Behaviour of methylmethacrylate–acrylonitrile random copolymers in dilute solution

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Studies on the dilute solution properties of methylmethacrylate–acrylonitrile random copolymers of three different compositions, 0.236, 0.5 and 0.74 mole fraction (m.f.) of acrylonitrile (AN) designated as MAa, MAb and MAc, respectively, have been made in good solvents and theta solvents. MAa has been studied in benzene (Bz) and ethylacetate (EAc). MAb in acetonitrile (MeCN), dimethyl sulphoxide (DMSO) and a binary solvent mixture of Bz and dimentyl formamide (DMF) in the volume ratio 6.5:1 designated as BM1 and MAc in MeCN, DMSO and Bz+DMF in the volume ratio 1.667:1 designated as BM2. The Mark–Houwink exponent '*a*' reveals that Bz is a theta solvent for MAa at 20°C. For MAb and MAc, BM1 and BM2, respectively have '*a*' values of 0.5 at all three temperatures studied (30°, 40° and 50°C). It is not clear whether they represent theta states or preferential adsorption plays a role complicating the behaviour in solution. The values of A_2 are very low in MeCN considering that it is a very good solvent for the copolymer, '*a*' values for MAb and MAc being 0.75 and 0.7, respectively.

Keywords Methylmethacrylate–acrylonitrile random copolymer; theta solvent; short-range interactions; long-range interactions; steric factor; expansion factor

INTRODUCTION

The conformational and thermodynamic properties of flexible polymers may be described by two independent parameters[1–3]. They are the short-range and long-range interaction parameters, and are related to the unperturbed average dimension and to the excluded volume, respectively, of a given polymer in a given environment. These two parameters can be determined from molecular weight dependences of intrinsic viscosity[3–8].

The assumptions of the two parameter theory have been adequately substantiated by experiments on homopolymers[4,9–12], and have been successfully extended to copolymer systems like methyl methacrylate–styrene (MMA–St)[13–16]. When these studies were directed to systems like methyl methacrylate–acrylonitrile (MMA–AN) copolymers[17–20], where both the monomer units are highly polar, the results obtained are interesting and they show that the existing theories for the evaluation of unperturbed dimensions are inadequate to explain certain anomalous behaviour of these copolymer systems in solution.

In the case of methyl methacrylate (MMA), the pendant group, $-COOCH_3$, had a high dipole moment, while the $-CN$ group of acrylonitrile (AN) has high electrostatic charge. Hence, the copolymer, MMA–AN, should show some interesting behaviour in solution. The investigations on this copolymer system in good solvents by Kashyap *et al.*[18–20] have shown that the copolymer behaves like a stiff chain polymer in solution. In this paper, the results obtained on the studies of MMA–AN random copolymer systems in both good and poor solvents are presented in order to compare their behaviour in both types of solvent.

EXPERIMENTAL

The copolymers (MAa, MAb and MAc) were prepared by solution polymerization using benzoyl peroxide as the initiator and dimethyl formamide (DMF) as the solvent. *Table 1* gives the compositions and degree of conversion of the copolymer.

The fractionation of the copolymers was carried out by the stepwise addition of a non-solvent to a 1% solution of polymer in a good solvent at 30°C. The solvent–nonsolvent pairs chosen were acetonitrile (MeCN)–diisopropylether (DIPE), acetone–methanol and MeCN–methanol, respectively, for MAa, MAb and MAc. All the fractions were dissolved in the respective solvents and reprecipitated with methanol. The precipitates were then vacuum-dried at 60°C.

The percentage composition was determined by the method of Pham[21]. *Table 2* shows the results obtained for the unfractionated and fractionated samples, chosen at

Table 1 Composition and degree of conversion of MMA–AN copolymers*

Copolymer sample	Monomer content in reaction mixture		Polymer obtained (g)	% Conversion	Mole fraction of AN in the sample
	MMA (g)	AN (g)			
MAa	83.9	15	18.5	18.71	0.236
MAb	44.6	52.2	22.5	23.3	0.5
MAc	18.0	78.1	18.1	18.8	0.74

* Initiator: benzoyl peroxide
Temperature 60 ± 0.05°C

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Table 2 Nitrogen content (%) of copolymer samples

Copolymer samples	% N_2	Copolymer samples	% N_2	Copolymer samples	% N_2
MAa*	4.4	MAb*	9.08	MAc*	15.7
MAa1	4.9	MAb11	9.6	MAc31	15.9
MAa3	4.53	MAb3	9.07	MAc42	15.86
MAa4	4.65	MAb5	9.13	MAc52	15.875

