

Dilute Solution Properties of Acrylonitrile/ Vinylidene Chloride Copolymer

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(Received March 17, 1986)

ABSTRACT: A copolymer of acrylonitrile (AN) and vinylidene chloride (VDC) was prepared using azobisisobutyronitrile as an initiator and was separated into 20 fractions by successive solution fractionation, using dimethyl sulfoxide (DMSO) as the solvent and toluene as the precipitant. The fractions had essentially the same chemical composition: 59 weight percent in AN. Light scattering for a fraction in dimethylacetamide (DMAc), γ -butyrolactone (γ -BL) and dimethylformamide (DMF) gave the same weight-average molecular weight M_w within an experimental error $\pm 2\%$, which was evaluated assuming homopolymer. Viscosity and light scattering were measured for 8 fractions in DMAc. The Mark-Houwink-Sakurada (MHS) equations for this polymer at 25°C were $[\eta]=0.100 M_w^{0.603}$ in DMAc, $[\eta]=0.102 M_w^{0.591}$ in DMF, $[\eta]=0.112 M_w^{0.576}$ in γ -BL, and $[\eta]=0.142 M_w^{0.521}$ in 70 wt% aq nitric acid. The molecular weight dependence of the radius of gyration $\langle S^2 \rangle_z^{1/2}$ and the second virial coefficient A_2 in DMAc at 25°C were represented by $\langle S^2 \rangle_z^{1/2}=3.84 \times 10^{-9} M_w^{0.53}$ and $A_2=5.77 \times 10^{-3} M_w^{-0.137}$. The unperturbed chain dimension A was determined by Baumann, Stockmayer-Fixman and Kamide-Moore methods. The value of a copolymer of AN and VDC was by ca. 10% smaller than that of polyacrylonitrile.

KEY WORDS Dilute Solution Property / Acrylonitrile-Vinylidene Chloride Copolymer / Light Scattering / Viscometry / Mark-Houwink-Sakurada Equation / Radius of Gyration / Second Virial Coefficient / Unperturbed Chain Dimension / Conformation Parameter /

As well known, acrylonitrile (AN) reacts readily with other monomers to give various copolymers. In fact, the copolymerization of AN with styrene (St), vinyl acetate (VAc), methyl acrylate (MA), vinyl chloride (VCl), and vinylidene chloride (VDC) has been widely employed for improving physical properties and processability in plastic or fiber-making process of polyacrylonitrile (PAN).

Studies on the molecular characterization of AN-copolymer have been carried out for AN/MA,¹ AN/St,^{2,3} AN/methyl methacrylate (MMA).⁴ AN/VDC copolymer is an interesting polymer from an industrial point of view, because of its high nonflammability.

Up to now, only sequence distribution of model copolymer was analyzed,⁵ but no systematic study has been made on its dilute solution properties in connection with its molecular characteristics. In this article an attempt is made to investigate the dilute solution properties of AN/VDC copolymer (with 58 weight percent in AN) in various solvents to compare the molecular characteristic of AN/VDC copolymer with those of PAN.

EXPERIMENTAL

Polymer Sample

A mixture of acrylonitrile (AN) and vinylidene chloride (VDC) (AN/VDC=58/42,

weight/weight, total monomer weight 180 g) was polymerized in a 540 ml of dimethylformamide (DMF) by free radical solution polymerization at 50°C for 2 h, using azobisisobutyronitrile as an initiator. AN/VDC copolymer was isolated by pouring the DMF solution into approximately 5 liters of methanol. The mixture was stirred for 10 min and the precipitate was filtered, rinsed with methanol, filtered, and then dried at room temperature and *in vacuo* for 30 h at 50°C. The polymerization yield was 71 wt% and a whole sample obtained had the viscosity-average molecular weight M_v , determined from the limiting viscosity number $[\eta]$ using the MHS equation (eq 1) at 25°C in dimethylacetamide (DMAc) (Table IV), of 16.3×10^4 and had a VDC content of 43 wt% from the ^{13}C NMR method.

