

# polymer review

## Glass transition behaviour of compatible polymer blends

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It is shown that compatible polymer blends exhibit specific glass transition–composition behaviour, reflected in deviations from the Gordon–Taylor equation for supposed volume additivity of the blend components. Besides the intensity of the interchain interaction, conformational redistributions in the neighbourhood of the hetero-contacts are mainly responsible for the  $T_g$  behaviour of compatible polymer blends. Chain orientation due to the hetero-contact interaction is responsible for interchain stiffening, accompanied by an increase in the  $T_g$  temperature. The stronger the hetero-interchain interaction, the more likely it is that there will be an orientation effect. Decrease of the molecular weight of the stiffer blend component acts in the same way. Since it is then more mobile, the accommodation with the mobile blend component will be improved, resulting also in a closer packing of the blend components. Compensation for hetero-interaction and chain orientation effects may be responsible for the apparent volume additivity behaviour reflected by the Gordon–Taylor equation.

(Keywords: blends; glass transition; compatibility)

### INTRODUCTION AND THEORY

The Gordon–Taylor equation<sup>1</sup> was proposed to predict the second-order transition temperature of binary random copolymers from the respective temperatures of the homopolymers, their volume fractions and their coefficients of expansion in the glassy and rubbery states. Ideal volume additivity was assumed for the repeat units in the copolymer. The equation was subsequently used in the form:

$$T_g = (w_1 T_{g1} + K w_2 T_{g2}) / (w_1 + K w_2) \quad (1)$$

to explain the composition dependence of the glass transition temperature  $T_g$ , of binary compatible polymer blends, where  $w_i$  is the weight fraction and  $T_{gi}$  the glass transition temperature of the blend component  $i$  and  $K$  is supposed to be an arbitrary fitted parameter.

The original equation was derived assuming volume additivity, and  $K$  is defined as the ratio of the differences of the coefficients of expansion,  $\Delta\alpha$ , at  $T_g$  of the glassy (G) and rubbery (L) states.

Applied to blends the condition of volume additivity implies also the additivity of the fractional free volumes<sup>2,3</sup>. If weight fractions are used instead of volume fractions, the constant  $K$  includes in addition the ratio of their respective densities,  $\rho_i$  (ref. 4):

$$K = \rho_1 \Delta\alpha_2 / \rho_2 \Delta\alpha_1 \quad (2)$$

where  $\Delta\alpha_i = (\alpha_L - \alpha_G)_i$ .

Taking into account the general lack of exact expansion and density data in the  $T_g$  range, it was assumed that the  $K$  parameter for volume additivity can be expressed by:

$$K = K'(T_{g1}/T_{g2}) \quad (2a)$$

assuming the validity of the Simha–Boyer rule<sup>5</sup>,  $\Delta\alpha T_g = 0.113$  ('0.113' being a 'universal' constant). Considering the very similar densities of most polymers, the coefficient  $K' = \rho_1/\rho_2$  can for simplicity be admitted equal to unity. It has been shown that under these conditions the Gordon–Taylor equation transforms to the much simpler Fox relation<sup>6</sup>, and this can be considered an 'ideal' volume additivity equation for the  $T_g$  of compatible polymer blends.

Using values of the coefficient  $K' \neq 1$ , the parameter  $K$  becomes a fitting parameter of the Gordon–Taylor equation.

There have been various attempts to derive thermodynamic support for the Gordon–Taylor equation, assuming continuity at  $T_g$  of the extensive thermodynamic functions and of the excess functions of mixing<sup>7,8</sup>. It has been shown that, depending on the selected thermodynamic extensive function, the constant  $K$  is connected with the ratio either of the differences of the coefficients of expansion or of the heat capacities in the rubbery and glassy states. The kinetic nature of the glass transition state is, however, neglected. Contradictions related with this thermodynamic approach are discussed by Goldstein<sup>9</sup>.

Simultaneous with Gordon and Taylor's derivation of their equation, Jenckel and Heusch<sup>10</sup> suggested the expression:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + w_1 w_2 b (T_{g2} - T_{g1}) \quad (3)$$

to explain the lowering of the  $T_g$  of polymers by plasticizers. The constant  $b$  in the concentration cross-term characterizes the solvent quality of the plasticizer, i.e. the interaction between polymer and plasticizer. Saeki *et al.*<sup>11</sup> have used this expression to explain the  $T_g$  behaviour of polystyrene/poly( $\alpha$ -methylstyrene) blends, because of the failure of the Gordon–Taylor equation.

Later a quadratic concentration correction term ( $qw_1w_2$ ) was also added by Kwei<sup>12</sup> to the Gordon-Taylor equation to account for specific interactions between the blend components. Thermodynamic support for the quadratic concentration term was given by Kanig<sup>13</sup>.

Assuming the polymer melt above  $T_g$  to be a saturated mixture of polymer chains and holes (the 'overall free volume') in thermodynamic equilibrium, the interaction energy is directly related to the contact surface between the polymer segments. Holes inserted between polymer segments suppress, in a first approximation, this segmental interaction. The overall free volume is composed of the specific vibration free volume and the specific hole volume. Only the latter contributes to the segment separation and is frozen at  $T_g$ . Both molecular-weight and composition dependences of  $T_g$  can be explained using these assumptions.

The final equation derived by Kanig for the  $T_g$  of polymer blends is of the form<sup>13</sup>:

$$\frac{T_{g2} - T_g}{\Phi_{f1}} = \frac{\Psi_v^2(2A_{12} - A_{11}A_{22})}{R(\ln \Psi_h + \Psi_v)} \Phi_{f1} - \frac{\Psi_v^2 2(A_{22} - A_{12})}{R(\ln \Psi_h + \Psi_v)} \quad (4)$$

where  $\Psi_h$  is the fraction of holes at  $T_g$  (about 0.64 of the overall free volume),  $\Psi_v$  is the fraction of specific vibration free volume at  $T_g$  (about 0.36) and  $\Phi_{f1}$  is the fraction of specific vibration free volume appertaining to component 1. The latter is related to the corrected weight fraction of the components, taking into account the different coefficients of expansion:

$$\Phi_{f1} = [N_1 \Psi_v / (N_1 \Psi_v + N_2 \Psi_h)] = w_1 / (w_1 + Kw_2) \quad (5)$$

Finally, in equation (4),  $A$  are material-specific constants, representing the standard Gibbs free energy for generating one mole of holes in the equilibrium polymer melt. For pure components, these constants are related to the corresponding molecular-weight-independent  $T_{g\infty}$  of the high-molecular-weight polymer:

$$A = -\frac{R(\ln \Psi_h + \Psi_v)}{\Psi_v^2} T_{g\infty} = 0.664RT_{g\infty} \quad (6)$$

For  $A_{12} = \frac{1}{2}(A_{11} + A_{22})$ , the Kanig equation transforms into the Gordon-Taylor equation. The quadratic concentration term is thus related to the specific interaction between the blend components, i.e. with deviations from additivity of the interaction between the two blend components.