* Unfractionated

Table 3 Light scattering data λ_0 = 5460 Å, solvent MeCN

Fraction	$\bar{M}_w \times 10^{-6}$	$\langle \bar{S}^2 \rangle_z^{1/2}$	$A_2 \times 10^4$ (ml g^{-2} mol)
MAa1	1.56	805.6	0.991
MAa21	1.24	786.9	1.24
MAa22	1.016	689.4	1.304
MAa23	0.75	611.5	1.415
MAa3	0.58	657.6	1.46
MAa4	0.44	523.9	1.52
MAa5	0.4	500.0	1.522
MAb11	1.83	1556.5	0.315
MAb12	1.2	1465.9	0.4
MAb21	1.15	1171.9	0.422
MAb22	0.676	1112.4	0.478
MAb3	0.758	1132.8	0.45
MAb4	0.46	1096.7	0.51
MAb5	0.27	1046.4	0.525
MAc2	1.7	2247.1	0.14
MAc31	1.53	2048.0	0.16
MAc33	1.047	1619.0	0.225
MAc42	1.352	1932.3	0.185
MAc51	1.175	1718.0	0.2075
MAc53	1.000	1630.5	0.234
MAc62	0.871	1595.4	0.248
MAc63	0.832	1612.0	0.255
MAc64	0.6	1482.5	0.292

random. The similarity in the values for fractionated and unfractionated samples shows that fractionation has taken place with respect to molecular weight only.

Light scattering

The molecular weights of the fractions were determined using a Brice Phoenix light scattering photometer (type 1000D) over the angular range of 45°–135° using a cylindrical cell. The instrument was calibrated using well purified and freshly distilled analar benzene and the solvents and the solutions were rendered dust-free by repeated filtration through sintered crucibles. The concentration (2×10^{-3} to 0.5×10^{-3} g/dl) was changed by successive dilution. All light scattering measurements were carried out in MeCN because of the high dn/dc values of the copolymer solution in MeCN[18]. The refractive index increments, dn/dc, were measured in a Brice–Phoenix differential refractometer.

The molecular weights, $\bar{M}_w$, the mean square radius of gyration $\langle \bar{S}^2 \rangle_z$ and the second virial coefficient A_2 were determined from Zimm plots[22].

The measurement of the light scattering of a heterogeneous copolymer gives only an apparent molecular weight, which depends on the refractive index of the solvent, and measurements in several solvents with different refractive indices are required to obtain the true molecular weights[14,23–25]. But in the present case, the apparent molecular weights determined in three different solvents, MeCN, methyl ethyl ketone and DMF, gave the same values within experimental error. This suggests that the copolymer prepared is homogeneous in composition. Hence, the true molecular weight is given by the usual treatment applicable to homopolymers[26,27].

Table 3 gives the light scattering results in MeCN for all the copolymers and a typical Zimm plot is shown in *Figure 1.*

Viscosity

The viscosities of the copolymer solutions were measured at three different temperatures in the concentration range 0.1 to 0.5 g/dl with a suspended level dilution viscometer. The kinetic energy and shear corrections were not needed since the values of $[\eta]$ were less than 3 dl/g and the flow times of the solvents were all more than 100 seconds[28]. *Table 4* gives the viscosity data.

RESULTS AND DISCUSSION

Mark–Houwink relationships

The Mark–Houwink parameters, K' and 'a', were evaluated for all the copolymers in at least one good solvent and one poor solvent. Ethyl acetate (EAc) and benezene (Bz) were used for MAa, MeCN, dimethyl sulphoxide (DMSO) and a binary mixture of Bz and DMF in the ratio of 6.5:1 by volume (BM1) for MAb, and MeCN, DMSO and Bz+DMF in the ratio 1.667:1 by volume (BM2) for MAc. A Mark–Houwink plot for one of the copolymer systems is shown in *Figure 2* and the values are summarized in *Table 5.*

The value of 'a' for MAa in Bz is found to be 0.5 at 20°C indicating that it is in the theta state at this temperature. The high molecular weight fractions of MAa did not dissolve in Bz below 20°C. The other two copolymers, MAb and MAc, were insoluble in Bz even at high temperature. The 'a' value of PMMA in Bz is 0.76 at 30°C [29]. The incorporation of even 23.5% of AN into the chain has decreased the solubility considerably. At 40°C, Bz is a good solvent for MAa.

EAc is a good solvent for MAa (the value of 'a' being 0.73 at 30°C). There is a marked increase in 'a' value with a rise in temperature from 30°C to 40°C (from 0.73 to 0.8), but with a further rise to 50°C, it remains constant at 0.8.

