Temperature influence on the excess interaction parameter of styrene-methyl methacrylate copolymer

C. Rami Reddy*, A. K. Kashyap and V. Kalpagam

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

(Received 29 June 1976; revised 13 September 1976)

Intrinsic viscosity data for polystyrene, poly(methyl methacrylate) and styrene–methyl methacrylate copolymer of azeotropic composition have been used to evaluate the excess interaction parameters at different temperatures in γ-butyrolactone and dimethylformamide. It is found that these values are positive and show a negligible increase with increase in temperature, indicating therefore that the hetero-contact interactions are not influenced by temperature, contrary to the results obtained by Dondos and Benoit for the same copolymer system in *p*-xylene and iso-amyl acetate.

INTRODUCTION

Non-polar copolymers, in general, exhibit large expansion in solution as a result of repulsive interactions of unlike monomer units[1] in the copolymer chain. These repulsive interactions influence both the short range and long range parameters. Hence it is important to evaluate the excess interaction parameters which are responsible for the expansion of the chain, from intrinsic viscosity data. Styrene–methyl methacrylate copolymers (SM1) were used by a number of workers[1–7] to evaluate the excess interaction parameter in different solvents[1–5] and at different temperatures[5], but there is no data on γ-butyrolactone (γ-BL) at different temperatures. In this article, evaluation of excess interaction parameter χ_{AB} at different temperatures in γ-BL and in dimethylformamide (DMF), in addition to other results viz. Mark–Houwink relationship, effect of temperature on intrinsic viscosity ($[\eta]$), unperturbed dimensions etc., are reported.

EXPERIMENTAL

Styrene–methyl methacrylate copolymer, of azeotropic composition[1] (SM1) was prepared by free radical polymerization at 60°C. Estimation of polydispersity, fractionation, weight-average molecular weight etc. has been reported earlier[8]. Determinations of $[\eta]$ in γ-BL, and DMF were carried out in suspended level viscometers at 30°, 40°, 50° and 60°C and in ethyl acetate (EtAc) at 30°C. Parent homopolymers polystyrene (PS) and poly(methyl methacrylate) (PMMA) were prepared by free radical polymerization, fractionated and their weight-average molecular weights ($\bar{M}_w$) were determined. The $[\eta]$ for these polymers were determined in the above mentioned solvents, which were purified in accordance with the standard procedure[9]. The solvents were distilled just prior to use.

Tables 1–3 give the $[\eta]$ values at different temperatures for all the copolymer and homopolymers in these three solvents.

RESULTS AND DISCUSSION

Mark–Houwink relation

From the plots of log $[\eta]$ *versus* log $\bar{M}_w$(MH plot), Mark–Houwink relations were established for SM1, PS and PMMA in EtAc, DMF and γ-BL at different temperatures. Values of K' and a are given in *Table 4*.

From the values of a, it is evident that all the three solvents are good solvents, in general, the best being DMF

Table 1 $[\eta]$ values for SM1

Copolymer fraction	$\bar{M}_w \times 10^{-5}$	EtAc 30°C	DMF 30°C	DMF 40°C	DMF 50°C	DMF 60°C	γ-BL 30°C	γ-BL 40°C	γ-BL 50°C	γ-BL 60°C
SM12	11.130	1.680	–	–	–	–	–	–	–	–
SM13	8.800	1.510	1.740	1.796	1.780	1.719	1.466	1.530	1.570	1.550
SM15	6.119	–	1.360	1.413	1.400	1.350	1.119	1.208	1.235	1.215
SM16	5.400	1.097	1.238	1.273	1.255	1.200	1.025	1.053	1.091	1.076
SM17	4.662	0.974	1.095	1.131	1.140	1.110	0.950	0.970	–	–
SM18	4.225	0.903	1.012	1.047	1.027	0.985	0.830	0.860	0.918	0.887
SM19	3.721	0.789	0.887	0.917	0.914	0.898	0.763	0.790	0.804	0.797

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*Present Address: Central Leather Research Institute, Madras 600020, India.

