

The glass transition temperature of random copolymers: 2. Extension of the Gordon–Taylor equation for asymmetric T_g vs composition curves

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It is obvious that asymmetric T_g vs composition curves of random copolymers cannot be adapted by the Gordon–Taylor equation based on volume additivity, even if instead of the model-specific additivity parameter $K_{G-T} = (\rho_1/\rho_2)(\Delta\alpha_2/\Delta\alpha_1)$ a curve fitting parameter, K , is considered. Therefore contributions of diad- and triad-sequences to the copolymer T_g were considered. Assuming, by lack of copolymerization kinetics data, that the diad- and triad-sequence distribution can be related in a first approximation to the respective weight fractions of the copolymer components a concentration power equation is deduced for adapting the composition dependence of the glass temperature of copolymers. The two fitting parameters, K_1 and K_2 , of this concentration power equation characterize the contributions to the copolymer T_g of the hetero-diads and -triads, respectively. Values of $K_1 > 0$ are generally typical for positive deviations of the copolymer T_g from additivity, suggesting stiffening effects induced by attractive interactions between the different repeating units of the copolymer. Negative values of K indicate negative deviations due to repulsions within the hetero-diads. The corresponding T_g vs composition curves may exhibit maxima or minima, respectively. The different influences on the copolymer T_g of hetero-triads, are characterized by values of K_2 different from zero. Depending on whether K_2 is smaller or larger than K_1 the results are either pronounced asymmetric or S-shaped T_g vs composition curves, suggesting that the influence on T_g of the hetero-triads is dependent on their composition, taking into account the hetero-triads may contain either two repeating units of the one or of the second component. Although fundamental relationships between the fitting parameters and a molecular property are not yet available, it is shown, that in a first approximation the values of K_1 are related to differences between the solubility parameters of the copolymer components. The T_g vs composition behaviour is analysed for copolymers of acrylates and methacrylates among each other and with styrene, acrylonitrile and vinyl chloride, respectively. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In the literature essentially two basic concepts are discussed to explain the composition dependence of the glass temperature of random copolymers. Gordon and Taylor¹ assumed volume additivity of the repeating units in copolymers, analogous to the interpretation of packing phenomena in ideal solutions of small molecules. Di Marzio and Gibbs², on the other hand, based on the idea that chain stiffness is the main determinant of the glass transition, supposed additivity of 'rotatable' ('flexible') bonds, i.e. of those simple bonds which by rotation contribute to conformational changes of the molecule. Incidentally the resulting expression of both models are formally of the same 'Gordon–Taylor' type.

$$T_g = [w_1 T_{g_1} + K w_2 T_{g_2}] / [w_1 + K w_2] \quad (1)$$

with T_g the glass temperature of the copolymer and T_{g_i}

and w_i the glass temperatures and the weight fractions of the components, respectively. The parameter K is, however, model specific, i.e. $K_{G-T} = (\rho_1/\rho_2)(\Delta\alpha_2/\Delta\alpha_1)$ for the Gordon–Taylor volume additivity model and $K_{DM-G} = [\mu_1/\gamma_1]/[\mu_2/\gamma_2]$ for the Di Marzio–Gibbs 'flexible' bond additivity model. ρ_i are the densities and $\Delta\alpha_i = (\alpha_{\text{melt}} - \alpha_{\text{glass}})_{T_g}$ the increments of the expansion coefficients at T_g , whereas μ_i and γ_i are the masses and the numbers of 'flexible' bonds, respectively, of the monomeric units.

In the assumption of validity of the Simha–Boyer rule, $\Delta\alpha T_g = 0.113^3$, and neglecting in a first approximation the differences between the mostly very similar densities of polymers, i.e. supposing $\rho_1/\rho_2 = 1$, the constant K_{G-T} for volume additivity can be substituted in a first approximation by $K_F = T_{g_1}/T_{g_2}$. Accordingly, the Gordon–Taylor equation can be reformulated

$$(1/T_g) = (w_1/T_{g_1}) + (w_2/T_{g_2}) \quad (2)$$

the result being the well known Fox relation⁴.

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Without further transformations the above equations have also been used for the prediction of the composition dependence of the glass temperature of compatible polymer blends. Schneider and Di Marzio⁵ have shown, however, that both additivity models result in the same composition dependence of the glass temperature of polymer blends. The values of the respective constants of equation (1), K_{G-T} and K_{DM-G} , must thus be equal, i.e. $\rho/\Delta\alpha = \mu/\gamma$. The latter equality can be substituted in a first approximation by $T_g \sim \mu/\gamma$ considering the above-mentioned Simha-Boyer rule and replacing the Gordon-Taylor constant, K_{G-T} , by K_F . Consequently the glass temperature of polymers is related to the mass per 'flexible' bond of the monomeric unit, i.e. $T_g = C\mu/\gamma$. It was initially supposed that C is a 'universal' constant, but recently Schneider⁶ has shown that C is a characteristic parameter for the different classes of polymers.

Taking into account that both the volume and the 'flexible' bond additivity models assume ideal behaviour, thus neglecting any kind of interaction between the components, it is not surprising that the glass temperature vs composition dependence of both copolymers and polymer blends exhibit more or less significant deviations of the glass temperature from the predicted additivity values. Consequently, in order to adapt experimental T_g data, the additivity models were extended to account for the effect of interactions between the components of both copolymers and compatible polymer blends. The simplest way, is, however, to consider the K parameter of the Gordon-Taylor equation to be a real fitting parameter. This procedure has been used in the first paper of this series. It resulted, however, that only symmetrical T_g vs composition curves can be adapted by this method⁷.

To improve the fit of asymmetrical T_g vs composition data of copolymers, effects of the sequence distribution on the glass temperature were taken into account and both, the volume additivity and the 'flexible' bond model have been extended to account for influences of sequence distribution on T_g .

Starting with the original Di Marzio-Gibbs² expression for the glass temperature of copolymers

$$T_g = n'_1 T_{g_1} + n'_2 T_{g_2} \quad (3)$$

where $n'_i = w_i(\gamma_i/\mu_i)$ are the weight fractions of 'flexible' bonds of the respective components, Barton⁸ extended the relation to account for diad sequences contributions to T_g .

$$T_g = n'_{11} T_{g_1} + n'_{22} T_{g_2} + (n'_{12} + n'_{21}) T_{g_{12}} \quad (4)$$

n'_{ij} are the mole fractions of 'flexible' bonds of the respective diads, and $T_{g_{12}}$ is the glass temperature of the strictly alternating copolymer. Taking into account that $T_{g_{12}}$ is generally not accessible experimentally, it is in fact treated as a fitting parameter of the extended diad sequence contribution equation. The mole fractions of 'flexible' bonds of the different diads are estimated via the corresponding reactivity ratios, r_i , and the monomer feed composition. Moreover, Ham⁹ has shown that for the better fit of S-shaped experimental T_g vs composition curves it is more convenient to use an equation extended to account for the contributions of triad sequences to the glass temperature of copolymers. The glass temperatures of the respective hetero-triads become now, however, real fitting parameters of the

experimental T_g vs copolymer composition curves without any physical meaning.

Johnston¹⁰, on the other hand, has extended the Fox equation (2) of the volume additivity model to account for diad sequence contributions to the glass temperature of copolymers.

$$\begin{aligned} (1/T_g) = & [w_1 p_{11}/T_{g_1}] + [w_2 p_{22}/T_{g_2}] \\ & + [(w_{12} p_{12} + w_{21} p_{21})/T_{g_{12}}] \end{aligned} \quad (5)$$

p_{ij} are the probabilities of formation of the respective diads, depending on the conditions of copolymerization, i.e. on the monomer feed composition and the monomer reactivity ratios of the copolymerization reaction.

All the above discussed equations based on the concept of diad and triad sequence contributions to the glass temperature of copolymers suppose, independent of the used additivity model, the knowledge of the copolymerization kinetics, i.e. of the monomer feed composition and of the reactivity ratios. If kinetic data are not accessible and only the composition of the copolymers is known, there is another possibility to extend the Gordon-Taylor equation (1) in order to adapt experimental T_g data which show deviations from additivity because of specific interactions between the copolymer repeating units.

CONCENTRATION POWER COPOLYMER T_g VS COMPOSITION EQUATION

Using corrected weight fractions to include the additivity effects, i.e. introducing the notations

$$w_{1c} = (1 - w_{2c}) = [w_1/(w_1 + Kw_2)] \text{ and}$$

$$w_{2c} = [Kw_2/(w_1 + Kw_2)] \text{ with } w_{1c} + w_{2c} = 1$$

the Gordon-Taylor equation (1) can be reformulated as

$$T_g = (1 - w_{2c}) T_{g_1} + w_{2c} T_{g_2}$$

The latter equation can be rearranged in a linear relationship to express the relative increase of the blend T_g depending on the corrected weight fraction, w_{2c} , of the copolymer component with the higher T_{g_2}

$$(T_g - T_{g_1})/(T_{g_2} - T_{g_1}) = w_{2c} \quad (6)$$

In the subsequent discussions concerning the experimentally observed deviations of the copolymer T_g from the additivity values predicted by the Gordon-Taylor equation in a first approximation for K the most accessible value $K_F = T_{g_1}/T_{g_2}$ is used to estimate the corrected weight fractions. That means the deviations from additivity of the glass temperature are analysed by comparison with the additivity rule of Fox (2).