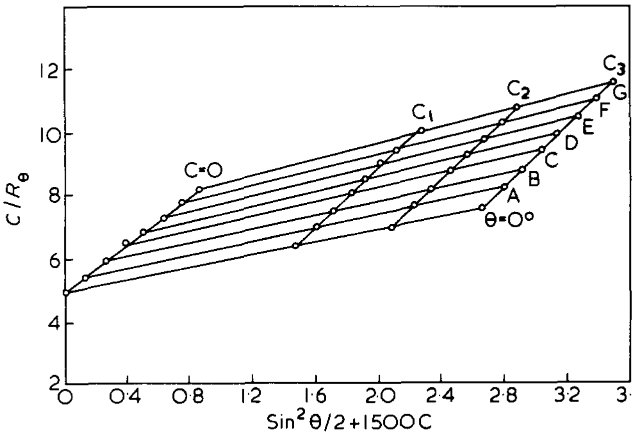

Figure 1 Zimm plot for the fraction MAa1. A, 45°; B, 60°; C, 75°; D, 90°; E, 105°; F, 120°; G, 135°C. $K^* = -13.1 \times 10^{-8}$ mol. gm^{-2} cm^2

Table 4 Viscosity data
(a) MAa

		[η] EAc (dl/g)			[η] Bz (dl/g)		
Fraction	$\bar{M}_w \times 10^{-6}$	30°	40°	50°C	20°	30°	40°C
1	1.56	1.53	1.515	1.45	1.047	1.385	1.46
21	1.24	1.34	1.28	1.17	0.933	1.12	1.165
22	1.016	1.245	1.105	1.025	0.85	0.99	1.01
23	0.75	0.94	0.915	0.88	0.75	0.82	0.87
3	0.578	0.74	0.705	0.67	0.69	0.71	0.73
4	0.44	0.6	0.55	0.52	0.53	0.55	0.53
5	0.4	0.55	0.525	0.49	0.47	0.51	0.47

(b) MAb

		[η] MeCN (dl/g)			[η] DMSO (dl/g)			[η] BM1 (dl/g)		
Fraction	$\bar{M}_w \times 10^{-6}$	30°	40°	50°C	30°	45°	60°C	30°	40°	50°C
11	1.83	2.17	2.06	1.97	2.94	2.9	2.88	1.035	1.01	0.96
12	1.2	1.565	1.51	1.38	2.14	2.09	2.00	0.89	0.84	0.81
21	1.15	1.475	1.42	1.3	2.05	1.95	1.8	0.875	0.83	0.785
22	0.676	1.0	0.965	0.89	1.26	1.23	1.26	0.685	0.63	0.615
3	0.76	1.055	1.02	0.93	1.41	1.35	1.32	0.705	0.675	0.64
4	0.46	0.77	0.72	0.685	0.89	0.86	0.8	0.51	0.48	0.46
5	0.27	0.51	0.48	0.465	0.6	0.59	0.56	0.4	0.385	0.36

(c) MAc

		[η] MeCN (dl/g)			[η] DMSO (dl/g)			[η] BM2 (dl/g)		
Fraction	$\bar{M}_w \times 10^{-6}$	30°	40°	50°C	30°	45°	60°C	30°	40°	50°C
1	3.8	–	–	–	–	–	–	2.08	2.06	2.03
2	1.7	1.57	1.53	1.43	2.3	2.25	2.24	1.45	1.385	1.37
31	2.53	1.4	1.33	1.29	2.18	2.16	2.14	1.355	1.31	1.28
32	–	–	–	–	2.1	2.1	2.08	–	–	–
33	1.047	1.115	1.04	0.97	1.74	1.62	1.72	1.03	1.02	1.01
41	–	–	–	–	1.98	1.96	1.9	–	–	–
42	1.35	1.31	1.22	1.17	–	–	–	1.27	1.25	1.23
51	1.175	1.2	1.12	1.07	1.82	1.78	1.83	1.21	1.16	1.14
53	1.00	1.07	0.97	0.95	–	–	–	–	–	–
61	–	–	–	–	1.62	1.56	1.46	–	–	–
62	0.87	0.95	0.9	0.88	1.52	1.46	1.42	1.05	0.98	0.945
63	0.83	–	–	–	1.48	1.407	1.39	1.015	1.0	0.975
64	0.6	–	–	–	–	–	–	0.87	0.8	0.73

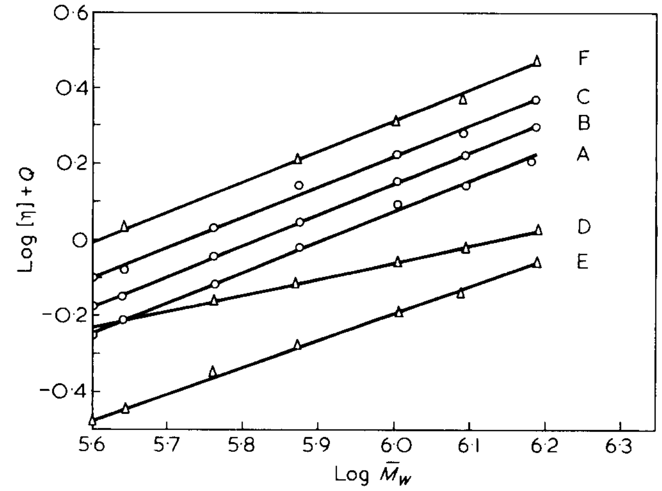

Figure 2 Mark–Houwink plot for MAa. A: 30°C, Q = 0.0; B: 40°C, Q = 0.1; C: 50°C, Q = 0.2; D: 20°C, Q = 0.0; E: 30°C, Q = –0.2; F: 40°C, Q = 0.3. ○ EAc; △ Bz