Table 2 [η] values for PS

Polymer fraction	$\bar{M}_w \times 10^{-5}$	EtAc	DMF				γ-BL			
		30°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
PS1	6.236	0.856	1.025	1.025	0.997	0.974	0.767	0.760	0.745	0.730
PS2	5.066	0.748	0.878	0.872	0.853	0.820	0.692	0.674	0.680	0.656
PS3	4.120	0.654	0.778	0.760	0.760	0.705	0.602	0.592	0.600	0.584
PS4	3.515	0.592	0.678	0.658	0.663	0.647	0.524	0.540	0.525	–
PS6	2.366	0.540	0.527	0.520	0.507	0.483	0.430	0.423	0.415	0.400

Table 3 [η] values for PMMA

Polymer fraction	$\bar{M}_w \times 10^{-5}$	DMF			γ-BL			
		30°C	45°C	60°C	30°C	40°C	50°C	60°C
M11	29.040	–	–	–	2.898	–	–	–
M21	13.740	–	–	–	1.673	1.783	1.878	2.182
M31	3.122	0.634	0.659	0.756	0.576	0.629	0.646	0.730
M23	2.080	0.486	0.500	0.534	–	–	–	–
M33	1.941	0.465	0.477	0.486	–	–	–	–
M41	1.714	–	–	–	0.395	0.428	0.436	0.482
M51	1.291	–	–	–	0.320	0.340	0.350	0.405
M43	1.045	0.311	0.330	0.350	–	–	–	–
M53	0.820	0.265	0.289	0.296	–	–	–	–

Table 4 Mark–Houwink Parameters

Polymer	Solvent	$K' \times 10^4$				a			
		30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
SM1	EtAc	0.96	–	–	–	0.706	–	–	–
	DMF	1.01	0.88	0.84	0.76	0.712	0.725	0.728	0.733
	γ-BL	0.98	0.85	0.75	0.64	0.702	0.715	0.727	0.737
PS	EtAc	2.03	–	–	–	0.625	–	–	–
	DMF	1.05	0.94	0.71	0.59	0.688	0.697	0.716	0.728
	γ-BL	1.67	1.49	1.15	0.74	0.632	0.640	0.660	0.692
PMMA	EtAc†	1.07	–	–	–	0.680	–	–	–
	DMF	1.70	1.62*	–	1.58	0.650	0.657*	–	0.667
	γ-BL	1.07	1.08	1.06	1.11	0.680	0.686	0.690	0.696

* At 45°C; †calculated from ref 10

for SM1. Increase in temperature increases the values of a, indicating that the chains are in an expanded state at higher temperatures. It is also seen that the value of a for the copolymer is larger than that for the parent homopolymers at each temperature which indicates that these solvents are quite good for the copolymer. This is in accordance with the prediction that the copolymer attains more extended configuration in the solvents than the parent homopolymers[1].

Temperature variation of [η]

The behaviour of the linear deformation of the polymer chain, due to polymer–solvent interaction in good solvent media, is represented by the Flory–Fox equation[11]:

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

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

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

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

For flexible chain polymers in poor solvents, [η] increases with increase in temperature and in solvents, where $\theta \ll 0°C$, [η] decreases with increase in temperature[12]. It was pointed out by Kawai and Ueyama[13] that the chains are most expanded at the temperature at which [η] is maximum. The decrease of [η], after the maximum is explained by the decrease of $\langle r_0^2 \rangle$.

For SM1 fractions, in DMF and γ-BL, [η] increases with increase in temperature, attains a maximum and finally falls off. Maximum value of [η], is attained at ~40°C in DMF whereas in γ-BL, the maximum is at ~50°C. It is, therefore evident that the copolymer chains exhibit the maximum expansion in both the solvents at these temperatures. The [η] values of PS are observed to decrease with increase in temperature in DMF and in γ-BL, whereas in the case of PMMA the [η] values increase in both the solvents. Similar results were obtained for PS and PMMA in DMF[7]. *Figure 1* gives the plots of $[\eta]$ *versus* temperature.

