\eta] = 0.266 m_v^{0.50} \quad \text{at } 29.3^\circ\text{C} \quad (\text{g})$$

Equation g is very similar to that established in this article, although temperature is about 4°C higher (see Appendix).

Kamide *et al.*¹⁰ have pointed out that for PAN polymerized by γ -ray irradiation of urea canal complex at -78°C (γ -PAN) the exponent a becomes 0.50 in EC at 60°C , and γ -PAN has 75% isotacticity. That is, the Flory theta temperature of PAN varies with the stereoregularity of the polymer.

$[\eta]$ at constant M_w in 67 wt% aqueous nitric acid is larger than that in DMF, but a in the former solvent is slightly smaller than that in the latter. Interestingly, $[\eta]$ values at constant M_w in two theta solvents differ from each other: $[\eta]$ in 55 wt% aqueous nitric acid is larger than $[\eta]$ in EC/water mixture with $w_e = 85 \text{ wt}\%$. This indicates that the dissolved state, including the unperturbed chain dimension and the degree of solvation (*i.e.*, the specific interaction between the functional group CN in the polymer and solvent),

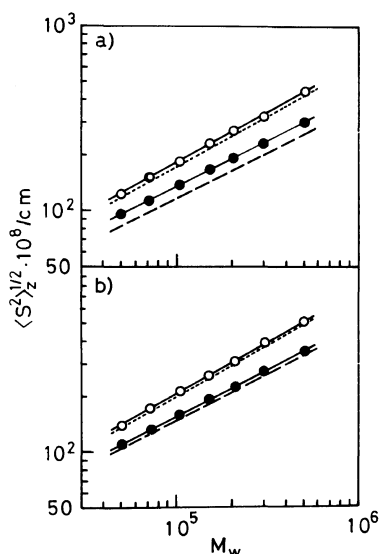


Figure 7. Plots of the radius of gyration $\langle S^2 \rangle_z^{1/2}$ as a function of weight-average molecular weight M_w for PAN at 25°C: a) \circ , in DMF; \bullet , in the EC/water mixture ($w_e = 85 \text{ wt}\%$); dotted line, the AN/MA copolymer in DMF¹; broken line, the AN/MA copolymer in the EC/water mixture ($w_e = 82.5 \text{ wt}\%$).¹ b) \circ , in aqueous nitric acid ($w_n = 67 \text{ wt}\%$); \bullet , in aqueous nitric acid ($w_n = 55 \text{ wt}\%$); dotted line, the AN/MA copolymer in aqueous nitric acid ($w_n = 67 \text{ wt}\%$); broken line, the AN/MA copolymer in aqueous nitric acid ($w_n = 51 \text{ wt}\%$).¹

varies with the nature of the theta solvent.

Figure 7 shows the molecular weight dependence of $\langle S^2 \rangle_z^{1/2}$ for the PAN polymer in various solvents at 25°C. The data for the AN/MA copolymer, obtained in the previous paper,¹ are shown by the dotted and broken lines. $\langle S^2 \rangle_z^{1/2}$ of PAN is larger than that of AN/MA copolymer, when both polymers with constant M_w are dissolved in the same solvent. The above finding was observed for both DMF and all other solvents investigated. $\langle S^2 \rangle_z^{1/2}$ is empirically related to M_w by

$$\langle S^2 \rangle_z^{1/2} = K_\gamma M_w^\gamma \quad (4)$$

The parameters K_γ and γ in eq 4 for PAN solution were determined by the least-squares method and are summarized in Table III. If the partially free draining effect is neglected, the following relation

