Composition and molecular-weight dependence of the glass transition in polystyrene–poly(2,6-dimethylphenylene ether) blends*

Marco Aurelio de Araujo†, Reimund Stadler‡ and Hans-Joachim Cantow
Institut für Makromolekulare Chemie, Hermann Staudinger Haus,
Stefan Meier Strasse 31, D-7800 Freiburg, FRG
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The glass transition behaviours of a series of poly(2,6-dimethylphenylene ethers) with various molecular weights and their blends with polystyrene have been studied. The data are analysed according to the Fox–Flory equation (M_n dependence) and the Gordon–Taylor equation (composition dependence). A more rigorous treatment according to the theory developed by Kanig is presented and data of polystyrene–poly(vinyl methyl ether) blends, as well as polystyrene–poly(methyl vinylether) blends which do not obey the Gordon–Taylor equation, are discussed in the framework of this theory. The theory allows the estimation of the energy required to separateA–B contacts.

(Keywords: glass transition; polystyrene–poly(2,6-dimethylphenylene ether) blends; polystyrene–poly(vinyl methyl ether) blends; free-volume concept; Kanig theory)

INTRODUCTION

The composition dependence of the glass transition temperature T_g of many copolymers can be described by an equation first developed by Gordon and Taylor[1]:

$$T_g = \frac{w_A T_{gA} + K w_B T_{gB}}{w_A + K w_B} \tag{1}$$

where $w_{A,B}$ are the weight fractions of the components. The constant K is given by the ratio of the changes in the expansion coefficient $\Delta\alpha_B/\Delta\alpha_A$, where $\Delta\alpha_i = \alpha_1 - \alpha_g$, or the corresponding change in the heat capacities at T_g. This equation has also been used to describe the composition dependence of T_g in miscible polymer blends. Several systems like polystyrene–poly(2,6-dimethylphenylene ether) (PS/PPE) can be described by equation (1), while the data for other systems like polystyrene–poly(vinyl methyl ether) (PS/PVME) are not in agreement with equation (1).

Several modifications of equation (1) have been published to describe the T_g behaviour of more complex systems involving strong intermolecular interactions like in polymers with electron donor/acceptor interactions or hydrogen bonds. A very common approach is the Kwei equation[2]:

$$T_g = \frac{w_A T_{gA} + K w_B T_{gB}}{w_A + K w_B} + q w_A w_B \tag{2}$$

According to Kwei q depends on the strength of the interaction. Another approach[3] to describe the T_g of blends uses the Gordon–Taylor equation (1) as the first factor (linear in the concentration) of a series expansion, while higher terms involve quadratic (as in equation (2)) and cubic terms of the composition.

A more fundamental approach to describe the molecular-weight dependence of the glass transition temperatures of homopolymers and the composition dependence of copolymers and polymer/plasticizer mixtures has been developed by Kanig[4]. Apparently his approach, based on thermodynamic considerations, has been overlooked by many authors. In the following a brief discussion of Kanig's attempt will be given.

Molecular-weight dependence

In 1950 Fox and Flory[5] described the glass transition temperature as a state of 'iso free volume'. According to their description the molecular-weight dependence of T_g can be described by:

$$T_g = a - b/P_n \tag{3}$$

where a is T_g at infinite chain length P_n and b is a constant. This equation fails for very low molecular weights. Kanig and Ueberreiter[6,7] showed that an equation of the form:

$$1/T_g = m + n/P_n \tag{4}$$

is able to describe the molecular-weight dependence of T_g down to dimers. This equation could be derived by Kanig along the following lines.

A polymer melt above T_g is considered as a saturated mixture of polymer chains with holes in thermodynamic equilibrium[8]. This saturated solution is treated according to the thermodynamics of mixing. It is assumed that the interactions between molecules are weak dispersive forces; thus it cannot be expected that systems with strong interactions (i.e. Coulombic forces) can be described with this approach. In addition Kanig proposed that the interaction energy is directly proportional to the contact

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† Permanent address: Instituto de Quimica, Universidade Federal do Rio Grande do Sul (UFRGS), Av. Bento Gonçalvez 9500, 9000 Porto Alegre, RS, Brazil

‡ To whom correspondence should be addressed

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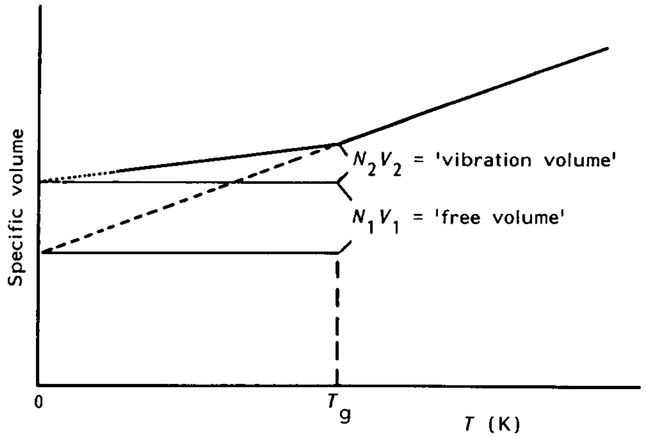

Figure 1 Schematic representation of the distinction between the vibrational free volume and the hole free volume

surface area between segments, an approach used earlier by Huggins[9] and in the mean-field lattice gas theory[10] to describe the phase behaviour of multicomponent mixtures. The thermodynamic equilibrium considerations are valid down to the glass transition temperature. Below, the material is frozen, and no thermodynamic equilibrium can be reached. Thus T_g is the lower boundary for which a thermodynamic equilibrium theory for a polymer melt can be applied.

According to a concept originally developed by Frenkel[11] the free volume in a liquid is separated into two parts:

(a) A continuous part, given by the expansion of the polymer by the chain due to the increasing vibrations of the atoms around their mean positions with temperature. This part is given by the specific vibration free volume V_{f2}, which increases with temperature according to the expansion coefficient of the glass. V_{fM} is the vibration free volume of a monomer unit within the chain:

$$V_{f2}=2V_{fE}+(P-2)V_{fM}$$

where P = degree of polymerization and V_{fE} = specific vibration volume of an end group.

(b) A discontinuous part, given by the holes, with specific hole volume V_{f1}. Below T_g the contribution of the holes to the specific volume of the material does not change. Above T_g the number of holes increases.