A third-power equation for the composition dependence of the  $T_g$  of polymer blends is obtained, if it is assumed that the binary contact interaction influences both conformation and 'free-volume' distribution in the polymer blend<sup>4</sup>:

$$\frac{T_g - T_{g1}}{T_{g2} - T_{g1}} = (1 + K_1)w_{2c} - (K_1 + K_2)w_{2c}^2 + K_2w_{2c}^3 \quad (7)$$

where  $w_{2c} = Kw_2 / (w_1 + Kw_2)$  represents the corrected weight fraction of component 2 (with the higher glass transition temperature  $T_{g2}$ ), assuming volume additivity for the blend components.  $K_1$  is essentially related to the differences between the shares of the interaction energies  $E_{ij}$  of hetero- and homo-contacts to be overcome at  $T_g$  to allow the characteristic conformational mobilities in the polymer melt. In addition it includes the energetic perturbations in the molecular surroundings of the binary

contacts:

$$K_1 = [(2E_{12} - E_{11} - E_{22}) + (2e_{12-1} - e_{11-1} - e_{22-1}) + (e_{11-2} - e_{11-1}) + (e_{22-1} - e_{22-2})] / (T_{g2} - T_{g1}) = K_1^* / (T_{g1} - T_{g2}) \quad (8)$$

where  $e_{ij-k}$  is the energetic perturbation in the molecular surrounding  $k$  ( $k=i$  or  $k=j$ ) of the binary contact  $ij$ . The first two terms consider the energetic interactions of the blend component in the environment of the pure component 1 only; the last two terms account for the substitution of one component by the second one in the neighbourhood of the binary contacts.

Also, in equation (7)  $K_2$  considers the differences only between the energetic perturbations in the molecular surroundings of the binary contacts:

$$K_2 = \frac{[(2e_{12-1} - e_{11-1} - e_{22-1}) - (2e_{12-2} - e_{11-2} - e_{22-2})]}{(T_{g2} - T_{g1})} = K_2^* / (T_{g2} - T_{g1}) \quad (9)$$

It has been shown that the parameters  $K_1^*$  and  $K_2^*$  are still molecular-weight-dependent. They are related to orientation effects of the hetero-interaction in the blend<sup>14</sup>.

For identical effects of the neighbourhood perturbations  $K_2 = 0$  and  $K_1$  is then given by the simple expression:

$$K_1 = (2E_{12} - E_{11} - E_{22}) / (T_{g2} - T_{g1}) \quad (10)$$

Equation (7) then is identical with the Kanig expression (4). This can be shown by rearranging the Kanig equation (4) to:

$$T_{g2} - T_g = -\frac{\Psi_v^2(2A_{12} - A_{11}A_{22})}{R(\ln \Psi_h + \Psi_v)} \Phi_{f1}^2 - \frac{\Psi_v^2(-2A_{12} + A_{11} + A_{22}) + \Psi_v^2(A_{22} - A_{11})}{R(\ln \Psi_h + \Psi_v)} \Phi_{f1} \quad (11)$$

Taking into account that expression (6) is valid for the pure components, the very last term,  $-\Psi_v^2(A_{22} - A_{11}) / R(\ln \Psi_h + \Psi_v)$ , can be replaced by the difference  $(T_{g2} - T_{g1})$  and equation (11) becomes finally:

$$(T_{g2} - T_g) / (T_{g2} - T_{g1}) = (1 + K_1)\Phi_{f1} - K_1\Phi_{f1}^2 \quad (12)$$

$$K_1 = \frac{\Psi_v^2(2A_{12} - A_{11} - A_{22})}{R(\ln \Psi_h + \Psi_v)(T_{g2} - T_{g1})} \quad (13)$$

Equation (12) written in terms of  $\Phi_{f1}$  is identical to equation (7) formulated in terms of  $w_{2c}$ , assuming  $K_2 = 0$ .

Comparing equations (13) and (10) it is evident that the supposed shares of interaction energies  $E_{ij}$  which have to be overcome at  $T_g$  to assure the characteristic conformational mobilities of the polymer melt are related to the standard Gibbs free energies defined by Kanig of generating one mole of holes:

$$E_{ij} = \Psi_v^2 / R(\ln \Psi_h + \Psi_v) \quad (14)$$

Finally we remind the reader that equation (12) is also identical with the Kwei relation<sup>12</sup>. As has already been shown<sup>13</sup>, the fitting parameter of the latter,  $q$ , is related to the parameter  $K_1$  by:

$$q = KK_1(T_{g2} - T_{g1}) / (w_1 + Kw_2)^2 \quad (15)$$

Taking into account the molecular-weight dependence of

$T_g$ , which according to Kanig<sup>13</sup> is given by the expression:

$$\frac{1}{T_g} = \frac{RV_{fh}^*}{\Psi_v^2 A V_{fm}^* P} - \frac{R(\ln \Psi_h + \Psi_v)}{\Psi_v^2 A} \quad (16)$$

it is evident that equation (6) holds only for high degrees of polymerization,  $P$ , for which the glass transition temperature achieves a constant value,  $T_{g\infty}$ . In (16),  $V_{fh}^*$  is the hole volume and  $V_{fm}^*$  the vibrational free volume of the monomeric unit. Their ratio is constant at  $T_g$ :  $V_{fh}^*/V_{fm}^* = 0.46$ .

As a consequence in the case of lower-molecular-weight blend components, the very last term  $-\Psi_v^2(A_{22} - A_{11})/R(\ln \Psi_h + \Psi_v)$  of equation (11) has to be replaced by a corrected  $(T_{g2} - T_{g1})$  difference of the form:

$$T_{g2} \left(1 + \frac{5.33T_{g2}}{P_2 T_{g2\infty}}\right)^{-1} - T_{g1} \left(1 + \frac{5.33T_{g1}}{P_1 T_{g1\infty}}\right)^{-1} \quad (17)$$

## RESULTS AND DISCUSSION

Recently<sup>15</sup> it has been shown that both the Gordon-Taylor and the Kwei relations can be linearized and used to discern between representations of the  $T_g$ -composition data. Except for blends of homo- and copolymers of styrene with poly(2,6-dimethylphenylene oxide) (PPO), all other compatible blends show serious deviations from Gordon-Taylor behaviour.

The more powerful method of classifying the  $T_g$ -composition behaviour of compatible polymer blends, however, is obtained using the third-power equation (7) reformulated in the following manner:

$$(T_g - T_{g1})/(T_{g2} - T_{g1})w_{2c} = (1 + K_1) - (K_1 + K_2)w_{2c} + K_2w_{2c}^2 \quad (7a)$$

For volume additivity both  $K_1=0$  and  $K_2=0$  and equation (7a) reduces to the simple form:

$$(T_g - T_{g1})/(T_{g2} - T_{g1})w_{2c} = 1 \quad (7b)$$

The result will be a straight horizontal line about unity in the  $(T_g - T_{g1})/(T_{g2} - T_{g1})w_{2c}$  vs.  $w_{2c}$  representation; otherwise straight lines of slope  $K_1$  ( $K_2=0$ ) or curved lines ( $K_2 \neq 0$ ) are obtained.

Taking into account the uncertainty in the value of the  $K$  parameter from volume additivity, the reformulated third-power equation (7a) was used in a first attempt to check  $T_g$ -composition data of a blend of homopolymers of styrene, i.e. (PS,  $M_n=800$ ,  $M_w/M_n=1.3$ )/(PS,  $M_n=75000$ ,  $M_w/M_n=1.06$ ). Owing to the identical interactions between the chain segments of the blend components, both  $K_1=0$  and  $K_2=0$ , i.e. the  $T_g$ -composition data obeyed the simplified equation (7b).

Assuming similar densities and expansion behaviour in the  $T_g$  range the  $K$  parameter can be replaced, in accordance with the Simha-Boyer rule, by the ratio of the respective glass transition temperatures  $T_{g1}/T_{g2}$ , i.e. the  $T_g$  data will obey the Fox relation characterized by the value of the coefficient  $K'=1$ . These assumptions are justified by the experimental data shown in Figure 1. Both the intercept related to unity (0.01) and the slope of the calculated straight line ( $-0.05$ ) about unity confirm the absence of any specific interactions between the blend components. This is consistent with the PS/PS blend obeying the ideal volume additivity behaviour, reflected by the Fox relation.

