

# Thermodynamics of polymer mixtures: study on the mixing process of the poly(styrene)/poly(vinylmethylether) system

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## Abstract

The miscibility of poly(styrene) and poly(vinylmethylether) is studied both by measuring the glass transition temperatures of the mixture and with the application of the Flory–Prigogine theory in the approximated form due to Patterson. For these calculations, the enthalpy of mixing of the two polymers is evaluated by measuring the enthalpies of solution of the pure polymers and of the mixture. The trend of the interaction parameters with the temperature for two samples of poly(styrene) of different molecular weight is discussed. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The experimental study of polymer mixtures has required the research of a theoretical model that is able to reproduce the fundamental characteristics of the mixture and particularly the aspects that regard its thermodynamic stability.

The first model was proposed by Flory–Huggins [1–3]. It is based on the reticular theory and involves some simplifying hypotheses:

1. same lattice for the two polymers that form the mixture and for all the mixtures deriving from them independently from the composition of the mixture itself;

2. division of the polymeric chain into identical spherical structural units each of which occupies only one position of the lattice;
3. random distribution of the structural units of the two polymers on the adjacent positions of the lattice;
4. the volume variation is zero during the mixing process in virtue of hypotheses 1 and 2.

The mixing entropy  $\Delta S_M$  is therefore formed only by the combinatorial contribution due to the number of different ways in which the system can be formed. It is possible to calculate that

$$\Delta S_M = -R(V_1 + V_2) \left[ \left( \frac{\varphi_1}{\bar{V}_1} \right) \ln \varphi_1 + \left( \frac{\varphi_2}{\bar{V}_2} \right) \ln \varphi_2 \right] \quad (1)$$

where  $R$  is the gas constant,  $V_i$  the volume of the component  $i$  inside the mix,  $\varphi_i$  the volume fraction of the component  $i$ , and  $\bar{V}_i$  the molar volume of the component  $i$ .

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So,  $\Delta S_M$  is always positive and independent of the nature of the polymers that are mixed. Its value is though small due to the big dimensions of the macromolecules, i.e. the high value of  $\bar{V}_i$ .

The mixing enthalpy  $\Delta H_M$  is associated to the formation in the mixture of a new type of mixed contacts (1–2) that substitute some of the homogeneous contacts (1–1) or (2–2) between the pure components in a “nearly chemical” process:

$$\frac{1}{2}(1-1) + \frac{1}{2}(2-2) \rightarrow (1-2)$$

$\Delta H_M$  is therefore proportional to the exchange energy  $\Delta \varepsilon$  whose value is given by the following equation:

$$\Delta \varepsilon = \frac{1}{2}(\varepsilon_{1,1} + \varepsilon_{2,2}) - \varepsilon_{1,2}$$

where  $\varepsilon_{1,1}$  is the interaction energy of the homogeneous contact (1–1),  $\varepsilon_{2,2}$  the interaction energy of the homogeneous contact (2–2), and  $\varepsilon_{1,2}$  the interaction energy of the mixed contact (1–2), and that

$$\Delta H_M = z\Delta \varepsilon N_1 \phi_2 \quad (2)$$

where  $z$  is the co-ordination number of the lattice,  $N_1$  the number of macromolecules of component 1. Eq. (2) can be manipulated in order to introduce the interaction parameter of Flory–Huggins defined as

$$\chi_{1,2} = \frac{z\Delta \varepsilon}{RT}$$

where  $T$  is the absolute temperature. In the end, we have that

$$\Delta H_M = RTN_1 \phi_2 \chi_{1,2} \quad (3)$$

The enthalpic content is favourable or unfavourable to the mixing process depending on the sign of  $\chi_{1,2}$ . This value is related to the chemical nature of the macromolecules.

For what previously said, the main limitation to the Flory–Huggins theory is that it is not able to foresee a phase diagram with an LCST, i.e. the experimentally verified fact that mixtures of two polymers can give separation of the phases if the temperature raises.

To overcome this problem, some mainly formal changes have been introduced [4] particularly those regarding the interaction parameter whose nature is no more only enthalpic but also entropic: in this way, hypothesis 3 is modified.