The differentiation between the two parts is shown in *Figure 1*. $\varphi_{f1,2}$ are the corresponding fractions of the vibrations and the holes to the overall free volume:

$$\varphi_{f1,2}=\frac{N_{1,2}V_{f1,2}}{N_1V_{f1}+N_2V_{f2}} \qquad (5)$$

where N_1 = number of holes and N_2 = number of chain molecules.

For the limit of T_g, Kanig derived the following equation:

$$\frac{1}{T_g}=\frac{RV^*_{f1}}{\varphi^*_{f2}A^*_{MM}V^*_{fM}}\frac{1}{P_n}-\frac{R(\ln\varphi^*_{f1}+\varphi^*_{f2})}{\varphi^*_{f2}\mathrm{A}^*_{MM}} \qquad (6)$$

This equation has the same form as equation (4). The asterisks in equation (6) indicate that these quantities are constants for a given polymer at T_g. An important conclusion from Kanig's work is that the fraction of holes (φ^*_{f1}) from the total free volume at T_g is about 0.64, while the fraction of the vibration free volume (φ^*_{f2}) is 0.36. These contributions were assumed to be independent of the molecular weight and of the molecular structure. Thus T_g is characterized by a constant ratio of hole volume to vibration free volume of 2:1. According to this treatment T_g is not characterized by the same iso free volume, independent of the molecular structure of the polymer, but by a state where the volume of the holes N_1V_{f1} just has the critical value of $2N_2V_{f2}$. This definition gives a value for the hole free volume at T_g close to the average value for many polymers according to Williams, Landel and Ferry[12] (0.0235 compared to 0.025). This different definition of the glass transition state can explain the rather large scatter of the 'iso free volume' data at T_g.

In a later paper[13] Kanig used the more common terminology, where only the contribution of the holes is defined as the 'free volume'. The two quantities are interrelated according to:

$$\varphi_{f1}\approx\varphi_1 a \qquad (7)$$

where a is a geometric parameter, which is related to the specific interacting surfaces of holes and monomer segments $O^V_{1,2}=O_{1,2}/V_{1,2}$, according to:

$$a=O^V_1/O^V_2 \qquad (8)$$

The quantity A^*_{MM}, a standard free enthalpy, is material-dependent. It is a direct measure of the affinity between chain molecules. A^*_{MM} is the standard free enthalpy to generate one mole of holes. For high degrees of polymerization A^*_{MM} is obtained from equation (6) according to:

$$A^*_{MM}=0.664RT^\infty_g \qquad (9)$$

i.e. the glass transition temperature is a direct measure of the affinity between chain molecules.

In the later paper[13], Kanig related the glass transition to the enthalpy ΔH^*_1, which is required to generate one mole of holes in a polymer melt where holes are already present:

$$T_g=-\frac{\Delta H^*_1}{R(\ln\varphi^*_1+\varphi^*_2)} \qquad (10)$$

The glass transition of copolymers and blends

Similar to the ideas given in the previous section, a copolymer melt has been treated by Kanig as a saturated mixture of holes and chain molecules[4]. He considered copolymers where segments of two components (A and B) are statistically distributed. If there are only weak interactions between A and B, the assumption may be valid that the mixing entropy (holes with chain of A and B) is the same as for the previous case.

The final equation derived by Kanig is:

$$\frac{T_{gB}-T_g}{\Phi_{fA}}=-\frac{\varphi^{*2}_{f2}(2A^*_{AB}-A^*_{AA}-A^*_{BB})}{R(\ln\varphi^*_{f1}+\varphi^*_{f2})}\Phi_{fA}-\frac{\varphi^{*2}_{f2}2(A^*_{BB}-A^*_{AB})}{R(\ln\varphi^*_{f1}+\varphi^*_{f2})} \qquad (11)$$

Here Φ_{fA} is the fraction of overall vibration volume arising from component A and is given by:

$$\Phi_{fA}=\frac{N_AV_{fA}}{N_AV_{fA}+N_BV_{fB}}=\frac{m_A}{m_A+m_BK} \qquad (12)$$

where K has the same meaning as in equation (1). Thus

Φ_{fA} is a modified weight fraction.

Again $\varphi^*_{f1,2}$ are material-independent quantities (0.64 and 0.36 respectively) and A^*_{AA}, A^*_{BB} and A^*_{AB} are material-specific quantities describing the standard free enthalpy to generate one mole of holes from pure AA, BB or AB contacts.

According to equation (11) a plot of $(T_{gB}-T_g)/\Phi_{fA}$ *versus* Φ_{fA} should give a straight line. The slope will be zero if A^*_{AB} is given by the arithmetic mean:

$$A^*_{AB}=(A^*_{AA}+A^*_{BB})/2 \qquad (13)$$

As already discussed by Kanig[4], equation (11) reduces to the Gordon–Taylor equation for that special case (high-molecular-weight limit). A positive slope corresponds to A^*_{AB} being higher than the arithmetic mean. Equation (11) has been successfully applied to copolymers even when the Gordon–Taylor equation failed[14].

If mixtures of homopolymers are considered, the additional small mixing entropy might be neglected and the result for copolymers should also be applicable for polymer blends, while in the case of polymers plasticized with a low-molecular-weight plasticizer additional entropic contributions must be taken into account[4]. In the following, experimental data on PPE and PS/PPE blends will be used to test the validity of equations (5)/(3) and (11)/(1).

EXPERIMENTAL

Narrow distributed PPE samples have been prepared to study in detail the thermal and linear viscoelastic properties of PS/PPE blends. The results of the linear viscoelastic measurements are reported elsewhere[15,16]. All samples were characterized by vapour-pressure osmometry (Hitachi–Perkin–Elmer vapour-pressure osmometer 115) or membrane osmometry (Hewlett-Packard high-speed osmometer 502) and size exclusion chromatography (gel permeation chromatography, g.p.c.). G.p.c. data were obtained using a set of styragel columns. The system was calibrated with commercially available PS standards. The number-average molecular weights for the PPEs as determined by g.p.c. in chloroform using polystyrene calibration were about 1.5 times the absolute values using osmometric methods.

Sample preparation

Polystyrene (*PS*). The polystyrene was obtained by standard high-vacuum anionic polymerization techniques using s-butyllithium as initiator and cyclohexane as solvent. The polymerization temperature was kept at about 40°C. The polymerization was terminated by adding a small amount of methanol. The polymer was precipitated in methanol and dried under high vacuum.