The high values of '*a*' for MAb and MAc in MeCN show that it is a very good solvent for this copolymer system. The value of '*a*' is reported as 0.5 for PMMA in MeCN at 30°C[29]. Kashyap *et al.* have obtained '*a*' values of 0.75, 0.53, 0.78 and 0.84, respectively, for copolymers containing 0.289, 0.422, 0.541 and 0.651 m.f. of AN[18–20]. It is found in the present investigation that with a further rise in AN to about 75%, the '*a*' value falls to 0.7, showing that increase of AN content first increases the solvent power, and with a further rise in AN, the solvent power is decreased. From the plot of '*a*' vs. percentage composition (*Figure 3*), it can be seen that there are two maxima corresponding to the composition of 0.415 and 0.65 m.f. of AN, and one minima corresponding to the composition of 0.566 m.f. of AN.

DMSO is reported to be a good solvent for PAN (a=0.75)[30]. In the present study, it is found that for a copolymer with about 50% of AN, the '*a*' value is very high (0.875) whereas with a further increase in AN to about 75%, the value falls off considerably (to 0.6) and it is a poor solvent. In other words, on introduction of MMA into the PAN sequences, the solvent power first reduces, reaches a minimum, after which it rises abruptly. There is a marked increase in the '*a*' values with rise in temperature.

It is interesting to note that the '*a*' values for the copolymers MAb and MAc, in the binary solvent mixtures, BM1 and BM2, respectively, are 0.5 at all the

Table 5 Mark–Houwink parameters

Solvent	Temperature (°C)	MAa $K' \times 10^4$	MAa a	MAb $K' \times 10^4$	MAb a	MAc $K' \times 10^4$	MAc a
EAc	30	0.44	0.73	–	–	–	–
	40	0.17	0.8	–	–	–	–
	50	0.1	0.8	–	–	–	–
Bz	20	9.12	0.5	–	–	–	–
	30	0.97	0.667	–	–	–	–
	40	0.455	0.72	–	–	–	–
MeCN	30	–	–	0.437	0.75	0.69	0.7
	40	–	–	0.34	0.767	0.305	0.75
	50	–	–	0.287	0.773	0.24	0.75
DMSO	30	–	–	0.094	0.875	4.23	0.6
	45	–	–	0.094	0.875	2.07	0.65
	60	–	–	0.05	0.92	1.016	0.7
BM1 & BM2	30	–	–	7.94	0.5	11.22	0.5
	40	–	–	7.6	0.5	10.84	0.5
	50	–	–	4.8	0.5	10.84	0.5

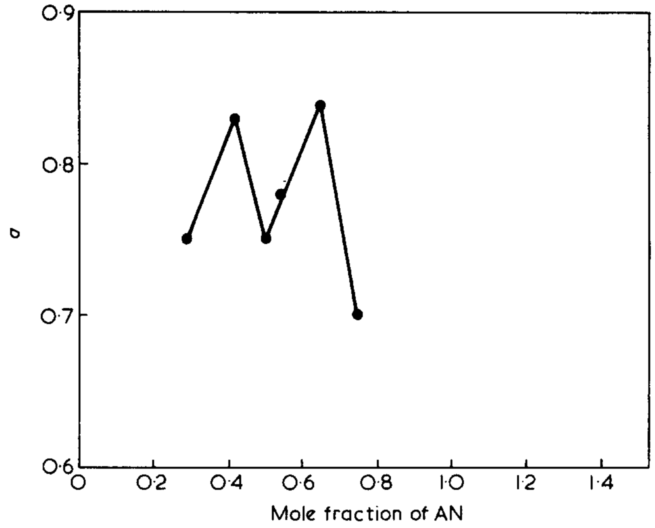

Figure 3 a vs. composition of AN in MMA–AN copolymer in MeCN. (Values for 0.289, 0.422, 0.541 and 0.651 m.f. are taken from refs. 18, 19 and 20)

