Dilute Solution Properties of Poly(methacrylonitrile-co-styrene) and Poly(acrylonitrile-co-styrene)

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ABSTRACT

Poly(methacrylonitrile-co-styrene) (PMANS) and Poly(acrylo-nitrile-co-styrene) (PANS) having 1:1 composition were pre-pared with free-radical initiators. The polymers were frac-tionated into fractions having narrow molecular weight distribution. The dilute solution properties of the fractionated copolymers were studied by light scattering, viscometry, and osmometry in solvents (methyl ethyl ketone, dimethylformamide, and acetone), $[\eta]$-$\overline{M}_w$ and $(\overline{r^2})_w^{1/2}$-$\overline{M}_w$ relationships have been established. The validity of the various graphical methods for the determination of Flory's constant, K_θ were observed.

From the values of the steric factors it was noticed that the copolymer coil of PANS is stiffer than that of PMANS.

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INTRODUCTION

Studies on configurational and frictional properties of copolymers are few, in spite of the increasing technological importance of copolymers. This may be due to the experimental difficulties encountered in the investigation of copolymer solutions. Determination of weight-average molecular weight is complicated by the heterogeneity due to composition as well as the sequence length of monomer units in the copolymer molecule. Stockmayer et al. [1] have shown that copolymer molecules are usually more expanded in solution than would be expected from the averaged behavior of the corresponding homopolymers, because of the repulsive interactions between the unlike monomer units. Utiyama and Kurata [2] found that neither the long-range interaction parameter nor the unperturbed dimensions coincide with the simple averages of the parent homopolymers and they suggested that the unperturbed dimension depends upon the arrangement of three successive monomer units in the copolymer. Similar observations have been reported for other copolymers [3-5]. However, for block copolymers, several experimenters found [6-10] that the "sequence length" of the monomer units play a significant role in influencing the dilute solution properties. Also, it has been observed that the substituents affect the unperturbed dimensions and other thermodynamic parameters in solution. We have prepared poly-(acrylonitrile-co-styrene) and poly(methacrylonitrile-co-styrene) of 1:1 composition and investigated their solution behavior in different solvents.

EXPERIMENTAL

Materials

Methyl ethyl ketone (L. R., B. D. H.), dimethylformamide (L. R., B. D. H.), acetone (A. R., B. D. H.), ethyl acetate (A. R., B. D. H.), chloroform (L. R., B. D. H.) and methanol (Fertilizer Corporation of India, Bombay) were purified according to standard procedures [11]. Methacrylonitrile (E. Merck, Darmstadt, Germany), acrylonitrile (L. R., B. D. H.), were purified by washing with sodium hydroxide (5%) and with orthophosphoric acid followed by distilled water. Styrene (Hindustan Polymers Ltd., Vizag, India) was washed three times with sodium hydroxide (5%) followed by distilled water. The washed monomers were dried over anhydrous sodium sulfate and distilled under reduced pressure in an atmosphere of dry nitrogen prior to use.

Copolymerization

Bulk copolymerization of methacrylonitrile and styrene was carried out with calculated amounts of monomers [12] at 60°C in an atmosphere of pure dry nitrogen with the use of benzoyl peroxide (0.1% by weight) as free-radical initiator in order to get nearly alternating copolymer, poly(methacrylonitrile-co-styrene) (PMANS) of 1:1 composition. The conversion was restricted approximately to 10% in order to get nearly homogeneous composition. The polymer was precipitated in methanol and purified by reprecipitation from methyl ethyl ketone solution and dried under vacuum at 55°C. Similarly 1:1 poly(acrylonitrile-co-styrene) (PANS) [13] was prepared by bulk copolymerization from the calculated quantities of monomers, calculated from the reactivity ratios of acrylonitrile (0.04) and styrene (0.40). The conversion was restricted to < 10% to avoid composition heterogeneity. Methyl ethyl ketone and methanol were used as solvent and nonsolvent, respectively.

Fractionation

Fractionations [14] of PANS and PMANS were carried out by using methyl ethyl ketone as solvent and methanol as nonsolvent. Also fractionation of PANS was done with chloroform as solvent and methanol as nonsolvent. Fifteen fractions, each varying from 0.4 to 0.6 g in weight were obtained.