Poly(*2,6-dimethyl-4-phenylene ether*) (*PPE*). Samples of technical-grade PPE were kindly supplied by BASF. Some samples were prepared by phase-transfer-catalysed polymerization of 4-bromo-2,6-dimethylphenol according to the procedure described by Percec and Mühlbach[17,18]. The technical-grade PPE was fractionated by subsequently adding small amounts of non-solvent (ethanol) to a 1 wt% solution of PPE in benzene. The polymer-rich phase was collected in a separate flask, diluted and the PPE was precipitated in methanol. The characterization of the samples is given in *Table 1*.

Blend preparation. Blends of PS and PPE were prepared by freeze drying of benzene solutions of the appropriate mixtures of the polymers. The samples were finally dried under high vacuum at about 60°C to remove final traces of solvent.

D.s.c. measurements and data analysis

Glass transition temperatures and heat capacities were determined using a calibrated Perkin–Elmer DSC-7 system. Sample pans were filled with 12–18 mg of homopolymers or blends. The samples were first heated above T_g to allow for good thermal contact in the sample pan and to remove crystallinity (only for the high-molecular-weight samples). Several runs with different heating rates were made for each sample. The inflection point of the d.s.c. traces was chosen as the heating-rate-dependent T_g value. The final T_g values were obtained by extrapolation to zero heating rate. The results for the blends with PPE of various molecular weights are listed in *Tables 2–6*. The glass transition of the trimer, which is a crystalline material, was obtained by quenching the molten material with liquid nitrogen. The sample pan was then transferred at low temperatures into the d.s.c. instrument. For each heating rate the same procedure was applied.

RESULTS AND DISCUSSION

The molecular-weight dependence of the glass transition temperature of PPE

In a previous paper the molecular-weight dependence of the glass transition temperature of PPE has been analysed according to the Fox–Flory equation (3). Equation (3) holds down to molecular weights of about

Table 1 Characterization of the polymer samples

Sample	M_n[a]	M_w/M_n[b]	T_g (°C)	Sample preparation[c]
PS	144 000	1.04	103	A
PPE-00	8 150	4.7	214	Technical grade
PPE trimer	362	1.0	−20	Direct synthesis
PPE-1100	1 120	1.1	93	C
PPE-1200	1 190	1.1	111	C
PPE-1500	1 500	1.1	127	C
PPE-2000	1 960	1.2	136	C
PPE-3100	3 100	1.2	179	B
PPE-5900	5 900	1.3	200	B
PPE-36000	36 000	1.4	224	B
PPE-44000	44 000	1.3	225	B

[a] Osmometry (v.p.o. for $M_n < 10\,000$)

[b] G.p.c. in $CHCl_3$

[c] A = anionic polymerization; B = fractionation; C = polymerization of 2,6-dimethyl-4-bromophenol[17,18]

Table 2 Glass transition temperatures and heat-capacity changes at T_g of PS/PPE-44000 mixtures

Sample $x=$	PPE (wt%)	T_g (°C)	Δc_p (J mol^{-1} K^{-1})
0	0	103	30.4
5	5	108	30.4
10	10	113	30.6
20	20	124	30.8
30	30	134	31.1
100	100	225	32.4

Table 3 Glass transition temperatures and heat-capacity changes at T_g of PS/PPE-5900 mixtures

Sample $x=$	PPE (wt%)	T_g (°C)	Δc_p (J mol^{-1} K^{-1})
10	10	111	30.6
20	20	120	30.7
40	40	135	30.9
60	60	154	31.0
80	80	178	31.6
100	100	200	31.7

Table 4 Glass transition temperatures and heat-capacity changes at T_g of PS/PPE-3100 mixtures

Sample $x=$	PPE (wt%)	T_g (°C)	Δc_p (J mol^{-1} K^{-1})
10	10	109	30.5
20	20	117	30.6
40	40	130	30.9
60	60	144	31.2
80	80	160	31.5
100	100	179	31.6

1000. The trimer ($M=362$ g mol^{-1}) does not fit equation (3). T_g^{∞} has been determined to be 227°C, and the constant b was 1.5×10^5. This value is about twice the value reported for PS. In *Figure 2* the reciprocal PPE glass transition temperatures are plotted *versus* $1/P_n$ according to Kanig's theory (equation (4) or (5)). A straight line results including also the trimer. As in the case of PS the validity range of equation (4) is apparently larger than the Fox–Flory equation. The limiting value for infinite molecular weights does not change. From the intercept of *Figure 2*, the free energy A_{AA}^* is obtained (equations (5) and (7)). For PPE the work required to separate PPE units and generate one mole of holes (energy of dilution) is 2770 J mol^{-1}. The corresponding value for PS is 2060 J mol^{-1}.

From the slope of *Figure 2* the ratio of the specific free volume of the holes and the free volume due to the vibration V_{f1}^*/V_{fM}^* is obtained. The value is 0.46 for PS[4] and 0.72 for PPE*. It has been discussed by Kanig[4] that the specific volume of a hole at T_g (V_{f1}^*) is not a constant for a variety of polymers. From the changes in the expansion coefficient and the heat capacity at T_g the ratio of the specific volumes of the repeating unit V_2^* and the hole V_{f1}^* at T_g are obtained according to:

$$\frac{V_2^*}{V_{f1}^*}=-\frac{\varphi_2^*}{R(\ln\varphi_1^*+\varphi_2^*)}\frac{\Delta c_p^*}{\Delta\alpha^* T_g}$$

These ratios are 9.2 for PS[4] and 4.5 for PPE, Compared to other polymers, the value for PPE is rather low, i.e. the holes in PPE are rather large. This result is in qualitative agreement with the results from Zoller[19], who found that in PS/PPE blends the free volume change at T_g strongly increases with increasing PPE content.

To look at the effect of a possible interaction on the local packing in the PS/PPE blend the analysis of the phenyl group rotation in PS[20] might be used. We have shown that the fraction of 'mobile' phenyl groups is not influenced by the presence of PPE[21].

In *Table 7* the heat-capacity changes of the PPEs at T_g are collected. Within experimental error no changes down to $P_n=9$ are observed, while the trimer behaves differently. The Δc_p values are in good agreement with those reported by Wunderlich[30], Zoller[19] and Fried[31].