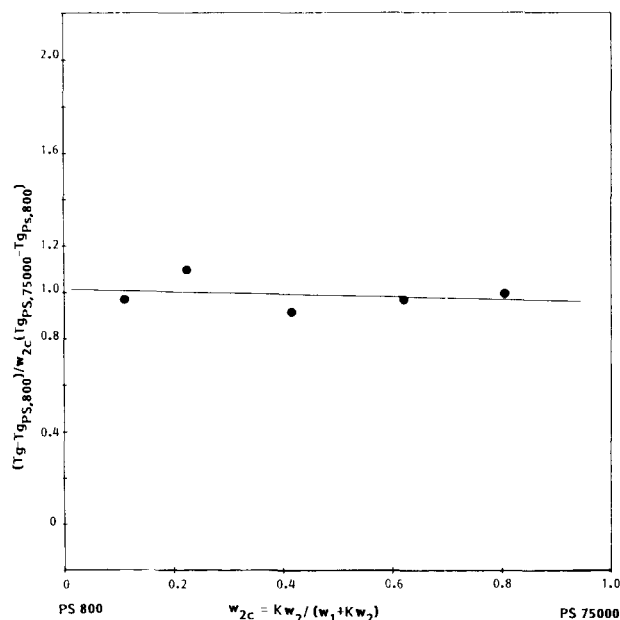


Figure 1 Representation of the  $T_g$ -composition behaviour of blends of anionic (PS,  $M_n=800$ )/(PS,  $M_n=75000$ ) according to equation (7a) using values of the  $K$  parameter,  $K=K'T_{g1}/T_{g2}$  and  $K'=1$

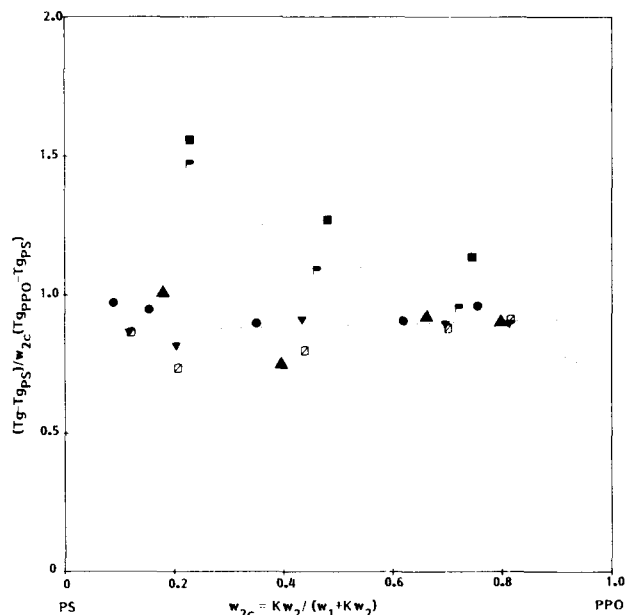


Figure 2 Representation of the  $T_g$ -composition data of Gräter<sup>16</sup> for blends of PS/PPO according to equation (7a).  $K$  parameter as in Figure 1. Blends: ( $\blacktriangledown$ ) PS 800/PPO 17 000; ( $\bullet$ ) PS 40 000/PPO 17 000; ( $\circ$ ) PS 600 000/PPO 17 000; ( $\blacktriangle$ ) PS 800/PPO 1500; ( $\blacksquare$ ) PS 2900/PPO 1500; ( $\blacksquare$ ) PS 40 000/PPO 1500. (Numerals behind polymer abbreviations denote the weight-average molecular weights)

Similar behaviour is shown by the PS/PPO blends, except for the blends with low-molecular-weight PPO component.

For illustration the  $T_g$ -composition data of PS/PPO blends are shown in Figure 2<sup>16</sup> and in Figure 3<sup>17</sup>. It is evident that for both series of  $T_g$ -composition data the volume additivity condition is obeyed, with the exception of those blends with PPO of molecular weights  $M_n < 1500$ . These deviations are explained by de Araujo<sup>17</sup> by increase in the measured ratio of the heat capacities,  $\Delta c_{p2}/\Delta c_{p1}$ , for low-molecular-weight components. Inexplicable, however, are the opposite deviations from the volume

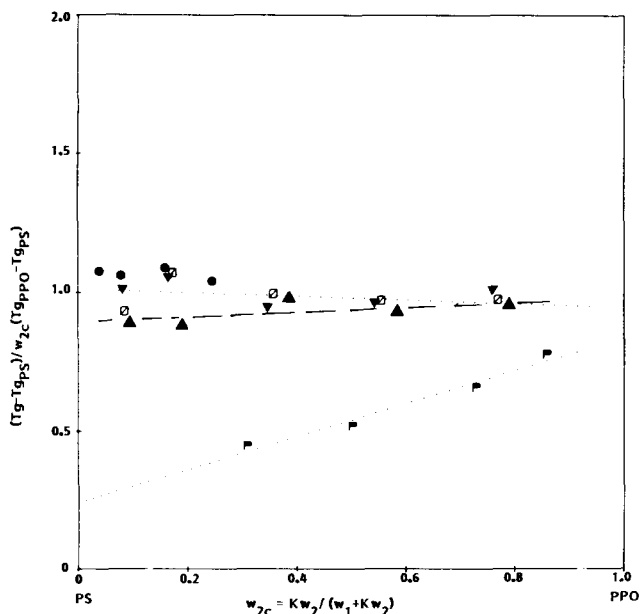


Figure 3 Representation of the  $T_g$ -composition data of de Araujo *et al.*<sup>17</sup> for blends of PS/PPO according to equation (7a).  $K$  parameter as in Figure 1. Blends of PS 144 000 with: (●) PPO 44 000; (▼) PPO 5900; (○) PPO 3100; (▲) PPO 1500; (■) PPO 360. (Numerals denote the number-average molecular weights)

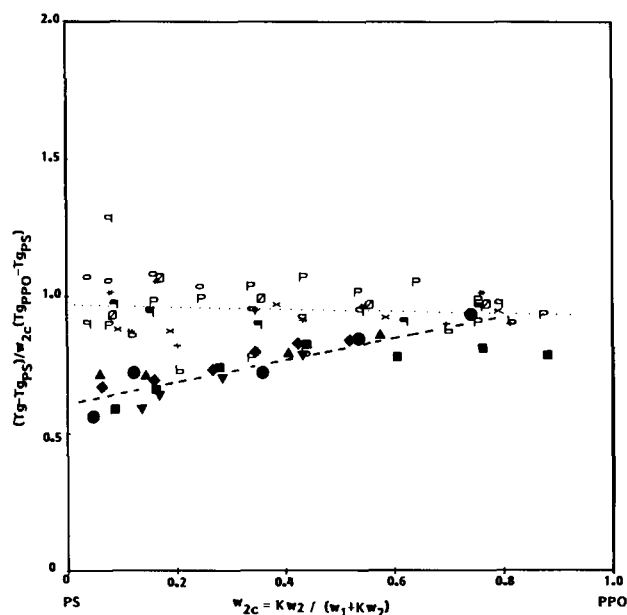


Figure 4 Representation of the  $T_g$ -composition data of blends of PS/PPO according to equation (7a).  $K$  parameter as in Figure 1. Blends of PPO 17 000 with: (■) PS 600 000; (b) PS 40 000; (+) PS 800<sup>16</sup>. Blends of PS 144 000 with: (●) PPO 44 000; (\*) PPO 5900; (○) PPO 3900; (x) PPO 1500<sup>17</sup>. Other blends: (q) PS 97 000/PPO 69 000<sup>3</sup>; (p) PS 97 200/PPO 37 200<sup>18</sup>. (Numerals denote the weight-average molecular weights for the last two blends, and the number-average molecular weights for all other blends.) Full signs are data of Kwei *et al.*<sup>19,20</sup>: (■) PS 300 000/PPO 35 000<sup>19</sup> and blends of PPO 45 000 with (●) PS 800, (▲) PS 2200, (◆) PS 10 000 and (▼) PS 37 000<sup>20</sup>. (Numerals denote the weight-average molecular weights)

additivity exhibited by the blends with the lower-molecular-weight PPO, studied by Gräter<sup>16</sup> and by de Araujo<sup>17</sup>, respectively.

