

# Polymer–polymer interaction parameters in the ternary system polystyrene/poly( $\alpha$ -methyl styrene)/n-butyl chloride

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The polymer–polymer interaction parameter  $\chi'_{12}$ , for the polystyrene/poly( $\alpha$ -methyl styrene)/n-butyl chloride ternary system, has been determined from activity coefficients of the solution measured using piezoelectric vapour sorption methods in the temperature range 30°–60°C. (These measurements were carried out in the concentration range  $0.06 < \psi_0 < 0.26$ , where  $\psi$  is the segment fraction of the solvent). The values of  $\chi'_{12}$  extrapolated to zero solvent concentration over the range 30°–60°C, are large and negative ( $-0.2$  to  $-0.9$ )  $\chi'_{12}$  was found to increase with  $\psi_0$ . The negative values of  $\chi'_{12}$  in this work are in agreement with the  $T_g$  in the polystyrene ( $M_w = 2.04 \times 10^4$ )/poly( $\alpha$ -methyl styrene) ( $M_w = 9.09 \times 10^4$ ) blends on the point of blend compatibility. The polymer–polymer interaction parameters obtained in this work are discussed by taking into account the high susceptibility of polymers in the glassy state to solution of organic solvents.

(Keywords: polymer–polymer interaction parameter  $\chi'_{12}$ ; polystyrene/poly( $\alpha$ -methyl styrene) blend; piezoelectric vapour sorption methods; compatibility phenomena)

## INTRODUCTION

The compatibility phenomena between the polymers or oligomers have been investigated using gas-liquid chromatography<sup>1–3</sup>, melt-titration<sup>4</sup>, differential scanning calorimetry<sup>5–7</sup> (d.s.c.), differential thermal analysis<sup>8</sup> (d.t.a.), neutron<sup>9–11</sup> and light scattering<sup>12</sup>. The measurements of phase diagrams<sup>13–23</sup>, vapour sorption<sup>24</sup>, osmotic pressure<sup>25</sup>, and mechanical strength<sup>26</sup> in the polymer blend systems have been carried out extensively. The available data indicate that many compatible polymer systems are characterized by a specific interaction between the polymers. The free volume effect is not large as in the usual polymer–solvent systems. The phase separation at the lower critical solution temperature in the polymer blend has been predicted by using the recent theories of polymer solution thermodynamics<sup>17,27</sup>. The importance of the  $|\Delta\chi|$  effect in explaining the polymer compatibility in ternary solutions<sup>1,13,15</sup> has been recognized. The  $|\Delta\chi|$  effect is due to the difference between the strengths of interactions of the two polymers with the solvent. The chain dimensions in a binary mixture of compatible polymers have been determined using neutron scattering and discussed by comparisons with the polymer dimension in the compatible state with those in the unperturbed state<sup>9–11</sup>.

Whether the phenomena of both the upper and lower critical solution temperatures in the polymer system observed in the polystyrene/poly(vinyl methyl ether) system<sup>19,24</sup> can be explained by the recent theories is an open question. The compatibility in the non-polar polymer blend such as polystyrene/poly( $\alpha$ -methyl styrene)<sup>5,6,8</sup> and its molecular weight dependence<sup>5,6</sup> has not been predicted theoretically. However, the large variation in the location of the miscibility gap in oligomeric

mixtures is achieved with the combinatorial entropy term<sup>22</sup>. In order to discuss these experimental results, reliable values of the polymer–polymer interaction parameter are needed over the wide range of temperature and molecular weight of the polymer.

In this work the interaction parameter between polystyrene and poly( $\alpha$ -methyl styrene) has been determined from the activity coefficient of solvent in the ternary and binary solutions at very high concentrations of polymer, so that the parameter obtained may reflect closely the properties of polymer blend in bulk state. The polystyrene and poly( $\alpha$ -methyl styrene) were selected to elucidate the general properties of the polymer blend system<sup>17,22,27</sup> and also because the blend is non-polar and compatible, and the result in this work can be compared with data available such as those from the glass transition temperature<sup>5,6,8</sup> and neutron scattering<sup>11</sup> studies.

