Dilute solution properties of methyl methacrylate—acrylonitrile copolymer (MA1)

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This paper deals with studies on the dilute solution properties of methyl methacrylate—acrylonitrile copolymer of 0.289 mole fraction (*mf*) of acrylonitrile composition. Mark—Houwink parameters for this copolymer have been evaluated in acetonitrile (MeCN), 2-butanone (MEK), dimethylformamide (DMF) and γ-butyrolactone (γ-BL). The solvent power is found to be in the order of MEK < MeCN < DMF < γ-BL at 30°C. Herein, probably for the first time, the steric factor for the copolymer is found to be lower than that for the parent homopolymers and the excess interaction parameter, χ_{AB} is found to be negative. This probably suggests that the units are compatible to each other.

INTRODUCTION

The behaviour of copolymers in solution is very complex compared to that of their parent homopolymers. Earlier studies of their solution properties have been mainly directed towards the study of the styrene/methyl methacrylate copolymer[1,10] system where styrene is a non-polar unit. The theory developed by Stockmayer *et al.*[1] could successfully explain the properties of this system. More recently, this theory has been extended to explain the properties of other copolymer systems such as styrene—acrylonitrile copolymer[2]. However, very little work has been done on the copolymer systems like methyl methacrylate/acrylonitrile (MMA—AN) copolymer[7], where both the constituents are polar. The nature of the intramolecular interactions may be quite different from those of the other systems.

With this in view, studies were undertaken on the solution properties of MMA—AN copolymers. In this paper, we report the results of these studies on a copolymer of 0.289 *mf* of AN, denoted as MA1.

EXPERIMENTAL

Polymerization and fractionation

MA1 was prepared by the solution polymerization method using benzoyl peroxide (0.05 mol %) as the initiator. MA1 was fractionated using acetonitrile—di-isopropylether as the solvent/non-solvent system. The γ-values ranged from 0.363 to 0.535. The details of the preparation of the copolymer, and the criteria for selecting this solvent/non-solvent pair, have been described elsewhere[3]. The fractionation was effected with respect to molecular weight only.

Specific refractive index increment

The specific refractive index increment (dn/dc) of the copolymer was measured in MEK, MeCN and DMF with a Brice—Phoenix type of differential refractometer (constructed in this laboratory) at 30°C with green light (λ = 5460 Å). The values (in ml/g) in MEK, MeCN, and DMF are 0.117, 0.141 and 0.063 respectively.

Light scattering

Light scattering measurements were carried out at 30°C with green light (λ = 5460 Å) using a Brice—Phoenix light scattering photometer (Type 1000-D) over the angular range of 45° to 135° with a cylindrical cell. The instrument was calibrated with well purified and distilled benzene ($R_{90} = 16.5 \times 10^{-6}$ cm^{-1}). The solutions were prepared in purified and freshly distilled solvents and the solvents and solutions were rendered dust-free by repeated filtration. The concentration (2×10^{-3} to 0.5×10^{-3} g/ml) was changed by successive dilution.

The weight-average molecular weight $\bar{M}_w$, the mean square radius of gyration $\langle S^2 \rangle_z$, and the second virial coefficient A were determined from Zimm plots[4]. Beattie *et al.*'s programme[5] was modified as an aid to the manual construction of these plots.

The molecular weights obtained from all three solvents (MeCN, MEK and DMF) agree well within experimental error. This suggests that any polydispersity in composition which may be present in this copolymer system poses no problem in obtaining the true molecular weight. It could also be due to the fact that, for such a small difference in the refractive indices of the parent homopolymers itself (i.e. 0.025), the Bushuk—Benoit theory[6] is no longer effective. Similar conclusions were drawn by Shimura[7] for a copolymer of MMA—AN of 0.48 *mf* of AN, and by Spatorico[8] for a copolymer of poly(ethylene oxide) and polycarbonate.

Hence all the remaining measurements of the light scattering of copolymer solutions were carried out in MeCN only, because of its high dn/dc value.