Solvent

N-methyl-2-pyrrolidone (*n*-MP), dimethylacetamide (DMAc), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), γ -butyrolactone (γ -BL), and toluene were used in this study. All these solvents were of reagent grade and used as received. A 70 wt% aq nitric acid was also employed.

Molecular Weight Fractionation

The polymer sample was fractionated by the successive solution fractionation method into 20 fractions: 110 g of the polymer were dissolved in a 2800 ml of DMSO to give a starting concentration of 0.039 g ml^{-1} at 30°C. To the solution 6–9 liters of toluene were gradually added with agitation to bring about a two-liquid phase separation and a polymer-lean phase was separated and concentrated by evaporating toluene contained in the phase and the polymer was completely precipitated by addition of methanol to the concentrated solution, washed with a large amount of methanol and dried *in vacuo*. Eight fractions having the weight-average molecular weight M_w , ranging 4.2×10^4 – 50×10^4 , were

selected for further study.

Solution Viscosity

Solution viscosity was measured in *n*-MP, DMAc, DMF, γ -BL, and aqueous nitric acid (nitric acid content $w_n = 70 \text{ wt}\%$) with a modified Ubbelohde suspension type viscometer at $25 \pm 0.01^\circ\text{C}$. $[\eta]$ was determined by Huggins plot.

Light Scattering

Light scattering measurements were made in DMAc, DMF, γ -BL, and aq nitric acid ($w_n = 70 \text{ wt}\%$) at 25°C on a FICA photogoniometer 42000. Unpolarized natural light of the wave length $\lambda_0 = 546 \text{ nm}$ was used as an incident light. The specific refractive index increment dn/dc for AN/VDC copolymer was determined to be $0.080 \text{ ml}^{-1} \text{ g}$, $0.086 \text{ ml}^{-1} \text{ g}$, and $0.086 \text{ ml}^{-1} \text{ g}$ for DMF, DMAc, and γ -BL at 25°C. Calibration of the apparatus was made using benzene (the Rayleigh ratio at scattering angle $\theta = 90^\circ$, $R_{90} = 16.3 \times 10^{-6}$ at $\lambda_0 = 546 \text{ nm}$).⁶ The data were analyzed according to Zimm's procedure to evaluate M_w , the *z*-average mean-square radius of gyration $\langle S^2 \rangle_z^{1/2}$ and the second virial coefficient A_2 . Here, the polymer was assumed homopolymer. In aq nitric acid ($w_n = 70 \text{ wt}\%$) solution, $\langle S^2 \rangle_z^{1/2}$ and A_2 were evaluated using M_w obtained in DMAc. The detailed experimental procedure is the same as that described for PAN previously.⁷

^{13}C NMR Measurement

^{13}C NMR measurements on AN/VDC copolymer were made on a FT-NMR JEOL FX-200 using a 1/2 (by volume at 25°C) mixture of DMSO- d_6 /DMSO: sample weight, 200 mg; measuring temperature, 80°C; internal standard, tetramethylsilane (TMS). The monomer sequence distribution and stereoregularity of the polymer were evaluated according to the method of Bailey and Henrichs.⁵

RESULTS AND DISCUSSION

The monomer reactivity ratio of acrylonitrile and vinylidene chloride, r_N and r_V , in AN/VDC/DMF system were determined by Guyot *et al.*⁸ to be 0.8 and 0.6, respectively. Putting these values of r_N and r_V and experimental initial monomer feed composition $f_N (=0.716)$ and $f_V=(1-f_N)$ into Mayo-Lewis equation,⁹ we can calculate the AN content of the polymer F_N to be 0.712 corresponding to $f_N =$

0.716. The estimated F_N value is very near the experimental value (0.708), determined by ¹³C NMR method. The above experimental fact of $F_N \cong f_N$ means that the monomer compositions of AN and VDC, employed in this study, are fortunately a close to an azeotrope composition.

