The glass transition temperature of polymer–diluent systems

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The theoretical treatment proposed by Couchman to describe the compositional dependence of T_g for polymer–diluent systems has been applied, in its several forms, to selected pairs for which heat capacity data are found in the literature. The most accurate equation gives the least satisfactory description of the experimental T_g data. This result seems to be accounted for by the assumption, first suggested by Couchman, that in some cases the entropy of mixing is not continuous at T_g.

(**Keywords: glass transition; polymer–diluent system; heat capacity increment; entropy of mixing**)

INTRODUCTION

The glass transition of polymeric systems has been explored in a very large number of papers: more than 10 000 citations in the past 20 years have been collected by McKenna[1], under the keyword 'polymer glasses'. A proportionate number are devoted to the glass transition of polymer–diluent mixtures, a subject related to the plasticization of polymeric systems, as well as to the theory of the glass transition itself. When the subject is scrutinized closely, one finds, from the experimental point of view, that only a few systems have been explored over the full range of composition, and, from the theoretical point of view, not only that there are scores of rather different treatments that can be applied to the experimental data with 'reasonable' results[2–24], but also that they are often applied making use of one or more adjustable parameters in the comparison with experimental data. The basic physical parameters that enter in some theoretical equations are either 'free volumes' and the related temperature coefficients, known to be rather poorly defined, or heat capacity data of the components of the mixture. Very seldom are these data directly available. In the present paper, which is intended as a tentative clarification of some peculiarities of the problem, after a concise review of the theoretical equations previously obtained by Couchman *et al.*[10–17], a comparison will be presented between such a theory and experimental data pertaining to the very rare series of polymer and diluent mixtures for which relatively accurate heat capacity data in the pure state are available over a large range of temperature.

THEORETICAL TREATMENT

In the treatment of Couchman[10–17], the solutions are taken as 'regular', i.e. solutions in which specific interactions are absent and the entropy of mixing is approximately the same as that of ideal solutions. In fact, the regular solution concept is based upon the concept of maximum randomness, so that, at a fixed composition, the entropy of mixing, which should include all entropy changes due to mixing, is simply configurational, or combinatorial, and so continuous at T_g.

If the glass transition is treated as an Ehrenfest second-order transition, and if S^l and S^g are the entropy of the liquid and glass respectively (expressed in J mol^{-1} K^{-1}), in a solution where the molar fraction of solvent is x_1, one has therefore at T_g:

$$S^l(T_g, x_1) = S^g(T_g, x_1) \tag{1}$$

Since:

$$S^l(T, x_1) = x_1 S_1^l(T) + x_2 S_2^l(T) + \Delta S_m^l \tag{2a}$$

$$S^g(T, x_1) = x_1 S_1^g(T) + x_2 S_2^g(T) + \Delta S_m^g \tag{2b}$$

(where S_i^l and S_i^g are the liquid and glassy entropies of pure components, while ΔS_m^l and ΔS_m^g are the liquid and glassy entropies of mixing), one obtains:

$$S^l(T, x_1) = x_1\left(S_1^{0l} + \int_{T_{g1}}^{T} C_{p1}^l(T)\,\mathrm{d}\ln T\right) + x_2\left(S_2^{0l} + \int_{T_{g2}}^{T} C_{p2}^l(T)\,\mathrm{d}\ln T\right) + \Delta S_m^l \tag{3a}$$

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$$S^g(T,x_1)=x_1\left(S_1^{0g}+\int_{T_{g1}}^{T}C_{p1}^g(T)\,\mathrm{d}\ln T\right)+x_2\left(S_2^{0g}+\int_{T_{g2}}^{T}C_{p2}^g(T)\,\mathrm{d}\ln T\right)+\Delta S_m^g \tag{3b}$$

where S_i^{0l} and S_i^{0g} are the molar entropies at the respective T_{gi} of the pure components, and $C_{pi}^l(T)$ and $C_{pi}^g(T)$ the corresponding molar heat capacity functions. At the glass transition of the solution:

$$x_1\left(S_1^{0l}+\int_{T_{g1}}^{T_g}C_{p1}^l(T)\,\mathrm{d}\ln T\right)+x_2\left(S_2^{0l}+\int_{T_{g2}}^{T_g}C_{p2}^l(T)\,\mathrm{d}\ln T\right)+\Delta S_m^l$$
$$=x_1\left(S_1^{0g}+\int_{T_{g1}}^{T_g}C_{p1}^g(T)\,\mathrm{d}\ln T\right)+x_2\left(S_2^{0g}+\int_{T_{g2}}^{T_g}C_{p2}^g(T)\,\mathrm{d}\ln T\right)+\Delta S_m^g \tag{4}$$

which becomes:

$$x_1\int_{T_{g1}}^{T_g}\Delta C_{p1}(T)\mathrm{d}\ln T+x_2\int_{T_{g2}}^{T_g}\Delta C_{p2}(T)\mathrm{d}\ln T+\Delta S_m^l-\Delta S_m^g=0 \tag{5}$$

where ΔC_{p1} and ΔC_{p2} are the molar pure component heat capacity increments ($\Delta C_{pi}=C_{pi}^l-C_{pi}^g$).