Table 1 gives the light scattering results. A typical Zimm plot is shown in *Figure 1.*

Viscosity

The intrinsic viscosities, $[\eta]$, of the copolymer solutions were determined at different temperatures in the concentration range 0.1 to 0.5 g/dl, with suspended level dilution viscometers. The kinetic energy and shear correction factors were not applicable. *Table 2* gives the viscosity data.

RESULTS AND DISCUSSION

Mark–Houwink relation

From the plots of log [η] *versus* log$\bar{M}_w$ in *Figure 2*, Mark–Houwink relations were established for MA1 in MeCN, MEK, DMF and γ-BL at different temperatures. Values of K' and a are given in *Table 3*.

From the values of a we see that, for the copolymer, the solvent power is in the order MEK < MeCN < DMF < γ-BL at the same temperature, though all the solvents seem to be good solvents.

The a values for PMMA in MEK[9], DMF[10] and γ-BL[10] at 30°C are 0.72, 0.65 and 0.68 respectively and the values for PAN in DMF[11] and γ-BL[12] are 0.72 and 0.69 respectively. From this, it is clear that the a values obtained for the copolymer in these solvents are higher than those for both the parent homopolymers. Even in MeCN, which is a θ-solvent for PMMA[13] and a non-solvent for PAN, the a value for the copolymer in this solvent is 0.746 which is comparable to the values obtained in the other solvents.

The effect of temperature on the values of a is not of uniform nature. In the case of DMF, the a value shows a minimum at 45°C, whereas for γ-BL, a maximum is observed at 45°C.

Table 1 Light scattering results for MA1

Fraction	$\bar{M}_w \times 10^{-5}$	$\langle S^2\rangle_z$	$A_2 \times 10^4$
MA 111	79.03	0.039	0.40
MA 112	63.23	0.031	0.37
MA 121	47.72	0.024	0.55
MA 14	31.61	0.016	0.69
MA 15	23.71	0.012	0.65
MA 16	21.68	0.011	0.70

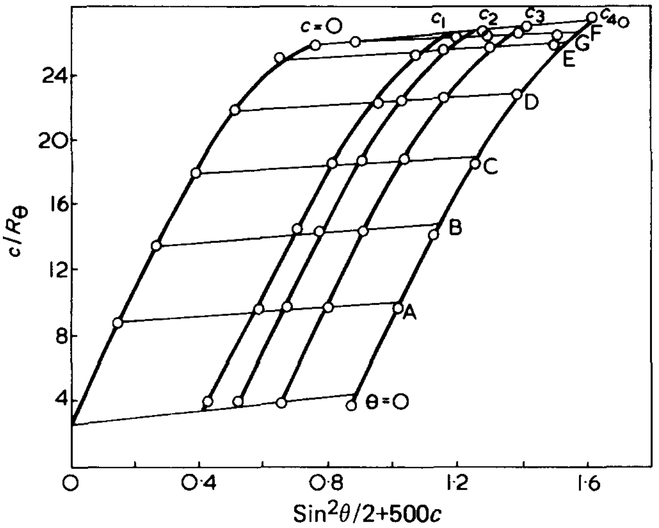

Figure 1 Zimm plot for the fraction MA 14. A, 45°; B, 60°; C, 75°; D, 90°; E, 105°; F, 120°; G, 135°. $K^* = 13.18 \times 10^{-8}$ mol g^{-2} cm^2