## EXPERIMENTAL

Polystyrene (PS) was obtained from Pressure Chemical Co. and characterized by  $M_w = 1.75 \times 10^4$ ,  $M_w/M_n < 1.04$  and poly( $\alpha$ -methyl styrene) (P $\alpha$ MS) from Polysciences and  $M_w = 9.00 \times 10^4$ ,  $M_w/M_n < 1.1$ . n-Butyl chloride (n-BuCl) was of reagent grade, obtained from Wako Pure Chemicals. The solvent was dried by potassium anhydride and distilled before use. Chloroform was used as a casting solvent and was obtained from Wako Pure Chem. It was used as received. The piezoelectric vapour sorption apparatus is described elsewhere<sup>28</sup>.

## DATA REDUCTION

Sauerbrey showed that there is a linear relationship between the frequency decrease and the mass of material

deposited on a piezoelectric crystal surface<sup>29</sup>. Using Sauerbrey's relationship, the weight fraction of solvent sorbed by polymer in the binary solution is calculated using

$$w_0 = m_0 / (m_1 + m_0) = \Delta F_0 / (\Delta F_1 + \Delta F_0) \quad (1)$$

where  $\Delta F_0$  is the frequency decrease due to the solvent mass  $m_0$  sorbed by polymer on the crystal, and  $\Delta F_1$  is the frequency decrease due to the initially applied polymer coating of mass  $m_1$ . In a ternary system of solvent(0)/polymer(1)/polymer(2), the weight fraction of the component ( $i$ ) is given by introducing a blend concentration of component (1),  $w_b$ ,

$$w_b = m_1 / (m_1 + m_2) = \Delta F_1 / (\Delta F_1 + \Delta F_2) \quad (2)$$

$$w_0 = m_0 / (m_0 + m_1 + m_2) = \Delta F_0 / (\Delta F_0 + \Delta F_1 + \Delta F_2) \quad (3a)$$

$$w_1 = w_b(1 - w_0) \quad (3b)$$

$$w_2 = 1 - w_0 - w_1 \quad (3c)$$

where  $\Delta F_i$  is the frequency decrease due to the mass of material ( $i$ ) deposited on the crystal. With a knowledge of  $w_b$  and  $w_0$ , values of  $w_1$  and  $w_2$  are determined by the above equations.

At modest pressures, the activity  $a_0$  of the solvent at a given solution temperature is expressed by<sup>30</sup>

$$a_0 = (P_0/P_0^s) \exp\{-B_{00}(P_0^s - P_0)/RT\} \quad (4)$$

where  $P_0$  is the partial pressure of solvent above the polymer solution,  $P_0^s$  is the saturated vapour pressure of solvent at the solution temperature,  $B_{00}$  is the second virial coefficient of solvent,  $T$  is the absolute temperature, and  $R$  is the gas constant. The values of  $P_0^s$  for the pure solvent were obtained from the literature<sup>31</sup>. The detailed procedure to determine  $a_0$  and  $w_0$  is described in detail elsewhere<sup>28</sup>.

The vapour sorption data for n-butyl chloride obtained by coating the PS/P $\alpha$ MS blend from chloroform solutions agreed with those by coating the PS/P $\alpha$ MS from n-butyl chloride solutions. Therefore, the vapour sorption isotherm in this work will not depend on the solvent. Errors caused by the temperature dependence of the frequency of the quartz crystal in the measurement have been minimized by monitoring the frequency of uncoated crystal at measuring temperatures before the vapour sorption experiment.

## RESULTS

The polymer-solvent interactions in the binary system are often analysed using the Flory-Huggins formulation for the activity coefficients<sup>32</sup>

$$a_0/\phi_0 = \exp\{(1-1/r)\phi_1 + \chi\phi_1^2\} \quad (5)$$

where the  $\phi$ 's represent volume fraction of solvent ( $\phi_0$ ) and polymer ( $\phi_1$ ), and  $r$  is the ratio of the molar volume of the polymer to that of the solvent. Following recent polymer solution theories<sup>33,34</sup>, the volume fractions in equation (5) are replaced by segment fractions ( $\psi_i$ ),

$$\psi_i = w_i v_{i,sp}^* / \left( \sum_{i=0}^1 w_i v_{i,sp}^* \right) \quad (6)$$

where the quantity  $v_{i,sp}^*$  is the specific characteristic volume reduction parameter of component ( $i$ ). The values of  $v_{i,sp}^*$  reflecting the hard-core volume of each component are 0.8742 cm<sup>3</sup> g<sup>-1</sup> for n-BuCl<sup>35</sup>, 0.770 for P $\alpha$ MS<sup>36</sup> and 0.8098 for PS<sup>37</sup>. In Figures 1 and 2, values of the polymer-solvent interaction parameter  $\chi_{10}$  for PS/n-BuCl and  $\chi_{20}$  for P $\alpha$ MS/n-BuCl calculated using equation (5) are plotted against  $\psi_0$ .