Estimation of unperturbed dimensions

The dependence of $[\eta]$ on $\bar{M}_w$ in good solvent data, 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 $[\eta]$ in non-ideal solvents[14]. The simplest one is due to Stockmayer and Fixman (SF)[15]. The relation is given by:

$$[\eta]/\bar{M}_w^{1/2} = K_0 + 0.51B\phi_0\bar{M}_w^{1/2} \qquad (5)$$

where K_0 is the Flory constant related to unperturbed dimensions, and B is given by:

$$B = 2\bar{v}^2(\tfrac{1}{2} - \chi_1)/N_A V_1 \qquad (6)$$

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

K_0 values were evaluated by this method for SM1, PS and PMMA in DMF, γ-BL and EtAc at the respective temperatures and are given in *Table 5*.

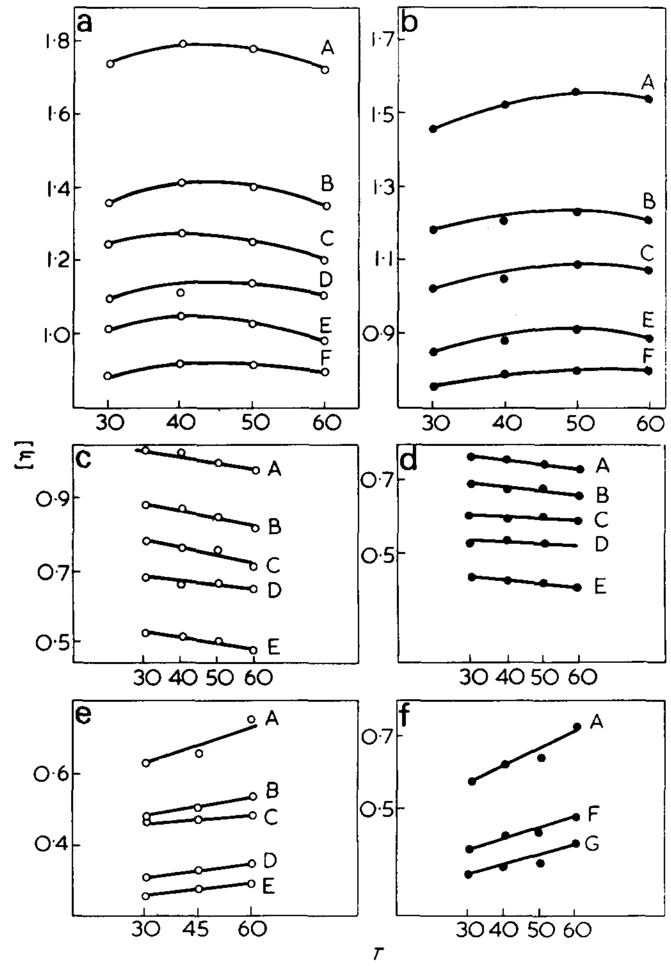

Figure 1 Temperature variation of $[\eta]$. (a) and (b) plots for SM1: A, SM13; B, SM15; C, SM16; D, SM17; E, SM18; F, SM19. (c) and (d) are plots for PS: A, PS1; B, PS2; C, PS3; D, PS4; E, PS6. (e) and (f) are plots for PMMA: A, M31; B, M23; C, M33; D, M43; E, M53; F, M41; G, M51. ○, DMF; ●, γ-BL