All the available data on  $T_g$ -composition of PS/(PPO,  $M_n > 1500$ ) blends are presented in Figure 4. Except for the blends studied by Kwei *et al.*<sup>19,20</sup>, for the other PS/PPO blends shown in Figure 4 both the slope of the

dotted straight line ( $-0.04$ ) and the intercept related to unit value ( $-0.03$ ) suggest the absence of specific interactions between the blend components, i.e.  $K_1 = 0$ . The blends analysed by Kwei, however, are characterized by molecular-weight dependent values of the  $K_1$  parameter (broken line), ranging between  $-0.25$  and  $-0.45$  for the assumed Gordon-Taylor parameter  $K = T_{g1}/T_{g2}$  (i.e.  $K' = 1$ ).

It is interesting to notice that the observed negative deviations of the  $T_g$ -composition data from the volume additivity rule characterized by  $K = K'T_{g1}/T_{g2}$  ( $K' = 1$ ) can be almost compensated for by an appropriate change in the  $K'$  coefficient, as shown in Figure 5. (The coefficient is about 0.55 for the blend (PS,  $M_n = 800$ )/(PPO,  $M_n = 45 000$ )). This suggests that possible specific interactions between the blend components can be included in an arbitrary fitting  $K$  parameter of the Gordon-Taylor equation, as has been suggested by Walsh and McKeown<sup>21</sup> and demonstrated previously<sup>15</sup>.

The different methods used in blend preparation could be a possible explanation for the observed discrepancies between the  $T_g$ -composition behaviour of the PS/PPO blends studied by Kwei *et al.*<sup>19,20</sup> (blend films obtained by solution casting) and the other blends shown in Figure 4 (blends obtained by freeze drying). Residual solvent in films obtained by solution casting would then be responsible for the observed lowering of the  $T_g$ .

Several studies have been made of the miscibility of copolymers of styrene and PPO, claiming a gradual decrease of the compatibility with increasing comonomer content. Although the  $T_g$ -composition behaviour of the blends can be fitted to the Gordon-Taylor equation<sup>15</sup>, the observed negative deviations from volume additivity increase with increasing comonomer content. This general behaviour is exemplified in Figure 6 for blends of poly(styrene-*co*- $\alpha$ -methylstyrene)/PPO, using  $T_g$  data published by Shultz and Young<sup>22</sup>.

Negative deviations of the  $T_g$ -composition data from volume additivity are also characteristic of the compatible poly(vinyl methyl ether)/polystyrene (PVME/PS) blends.

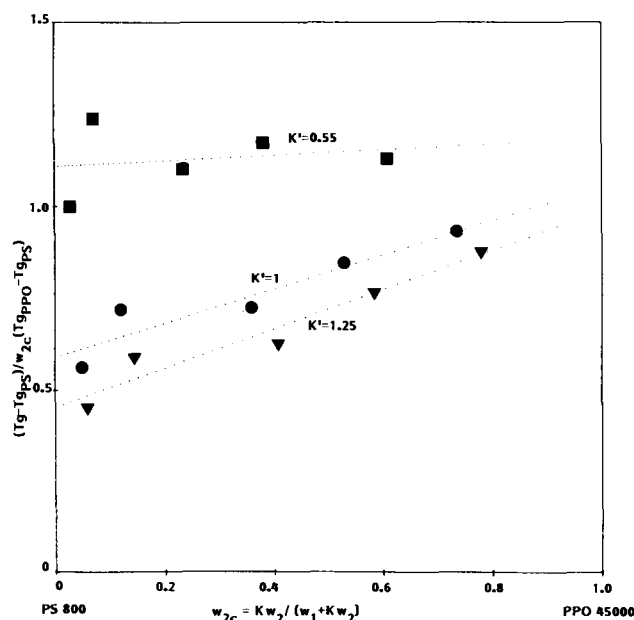
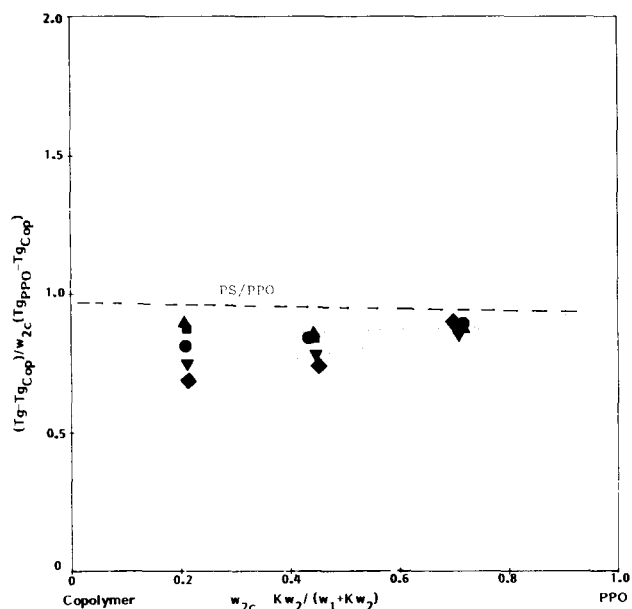
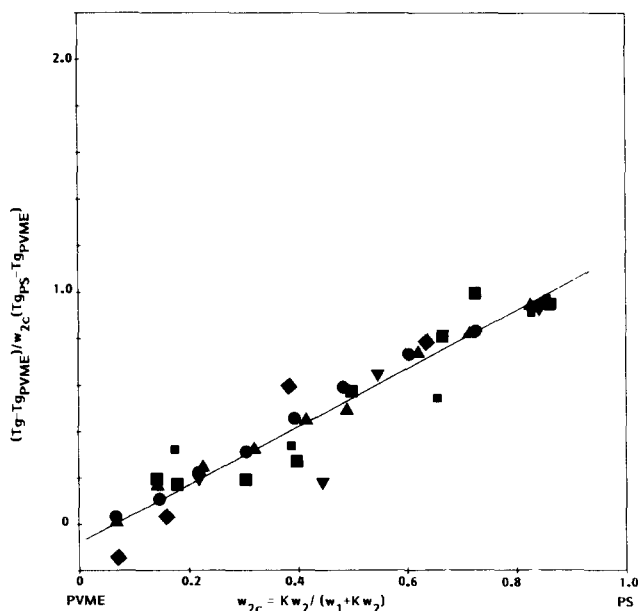


Figure 5 Representation of the  $T_g$ -composition data of (PS,  $M_w = 800$ )/(PPO,  $M_w = 45 000$ )<sup>20</sup> according to equation (7a) using different values of the  $K$  parameter.  $K = K'T_{g1}/T_{g2}$ , values of  $K'$  shown on the curves



**Figure 6** Representation of the  $T_g$ -composition data of Shultz and Young<sup>22</sup> for blends of statistical poly(styrene-co- $\alpha$ -methylstyrene)/PPO according to equation (7a).  $K$  parameter as in Figure 1. Blends of PPO,  $M_w = 37\,200$ /P(S-co- $\alpha$ MS). Weight fraction of  $\alpha$ MS: (●) 0.09,  $M_n = 20\,000$ ; (▲) 0.17,  $M_n = 39\,000$ ; (■) 0.26,  $M_n = 24\,000$ ; (▼) 0.36; (◆) 0.44;  $M_n = 13\,000$ . Broken line: representative curve of PS/PPO blends in Figure 4