Supposing that the probabilities of finding diad and triad sequences in the copolymers are related to the respective weight fractions of components, the contributions to T_g of the different sequences can be considered by extending equation (6) into a concentration power equation

$$\begin{aligned} T_g = & w_{1c} T_{g_1} + w_{2c} T_{g_2} + k_1 w_{1c} w_{2c} + k_2 w_{1c}^2 w_{2c} \\ & + k_3 w_{1c} w_{2c}^2 \end{aligned} \quad (6a)$$

Expressing in the concentration power terms w_{1c} by $(1 - w_{2c})$ an extended Gordon-Taylor equation results

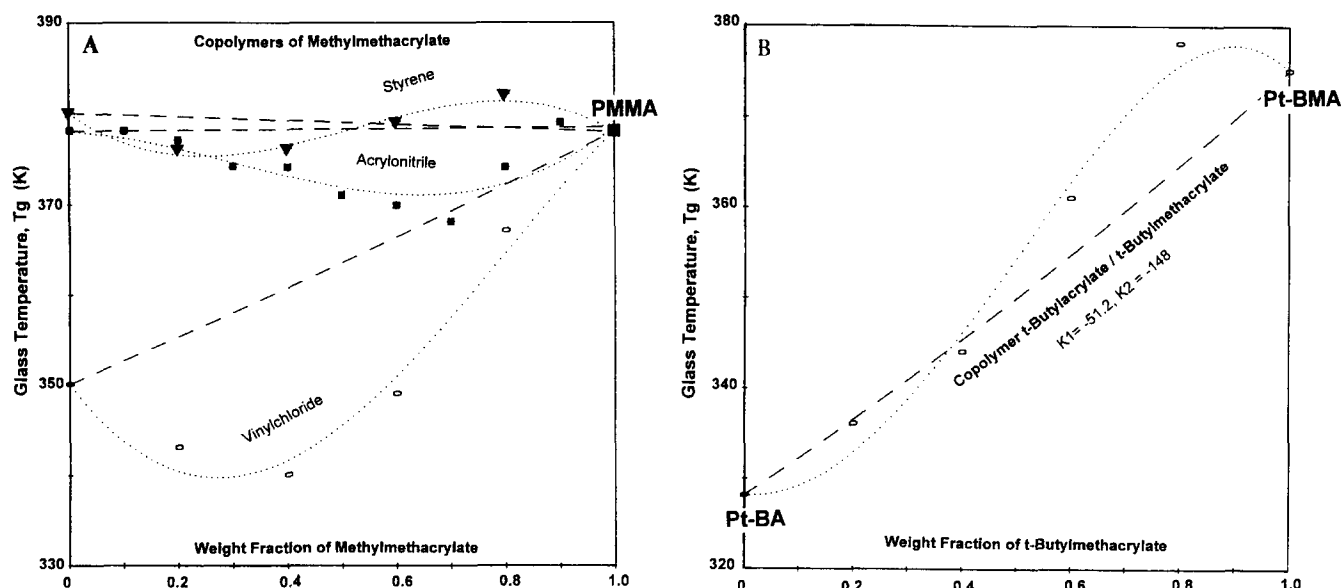


Figure 1 T_g vs composition curves of copolymers, dashed lines—Fox additivity rule (2); dotted lines—fit by concentration power equation (8). (A) Copolymers of methyl methacrylate with styrene, acrylonitrile and vinyl chloride; (B) poly(*t*-butyl acrylate-*co*-*t*-butyl methacrylate)

as:

$$T_g = w_{1c}T_{g1} + w_{2c}T_{g2} + (k_1 + k_2)w_{2c} \\ \downarrow \\ \text{Gordon-Taylor equ.} \\ -(k_1 + 2k_2 - k_3)w_{2c}^2 + (k_2 - k_3)w_{2c}^3 \quad (6b)$$

↓
extension for contributions of diads and triads

From equation (6a) it results, that k_1 characterizes the contributions of the hetero-diad sequences to T_g , whereas k_2 and k_3 of the respective different hetero-triad sequences, containing either two repeating units of the first, or of the second component, respectively.

Remembering that $w_{1c} = (1 - w_{2c})$, finally the following concentration power equation in w_{2c} is obtained by reformulation of equation (6b)

$$(T_g - T_{g1})/(T_{g2} - T_{g1}) = (1 + \kappa_1 + \kappa_2)w_{2c} \\ - (\kappa_1 + 2\kappa_2 - \kappa_3)w_{2c}^2 + (\kappa_2 - \kappa_3)w_{2c}^3 \quad (7)$$

with $\kappa_i = k_i/(T_{g2} - T_{g1})$.

The values of the coefficients of the concentration power equation (7), κ_i , depend via the coefficients k_i of equation (6a) on the kinetic parameters of the copolymerization reaction which control the sequence distribution of the copolymer as well on the contributions of the respective sequences to the glass temperature of the copolymers. Since the two contributions are not separately accessible without knowledge of the copolymerization kinetics, the coefficients of equation (7) can be combined as

$$(T_g - T_{g1})/(T_{g2} - T_{g1}) = (1 + K_1)w_{2c} \\ - (K_1 + K_2)w_{2c}^2 + K_2w_{2c}^3 \quad (8)$$

The new introduced parameters, $K_1 = (\kappa_1 + \kappa_2)$ and $K_2 = (\kappa_2 - \kappa_3)$ are accessible by least squares fitting procedures by applying the concentration power equation (8) to experimental copolymer T_g data. Unfortunately, to our knowledge no relationships between the fitting parameters and physical characteristics of the copolymer components are available.

By multiplying with $(T_{g2} - T_{g1})$ the concentration power equation (8) can be rearranged to concentration power extended Gordon-Taylor equation

$$T_g = w_{1c}T_{g1} + w_{2c}T_{g2} + K^1w_{1c}w_{2c} + K^2w_{1c}w_{2c}^2 \\ \downarrow \qquad \qquad \qquad \downarrow \\ \text{Gordon-Taylor equ.} \quad \text{concentration power extension.} \quad (9)$$

The new introduced parameters K^1 and K^2 are related to the fitting parameters of the concentration power equation (8) by

$$K^1 = (T_{g2} - T_{g1})K_1 = k_1 + k_2$$

and

$$K^2 = (T_{g2} - T_{g1})K_2 = k_2 - k_3$$

[for significance of the respective k_i parameters see equation (6a)].

Unfortunately there is no alternative way for an independent evaluation of the sequence dependent parameters k_i of equation (6a). Thus only a rough estimation of the significance can be presented for the experimentally derived fitting parameters K_1 and K_2 of the concentration power equation (8).

If the specific contributions of the different hetero-triads to T_g are negligible, i.e. if the respective contributions of the hetero-triads are independent of composition (i.e. if $k_2 = k_3$) the fitting parameter $K_2 = 0$ and equation (8) becomes

$$(T_g - T_{g1})/(T_{g2} - T_{g1}) = (1 + K_1)w_{2c} - K_1w_{2c}^2 \\ = w_{2c} + K_1w_{1c}w_{2c} \quad (10)$$

K_1 depends then only on the contributions of the hetero-diads to the copolymer T_g and generally symmetrical T_g vs composition curves are obtained, which even can show more or less accentuated maxima or minima. In that case values of $K_1 > 0$ characterize positive deviations of the copolymer glass temperature from additivity, suggesting stiffening effects induced by attractive interactions between the repeating units of the hetero-diads. $K_1 < 0$ indicates correspondingly negative deviations

Table 1 Parameters of the T_g vs composition curves of copolymers

Copolymer	$(T_{g_2} - T_{g_1})$	Fitting parameters of equation (8)		Parameters of equation (6a)		
		K_1	K_2	$(k_1 + k_2)^a$ K^1	$(k_2 - k_3)^b$ K^2	$(k_1 + k_3)^c$ K^3
<i>Copolymers of Fig. 1</i>						
AN/MMA	0.5	-85.72	-72.24	-42.9	-36.1	-6.8
VC/MMA	28.0	-0.94	3.85	-26.3	+107.5	-133.8
S/MMA	-2.0	16.33	37.04	-32.7	-74.1	+41.4
<i>t</i> -BA/ <i>t</i> -BMA	47.0	-1.09	-3.5	-51.2	-164.5	+113.3
<i>Acrylic/metaacrylic copolymers</i>						
MMA/ <i>t</i> -BMA	3.0	5.61	14.12	+16.83	+42.36	-26.0
MA/ <i>n</i> -BA	65.0	0.69	0.54	+44.85	+53.1	+9.8
EA/ <i>n</i> -BA	35.0	1.03	0.97	+36.05	+33.95	+2.1
2E-HA/ <i>t</i> -BA	113.0	0	0	0	0	0

$$^a k_1 + k_2 = K^1 = K_1(T_{g_2} - T_{g_1})$$

$$^b k_2 - k_3 = K^2 = K_2(T_{g_2} - T_{g_1})$$

$$^c k_1 + k_3 = K^3 = (K_1 - K_2)(T_{g_2} - T_{g_1})$$

from additivity of the copolymer T_g , because of an increased mobility due to repulsions within the hetero-diads. Kanig¹², relating the changes of interaction energies to the respective Gibbs energies for generating one mole of holes in the equilibrium polymer melt, has shown already in 1963, that the second power concentration equations of type (10) allow the fit of experimental T_g vs composition curves of copolymers showing maxima or minima. This is not possible using the Gordon–Taylor equation [which results for both $K_1 = 0$ and $K_2 = 0$ —see equation (9)] even if the K parameter is considered a real fitting parameter. That means the Gordon–Taylor equation works only if the glass temperature of the copolymer is not depending on the sequence distribution of the repeating units within the copolymer, the composition dependence of T_g being almost additive.

Contributions of the hetero-triads to the glass temperature of the copolymers are characterized by both K_2 values different from zero and asymmetric T_g vs composition curves. This is illustrated in *Figure 1* for the copolymers of methyl methacrylate (MMA) with styrene (S), acrylonitrile (AN) and vinyl chloride (VC), respectively (*Figure 1A*) as well as for the copolymers of *t*-butyl acrylate/*t*-butyl methacrylate (*Figure 1B*).

For further discussions it is, however, more convenient to use instead of the fitting parameters K_1 and K_2 of the concentration power equation (8) and which depend on the difference between the glass temperatures of the copolymer components, the related parameters K^1 and K^2 of the extended Gordon–Taylor equation (9), which characterize the deviations of the copolymer T_g from the values predicted by the Gordon–Taylor equation, due to interactions between the different monomeric units of the copolymer.

Taking into account that the parameter of the extended Gordon–Taylor equation (8), $K^2 = (T_{g_2} - T_{g_1}) K_2 = k_2 - k_3$, is given by the difference between the contributions of the hetero-triads containing either two repeating units of component 1 with the lower T_{g_1} [characterized by the parameter k_2 —see equation (6a)] or two repeating units of the component 2 with the higher T_{g_2} (characterized by k_3), positive values of K^2 indicate a prevailing

effect on the copolymer T_g of the hetero-triads containing two repeating units of component 1. The predominant effect of the hetero-triads containing two repeating units of component 2 will be reflected by negative values of the parameter K^2 .

