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RELATION OF GLASS TRANSITION TEMPERATURE TO MOLECULAR STRUCTURE OF ADDITION COPOLYMERS

by

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SUMMARY

An equation is proposed relating the glass transition temperature (T_G) of copolymers to the molecular structure in terms of the mole fractions of the various diad sequences of monomer units combined in the copolymer chains. The equation, which can account for the occurrence of a maximum or a minimum in plots of T_G versus copolymer composition, is applied to eleven addition copolymer systems and found to give good agreement with the experimental data. Application of the equation to obtain homopolymer T_Gs by extrapolation is demonstrated.

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CONTENTS

1 INTRODUCTION

Many of the elastomers in current service, for example Viton and ethylene-propylene rubbers, are based on copolymers which are often less crystalline than the corresponding homopolymers and which may also have lower glass transition temperatures (T_Gs). The T_G of an elastomer is of great significance as it determines the lower temperature limit of elastomeric behaviour and influences the physical properties in the rubbery state. Therefore, a knowledge of the factors governing T_G is essential in designing new elastomeric materials.

In this Report an equation is proposed which relates the T_G of a copolymer to its molecular structure, and the equation is accurately applied to published experimental data for eleven different addition copolymer systems. It is shown that homopolymer T_Gs may be obtained by extrapolation, and by this method the T_Gs of polyacrylonitrile and polyacrylic acid are estimated to be 380° and 413°K, respectively. The relationship of the equation to other theories is discussed.

2 THE DEPENDENCE OF T_G ON COPOLYMER COMPOSITION

2.1 The importance of sequence distribution in determining the T_Gs of copolymers

Boyer[1] has reviewed some of the factors which govern the T_Gs of copolymers. Several semi-empirical equations have been suggested which give the T_G of a copolymer in terms of the T_Gs of the homopolymers of the corresponding monomers and the overall copolymer composition[2-9]. These equations are based on the assumption that certain properties of the copolymer, e.g., specific volume, molar cohesive energy, chain stiffness, are additive combinations of the properties of the homopolymers of the corresponding monomers. The equations involve functions of either the weight- or mole-fractions of the comonomers combined in the copolymer.

Many addition copolymer systems exhibit a minimum or maximum value of T_G in plots of T_G versus copolymer composition, yet only three of the equations mentioned above[7-9] can be used to describe such phenomena. In a copolymer formed from monomers A and B there are four possible sequences of pairs of repeating units, which may be represented as aa, bb, ab, and ba pairs. DiMarzio and Gibbs[2] pointed out that the properties (e.g. chain stiffness) of an ab or ba sequence may well be different from those of an aa or bb sequence and that it may be necessary to take account of the sequence distribution in order to make accurate predictions of copolymer T_G when the fraction of ab + ba sequences is large. Beevers[10] found a minimum in the T_G-composition curve for random styrene/methyl methacrylate copolymers, and suggested that this may be due to the presence of ab sequences in which there is a greater freedom of rotation than in aa or bb sequences. This idea has not hitherto been tested quantitatively.

Kanig[7] has formulated a thermodynamic theory of the glass transition based on the treatment of a polymer melt as a mixture of molecules and voids. The equation derived for copolymers is complex and relates T_G to a function of the weight fraction of comonomers combined in the copolymer, and the work required to produce holes in the melt by the separation of aa, ab, or bb associations. The assumption is made that the components A and B are "statistically distributed" in the copolymer, and does not allow for the variation in the sequence distribution with copolymer composition. Illers[11] found that the T_G-composition data for thirteen copolymer systems could be fitted to the Kanig equation. The relationship of these results to the present work are discussed later in this Report.

Lee and O'Mahony[12] have treated homopolymers as ideal multicomponent "copolymers" in which the sequence distribution of any one group is fixed with respect to its nearest neighbours. A group is defined as the smallest atom or group of atoms capable of independent torsional oscillation with respect to its nearest neighbours and the groups may be considered to be the monomer units of the "copolymer". Several equations were evaluated, which related T_G to molecular structure on the basis of additive contributions of the groups on a mole- or weight-fractional basis. For a set of 32 homopolymers it was found that a simple additive mole fractional equation gave the best agreement between calculated and observed T_Gs. Although different in application, this equation is of the same form as generalized versions of the Hayes[6] and DiMarzio and Gibbs[2] copolymer equations.

The extension of the DiMarzio and Gibbs copolymer equation to include the effects of the different properties of aa, ab, ba and bb sequences, and the applicability of the resulting equation to experimental data is demonstrated in the following sections.