The composition dependence of the glass transition temperature in PS/PPE mixtures

In *Figure 3* the d.s.c. traces of the blend series PS/PPE-3100 are shown. As has already been discussed in a previous paper[15], the glass transition regions in PS/PPE blends are rather narrow if PPEs of narrow molecular-weight distribution are used. In contrast, in PS/PVME blends, rather broad glass transition regions are observed. In *Figure 4* the glass transition temperatures for all blends with varying PPE molecular weights are

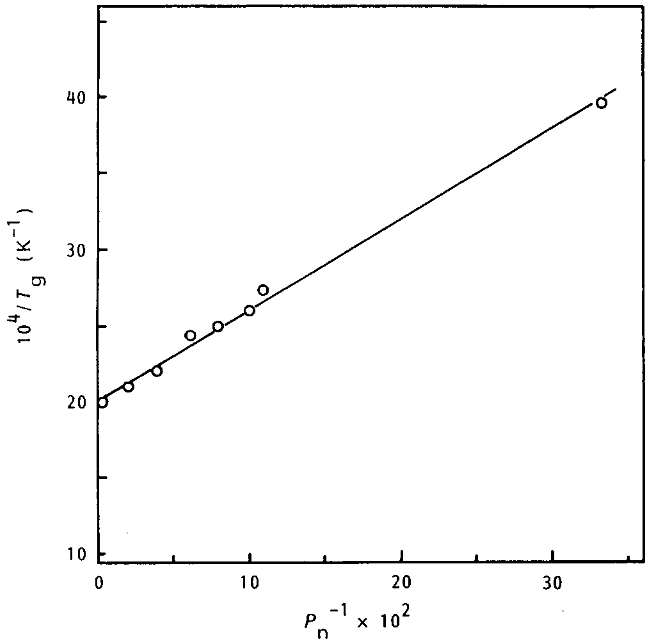

Figure 2 Molecular-weight (degree of polymerization) dependence of the PPE glass transition temperature according to equations (4) and (5); from the intercept $T_g^{\infty}=227$°C

Table 5 Glass transition temperatures and heat-capacity changes at T_g of PS/PPE-1500 mixtures

Sample $x=$	PPE (wt%)	T_g (°C)	Δc_p (J mol^{-1} K^{-1})
10	10	105	30.5
20	20	107	30.4
40	40	112	30.8
60	60	116	30.8
80	80	121	31.0

Table 6 Glass transition temperatures and heat-capacity changes at T_g of PS/PPE trimer mixtures

Sample $x=$	PPE (wt%)	T_g (°C)	Δc_p (J mol^{-1} K^{-1})
10	10	62	35.6
20	20	39	37.2
40	40	12	46.1
60	60	−3	55.4
100	100	−20	58.4

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* The calculation for PPE has been performed using the $\Delta\alpha$ value given by Zoller[19], and constant free volume fraction $\varphi_{f1}=0.0235$

Table 7 Comparison of $\Delta c_p(B)/\Delta c_p(A)$ for PS/PPE and PS/PVME blends (A = PS) (Δc_p in J g^{-1} K^{-1})

Blend	From $\Delta c_p(B)/\Delta c_p(A)$ (d.s.c.)	From Eq. (15) (Gordon–Taylor)
PS/PPE		
Our data	0.81	0.79
Prest and Porter[22a]		0.68
Kwei[23]		0.5
Schultz[24]		0.79
Fried[25]	0.78	0.76
From thermal expansion		$\rho_2\Delta\alpha_2/\rho_1\Delta\alpha_1$
Zoller[19]		0.55
Sharma[26b] and Rehage[27c]		0.9
PS/PPE trimer[d]	1.65	4.17
PS/PVME[28,29]		5.0

[a] T_g obtained at constant heating rate. No extrapolation to zero heating rate

[b] $\Delta\alpha_{PPE}$ value determined

[c] $\Delta\alpha_{PS}$ value determined

[d] The large difference of the values probably arises from the fact that the value obtained directly from the d.s.c. trace is altered by the onset of crystallization of the trimer after heating above T_g

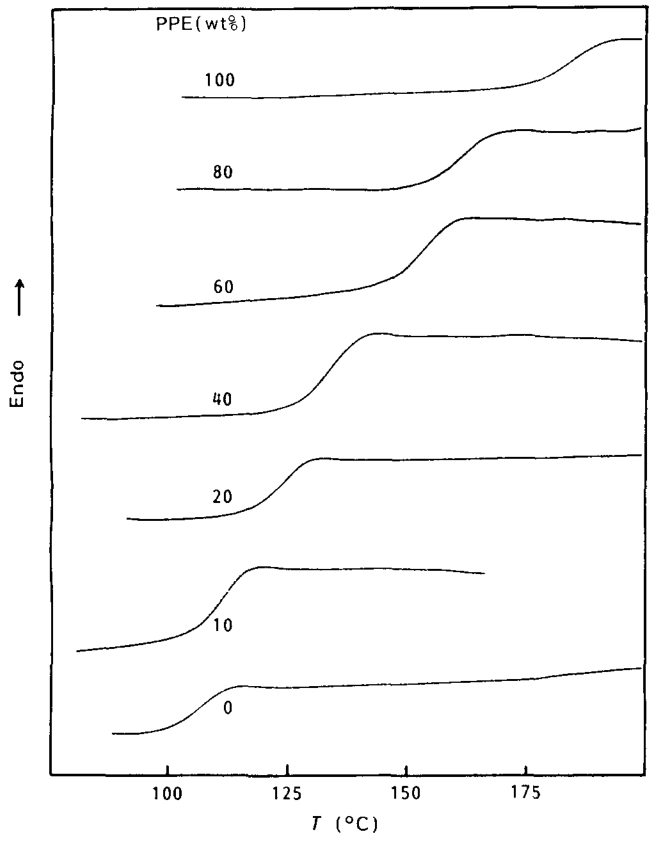

Figure 3 D.s.c. traces for PS/PPE-3100 mixtures of various compositions; heating rate 20 K min^{-1}

shown. Apparently the deviation from a linear behaviour is most pronouned for the PS/PPE trimer blends, where the glass transition temperatures are far below a linear additive behaviour. Only slight deviations are observed for the higher molecular weights. In the following an analysis of the T_g behaviour is given.