According to Couchman, if ΔS_m is continuous at T_g, equation (5) reduces to:

$$x_1\int_{T_{g1}}^{T_g}\Delta C_{p1}(T)\mathrm{d}\ln T+x_2\int_{T_{g2}}^{T_g}\Delta C_{p2}(T)\mathrm{d}\ln T=0 \tag{6}$$

Equation (1) can also be written in terms of weight fractions w_i, so that it becomes:

$$s^l(T_g,w_1)=s^g(T_g,w_1) \tag{1'}$$

where s is the entropy expressed in J g^{-1} K^{-1}. All the above equations can also be written using the specific heat increments Δc_{pi} and the weight fractions w_i. Particularly equation (6) becomes:

$$w_1\int_{T_{g1}}^{T_g}\Delta c_{p1}(T)\mathrm{d}\ln T+w_2\int_{T_{g2}}^{T_g}\Delta c_{p2}(T)\mathrm{d}\ln T=0 \tag{6'}$$

From equation (6′) by assuming various functional dependences of the specific heat on T, various equations can be derived. The zeroth-order approximation, $\Delta c_{pi}=\text{constant}=\Delta c_{pi}(T_{gi})$, gives, from equation (6′):

$$\ln T_g=\frac{w_1\Delta c_{p1}\ln T_{g1}+w_2\Delta c_{p2}\ln T_{g2}}{w_1\Delta c_{p1}+w_2\Delta c_{p2}} \tag{7}$$

an equation that has been used extensively[10–17,25–28] with reasonable results. A better approximation to the real temperature dependence of Δc_{pi} is, however[16–18]:

$$\Delta c_{pi}=\text{constant}/T=\Delta c_{pi}(T_{gi})T_{gi}/T \tag{8}$$

from which one obtains:

$$T_g=\frac{w_1\Delta c_{p1}T_{g1}+w_2\Delta c_{p2}T_{g2}}{w_1\Delta c_{p1}+w_2\Delta c_{p2}} \tag{9}$$

The functional dependence of Δc_{pi} on T that appears to be the most correct from a physical point of view, since c_{pi} is known[29–38] to be approximately linearly dependent on T both just below and above T_{gi}, is:

$$\Delta c_{pi}=a_i+b_iT \tag{10}$$

After substitution in equation (6′), one obtains the following transcendental implicit equation:

$$w_1[a_1\ln(T_g/T_{g1})+b_1(T_g-T_{g1})]+w_2[a_2\ln(T_g/T_{g2})+b_2(T_g-T_{g2})]=0 \tag{11}$$

COMPARISON WITH EXPERIMENTAL DATA

As pointed out, the fundamental equation of Couchman's treatment, equation (5), with the assumption $\Delta S_m^l=\Delta S_m^g$, gives equation (6) and, in terms of weight fractions equation (6′), which can then be transformed into the explicit equations (7) and (9) or the implicit equation (11), which correspond respectively to different functional dependences of Δc_{pi} on temperature.

A test of the applicability of the above fundamental equations therefore requires knowledge of the relations between Δc_{pi} and T in the range of temperature from T_{g1} to T_{g2}, for both components of the mixture (1 = diluent, 2 = polymer). As far as the Δc_{p2} data are concerned, it is known that recently Wunderlich *et al.*[29–37] have published extensive data on the $c_p(T)$ function for a variety of polymers. On the contrary, $c_p(T)$ data for diluents are rare, but some are available for typical 'plasticizers' such as tricresyl phosphate (TTP)[39], dimethyl phthalate (DMP)[40], diethyl phthalate[41], dibutyl phthalate[42] and di-2-ethylhexyl phthalate[42].

The polymer–diluent system (bisphenol-A polycarbonate)–tricresyl phosphate (PC–TTP) appears to be suitable for the purpose of the present work, having being studied by Onu *et al.*[43], who determined the T_g of the system over the full range of composition, i.e. from about 420 K to about 220 K.

The $c_p(T)$ data for PC are found in Wunderlich's paper[37]. To obtain a reasonable $\Delta c_{p2}(T)$ function, one has to extrapolate linearly below T_{g2} the liquid polycarbonate $c_p^l(T)$ data. The resulting $\Delta c_{p2}(T)$ is given by the linear equation:

$$\Delta c_{p2}(T)=0.929-1.75\times10^{-3}T\ \ \mathrm{J\,g^{-1}\,K^{-1}}$$

This equation should be applicable between T_{g1} and T_{g2}, unless fundamental thermodynamic reasons are invoked to limit its validity below a characteristic temperature T_0 (refs 44–46). This argument will be the subject of a future paper.

