Solvent effect on the equilibrium polymerization of α-methylstyrene

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The Flory-Huggins interaction parameter χ has been determined from static vapour-pressure measurements for four binary mixtures: α-methylstyrene in *p*-dioxane or cyclohexane, and poly(α-methylstyrene) in *p*-dioxane or cyclohexane. For the first system, measurements were carried out at 25 and 40°C, yielding values between 0.12 and 0.18 for χ. The second one was investigated at 30, 35 and 40°C leading to χ values between 0.50 and 0.58. The values at 40°C for the third system lie between 0.40 and 0.46 when the polymer volume fraction varies from 0.10 to 0.35. The last system, also at 40°C, has χ values of 0.49 and 0.60 for polymer volume fraction of 0.10 and 0.27, respectively. These parameters were used to compute the equilibrium compositions of monomer and polymer, at any solvent concentration, for the polymerization of α-methylstyrene in different solvents.

(Keywords: α-methylstyrene; cyclohexane; equilibrium polymerization; free energy change; interaction parameter; *p*-dioxane; poly(α-methylstyrene); solvent effect; vapour pressure)

INTRODUCTION

The free energy change upon the conversion of 1 mole of pure liquid monomer to 1 base mole of pure amorphous polymer ΔG_{lc}, can be obtained from the experimental values of monomer and polymer concentrations measured under equilibrium conditions for a polymerization in solvent through the equation[1,2]:

$$\frac{\Delta G_{lc}}{RT} = \ln \phi_m + 1 + [\chi_{ms} - \chi_{sp}(\bar{V}_m/\bar{V}_s)]\phi_s + \chi_{mp}(\phi_p - \phi_m) \tag{1}$$

In this equation R is the gas constant, T is the absolute temperature, $\bar{V}$ is the molar volume, ϕ is the volume fraction, χ is the Flory–Huggins parameter and the subscripts m, s and p refer to monomer, solvent and polymer respectively. The equation is valid when the number of segments in a polymer chain is large, and it has been shown[3] that the use of the Flory–Huggins binary interaction parameter[4] χ is adequate in order to obtain the right value of ΔG_{lc}.

The solvent effect on the equilibrium polymerization is summed up in the term

$$\beta = \chi_{ms} - \chi_{sp}(\bar{V}_m/\bar{V}_s) \tag{2}$$

χ_{ms} is the most important parameter, owing to large variations in its value from one solvent to another, while the corresponding change in the χ_{sp} parameter is usually less pronounced.

Equation (1) may now be rearranged in such a manner that the relationship between ϕ_m and ϕ_s is explicit. With

$$\phi_m + \phi_s + \phi_p = 1.0 \tag{3}$$

upon rearrangement, equation (1) becomes

$$\ln \phi_m - 2\phi_m\chi_{mp} = \left(\frac{\Delta G_{lc}}{RT} - \chi_{mp} - 1\right) + (\chi_{mp} - \beta)\phi_s \tag{4}$$

Given that $\Delta G_{lc}/RT$ and the interaction parameters are known at any temperature, equation (4) may then be solved to yield the equilibrium monomer and polymer compositions, ϕ_m and ϕ_p, for any value of ϕ_s. This way, equation (4) allows us to evaluate whether or not a high conversion of monomer into polymer can be achieved with the selected solvent. This condition is fulfilled when the ϕ_m value is as small as possible and hence the right-hand side of equation (4) should be as negative as possible. This requirement may be satisfied if ΔG_{lc} is large and negative. In this case ϕ_m is small and the solvent has little effect on the equilibrium position. However, if ΔG_{lc} approaches zero, the last term of equation (4) becomes very important and the value of ϕ_m is likely to change by a great deal with a change of solvent, which would be expressed through the variation of β (equation (2)) with the solvent.

In order to study the solvent effect on an equilibrium polymerization, three solvents have been selected for the polymerization of α-methylstyrene (αMS): tetrahydrofuran (THF), *p*-dioxane (DOX) and cyclohexane (CH). The χ_{ms} and χ_{sp} values for the first solvent have been reported elsewhere[3]; the determination of the χ parameters for DOX and CH from static vapour-pressure measurements is described in the present work and the equilibrium compositions ϕ_m and ϕ_p, have been calculated at 25 and 40°C through equation (4) using the available values for $\Delta G_{lc}/RT$.