Asymmetries of the T_g vs composition curves due to the different hetero-triad contributions can be, however, more conveniently discussed by comparison of the values of the sums $(k_1 + k_2)$ and $(k_1 + k_3)$, respectively, which characterize the additional different contributions to the copolymer T_g of the asymmetric hetero-triads [see equation (6a)] in addition to those of the hetero-diads (k_1). These sums are accessible via the fitting parameters K_1 and K_2 of the concentration power equation (8)

$$(k_1 + k_2) = K^1 = K_1(T_{g_2} - T_{g_1})$$

and

$$(k_1 + k_3) = K^3 = (K_1 - K_2)(T_{g_2} - T_{g_1}) \quad (11)$$

The respective parameters are listed in *Table 1* for the copolymers shown in *Figure 1*.

The dashed lines in *Figure 1* represent the additive T_g vs composition behaviour predicted by the simple Fox relation (4), whereas the dotted lines are obtained by fitting the experimental T_g data using the concentration power equation (8).

The glass temperatures of the copolymers of methyl methacrylate with acrylonitrile and vinyl chloride, respectively, show both negative deviations from additivity. The respective T_g vs composition curves exhibit, however, different asymmetries although they are characterized both by negative K^1 and K^3 values, respectively. But the K^2 parameters have different signs. So the T_g vs composition curve of poly(AN-*co*-MMA)—showing the more pronounced negative deviations for higher MMA weight fractions—is characterized by a negative K^2 parameter, whereas the respective curve of poly(VC-*co*-MMA) adapts to positive K^2 and exhibits the more pronounced negative deviations for lower MMA weight fractions, i.e. higher VC weight fractions. It may thus be supposed that in poly(AN-*co*-MMA) the influence on T_g of the hetero-triads

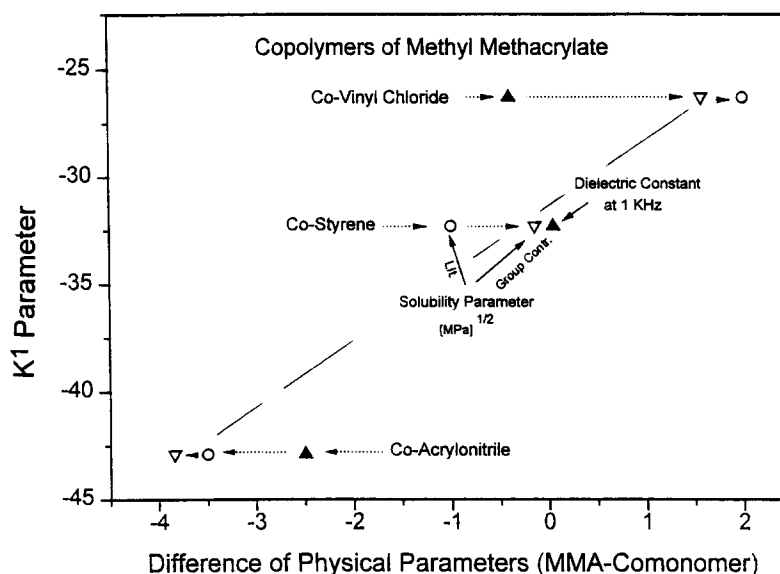


Figure 2 Correlation of the K^1 fitting parameters of the concentration power equation (8) with the differences between: solubility parameters (open circles—literature data, open triangles values estimated by group contributions); and dielectric constants (full triangles) of copolymer components

containing two MMA repeating units predominates (i.e. $k_3 > k_2$), whereas in poly(VC-*co*-MMA) the influence of the hetero-triads containing two VC repeating units (i.e. $k_2 > k_3$) prevails. To obtain negative values of both parameters K^1 and K^3 , which are characteristic for T_g vs composition characterized by negative deviations from additivity, negative K^2 parameters have to be always smaller than the negative K^1 parameters.

The S-shaped T_g vs composition curves of the copolymers (S-*co*-MMA)—Figure 1a—and (*t*-BA-*co*-*t*-BMA)—Figure 1b—are also characterized by negative K^1 parameters. But in contrast to the previous discussed (AN-*co*-MMA) and (VC-*co*-MMA) copolymers, the K^3 parameters are no longer negative but positive, because of the larger negative K^2 values than the negative K^1 values, suggesting an overwhelming contribution to T_g of the hetero-triads containing respectively either two MMA or two *t*-BMA repeating units. Accordingly the T_g vs composition curves show in the high weight fraction range of MMA and *t*-BMA, respectively, positive deviations from additivity, although the K^1 parameter has a negative value.

Reversed S-shaped asymmetric curves are obtained if K^1 is positive and K^3 has negative values. This situation happens if both K^1 and K^2 are positive, but K^2 has the larger positive values than K^1 as in the case of poly(*t*-BMA-*co*-MMA), for instance. If both, K^1 and K^3 are

positive, the T_g vs composition curves show positive deviations from additivity. Typical examples are the copolymers of *n*-butyl acrylate with methyl acrylate or ethyl acrylate. Values of K^1 and K^2 near zero are characteristic for copolymers with almost additive glass temperatures. The values of the corresponding K^i parameters are shown in Table 2. The respective T_g vs composition curves will be presented together with those of the other copolymers of acrylates and methacrylates among each other.

Subsequently an attempt has been made to correlate the K^1 parameter, which is essentially characteristic for the influence of hetero-diads on the copolymer glass temperature, with specific physical constants, i.e. dielectric constants and solubility parameters¹³. The result of this attempt is illustrated in Figure 2, where the K^1 fitting parameters of the T_g vs composition curves—shown in Figure 1a—for the copolymers of methyl methacrylate with styrene, acrylonitrile and vinyl chloride, respectively, are presented vs the differences of the respective physical parameters of the monomers. Taking into account that in literature solubility parameters are not available for all monomers used in this study two series of values were employed. On the one hand values (in [MPa]^{1/2}) listed in literature¹³ were used and on the other hand, the solubility parameters were estimated by applying the

Table 2 Parameters of the T_g vs composition curves of acrylic/methacrylic copolymers

Copolymer	$(T_{g_2} - T_{g_1})$	Fitting parameters of equation (8)		Parameters of equation (6a)		
		K_1	K_2	$(k_1 + k_2)^a$ K^1	$(k_2 - k_3)^b$ K^2	$(k_1 + k_3)^c$ K^3
MMA/ <i>t</i> -BMA	3.0	5.61	14.12	16.83	42.36	-26.0
MA/ <i>n</i> -BA	65.0	0.69	0.54	44.85	35.1	9.8
EA/ <i>n</i> -BA	35.0	1.03	0.97	36.05	33.95	2.1
2E-HA/ <i>t</i> -BA	113.0	0	0	0	0	0
2E-HA/ <i>t</i> -BMA	160.0	0.18	-0.14	28.8	-22.4	51.2

$$^a k_1 + k_2 = K^1 = K_1(T_{g_2} - T_{g_1})$$

$$^b k_2 - k_3 = K^2 = K_2(T_{g_2} - T_{g_1})$$

$$^c k_1 + k_3 = K^3 = (K_1 - K_2)(T_{g_2} - T_{g_1})$$

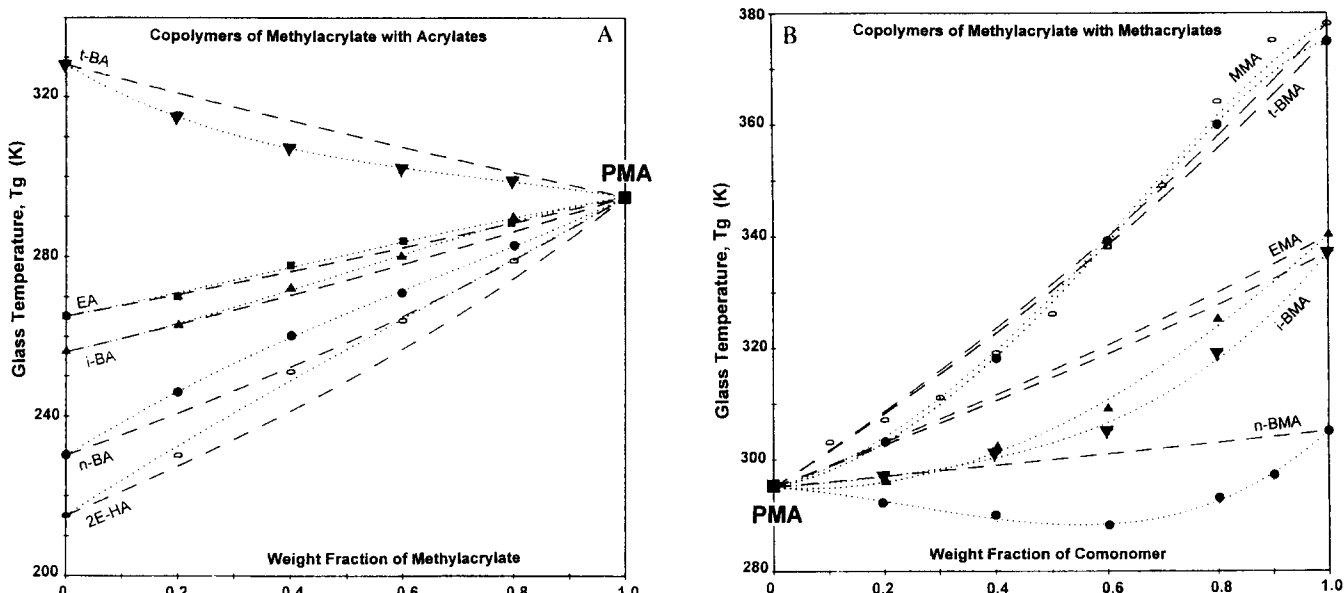


Figure 3 T_g vs composition curves of copolymers of methyl acrylate with (A) acrylates and (B) methacrylates (for significance of dashed and dotted lines see Figure 1)