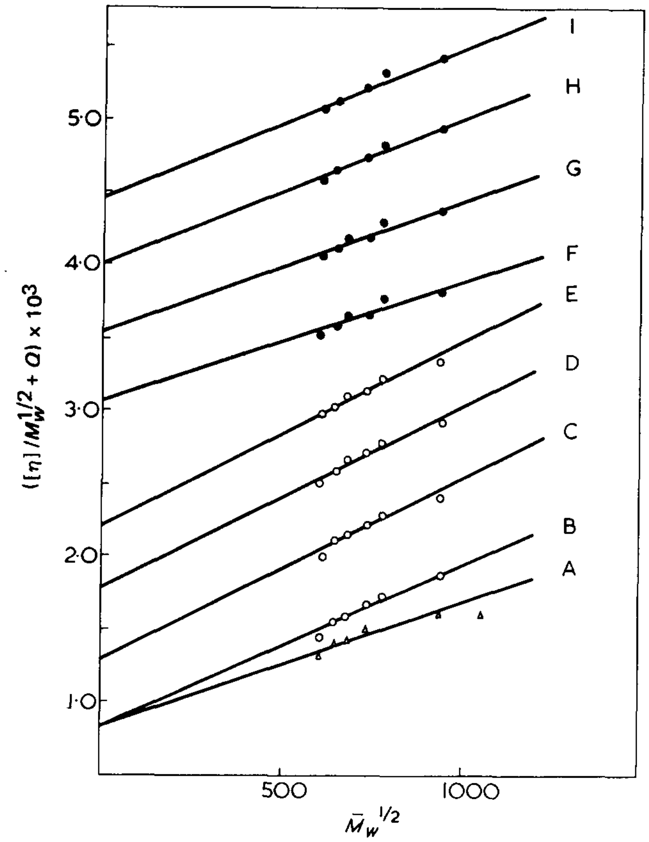

Figure 2 Stockmayer–Fixman plot for SM1. A, 30°C; Q = 0.0; B, 30°C, Q = 0.0; C, 40°C, Q = 0.5; D, 50°C, Q = 1.0; E, 60°C, Q = 1.5; F, 30°C, Q = 2.25; G, 40°C, Q = 2.75; H, 50°C, Q = 3.25; I, 60°C, Q = 3.75. Δ, EtAc; ○, DMF; ●, γ-BL

Table 5 Evaluation of K_0 and $[\langle r_0^2\rangle/\bar{M}_w]$ (for the copolymer only) by Stockmayer–Fixman equation

Polymer	Temperature (°C)	$K_0 \times 10^3$			$[\langle r_0^2\rangle/\bar{M}_w] \times 10^{17}$		
		EtAc	DMF	γ-BL	EtAc	DMF	γ-BL
SM1	30	0.84	0.85	0.82	4.60	4.67	4.54
	40	–	0.82	0.79	–	4.53	4.43
	50	–	0.78	0.76	–	4.40	4.30
	60	–	0.72	0.71	–	4.16	4.13
PS	30	0.74	0.75	0.73	–	–	–
	40	–	0.72	0.70	–	–	–
	50	–	0.70	0.69	–	–	–
	60	–	0.67	0.66	–	–	–
PMMA	30	0.78	0.78	0.72	–	–	–
	40	–	0.80*	0.75	–	–	–
	50	–	–	0.75	–	–	–
	60	–	0.80	0.75	–	–	–