The Flory–Huggins model is very intuitive and gives equations that are very simple to use but nevertheless

it is still unable to reproduce the real situation even with the modifications that have been introduced. For this reason, Flory has proposed a new model [5] after Prigogine’s molecular theories for solutions [6].

The Flory–Prigogine theory is based on the hypothesis that every thermodynamic system can be described by a state equation that relates the reduced variables of temperature, volume and pressure. This equation can be calculated with the aid of statistic thermodynamics and by determining the repartition function of the pure components and those of the mixtures. In other terms, it is equivalent to a cell model for the liquid state knowing the intermolecular forces, and so it is that

$$\Delta G_M = \Delta G_{M,\text{comb}} + G_R, \quad G_R = H_R - TS_R$$

with  $\Delta G_{M,\text{comb}}$  is the free mixing energy (only combinatorial),  $G_R$  the residual free energy due to interactions,  $H_R$  the residual enthalpy due to interactions, and  $S_R$  the residual entropy due to interactions, and that

$$\begin{aligned} H_R &= \Delta H_M \\ &= Nr\nu^* \left[ \frac{\psi_1 P_1^*}{1/\tilde{v}_1 - 1/\tilde{v}} + \frac{\psi_2 P_2^*}{1/\tilde{v}_2 - 1/\tilde{v}} + \left( \frac{\psi_1 \phi_2}{\tilde{v}} \right) X_{1,2} \right] \end{aligned} \quad (4)$$

$$\begin{aligned} S_R &= -3Nr\nu^* \left\{ \frac{\psi_1 P_1^*}{T_1^*} \ln \left[ \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right] \right. \\ &\quad \left. + \frac{\psi_2 P_2^*}{T_2^*} \ln \left[ \frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right] \right\} \end{aligned} \quad (5)$$

where  $N$  is the total number of molecules,  $r$  the number of segments of the macromolecular chain,  $\nu^*$  the characteristic volume of the mixture,  $P_i^*$  the characteristic pressure of the component  $i$ ,  $T_i^*$  the characteristic temperature of the component  $i$ ,  $\psi_i$  the fraction (in segments) of the component  $i$ ,  $\tilde{v}_i$  the reduced volume of the component  $i$ ,  $\tilde{v}$  the reduced volume of the mixture, and  $X_{1,2}$  the exchange parameter.

As shown, these equations are difficult to understand and to handle and for this reason, the Flory–Prigogine theory has been applied only once in the complete form [7]. Generally, the simplified Patterson form [8,9] is used: in this case, the interaction parameter is written in a simple way thanks to the fact that

1. the dependence of  $\chi_{1,2}$  from the composition foreseen by the Flory–Prigogine theory is ignored;
2.  $\chi_{1,2}$  is assumed as constant, as in the Flory–Huggins model.

In this way:

$$\frac{\chi_{1,2}}{M_1 v_1^*} = \frac{P_1^*}{RT_1^*} \left\{ \left[ \frac{\tilde{v}_1^{1/3}}{\tilde{v}_1^{1/3} - 1} \right] \left[ \frac{X_{1,2}}{P_1^*} \right] + \left[ \frac{\tilde{v}_1^{1/3}}{2(\frac{4}{3} - \tilde{v}_1^{1/3})} \right] \tau^2 \right\} \quad (6)$$

$$X_{1,2} = \frac{\tilde{v}}{m_1 v_1^* \theta_2} \left[ \Delta H_M - m_1 v_1^* P_1^* \left( \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right) - m_2 v_2^* P_2^* \left( \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right) \right] \quad (7)$$

with  $m_i$  being the weight fraction of the component  $i$

$$\theta_2 = \frac{\phi_2}{\phi_2 + \phi_1 (v_1^*/v_2^*)^{-1/3}} \quad \text{with } \phi_2 = 1 - \phi_1$$

$$= \frac{1}{1 + (m_1 v_1^*/m_2 v_2^*)}$$

The first term is due to the interaction between the structural elements of the two different macromolecular species and the sign is positive or negative depending on the fact that either the specific interaction forces or the dispersion forces are active. The second term is due to the variation of the free volume ( $\tau = 1 - T_1^*/T_2^*$  represents the difference in terms of free volume of the two components) and is always positive and therefore unfavourable to the mixing process.