The linearized Gordon–Taylor equation . To test the validity range of an equation like that proposed by Gordon and Taylor[1], it is quite convenient to look for a linearization. Wood[32] and recently Schneider[33] proposed the following linearized version of equation (1) (called the Wood equation by Fried[31]):

$$\frac{T_g - T_{gA}}{T_{gB} - T_g} = K\frac{w_B}{1 - w_B} \qquad (14)$$

Thus a plot of $(T_g - T_{gA})/(T_{gB} - T_g)$ *versus* $w_B/(1 - w_B)$ has to give a straight line with slope K if the Gordon–Taylor equation is applicable. Of course, it is evident that the left-hand side of equation (14) is very sensitive to experimental errors if T_{gA} and T_{gB} differ only slightly. Additional problems in the use of equation (14) arise from the right-hand term. In the usual composition ranges, the data are not uniformly distributed along the $w_B/(1 - w_B)$ axis. Thus a check on the validity of the Gordon–Taylor approach might not be conclusive. The second difficulty can be eliminated by using the logarithmic form:

$$\log\left(\frac{T_g - T_{gA}}{T_{gB} - T_g}\right) = \log K + \log\left(\frac{w_B}{1 - w_B}\right) \qquad (15)$$

Using this form a rather unambiguous check on the applicability of the Gordon–Taylor equation can be made. A plot of $\log[(T_g - T_{gA})/(T_{gB} - T_g)]$ *versus* $\log[w_B/(1 - w_B)]$ must give a straight line with a slope 1. From the intercept K is obtained.

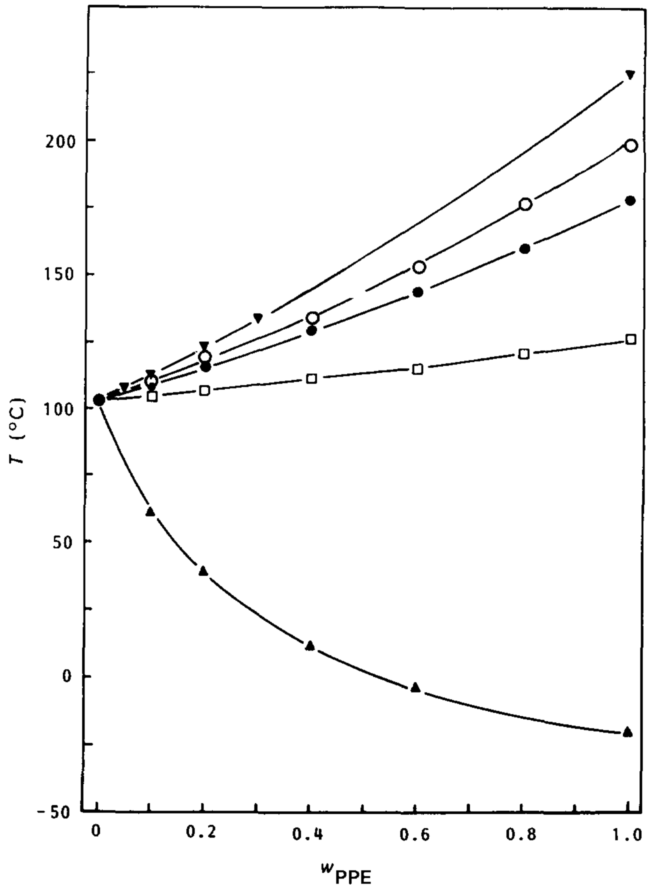

Figure 4 Composition dependence of the glass transition temperatures of PS/PPE with variable PPE molecular weight: M_n (PS) = 144 000; (▼) PS/PPE-44000; (○) PS/PPE-5900; (●) PS/PPE-3100; (□) PS/PPE-1500; (▲) PS/PPE trimer

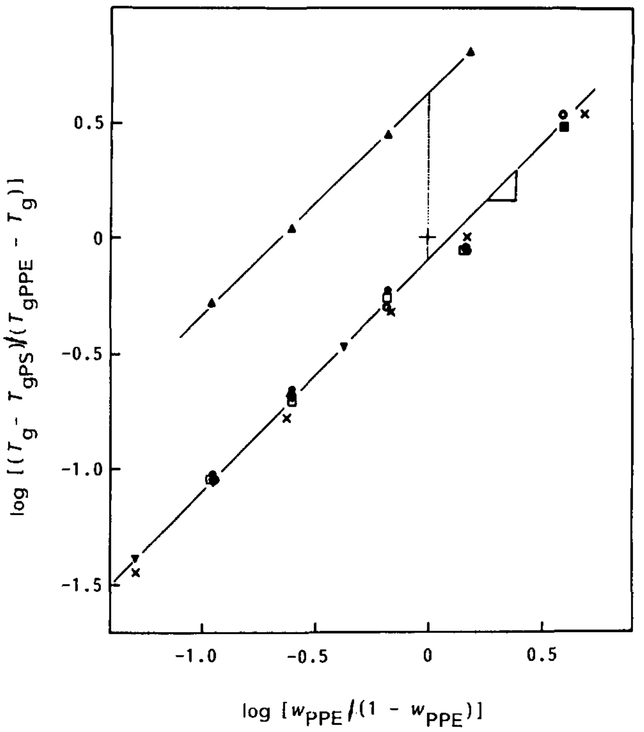

Figure 5 Analysis of the composition dependence of PS/PPE glass transition temperatures according to the linearized Gordon–Taylor equation (15): (▼) PS/PPE-44000; (○) PS/PPE-5900; (●) PS/PPE-3100; (□) PS/PPE-1500; (▲) PS/PPE trimer; (×) data from Prest and Porter[22]

In *Figure 5* all T_g data of our PS/PPE blends are represented according to equation (15). For all PS/PPE blends with P_n(PPE)>9 the data fall onto a single straight line with slope 1. Included are the T_g data from the work of Prest and Porter[22]. Especially for the lower PPE molecular weights with a T_g not far from PS, the small scatter of the data is quite astonishing. From the intercept the ratio of the heat-capacity changes of the pure homopolymers at T_g should be obtained. As can be seen in *Table 7*, the value obtained directly from d.s.c. and the value from *Table 5* are in very good agreement. These experimental findings indicate that the different chain lengths do not change the interaction strength between PS and PPE chain segments. It is evident from *Figure 5* that the PS/PPE trimer blends behave differently from the higher molecular weights. Nevertheless a 'Gordon-Taylor behaviour' with a slope of 1 is observed, but the intercept is very much different from the 'polymers'. The value of $\Delta c_{pB}/\Delta c_{pA}$ obtained from *Figure 5* is 4.7; using the Δc_p value of PS the corresponding Δc_p of the trimer is 146 J mol^{-1} K^{-1}. The directly measured Δc_p value at T_g for the trimer is much lower (60 J mol^{-1} K^{-1}). This lower value can be explained by the onset of exothermic crystallization of the trimer after passing the glass transition.