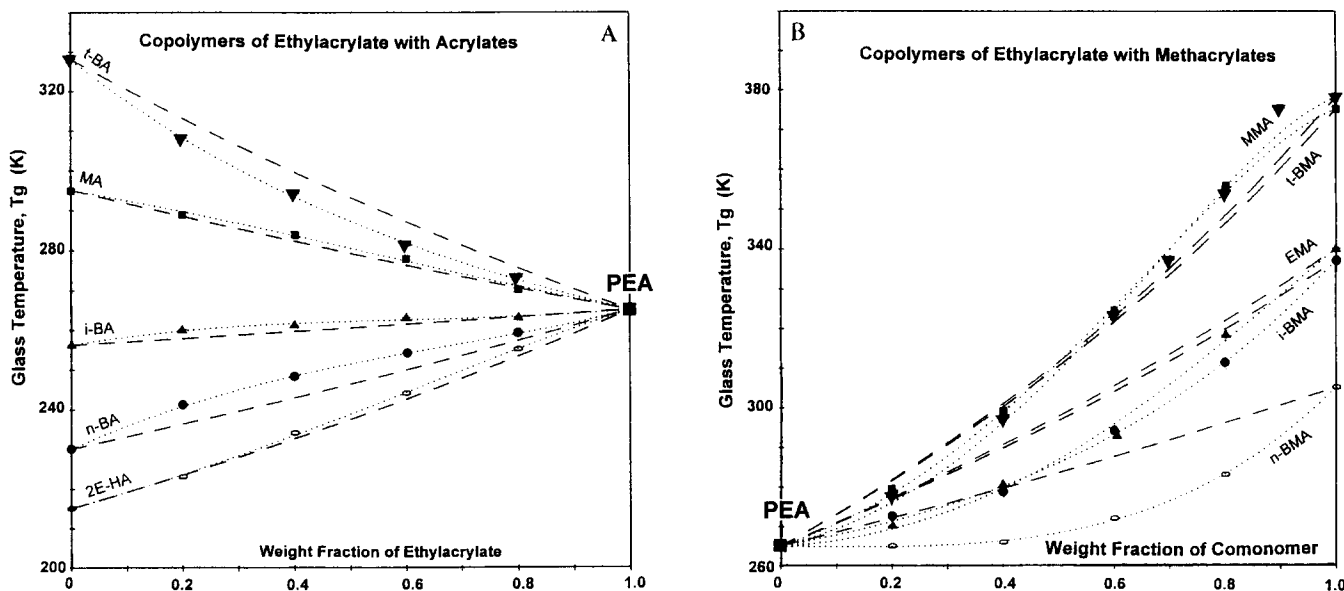


Figure 4 T_g vs composition curves of copolymers of ethyl acrylate with (A) acrylates and (B) methacrylates (for significance of dashed and dotted lines see Figure 1)

group contribution method of Small¹⁴.

$$\delta_i = \left(\rho_i \sum F_j \right) / M_i \quad (12)$$

where ρ_i is the density, M_i the molecular weight and F_j the group contribution to the cohesive energy density of the respective monomer, derived from measurements of heats of vaporization.

It results from the data shown in Figure 2 that the K^1 parameters of the T_g vs composition curves correlate better with the differences between the solubility parameters than with the dielectric constants of the copolymer components. Thus in all following representations this criterion will be used in the attempt to correlating the K^1 fitting parameters of the T_g vs composition curves for the different families of copolymers studied.

The observed tendencies of the K^1 variation depend, however, on the manner how the differences between the solubility parameters are calculated. Thus, if instead of the difference between the solubility parameters of MMA and the respective comonomers ($\delta_{MMA} - \delta_{Comonomer}$) the inverted difference ($\delta_{Comonomer} - \delta_{MMA}$), is used, then the sign of the difference is also inverted. The same is valid if for evaluation of the K^1 parameter the order of the glass temperatures is inverted, i.e. if instead of $K^1 = k_1(T_{g2} - T_{g1})$ the value $K^1 = k_1(T_{g1} - T_{g2})$ is used.

Although the representation of the K^1 parameters vs the difference of solubility parameters of the copolymers depends on the modality of evaluation of the respective T_g and solubility parameter differences, some general valid rules can be formulated for the different classes of copolymers, with the condition that the

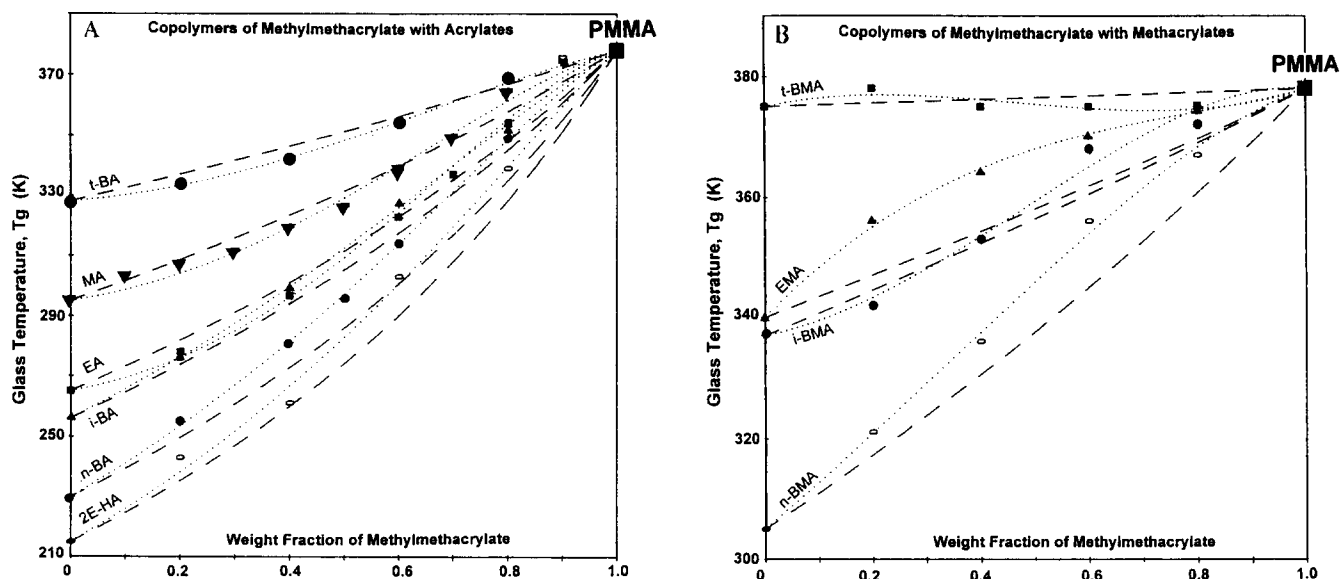


Figure 5 T_g vs composition curves of copolymers of methyl methacrylate with (A) acrylates and (B) methacrylates (for significance of dashed and dotted lines see Figure 1)

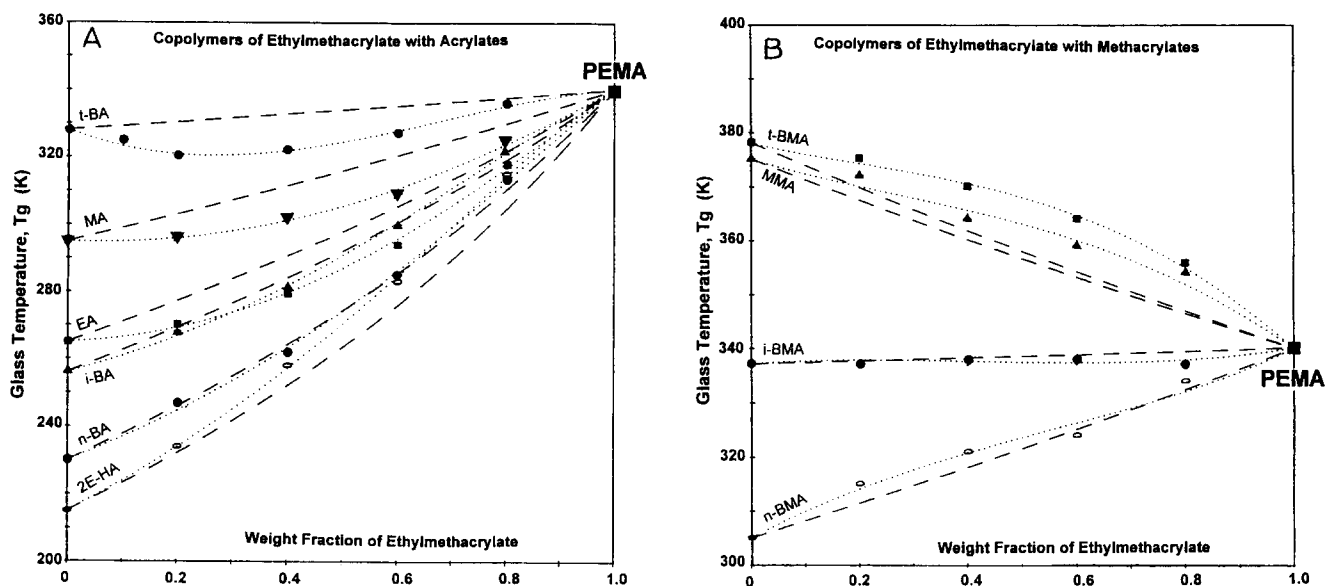


Figure 6 T_g vs composition curves of copolymers of ethyl methacrylate with (A) acrylates and (B) methacrylates (for significance of dashed and dotted lines see Figure 1)

respective differences are evaluated always in the same manner.

EXPERIMENTAL

Copolymers of methyl- (M), ethyl- (E), *n*-butyl- (*n*-B), iso-butyl (*i*-B), *t*-butyl- (*t*-B) and ethyl-hexyl- (E-H) acrylates (A) and methacrylates (MA) (the latter without EHMA) among each other and with styrene, acrylonitrile and vinyl chloride, respectively, were synthesized by emulsion polymerization under starved conditions to assure constant compositions of the copolymers dependent on the monomer ratio only. The glass temperatures were recorded using the Mettler TA 4000 instrument at a heating rate of 20 K min^{-1} . The presented T_g -data are the temperatures corresponding to the half height of the thermal capacity increment during the second heating scan. Details concerning the synthesis of the copolymers

and the d.s.c. measurements are presented in the first part of this series⁷.

RESULTS AND DISCUSSION

Copolymers of acrylates and methacrylates among each other

The T_g vs composition curves of methyl acrylate and ethyl acrylate with the different acrylates and methacrylates are shown in Figures 3 and 4, respectively. Whereas for the copolymers of MA and EA with acrylates an inversion of the initial negative to positive deviations from additivity of the copolymers glass temperatures is observed with increasing length of the alkyl ester group, for the copolymers with methacrylates the negative deviations from additivity prevail, excepting the copolymers with MMA and *t*-BMA which show S-shaped T_g vs composition curves.