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EXPERIMENTAL

Materials

α-Methylstyrene, *p*-dioxane and cyclohexane were the best grade reagents. They were first distilled over CaH_2 and degassed over a period of several days on a vacuum manifold. They were then distilled under vacuum, the head and the tail fractions being discarded. The middle fractions of DOX and CH were distilled onto a first sodium mirror and kept over a second one. The poly(α-methylstyrene) (PαMS) samples had been previously prepared by anionic polymerization of αMS in THF[3]. They had been characterized by gel permeation chromatography (size exclusion chromatography) yielding weight-average molecular weights of 26 500 and 45 000 with a polymolecularity index smaller than 1.10.

Apparatus and measurements

The apparatus used for measurements of static vapour pressure of liquid mixtures and polymer mixtures has been described elsewhere[3]. Differential pressures of up to 300 ± 0.001 mmHg (40.0 kPa) could be obtained with this apparatus.

All manipulations were performed according to high-vacuum techniques. Purified αMS and DOX (or CH) were distilled successively into the vapour-pressure cell to form the binary liquid mixture. The amount of each component was determined by weighing its ampoule before and after distillation. The stirring of the mixture was achieved with a magnetic bar coupled to an external rotor driven by compressed air. For measurements carried out on polymer solutions, ~2.0 g of previously dessicated PαMS was inserted into the cell and degassed slowly through the 'bellows' stopcock. A desired amount of DOX (or CH) was then distilled into the cell to form the polymer mixture. It was observed that PαMS samples were completely dissolved in DOX as well as in CH at 40°C within the working concentration range, and the resulting solutions could be easily stirred.

RESULTS AND DISCUSSION

The liquid mixtures

Static vapour pressures P of αMS–DOX mixtures for various mole fractions x_m are listed in *Table 1* for 25 and 40°C, while those of αMS–CH mixtures are presented in *Table 2* for 30, 35 and 40°C. The values of x_m have been corrected[3] for the loss of material occurring through evaporation taking place in the cell. *Tables 1* and *2* and *Figure 1* show the 'excess vapour pressure' P^E for both systems for various compositions and temperatures. P^E is defined here as

$$P^E = P - P_m^\circ x_m - P_s^\circ x_s \tag{5}$$

where subscripts m and s refer to αMS and DOX (or CH), respectively. P^E, with its positive values for both systems, reflects the extent of positive deviation from Raoult's law.

Table 1 Vapour pressure P and 'excess vapour pressure' P^E of α-methylstyrene–*p*-dioxane mixtures at various mole fractions x_m (m = αMS, s = DOX)

	25°C		40°C	
x_m	P(kPa)	P^E(kPa)	P(kPa)	P^E(kPa)
0	4.773	–	9.979	–
0.211	3.866	0.032	–	–
0.293	3.520	0.051	7.426	9.148
0.389	3.311	0.068	6.594	0.197
0.468	2.766	0.081	5.153	0.253
0.553	2.413	0.093	4.280	0.247
0.689	1.800	0.089	3.886	0.239
0.772	1.420	0.080	3.096	0.209
0.856	1.036	0.061	2.230	0.117
1.000	0.331	–	0.793	–

Table 2 Vapour pressure P and 'excess vapour pressure' P^E of α-methylstyrene–cyclohexane mixtures at various mole fractions x_m (m = αMS, s = CH)