The polymer-polymer interaction is analysed using the Flory-Huggins expression for a system of two polymers and one solvent<sup>32</sup>

$$a_0/\psi_0 = \exp[(1-r_{10}^{-1})\psi_1 + (1-r_{20}^{-1})\psi_2 + \chi_{10}\psi_1^2 + \chi_{20}\psi_2^2 + (\chi_{10} + \chi_{20} - \chi'_{12})\psi_1\psi_2] \quad (7)$$

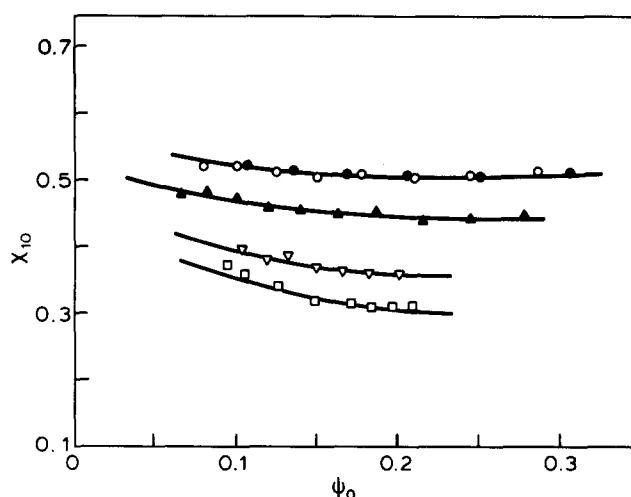


Figure 1 Interaction parameter  $\chi_{10}$  plotted as a function of the segment fraction of solvent  $\psi_0$  for solutions of n-butyl chloride in polystyrene at various temperatures; (●) 30.0°C, (○) 35.0°C, (▲) 40.0°C, (△) 50.0°C, and (□) 60.0°C

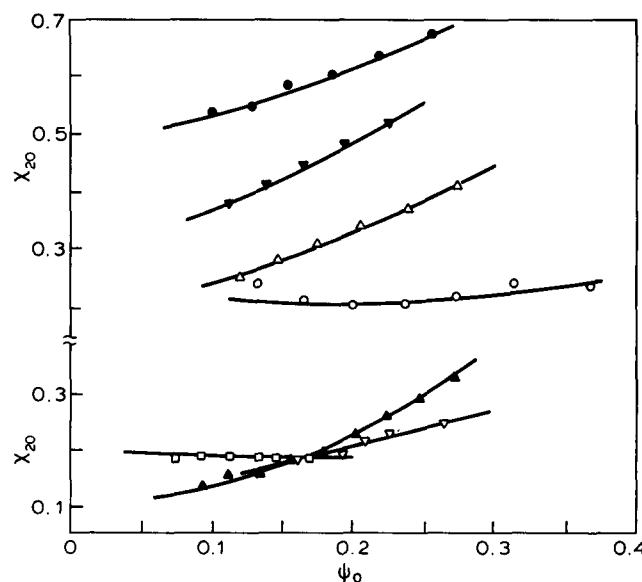
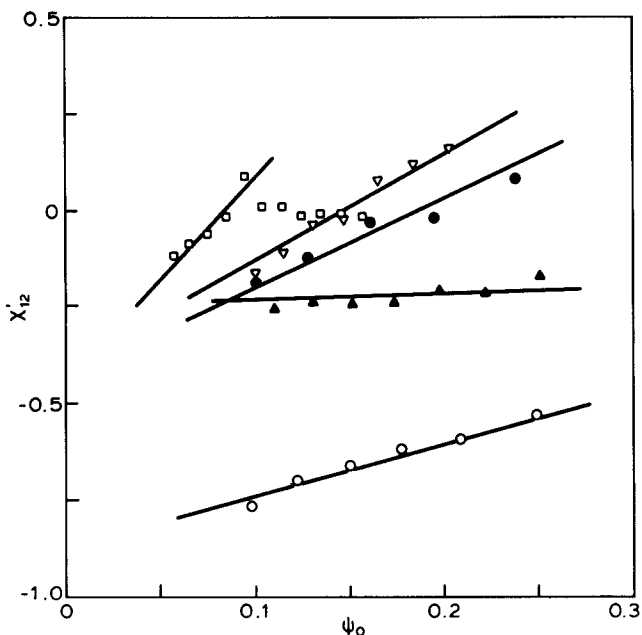