* At 45°C

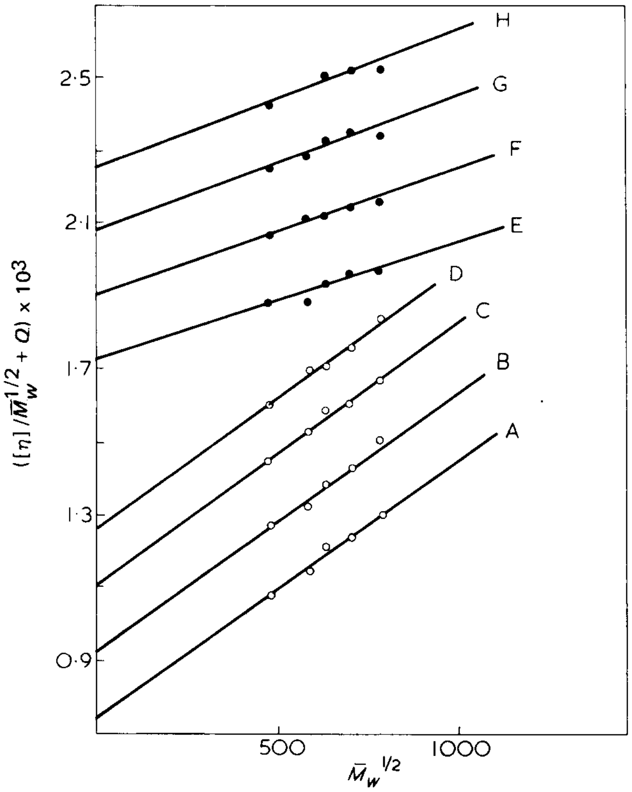

Figure 3 Stockmayer–Fixman plot for PS. A, 30°C, Q = 0.0; B, 40°C, Q = 0.2; C, 50°C, Q = 0.4; D, 60°C, Q = 0.6; E, 30°C, Q = 1.0; F, 40°C, Q = 1.2; G, 50°C, Q = 1.4; H, 60°C, Q = 1.6. ○, DMF; ●, γ-BL

The values of K_0 in all the three solvents are in good agreement with each other indicating that the effect of solvent on K_0 is negligible. The values of K_0 for SM1 decrease with increase in temperature and reduce from 0.85 x 10^{-3} (30°C in DMF) to 0.72 x 10^{-3} (60°C in DMF) approaching the ideal value of 0.65 x 10^{-3} calculated by Dondos and Benoit[5]. Therefore, this decrease may be attributed to the decrease in the hetero-contact interaction[5].

The values of K_0 for PS also decrease with increase in temperature indicating that a reduction in the unperturbed chain dimension is taking place with increase in temperature. The values of K_0 for PMMA, are noticed to increase slightly with increase in temperature. However, this increase is negligible and it can therefore be treated as constant in the light of the errors involved in the measurement of $[\eta]$ and molecular weight[7].

Unperturbed dimensions

The average mean square unperturbed end-to-end distances were calculated from the K_0 values for the copolymer at all the temperatures in the solvents studied. *Table 5* includes the respective $\langle r_0^2\rangle/\bar{M}_w$ values.

The idealized values of $\langle r_0^2\rangle/\bar{M}_w$ for the copolymer is calculated from the relation:

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

where W_A and W_B are the weight fractions of the respective homopolymers. For SM1, the idealized value at 30°C is 3.91 x 10^{-17} cm^2 [16]. The experimental values are much higher for the copolymer in the respective solvents and the observed values are noticed to decrease with an increase in temperature. This decrease may be a result of (a) the reduction in chain dimensions, or (b) reduction in unlike monomer unit interactions.

The changes in unperturbed dimensions of the homopolymers is different in the two cases. For PS unperturbed dimensions decrease with increase in temperature, while for PMMA it may be taken as independent of temperature. Hence, the changes in the unperturbed dimension of the copolymer may be due to the change in the skeletal dimensions alone.

Long range interactions

Long range interaction parameter B was evaluated from the plots of the SF equation (equation 5). *Table 6* gives the values of B.

The long range interaction parameter B, increases with increase in temperatures in DMF and in γ-BL, for SM1 copolymer. In other words, the solute–solvent interaction is increased with the increase in temperature in both the solvents. The parent homopolymers, PS and PMMA, show different types of interactions with the solvents. The values of B for PS remain unchanged with temperature in both the solvents indicating that the chain expansion of PS is unaltered with increase in temperature. The B values of PMMA, on the other hand, are increased with increase in temperature indicating that the chain expansion is influenced by temperature to the same extent in both the solvents. The energy parameter χ_1, which represents the solute–solvent interactions, is calculated for SM1, PS and PMMA at different temperatures (*Table 6*). The decreasing tendency of these values for SM1 copolymer system indicates the increase in solute–solvent affinity. From these results, it can be concluded that the incorporation of MMA