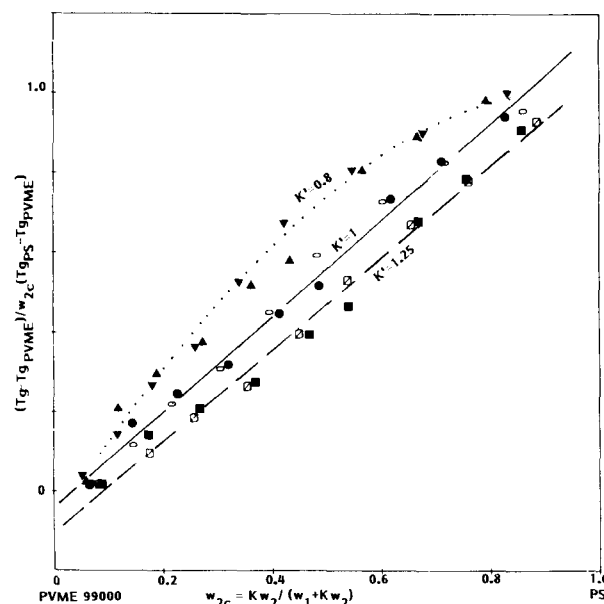
**Figure 7** Representation of the  $T_g$ -composition data of PVME/PS blends according to equation (7a).  $K$  parameter as in Figure 1. Blends: (◆) PVME 97 500/PS 73 500<sup>27</sup>; (■) PVME 73 000/PS 75 000<sup>26</sup>; (●) PVME 99 000/PS 35 000 and (▲) PVME 99 000/PS 233 000<sup>23</sup>; (■) PVME 524 000/PS 150 000<sup>24</sup>. (Numerals denote the weight-average molecular weights.) Other blend: (▼) PVME 0.51/PS 0.94<sup>25</sup>. (Numerals denote the intrinsic viscosity in benzene at 25°C)

This is exemplified in Figure 7. Although the scatter of the experimental data is noticeable, it is supposed that for the blends of the high-molecular-weight components the overall behaviour is reflected by the straight line (slope 1.21, intercept  $-1.04$ ) giving a  $K_1$  mean value of about  $-1.1$  (with  $K$  parameter assumed for volume additivity, i.e.  $K = K'T_{g1}/T_{g2}$  and  $K' = 1$ ).

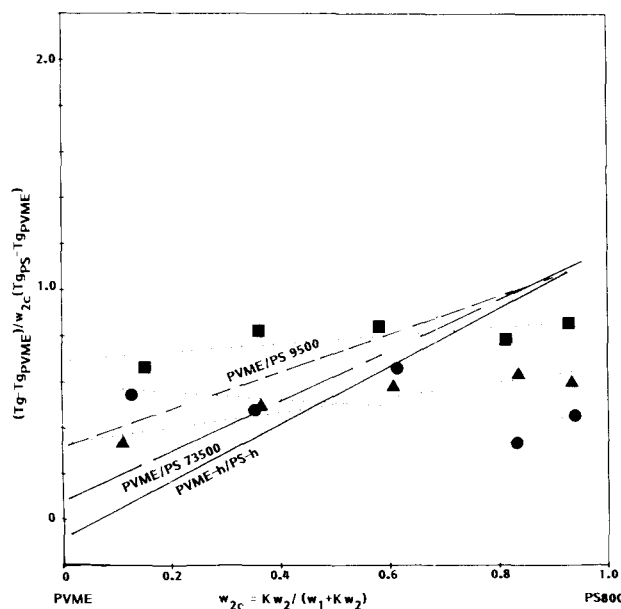
Any attempt to approach Gordon-Taylor like

behaviour (a horizontal straight line about 1.0) by changing the  $K$  parameter (i.e. using values of  $K' \neq 1$ ) fails, as is evidenced in Figure 8 using the  $T_g$ -composition data of Halary *et al.*<sup>23</sup>. Instead of an improvement for  $K' = 1.2$  a shift of the  $T_g$  data is observed towards increased negative deviations from additivity, whereas for  $K' = 0.8$  the bending of the  $T_g$ -composition data indicates further removal from the Gordon-Taylor behaviour. The data thus confirm the existence of real specific interactions between blend components and support the previously reported failure of the Gordon-Taylor equation<sup>26,27</sup>.

The data in Figure 9 show the influence of the



**Figure 8** Representation of the  $T_g$ -composition data of Halary *et al.*<sup>23</sup> for blends of PVME/PS according to equation (7a) using different values of the  $K$  parameter ( $K'$  values shown on the curves): (▼, ○, ∅) PVME 99 000/PS 35 000 and (▲, ●, ■) PVME 99 000/PS 233 000. (Numerals denote the weight-average molecular weights)



**Figure 9** Representation of the  $T_g$ -composition data of Schneider and Leikauf<sup>27</sup> for blends of PVME/PS 800 according to equation (7a).  $K$  parameter as in Figure 1. Blends of PS 800 with: (■) PVME 1000; (▲) PVME 10 000; (●) PVME 97 500. Representative straight lines of the blends of the same PVME with (---) PS 9500 and (—) PS 75 000. Full line of the blends PVME/PS in Figure 7

molecular weight of the blend components and it is noticeable that, as with the PS/PPO blends, the molecular weight of the stiffer blend component (PS this time) seems to be mainly decisive in determining the  $T_g$  behaviour of the PVME/PS blends. With increasing molecular weight of the PS component, both the  $K_1$  and  $K_2$  coefficients of the third-order equation (7) decrease in magnitude<sup>4</sup> whereas the slope of the  $T_g$ -composition curves shown in Figure 9 increases (i.e. smaller  $K_1$  values). These changes in the  $K_1$  and  $K_2$  coefficients are almost independent of the molecular weight of the PVME, indicating that the negative deviations from volume additivity are the greater the higher the molecular weight of the PS.

The  $T_g$  data of Saeki *et al.*<sup>11</sup> for the polystyrene/poly( $\alpha$ -methylstyrene) (PS/P $\alpha$ MS) blends show much more pronounced negative deviations from volume additivity. These deviations are important in that the  $T_g$  of all blends in the composition range above 50% w/w PS are lower than those of the two blend components. The data are presented according to equation (7a) in Figure 10. The scatter of the data is considerable and it seems that the molecular weight of P $\alpha$ MS has a decisive influence, but the number of blends studied is too small for a more definitive statement. It is obvious that the  $T_g$  data fit better on a curve than on a straight line, suggesting important influences of the contact interactions in the neighbourhood of the binary contacts (i.e.  $K_2 \neq 0$ ).