Figure 1 shows ¹³C NMR spectrum of sample cord AV-1-3. Assignment of these peaks by Bailey and Henrichs⁵ is shown on the spectrum. The relative mole fractions of

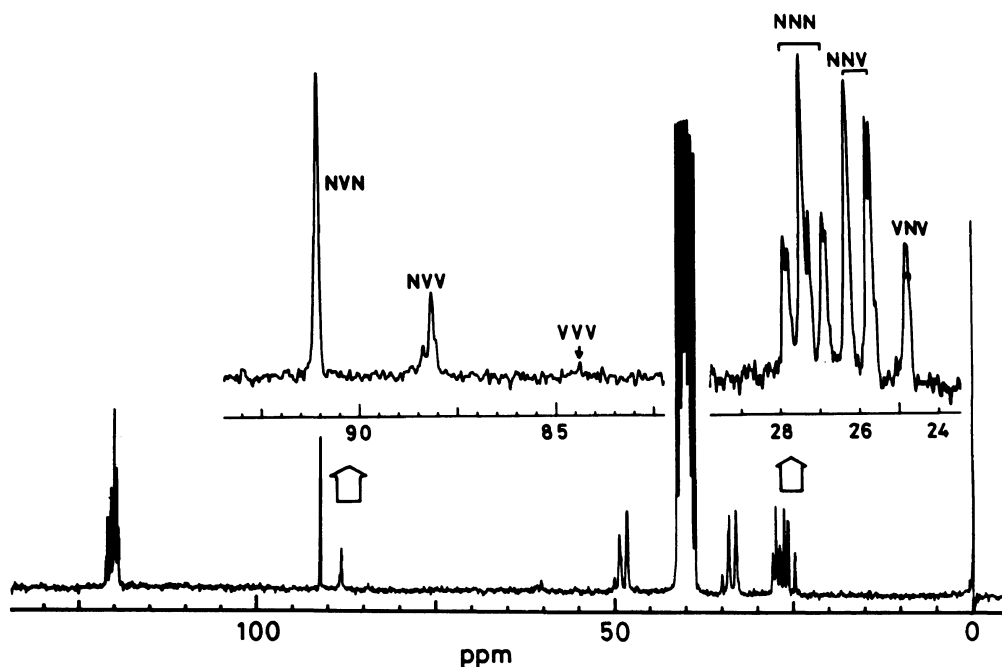


Figure 1. ¹³C NMR spectrum of a AN/VDC copolymer fraction AV-1-3.

Table I. The relative mole fractions of V-centered triads and N-centered triads and VDC content for the AN/VDC copolymer fractions determined by ¹³C NMR

Sample	$M_w \times 10^{-4}$	V-Centered triads			N-Centered triads			VDC content wt%
		VVV	NVV	NVN	NNN	NNV	VNV	
AV-1-3	27.0	0.04	0.26	0.70	0.50	0.39	0.11	38
AV-1-6	9.0	0.05	0.27	0.67	0.48	0.40	0.12	40
AV-1-8	4.2	0.04	0.31	0.65	0.49	0.40	0.11	41
Assignment of peaks/ppm		84.3	88.1	91.1	26.5 28.0	25.5 26.5	24.8	

V-centered triads of VVV, VVN, and NVN, and N-centered triads of NNN, NNV, and VNN were estimated from the peaks of the dichloro-substituted carbons of VDC and methine carbon of AN, respectively. Here, V means VDC and N is AN monomer.