To obtain $\Delta c_{p1}(T)$ for the diluent TTP (experimental $c_p(T)$ data from Ovchinnikov *et al.*[39]), one has to make two extrapolations, one based on the linearity of the $c_p^g(T)$ data in the range 100–200 K, and the second on the good linearity of the $c_p^l(T)$ data up to 320 K. The result is given by:

$$\Delta c_{p1}(T)=0.677-1.23\times10^{-3}T\ \mathrm{J\,g^{-1}\,K^{-1}}$$

which again should be applicable without restraints from T_{g1} to T_{g2}.

An understanding of the physical meaning of the above

Δc_{pi} data, as compared with the usual approximations Δc_{pi} = constant and Δc_{pi} = constant/T, can be achieved from the plot of the above relations, shown in *Figure 1*. It is seen that, for both polymer and diluent, the approximate equation Δc_{pi} = constant should not be considered acceptable; the approximation Δc_{pi} = constant/T appears reasonable for the diluent, but not for the polymer.

In order to evaluate the applicability of Couchman's fundamental treatment and of the relative equations, the T_g data of Onu *et al.* for the PC–TTP system are now compared in *Figure 2* with:

(a) the explicit T_g vs. w_1 function given by equation (7), corresponding to the zeroth approximation Δc_{pi} = constant;

(b) the explicit T_g vs. w_1 function given by equation (9), corresponding to the approximation Δc_{pi} = constant/T;

(c) the implicit equation (11), applied with the method of successive approximations, with Δc_{pi} given by equation (10), where the numerical data are those obtained from experimental $c_{pi}(T)$ data through suitable extrapolations, as described above.

The unexpected result of the comparison is that the implicit equation (11), in which use is made of the Δc_{pi} functions obtained from experiments, is clearly the farthest away from the experimental T_g vs. w_1 data, whereas a reasonable description of the latter is given by the zeroth approximation, equation (7), the intermediate curve being that given by the approximation Δc_{pi} = constant/T, equation (9). To make the differences more visible, the differences ΔT_g between the forecast of equations (11) and (9) and that of equation (7), taken as a reference, are shown inserted in the figure. The maximum deviations, about 27 and 16 K respectively, seem to be much larger than any kind of experimental error.

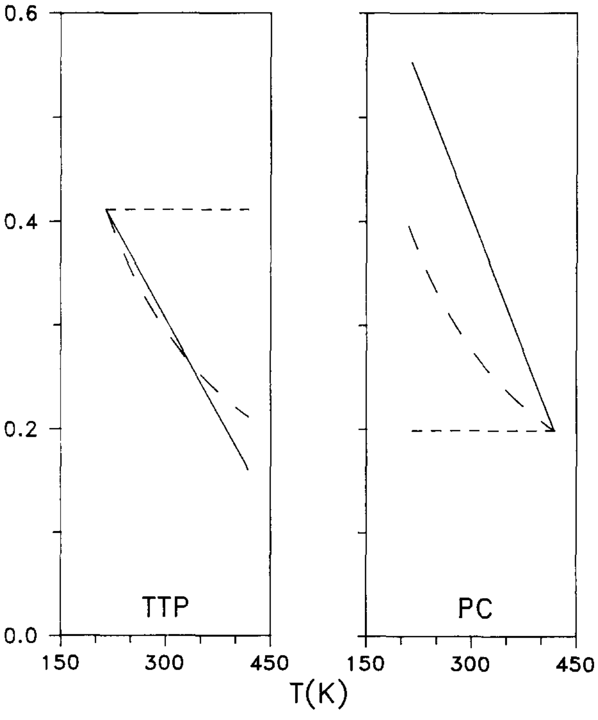

Figure 1 The function $\Delta c_{pi}(T)$ for polycarbonate and tricresyl phosphate obtained by linear extrapolations from experimental data (full line), and given by the approximation Δc_{pi} = constant/T (long broken curve) and the zeroth approximation Δc_{pi} = constant (short broken line)