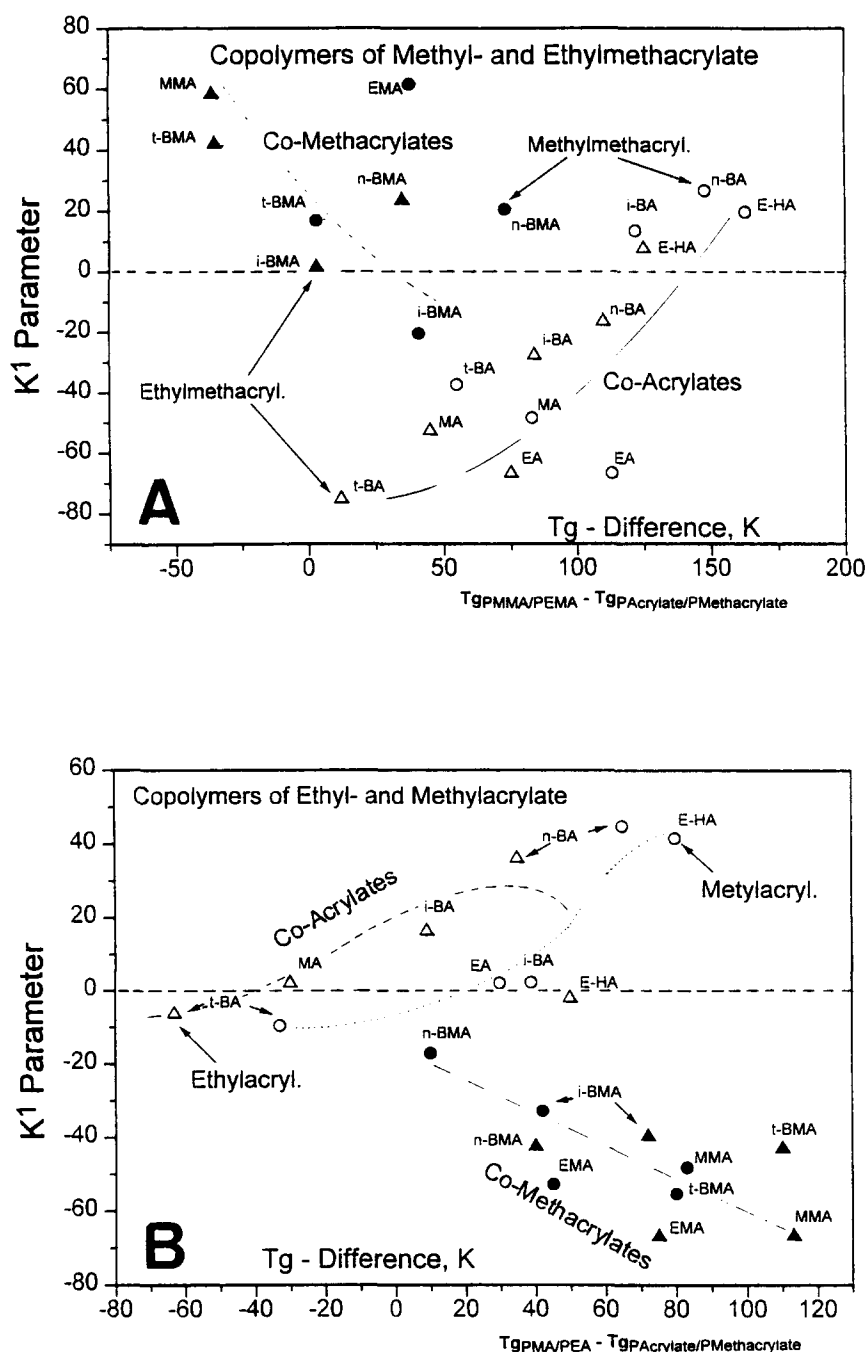


Figure 7 Correlation of the K^1 fitting parameters of concentration power equation (8) with the difference of the glass temperatures of the copolymer components. (A) Copolymers of methyl methacrylate with acrylates (open triangles) and methacrylates (full circles) and copolymers of ethyl methacrylate with acrylates (open triangles) and methacrylates (full circles); (B) copolymers of methyl acrylate with acrylates (open circles) and methacrylates (full circles) and copolymers of ethyl acrylate with acrylates (open triangles) and methacrylates (full triangles)

The same inversion of the initial negative to positive deviations of the copolymer glass temperature from additivity with increasing length of the alkyl ester group is observed for the copolymers of MMA and EMA with acrylates (see Figures 5 and 6). For the copolymers of MMA and EMA with methacrylates, however, the positive deviations from additivity prevail this time. Again S-shaped curves are observed for the copolymers with *n*-BMA and *i*-BMA, respectively.

The peculiar behaviour concerning the deviations from additivity of the glass temperatures of the copolymers of acrylates and methacrylates among each other is reflected in the K^1 parameters of the respective T_g vs composition curves as it results from the data shown in Figure 7. Thus for the copolymers of methacrylates and acrylates,

respectively, among each other, positive values of the K^1 parameters are characteristic, whereas for the cross-copolymers poly(acrylate-*co*-methacrylate) negative K^1 values are obtained.

There is, however, a remarkable difference in the variation of the K^1 parameters with increasing length of the alkyl ester group. Thus the K^1 parameters of the methacrylate-methacrylate copolymers decrease, whereas those of the acrylate-acrylate copolymers increase with increasing alkyl ester length. For instance, the copolymers P(MMA-*co*-EMA) and P(MA-*co*-EHA) show the largest positive K^1 values, whereas P(MMA-*co*-*n*-BMA) and P(MA-*co*-EA) exhibit, on the contrary, the smallest K^1 values. The negative values of the K^1 parameters of the copolymers acrylates/methacrylates on the contrary

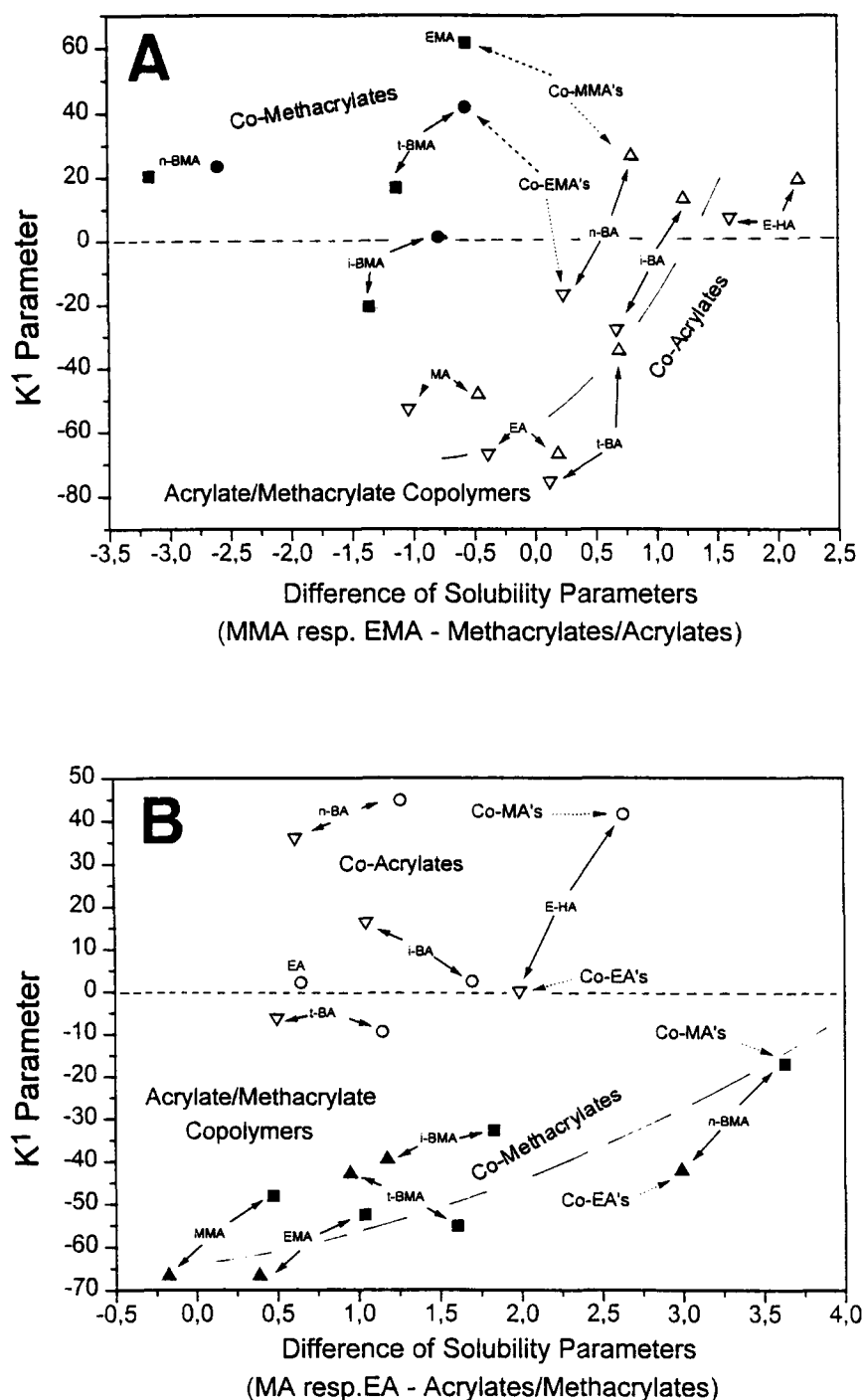


Figure 8 Correlation of the K^1 fitting parameters of concentration power equation (8) with the difference of the solubility parameters of the copolymer components. (A) ■, $\delta_{\text{MMA}} - \delta_{\text{methacrylates}}$; △, $\delta_{\text{MMA}} - \delta_{\text{acrylates}}$; ●, $\delta_{\text{EMA}} - \delta_{\text{methacrylates}}$; ▽, $\delta_{\text{EMA}} - \delta_{\text{acrylates}}$. (B) ■, $\delta_{\text{MA}} - \delta_{\text{methacrylates}}$; ○, $\delta_{\text{MA}} - \delta_{\text{acrylates}}$; ▲, $\delta_{\text{EA}} - \delta_{\text{methacrylates}}$; △, $\delta_{\text{EA}} - \delta_{\text{acrylates}}$

increase with increasing length of the alkyl ester group. This increase is, however, more accentuated for the copolymers of MMA and EMA with acrylates (the K^1 parameters becoming even positive for the longer alkyl esters *n*-BA and E-HA), than for the copolymers of MA and EA with methacrylates.