The experimental application of Eq. (6) is quite simple [10–12]: in fact, the polymer mixture is homogeneous if  $\chi_{1,2}$  is smaller than the critical value of

$$\left( \frac{\chi_{1,2}}{M_1 v_1^*} \right)_{CR} = \frac{1}{2} \left[ \frac{1}{v_1^{*1/2}} + \frac{1}{v_2^{*1/2}} \right] \quad (8)$$

For values of  $\chi_{1,2}$  bigger than  $(\chi_{1,2})_{CR}$ , the separation of the phases is achieved.

In the present paper, the Patterson theory is applied to the poly(styrene)/poly(vinylmethylether) system whose mixing values [13] in the whole composition interval and for a wide range of molecular weights are known.

## 2. Experimental

### 2.1. Materials

The two poly(styrene) (PS) samples that have been used were from Poliscience, whereas the sample of poly(vinylmethylether) (PVME) was a 50% water solution from Aldrich.

The molecular weight of the first sample of PS was determined via GPLC with the following results:  $\overline{M}_W = 210\,000 \text{ g mol}^{-1}$ ,  $\overline{M}_N = 105\,000 \text{ g mol}^{-1}$ , and polydispersion index  $q = 2$ .

For the second sample of PS, the molecular weight was determined by viscosity measurements in toluene at 30°C [14] and a value of  $\overline{M}_V = 38\,200 \text{ g mol}^{-1}$  was obtained.

The molecular weight of PVME was determined by viscosity measurements in butanone at 30°C [14] and the result was  $\overline{M}_V = 32\,500 \text{ g mol}^{-1}$ .

The mixtures of PS with PVME in the desired weight ratios were obtained from solutions in toluene at 5% in weight of the two polymers followed by evaporation of the solvent in order to obtain thin films of the desired depth (about 0.2 mm).

The evaporation was carried out first under a ventilated hood at room temperature (for 2–3 days) and then in a vacuum oven at 60°C for a week in order to remove all the residual solvent.

In the rest of this paper, the mixtures containing PS with a higher molecular weight will be called “mixtures A”, whereas those with PS with minor molecular weight will be indicated as “mixtures B”.

### 2.2. Techniques

#### 2.2.1. Differential scan calorimetry (DSC)

To determine the temperature of glass transition  $T_g$ , DSC measurements have been carried out under nitrogen flux using a Mettler calorimeter model DSC 30. The thermograms were obtained with the following thermal cycle:

1. heating of the system above its  $T_g$  at the speed of 20°C/min and maintaining the isotherm for 5 min in order to cancel eventual previous thermal histories of the sample and to eliminate the last traces of the solvent;
2. cooling below the  $T_g$  at the speed of 10°C/min;

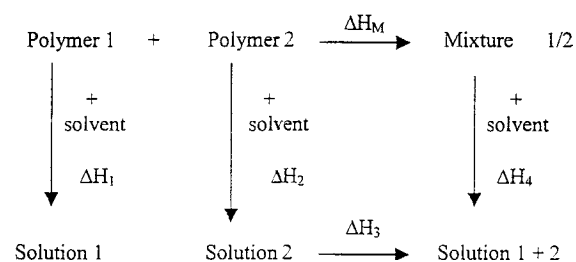
- scan from the initial temperature, below the  $T_g$  to the final one, above the  $T_g$ , at the speed of 20°C/min.

Conventionally, the  $T_g$  is the mean point of the flexure of the thermogram.

### 2.2.2. Dissolution calorimetry

In order to determine the mixing heat  $\Delta H_M$  of the PS/PVME mixtures, measurements of the solution heats of the mixtures and of the pure components in an appropriate solvent have been carried out.