Osmometry

The number-average molecular weights were determined by the use of a Pinner-Stabin osmometer (Colchester Instruments Ltd., U. K.) with preconditioned gel cellulose (Pcel 600) membranes. The osmotic pressure π of the polymer samples, $PMANS_2$, $PMANS_6$, $PANS_1$, and $PANS_D$ were measured at 30 ± 0.01°C and the number-average molecular weights were obtained from the plots of $(\pi/c)^{1/2}$ versus c. Methyl ethyl ketone and acetone were used as solvents for study. The polydispersity of the fractions was calculated from the ratio of molecular weights obtained by light scattering and osmometry and was found to be 1.09, 1.13, 1.38, and 1.27 for $PMANS_2$, $PMANS_6$, $PANS_1$, and $PANS_D$, respectively.

Viscosity

Intrinsic viscosity of the fractions were determined at 30°C by the use of a suspended-level dilution viscometer (Colchester Instruments Ltd., U. K.). The limiting viscosity numbers $[\eta]$ were obtained as the mean of the three values obtained from Eqs. (1), (2), and (3) [15],

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2 c \tag{1}$$

due to Huggins [16]

$$(\ln \eta_{rel})/c = [\eta] - k_2[\eta]^2 c \tag{2}$$

due to Kraemer [17], and

$$(\eta_{sp}/c = [\eta] + k_3\eta_{sp}[\eta] \tag{3}$$

due to Schulz and Blascke [18].

Light Scattering

The weight-average molecular weights of the polymer fractions were determined by light scattering measurements, with a Brice-Phoenix universal light scattering photometer [19] (1000 series, Phoenix Precision Instruments Company, Philadelphia) over the angular range 45° to 135° with a cylindrical cell and with unpolarized light of wavelength 4356 Å. The instrument was standardized by Standard polystyrene supplied by International Bureau of Standards, Washington. The solvents and solutions were filtered directly into the cell and the variation in concentration (2×10^{-3} to 5×10^{-4} g/ml) of the polymer was achieved by successive dilutions. Corrections were made for the measurements made with DMF as solvent for fluorescence.

Refractive index increments (dn/dc), of the samples in various solvents were determined in a Brice-Phoenix differential refractometer [20] at 4356 Å (No. 1974, Phoenix Precision Instruments Company, Philadelphia). The dn/dc values for PMANS/MEK, PMANS/DMF, PMANS/ethyl acetate, PANS/MEK, and PANS/DMF systems were found to be 0.183 ± 0.003, 0.105 ± 0.003, 0.183 ± 0.004, 0.182 ± 0.003, and 0.105 ± 0.003, respectively.

Treatment of Data

Light scattering data were treated according to Zimm [21]. Plots of Kc/R_θ versus $\sin^2 \theta/2 + 100C$ were made to get the weight-average molecular weight $\overline{M}_w$, the second virial coefficient A_2, and the z-average mean-square radius of gyration $(\overline{S^2})_z$; the latter was converted to $(\overline{S^2})_w$ by Eq. (4) [22]

$$(S^2)_w = (S^2)_z \, (h + 1)/(h + 2 + \beta) \tag{4}$$

where $h = [(M_w/M_n) - 1]^{-1}$ in Schulz-Zimm distribution

$$f(N) = [Y^{(h + 1)}/\Gamma(h + 1)] \, e^{-YN}N^h dN$$

and β is obtained from

$$(\overline{r^2})_w = AM^{1 + \beta}$$

or

$$\beta = (2a - 1)/3$$

In the above relations, M is the molecular weight and a is the exponent in the Mark-Houwink equation. The values of β for the systems under investigation were calculated by using the exponents of the respective Mark-Houwink relations, and $(\overline{S^2})_w$ was then converted to $(\overline{r^2})$ by Eq. (5) [23]:

$$(\overline{r^2})_w = (\overline{S^2})_w \, (2 + \beta)(3 + \beta) \tag{5}$$

Analysis of Copolymers

The copolymers were analyzed for nitrogen by the Kjeldahl method to estimate the percentage composition of $-C\equiv N$ in the copolymer chains and by NMR spectral analysis recorded with Varian A-60D spectrometer in deuterochloroform at 60°C, tetramethylsilane being used as internal standard.