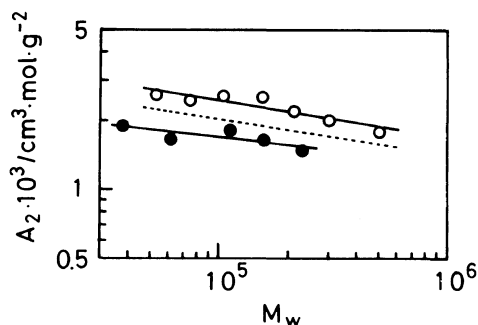


Figure 8. Molecular weight dependence of the second virial coefficient A_2 for PAN in DMF at 25°C: \circ , $A_{2,L}$ by light scattering; \bullet , $A_{2,O}$ by osmometry; dotted line, $A_{2,L}$ by light scattering for the AN/MA copolymer in DMF.¹

$$\gamma = (1 + a)/3 \quad (5)$$

holds between a eq 1 and γ in eq 4. The γ values calculated by eq 5 from the experimental a (0.69 and 0.62) in DMF and 67 wt% nitric acid are 0.56 and 0.54, respectively, both in fairly good agreement with the experimental values (0.55 for both solvents). The PAN polymer, like the AN/MA copolymer, behaves as a gaussian chain in Flory theta solvents and PAN expands more in 55 wt% aqueous nitric acid than in the EC/water mixture ($w_e = 85 \text{ wt}\%$).

Figure 8 shows the molecular weight dependence of A_2 , determined by light scattering (open circles) and membrane osmometry (closed circles) for PAN in DMF at 25°C. The empirical relations derived are as follows.

$$A_{2,L} = 1.68 \times 10^{-2} M_w^{-0.17} \quad \text{in DMF at } 25^\circ\text{C} \quad (h)$$

$$A_{2,O} = 4.80 \times 10^{-3} M_w^{-0.09} \quad \text{in DMF at } 25^\circ\text{C} \quad (i)$$

When the molecular weight dependence of A_2 and the ratio $A_2 M_w / [\eta]$ can be semi-empirically expressed respectively as

$$A_2 = K_v M_w^{-v} \quad (6)$$

and

$$A_2 M_w / [\eta] = K_e M_w^e \quad (7)$$

ν in eq 6 is related to a and ε by the relation

$$\nu = 1 - a - \varepsilon \quad (8)$$

Substituting the experimental values of a (0.69) and ε (0.15), both obtained in DMF, into eq 8, we obtain $\nu = 0.16$, which is comparable to the experimental value ν (0.17). This shows sufficient experimental accuracy.

Equation h differs somewhat from the relation⁷

$$A_{2,L} = 4.94 \times 10^{-2} M_w^{-0.29} \quad \text{in DMF at } 20^\circ\text{C} \quad (\text{h})'$$

established in the previous paper⁷ for the PAN-DMF system, to which no LiCl was added and the fluorescence contaminating the scattered light was eliminated by procedure described elsewhere.⁷ The figure shows the molecular weight dependence of $A_{2,L}$ for the AN/MA copolymer in DMF.

The values of Flory's viscosity parameter,

$$\Phi \equiv [\eta] M_w q_{w,z} / 6^{3/2} \langle S^2 \rangle_z^{3/2}$$

($q_{w,z}$ is a correction factor for polydispersity), was calculated for PAN in DMF, 67 and 55 wt% aqueous nitric acid, and the EC/water mixture with $w_e = 85$ wt%, all at 25°C. $q_{w,z}$ was calculated assuming the Schulz-Zimm molecular weight distribution for the fractions. The Φ values in aqueous nitric acid and EC/water mixture were calculated using the M_w values obtained in DMF. It is obvious that the Φ values are almost constant, averaging $(2.3 \pm 0.1) \times 10^{23}$, $(1.5 \pm 0.1) \times 10^{23}$, and $(2.8 \pm 0.1) \times 10^{23}$ for DMF, 67 wt% aqueous nitric acid and two theta solvents, and the last value is almost equivalent to the theoretical value. The Φ values, except for 67 wt% aqueous nitric acid, are comparable to those obtained for flexible polymer in good and theta solvents. Note that the Φ values for the AN/MA copolymer in 51 wt% aqueous nitric acid (theta solvent) was only 70% of the theoretical value (2.87×10^{23}). The Φ values for PAN in 67 wt% aqueous nitric acid are unusually small for reasons not completely understood.

The unperturbed chain dimension

$$A = (\langle R^2 \rangle_0 / M)^{1/2},$$

[$\langle R^2 \rangle_0^{1/2}$ is the mean-square end-to-end distance in the unperturbed state] was evaluated by the following method:

Method 2A

Measurements of $\langle S^2 \rangle_z^{1/2}$ of a polymer in Flory theta solvent allow A to be determined from

$$A = 6^{1/2} (\langle S^2 \rangle_0 / M)^{1/2} \quad (9)$$

where the subscript zero indicates the unperturbed state.