Gordon-Taylor like behaviour accompanied by more or less accentuated negative deviations from volume additivity is shown by most of the compatible blends of polyesters studied by Barlow and Paul *et al.* This can be seen in Figure 11 for blends of various aliphatic polyesters with poly(vinyl chloride) (PVC)<sup>28,29</sup> (including the data of Goh and Sion<sup>30</sup> for poly(tetrahydrofurfuryl methacrylate)/poly(vinyl chloride) (PHFM/PVC)), a vinyl chloride-co-vinylidene chloride copolymer (P(VC/VDC)) (containing 13.5% w/w VC)<sup>31</sup> and poly(epichlorhydrin)<sup>32</sup> (PEC). In Figure 12 are shown the  $T_g$  data of blends of the aliphatic polyesters with poly(hydroxy ether of

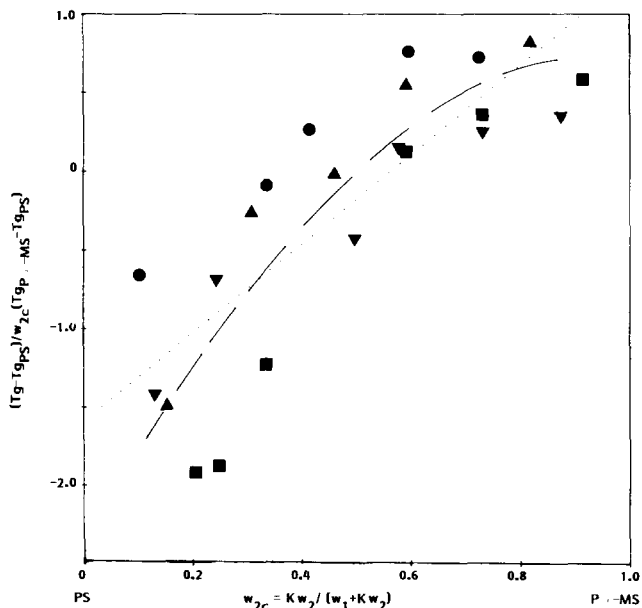


Figure 10 Representation of the  $T_g$ -composition data of Saeki *et al.*<sup>11</sup> for blends of PS/P $\alpha$ MS according to equation (7a).  $K$  parameter as in Figure 1. Blends of P $\alpha$ MS 17 000 with (▼) PS 17 000 and (■) PS 37 000 and of P $\alpha$ MS 84 000 with (●) PS 10 000 and (▲) PS 63 000. (Numerals denote the weight-average molecular weights)

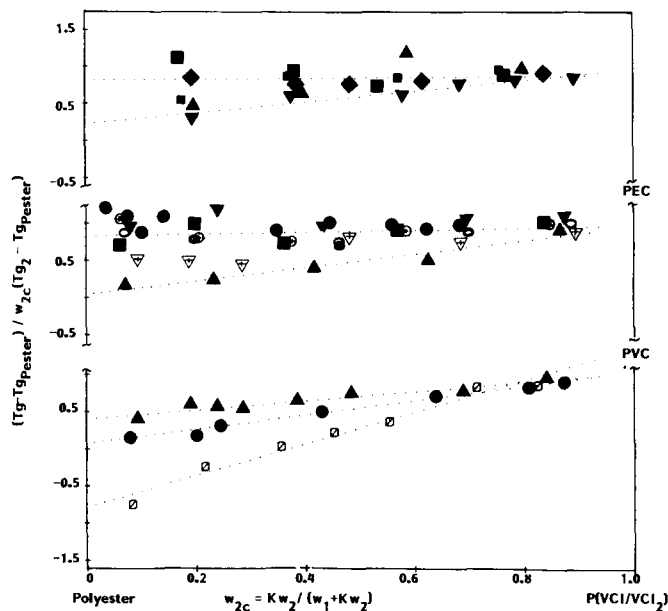


Figure 11 Representation of the  $T_g$ -composition data of blends of polyesters (PES) with commercial poly(vinyl chloride) (PVC)<sup>28,29</sup>, (vinyl chloride-co-vinylidene chloride) copolymer (P(VC/VDC)) with 13.5 wt% VC<sup>31</sup>, and poly(epichlorhydrin),  $M_w = 700\,000$  (PEC)<sup>32</sup> according to equation (7a).  $K$  parameter as in Figure 1. PES: (●) poly( $\epsilon$ -caprolactone),  $M_w = 46\,700$ . Polysuccinates: (▲) 2,2'-dimethyl-1,3-propylene; (▼) 1,4-cyclohexanedimethylene. Polyadipates: (■) ethylene; (■) 1,4-butylene; (○) 2,2'-dimethyl-1,3-propylene; (◆) neopentylglycol. Polysebacates: (●) butylene; (⊙) hexamethylene,  $M_w = 16\,500$ . (For all other PES viscosity-average molecular weights in the range 1000–6000.) (▽) Poly(tetrahydrofurfuryl methacrylate), intrinsic viscosity 0.31 in benzene at 30°C<sup>30</sup>

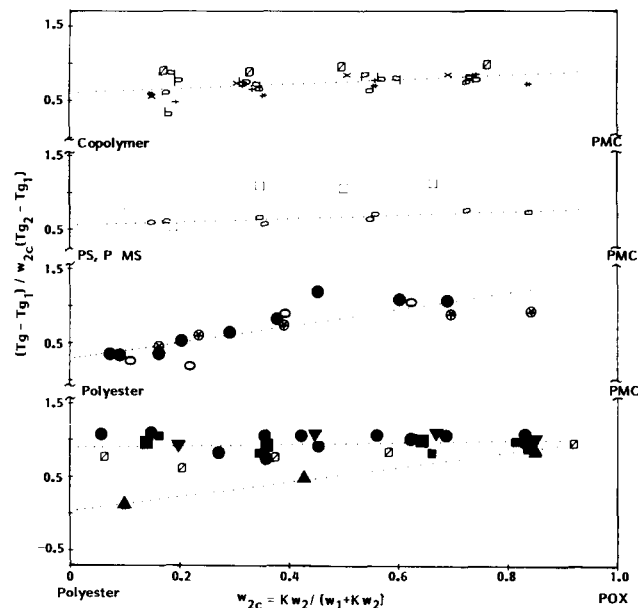


Figure 12 Representation of the  $T_g$ -composition data of PES with poly(hydroxy ether of bisphenol A),  $\eta_{rel} = 0.29\text{ dl g}^{-1}$  (POX)<sup>33</sup> and with tetramethylbisphenol A polycarbonate,  $\eta_{rel} = 1.29\text{ dl g}^{-1}$  (MPC)<sup>34</sup> and of MPC with styrenic polymers<sup>35</sup> according to equation (7a).  $K$  parameter as in Figure 1. Styrenic polymers: (○) PS, commercial; (□) P $\alpha$ MS,  $M_n = 940$ . Copolymers: styrene-co-acrylonitrile—(x) 2% AN,  $M_w = 204\,000$ ; (p) 5.5% AN,  $M_w = 270\,000$ ; (+) 9% AN, —; styrene-co-allyl alcohol—(\*) 4.4% AA,  $M_w = 2100$ ; (○) 8.4% AA,  $M_w = 1420$ ; (q) 19.1% AA,  $M_w = 2340$ ; (b) 25.8% AA,  $m_w = 1700$ ; (●) styrene-co-maleic anhydride—8% MA,  $M_w = 200\,000$

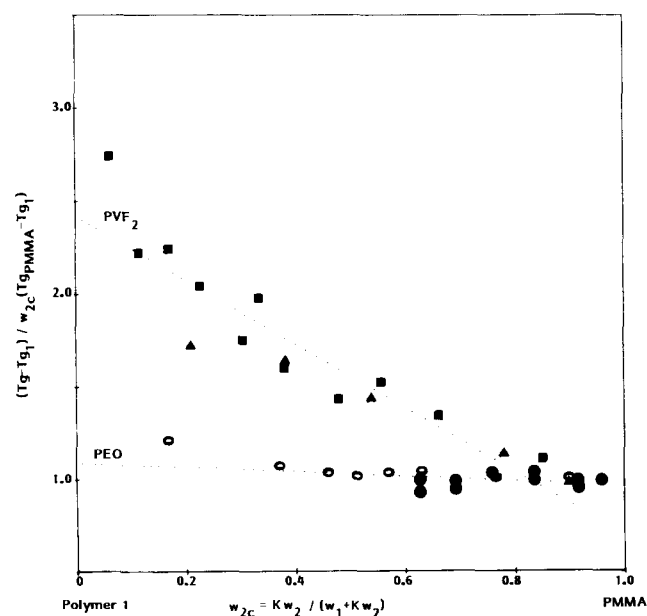
bisphenol A) (POX)<sup>33</sup> and tetramethylbisphenol A polycarbonate (MPC)<sup>34</sup> as well of MPC with styrene copolymers (PS, P $\alpha$ MS and P(S-co- $\alpha$ MS))<sup>35</sup>. Although there are observed deviations from volume additivity, no correlation is possible between these deviations and the nature of the blend components.