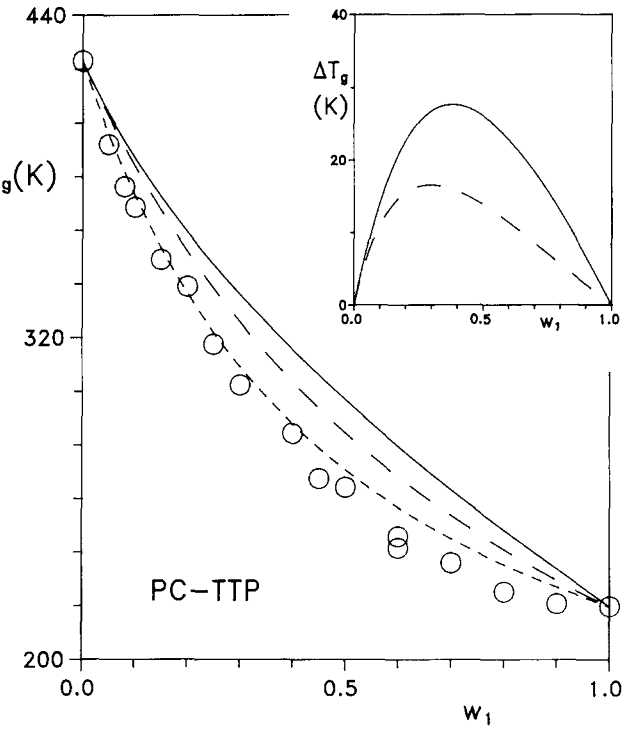

Figure 2 Experimental T_g data for the polycarbonate–tricresyl phosphate system from Onu *et al.*[43], as a function of diluent weight fraction w_1 (○), compared with the theoretical curves predicted by equation (7) (short broken curve), equation (9) (long broken curve) and equation (11) (full curve). In the insert the differences ΔT_g between the forecast of equations (9) and (11) and that of equation (7), taken as reference, are also shown

To confirm the above unexpected results, a second polymer–diluent system was investigated. The data plotted in *Figure 3* refer to the polystyrene–tricresyl phosphate pair[47] (PS–TTP). At low temperatures, two glass transitions are found, so that only the experimental data in the range of composition where the system is homogeneous, i.e. from T_{g2} down to about 300 K, are available for the present analysis.

The c_p data for PS, taken from ref. 33, give:

$$\Delta c_{p2}(T) = 1.036 - 1.96 \times 10^{-3} T \text{ J g}^{-1} \text{ K}^{-1}$$

In *Figure 3* it has to be noted that the experimental data are again rather close to the forecast of the zeroth approximation, equation (7), rather than to that of the correct equation (11). It is interesting to note that the latter is close to the curve relative to equation (9), as clearly seen in the insert of *Figure 3*, since for both polymer and diluent the approximation Δc_{pi} = constant/T is quite close to the linear one (equation (10)).

The data plotted in *Figure 4* refer to the third polymer–diluent pair investigated, i.e. to the poly(vinyl chloride)–dimethyl phthalate system (PVC–DMP) (experimental data from Scandola *et al.*[25]). As far as the PVC c_p data are concerned, they are given with good accuracy only for the glassy state. It is known in fact that, above T_g, the calorimetric measurements are strongly influenced by fusion and crystallization processes[48]. It seems reasonable to assume for Δc_{p2} the general equation suggested by Van Krevelen[38,49]:

$$\Delta c_p(T) = \Delta c_p(T_g) - 1.87 \times 10^{-3}(T - T_g) \text{ J g}^{-1} \text{ K}^{-1}$$

where $\Delta c_{p2}(T_{g2}) = 0.31$ J g^{-1} K^{-1} (ref. 35).

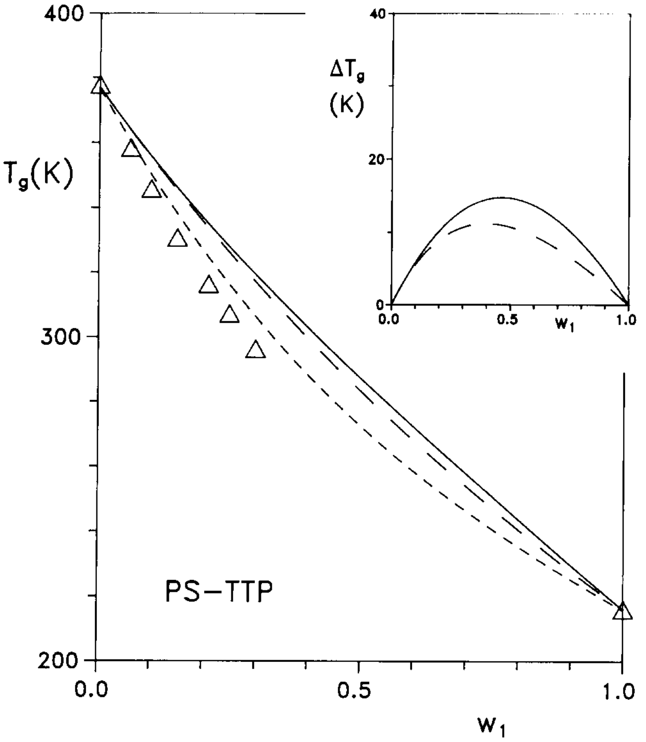

Figure 3 Experimental T_g data for the polystyrene–tricresyl phosphate system from Pizzoli *et al.*[47], as a function of diluent weight fraction w_1 (△), compared with the theoretical curves predicted by equation (7) (short broken curve), equation (9) (long broken curve) and equation (11) (full curve). In the insert the differences ΔT_g between the forecast of equations (9) and (11) and that of equation (7), taken as reference, are also shown