T (°C)	x_m	P(kPa)	P^E(kPa)	x_m	P(kPa)	P^E(kPa)
30	0	16.203	–	0.6206	7.815	1.387
	0.1963	13.506	0.393	0.6918	6.717	1.407
	0.2908	12.322	0.700	0.7071	6.461	1.393
	0.3688	11.311	0.916	0.7167	6.279	1.363
	0.4578	10.146	1.152	0.7838	5.096	1.236
	0.4706	10.026	1.233	0.8326	4.157	1.067
	0.5357	9.109	1.340	0.8846	3.100	0.827
	0.5817	8.419	1.379	1.000	0.456	–
35	0	20.061	–	0.6214	9.593	1.619
	0.1970	16.692	0.464	0.6924	8.223	1.631
	0.2913	15.198	0.800	0.7075	7.930	1.631
	0.3694	13.929	1.053	0.7171	9.561	1.600
	0.4585	12.484	1.340	0.7845	6.246	1.444
	0.4710	12.332	1.433	0.8333	5.090	1.240
	0.5364	11.192	1.567	0.8852	3.784	0.940
	0.5823	10.342	1.606	1.0	0.611	–
40	0	24.547	–	0.6226	11.646	1.893
	0.1979	20.405	0.561	0.6931	9.990	1.907
	0.2919	18.525	0.920	0.7080	9.629	1.899
	0.3702	16.980	1.232	0.7176	9.389	1.887
	0.4593	15.198	1.560	0.7853	7.593	1.700
	0.4714	15.025	1.676	0.8341	6.166	1.433
	0.5372	13.599	1.813	0.8860	4.580	1.080
	0.5831	12.552	1.856	1.000	0.793	–

Experimental values of P were used for the computation of the 'excess free energy of mixing', ΔG^E, according to an iterative method[3] which makes use of Wilson's equation[5] as the pivot of the iteration process. Hence the χ_{ms} parameter was readily calculated using[4]

$$\chi_{ms} = \frac{\Delta G^E}{RTx_m\phi_s} \tag{6}$$

where x_m is the mole fraction of αMS and ϕ_s is the volume fraction of DOX (or CH) in the binary liquid mixture. The calculated χ_{ms} parameters for both systems are plotted against ϕ_s for various temperatures in *Figure 2*.

In contrast with the results obtained previously for the αMS–THF mixture[3], the χ_{ms} positive values indicate that αMS–CH and αMS–DOX interactions are relatively weak. In the case of αMS–CH mixture, the value of χ_H, the enthalpy contribution[2,6], is about 1.20 at 26.9°C and it suggests that the contact energy is small; consequently the mixing process between αMS and CH molecules should be mainly assumed by the entropy contribution. Regarding the DOX solvent, the mixing process involves the break-up of electrostatic interactions[7] (mainly quadrupoles) between DOX molecules and the formation of interactions between αMS and DOX molecules due to dispersion forces.

A further point of interest observed here is the virtual constancy of the χ_{ms} parameter over the whole range of concentration. The same behaviour has also been observed in the αMS–THF mixture[3] for temperatures

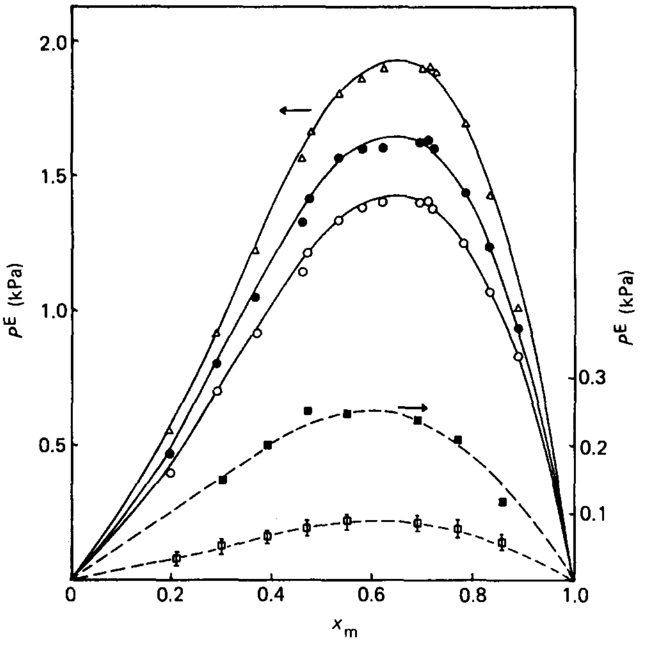

Figure 1 Excess vapour pressure P^E plotted against the mole fraction x_m: full curves for α-methylstyrene–cyclohexane mixtures at 30°C (○), 35°C (●) and 40°C (△); broken curves for α-methylstyrene–*p*-dioxane mixtures at 25°C (□) and 40°C (■) (m = αMS, s = CH or DOX)