Table I lists the relative mole fraction of VVV, VVN, and NVN, and NNN, NNV, and VNV, determined thus, and the VDC content for some fractions. The VDC content of the fractions only slightly decreased with an increase in M_w and was smaller than that (0.43) of the whole copolymer. This is consistent with the experimental fact that the first fraction with an extremely low molecular weight has a high VDC content. The relative mole fractions of V- and N-centered triads remain almost constant, except for NVV, over a wide M_w range of the fractions, although NVV triad content increased gradually with decreasing M_w . VVV triad content is only a few percent and VVVV tetrad content is too low to de-

tect by ^{13}C NMR method.¹⁰ Therefore, we can conclude that the distribution of monomer composition in AN-VDC copolymer, employed here, may be sufficiently narrow.

The isotactic, heterotactic and syndiotactic triad probabilities of NNN sequence were analyzed from methine carbon peaks (24–28 ppm) and found to be 28, 47, and 25 mol%, respectively. These values are in good agreement with those of the PAN polymerized with redox catalyst.⁷ Therefore, this polymer can be regarded as a random AN/VDC copolymer.

The AN/VDC copolymer dissolves in all solvents (*n*-MP, 70 wt% HNO_3 , DMAc, DMF, DMSO, and γ -BL) for PAN. Figure 2 shows some typical Zimm plots of a fraction AV-1-4 in DMAc, DMF, and γ -BL. All plots have diamond shape.

Table II illustrates M_w , $\langle S^2 \rangle_z^{1/2}$ and A_2 of a AN/VDC copolymer fraction AV-1-4 in DMF, γ -BL, 70 wt% aq nitric acid and DMAc

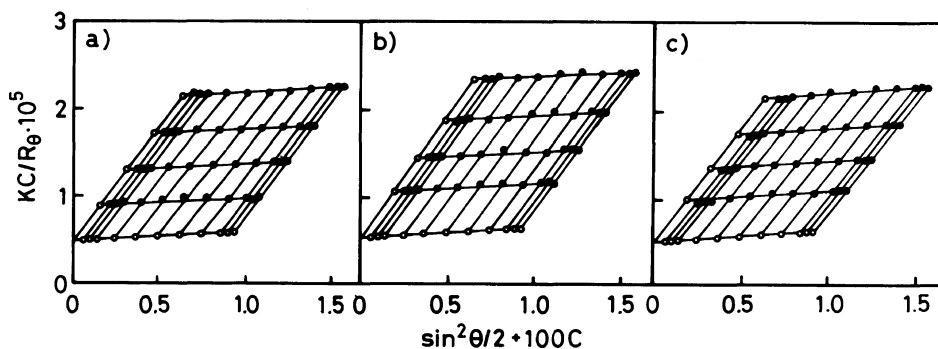


Figure 2. Zimm plots for a AN/VDC copolymer fraction AV-1-4 at 25°C: a) in DMAc; b) in DMF; c) in γ -butyrolactone.

Table II. Light scattering data for a AN/VDC copolymer fraction (AV-1-4) in various solvents at 25°C

Solvent	$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2} \times 10^8$ ^a	$A_2 \times 10^3$ ^b	Dielectric constant
Dimethylformamide	19.6	248	1.37	36.7
γ -Butyrolactone	20.0	232	1.19	39.0
70 wt% HNO_3	—	211	0.075	—
DMAc	20.4	248	1.15	37.8

^a cm. ^b $\text{cm}^3 \text{mol} \cdot \text{g}^{-2}$.

Table III. Results of light scattering and intrinsic viscosity numbers for AN/VDC fractions in various solvents at 25°C

Sample	$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2} \times 10^8$ ^a	$A_2 \times 10^3$ ^b	$[\eta]/\text{cm}^3\text{g}^{-1}$				
				DMAc	DMF	γ -BL	<i>n</i> -MP	70 wt% HNO ₃
AV-1-1	50.0	405	0.90	270	239	213	280	132
AV-1-2	34.8	335	0.95	223	195	174	230	111
AV-1-3	27.0	283	1.10	188	169	153	196	96
AV-1-4	20.4	248	1.15	156	140	124	162	82
AV-1-5	14.0	205	1.20	126	112	104	129	67
AV-1-6	9.0	163	1.20	97	88	80	102	54
AV-1-7	6.2	133	1.21	76	69	63	81	44
AV-1-8	4.2	108	1.32	62	56	52	65	37