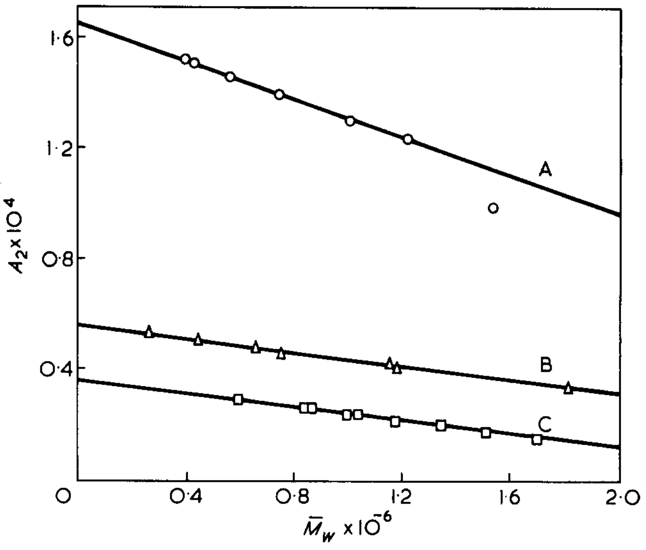

Figure 4 A_2 vs. $\bar{M}_w$ for MMA–AN copolymers in MeCN. A, MAa; B, MAb; C, MAc

three temperatures. These solvents were chosen for studying the copolymers in the θ state since a pure θ solvent was not available. It is not clear whether they are to be considered as representing true theta conditions or whether preferential adsorption plays a role in it. The copolymer being highly polar, the possibility of the existence of preferential adsorption cannot be ruled out completely and so the theta condition in the present case may not be representing the true theta state[31]. However, the copolymers cease to go into solution below 30°C.

The K' values are found to increase with rise in temperature. A similar trend was observed by other workers[19,32]. For MAa in Bz at 20°C, the K' value gives the unperturbed dimensions directly, as it is in the theta state. For the binary solvent mixtures, it is difficult to say which is the theta temperature due to the reasons stated earlier.

Virial coefficients

The values of A_2, the second virial coefficient, in MeCN are given in *Table 3*. The ranges of A_2 values are 0.99×10^{-4} – 1.522×10^{-4} for MAa, 0.315×10^{-4} – 0.525×10^{-4} for Mab and $0.14 \times 10^{-4} - 0.292 \times 10^{-4}$ ml g^{-2} mol for MAc. These values are extremely low considering that MeCN is a good solvent for the copolymers. The variation of A_2 with $\bar{M}_w$ is found to be linear (*Figure 4*). The values are seen to decrease with increase in AN content contrary to the results obtained by Kashyap *et al.*[18–20]. *A plot of* $(A_2)_{\bar{M}_w} = 0$ *versus* composition of copolymer (*Figure 5*) shows a minimum corresponding to the m.f. of AN of 0.415, in contrast to that observed for the behaviour of 'a' with composition (*Figure 3*). Usually both 'a' and A_2 are considered to be measures of solvent power. Hence, one expects large A_2 values when 'a' values are high. But in the present system, the observed low values of A_2 and high values of 'a' cannot be explained by the existing theories.

Short-range interaction parameters

Evaluation of K, *the Flory constant.* The unperturbed mean square radius $\langle \bar{r} \rangle_0^2$ is one of the two basic parameters which represents the short-range interferences

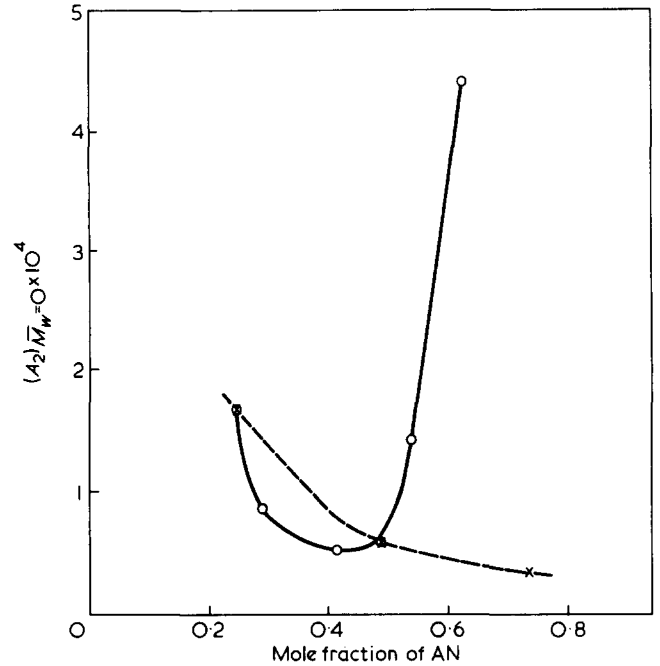

Figure 5 $(A_2)_{\bar{M}_w=0}$ vs. composition for MMA–AN copolymers in MeCN

in the chain. It is evaluated from intrinsic viscosity molecular weight data. The treatment is based on Flory's excluded volume treatment[33,34] of dilute polymer solutions and its main results are summarized in the following equations:

$$[\eta] = K\bar{M}_w^{1/2}\alpha_\eta^3 = [\eta]_\theta \alpha_\eta^3 \qquad (1)$$

$$K = \varphi[\langle \bar{r}\rangle_0^2/\bar{M}_w]^{3/2} \qquad (2)$$

Here α_η is the hydrodynamic expansion factor given by

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \qquad (3)$$

where $[\eta]_\theta$ is the intrinsic viscosity at θ temperature and φ is the hydrodynamic constant. This dependence of $[\eta]$ on $\bar{M}_w$ is made use of for calculating K and α_η^3 for a given polymer–solvent system.