RESULTS AND DISCUSSION

Characterization of Copolymer Samples

Generally, a statistical copolymer has three kinds of heterogeneity, that is, molecular weight distribution, composition fluctuation among different molecules, and sequence length distribution. It was expected that because of the reaction mechanism the copolymers prepared in this experiment would be practically homogeneous in both composition and sequence length (1:1). The copolymer fractions found to contain 49.8 and 49.9 mole % of nitriles in the PMANS and PANS chains, respectively, as determined by elemental analysis for nitrogen for the methacrylonitrile and acrylonitrile contents (standard Kjeldahl analysis).

The NMR spectra in deuterochloroform at 60°C were recorded to ascertain the microstructures and compositons of PMANS and PANS. The NMR spectrum of PMANS showed a phenyl proton peak at 3.02 τ without a shoulder, peaks due to $-CH$ and $-CH_2$ protons at 7.25 τ and 8.60 τ, and a peak due to $-CH_3$ protons at 9.22 τ. The ratio of the relative areas of the phenyl proton peak and peaks due to $-CH$, $-CH_2$, and $-CH_3$ protons of both the monomer units in the copolymer chain was found to be 1:1 as expected from kinetics. The absence of a shoulder in the phenyl proton peak at 3.02 τ, characteristic of the ortho proton, clearly indicated that the sequence length of styrene unit is less than three in the copolymer, and hence the copolymer has nearly an alternating nature [24-26]. In the NMR spectrum of PANS, peaks due to phenyl protons of styrene units appeared at 2.80 τ without any shoulder, indicating the absence of blocks in the copolymer [24-26]; the peaks due to $-CH$ and $-CH_2$ protons of both the monomer units in the copolymer chain appeared at 7.25 τ and 8.20 τ, respectively. From the ratio of the relative areas of the above peaks, the composition of copolymer was found to be 1:1.

The heterogeneity in composition of the copolymer was further examined by light scattering measurements. Stockmayer et al. [1], and Bushuk and Benoit [27] showed that molecular weights obtained by light scattering for copolymers were only apparent molecular weights. Leng and Benoit [28] derived an equation to obtain the dimensions of copolymers (heterogeneous in composition) by light scattering. Light scattering measurements of single fraction of copolymer PMANS were made in various solvents, chloroform (dn/dc = 0.132, $\overline{M}_{app}$ = 3.427 × 10^5); methyl ethyl ketone (dn/dc = 0.186; $\overline{M}_{app}$ = 3.354 × 10^5), acetone (dn/dc = 0.216, $\overline{M}_{app}$ = 3.151 × 10^5). The values of $\overline{M}_{app}$ obtained were almost independent of solvent used, which suggested that the composition distribution of the copolymer sample was narrow.

So, the value of $\overline{M}_{app}$ determined in single solvent may be regarded as true molecular weight. Thus the light scattering equation, [Eq. (4)] could be used for the determination of molecular dimensions of the copolymer. The (dn/dc) values of the different fractions of the same copolymer in the same solvent vary a little about the mean value, which also showed that the composition distribution with respect to molecular weight was negligible. The light scattering measurements of PMANS were made in methyl ethyl ketone (9 samples designated $PMANS_1$ to $PMANS_9$); in dimethylformamide (6 samples designated $PMANS_A$ to $PMANS_F$), and in ethyl acetate (5 fractions designated $PMANS_I$ to $PMANS_V$). The molecular weights of PANS fractions were determined in methyl ethyl ketone (6 samples designated $PANS_1$ to $PANS_6$) and dimethylformamide (6 samples designated $PANS_A$ to $PANS_F$) by light scattering measurements.

Limiting Viscosity Number-Molecular Weight Relationships

The double logarithmic plots of $[\eta]$ and $\overline{M}_w$ for PMANS in methyl ethyl ketone, dimethylformamide, acetone, and ethyl acetate at 30°C yielded the Mark-Houwink relations (6), (7), (8), and (9), and the double logarithmic plots of $[\eta]$ and $\overline{M}_w$ for PANS in methyl ethyl ketone, dimethylformamide, and acetone at 30°C yielded the Mark-Houwink relations (10), (11), and (12) respectively (Figs. 1 and 2, Tables 1, 2, and 3).