Similar behaviour is shown by the  $T_g$  data of the aliphatic polyester blends with various oligomeric copolymers of styrene/allyl alcohol<sup>36</sup>. Nevertheless, the analysis showed that the  $K_1$  and  $K_2$  parameters computed using the third-order fitting relation (7) are related with both the wt% OH content of the (styrene-co-allyl alcohol) copolymer and the CH<sub>2</sub>/COO ratio of the aliphatic polyesters<sup>14</sup>.

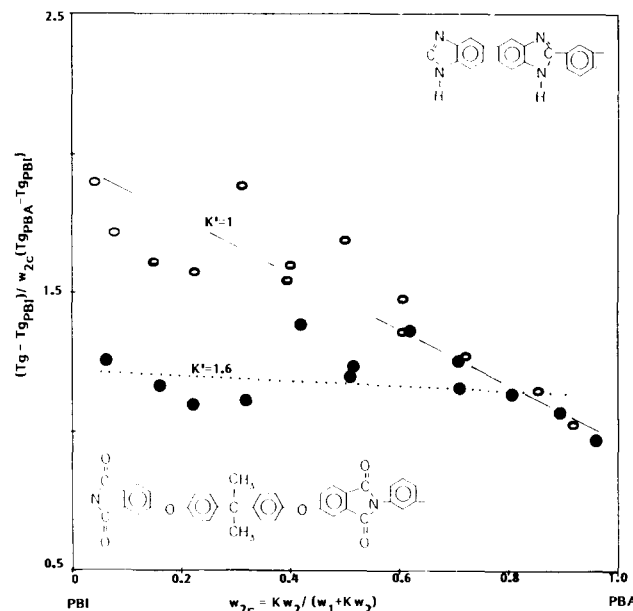
The study of Kwei on the miscibility of Novolac resins with poly(methyl methacrylate) (PMMA) of different tacticities was perhaps one of the first studies indicating large positive deviations from volume additivity<sup>12</sup>. In particular blends of Novolac resins with isotactic PMMA exhibited  $T_g$  values higher than those of both of the blend components. This behaviour is explained by formation of hydrogen bonds between the components and required an extension of the Gordon-Taylor equation by the incorporation of the quadratic concentration term.

Positive deviations from volume additivity are also characteristic of the  $T_g$  data of other PMMA blends, as can be seen in Figure 13. The blends of PMMA with poly(ethylene oxide) (PEO)<sup>37,38</sup> still show additive volume behaviour, whereas the blends with poly(vinylidene fluoride) (PVF<sub>2</sub>) are marked by serious positive deviations<sup>39</sup>; the blends with poly(styrene-co-acrylonitrile) behave in between, depending on the acrylonitrile (AN) content of the styrene copolymer<sup>40-42</sup>. There are, however, indications of a miscibility gap in the range of 20-50 wt% PEO in the compatibility of PMMA/PEO blends<sup>43</sup>.

The compatible polymer blends of poly(2,2'-bis(3,4-



**Figure 13** Representation of the  $T_g$ -composition data of blends of PMMA with PEO<sup>37,38</sup> and PVF<sub>2</sub><sup>39</sup> according to equation (7a).  $K$  parameter as in Figure 1. Blends: (○) PEO,  $M_w = 10\,000$ /PMMA,  $M_w = 106\,000$ <sup>37</sup>; (●) PEO,  $M_{vis} = 20\,000$ /PMMA,  $M_{vis} = 116\,000$ <sup>38</sup>; (■) PVF<sub>2</sub>, 1.45/PMMA, 0.303 (intrinsic viscosities in DMF at 25°C)<sup>39</sup>; (▲) data of Noland *et al.* cited in ref. 39



**Figure 14** Representation of the  $T_g$ -composition data of Leung *et al.*<sup>44</sup> of poly(ether imide)/(poly(benzimidazole)) blends, according to equation (7a), using different values of the  $K$  parameter.  $K = K' T_{g1} / T_{g2}$ , values of  $K'$  shown on the curves. (PBI,  $M_w = 30\,000$ ; PBA, commercial product)

dicarboxyphenoxy)phenylpropane-2-phenylene bisimide) (PBI) and poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole) (PBA) studied by Leung *et al.* also show positive deviations from volume additivity<sup>44</sup>. The data are presented in Figure 14. By increasing the  $K$  parameter the  $T_g$  data of the blend can be fitted to the Gordon-Taylor equation. The respective correction factor of equation (2a) is  $K' = 1.6$ .

Besides hydrogen-bond formation, charge-transfer interchain complexation between electron-donor and electron-acceptor side-groups is also accompanied by significant positive deviations from volume additivity. Important conformational rearrangements in the neighbourhood of the binary hetero-contacts are suggested by the deviations from linearity of the experimental  $T_g$ -composition data. This behaviour is evidenced in Figure 15 for blends of the polydonor poly(*N*-(2-hydroxyethyl)-carbazolyl methacrylate) (PHECM) and the polyacceptor poly( $\omega$ -(hydroxyethyl)-3,5-dinitrobenzoyl methacrylate) (PDNBM-n)<sup>45</sup>, and in Figure 16 for blends of the polydonor poly(*N*-ethylcarbazol-3-yl-methyl methacrylate) (PHMCM-2) and the polyacceptor poly( $\beta$ -hydroxyethyl-3,5-dinitrobenzoyl methacrylate) (PDNBM-2) of different molecular weights<sup>46</sup>. For both series of polydonor/polyacceptor blends specific deviations from linearity are observed in the 0 to 0.4 concentration range of the polydonor.

It has been shown that the  $K_1$  and  $K_2$  parameters of the third-power equation (7) are related with the heat of mixing of the compatible polydonor/polyacceptor (PDNBM-n/PHECM) blends<sup>12</sup>.

The negative deviations from linearity are smaller the longer the spacer of the acceptor side-group in the blends with PDNBM-n, suggesting decoupling effects between the interacting side-groups and the polymeric main chain. Because of this decoupling effect, influences of conformational redistributions of the main chain will be reduced and the alignment of the side-chains by hetero-contact interaction improved. Molecular-weight influences of the