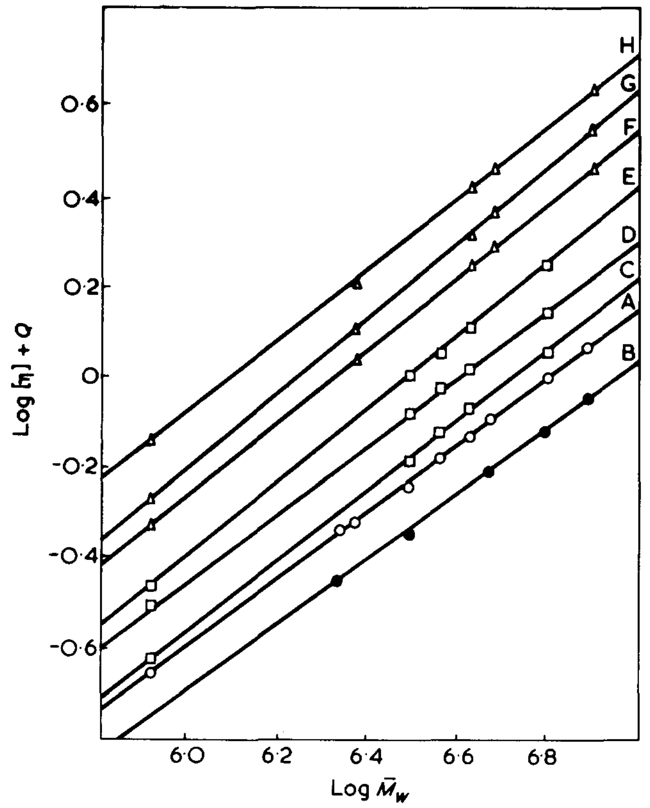

Figure 2 Mark–Houwink plot. A, 30°C, Q = 0.0; B, 30°C, Q = −0.1; C, 30°C, Q = 0.0; D, 45°C, Q = 0.1; E, 60°C, Q = 0.2; F, 30°C, Q = 0.2; G, 45°C, Q = 0.3; H, 60°C, Q = 0.4. ○, MeCN; ●, MEK; □, DMF; △, γ-BL

Table 2 Viscosity results for MA1 ([η] values)

				DMF			γ-BL		
Fraction	$\bar{M}_w \times 10^{-5}$	MeCN 30°C	MEK 30°C	30°C	45°C	60°C	30°C	45°C	60°C
MA 111	79.03	1.190	1.150	–	–	–	1.870	1.800	1.800
MA 112	63.23	1.010	0.980	1.200	1.135	1.160	–	–	–
MA 121	47.72	0.820	0.795	–	–	–	1.257	1.190	1.190
MA 122	42.95	0.750	–	0.870	0.850	0.840	1.135	1.070	1.070
MA 113	37.07	0.670	–	0.775	0.768	0.740	–	–	–
MA 14	31.61	0.580	0.570	0.670	0.670	0.650	–	–	–
MA 15	23.71	0.480	–	–	–	–	0.700	0.650	0.660
MA 16	21.68	0.460	0.450	–	–	–	–	–	–
MA 17	8.38	0.220	–	0.238	0.256	0.218	0.299	0.269	0.289