Equation (1) should permit the evaluation of K from the value of $[\eta]_\theta$ obtained using a polymer fraction of known molecular weight at the theta temperature. Under non-theta conditions, the expansion factor is an increasing function of the excluded volume parameter, z. Several graphical procedures have been proposed to evaluate K from $[\eta]$ values obtained under non-theta conditions[3,5,12,34–39]. Cowie[40] has critically reviewed the various methods for evaluation of K.

The experimental data of this investigation were used to evaluate K by the Stockmayer–Fixman method (S.F.) which is the simplest of all the methods. The S.F. equation is given by[5]

$$[\eta]/\bar{M}_w^{1/2} = K + 0.51\,\varphi B \bar{M}_w^{1/2} \qquad (4)$$

From the $[\eta]/\bar{M}_w^{1/2}$ *versus* $\bar{M}_w^{1/2}$ plots (*Figure 6*), K was evaluated from the intercept for all the copolymers.

The values of K are given in *Table 6*. From the table it is seen that K is dependent on the nature of the solvent contrary to earlier beliefs that it is independent of the solvent. It is observed that in a solvent with larger value of 'a', the MH exponent, K value is lower. Kashyap *et al.* have also obtained similar results with MMA-AN copolymers[18]. For MAa, the solvent effect seems to be negligible. The values obtained at 30°C and 40°C in Bz are almost identical with the values obtained in EAc at the corresponding temperatures. This may be due to the fact that in MAa, the m.f. of AN being very small, intramolecular interactions may be negligible.

Unperturbed dimensions. Values of $\langle \bar{r}\rangle_0^2/\bar{M}_w$ were evaluated from the K values using a value of 2.68×10^{21} dl/g for φ[41]. The results are included in *Table 6*.

If the unperturbed average dimensions of a copolymer chain conformed to an idealized random flight model and consisted of two independent statistical chain elements, the unperturbed mean square end to end distance would obey the relation,

$$[\langle \bar{r}\rangle_0^2/\bar{M}_w]_{co} = W_A[\langle \bar{r}\rangle_0^2/\bar{M}_w]_A + W_B[\langle \bar{r}\rangle_0^2/\bar{M}_w]_B \qquad (5)$$

where W_A and W_B are the weight fractions and the quantities in brackets are characteristic of homopolymers. The values computed from this equation are 4.67×10^{-17} cm^2, 5.47×10^{-17} cm^2 and 6.5×10^{-7} cm^2, respectively, for MAa, MAb and MAc, assuming the values for PMMA and PAN to be 4.096×10^{-17} cm^2 and 8.1×10^{-17} cm^2, respectively. The experimental values are much lower than these ideal values. This is contrary to the expected results. It is quite interesting to note that the extension is maximum in the poorest solvent! This cannot be explained by the existing theories. The value for MAa in benzene at the θ state is found to be equal to the ideal value showing that in this case A–B interactions are very low or absent.

Steric factor, σ. The short-range interactions result from side group steric effects and bond angle restrictions. These short-range interactions are reflected in a parameter, σ, the steric factor or stiffness parameter, which is a measure

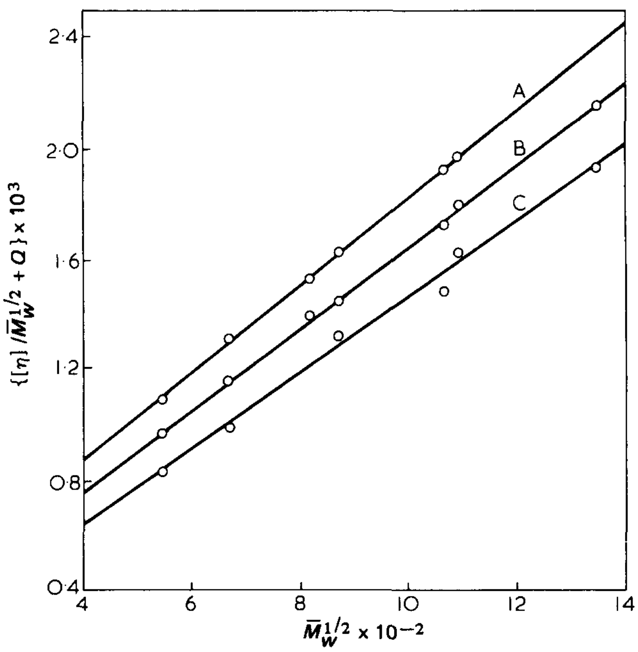

Figure 6 Stockmayer–Fixman plot for MAb in DMSO. A: 30°C, Q = 0.0; B: 45°C, Q = –0.1; C: 60°C, Q = –0.2