The dependence of the K^1 parameter on the difference of the solubility parameters of the acrylate/methacrylate copolymers (evaluated by the group contribution method) is illustrated in Figure 8. Comparing with the data presented in Figure 7, it results that the behaviour is quite similar. The scatter of the data of the acrylate/acrylate and methacrylate/methacrylate copolymers, respectively, is, however, too large for evidencing as clear tendencies

as observed in Figure 7. For the cross-copolymers acrylate/methacrylate, on the contrary, clear dependences are visible. The negative K^1 parameters of the copolymers of methyl and ethyl methacrylate with acrylates increase with both the increasing length of the alkyl ester group (i.e. with the decrease of the glass temperature of the respective homopolymer) and the difference of the solubility parameters (see Figures 7A and 8A). The same is valid for the K^1 parameters of the copolymers of methyl and ethyl acrylate with methacrylates.

The fact that in Figures 7B and 8B apparently the tendencies are inverted is explained by the change in the order of evaluation of the respective differences of the T_{gs} and solubility parameters. The absolute tendencies

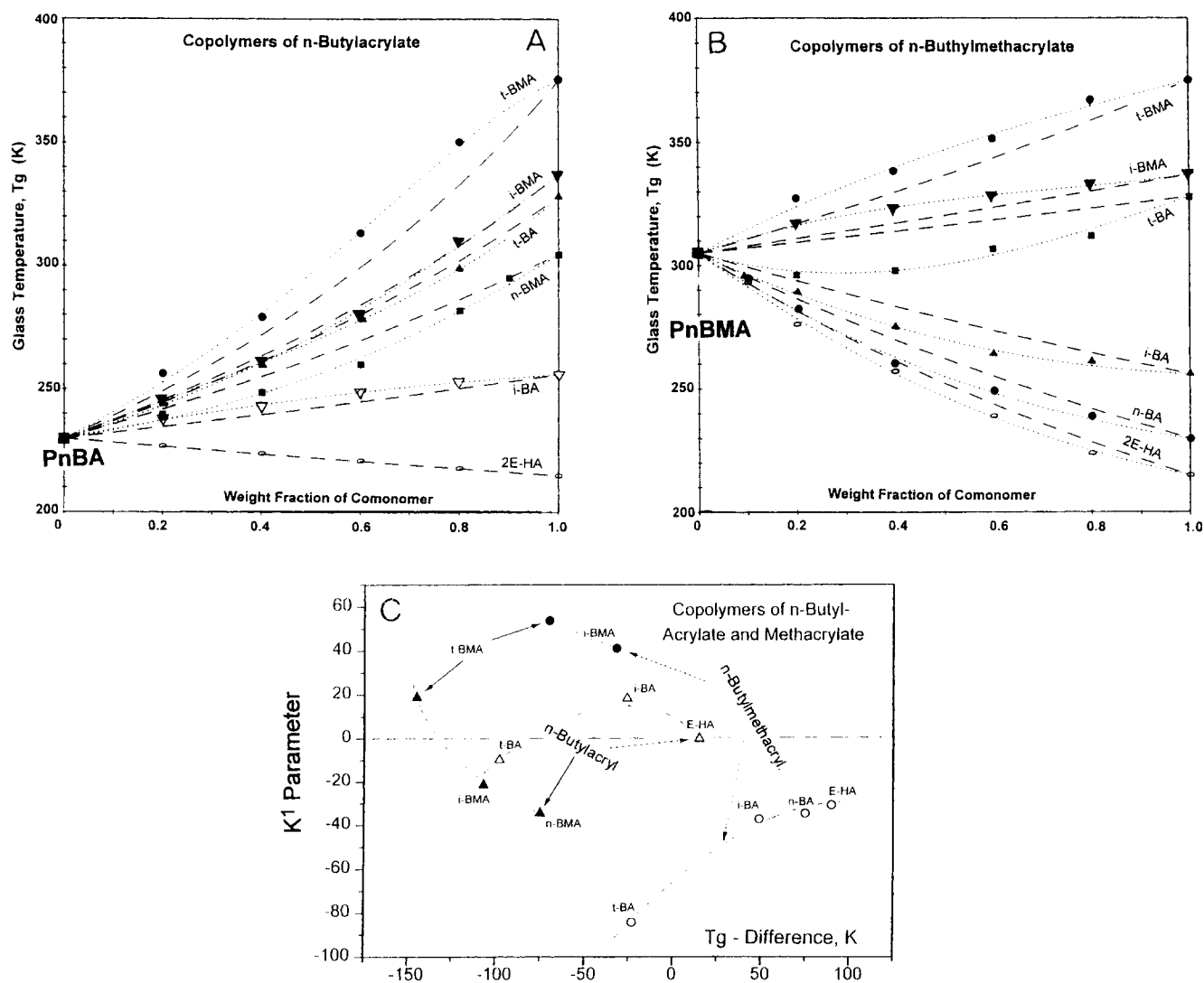


Figure 9 Copolymers of *n*-butyl acrylate and *n*-butyl methacrylate. (A) T_g vs composition curves of copolymers of *n*-butyl acrylate; (B) T_g vs composition curves of copolymers of *n*-butyl methacrylate (for significance of dashed and dotted lines see Figure 1); (C) K^1 fitting parameters vs differences of glass temperatures: \circ $T_{g\text{methacrylates}} - T_{g\text{nBMA}}$; \square , $T_{g\text{acrylates}} - T_{g\text{n-BMA}}$; \triangle , $T_{g\text{methacrylates}} - T_{g\text{nBMA}}$; \diamond , $T_{g\text{acrylates}} - T_{g\text{n-BMA}}$

are, however, the same, i.e. K^1 increases with both the length of the alkyl ester group and the difference of the solubility parameters.

The observed regularities are also reflected by the copolymers of *n*-butyl (Figure 9) and iso-butyl (Figure 10) acrylates and methacrylates, respectively.

In conclusion for the cross-copolymers acrylate/methacrylate clear tendencies for the change of the shape of the T_g vs composition curves are observed which are reflected essentially in the dependencies of the K^1 parameter on both the differences of the glass temperatures and solubility parameters, respectively. For the copolymers acrylate/acrylate and methacrylate/methacrylate, respectively, changes of the deviations of the copolymer T_g from additivity are observed too. The scatter of the K^1 data is, however, too large for unequivocal statements.

Copolymers of styrene, acrylonitrile and vinyl chloride with acrylates and methacrylates

The T_g vs composition curves of the copolymers of methacrylates and acrylates with styrene are presented in Figure 11, those with acrylonitrile are shown in Figure 12, whereas those with vinyl chloride in Figure 13.

It is evident that the glass temperatures of the copolymers with methacrylates show rather pronounced negative deviations from additivity, whereas the copolymers with acrylates are characterized by glass temperatures which exhibit positive deviations from additivity. The negative deviations of the glass temperatures of the copolymers with methacrylates generally decrease with increasing length of the alkyl ester group. Some irregularities in this general behaviour are observed for the copolymers of the methacrylates with acrylonitrile. The positive deviations of the glass temperatures of the copolymers with acrylates, on the other hand, increase with increasing length of the alkyl ester group. It seems, however, that the length of the alkyl of the ester group and not the number of C atoms is the determinant factor for the observed deviations of the copolymers glass temperature from additivity. Thus similar T_g vs composition curves are exhibited by the methylic and *t*-butylic esters and by the ethylic and *i*-butylic esters, respectively. This peculiar glass temperature behaviour of the copolymers is reflected by the fitting parameters of the respective T_g vs composition curves as it is illustrated in Figure 14 where the fitting parameters are presented vs the difference of the glass

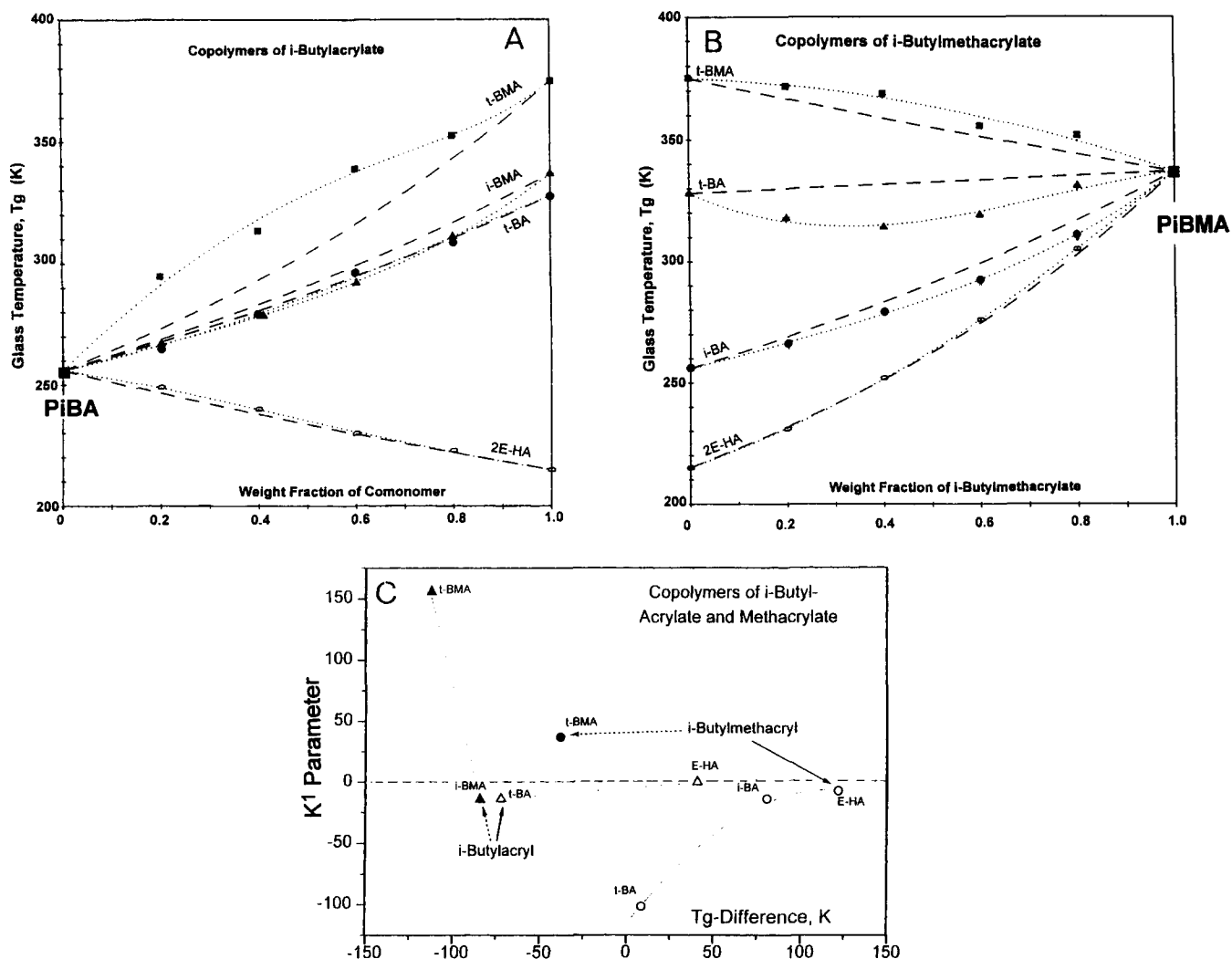


Figure 10 Copolymers of *i*-butyl acrylate and *i*-butyl methacrylate: (A) T_g vs composition curves of copolymers of *i*-butyl acrylate; (B) T_g vs composition curves of copolymers of *i*-butyl methacrylate; (C) K^1 fitting parameters vs differences of glass temperatures: \circ , $T_{g(i-BMA)} - T_{g(i-BMA)}$; \triangle , $T_{g(i-methacrylates)} - T_{g(i-BA)}$; Δ , $T_{g(acrylates)} - T_{g(i-BA)}$