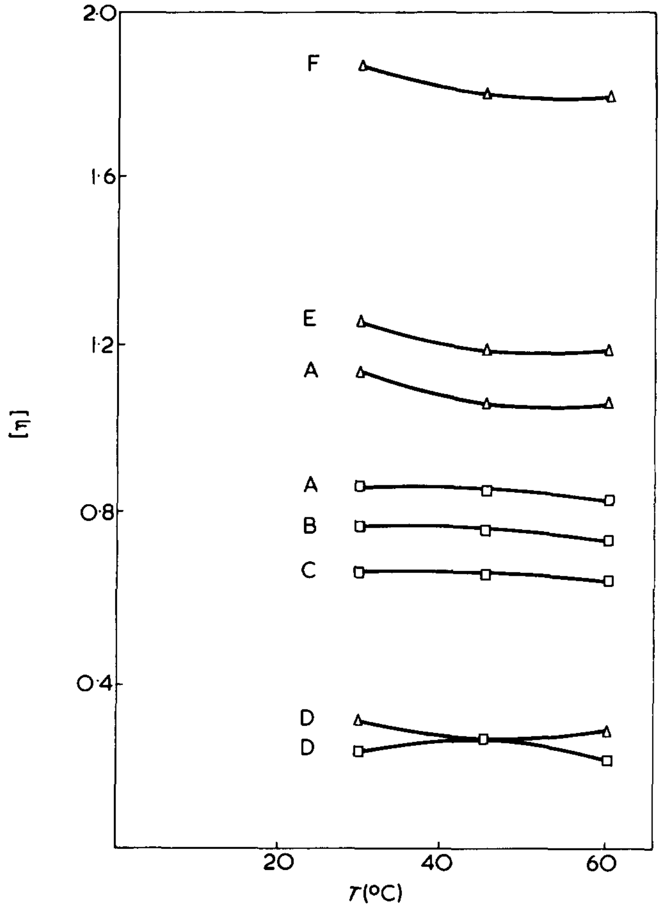

Figure 3 Temperature variation of [η]. A, MA 122; B, MA 113; C, MA 14; D, MA 17; E, MA 121; F, MA 111. □, DMF; △, γ-BL

Table 3 Mark–Houwink parameters for MA1

Solvent	Temperature (°C)	$K' \times 10^4$	a
MeCN	30	0.085	0.746
MEK	30	0.111	0.727
DMF	30	0.050	0.791
	45	0.073	0.764
	60	0.029	0.824
γ-BL	30	0.044	0.817
	45	0.027	0.845
	60	0.053	0.800

Temperature variation of [η]

The behaviour of the linear deformation of the polymer chain, due to polymer–solvent interaction in a good solvent medium, is represented by the Flory–Fox equation[14]:

$$[\eta] = K_0\bar{M}_w^{1/2}\alpha_\eta^3 \qquad (1)$$

where

$$K_0 = \phi_0[\langle r_0^2\rangle/\bar{M}_w]^{3/2} \qquad (2)$$

and α_η, the hydrodynamic expansion factor is given by:

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

where $[\eta]_\theta$ is the value of $[\eta]$ at θ-temperature, ϕ_0 is the hydrodynamic constant, and $\langle r_0^2\rangle$ is the unperturbed mean-square end-to-end distance.

For flexible chain polymers in poor solvents, [η] increases with an increase in temperature; in good solvents, [η] decreases with an increase in temperature; and in athermal solvents, [η] is independent of temperature[15]. It was pointed out by Kawai and Ueyama[16] that the chains are expanded most at the temperature at which [η] is maximum. The decrease of [η] after the maximum is explained by the decrease of $\langle r_0^2\rangle$.

Figure 3 shows plots of [η] *versus* temperature T. In DMF, [η] is almost the same at 30° and 45°C. The further decrease in [η] could be viewed as being due to the skeletal decrease of chain dimensions. In the case of γ-BL, a different trend is noticed; [η] decreases with increase in temperature, which seems to be characteristic of the behaviour of the copolymers in a good solvent, and then remains almost constant.

Short range interactions

The dependence of [η] on $\bar{M}_w$ in a good solvent is made use of in calculating the unperturbed dimensions (K_0) and the long range interaction parameter B. Several graphical procedures are available for the estimation of K_0 from [η] in non-ideal solvents[17]. The simplest one is due to Stockmayer and Fixman[18], and is widely used for studies on polymers and copolymers. The relation is given by:

$$[\eta]/M_w^{1/2} = K_0 + 0.51\,B\phi_0\bar{M}_w^{1/2} \qquad (4)$$

B is given by

$$B = 2\bar{v}^2(½ - \chi_1)/N_A V_1 \qquad (5)$$

where $\bar{v}$ is the specific volume of the polymer, V_1 is the molar volume of the solvent, N_A is Avogadro's number, and χ_1 is the solute–solvent interaction parameter.

K_0 values were evaluated by this method and are given in *Table 4*. *Figure 4* gives the Stockmayer–Fixman plots.

From the Table, it can be seen that the unperturbed dimensions depend on the solvent as well as on the temperature. The values of K_0 in MeCN and MEK at 30°C are the same within the limits of experimental error, while the values in DMF and γ-BL (the solvents for the parent homopolymers) are smaller at this temperature. The corresponding K_0 values for PMMA[10] and PAN[19] are 0.78×10^{-3} and 2.05×10^{-3}. For the copolymer, the K_0 values in all the solvents are lower than the K_0 values for the parent homopolymers. In general, it is observed that in a solvent with larger value of a (the Mark–Houwink exponent) K_0 values are lower.