Figure 2 Interaction parameter  $\chi_{20}$  as a function of segment fraction of solvent  $\psi_0$  for solutions of n-butyl chloride in poly( $\alpha$ -methyl styrene) at various temperatures, (●) 30.0°C, (▼) 31.2°C, (△) 32.5°C, (○) 35.0°C, (▲) 40.0°C, (▽) 50.0°C, (□) 60.0°C

$$\text{and } \psi_i = w_i v_{i,sp}^* / \sum_{i=0}^2 w_i v_{i,sp}^* \quad (8)$$

$$\chi'_{12} = \chi_{12} / r_{10} \quad (9)$$

where  $r_{10}$  is the ratio of characteristic molar volume reduction parameter ( $M_w v_{i,sp}^*$ ) of polymer ( $i=1$  or  $2$ ) to that solvent ( $i=0$ ),  $\chi_{i0}$  is the polymer( $i$ )-solvent( $0$ ) interaction parameter, and  $\chi'_{12}$  is the polymer( $1$ )-polymer( $2$ ) interaction parameter per segment of polymer( $1$ ). In Figure 3, values of  $\chi'_{12}$  for the PS-P $\alpha$ MS



**Figure 3** Interaction parameter  $\chi'_{12}$  (between polystyrene and poly( $\alpha$ -methyl styrene)) plotted as a function of segment fraction of solvent  $\psi_0$  in the ternary polystyrene/poly( $\alpha$ -methyl styrene)/ $n$ -butyl chloride system at various temperatures, (●) 30.0°C, (○) 35.0°C, (▲) 40.0°C, (▽) 50.0°C, and (□) 60.0°C. The blend concentration of PS=0.5

(calculated using equation (7) and  $\chi_{10}$  and  $\chi_{20}$  in Figures 1 and 2) are plotted against  $\psi_0$ .

Experimental values of the ratio  $[\partial(a_0/\psi_0)/\partial a_0]_T$  for the PS/ $n$ -BuCl, P $\alpha$ MS/ $n$ -BuCl, and PS/P $\alpha$ MS/ $n$ -BuCl systems are observed to be constant over the concentration and temperature range measured. The empirical relation between the activity coefficient and the concentration of solvent can be derived assuming that values of  $[\partial(a_0/\psi_0)/\partial a_0]_T$  are independent of concentration<sup>38</sup>:

$$[\partial(a_0/\psi_0)/\partial a_0]_T = C \quad (10)$$

$$a_0/\psi_0 = B/(1 - C\psi_0) \quad (11)$$

where  $C$  and  $B$  are constant. The value of  $B$  in equation (11) corresponds to that of  $a_0/\psi_0$  extrapolated to  $\psi_0=0$ . In Tables 1 and 2, values of  $B$  and  $C$  and  $\chi_{10}^0$ ,  $\chi_{20}^0$  and  $\chi_{12}^{10}$  at the limit of  $\psi_0=0$  calculated using equations (5) and (7) are listed. In Figures 4 and 5, values of  $\chi_{10}$ ,  $\chi_{20}$  and  $\chi_{12}^{10}$  are plotted against temperature. The temperature dependence of  $\chi_{20}$  for the P $\alpha$ MS/ $n$ -BuCl system at temperatures lower than 40°C is complicated, while  $\chi_{10}$  for the PS/ $n$ -BuCl system decreases with increasing temperature linearly.

## DISCUSSION

The negative values of  $\chi_{12}^0$  observed in the PS/P $\alpha$ MS suggest that the blend of PS ( $M_w=1.75 \times 10^4$ ) and P $\alpha$ MS ( $9.0 \times 10^4$ ) is compatible (at least at temperatures between 30°–60°C, which is consistent with the presence of a single glass transition temperature in the PS ( $M_w=2.04 \times 10^4$ )/P $\alpha$ MS ( $9.09 \times 10^4$ ) system<sup>6</sup> and also the result that the polymer chain dimension of PS in solutions of PS in P $\alpha$ MS is slightly less than the unperturbed value<sup>11</sup>.