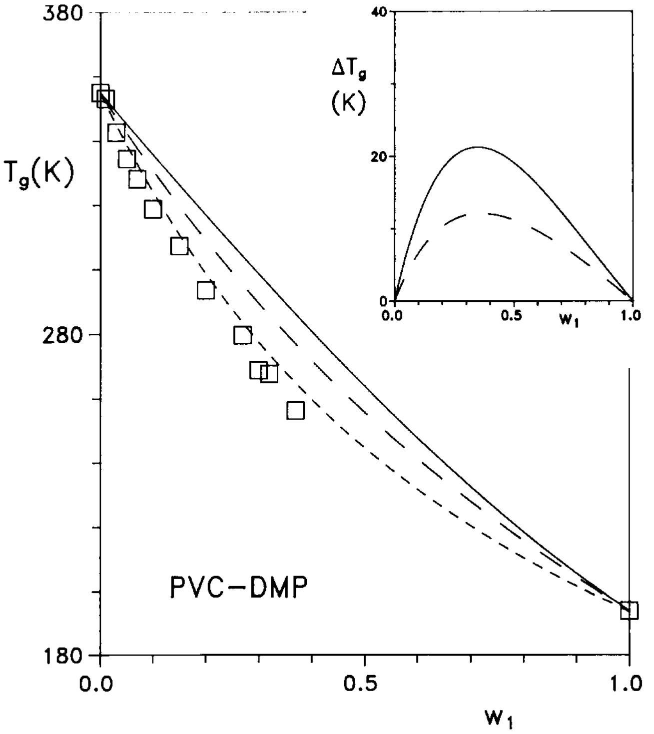

Figure 4 Experimental T_g data for the poly(vinyl chloride)–dimethyl phthalate system from Scandola *et al.*[25], as a function of diluent weight fraction w_1 (□), compared with the theoretical curves predicted by equation (7) (short broken curve), equation (9) (long broken curve) and equation (12) (full curve). In the insert the differences ΔT_g between the forecast of equations (9) and (11) and that of equation (7), taken as reference, are also shown

Specific heat data for the diluent are known for the liquid state above 270 K, as well as for the amorphous phase up to T_{g1} (ref. 40). The Δc_{p1} value at T_{g1}, measured by Scandola *et al.*[25], was found to be 0.50 J g^{-1} K^{-1}, which is about 20% higher than that obtainable from a linear extrapolation, down to T_{g1}, of the liquid c_p^l data. The reasonable choice for the $\Delta c_{p1}(T)$ function appears to be that of accepting the numerical value of 0.50 J g^{-1} K^{-1} at T_{g1}, and of interpolating the liquid DMP specific heat data with a second-degree polynomial, since a similar $c_p^l(T)$ function has been found for other phthalates[41,42]. As far as the glassy DMP specific heat is concerned, the extrapolation carried out is a linear one, and the result is:

$$\Delta c_{p1}(T) = 1.432 - 6.043 \times 10^{-3}T + 6.257 \times 10^{-6}T^2 \quad \text{J g}^{-1}\,\text{K}^{-1}$$

When use is made of the polynomial:

$$\Delta c_{p1} = a_1 + b_1 T + c_1 T^2$$

together with the linear equation:

$$\Delta c_{p2} = a_2 + b_2 T$$

one obtains from equation (6′) the new implicit equation:

$$w_1[a_1 \ln(T_g/T_{g1}) + b_1(T_g - T_{g1}) + \tfrac{1}{2}c_1(T_g^2 - T_{g1}^2)] + w_2[a_2 \ln(T_g/T_{g2}) + b_2(T_g - T_{g2})] = 0 \quad (12)$$

The comparison with experimental data is shown in *Figure 4*, and again one finds that the zeroth approximation, equation (7), is the closest to them, whereas equation (12) is the farthest away.