$$[\eta] = 1.635 \times 10^{-2} \ \overline{M}_w^{0.67} \tag{6}$$

$$[\eta] = 4.732 \times 10^{-3} \ \overline{M}_w^{0.80} \tag{7}$$

$$[\eta] = 1.059 \times 10^{-2} \ \overline{M}_w^{0.70} \tag{8}$$

$$[\eta] = 5.278 \times 10^{-2} \ \overline{M}_w^{0.55} \tag{9}$$

$$[\eta] = 13.710 \times 10^{-2} \ \overline{M}_w^{0.53} \tag{10}$$

$$[\eta] = 5.750 \times 10^{-2} \ \overline{M}_w^{0.60} \tag{11}$$

$$[\eta] = 4.17 \times 10^{-2} \ \overline{M}_w^{0.65} \tag{12}$$

FIG. 1. Plot of molecular weight vs. intrinsic viscosity for poly(methacrylonitrile-co-styrene) in various solvents: (A) methyl ethyl ketone; (B) acetone; (C) dimethylformamide; (D) ethyl acetate.

The values of the exponents a in Eqs. (6)-(9) show the solvent power for PMANS in the order, DMF > acetone > MEK > ethyl acetate. The values of the exponents a in the Mark-Houwink relations for PANS [Eqs. (10)-(12)] show the solvent power in the order DMF > acetone > MEK.
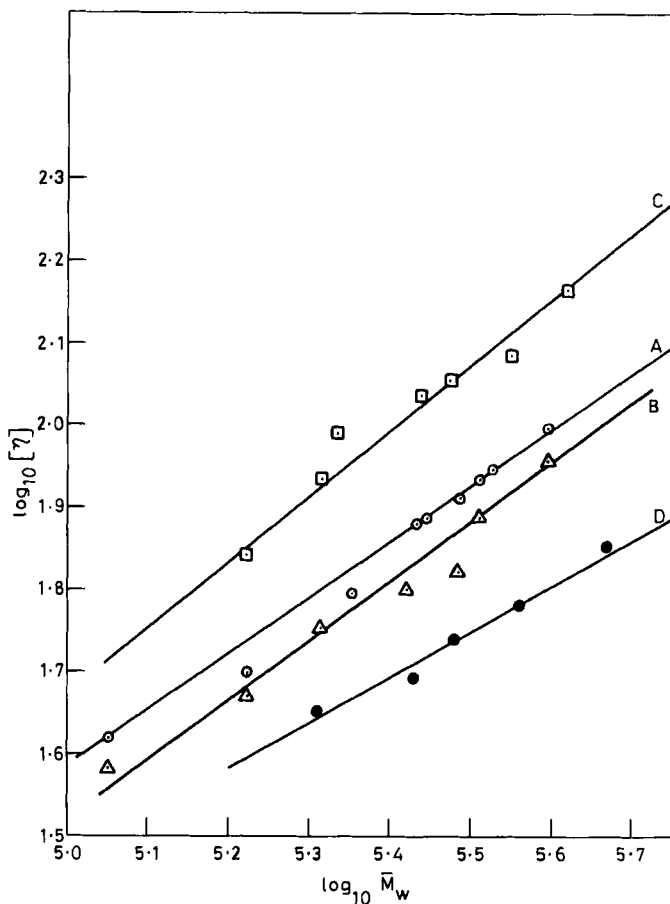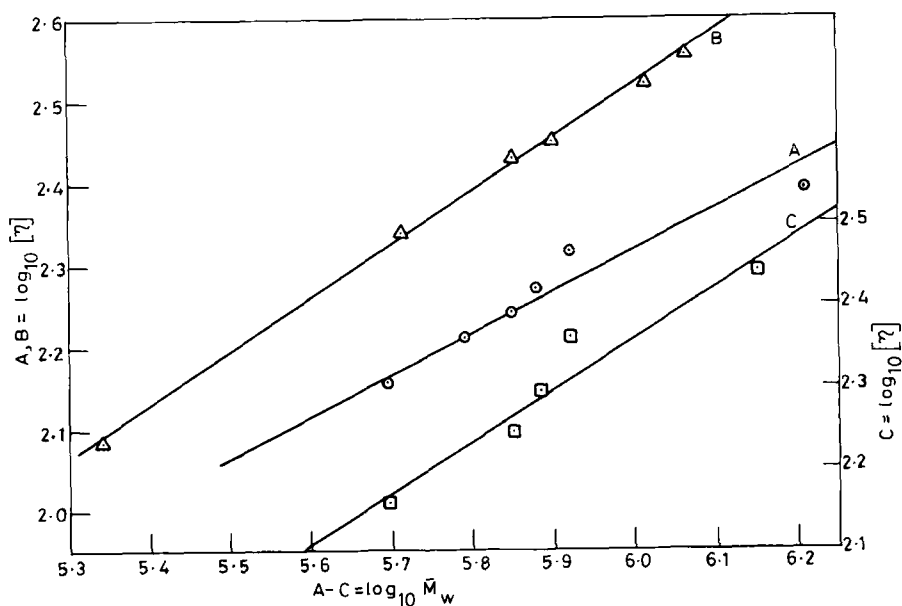
FIG. 2. Plot of molecular weight vs. intrinsic viscosity for Poly-(acrylonitrile-co-styrene) in various solvents: (A) methyl ethyl ketone; (B) dimethylformamide; (C) acetone.