In *Figure 6* T_g data from the literature for blends of PPE with PS, chlorinated PS and poly(styrene-α-methylstyrene) P(S-αMS) are represented according to equation (15). In *Figure 6a* PS/PPE data from Shultz and Gendron[24] are shown (PS M_w = 97 200, M_w/M_n = 1.06; PPE M_w = 18 500, M_w/M_n = 2.02). The heating rate was kept at 20 K min^{-1}; data from the first and second runs are shown. Apparently these data show a much larger scatter than the data given in *Figure 5*, but again a linear representation with slope = 1 is possible. The value of K is the same as from our own data. The data of Fried, Karasz and MacKnight[25] for PS/PPE and P(S-*co*-*p*ClS)/PPE blends are included. They also show 'Gordon–Taylor' behaviour (see *Table 7* for K values). In *Figure 6b* PS/PPE data from Kwei and Frisch[23] for various PS molecular weights are shown for a heating rate of 10 K min^{-1} and a PPE of rather broad *MWD* (M_w/M_n = 3.95). For M_n(PS)⩾2200 all data fit the same line with slope 1, while the PS-800 data deviate slightly. This deviation might be within experimental error due to a broad glass transition region. The value of K obtained from these data is around 0.5, a value much lower than from the other data.

In *Figure 6c* the data of blends of styrene/α-methylstyrene copolymers with PPE from Shultz[34] are shown for two different copolymer compositions. Though the number of data points is rather limited, the Gordon–Taylor equation is applicable to these data.

These examples demonstrate that the representation of T_g data of miscible polymer blends according to equation (15) might be quite useful to decide directly whether the Gordon–Taylor equation can describe the composition dependence or not. On the other hand, this representation also shows how sensitive the T_g data and their quantitative interpretation are to experimental errors.

The Kanig equation. In *Figure 7* the data for the PS/PPE blends are presented according to the result of Kanig's theory (equation (11)). For all PPE molecular weights horizontal straight lines are obtained. This is expected for the special case when A^*_{AB} is given by the arithmetic mean of A^*_{AA} and A^*_{BB}, in agreement with the previous statement that equation (11) reduces to the Gordon–Taylor equation for that situation. A cross-check can be made from the analysis of the intercept for high-molecular-weight PPE/PS blends. The standard free enthalpy to generate one mole of holes is 2400 J mol^{-1}, a value which is in good agreement with the arithmetic mean (2415 J mol^{-}1).

The composition dependence of PS/PVME

A critical check of Kanig's relation can be made for PS/PVME blends, for which the Gordon–Taylor approach fails. For this analysis we have used data of Halary *et al.*[28] and of Banks *et al.*[29]. Both sets of T_g data were not extrapolated to zero heating rate. A more detailed analysis including other data will be given elsewhere[35].

To check again the inadequacy of equation (1), we used the logarithmic linearized version (equation (15)). The result is shown in *Figure 8*. As we expected, no straight line with slope 1 (Gordon–Taylor behaviour) is found. Surprisingly all the data fall on a straight line with slope ~1.4–1.5. Thus the composition dependence of the PS/PVME glass transition temperatures can be given empirically by:

$$\log\left(\frac{T_g - T_{gA}}{T_{gB} - T_g}\right) = \log K + b\log\left(\frac{w_B}{1 - w_B}\right) \qquad (16)$$

Rearranged into the form of equation (1), this empirical equation gives equation (17), i.e. the composition variable enters to a higher power than 1. Of course, in both the Kwei equation as well as Kanig's equation for