^a cm. ^b cm³mol⁻¹g⁻².

at 25°C. M_w was constant in various solvents and $(20 \pm 0.4) \times 10^4$ was obtained as M_w for the fraction. This means that at least in this case the light scattering data can be, to the first approximation, analyzed assuming AN/VDC copolymer as homopolymer. Note that dielectric constants ϵ of the solvents used here lie in the narrow range (36.7–39.0) and the solvents having different ϵ were not available for light scattering measurements.

Table III collects M_w , $\langle S^2 \rangle_z^{1/2}$, and A_2 , all evaluated from Zimm plots, and $[\eta]$ for 8 fractions in various solvents at 25°C.

The MHS equation between $[\eta]$ and M_w can be expressed by

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

where K_m and a are constants characteristic of a combination of polymer and solvent at a given temperature.

Figure 3 shows the log–log plots of $[\eta]$ and M_w . K_m and a in eq 1 were calculated using the least-squares method and the results are summarized in Table IV. In the table, the data for PAN⁷ were compiled for comparison. The magnitude of $[\eta]$ for a given fraction decreases in the following order: DMAc \cong *n*-MP > DMF > γ -BL > 70 wt% aq nitric acid. Change in the exponent a with solvent is almost in parallel to that of $[\eta]$. DMAc can be regarded as the best solvent for AN/VDC co-

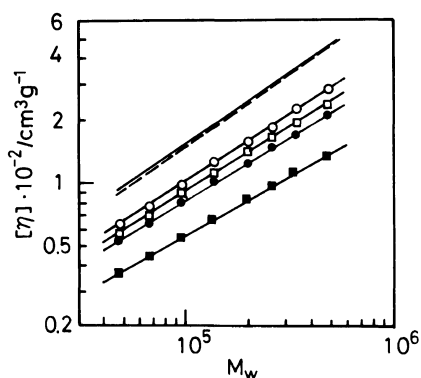


Figure 3. Log-log plots of limiting viscosity number $[\eta]$ versus weight-average molecular weight M_w for AN/VDC copolymer at 25°C: ○, in DMAc; □, in DMF; ●, in γ -butyrolactone; ■, in 70 wt% aq nitric acid; full line, PAN in DMAc; broken line, PAN in DMF.

polymer and 70 wt% nitric acid is expected to be near to a Flory's theta solvent (see, also Table III). In Figure 3 the relations for PAN/DMAc and PAN/DMF are shown as full and broken lines, respectively. In the same solvent PAN has 50–70% larger $[\eta]$ than that of AN/VDC copolymer, if these polymers have the same M_w . The exponent a for PAN is some 15% larger than for AN/VDC copolymer.

Figure 4 shows the log–log plots of $\langle S^2 \rangle_z^{1/2}$ and M_w for AN/VDC copolymer in DMAc at 25°C. The plots are linear and semiempirically expressed as

Table IV. K_m and a in the Mark-Houwink-Sakurada equations (eq 1), K_γ and γ in the relation between $\langle S^2 \rangle_z^{1/2}$ and M_w (eq 2) and K_β and β in the relation between A_2 and M_w (eq 3) for AN/VDC copolymer and PAN in various solvents at 25°C

Polymer	Solvent	K_m	a	$K_\gamma \times 10^8$	γ	$K_\beta \times 10^3$	β
AN/VDC copolymer	DMAc	0.0999	0.603	0.384	0.530	5.77	-0.137
	DMF	0.102	0.591	—	—	—	—
	γ -BL	0.112	0.576	—	—	—	—
	<i>n</i> -M-P	0.114	0.595	—	—	—	—
	70 wt% HNO ₃	0.142	0.521	—	—	—	—
R-PAN	DMAc	0.0636	0.674	—	—	—	—
	DMF ^a	0.0520	0.690	0.317	0.551	16.8	-0.17
	DMSO ^b	0.153	0.600	0.337	0.54	—	—

^a Reference 7. ^b Reference 15.