Method 2C (Baumann Plot)¹⁹

Using $\langle S^2 \rangle_z^{1/2}$ of a polymer in a non-theta solvent, we can evaluate A by the relation,

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

Here, B is a long-range interaction parameter.

Method 2E (Stockmayer-Fixman Plot)²⁰

$$[\eta] / M^{1/2} = K + 2(3/2\pi)^{3/2} \Phi_0(\infty) B M^{1/2} \quad (11)$$

with

$$K = \Phi_0(\infty) A^3$$

Method 2F (Kamide et al. Plot)²¹

$$\begin{aligned} & -\log k_m + \log [1 + 2\{(a-0.5)^{-1} - 2\}^{-1}] \\ & = -\log K + (a-0.5) \log M_0 \end{aligned} \quad (12)$$

M_0 can be approximated with a geometric average of the lower- and upper-limit of M .

$\langle S^2 \rangle_0^{1/2}$ or $\langle S^2 \rangle^{1/2}$ in eq 9 and 10 is the weight-average quantity, which is converted from the z -average quantity, using the experimental values of M_w/M_n and assuming the Schulz-Zimm distribution for each fraction.

Method 2A was applied to PAN in two theta solvents and the results are listed in Table IV. The A value in the EC/water mixture with w_e of 85 wt% is about 15% smaller than that in 55 wt% aqueous nitric acid. A similar difference was observed for the AN/MA copolymer.

Figures 9 and 10 show the Baumann and Stockmayer and Fixman plots for PAN in various solvents. Both plots are well represented by straight lines, even at the highest molecular weight fraction. The A values obtained from the intercept are summarized in Table IV. Table IV also includes the A values evaluated by method 2F. In applying methods 2E and 2F, the experimental Φ values were corrected for the excluded volume effect ($\Phi/\alpha_s^{-0.57}$) and taken to be $\Phi_0(\infty)$ for 67 wt% aqueous nitric acid and the DMF solution. Here, α_s was estimated conventionally from the ratio

$$\langle S^2 \rangle^{1/2} / (A (\text{method 2C}) / 6^{1/2} M^{1/2}).$$

Table IV indicates all the methods including thermodynamic and hydrodynamic approaches to yield almost the same A values in each solvent.

The conformation parameter σ and characteristic ratio C_∞ are expressed by

$$\sigma = A/A_f \quad (13)$$

$$C_\infty = A^2 M_b / l^2 \quad (14)$$

where A_f is the A of a hypothetical chain with free internal rotation, M_b is the mean molecular weight per skeletal bond (26.5), and l is the mean bond length (1.54×10^{-8} cm). The values of σ and C_∞ calculated using the most probable A values are tabulated in the seventh and eighth columns of Table IV.

The most probable A is the average of

values obtained by thermodynamic approaches (method 2A and 2C) and is given in the sixth column of Table IV. This table also gives B values estimated from the slopes of the plots in Figures 9 and 10. The B values by method 2C (thermodynamic approach) are in fairly good agreement with those by method 2E

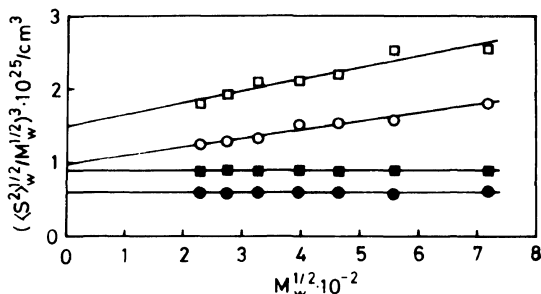


Figure 9. Baumann plot (method 2C) for PAN at 25°C: \circ , DMF; \square , aqueous nitric acid ($w_n=67$ wt%); \bullet , EC/water mixture ($w_e=85$ wt%); \blacksquare , aqueous nitric acid ($w_n=55$ wt%).