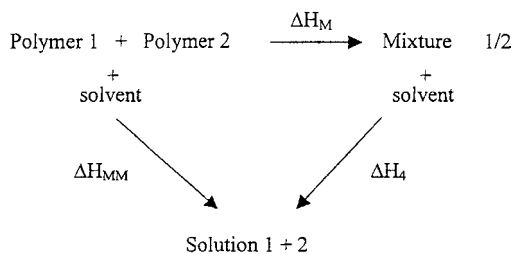
Under these conditions, the mixing enthalpy is calculated by using a Hess cycle:



and

$$\Delta H_M = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4$$

In order to reduce the number of experiments and therefore the final error, we have used a modified version that measures the difference between the solution heat of the mixture 1/2 and that of a mechanical mix that contains the two polymers in the same ratio of the mixture 1/2:



In this case, the mixing heat is

$$\Delta H_M = \Delta H_{MM} - \Delta H_4 \quad (9)$$

Since all the theories previously seen describe the mixing process of fluid polymers above their  $T_g$ , it is necessary to consider that PS is glassy under 105°C and that our experiments have been carried out at 50°C. For this reason, to use the theoretical equations,

it has been necessary to introduce a suitable correction term that is able to estimate the excess enthalpy of the glass compared to that of the corresponding under-cooled liquid.

In the Petrie–Marshall theory [15], this correction term  $\Delta H_\infty$  is calculated as the integral of the difference between the specific heat of the liquid  $c_{p,l}$  and that of the glass  $c_{p,g}$  at the required temperature:

$$\Delta H_\infty = \int_{T_a}^{T_u} (c_{p,l} - c_{p,g}) dT \quad (10)$$

where the integration limits are a generic temperature  $T_u$  (always higher than  $T_g$ ) and  $T_a$ , temperature at which the correction is evaluated (in our case, 50°C).

Our experiments have been carried out with a mixing calorimeter SETARAM C80D at 50°C with toluene as the solvent for both the polymers. The values of the specific heats for the correction were obtained from DSC measurements.

## 3. Results and discussion

### 3.1. Study of the miscibility through the $T_g$

The experimental results of the  $T_g$  (measured with the DSC) of the two series of mixtures are listed in Table 1 together with the values of the theoretical equations.

As shown, for both the mixtures and for all the considered compositions, the thermograms are characterised by only one glass transition in which the  $T_g$  is intermediate of those of the pure components. As a consequence, the two polymers are mixable in the whole concentration interval, even if the molecular weight varies.

Fig. 1 shows that the experimental outline of the  $T_g$  vs. the composition of the mixture is characterised by negative variations from linearity. This indicates that the PVME chains influence (thanks to their higher flexibility) in a relevant grade the mobility of the macromolecules of PS enhancing their movement possibilities.

The theoretical equations that have been considered foresee negative deviations from linearity and are:

- the Flory–Fox equation [16]

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

Table 1  
 $T_g$  values experimental and calculated

PS/PVME (%)	Experimental values of $T_g$ (K)		Calculated values of $T_g$ (K)	
	Mixture A	Mixture B	Fox–Flory	Gordon–Taylor, $K = 0.25$
100/0	378	372	378	378
90/10	340	253	359	337
80/20	315	318	341	312
70/30	296	298	325	295
60/40	283	281	311	282
50/50	269	265	298	273
40/60	263	256	286	265
30/70	258	251	275	259
20/80	254	250	265	254
10/90	251	249	255	250
0/100	246	249	246	246

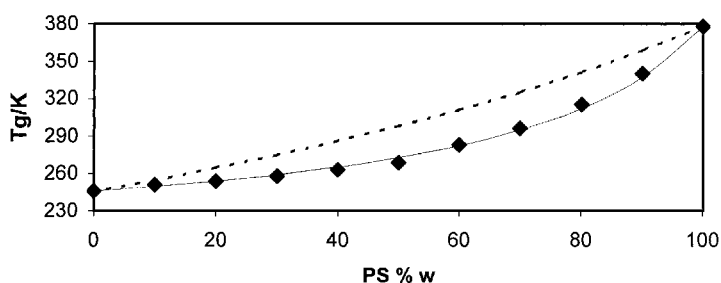


Fig. 1. Experimental and calculated  $T_g$  values: (---) Fox–Flory, (—) Gordon–Taylor, (◆) experimental values.

where  $W_1$  and  $W_2$  are the fractions in weight of the two polymers 1 and 2,  $T_{g1}$  and  $T_{g2}$  are, respectively, their glass transition temperatures.