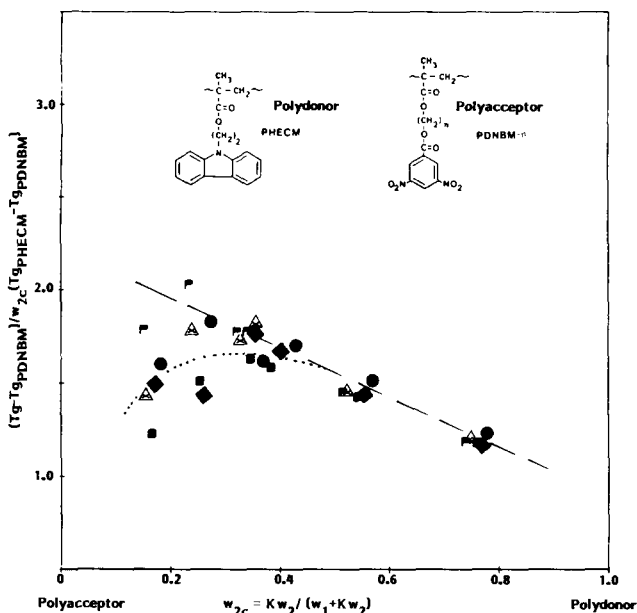


Figure 15 Representation of the  $T_g$ -composition data of Rodriguez-Parada and Percec<sup>45</sup> for blends of polydonor (PHECM)/polyacceptor (PDNBM-n) blends.  $K$  parameter as in Figure 1. Blends of PHECM 31 000 with: (●) PDNBM-2, 24 200; (◆) PDNBM-3, 18 300; (■) PDNBM-4, 19 300; (△) PDNBM-5, 19 900; (◻) PDNBM-6, 20 400. (Numerals denote the weight-average molecular weights)

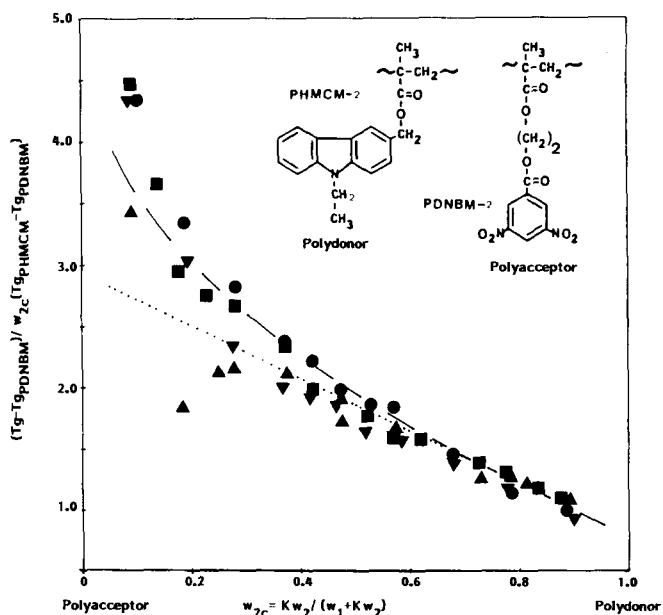


Figure 16 Representation of the  $T_g$ -composition data of Percec *et al.*<sup>46</sup> for blends of polydonor (PHMCM-2)/polyacceptor (PDNBM-2) according to equation (7a).  $K$  parameter as in Figure 1. Blends of PDNBM-2, 19 000 with (▼) PHMCM-2, 6800, (■) PHMCM-2, 16 900 and (●) PHMCM, 35 000; (▲) PDNBM-2, 24 200/PHMCM-2, 35 800. (Numerals denote the weight-average molecular weights)

interacting components seem to be less significant (Figure 16).

Any attempt to verify Gordon-Taylor behaviour by using an extreme fitting parameter  $K$  fails, as is demonstrated in Figure 17. With increasing coefficient  $K'$  the horizontal line about unity will be approached, but at the same time both the experimental  $T_g$  data and the curvature of the line are shifted into the range of the higher polydonor concentrations.

Finally in Figure 18, some of the previously discussed

compatible blend systems are compared. The most striking fact is the very different  $T_g$  behaviour, reflected in both negative and positive deviations from volume additivity. The  $T_g$  behaviour of the compatible blends suggests that the miscibility is influenced not only by the energetic interaction of the hetero-contacts, but also by associated free-volume effects due to conformational rearrangements in the neighbourhood of the binary hetero-contacts.

It was assumed that segment alignment by the hetero-interchain interaction contributes to a reduction of the available free volume and consequently to a decrease of the mobility in the polymer blend<sup>14</sup>. This effect is favoured by both the strengths of the interacting contacts and by the molecular weight of the components. As a

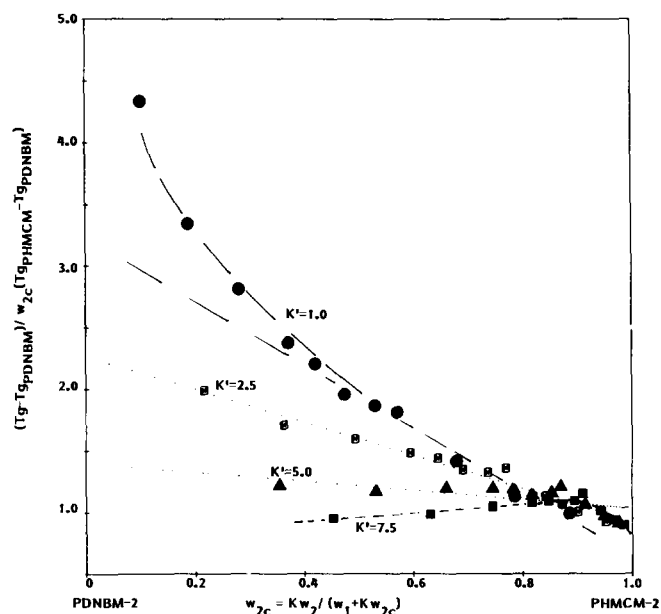


Figure 17 Representation of the  $T_g$ -composition data of the polydonor/polyacceptor blends PDNBM-2, 19 200/PHMCM-2, 35 000 according to equation (7a) using different values of the  $K$  parameter. Values of the  $K'$  coefficient shown on the curves

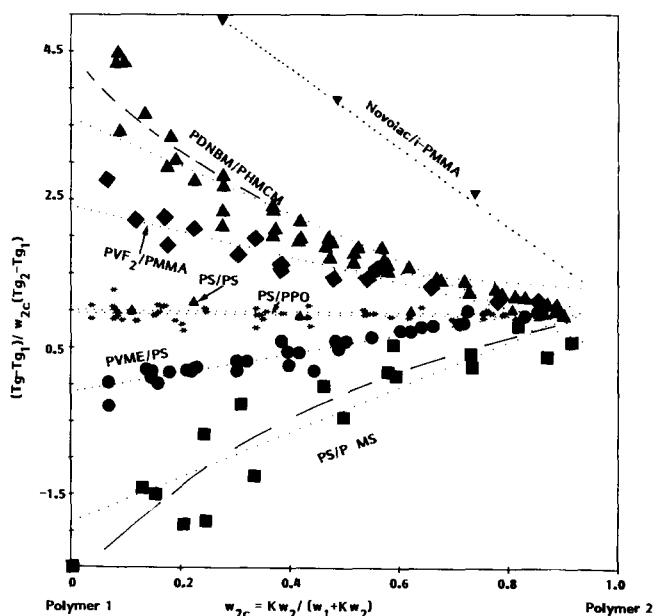


Figure 18 Comparison of the  $T_g$ -composition behaviour of compatible polymer blends using the representation of the data according to the reformulated third-power equation (7a)



consequence, an increase of the  $T_g$  temperature of the blends will be observed as the interaction between the blend components becomes stronger. This may explain the observed order for positive deviation for hydrogen bridges and charge-transfer interaction. At the same time the stronger directional effect of the hetero-contacts will be accompanied by stronger perturbations of the conformational rearrangements in the neighbourhood of the contacts. However, decrease in molecular weight, mainly by the stiffer blend component, may act in the same direction. The lower the molecular weight, the better the segment alignment due to the increased mobility of the stiffer component.

On the other hand, the lack of segment alignment due to hetero-interaction will increase the mobility of the polymeric chain, resulting finally even in a decrease of the  $T_g$  temperature of the blend below the respective temperatures of the blend components as observed for instance in the PS/P $\alpha$ MS blends.

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