Root-Mean-Square End-to-End Distance-Molecular Weight Relations

From the log-log plots of $(\overline{r^2})_w^{1/2}$ and $\overline{M}_w$ for PMANS and PANS in MEK and DMF the relations (13)-(16) have been established.

For PMANS/MEK:

$$(\overline{r^2})_w^{1/2} = 1.862\ \overline{M}_w^{0.50} \tag{13}$$

For PMANS/DMF:

$$(\overline{r^2})_w^{1/2} = 1.718\ \overline{M}_w^{0.50} \tag{14}$$

For PANS/MEK:

$$(\overline{r^2})_w^{1/2} = 2.07\ \overline{M}_w^{0.50} \tag{15}$$

For PANS/DMF:

$$(\overline{r^2})_w^{1/2} = 1.99\ \overline{M}_w^{0.51} \tag{16}$$

TABLE 1. Parameters Obtained from Light Scattering and Viscosity[a]

Fraction	$M_w \times 10^{-5}$ (g/mole)	$[\eta]$ (ml/g)	k_1	$(\overline{r^2})_w \times 10^{11}$ (cm²)	$(\overline{r^2})_w^{1/2}$ (Å)	$(\overline{r_0^2})_w^{1/2}$ (Å)[b]	$A_2 \times 10^4$ cc-mole/g²	α	$\Phi \times 10^{23}$ (cgs)
PMANS$_1$	3.98	98.4	0.33	11.50	1070	419	2.89	1.286	0.247
PMANS$_2$	3.29	86.2	0.32	11.80	1090	379	1.88	1.270	0.268
PMANS$_3$	3.09	81.4	0.39	7.85	890	369	1.44	1.254	0.231
PMANS$_4$	2.79	75.8	0.40	7.49	870	347	2.46	1.247	0.211
PMANS$_5$	3.46	88.3	0.36	-	-	387	3.18	-	-
PMANS$_6$	2.27	62.3	0.20	9.58	980	317	2.16	1.195	0.200
PMANS$_7$	1.67	50.1	0.56	-	-	273	-	-	-
PMANS$_8$	1.12	41.5	0.46	-	-	224	-	-	-
PMANS$_9$	2.76								

[a]Polymer, poly(methacrylonitrile-co-styrene); solvent, methyl ethyl ketone; temperature, 30°C; $\lambda = 4358$ Å; $dn/dc = 0.183 \pm 0.003$; $h = \overline{10}$; $a = 0.675$; $\beta = 0.117$; $\overline{M}_w/\overline{M}_n = 1.11$.

[b]From Flory's equation.