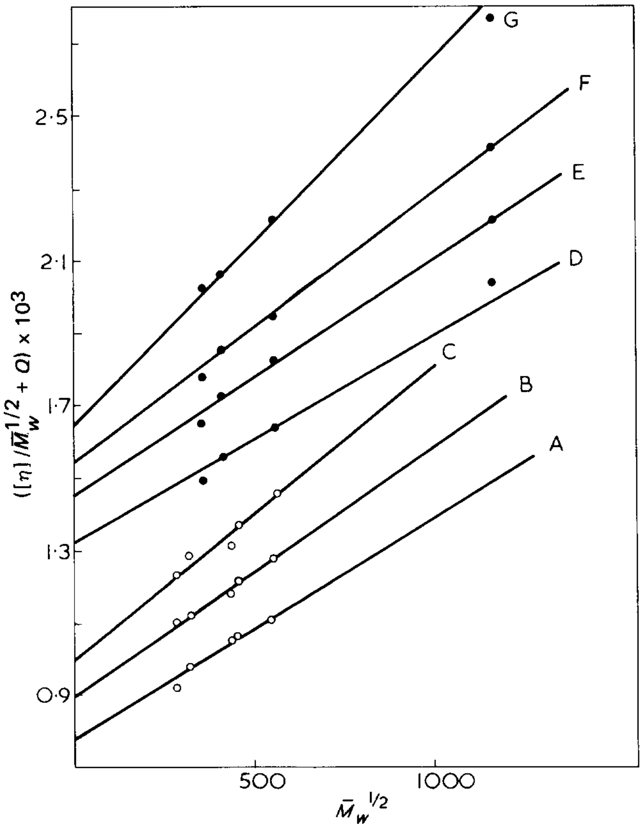

Figure 4 Stockmayer–Fixman plot for PMMA, A, 30°C, Q = 0.0; B, 45°C, Q = 0.1; C, 60°C, Q = 0.2; D, 30°C, Q = 0.6; E, 40°C, Q = 0.7; F, 50°C, Q = 0.8; G, 60°C, Q = 0.9. ○, DMF; ●, γ-BL

Table 6 Evaluation of parameters B and χ_1

Polymer	Temperature (°C)	$B \times 10^{27}$			χ_1		
		EtAc	DMF	γ-BL	EtAc	DMF	γ-BL
SM1	30	0.61	0.80	0.58	0.477	0.476	0.483
	40	–	0.88	0.67	–	0.474	0.480
	50	–	0.89	0.71	–	0.473	0.479
	60	–	0.93	0.74	–	0.472	0.478
PS	30	0.32	0.51	0.24	0.488	0.486	0.494
	40	–	0.51	0.26	–	0.486	0.493
	50	–	0.51	0.27	–	0.486	0.493
	60	–	0.51	0.28	–	0.486	0.493
PMMA	30	0.31	0.35	0.41	0.487	0.486	0.487
	40	–	0.49	0.48	–	0.484	0.485
	50	–	0.53	0.53	–	0.483	0.483
	60	–	0.58	0.66	–	0.481	0.479

Table 7 Values of χ_{AB} for SM1

Temperature (°C)	EtAc	DMF	γ-BL
30	0.045	0.042	0.031
40	–	0.047	0.037
50	–	0.045	0.038
60	–	0.047	0.033

units, actually brings about a greater affinity towards the solvents like DMF and γ-BL. This observation is not in harmony with the conclusions drawn by Shimura[7] who pointed out that the long and short range interactions are unaffected by the random introduction of MMA units, in the PS chain.