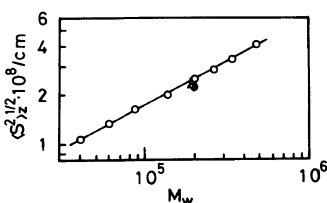


Figure 4. Plots of the radius of gyration $\langle S^2 \rangle_z^{1/2}$ as a function of weight-average molecular weight M_w for AN/VDC copolymer at 25°C: \circ , in DMAc; \square , in DMF; \triangle , in γ -butyrolactone; \bullet , 70 wt% aq nitric acid.

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

K_γ and γ are constants for a given combination of polymer and solvent at constant temperature and summarized in the 5th and 6th columns of Table IV. The figure also includes $\langle S^2 \rangle_z^{1/2}$ data for a fraction AV-1-4 in other solvents. $\langle S^2 \rangle_z^{1/2}$ decreases in the order: DMAc > DMF > γ -BL > 70 wt% aq nitric acid. This is the same order as $[\eta]$. γ can be indirectly evaluated from a , using the relation $\gamma = (1 + a)/3$ and $\gamma = 0.534$ was calculated from $a = 0.603$ for DMAc and this agrees well with the experimental value (0.530).

Figure 5 shows the molecular weight dependence of A_2 by the light scattering for AN/VDC copolymer in DMAc at 25°C. A_2 is related to M_w through the relation,

$$A_2 = K_\beta M_w^\beta \quad (3)$$

The values of K_β and β are given in Table IV. with

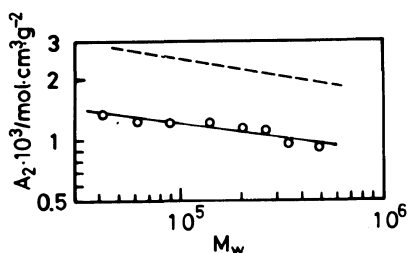


Figure 5. Molecular weight dependence of the second virial coefficient A_2 for AN/VDC copolymer in DMAc at 25°C; broken line, PAN/DMF at 25°C.

In Figure 5 the relation for PAN/DMF⁷ is shown as a broken line. A_2 of AN/VDC copolymer in DMAc is almost half that of PAN in DMF. This can be explained by the lower thermodynamic interaction of VDC component with DMAc or DMF, as estimated from lower solubility of poly(vinylidene chloride) in these solvents.

The unperturbed chain dimension A was evaluated using the following methods:

*Method 2C (Baumann plot)*¹¹

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

where B is the long-range interaction parameter.

*Method 2E (Stockmayer-Fixman plot)*¹²

$$[\eta] / M^{1/2} = K + 2(3/2\pi)^{3/2} \Phi_0(\infty) B M^{1/2} \quad (5)$$

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

Polymer	Solvent	$A \times 10^8/\text{cm}$				$B \times 10^{27}/\text{cm}^3$		σ	C_∞
		2C	2E	2F	Most probable	2C	2E		
AN/VDC copolymer	DMAc	1.11	0.98	0.98	0.98	1.36	0.88	2.57	14.4
	DMF	—	0.95	0.95	0.95	—	0.67	2.49	13.5
	γ -BL	—	0.94	0.94	0.94	—	0.49	2.46	13.2
	<i>n</i> -MP	—	1.00	1.00	1.00	—	0.90	2.62	15.0
	70 wt% HNO ₃	—	0.88	0.85	0.86	—	0.085	2.31	10.8
R-PAN	DMAc	—	1.05	1.05	1.05	—	2.23	2.49	12.3
	DMF ^a	1.09	1.05	1.05	1.06	2.33	2.32	2.51	12.6
	DMSO ^b	1.12	1.09	1.10	1.10	1.51	1.19	2.61	13.5