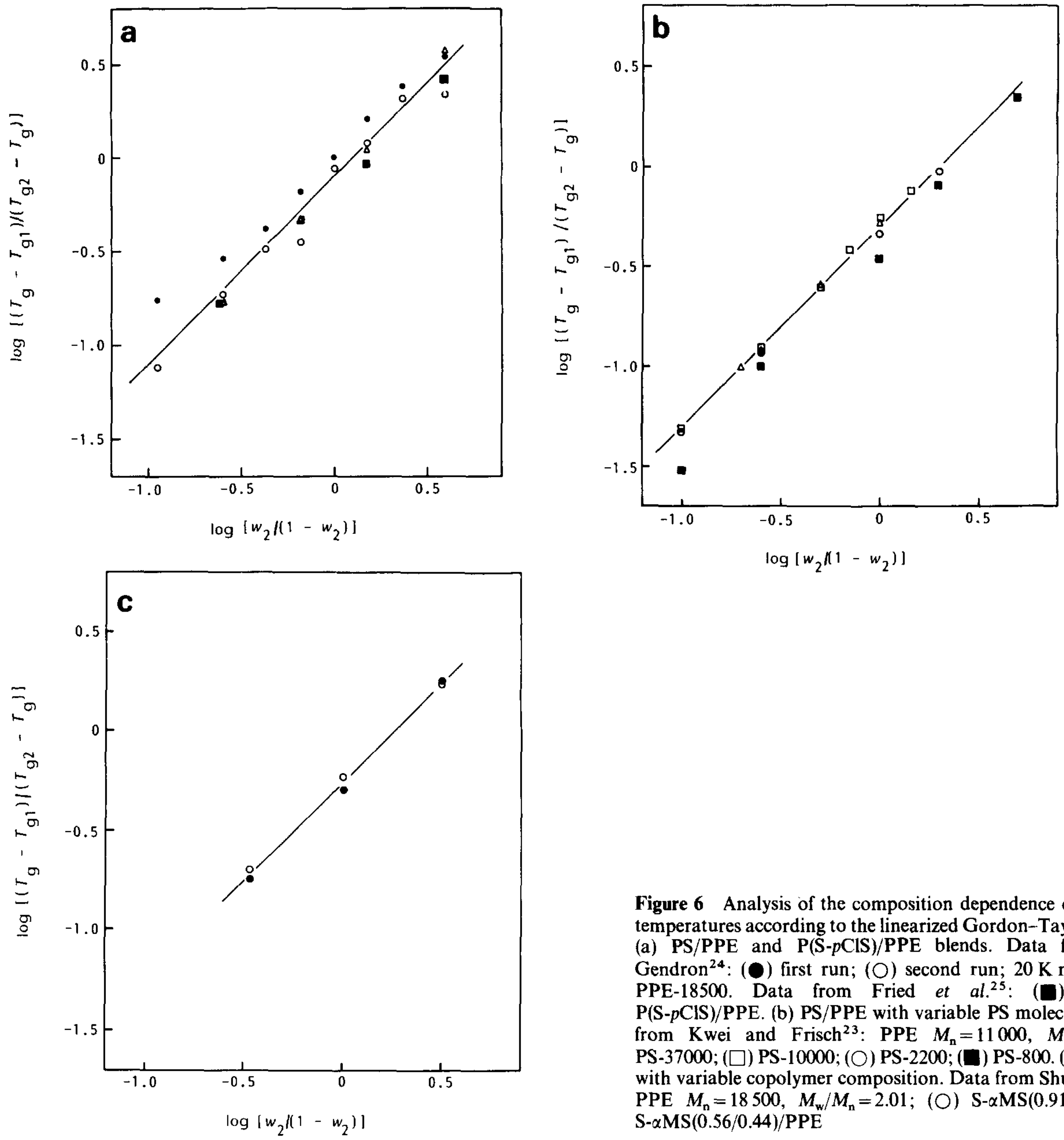

Figure 6 Analysis of the composition dependence of glass transition temperatures according to the linearized Gordon–Taylor equation (15). (a) PS/PPE and P(S-*p*ClS)/PPE blends. Data from Shultz and Gendron[24]: (●) first run; (○) second run; 20 K min^{-1}; PS-97200; PPE-18500. Data from Fried *et al.*[25]: (■) PS/PPE; (△) P(S-*p*ClS)/PPE. (b) PS/PPE with variable PS molecular weight. Data from Kwei and Frisch[23]: PPE $M_n = 11\,000$, $M_w/M_n = 3.95$; (△) PS-37000; (□) PS-10000; (○) PS-2200; (■) PS-800. (c) P(S-αMS)/PPE with variable copolymer composition. Data from Shultz and Young[34]: PPE $M_n = 18\,500$, $M_w/M_n = 2.01$; (○) S-αMS(0.91/0.09)/PPE; (●) S-αMS(0.56/0.44)/PPE

copolymers the composition enters in linear and quadratic terms:

$$T_g = \frac{w_A^b T_{gA} + K w_B^b T_{gB}}{w_A^b + K w_B^b} \tag{17}$$

Because no detailed data of Δc_p(PVME) could be obtained from the literature, we used the value obtained from the intercept of *Figure 8* ($K = 0.2$) to analyse the PS/PVME data according to Kanig's relation. The result for the data given by Halary[28] is given in *Figure 9*. The data of the blends can be described by a straight line within experimental error. From the positive slope and from the intercept the values for A_{AB}^* are obtained. This value is about 2000 J mol^{-1} from both slope and intercept, a value that is quite close to that of PS and much larger than the arithmetic mean of PS and PVME (1700 J mol^{-1}). No straight line is observed if K is taken too large (>0.3). The reduced weight fractions Φ_A are very sensitive to the value of K, if it departs from 1 as is the case for PS/PVME. It has to be discussed how the strong negative deviation from linearity of the PS/PVME glass transition values can be in agreement with an interaction energy A_{AB}^* that is larger than the arithmetic average. Such an interaction would rather increase the T_g of the blend. From the analysis according to equation (11), we actually obtain a rather high value for the work required to separate A–B contacts. Nevertheless these two results are not in contradiction: using equation (1) with the value of K obtained from *Figure 8* the calculated T_g data are even below the experimental values, i.e. the large gain of the free volume when PVME segments become mobile dominates the glass transition behaviour of PVME/PS blends. Contrary to this effect is the interaction that tends to increase the glass transition temperature. This is shown in *Figure 10*.

CONCLUSIONS

The analysis of the molecular-weight dependence of the glass transition temperatures of PPE from $P_n = 3$ to 370

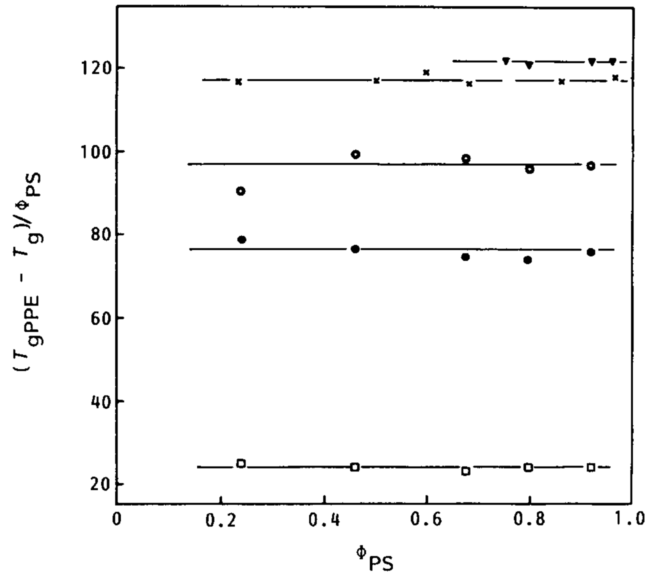

Figure 7 Analysis of the composition dependence of PS/PPE glass transition temperatures according to the Kanig equation (11): (▼) PS/PPE-44000; (○) PS/PPE-5900; (●) PS/PPE-3100; (□) PS/PPE-1500; (×) data from Prest and Porter[22]