The values of  $\chi'_{12}$  are negative in the vicinity of  $\psi_0=0$  and become positive with increase in  $\psi_0$  (see Figure 3). This suggests that the addition of 6–20% of the solvent brings about phase separation and that the phase diagram

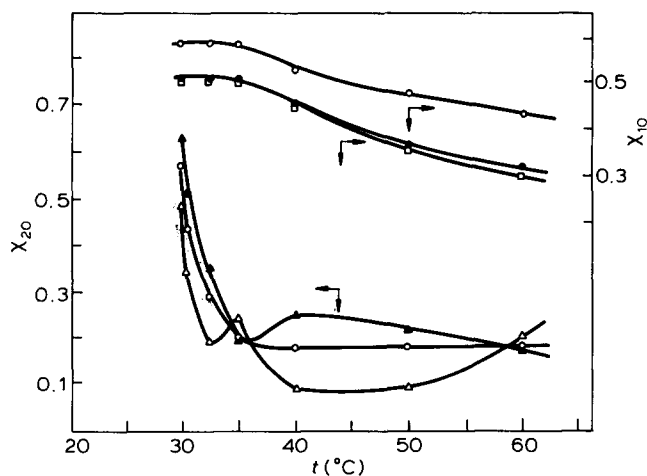
**Table 1** Experimental values of  $B$  and  $C$  in equation (11) for PS/ $n$ -BuCl, P $\alpha$ MS/ $n$ -BuCl and PS/P $\alpha$ MS/ $n$ -BuCl systems

Temperature	PS/ $n$ -BuCl		P $\alpha$ MS/ $n$ -BuCl		PS/P $\alpha$ MS/ $n$ -BuCl	
	$B$	$C$	$B$	$C$	$B$	$C$
30.0°C	4.83	- 2.9	4.42	- 1.7	5.16	- 3.2
32.5	4.83	- 2.9	3.29	- 1.0	4.39	- 2.4
35.0	4.83	- 2.9	3.45	- 1.8	5.09	- 3.3
40.0	4.59	- 2.8	2.98	- 0.8	3.95	- 1.9
50.0	4.36	- 2.8	2.97	- 0.9	3.99	- 2.7
60.0	4.18	- 2.8	3.34	- 1.3	4.21	- 2.8

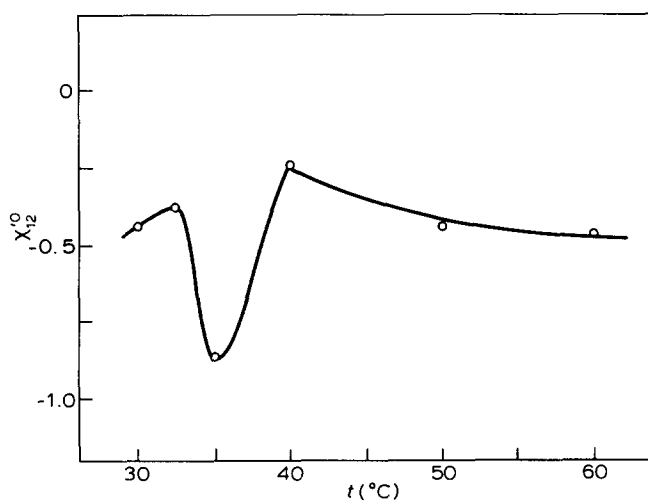
**Table 2** Values of  $\chi_{10}^0$  for PS/ $n$ -BuCl,  $\chi_{20}^0$  for P $\alpha$ MS/ $n$ -BuCl and  $\chi_{12}^{10}$  for PS/P $\alpha$ MS in the vicinity of  $\psi_0=0$  calculated from equations (5) and (7) and from the values in Table 1

Temperature	PS/ $n$ -BuCl	P $\alpha$ MS/ $n$ -BuCl	PS/P $\alpha$ MS
	$\chi_{10}^0$	$\chi_{20}^0$	$\chi_{12}^{10}$
30.0°C	0.58	0.49	- 0.44
32.5	0.58	0.19	- 0.37
35.0	0.58	0.24	- 0.87
40.0	0.53	0.09	- 0.24
50.0	0.48	0.09	- 0.39
60.0	0.44	0.21	- 0.47

$$T_g = w_0 T_{g,0} + w_i T_{g,i} + w_0 w_i b (T_{g,i} - T_{g,0}) \quad (12)$$



**Figure 4** Interaction parameters  $\chi_{10}$  and  $\chi_{20}$  plotted as a function of temperature at various concentrations in the PS/n-BuCl system, upper curves, (○)  $\psi_0=0$ , (●)  $\psi_0=0.16$ , (□)  $\psi_0=0.22$ ; the P $\alpha$ MS/n-BuCl system, lower curves, (△)  $\psi_0=0$ , (○)  $\psi_0=0.16$ , (▲)  $\psi_0=0.22$