- the Gordon–Taylor equation [17]

$$T_g = \frac{W_1 T_{g1} + K W_2 T_{g2}}{W_1 + K W_2}$$

where  $K$  is a parameter that derives from the ratio of the difference between the thermal expansion coefficients of the pure rubber and the glassy components:

$$K = \frac{\alpha_{1,2} - \alpha_{g,2}}{\alpha_{1,1} - \alpha_{g,1}}$$

As shown in Fig. 1, there is little agreement of the experimental data with the Flory–Fox equation. Instead there is a good agreement with the Gordon–Taylor equation, assuming  $K$  as an empirical parameter whose value is 0.25.

It has not been possible to use the correct value of  $K$  since the value of the thermal expansion of PVME in the glass state was not available with sufficient accuracy.

### 3.2. Miscibility studies through Patterson's equation

Table 2 contains the experimental results of the solution heats of the mixture 1/2 and of the mechanical

Table 2  
 Experimental solution heats (mJ/mg)

PS/PVME (%)	$\Delta H_{MM}$		$\Delta H_4$	
	Mixture A	Mixture B	Mixture A	Mixture B
25/75	0.68±0.1	0.73±0.1	0.90±0.1	0.92±0.1
50/50	-7.0±0.6	-7.4±0.6	2.6±0.2	-2.7±0.2
75/25	-13.6±1.1	-14.4±1.5	-5.3±0.4	-5.9±0.4

Table 3  
Corrected mixing heats (mJ/mg)

PS/PVME (%)	$\Delta H_M$	
	Mixture A	Mixture B
25/75	$-1.5 \pm 0.1$	$-2.0 \pm 0.2$
50/50	$-2.9 \pm 0.4$	$-3.8 \pm 0.4$
75/25	$-3.9 \pm 0.4$	$-4.0 \pm 0.4$

mix for mixtures A and B in three different compositions.

For the correction coefficient, the following values of specific heat ( $\text{J g}^{-1} \text{K}^{-1}$ ) have been used [18]:

$$c_{p,l} = 1.5234 + 2.18 \times 10^{-3}(T - 320),$$

$$c_{p,g} = 1.1781 + 4.21 \times 10^{-3}(T - 320)$$

and the value of the correction coefficient itself is  $\Delta H_\infty = -15.59 \text{ mJ/mg}$ .

Table 4  
Exchange parameter (calculated values)  $X_{1,2}$  ( $\text{J cm}^{-1}$ )

	T (K)						
	298	303	313	323	333	343	353
Mixture A							
25/75	-17.7	-17.4	-17.2	-16.6	-17.0	-16.9	-16.7
50/50	-45.0	-44.8	-44.7	-44.3	-44.3	-44.2	-44.9
75/25	-67.6	-67.1	-66.5	-65.0	-64.4	-64.4	-63.6
Mixture B							
25/75	-	-	-	-	-18.5	-18.3	-18.1
50/50	-	-	-	-	-46.8	-46.7	-46.7
75/25	-	-	-	-	-69.0	-68.8	-67.9

Table 5  
Interaction parameter (calculated values)  $\chi_{1,2} \times 10^2 / M_1 v_1^*$  ( $\text{mol cm}^{-3}$ )

	T (K)						
	298	303	313	323	333	343	353
Mixture A							
25/75	-2.28	-2.26	-2.22	-2.18	-2.14	-2.10	-2.07
50/50	-5.95	-5.89	-5.78	-5.68	-5.59	-5.49	-5.41
75/25	-8.78	-8.70	-8.54	-8.39	-8.24	-8.10	-7.98
Mixture B							
25/75	-	-	-	-	-3.40	-2.80	-2.40
50/50	-	-	-	-	-8.80	-7.40	-6.50
75/25	-	-	-	-	-13.10	-11.10	-9.50

Consequently, the corrected values of the mixing heats are listed in Table 3. As shown, the mixing heats are all negative (the mixing process is always exothermic) and these values increase, in their absolute value, when the percentage of PS increases. Considering the errors from which the experimental data are affected, we are able to state that no dependence of the mixing heat from the molecular weight of PS exists.