Such large differences in the unperturbed dimensions in different solvents have been reported for stiff chain polymers such as cellulose derivatives[20,21].

Table 4 Short range interaction parameters for MA1

solvent	Temperature (°C)	$K_0 \times 10^3$	$\langle r_0^2\rangle/M_w \times 10^{17}$	σ
MeCN	30	0.175	1.622	1.22
MEK	30	0.182	1.665	1.23
DMF	30	0.140	1.397	1.13
	45	0.180	1.652	1.23
	60	0.102	1.132	1.02
γ-BL	30	0.150	1.463	1.16
	45	0.132	1.344	1.11
	60	0.158	1.515	1.18

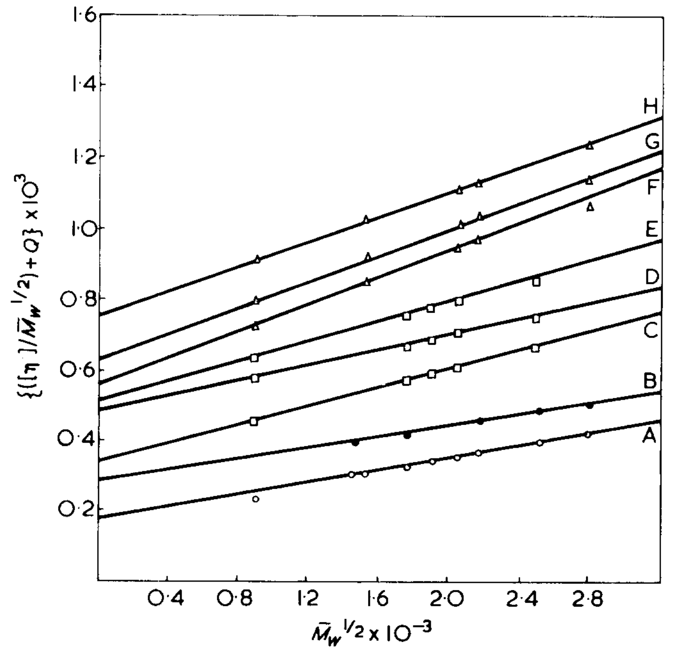

Figure 4 Stockmayer–Fixman plot. A, 30°C, Q = 0.0; B, 30°C, Q = 0.1; C, 30°C, Q = 0.2; D, 45°C, Q = 0.3; E, 60°C, Q = 0.4; F, 30°C, Q = 0.4; G, 45°C, Q = 0.5; H, 60°C, Q = 0.6. ○, MeCN. ●, MEK; □, DMF; △, γ-BL

Unperturbed dimensions

Values of $\langle r_0^2\rangle/\bar{M}_w$ were calculated from K_0 values obtained from the Stockmayer–Fixman equation using a value of 2.68 x 10^{21} dl/g for ϕ_0[22]. The results are included in *Table 4*.

If the unperturbed average dimensions of a copolymer chain conform to an idealized random-flight model, and the chain consists of two different kinds of independent statistical chain element, the unperturbed mean-square end-to-end distance would obey the relation[1]:

$$[\langle r_0^2\rangle/\bar{M}_w]_{C_0} = W_A[\langle r_0^2\rangle/\bar{M}_w]_A + W_B[\langle r_0^2\rangle/\bar{M}_w]_B \qquad (6)$$

where W_A and W_B are the weight fractions, and the quantities in brackets are characteristic of homopolymers.

The value of $[\langle r_0^2\rangle/\bar{M}_w]_{C_0}$ computed for MA1 from equation (6) is 1.096 x 10^{-17} cm^2, by taking 0.949 x 10^{-17} and 1.781 x 10^{-17} cm^2 as the values for PMMA and PAN[23]. The experimental values are higher than this ideal value.