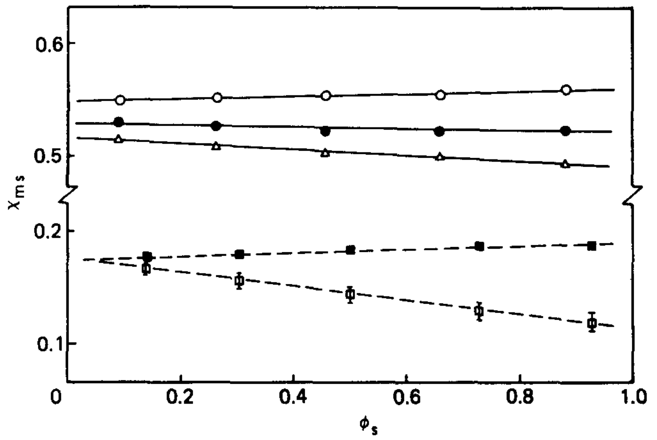

Figure 2 Variation of χ_{ms} with the volume fraction ϕ_s: full curves for α-methylstyrene–cyclohexane mixtures at 30°C (○), 35°C (●) and 40°C (△); broken curves for α-methylstyrene–*p*-dioxane mixtures at 25°C (□) and 40°C (■) (m = αMS, s = CH or DOX)

higher than 25°C. This constancy of χ_{ms}, which makes the use of equation (1) through the β term more convenient, may result from the fact that the intermolecular interactions in those systems are probably predominant in dispersion forces over the sufficiently high-temperature range (far from the component's freezing points) where the effect of polar attractions as well as that of molecular size difference become less important than that of molecular thermal agitation. For such mixtures, the extents of deviation from Raoult's law are rather moderate and only slight asymmetry in the P^E curves across the central axis $x_m = 0.5$ (*Figures 1* and *2*) is observed. It is interesting to note that, while the use of Wilson's equation requires at least two adjustable parameters in the iterative method for computing ΔG^E from P data[3], the final results of ΔG^E may be adequately represented by a unique χ_{ms} parameter over the whole concentration (expressed in volume fraction) range for temperatures above 25°C for all three systems under investigation. In other words, it seems that the Flory–Huggins polymer theory can be successfully applied to binary liquid mixtures using a concentration-independent interaction parameter under the conditions where intermolecular interactions are assumed to be of the van der Waals type.

The polymer mixtures

The χ_{sp} parameter for the DOX–PαMS and CH–PαMS solutions were directly obtained from their vapour-pressure data P using[4]

$$\ln a = \ln(1-\phi_p) + \phi_p + \chi_{sp}\phi_p^2 \qquad (7)$$

where ϕ_p is the polymer volume fraction in the binary mixture and a is the activity of either DOX or CH. The activity has been calculated from P/P° after correction for the non-ideal behaviour of the vapour phase[3].

Experimental data for P and calculated values for χ_{sp} for the DOX–PαMS mixture at 40°C are presented in *Table 3* and *Figure 3*. The parameter χ_{sp} varies slightly with concentration and its values are similar to the results obtained for the THF–PαMS mixture[3] at 35°C. Regarding the CH–PαMS system, measurements were carried out at 40°C yielding the values of $\chi_{sp} = 0.49$ and 0.60 for $\phi_p = 0.10$ and 0.27, respectively. This result seems to be in good agreement with the value of 0.533 calculated from critical miscibility measurements[8] for CH–polystyrene at 25°C. It is found from the above results that PαMS is less compatible with CH than with THF or DOX; this is in accordance with the fact that the theta temperature for the PαMS–CH system is 37°C[9].