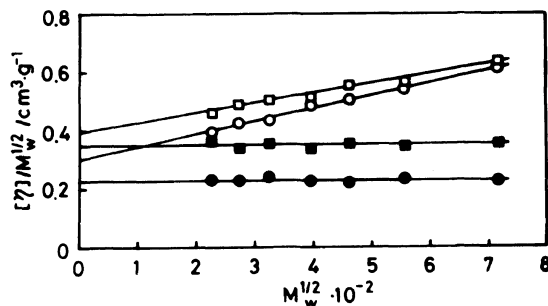


Figure 10. Stockmayer-Fixman plot (method 2E) for PAN at 25°C: Marks have the same meaning as in Figure 9.

Table IV. Unperturbed chain dimension A , long-range interaction parameter B , conformation parameter σ and characteristic ratio C_∞ of PAN in various solvents at 25°C

Solvent	$A \times 10^8 / \text{cm}$					σ	C_∞	$B \times 10^{27} / \text{cm}^3$	
	2A	2C	2E	2F	Most probable			2C	2E
DMF	—	1.09	1.05	1.05	1.06	2.51	12.6	2.33	2.32
85 wt% EC/W	0.95	—	—	—	0.95	2.25	10.1	0	0
67 wt% HNO ₃	—	1.29	1.29	1.30	1.29	3.06	18.5	3.17	2.69
55 wt% HNO ₃	1.06	—	—	—	1.06	2.51	12.6	0	0

(hydrodynamic approach), as expected.

The A values for PAN in the EC/water mixture with $w_e = 85$ wt% and 55 wt% aqueous nitric acid are 0.94 and 1.06×10^{-8} cm, respectively. These are comparable to 0.88 and 1.02×10^{-8} cm evaluated for the AN/MA copolymer in two corresponding theta solvents (EC/water mixture ($w_e = 82.5$ wt%) and 51 wt% aqueous nitric acid).

The A , σ and C_∞ values in Table IV are significantly dependent on the nature of solvent: they are larger for better solvents and the A value is maximum in 67 wt% aqueous nitric acid in which the B value also attains a maximum. This was also observed in AN/MA copolymer solutions.¹

The dependence of A on solvent nature is quite remarkable for aqueous nitric acid with various w_n . There may exist some specific interaction between nitric acid and the polymer chain. To gain a better understanding of the reasons for this, we investigated solvation phenomena.

Figure 11 shows the dependence of n on the polymer concentrations of PAN and AN/MA copolymer in various solvents. In DMF and the EC/water mixture, n was nearly always constant, irrespective of polymer concentration, but in aqueous nitric acid, it decreased linearly with an increase in concentration. n_0 was estimated as the intercept of the plot at infinite concentration in Figure 11. n_0 in organic solvents is relatively small: 0.4 for PAN and 0.3 for AN/MA copolymer. For PAN in organic solvents, solvation does not occur. n_0 increases with the concentration of nitric acid, suggesting that the degree of solvation is greater in much more concentrated nitric acid and the solvated molecule should not be water, but HNO_3 , NO_3^- or hydrated similar compounds. Interestingly, n_0 in aqueous nitric acid does not reduce to zero even in a theta solvent.

Figure 12 shows a plot of A against n_0 for PAN and the AN/MA copolymer in various solvents. The data points for the AN/MA

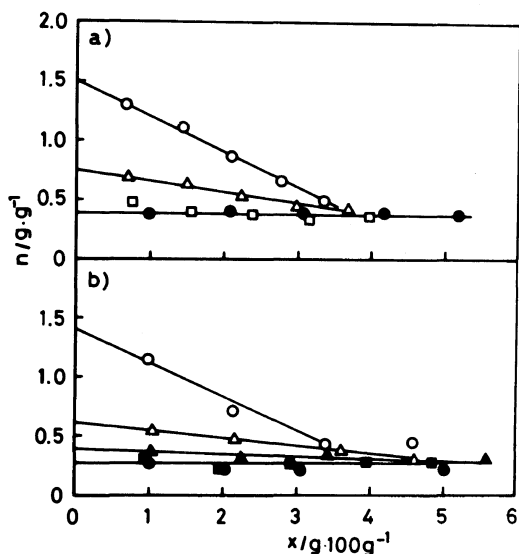


Figure 11. Plots of n versus concentration x for PAN (a) and the AN/MA copolymer (b) at 25°C: \circ , aqueous nitric acid ($w_n = 67$ wt%); \triangle , aqueous nitric acid ($w_n = 55$ wt%); \blacktriangle , aqueous nitric acid ($w_n = 51$ wt%); \bullet , DMF; \square , EC/water mixture ($w_e = 85$ wt%); \blacksquare , EC/water mixture ($w_e = 82.5$ wt%).