^a Reference 7. ^b Reference 15.

$$K = \Phi_0(\infty)A^3 \quad (6)$$

Method 2F (Kamide–Moore plot)¹³

$$\begin{aligned} -\log K_m + \log[1 + 2\{(a-0.5)^{-1} - 2\}^{-1}] \\ = -\log K + (a-0.5)\log M_0 \quad (7) \end{aligned}$$

where M_0 can be approximated with a geometrical average of the upper and lower limits of molecular weights, in which the MHS equation applies.

Figure 6 shows Baumann and Stockmayer–Fixman plots of AN/VDC copolymer and PAN in various solvents. Data for PAN were cited from literature.⁷

Table V summarizes A and B for AN/VDC copolymer, estimated by methods 2C, 2E, and 2F. A value estimated by method 2C is by *ca.* 10% larger than that by methods 2E and 2F. This small difference might be due to the homopolymer approximation employed in the light scattering measurement. A decreases in the following order: *n*-MP > DMAc > DMF > γ -BL > 70 wt% aq nitric acid. A increases gradually with B , but the solvent dependence is much more remarkable in B than in A . It is clear that 70 wt% aq nitric acid is near to a theta solvent, in which $B \cong 0$. In DMAc, B value of AN/VDC copolymer is about 1/3 of that of PAN, sug-

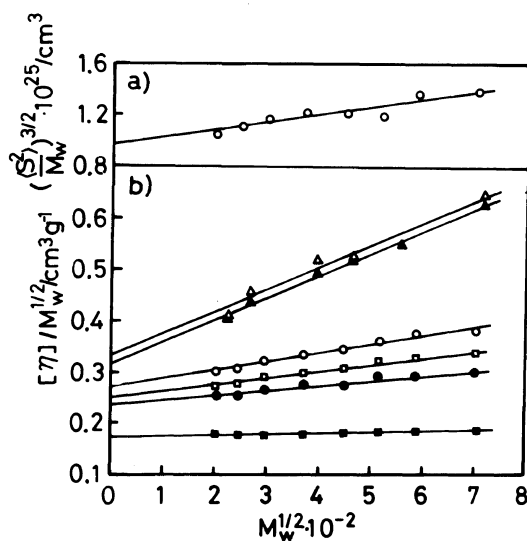


Figure 6. a) Baumann plot for AN/VDC copolymer in DMAc. b) Stockmayer–Fixman plots: \circ , for AN/VDC copolymer in DMAc; \square , in DMF; \bullet , in γ -butyrolactone; \blacksquare , in 70 wt% aq nitric acid; \triangle , for PAN in DMAc; \blacktriangle , in DMF.

gesting that an introduction of VDC monomer into PAN diminishes the solubility of the polymer in solvent suitable for PAN.

The conformation parameter σ and characteristic ratio C_∞ were calculated from A by using the relation,

$$\sigma = A/A_f \quad (8)$$

and

$$C_\infty = A^2 M_b / l^2 \quad (9)$$

A_f is A of a hypothetical chain with free internal rotation, l , the length of a repeating unit, and M_b , its molecular weight (= 35.5). A_f (0.381×10^{-8} cm) is given by^{1,14}

$$A_f^2 = w_a A_{a,f}^2 + (1 - w_a) A_{c,f}^2 \quad (10)$$

w_a is the weight fraction of AN (0.58), $A_{a,f}$, A_f of PAN ($= 0.422 \times 10^{-8}$ cm) and $A_{c,f}$, A_f of poly(vinylidene chloride) ($= 0.313 \times 10^{-8}$ cm). The values of σ and C_∞ appear in the 9th and 10th columns of Table V. These values are similar to those of PAN.

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