TABLE 2. Parameters Obtained from Light Scattering and Viscosity[a]

Fraction	$\bar{M}_w \times 10^{-5}$ (g/mole)	$[\eta]$ (ml/g)	k_1	$(r^2)_w \times 10^{11}$ (cm^2)	$(r^2)_w^{1/2}$ (Å)	$(r_0^2)_w^{1/2}$ (Å)[b]	$A_2 \times 10^4$ (cc-mole/g^2)	α	$\Phi \times 10^{-23}$ (cgs)
PMANS$_A$	4.16	146.2	0.24	10.73	1040	438	3.07	1.467	0.587
PMANS$_B$	3.62	121.2	0.17	10.85	1040	405	2.76	1.400	0.432
PMANS$_C$	3.00	112.7	0.18	7.68	880	372	3.37	1.406	0.425
PMANS$_D$	2.85	110.2	0.12	8.63	930	356	3.27	1.419	0.434
PMANS$_E$	2.29	98.0	0.11	7.62	870	316	3.37	1.420	0.335
PMANS$_F$	2.23	86.2	0.10	7.55	870	309	4.19	1.357	0.310

[a]Polymer, poly(methacrylonitrile-co-styrene); solvent, dimethylformamide; temperature, 30°C; λ = 4358 Å; M_w/M_n = 1.11; h = 10; dn/dc = 0.105 ± 0.003; a = 0.8; β = 0.2.

[b]From Flory's equation.

TABLE 3. Parameters Obtained from Light Scattering and Viscosity

Polymer	Solvent	$\bar{M}_w \times 10^{-5}$ (g/mole)	$(\bar{S}^2) \times 10^{11}$ (cm²)	$(\bar{r}^2)_w^{1/2}$ (Å)	$[\eta]$ (ml/g)	k_1	$(\bar{r_0}^2)_w^{1/2}$ (Å)[a]	$A_2 \times 10^4$ (cc-mole/g²)	α	$\Phi \times 10^{-23}$ (cgs)
PANS$_1$	MEK[b]	15.9	6.4	1690	241.6	0.37	993	3.90	1.104	0.824
PANS$_2$		8.13	4.42	1440	210.2	0.42	725	4.74	1.187	0.582
PANS$_3$		7.36	4.20	1410	190.8	0.36	714	3.62	1.147	0.516
PANS$_4$		6.73	4.02	1380	173.0	0.40	687	4.74	1.124	0.466
PANS$_5$		6.14	3.94	1360	163.2	0.38	643	3.63	1.123	0.400
PANS$_6$		4.93	2.81	1150	143.8	0.46	577	4.46	1.115	0.475
PANS$_A$	DMF[c]	11.10	6.96	1930	352.3	0.30	931	3.49	1.294	0.581
PANS$_B$		10.98	5.12	1650	332.0	0.21	874	4.34	1.298	0.764
PANS$_C$		7.48	3.36	1340	280.8	0.31	764	5.03	1.306	0.936
PANS$_D$		7.19	3.08	1280	274.2	0.28	707	4.60	1.347	0.885
PANS$_E$		4.66	3.02	1270	219.6	0.27	619	3.31	1.303	0.560
PANS$_F$		2.09	2.80	1220	122.0	0.13	403	2.16	1.210	0.148

[a]From Flory's equation.
[b]Polymer, poly(acrylonitrile-co-styrene); solvent, methyl ethyl ketone; temperature, 30°C; λ = 4358 Å; dn/dc = 0.182 ± 0.003; M_w/M_n = 1.376; h = 2.5; a = 0.53; β = 0.02.
[c]Polymer, poly(acrylonitrile-co-styrene); solvent, dimethylformamide; temperature, 30°C, λ = 4358 Å; dn/dc = 0.105 ± 0.003; M_w/M_n = 1.27; h = 4; a = 0.65; β = 0.1.

Molecular Weight Dependence of Second Virial Coefficient

From the log-log plots of the second virial coefficient A_2 and the weight-average molecular weight $\overline{M}_w$ the mathematical relations (17)-(19) have been established for the systems PMANS/MEK, PMANS/DMF and PANS/DMF (Tables 1-3).

For PMANS/MEK:

$$A_2 = 1.347 \times 10^{-2} \ \overline{M}_w^{-0.33} \tag{17}$$

For PMANS/DMF:

$$A_2 = 6.409 \times 10^{-4} \ \overline{M}_w^{-0.42} \tag{18}$$

For PANS/DMF:

$$A_2 = 13.40 \times 10^{-2} \ \overline{M}_w^{-0.42} \tag{19}$$

The values of second virial coefficient scattered too much to permit qualitative relation to be obtained between A_2 and $\overline{M}_w$ in MEK for PANS. It has been observed that A_2 decreases as the size of the molecule increases.