The above equations have been applied also to a polymer–polymer system, i.e. to the poly(2,6-dimethyl-1,4-phenylene oxide)–polystyrene (PPO–PS) pair, for which T_g data have been published by Fried *et al.*[50]. It is important to note that the extrapolation of the $c_p(T)$ data has to be carried out over a relatively narrow temperature range, so that its reliability should be high. The c_p data for PPO, taken from refs 33 and 51, give:

$$\Delta c_{p2}(T) = 0.978 - 1.58 \times 10^{-3}T \text{ J g}^{-1}\,\text{K}^{-1}$$

(In this case the assumption is: 1 = PS, 2 = PPO.) The corresponding $\Delta c_{p1}(T)$ data for PS are those previously obtained.

Comparison of equation (11) with experimental data is seen in *Figure 5*, and the results show again that equation (11) is far from being satisfactory, even though the differences are smaller than for the polymer–diluent mixtures described above.

DISCUSSION

It has been shown, for three different polymer–diluent systems, as well as for a polymer–polymer mixture, for which $c_p(T)$ data are available, that the fundamental equation of Couchman, equation (11), appears less apt to describe the T_g–composition data than the rather approximate equation (7).

In principle, there could be experimental errors in the measurements of T_g, carried out, as usual, by differential scanning calorimetry. In the above analysis, T_g data have been obtained by the so-called 'onset' method[52] (except for the PPO–PS blend, for which the temperature at half-height has been measured), a method known to give data close to the definition of T_g based on volumetric measurements. Other sources of errors are the possible

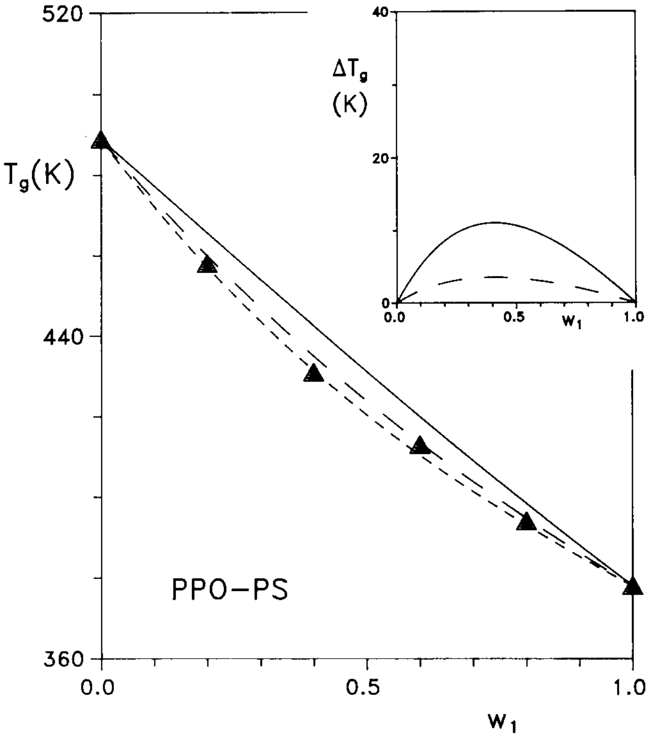

Figure 5 Experimental T_g data for the poly(2,6-dimethyl-1,4-phenylene oxide)–polystyrene system from Fried *et al.*[50], as a function of polystyrene weight fraction w_1 (▲), compared with the theoretical curves predicted by equation (7) (short broken curve), equation (9) (long broken curve) and equation (11) (full curve). In the insert the differences ΔT_g between the forecast of equations (9) and (11) and that of equation (7), taken as reference, are also shown

presence of two glass transitions at intermediate compositions or at low temperatures[27,47,53] and the appearance of a singularity, i.e. a 'cusp' in the T_g vs. w_1 curve, at a characteristic temperature below which the analytical T_g vs. w_1 function has been predicted to change form[4–6,54,55]. To avoid such problems, in the present work only the experimental data belonging to the upper, left-hand part of the T_g vs. w_1 curve have been used in the comparison with theory (see the PS–TTP and PVC–DMP systems in *Figures 3* and *4*).

As suggested by Couchman[10], when it is found that the experimental data are not described satisfactorily by the theory, one should take into consideration the possibility that the entropy of mixing Δs_m may not be continuous at T_g, in which case equations (11) and (12) have to be replaced by:

$$\begin{aligned} w_1[a_1 \ln(T_g/T_{g1}) + b_1(T_g - T_{g1})] \\ + w_2[a_2 \ln(T_g/T_{g2}) + b_2(T_g - T_{g2})] \\ + (\Delta s^l_m - \Delta s^g_m) = 0 \end{aligned} \quad (13)$$

$$\begin{aligned} w_1[a_1 \ln(T_g/T_{g1}) + b_1(T_g - T_{g1}) + \tfrac{1}{2}c_1(T_g^2 - T_{g1}^2)] \\ + w_2[a_2 \ln(T_g/T_{g2}) + b_2(T_g - T_{g2})] \\ + (\Delta s^l_m - \Delta s^g_m) = 0 \end{aligned} \quad (14)$$

The values of $(\Delta s^l_m - \Delta s^g_m)$ at the glass transition temperature of the mixtures, calculated from the above equations and making use of the experimental T_g data, are plotted in *Figure 6*, as a function of weight fraction of component 1, for the four systems investigated here. It is seen that the differences of entropy of mixing so calculated are all positive, and that their maximum values are about 5×10^{-2} J g^{-1} K^{-1} for the polymer–diluent solutions and about 7×10^{-3} J g^{-1} K^{-1} for the polymeric blend.