**Figure 5** Interaction parameter  $\chi_{12}^0$  (extrapolated to  $\psi_0=0$ ) plotted as a function of temperature for the PS/P $\alpha$ MS blend

of the PS/P $\alpha$ MS/n-BuCl system shows a closed region similar to that in the polystyrene/poly(vinyl methyl ether)/chloroform system<sup>13</sup>.

The polymer-polymer interaction parameter of  $\chi'_{12}$  can be obtained from equation (7) through the values of  $\chi_{10}$  and  $\chi_{20}$ , which were determined for a polymer in the liquid state. There is a report<sup>39</sup> that a polymer in the glassy state shows a high susceptibility to swelling and solution for organic solvents than it would as a liquid. The trend leads to a lower value of  $\chi_{i0}$  and a large negative value of  $\chi'_{12}$  (if  $\chi_{i0}$  was determined for a polymer in the glassy state<sup>1</sup>). Therefore it is important to examine whether or not the binary and ternary systems under measurements are in a state above the glass transition temperature ( $T_g$ ), when  $\chi'_{12}$  is evaluated using equation (7).

A rough estimation of  $T_g$  as a function of concentration of n-BuCl in the PS/n-BuCl, P $\alpha$ MS/n-BuCl, and PS/P $\alpha$ MS/n-BuCl systems has been carried out by using available experimental data. Numerous workers have examined the  $T_g$ -composition trend in polymer/diluent systems<sup>40,41</sup>. The equation developed by Jenkel *et al.*<sup>40</sup> is given by

where  $T_{g,i}$ (K) is the glass transition temperature for the pure component of diluent(0) and polymer(1), and  $b$  is an empirical parameter depending on the polymer-diluent interaction, and  $w_i$  is the weight fraction of (i). The  $T_g$  for pure polymers and blend are known to be 373K for PS<sup>6</sup>, 450K for P $\alpha$ MS<sup>6</sup> and 110°C for PS/P $\alpha$ MS blend<sup>6</sup> with a blend composition  $w_b=0.5$  in this work. The  $T_g$  of n-BuCl is estimated to be 90K through the melting temperature  $T_m=150K$ <sup>31</sup> and ratio of  $T_g/T_m=0.6$ , which is an average value for alcohols and carbon tetrachloride<sup>42</sup>. The ratio does not depend strongly on the materials, for example  $T_g/T_m$  for the majority of polymer are between 0.56 and 0.76<sup>43</sup>. The value of  $b$  in the systems studied in this work is assumed to be in the range of  $-0.8$  to  $-1.4$ . Data in 14 PS/diluent systems<sup>40</sup> have values between  $-0.42$  and  $-1.40$  with an average value of  $-0.92$ . The calculated values of  $T_g$  from equation (12) (with  $T_{g,0}=-183^\circ\text{C}$  and  $b=-0.8$  to  $-1.4$ ) are  $60^\circ\text{C}$  at  $\psi_0=0.08 \pm 0.01$ , and  $30^\circ\text{C}$  at  $\psi_0=0.14 \pm 0.02$  for the PS/n-BuCl system, and  $60^\circ\text{C}$  at  $\psi_0=0.19 \pm 0.03$  and  $30^\circ\text{C}$  at  $\psi_0=0.25 \pm 0.04$  for the P $\alpha$ MS/n-BuCl. The  $T_g$ 's in the PS/P $\alpha$ MS/N-BuCl system are  $60^\circ\text{C}$  at  $\psi_0=0.10 \pm 0.01$ , and  $30^\circ\text{C}$  at  $\psi_0=0.15 \pm 0.02$ . It is speculated from the above results that most of the values of  $\chi_{10}$  in the PS/n-BuCl system and of  $a_0/\psi_0$  in the PS/P $\alpha$ MS/n-BuCl system obtained in this work are determined at temperatures above  $T_g$ , while in the P $\alpha$ MS/n-BuCl system values of  $\chi_{20}$  are determined at or near the  $T_g$  (except those at  $35^\circ\text{C}$ ). It is possible that the values of  $\chi_{20}$  for the P $\alpha$ MS/n-BuCl in this work are smaller than those for a P $\alpha$ MS in the liquid state.