Concerning the χ_{mp} parameter, owing to the very weak volatility of αMS, the measurements of vapour pressure for the αMS–PαMS mixture in the temperature range allowed by our apparatus (< 50°C) could not provide a satisfactory value for that parameter. Fortunately, we can

Table 3 The χ_{sp} parameter for *p*-dioxane–poly(α-methylstyrene) mixtures at 40°C (s = DOX, p = PαMS)

Sample ($\bar{M}$)	ϕ_p	P(kPa)	χ_{sp}
26500	0.328	9.793	0.455
	0.186	9.950	0.420
	0.120	9.982	0.395
45000	0.239	9.922	0.440
	0.165	9.973	0.435
	0.096	9.995	0.405

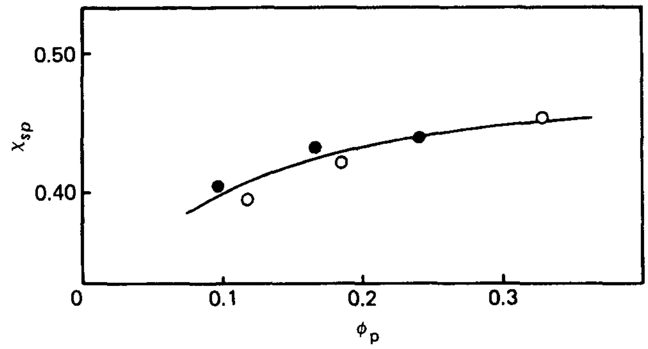

Figure 3 Variation of χ_{sp} with the volume fraction ϕ_p for *p*-dioxane–poly(α-methylstyrene) mixtures at 40°C: ●, $\bar{M}_w = 45000$; ○, $\bar{M}_w = 26500$ (s = DOX, p = PαMS)

benefit from the available activity data[10] corresponding to 65.04°C for that system. Those data were presented as a function of the mass fraction of a PαMS sample of $\overline{MW}=17400$. The correction for the non-ideality of the vapour phase has been taken into account in those data in the same manner as that reported[3].

From the mass fraction of PαMS, W_p, the volume fraction ϕ_p can be deduced from

$$\phi_p=\frac{W_p\bar{V}_p}{W_p\bar{V}_p+(1-W_p)\bar{V}_m} \tag{8}$$

where $\bar{V}_m$ is the molar volume of αMS and $\bar{V}_p$ is the base molar volume of PαMS whose values are available[1,10]. The activity a together with the ϕ_p values were substituted into equation (7) to yield values of the χ_{mp} parameters. The results are summarized in *Table 4* and *Figure 4*. It is found that χ_{mp} increases with increasing polymer concentration for ϕ_p ranging from 0.2 to 0.6, as observed in the THF–PαMS and DOX–PαMS mixtures. This behaviour seems to be common to systems where the solvent is a relatively good solvent for the polymer. It has also been noted[10] that the activity data for the αMS-PαMS system at 54.95°C were very close to those corresponding to 65.04°C. This means that the temperature dependence of the χ_{mp} parameter may be considered as being very slight. Since the χ parameter usually increases with decreasing temperature, from the above observations, a value of 0.40 for the χ_{mp} parameter appears to be reasonable when it is applied to the equilibrium polymerization system of αMS within the 25 to 40°C temperature range for ϕ_p smaller than 0.3

THE SOLVENT EFFECT

Equation (4) can be used for predicting the effect of the solvent, through the β parameter, on the equilibrium composition in monomer and polymer (ϕ_m and ϕ_p). This can be done if $\Delta G_{lc}/RT$ is known, the interaction parameters already being determined.

Table 4 The χ_{mp} parameter for the α-methylstyrene–poly(α-methylstyrene) mixture at 65.04°C (m = αMS, p = PαMS)

a	W_p	ϕ_p	χ_{mp}
0.983	0.2975	0.256	0.34
0.975	0.3459	0.300	0.35
0.977	0.3528	0.307	0.39
0.963	0.4233	0.374	0.41
0.897	0.6018	0.551	0.46
0.874	0.6168	0.567	0.42
0.673	0.7718	0.733	0.36

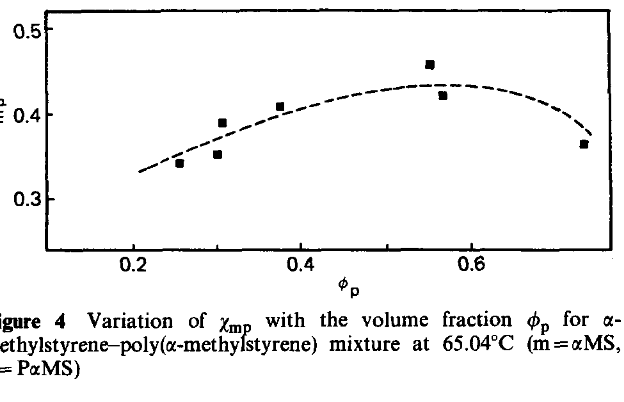

Figure 4 Variation of χ_{mp} with the volume fraction ϕ_p for α-methylstyrene–poly(α-methylstyrene) mixture at 65.04°C (m = αMS, p = PαMS)