If the above results are taken as physically meaningful, one is led to the conclusion that the entropy of mixing is not exclusively combinatorial, but originates in part from specific interactions, so that the solutions are not regular and non-random mixing plays a role[12] in the systems investigated here. Infra-red studies of poly(vinyl chloride) plasticized with dibutyl phthalate (DBP), a diluent very similar to dimethyl phthalate, seem to be indicative of the presence of molecular interactions between mainly the α hydrogens of PVC and the carbonyl groups of DBP[56]. Regarding the PPO–PS blend, there is some evidence of phenyl-group coupling and interactions between the methyl groups and the phenyl rings[57]. Similar specific interactions are likely to occur in PC–TTP and PS–TTP systems.

The problem of continuity of the entropy of mixing at the glass transition temperature has been discussed by Goldstein[58], who emphasized the fact that 'the assumption of continuity of Δs_m at T_g implies that T_g must coincide with the temperature T'_c at which the two lines $(w_1 s^l_1 + w_2 s^l_2)$ and $(w_1 s^g_1 + w_2 s^g_2)$ cross. It is obvious that T_c is the temperature calculated according to equation (6′), by assuming the functional dependences of the specific heat on T suggested above (equation (8) or, most correctly, equation (10)). If the experimental T_g differs from the calculated T_c, the difference $(\Delta s^l_m - \Delta s^g_m)$, which, as pointed out above, cannot be zero, at the glass transition temperature of the mixture is numerically equal to the difference between the glassy and liquid entropies of the unmixed system. A schematic representation is given in *Figures 7a* and *7b*. If T_c is higher than the experimental T_g, as we found for the systems investigated here, the difference $(\Delta s^l_m - \Delta s^g_m)$ is positive (see *Figure 7a*); on the contrary, if T_c is lower than T_g, then $(\Delta s^l_m - \Delta s^g_m)$ is negative, as shown in *Figure 7b*.

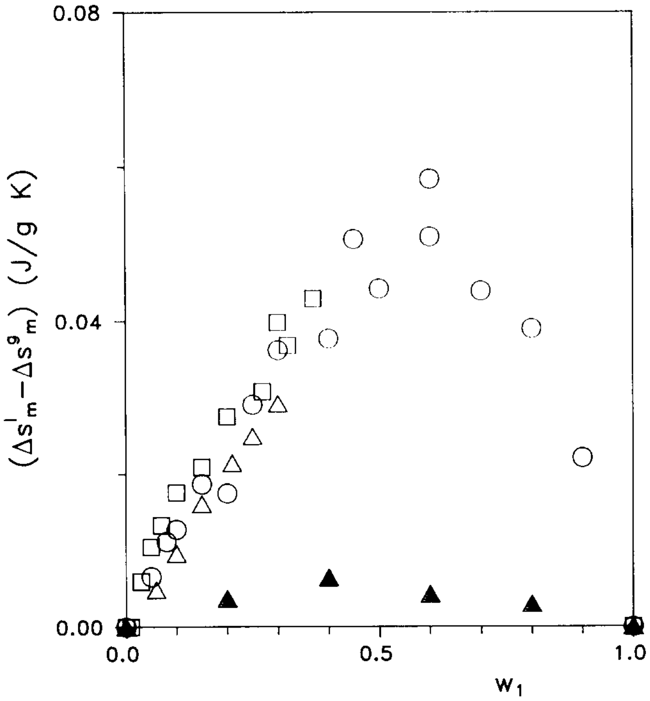

Figure 6 Difference $(\Delta s^l_m - \Delta s^g_m)$ calculated, as described in the text, at the T_g of the mixtures, as a function of weight fraction w_1: (○) PC–TTP; (△) PS–TTP; (□) PVC–DMP; (▲) PPO–PS