It is of interest to discuss the compatibility phenomena between polystyrene and poly( $\alpha$ -methyl styrene) from the viewpoint of a specific interaction between the polymers. The polymer-solvent interaction parameter in the PS/benzene and PS/toluene systems over very low solvent concentration provides useful information. Values of  $\chi$  in the PS/benzene system and PS/toluene system over the concentration  $0.2 < \psi_0 < 0.3$ <sup>28</sup> are small (0.25–0.35) and increase slightly with increases in  $\psi_0$ <sup>28,32</sup>. The same behaviour of  $d\chi/d\psi_0 > 0$  is also found in the PS/dichloromethane and PS/chloroform<sup>28</sup> systems where weak hydrogen bonding exists between the phenyl group of the PS and chloroform<sup>41</sup>. To our knowledge, the positive values of  $d\chi/d\psi_0$  and small or negative values of  $\chi$  are found in the systems with a specific interaction between polymer and solvent, while in nonpolar or moderately polar solvent systems  $\chi$  is positive and large and  $d\chi/d\psi_0$  is zero or negative<sup>28,38,44</sup>. The miscibility phenomena between PS and 2,6-dimethyl poly(phenylene oxide) (2MPPO) have been discussed from the structure and molecular basis. Wellinghoff *et al.* showed by using ultraviolet and Fourier transform infra-red spectroscopy<sup>45</sup> that the dispersion interaction between the phenyl ring of PS and phenylene ring of 2MPPO is quite strong. This is thought to be responsible for the compatibility. However, Djordjevic *et al.*<sup>46</sup> suggest that  $\pi$ -hydrogen bond between the methyl group of 2MPPO and the phenyl ring of PS in the compatible blend (from the analysis of the solvent-induced changes in n.m.r. chemical shifts) is responsible. The above results seem to relate the specific interaction between PS and P $\alpha$ MS in the compatible blend.

## CONCLUSIONS

Several features are evident from this work, (1) the interaction parameters  $\chi_{12}$  between PS and P $\alpha$ MS depend both on temperature and concentration of the solvent  $\psi_0$ . The  $\chi_{12}$ 's extrapolated to zero solvent concentration are negative and decrease slightly with temperature increases above 40°–60°C. (2) The temperature dependence of  $\chi_{20}$  for the P $\alpha$ MS/n-BuCl system at temperature lower than 40°C is very large and complicated compared to  $\chi_{10}$  in the PS/n-BuCl system. (3) Values of  $\chi_{10}$  slightly decrease with increasing values of  $\psi_0$ , while  $\chi_{20}$  increases with increasing values of  $\psi_0$  (except at 35° and 60°C, at which temperatures  $\chi_{20}$ 's are nearly constant with  $\psi_0$ ).