Extra interaction parameter, χ_{AB}

In order to understand the influence of temperature on repulsive interactions of unlike monomer units, the extra-interaction parameter χ_{AB} was evaluated from the values of χ_1 of copolymer and of homopolymers from the following expression[1]:

$$\chi_1 = x_A\chi_A + x_B\chi_B - x_Ax_B\chi_{AB} \qquad (7)$$

where x_A and x_B are the mole fractions of A and B in the copolymer and χ_A and χ_B are the interaction parameters for the homopolymers A and B, respectively in the same solvent. It is seen that χ_1 is smaller and the solvent therefore 'better' when χ_{AB} is positive, as for repulsive A–B interaction[1]. χ_{AB} decreases with increase in temperature in a given solvent for a copolymer when the hetero-contact interactions diminish[5]. *Table 7* gives the χ_{AB} values.

χ_{AB} values are positive and a tendency to increase is noticed, but the increase is negligible. Hence it can be concluded that the hetero-contact interactions of SM1 copolymer in DMF and in γ-BL, are not influenced by temperature up to 60°C, whereas for the same system in *p*-xylene and iso-amyl acetate, the decrease of χ_{AB} value has been reported with increase in temperature[5].

In *Table 8*, the values of χ_{AB}, determined by other workers, for SM1 copolymer are given along with the values obtained in the present work.

Except in dioxane, the χ_{AB} values in other solvents are equal to or lower than 0.05. The values of χ_{AB} in DMF, γ-BL and EtAc are in good agreement with the values of previous workers.

Table 8 Values of χ_{AB} in different solvents

Sample no.	Solvent	χ_{AB}	Reference
1	Butanone	0.050	1
	Dioxane	0.080	
2	Butanone	0.023	3
	Benzene	0.024	
	Dichloroethane	0.045	
	Ethyl acetate	0.026	
	Heptanone-4	0.034	
3	Benzene	0.031	5
	Tetrahydrofuran	0.046	
	p-xylene	0.053	
4	Dimethylformamide	0.042	Present work*
	γ-Butyrolactone	0.031	
	Ethyl acetate	0.045	

* At 30°C

ACKNOWLEDGEMENTS

The authors thank Council of Scientific and Industrial Research, New Delhi and Indian Institute of Science, Bangalore for the financial assistance during the course of this investigation.

REFERENCES

1 Stockmayer, W. H., Moore Jr, L. D., Fixman, M. and Epstein, B. N. *J. Polym. Sci.* 1955, **16**, 517

2 Bushuk, W. and Benoit, H. *Can. J. Chem.* 1958, **36**, 1616

3 Froelich, D. *J. Chim. Phys.* 1967, **64**, 1307

4 Dondos, A., Rempp, P. and Benoit, H. *Eur. Polym. J.* 1967, 3, 657

5 Dondos, A. and Benoit, H. *Makromol. Chem.* 1968, **118**, 165

6 Kotaka, T., Murakami, Y. and Inagaki, H. *J. Phys. Chem.* 1968, **72**, 829

7 Yuko Shimura-Kambe, *J. Phys. Chem.* 1968, **72**, 4104

8 Reddy, C. R. and Kalpagam, V. *J. Polym. Sci. (A-2)* 1976, **14**, 749

9 Weissberger, A. and Phoskauer, E. S. 'Organic Solvents, Physical properties and Methods of purification', Interscience New York, 1970

10 Rao, V. S. R. *J. Sci. Ind. Res. (B)* 1962, **21**, 422

11 Flory, P. J. and Fox Jr, T. G. *J. Am. Chem. Soc.* 1951, **73**, 1904

12 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953, pp 622–626

13 Kawai, T. and Ueyama, T. *J. Appl. Polym. Sci.* 1960, 3, 227

14 Cowie, J. M. G. *Polymer* 1966, 7, 487

15 Stockmayer, W. and Fixman, M. *J. Polym. Sci. (C.)* 1963, 1, 137

16 Reddy, C. R. and Kalpagam, V. *J. Polym. Sci. (A-2)* 1976, **14**, 759