Table 5 Correlation of $\Delta G_{lc}/RT$ by the least-squares method for different values of χ_{mp}

χ_{mp}	A	B	ΔH_{lc} (kJ mol^{-1})	ΔS_{lc} (J mol^{-1} K^{-1})
0.20	16.84	−5273	−43.84	−140.0
0.25	16.78	−5242	−43.58	−139.5
0.30	16.79	−5231	−43.49	−139.6
0.40	16.61	−5154	−42.85	−138.1

Table 6 The equilibrium compositions for the polymerization of α-methylstyrene in three solvents, with $\chi_{mp}=0.40$ and $\phi_s=0.50$

T (K)	$\Delta G_{lc}/RT$	Solvent	β	ϕ_m	ϕ_p	[M] (mol l^{-1})	[P] (base mol l^{-1})
298	−0.685	THF	−0.965	0.325	0.175	2.480	1.630
		DOX	−0.515	0.237	0.263	1.815	2.442
		CH	−0.050	0.178	0.322	1.358	3.00
313	+0.144	THF	−0.935	0.50	0	3.846	0
		DOX	−0.480	0.50	0	3.846	0
		CH	−0.085	0.50	0	3.846	0

Determination of ΔG_{lc}/RT

$\Delta G_{lc}/RT$ is independent of the solvent used for polymerization. However, it has been shown[2] how data obtained from equilibrium polymerization in solution can be used in order to obtain $\Delta G_{lc}/RT$. Using the equilibrium data for the polymerization of αMS in THF[1] and in DOX[11] for the −20 to 40°C temperature range, $\Delta G_{lc}/RT$ is found to vary in a linear fashion with $1/T$ according to

$$\Delta G_{lc}/RT=A+B/T \tag{9}$$

A can be identified as $\Delta S_{lc}/R$ and B as $\Delta H_{lc}/R$, with ΔS_{lc} and ΔH_{lc} being the polymerization entropy change and enthalpy change, respectively. In order to obtain $\Delta G_{lc}/RT$, values of χ_{mp} need to be assumed but it has little effect on the final results as can be seen from *Table 5*. This table shows the values of A, B, ΔS_{lc} and ΔH_{lc} obtained by the least-squares method for various values of χ_{mp}. According to these results, $\Delta G_{lc}/RT$ increases sharply with temperature and becomes positive slightly above room temperature, so that the conversion of αMS into high polymer would be limited in the high-temperature range. It is in that temperature range that the solvent effect becomes the determining factor for the equilibrium position of the polymerization system.

Illustration of effect

In order to illustrate the solvent effect through equation (4), we selected 25°C as the polymerization temperature of αMS, where $\Delta G_{lc}/RT$ is deduced from the above results as −0.685 (with $\chi_{mp}=0.40$). For an arbitrary value of solvent concentration, $\phi_s=0.50$, equation (4) can now be used to yield ϕ_m and ϕ_p values for the 3 solvents under consideration and the results are given in *Table 6*. The β terms are computed from the χ_{ms} and χ_{sp} values extrapolated from this work for DOX and CH, and from ref. 3 for THF, together with the available[12] experimental data of $\bar{V}_m/\bar{V}_s$. The equilibrium compositions expressed in terms of $[M]_e$ (mol l^{-1}) and [P] (base mol l^{-1}) may then be obtained by dividing ϕ_m by $\bar{V}_m$ and ϕ_p by $\bar{V}_p/n$ (ref. 1). At 40°C where

$\Delta G_{lc}/RT = 0.144$ (with $\chi_{mp} = 0.40$), equation (4) cannot be solved for a value of $\phi_s = 0.50$. This result indicates that under such conditions formation of high polymer would not take place in any of the three solvents.