Steric factor

The steric factor σ, which is a measure of the hindrance to internal rotation about the carbon–carbon single bond of the main chain of a flexible polymer molecule in the unperturbed state, is defined by:

$$\sigma = [\langle r_0^2\rangle/\langle r_{0f}^2\rangle]^{1/2} \qquad (7)$$

where $\langle r_{0f}^2\rangle$ is the mean-square end-to-end distance of the polymer chain with complete free internal rotation about the carbon–carbon bond of the main chain. *Table 4* includes the σ values as well.

It will be seen that the σ values of this copolymer are smaller than 2.2, the value reported for the parent homopolymers[23].

Long range interaction parameter

The long range interaction parameter B, evaluated from the Stockmayer–Fixman equation, is given in *Table 5*.

From the values of B, the solvent power for the various solvents can be arranged as MEK < MeCN < DMF < γ-BL, which is the same as deduced from the a values of MA1 in these solvents. B shows a minimum at 45°C in the case of DMF. In γ-BL, B decreases with an increase in temperature.

The interaction parameter χ_1 is related to B through the molar volume of the solvent. It can be seen from *Table 5*, where χ_1 values are also included, that χ_1 is independent of solvent and temperature. It is also interesting to note that the χ_1 values are high, in contrast to what would be expected from the present polymer theories for good solvents.

The excess interaction parameter, χ_{AB}, were calculated from the χ_1 values of copolymers and homopolymers using the expression[1]

$$\chi_1 = x_A\chi_A + x_B\chi_B - x_Ax_B\chi_{AB} \qquad (8)$$

where x_A and x_B are the mole fractions of A and B in the copolymer. χ_1, χ_A and χ_B are the interaction parameters for the copolymer and parent homopolymers. χ_A and χ_B values, interpolated from the data on PMMA[10] and PAN[24], are given in *Table 6*. χ_{AB} values calculated from equation (8) are included in *Table 5*. It will be seen from the *Table* that these values are negative. These values do show a solvent effect, but are practically independent of temperature. The χ_{AB} value calculated for the data given by Shimura[7] for MMA–AN copolymer of 0.48 *mf* of AN is also negative. This trend is opposite to what has been observed for other copolymer systems, such as styrene/methyl methacrylate copolymer[10].

The large values of a, the Mark–Houwink exponent, and the expansion factor α_η^3 obtained through the use of the

Table 5 Long range interaction parameters for MA1

Solvent	Temperature (°C)	$B \times 10^{27}$	χ_1	χ_{AB}
MEK	30	0.061	0.499	–
MeCN	30	0.067	0.498	–
DMF	30	0.098	0.497	−0.32
	45	0.082	0.498	−0.32
	60	0.107	0.497	−0.32
γ-BL	30	0.143	0.496	−0.24
	45	0.137	0.496	−0.25
	60	0.129	0.497	−0.26
Copolymer–DMF*	30	0.850	0.476	−0.35

* Calculated from Shimura's data on MMA–AN copolymer[7]

Table 6 Interaction parameters for homopolymers

Solvent	Temperature (°C)	χ_A	χ_B
DMF	30	0.486	0.285
	45	0.484	0.293
	60	0.481	0.295
γ-BL	30	0.487	0.335
	45	0.484	0.337
	60	0.479	0.340

Table 7 Evaluation of α_η^3 values by Stockmayer–Fixman equations

		MeCN	MEK	DMF			γ-BL		
Fraction	$\bar{M}_w \times 10^{-5}$	30°C	30°C	30°C	45°C	60°C	30°C	45°C	60°C
MA 111	79.03	2.417	2.248	–	–	–	4.435	4.853	4.058
MA 112	63.23	2.295	2.142	3.409	2.504	4.517	–	–	–
MA 121	47.72	2.147	1.996	–	–	–	3.833	4.135	3.450
MA 122	42.95	2.068	–	2.998	2.279	3.982	3.652	3.907	3.275
MA 113	37.07	1.986	–	2.869	2.212	3.775	–	–	–
MA 14	31.61	1.865	1.758	2.691	2.092	3.589	–	–	–
MA 15	23.71	1.776	–	–	–	–	3.030	3.203	2.715
MA 16	21.68	1.785	1.681	–	–	–	–	–	–
MA 17	8.38	1.375	–	1.861	1.553	2.342	2.182	2.222	1.996