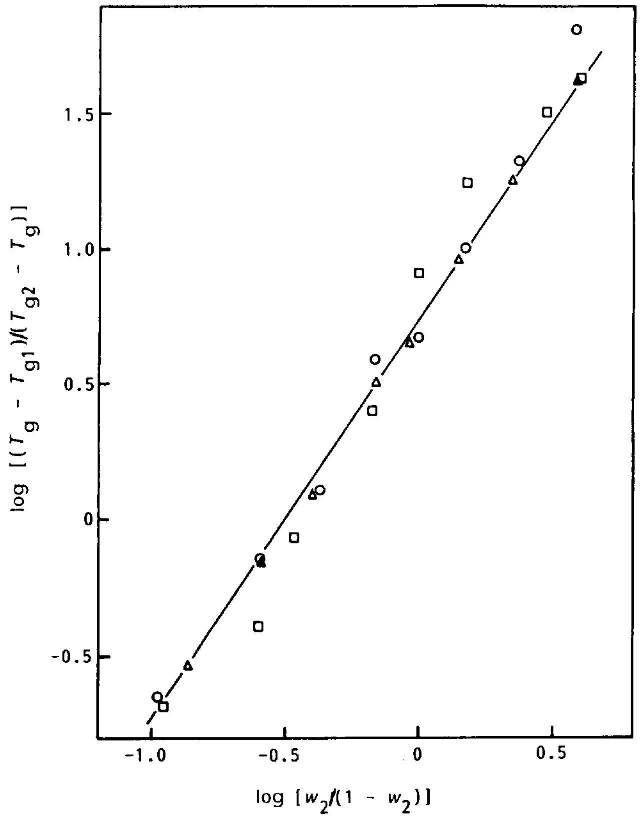

Figure 8 Analysis of the composition dependence of PS/PVME glass transition temperatures according to the linearized Gordon–Taylor equation (15). Data from Halary *et al.*[28]: (○) PS-35000; (△) PS-233000; heating rate 5 K min^{-1}. Data from Banks *et al.*[29]: (□); heating rate 20 K min^{-1}

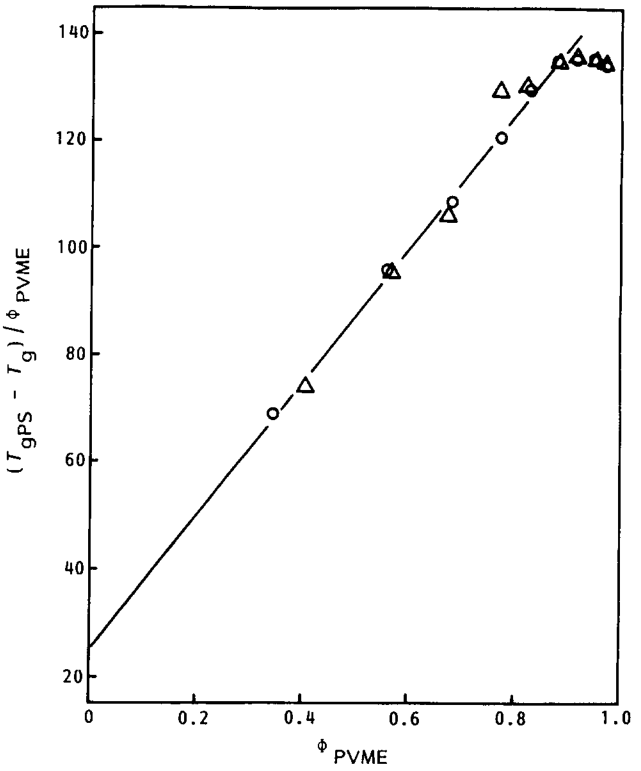

Figure 9 Analysis of the composition dependence of PS/PVME glass transition temperatures according to the Kanig equation (11). Data from Halary *et al.*[28]: (○) PS-35000; (△) PS-233000; heating rate 5 K min^{-1}

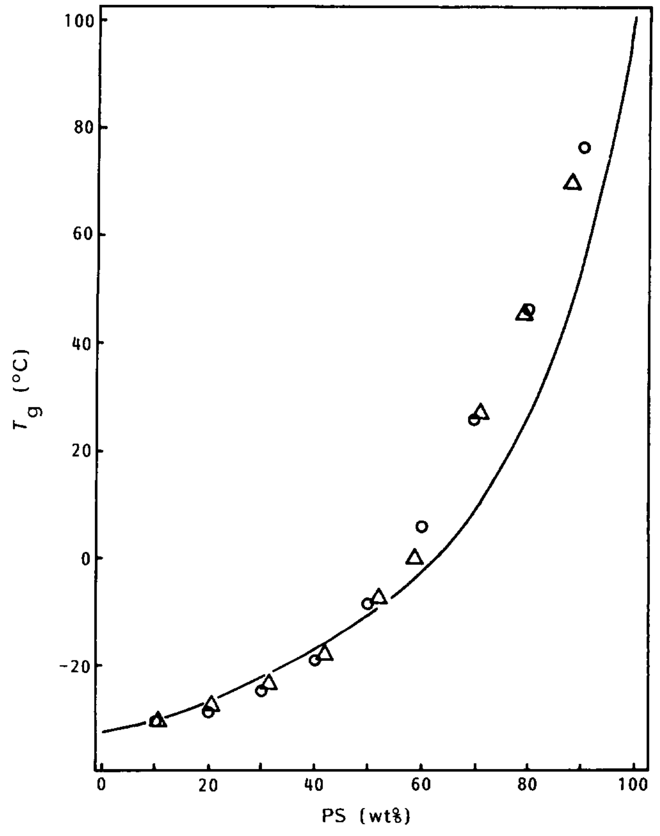

Figure 10 Composition dependence of PS/PVME glass transition temperatures: full curve calculated according to the Gordon–Taylor equation for $K = 0.2$. Data from Halary *et al.*[28]: (○) PS-35000; (△); PS-233000; heating rate 5 K min^{-1}

showed the validity of Kanig's relation. A polymer melt is considered as a saturated solution of holes and chains. To achieve thermodynamic equilibrium a reduction of holes with decreasing temperature results. The glass transition of various polymers is not described by a free volume that is constant for all polymers. In addition the theory allows the determination of the standard free energy required to generate one mole of holes in a polymer melt.

Kanig's equation for the composition dependence of copolymers has been applied to miscible polymer blends of PS and PPE. This equation reduces to the Gordon–Taylor equation, if the energy to separate A–B contacts is given by the arithmetic mean of the corresponding AA and BB energies. It seems that all modifications of the Gordon–Taylor equation given by Kwei[2] or Schneider *et al.*[3] are already included in Kanig's treatment, which apparently has been overlooked in the polymer blend field[36].

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Note added in proof

In the description of the Kanig theory we have used the equation for copolymers to describe the glass transition of polymer mixtures (equation (11)). According to a suggestion by Kanig*, this equation can also be obtained easily from the equation he derived for polymer–plasticizer mixtures[4] by increasing the plasticizer molecular weight. According to this line the mixing entropy is taken into account and this approach is more straightforward, than just using the equation for copolymers.

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* Kanig, G. personal communication, 1988