Flory Constant K_θ and Unperturbed Dimensions

Flory's constant K_θ and hence unperturbed dimensions were found by using graphical procedures, by Flory-Fox-Schaefgen (F-F) [29], Kurata-Stockmayer (K-S) [30], Stockmayer-Fixman (S-F) [31], and Ptitsyn-Inagaki (P-I) [32] from the intrinsic viscosity data of known molecular weight in nonideal solvents. The values of K_θ obtained for the systems PMANS/MEK and PMANS/acetone are more or less the same. All the methods gave same values of K_θ for each system. The value of K_θ obtained for the system PMANS/DMF, however was found to be higher than the value obtained for the PMANS/MEK and PMANS/acetone aystems. The K_θ values obtained for the systems PANS/MEK and PANS/acetone are same, except the P-I method gave
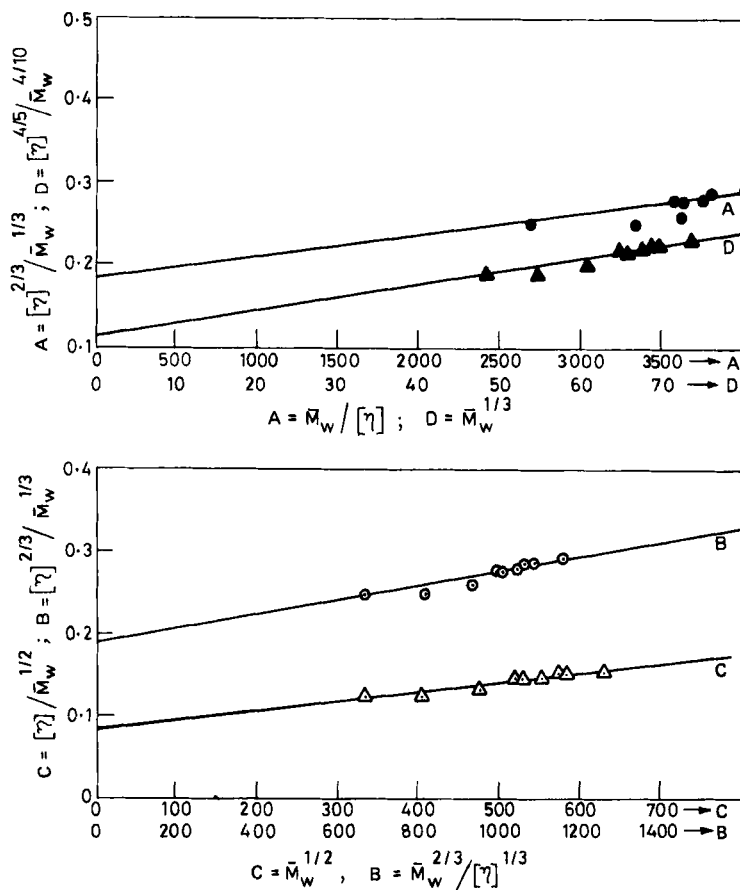
FIG. 3. Plots of (A) Flory-Fox, (B) Kurata-Stockmayer, (C) Stockmayer-Fixman and (D) Ptitsyn-Inagaki expressions for poly(methacrylonitrile-co-styrene); solvent: methyl ethyl ketone.

higher values in both solvents. The value of K_θ obtained for PANS/ DMF is higher than the value obtained for the systems PANS/MEK and PANS/acetone (Table 4). The higher values of K_θ in DMF than in MEK or acetone may be due to a specific solvent effect arising as a result of changes in the effective bond length for the unperturbed state of the copolymer in dimethylformamide and methyl ethyl ketone at the same temperature varying with apparent specific volume of the polymer in the solvent. The data were treated according to S-F. The

TABLE 4. Comparison of Calculated Values of K_θ Obtained from $[\eta]$-$\overline{M}_w$ Data