Table 6 Short-range interaction parameters for MMA–AN copolymers
(a) In EAc, Bz, MeCN, BM1 and BM2

Parameter	Temperature (°C)	MAa		MAb		MAc	
		EAc	Bz*	MeCN	BM1	MeCN	BM2
$K \times 10^3$	30	0.49	0.86	0.61	0.79	1.0	1.1
	40	0.46	0.47	0.58	0.754	0.88	1.06
	50	0.4	0.37	0.54	0.72	0.84	1.04
$\langle \bar{r} \rangle_0^2 \times 10^{17}$ cm^2	30	3.22	4.687	3.73	4.446	5.18	5.52
	40	3.09	3.13	3.6	4.3	4.76	5.39
	50	2.814	2.67	3.44	4.16	4.6	5.32
σ	30	1.73	2.09	1.735	1.9	1.885	1.945
	40	1.695	1.71	1.71	1.86	1.806	1.92
	50	1.62	1.576	1.667	1.834	1.78	1.91

* The values for Bz are at 20°, 30° and 40°C instead of at 30°, 40° and 50°C, respectively

(b) In DMSO

Parameter	MAb			MAc		
	30	45	60°C	30	45	60°C
$K \times 10^3$	0.26	0.285	0.3	1.32	1.112	0.84
$\langle \bar{r} \rangle_0^2 \times 10^{17}$ cm^2	2.93	2.7	2.45	6.24	5.59	4.614
σ	1.48	1.42	1.356	1.98	1.87	1.7

Table 7 Long-range interaction parameters for MMA–AN copolymers

Parameter	Temperature (°C)	MAa		MAb			MAc		
		EAc	Bz*	MeCN	DMSO	BM1	MeCN	DMSO	BM2
	30	0.465	0.0	0.55	0.997	0	0.133	0.271	0
$B \times 10^{27}$	40	0.457	0.366	0.52	0.967^a	0	0.183	0.322^a	0
	50	0.445	0.457	0.488	0.9145^b	0	0.183	0.54^b	0
	30	0.48	0.5	0.4875	0.4695	0.5	0.497	0.492	0.5
χ_1	40	0.481	0.486	0.488	0.47^a	0.5	0.496	0.49^a	0.5
	50	0.4815	0.483	0.49	0.472^b	0.5	0.496	0.484^b	0.5

* Values are at 20°C, 30°C and 40°C respectively, instead of at 30°C, 40°C and 50°C
[a] Values at 45°C
[b] Values at 60°C

of the hindrance to internal rotations about the carbon–carbon bond of the main chain. *Table 6* gives σ values for the systems studied.

The σ values of the copolymer are smaller than 2.2, the value reported for the parent homopolymers[17]. The small value for the copolymer in all the solvents signifies that in the unperturbed state, the copolymer is less extended than the corresponding homopolymers. This is in contrast to what was observed by Shimura[17] but Kashyap *et al.*[18–20] working with MMA–AN copolymers of four different compositions observed that σ values were all lower than those of the homopolymers.

Considering the above facts, it may be concluded that the interaction between the nitrile (–CN) groups of AN units and methoxy carbonyl groups and/or methyl group pendant to the MMA units is much less than the interactions between the methoxy carbonyl or methyl groups. The molar volumes of the substituents in the homopolymers are 38 cm^3 and 60 cm^3, respectively, for PAN and PMMA. From the smaller volume of PAN, one would expect smaller steric hindrance for a copolymer of MMA–AN compared to PMMA. Shimura[17] has pointed out that electrostatic interaction such as dipole–dipole force must be acting upon its conformation to increase the factor rather than the bulkiness of the substituent group. But from the present work and Kashyap's work, it may be concluded that the bulkiness of substituent groups is quite an important factor contributing to the steric factor in this system.

Long-range interactions. The dimensions of the polymer molecule in solution are determined by long-range thermodynamic interaction between the polymer and solvent. These are reflected in the values of the expansion factor, α_η (the ratio of the dimensions of the polymer molecules in the solvent system of interest to the corresponding value in the theta solvent) and the values of χ_1, where χ_1 is the solute–solvent interaction parameter.

A direct estimation of the long-range interaction is possible by the estimation of B which is connected to χ_1. B was calculated from the slopes of the S.F. plots for the copolymers.

B is connected to the χ_1 by the relation,

$$B = \frac{2\bar{v}^2(\frac{1}{2} - \chi_1)}{N_A V_1} \tag{6}$$

where $\bar{v}$ is the specific volume of the polymer, N_A is the Avogadro number and V_1 is the molar volume of the solvent. *Table 7* gives the values of B and χ_1 for the copolymers in all the solvents studied.