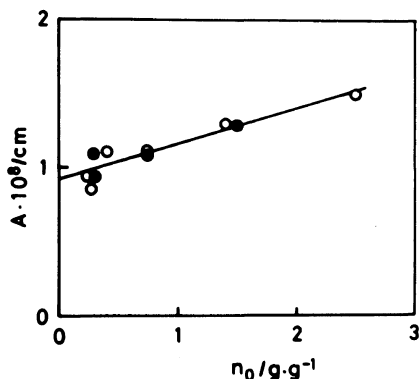


Figure 12. n_0 dependence of the short-range interaction parameter A for PAN (\circ) and the AN/MA copolymer (\bullet).

copolymer were cited from a previous paper.¹ The point of the largest n_0 corresponds to the AN/MA copolymer in 80 wt% nitric acid, extrapolated from the relations n_0 and $w_n \leq 67$ wt%, through lack of direct data due to the strong corrosive properties of the acid. A of both PAN and the AN/MA copolymer in-

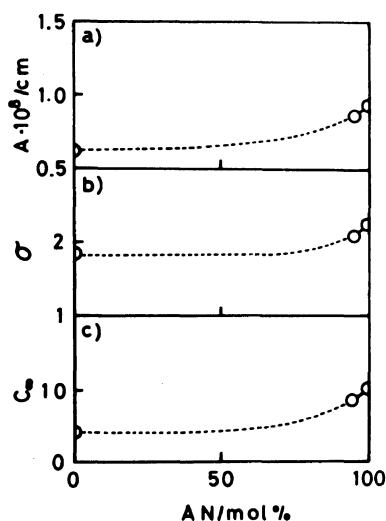


Figure 13. Effect of AN content in the polymer on the short range interaction parameter A , the conformation parameter σ and the characteristic ratio C_∞ .

creases significantly with an increase in n_0 . Similar conclusions have been reached by Kamide and Saito¹⁴ for the behavior of cellulose derivatives.

Figure 13 shows the dependence of A , σ and C_∞ on the AN content of PAN, the AN/MA copolymer and poly(methyl acrylate) (PMA). The former two polymers were dissolved in the EC/water mixture $w_e = 85$ and 82.5 wt% and latter in isoamyl acetate. The small variation in AN content in the AN/MA copolymer causes considerable variation in chain flexibility in the range where AN content is near to 100 mol%.

APPENDIX

$[\eta]_{20^\circ\text{C}}^{\text{DMF}}$ can be converted to $[\eta]$ of the DMF solution containing LiCl (0.1 wt%) at 25°C ($[\eta]_{25^\circ\text{C}}^{\text{DMF(LiCl)}}$)

$$[\eta]_{25^\circ\text{C}}^{\text{DMF(LiCl)}} = [\eta]_{20^\circ\text{C}}^{\text{DMF}} \times 1.17 \times M_w^{-0.022} \quad (\text{A-1})$$

The M_v values in Table I of ref 9 were converted to those of $[\eta]_{25^\circ\text{C}}^{\text{DMF(LiCl)}}$, from which M_v was recalculated using the MHS equation of the PAN solution in DMF, as indicated in Table II. Using the newly calculated M_v , we

can reconstruct the MHS equations of PAN in EC/water ($w_e = 85$ wt%) at 30 and 35°C as shown in ref 9 in the form,

$$[\eta] = 0.262 M_v^{0.502} \quad \text{at } 30^\circ\text{C} \quad (\text{A-2})$$

and

$$[\eta] = 0.201 M_v^{0.527} \quad \text{at } 35^\circ\text{C} \quad (\text{A-3})$$

The MHS equation (g) corresponding to $a = 0.5$ can be extrapolated from the above two equations.

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