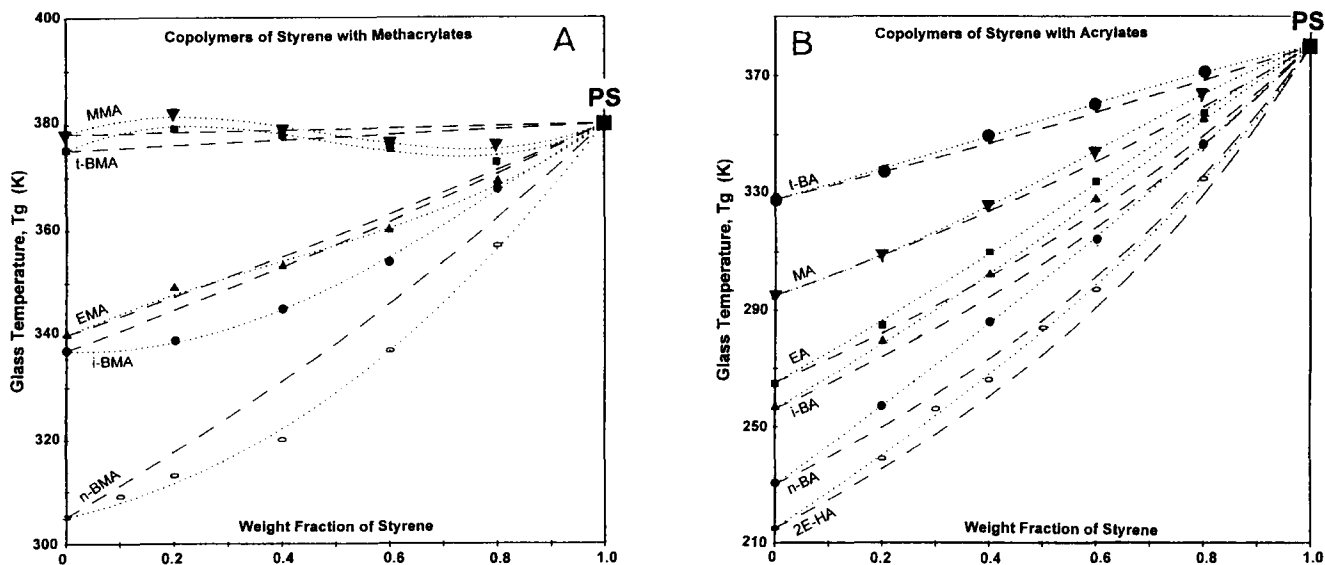


Figure 11 T_g vs composition curves of copolymers of styrene: (A) copolymers of styrene with methacrylates; (B) copolymers of styrene with acrylates (for significance of dashed and dotted lines see Figure 1)

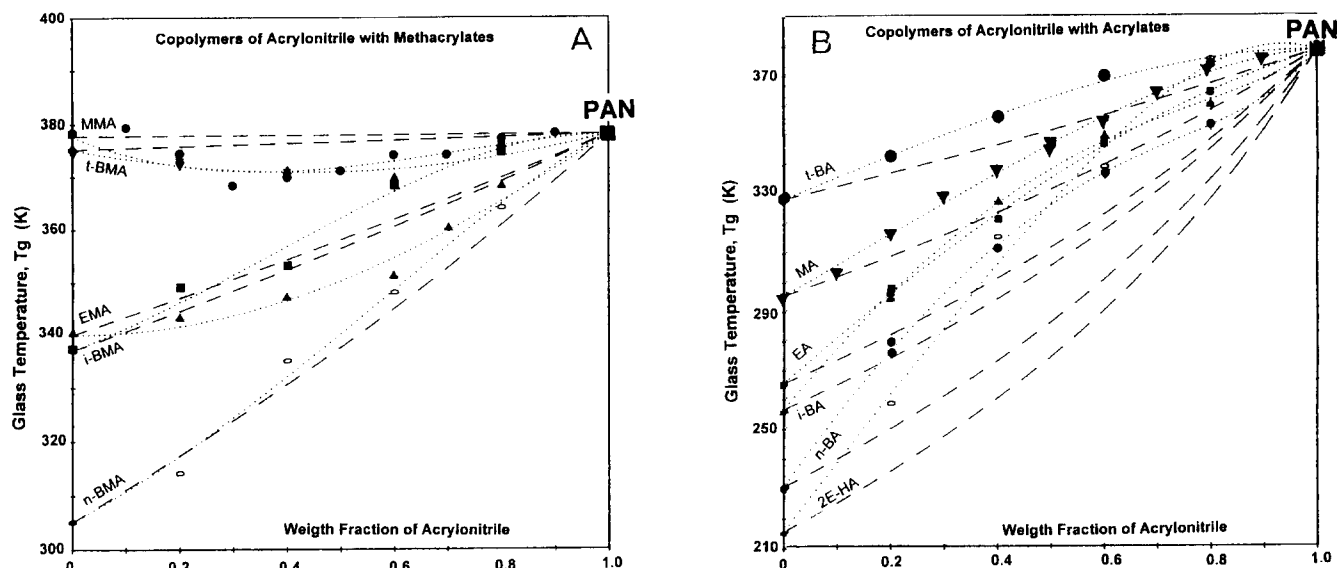


Figure 12 T_g vs composition curves of copolymers of acrylonitrile: (A) copolymers of acrylonitrile with methacrylates; (B) copolymers of acrylonitrile with acrylates (for significance of dashed and dotted lines see Figure 1)

temperature of the respective homopolymers. For the copolymers with methacrylates generally negative K^1 parameters are characteristic, whereas for the copolymers with acrylates positive K^1 values are obtained.

It is emphasized that all T_g vs composition curves characterized by both K^1 and K^2 parameters not too different from zero can be adapted by the simple Gordon–Taylor equation with the parameter K considered an overall fitting parameter as it was evidenced in a previous paper⁷. Asymmetric and mainly S-shaped T_g vs composition curves, however, cannot be reproduced by the Gordon–Taylor equation.

Data published by Barton⁸ for the composition dependence of the glass temperature of the copolymers AN/MMA, S/MMA, S/MA and S/BA are consistent with the corresponding curves presented in Figures 11 and 12, respectively. The same is valid for the copolymer system analysed by Ham⁹ (S/MMA), by Johnston¹⁰ (S/MMA, VC/MMA, VC/BMA, AN/MMA), by Podesva and

Prochazka¹⁵ (MMA/AN, MMA/VC, BMA(VC) and by Havlicek *et al.*¹⁶ (S/MMA). Even the observed asymmetries in the T_g vs composition curves are very similar.

The K^1 fitting parameters are correlated in Figure 15 with the difference of the solubility parameters, $\sigma_{(\text{comonomer-methacrylate})}$ and $\delta_{(\text{comonomer-acrylate})}$, respectively. Although the scatter of the data is relatively large, mainly for the copolymers of vinyl chloride, some general tendencies are, however, evident. Thus for the copolymers of vinyl chloride and styrene with the methacrylates, the K^1 parameter decreases with both the increasing length of the ester group of the methacrylate and the difference between the solubility parameters. For the copolymers of acrylonitrile, on the contrary, the K^1 parameter increases with increasing length of the ester group and of the difference between the solubility parameters.

For the copolymers with acrylates the tendency of

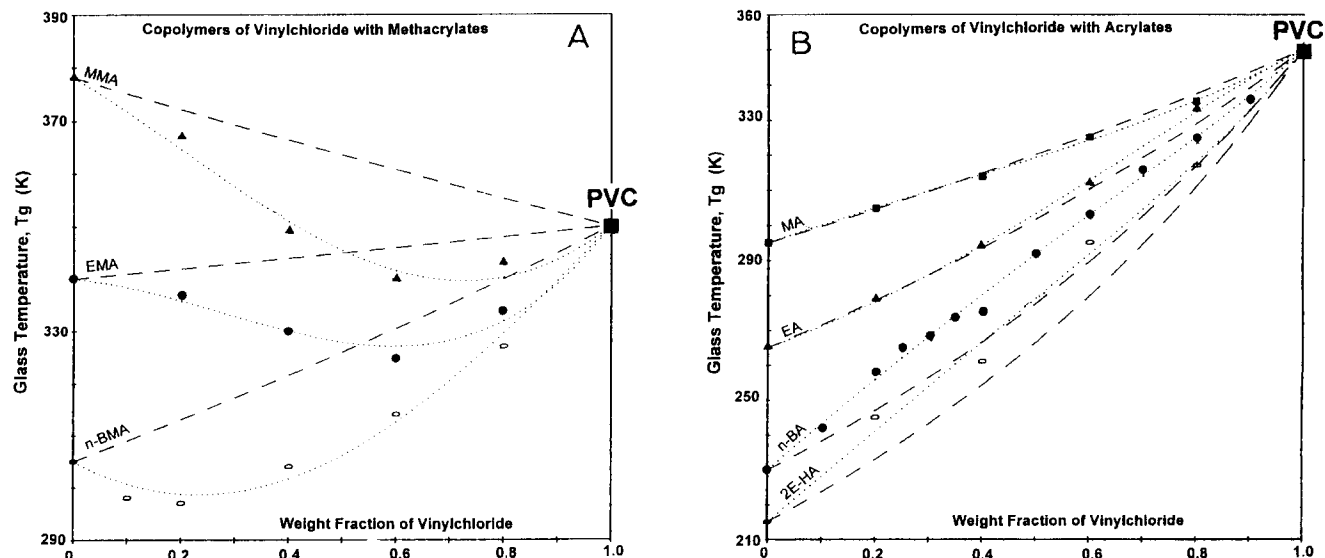


Figure 13 T_g vs composition curves of copolymers of vinyl chloride: (A) copolymers of vinyl chloride with methacrylates; (B) copolymers of vinyl chloride with acrylates (for significance of dashed and dotted lines see Figure 1)