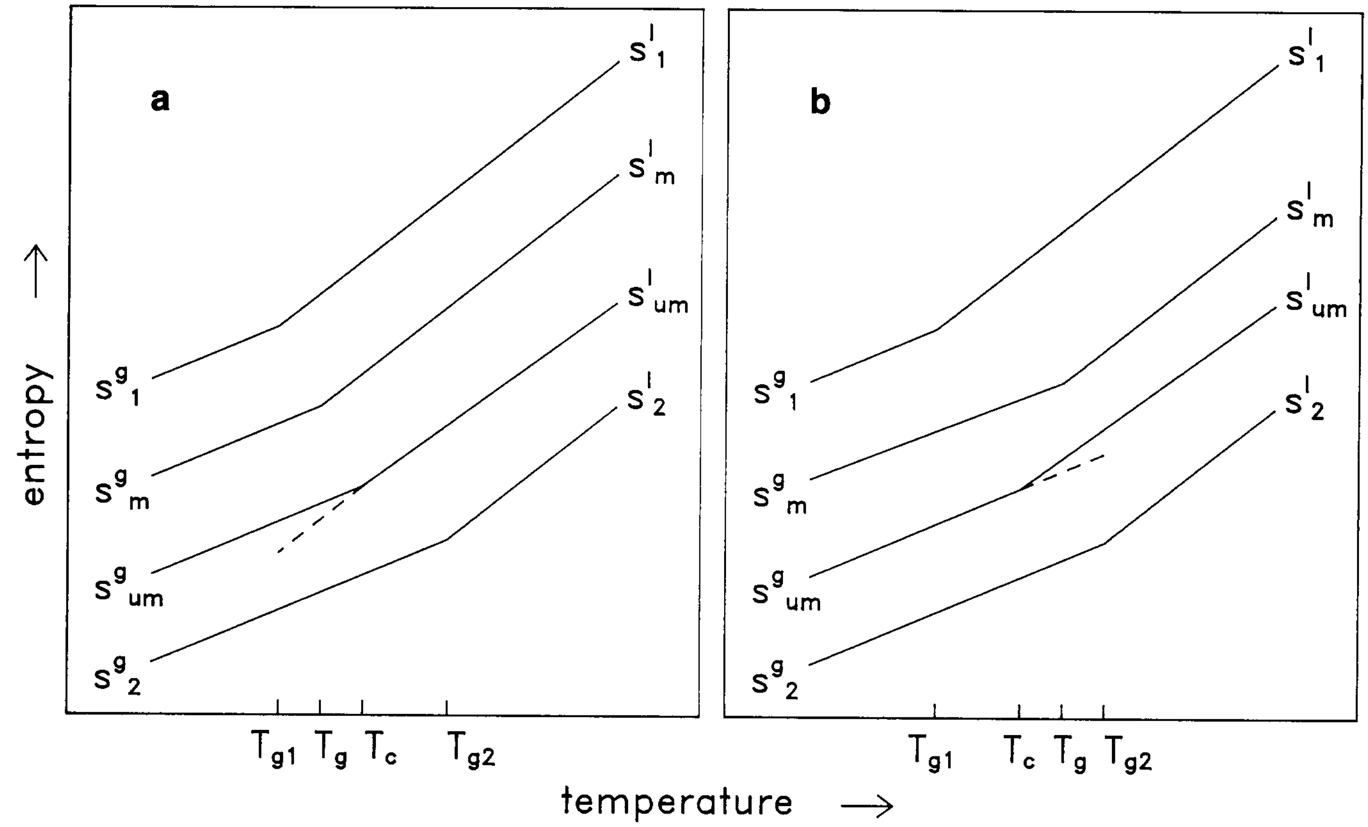

Figure 7 Schematic plots of: s^g_1 and s^l_1, glassy and liquid entropies of pure component 1 (lines crossing at T_{g1}); s^g_2 and s^l_2, glassy and liquid entropies of pure component 2 (lines crossing at T_{g2}); s^g_{um} and s^l_{um}, glassy and liquid entropies of the unmixed system, i.e. $(w_1 s^g_1 + w_2 s^g_2)$ and $(w_1 s^l_1 + w_2 s^l_2)$ (lines crossing at T_c); s^g_m and s^l_m, glassy and liquid entropies of the mixed system (lines crossing at T_g). In (a) $T_c > T_g$, whereas in (b) $T_c < T_g$

CONCLUSION

For the polymer–diluent systems examined, and for the PPO–PS polymeric blend, for which experimental $c_p(T)$ data are available, it has been shown that the zeroth approximation, equation (7), of the treatment proposed by Couchman describes the experimental compositional dependence of T_g better than the accurate equation (11). If one assumes the latter to be correct, from the experimental T_g–composition data one obtains values of the difference between the entropy of mixing in the liquid and glassy state $(\Delta s^l_m - \Delta s^g_m)$ that are not zero. As a consequence, one is led to the conclusion that for the systems investigated here, the entropy of mixing is not exclusively combinatorial, but originates in part from specific interactions, the solutions are not regular and non-random mixing plays a role.

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