To proceed in the discussion on the miscibility using Patterson's equation, the values of the exchange parameter  $X_{1,2}$  have been calculated by employing the mixing heats and other parameters that appear in Eq. (7) [19]. The results are shown in Table 4.

In the end, Table 5 lists the values of Patterson's interaction parameter that are calculated using Eq. (6) and, as before, referring to data published in a previous work [19].

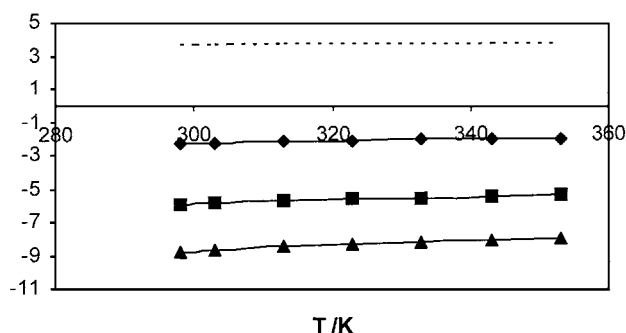


Fig. 2. Interaction parameters of mixture A vs.  $T$  (K): (◆) PS/PVME 25/75, (■) PS/PVME 50/50, (▲) PS/PVME 75/25, (---) critical value.

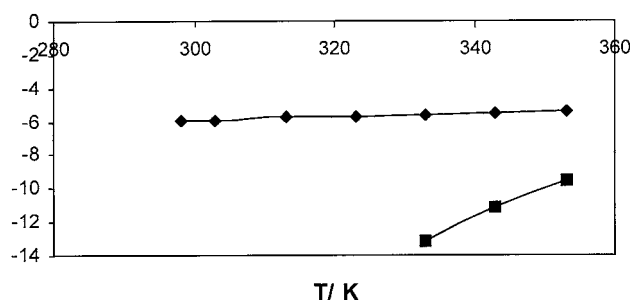


Fig. 3. Interaction parameters of mixture A 50/50 (◆) and mixture B 50/50 (■).

The critical values of the interaction parameters are calculated by using Eq. (8) and are

$$\text{mixture A : } \left( \frac{\chi_{1,2}}{M_1 v_1^*} \right)_{\text{CR}} = 3.8 \times 10^{-2} \text{ mol cm}^{-3},$$

$$\text{mixture B : } \left( \frac{\chi_{1,2}}{M_1 v_1^*} \right)_{\text{CR}} = 2.2 \times 10^{-2} \text{ mol cm}^{-3}$$

Fig. 2 describes the outline of the interaction parameters of mixture A in the three different compositions. The values of this parameter are, in all cases, negative and smaller than the critical value: this means that the two polymers are mixable in all ratios. The absolute values of this parameter also increase when the percentage of PS increases and this means that the miscibility of the system is better the higher the quantity of PS in the system. Finally, higher is the temperature, higher is the interaction parameter, according to the behaviour of an LCST type of system.

Similar considerations can be extended to mixture B. It has also to be observed (Fig. 3) that the miscibility of mixture B is higher than that of mixture A,

considering the fact that the values of the interaction parameter are different.

#### 4. Conclusions

Patterson's miscibility theory is able to predict the experimental behaviour of the PS/PVME system and particularly:

1. the PS/PVME system is mixable in every composition ratio;
2. the miscibility increases with the lowering of the molecular weight of PS;
3. the miscibility always lowers with the increase of the temperature, according to an LCST type of behaviour.

It has also been foreseen that the miscibility increases with the increase of the quantity of PS in the system; this result has still to be experimentally verified.

Overall, Patterson's theory can be considered a good theoretical support for the interpretation of the miscibility of polymers; nevertheless, some of its hypotheses seem not to be experimentally verified.

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