## REFERENCES

- 1 Su, C. S. and Patterson, D. *Macromolecules* 1977, **10**, 708
- 2 Olabisi, O. *Macromolecules* 1981, **14**, 1549
- 3 Baranyi, G. D. and Degre, P. *Macromolecules* 1975, **8**, 316
- 4 Somani, R. H. and Shaw, M. T. *Macromolecules* 1981, **14**, 1549
- 5 Lau, S. F., Pathak, J. and Wunderlich, B. *Macromolecules* 1982, **15**, 1278
- 6 Saeki, S., Cowie, J. M. G. and McEwen, I. J. *Polymer* 1983, **24**, 60
- 7 Shultz, A. R. and Young, A. L. *Macromolecules* 1980, **13**, 663
- 8 Dunn, D. J. and Krause, S. J. *Polym. Sci. Polym. Lett. Edn.* 1974, **12**, 591
- 9 Kruse, W. A., Kirste, R. G., Haas, J., Schmitt, B. J. and Stein, D. J. *Makromol. Chem.* 1976, **177**, 1145
- 10 Jelenic, J., Kirste, R. G., Schmitt, B. J. and Schmitt-Strecker, S. *Makromol. Chem.* 1979, **180**, 2057
- 11 Ballard, D. G. H., Rayner, M. G. and Schelten, J. *Polymer* 1976, **17**, 640
- 12 Derham, K. W., Goldsbrough, J. and Gordon, M. *Pure Appl. Chem.* 1974, **38**, 97
- 13 Robard, A., Patterson, D. and Delmas, G. *Macromolecules* 1977, **10**, 706
- 14 Hsu, C. C. and Prausnitz, J. M. *Macromolecules* 1974, **7**, 320
- 15 Robard, A. and Patterson, D. *Macromolecules* 1977, **10**, 1021
- 16 Roe, R. J. and Zin, W. C. *Macromolecules* 1980, **13**, 1221
- 17 McMaster, L. P. *Macromolecules* 1973, **6**, 760
- 18 Koningsveld, R., Kleintjens, L. A. and Onclin, M. H. *J. Macromol. Sci. Phys. Edn.* 1980, **B18**, 363
- 19 Cowie, J. M. G. and Saeki, S. *Polym. Bull.* 1981, **6**, 75
- 20 Saeki, S., Narita, Y., Tsubokawa, M. and Yamaguchi, T. *Polymer* 1983, **24**, 1631
- 21 Koningsveld, R. and Stepto, R. F. T. *Macromolecules* 1977, **10**, 1166
- 22 Koningsveld, R., Kleintjens, L. A. and Schoffeleers, H. M. *Pure Appl. Chem.* 1974, **39**, 1
- 23 Suzuki, Y., Miyamoto, Y., Miyaji, H. and Asai, K. *Polym. Prepr. Jpn.* 1982, **31**(4), 791
- 24 Kwei, T. K., Nishi, T. and Roberts, R. F. *Macromolecules* 1974, **7**, 667
- 25 Goldwasser, D. J. and Williams, D. J. *Macromolecules* 1973, **6**, 353
- 26 Barlow, J. W. and Paul, D. R. *Polym. Eng. Sci.* 1981, **21**, 985
- 27 Patterson, D. and Robard, A. *Macromolecules* 1978, **11**, 690
- 28 Saeki, S., Holste, J. C. and Bonner, D. C. *J. Polym. Sci. Polym. Phys. Edn.* 1981, **19**, 307
- 29 Sauerbrey, G. *Z. Z. Phys.* 1959, **155**, 206
- 30 Bonner, D. C. and Prausnitz, J. M. *J. Polym. Sci. Polym. Phys. Edn.* 1974, **12**, 51
- 31 Reid, R., Prausnitz, J. M. and Sherwood, E. K. in 'The Properties of Gases and Liquids', McGraw-Hill, New York, 1977
- 32 Flory, P. J. in 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, USA, 1953
- 33 Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 1833
- 34 Patterson, D. *J. Polym. Sci. (C)* 1968, **16**, 3379
- 35 Cowie, J. M. G. and McEwen, I. J. *Polymer* 1975, **16**, 244
- 36 Cowie, J. M. G. and Toporowski, P. M. *J. Macromol. Sci. (B)* 1969, **3**, 81
- 37 Hocker, H., Blake, G. J. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2251
- 38 Saeki, S., Holste, J. C. and Bonner, D. C. *J. Polym. Sci. Polym. Phys. Edn.* 1982, **20**, 793, 805
- 39 Kambour, R. P., Romagosa, E. E. and Cruner, C. L. *Macromolecules* 1972, **5**, 335
- 40 Jenckel, F. and Heusch, R. *Kolloid-Z.* 1953, **130**, 89
- 41 Adachi, K., Fujihara, I. and Ishida, Y. *J. Polym. Sci. Polym. Phys. Edn.* 1975, **13**, 2155
- 42 Lesikar, A. V. *Physics Chem. Glasses* 1975, **16**, 83
- 43 Van Krevelen, D. W. and Hoftyzer, P. J. in 'Properties of Polymers', Elsevier, Amsterdam, 1972, Ch. 7
- 44 Saeki, S., Holste, J. C. and Bonner, D. C. *J. Polym. Sci. Polym. Phys. Edn.* 1983, **21**, 2049
- 45 Wellinhoff, S. T., Koenig, J. L. and Baker, E. J. *Polym. Sci. Polym. Phys. Edn.* 1977, **15**, 1913
- 46 Djordjevic, M. and Porter, R. S. *Polym. Eng. Sci.* 1983, **23**, 650