Stockmayer–Fixman equation (*Table 7*), suggest that there is a large extension of these molecules in these solvents due to unusually favourable polymer–solvent interaction. On the other hand, the very low values of the second virial coefficient A_2, and the large values of χ_1, together with the observed high values of a, suggest that the large extension of these molecules can be understood in terms of unusual short range interactions which affect the unperturbed dimensions. Cellulose derivatives also exhibit high values of a and very low values of A_2, which have been interpreted as the typical properties of stiff-chain polymers. From the large values of α_η^3 obtained by applying the Flory–Fox equation[14], Kurata and Stockmayer[23] concluded that these molecules are highly extended mainly due to the unusually favourable polymer–solvent interactions rather than unusual short range interactions. Recent theoretical studies[20,21] suggest that these chains assume large extensions mainly due to the short range interactions, indicating that the Stockmayer–Fixman equation may not hold for stiff-chain polymers.

The present experimental data (low A_2 values and large χ_1, α_η^3 and a values) suggest that the incorporation of AN in MMA (0.289 *mf* of AN) might have introduced some stiffness in the chain and hence the Stockmayer–Fixman equation may have to be modified for such systems.

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REFERENCES

1 Stockmayer, W. H., Moore, L. D. Jr, Fixman, M. and Epstein, B. N. *J. Polym. Sci.* 1955, **16**, 517
2 Reddy, C. R. and Kalpagam, V. *J. Polym. Sci. (Polym. Phys. Edn.)* 1976, **14**, 749, 759 and references therein
3 Kashyap, A. K., Reddy, C. R. and Kalpagam, V. J. *J. Indian Chem. Soc.* 1976, **53**, 106
4 Zimm, B. H. *J. Chem. Phys.* 1943, **16**, 1093
5 Beattie, W. H., Laudenslager, R. K. and Moacanin, J. *NASA Tech. Memo.* No.33-242, Jet Prop. Lab. California, 1966
6 Bushuk, W. and Benoit, H. *Can. J. Chem.* 1958, **36**, 1616
7 Shimura, Y. *Bull. Chem. Soc. Jpn* 1967, **40**, 273
8 Spatorico, A. L. *J. Appl. Polym. Sci.* 1974, **18**, 1793
9 Chinai, S. N., Matlack, J. D., Resnick, A. L. and Sanuels, R. J. *J. Polym. Sci.* 1955, **17**, 391
10 Reddy, C. R., Kashyap, A. K. and Kalpagam, V. *Polymer* 1977, **18**, 32 and references therein
11 Krigbaum, W. R. and Tokita, N. *J. Polym. Sci.* 1960, **43**, 467
12 Shibukawa, T., Sone, M., Uchida, A. and Iwahari, K. *J. Polym. Sci. (A-1)* 1968, **6**, 147
13 Fox, T. G. *Polymer* 1962, **3**, 111
14 Flory, P. J. and Fox, T. G. Jr, *J. Am. Chem. Soc.* 1951, **73**, 1904
15 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953, pp.622–626
16 Kawai, T. and Ueyama, T. *J. Appl. Polym. Sci.* 1960, **3**, 227
17 Cowie, J. M. G. *Polymer* 1966, **7**, 487
18 Stockmayer, W. and Fixman, M. *J. Polym. Sci. (C)* 1963, **1**, 137
19 Inagaki, H., Hayashi, K. and Matsuo, T. *Makromol Chem.* 1965, **84**, 80
20 Yathindra, N. and Rao, V. S. R. *Biopolymers* 1970, **9**, 783
21 Yathindra, N. and Rao, V. S. R. *J. Polym. Sci. (A-2)* 1970, **8**, 2033
22 Kurata, M. and Yamakawa, H. *J. Chem. Phys.* 1958, **29**, 311
23 Kurata, M. and Stockmayer, W. H. *Fortschr. Hochpolym. Forsch.* 1963, 3, 244
24 Beevers, R. B. *Macromol Rev.* Vol 3, pp.113–254