Another manner of comparing the solvent effects is based on the linear relationship between ϕ_m and ϕ_p:

$$\phi_m = a + b\phi_p \tag{10}$$

where a and b are related[2] to $\Delta G_{lc}/RT$, β and χ_{mp} by

$$a = \frac{-(\Delta G_{lc}/RT) + \ln a + \beta}{\beta + \chi_{mp} - 1/a} \tag{11}$$

and

$$b = (\chi_{mp} - \beta)/(\beta + \chi_{mp} - 1/a) \tag{12}$$

Using the above values of $\Delta G_{lc}/RT$ and β and with different values of χ_{mp}, a and b were computed for the three solvents. Those results are presented in *Table 7*. It is also noted that when $\phi_p = 0$, $\phi_m = a$, and therefore the quantity $(1 - a)$ can be investigated as the superior limit of solvent concentration, ϕ_s°, beyond which the conversion of monomer into high polymer could no longer take place. This phenomenon may be caused by a very high interference of solvent molecules towards the whole polymerization system. Values of ϕ_s° are also found in *Table 7* together with a and b values.

Upon examination of the above results (*Table 6* and *7*) it is clear that CH is the best solvent to yield the highest extent of conversion of αMS into long-chain PαMS. This is in good agreement with the experimental polymerization equilibrium data[1,11,13]. On the molecular basis, this observation can be interpreted as follows: strong interactions between monomer and solvent molecules (which is the case for αMS–THF) should hinder the reactions between the monomer molecules and the living polymer chains, even though this trend may be outweighed by strong interactions between solvent molecules and living polymer chains (equation (2)). However, the χ_{sp} parameter usually does not vary too much from one solvent to another towards a given polymer, while the χ_{ms} parameter does well for a given monomer. Regarding the effect of the χ_{mp} parameter on the equilibrium position, it seems that the higher its values, or the lower the monomer–polymer interactions, the more pronounced will be the effect from the solvent.

Table 7 Values of a, b and ϕ_s° for the polymerization of α-methylstyrene in different solvents

T (K)	χ_{mp}	$\Delta G_{lc}/RT$	Solvent	a	b	ϕ_s°
273	0.25	−2.421	THF	0.079	−0.089	0.921
			DOX	0.052	−0.038	0.948
			CH	0.036	−0.012	0.964
	0.30	−2.371	THF	0.083	−0.097	0.917
			DOX	0.055	−0.042	0.945
			CH	0.038	−0.015	0.962
	0.40	−2.296	THF	0.093	−0.118	0.907
			DOX	0.061	−0.053	0.939
			CH	0.042	−0.021	0.958
298	0.25	−0.811	THF	0.332	−0.321	0.668
			DOX	0.251	−0.173	0.749
			CH	0.185	−0.064	0.815
	0.30	−0.764	THF	0.350	−0.354	0.650
			DOX	0.264	−0.197	0.736
			CH	0.196	−0.079	0.804

It is worth mentioning that in equations (2) and (4), only three binary interaction parameters have been used to describe the thermodynamic behaviour of the polymerization system while the probable ternary interactions have been neglected. It has been found[12] that such a ternary contribution, represented by the term $\phi_p\chi_{msp}$, is negligible in the case of the αMS–THF–PαMS system and the same result can be expected for the αMS–DOX–PαMS system. However, in the case of the αMS–CH–PαMS system, the ternary interactions may become considerable due to the relatively weak interactions between CH with αMS and also with PαMS. This suggestion may be justified by considering the benzene–CH–polystyrene system where the ternary interaction parameter χ_{123} has been determined[14] as 0.33. Such a positive value, if applied to the actual αMS–CH–PαMS system, would lead to a larger difference between the effect of CH on the equilibrium position with respect to that of DOX or THF.

CONCLUSIONS

For a given polymerization system at a given temperature, where the $\Delta G_{lc}/RT$ value is not strongly negative, a suitable choice of solvent would be the determining factor in yielding a good extent of conversion of monomer into long-chain polymer. If the χ_{ms} and χ_{sp} parameters for that solvent are known, equations (1) or (4) can be used to predict the equilibrium compositions of the system as well as the maximum value of solvent concentration to allow polymerization to take place.

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