		$K_\theta \times 10^2$			
Polymer	Solvent	F-F	K-S	S-F	P-I
PMANS	Methyl ethyl ketone	8.28	7.96	8.50	8.56
	Acetone	7.96	7.96	8.50	8.56
	Dimethylformamide	9.28	8.94	9.00	9.05
PANS	Methyl ethyl ketone	15.62	15.62	15.00	18.07
	Acetone	15.62	14.03	15.00	16.95
	Dimethylformamide	16.44	18.53	18.00	19.21

constant $(\overline{r_0^2}/M)^{1/2}$, which is the characteristic of the unperturbed dimension of the dissolved macromolecule [33, 34], was calculated for each copolymer in methyl ethyl ketone and dimethylformamide. The unperturbed mean-square end-to-end distance for the free rotation model of the polymer chain $\overline{r_{0f}^2}$ is given by

$$(\overline{r_{0f}^2}) = n\ell^2 \; (1 - \cos \theta)/(1 + \cos \theta)$$

where n is the number of carbon atoms in the chain, ℓ is the bond length, and θ is the valence angle. Taking $\ell = 1.54$ Å and $\theta = 109.5°$, values of $\overline{r_{0f}^2}$ were calculated. The ratio $(\overline{r_0^2}/\overline{r_{0f}^2}) = \sigma$ which may be taken as a measure of the hindrance to free rotation, was calculated in methyl ethyl ketone and dimethylformamide. The values of σ for PMANS in methyl ethyl ketone and dimethylformamide are 2.00 and 2.04. The values of steric factors for polystyrene and poly(methacrylonitrile (PMAN) are 2.22 and 1.90, respectively. It shows that the copolymer coil is stiffer than that of PMAN and more flexible than that of polystyrene. From the values of σ for PANS and PMANS, it can be noticed that the former is stiffer than latter.

Flory's Universal Parameter

The universal parameter, Φ for PMANS/MEK, PMANS/DMF, PANS/MEK, and PANS/DMF was found to be 1×10^{23} (Tables 1-3) which is less than the normal value 2.86×10^{23}. Such low values for

TABLE 5. Second Virial Coefficient of PMANS and PANS: Theoretical and Experimental Values

$A_2 \times 10^3$ (cc-mole/g^2)

Solvent	Fraction	PMANS		Fraction	PANS	
		Experi- mental	Calculated (0-F)		Experi- mental	Calculated (0-F)
MEK	PMANS$_1$	0.289	1.832	PANS$_1$	3.899	1.158
	PMANS$_2$	0.188	2.177	PANS$_2$	4.470	4.921
	PMANS$_3$	0.145	1.878	PANS$_3$	3.624	4.431
	PMANS$_4$	0.246	1.658	PANS$_4$	4.741	4.014
	PMANS$_6$	0.217	1.763	PANS$_5$	3.630	5.123
DMF	PMANS$_A$	0.307	1.676	PANS$_A$	3.486	6.151
	PMANS$_B$	0.276	1.935	PANS$_B$	4.342	5.192
	PMANS$_C$	0.338	2.203	PANS$_C$	5.035	5.629
	PMANS$_D$	0.327	2.358	PANS$_D$	5.211	8.273
	PMANS$_E$	0.338	3.433	PANS$_E$	3.195	12.069
	PMANS$_F$	0.420	2.975			

the universal parameter are not uncommon [35-39]. The possible factors that affect the magnitude of Φ are: (a) non-Gaussian distribution of chain segments, (b) branching; (c) molecular weight heterogeniety, and (d) chain stiffness. It has been found that in the case of vinyl polymers, the influence of non-Gaussian distribution is negligible. Under the conditions employed for the preparation of this copolymer, only a linear chain is expected and the effect of branching could be ruled out. Even after applying the correction for molecular weight heterogeneity and excluded volume effect, the values were low. The reasons for the low values of Φ obtained for the systems under investigation are not quite clear at present.

Second Virial Coefficient

The second virial coefficient, A_2, was calculated for PMANS and PANS in methyl ethyl ketone and dimethylformamide by the Orofino-Flory equation [40]:

$$A_2 = (2^{5/2} N\pi /27)[(\overline{r^2})_w^{3/2}/\overline{M}_w^2] \ln [1 + (\pi/2)^{1/2} (\alpha^2 - 1)] \qquad (20)$$

with known values of $(r^2)_w$, $\overline{M}_w$, and α, where α was computed from the relation $[\eta] = K_\theta \overline{M}_w^{1/2} \alpha^{2.43}$.

For the systems PMANS/MEK and PMANS/DMF, theoretically calculated values are higher than the experimental values, and for the systems PANS/MEK and PANS/DMF, the agreement between experimental and calculated values is fairly good (Table 5).

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