The B values are zero for MAb and MAc in the binary

Table 8 α_η^3 values
(a) MAa

		EAc			Bz		
Fraction	$\bar{M}_w \times 10^{-6}$	30°	40°	50°C	20°	30°	40°C
1	1.56	2.5	2.636	2.9	0.99	2.41	3.16
21	1.24	2.455	2.5	2.6	0.99	2.186	2.83
22	1.016	2.52	2.383	2.54	0.996	2.135	2.71
23	0.75	2.216	2.3	2.54	1.02	2.06	2.72
3	0.578	1,987	2.016	2.2	1.07	2.03	2.6
4	0.44	1.846	1.8	1.96	0.94	1.86	2.16
5	0.4	1.785	1.8	1.95	0.99	1.75	2.01

(b) MAb

		MeCN			DMSO			BM1		
Fraction	$\bar{M}_w \times 10^{-6}$	30°	40°	50°C	30°	45°	60°C	30°	40°	50°C
11	1.83	2.63	2.624	2.7	8.35	7.52	7.09	0.96	0.99	0.985
12	1.2	2.34	2.38	2.33	7.5	6.7	6.08	1.02	1.017	1.03
21	1.15	2.26	2.285	2.25	7.36	6.4	5.6	1.03	1.03	1.0
22	0.676	1.994	2.02	2.0	5.9	5.26	5.11	1.05	1.016	1.0
3	0.76	1.986	2.02	1.98	6.2	5.44	5.05	1.02	1.027	1.0
4	0.46	1.867	1.84	1.876	5.06	4.46	3.94	0.95	0.94	0.945
5	0.27	1.611	1.6	1.66	4.2	3.77	3.4	0.97	0.984	0.964

(c) MAc

		MeCN			DMSO			BM2		
Fraction	$\bar{M}_w \times 10^{-6}$	30°	40°	50°C	30°	45°	60°C	30°	40°	50°C
1	3.8	–	–	–	–	–	–	0.97	1.0	1.0
2	1.7	1.205	1.334	–	1.34	1.54	–	1.01	0.99	1.01
31	1.53	1.132	1.225	–	1.335	1.56	–	0.996	1.0	0.995
33	1.047	1.09	1.155	–	1.29	1.413	–	0.915	0.94	0.95
42	1.35	1.13	1.19	–	–	–	–	0.993	1.01	1.02
51	1.175	1.107	1.174	–	1.27	1.466	–	1.015	1.01	1.01
53	1.0	1.07	1.1	–	–	–	–	1.0	1.0	1.0
62	0.871	1.066	1.1475	–	1.234	1.4	–	1.023	1.01	0.974
63	0.832	–	–	–	1.23	1.377	–	1.012	1.013	1.03
64	0.6	–	–	–	–	–	–	1.017	0.97	0.9

solvent mixtures, BM1 and BM2, respectively. It is not clear whether this is an indication of θ condition due to reasons mentioned earlier. In all the solvents the χ_1 values are very close to 0.5, the value in a θ solvent. This is very difficult to explain since in good solvents where '*a*' values are high, the χ_1 values are expected to be low. For MAa in Bz, χ_1 is 0.5 at 20°C indicating again that it is in the theta state.

Expansion factor α_η^3

The values of α_η^3 which are a measure of the deviation of the solution from ideality, are given in *Table 8*. α_η^3 values are found to be very high, showing that the polymers are highly extended in solution. The high extensions of these chains are mainly due to unusually favourable solute–solvent interactions rather than due to short range interactions. Comparison of α_η^3 values and A_2 values shows that higher α_η^3 values are associated with higher A_2 values. MAc which has very low A_2 values has very low α_η^3 values too.

CONCLUSIONS

The large values of '*a*', the MH exponent, in good solvents suggest that these molecules are highly extended in solution. The low values of the unperturbed dimensions (i.e. low steric factor) and high α_η^3 values suggest that these molecules are extended mainly because of unusual solute–solvent interactions. However, if the high extensions of these molecules are mainly due to polymer solvent effect, then one would expect high A_2 and low χ_1 values. But A_2 values obtained by light scattering method for these systems are very low and the χ_1 values very high, opposite to that expected in a good solvent. Such high values of '*a*' and low values of A_2 have been reported for stiff chain polymers such as cellulose derivatives[3,42,43]. Hence, it is thought that the incorporation of AN into MMA chains must have introduced stiffness to the chain. It is observed that for none of the copolymer systems in good solvents does the S.F. method give the unperturbed dimension values obtained in the θ solvents, showing that this equation is not sufficient to eliminate the perturbation effects caused by the solvent.

All these experimental findings suggest that the theory for $[\eta]$ is not yet complete. It is hoped that these results may prove useful in the development of improved theoretical estimates of the dependence of $[\eta]$ on $\bar{M}_w$.

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