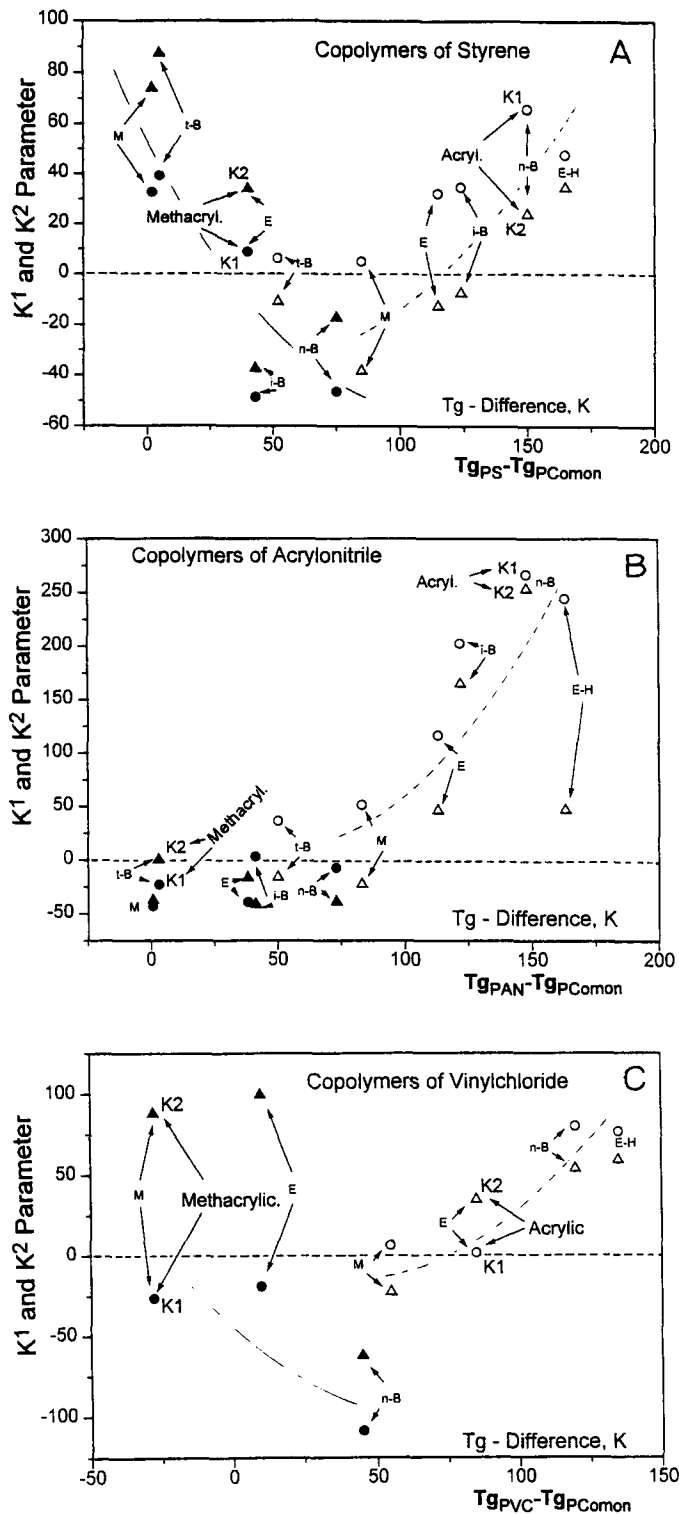


Figure 14 Correlation of K^1 and K^2 fitting parameters with the differences of the glass temperatures of the comonomers: (A) copolymers of styrene with acrylates and methacrylates; (B) copolymers of acrylonitrile with acrylates and methacrylates; (C) copolymers of vinyl chloride with acrylates and methacrylates. Full symbols—circles, K^1 values of copolymers with methacrylates; triangles, K^2 values of copolymers with acrylates. Open symbols—circles, K^1 values of copolymers with acrylates; triangles, K^2 values of copolymers with acrylates

increase of the predominant positive K^1 parameters prevails for both increasing length of the ester group and the difference between the solubility parameters indifferent of the nature of the comonomer. The increase of the K^1 parameter becomes, however, steeper in the order vinyl chloride (showing sooner negative values of the solubility parameter differences), styrene (with intermediate values of the solubility parameter differences)

and acrylonitrile (exhibiting the largest positive values of the solubility parameter differences).

CONCLUSIONS

In conclusion there is a rough correlation between the differences of the solubility parameters of the comonomers and the K^1 parameters, related to the K_1 fitting

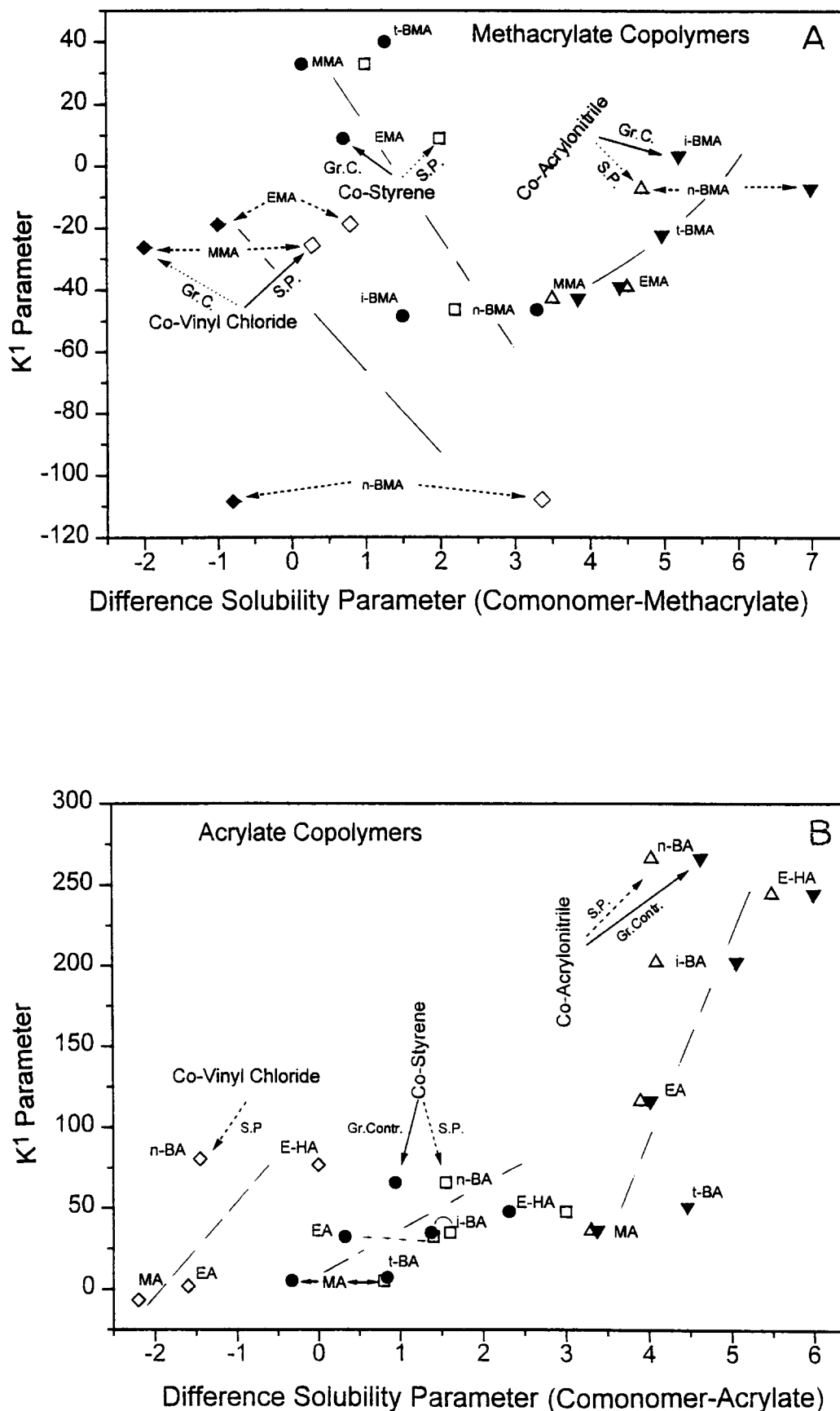


Figure 15 K^1 fitting parameters vs differences of solubility parameters (S.P., literature data; Gr.C., estimated by group contribution): (A) methacrylate copolymers with styrene, acrylonitrile and vinyl chloride; (B) acrylate copolymers with styrene, acrylonitrile and vinyl chloride

parameters of the T_g vs concentration power equation by $K^1 = K_1(T_{g_2} - T_{g_1})$ which characterizes for the different classes of copolymers the deviations from additivity of the T_g vs composition curves due mainly to the contributions of the binary heterosequences. A possible explanation for the observed relatively large scatter of the data could be, that the K^1 parameter includes beside hetero-diad also hetero-triad contributions to the copolymer T_g , whereas the difference between the solubility parameters refers to the two comonomers only. Additionally it seems that the observed correlation between the K^1 parameter and the difference of the solubility parameters is specific for the different classes of copolymers. The contributions of the hetero-triads to the copolymer T_g are expressed by the $K^2 = K_2(T_{g_2} - T_{g_1})$ parameters, K_2 like K_1 being the fitting parameter of the concentration power equation. Values of K^2 very different of zero are characteristic of asymmetric or of S-shaped T_g vs composition curves of the copolymers depending if the absolute value of K_2 is smaller or larger than of K_1 . *Although data indicate that the K^1 parameters are roughly correlated with the difference of the solubility parameters it is not possible to recommend a unique relationship for predicting the glass temperatures of copolymers knowing the solubility parameters of the components, because the observed interdependences are valid for given classes of polymers only.*

For the interested readers the values of the respective

fitting parameters of the concentration power equation (8) are available from HAS.

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