2.2 The proposed relationship between T_G and copolymer composition

For a copolymer composed of monomer units A and B, DiMarzio and Gibbs[2] obtained the following equation relating T_G and copolymer composition:

$$n'_a (T_G - T_{G_a}) + n'_b (T_G - T_{G_b}) = 0 \qquad (1)$$

where n'_a is the fraction of rotatable bonds in component A of the copolymer, n'_b is the fraction of rotatable bonds in component B, T_G refers to the copolymer, and T_{G_a} and T_{G_b} refer to the homopolymers of A and B, respectively. When A and B both contain the same number of rotatable bonds, n'_a and n'_b may be replaced by the mole fractions n_a and n_b. The equation was based on the proposition that the T_G of a copolymer depended mainly on chain stiffness. The stiffness energy of a bond was related to the energy difference between rotational isomers, and it was assumed that the stiffness energy of an A-B bond is the arithmetic mean of that of an A-A and a B-B bond. It was shown[2] that equation (1) is of the same form as the equations of Gordon and Taylor[3] and of Mandelkern, Martin, and Quinn[4], which involve the weight fractional composition of the copolymer. The terms n'_a and n'_b in equation (1) were defined more specifically as the fractions of rotatable bonds in a copolymer, which could change its configuration on rotation, thus excluding bonds connecting penultimate groups of side chains to the end group. As discussed in section 2.1, it was found that with certain provisions a generalized form of equation (1) could be applied to homopolymers[12]. It was further shown in an extension of this work[13] that better precision in calculated T_Gs was obtained by including the contributions of all groups, irrespective of whether or not their rotation could change the configuration of the molecule. The total numbers of groups and rotatable bonds in a copolymer are equal, and in the present discussion, by analogy with the work on homopolymers[13], all rotatable bonds are considered in calculating rotatable bond fractions.

Equation (1) may be rearranged in the following form:

$$T_G = n'_a T_{G_a} + n'_b T_{G_b} \qquad (2)$$

It is now proposed that equation (2) can be extended so as to differentiate between the contributions to the T_G of the aa, bb, ab, and ba sequences in the copolymer, as follows:

$$T_G = n'_{aa} T_{aa} + n'_{bb} T_{bb} + n'_{ab} T_{ab} + n'_{ba} T_{ba} \quad , \tag{3}$$

where n'_{ij} is the mole fraction of rotatable bonds (or groups) contained in ij sequences, and T_{ij} is an additive temperature parameter associated with an ij sequence. The terms T_{aa} and T_{bb} may be equated to the T_Gs of the homopolymers, T_{G_a} and T_{G_b}, respectively, while T_{ab} and T_{ba} may be equated to the T_G of the alternating copolymer $\{a - b\}_n$, so that the equation may be written as

$$T_G = n'_{aa} T_{aa} + n'_{bb} T_{bb} + (n'_{ab} + n'_{ba}) T_{ab} \quad . \tag{4}$$

This treatment can be readily extended to multicomponent copolymer systems and the general form of equation (4) is

$$T_G = \sum n'_{ij} T_{ij} \quad . \tag{4a}$$

The number of terms in the summation is the square of the number of different monomer components in the copolymer, and the values of the terms in equations (4) and (4a) are determined as follows. The n'_{ij} terms (rotatable bond fractions) are given by

$$n'_{ij} = n_{ij} \alpha_{ij} \Big/ \sum (n_{ij} \alpha_{ij}) \quad , \tag{5}$$

so that n'_{ij} is the mole fraction, n_{ij}, of ij sequences in a copolymer weighted according to the number of rotatable bonds, α_{ij}, in an ij sequence. The mole fractions of the diad sequences, n_{ij}, can be calculated from conventional addition copolymer theory and a knowledge of the comonomer reactivity ratios. The following treatment is restricted to binary copolymers.

From a consideration of the relative kinetic probabilities of the various copolymerisation propagation reactions it can be shown (see Appendix A) that the mole fractions of the aa and bb sequences are

$$n_{aa} = r_a X \Big/ [r_a X + (r_b/X) + 2] \quad , \tag{6}$$

and

$$n_{bb} = (r_b/X) \Big/ [r_a X + (r_b/X) + 2] \quad , \tag{7}$$

where r_a and r_b are the reactivity ratios of the comonomers A and B, respectively, X is the ratio of the molar concentrations of the two monomers in the monomer feed, [A]/[B], necessary to give the copolymer composition defined by n_{aa} and n_{bb}. The total mole fraction of monomer A combined in the copolymer, n_a, is given by the conventional copolymer composition equation:

$$n_a = (r_a X + 1) \Big/ [r_a X + (r_b/X) + 2] \quad . \tag{8}$$

Through equations (6), (7), and (8) the values of n_{aa} and n_{bb} may be found which correspond to the experimental values of the overall composition, n_a (or n_b), for which T_G is known or is required to be calculated from equation (4). The sum of the mole fractions of ab and ba sequences is readily obtained from the relation

$$n_{ab} + n_{ba} = 1 - n_{aa} - n_{bb} \quad . \tag{9}$$

If the T_Gs of the homopolymers, T_{aa} and T_{bb}, are known, equation (4) can now be applied graphically to experimental data in the following form

$$T_G - n'_{aa}\,T_{aa} - n'_{bb}\,T_{bb} = (n'_{ab} + n'_{ba})\,T_{ab} \quad , \qquad (10)$$

where T_G is the observed value for the copolymer. If the left hand side of equation (10) is plotted against $(n'_{ab} + n'_{ba})$, and if the theory is valid, the points should fall on a straight line with zero intercept and slope = T_{ab}. Alternatively, plots can be made of T_G calculated for different values of T_{ab} against n_a, to provide the T_{ab} value which gives the curve lying closest to the experimental T_Gs. The first of these two procedures is clearly more elegant and more easily applied.

If the va[illegible] of T_{aa} or T_{bb} is uncertain it is possible to construct a series of plots in the form of equation (10), but varying T_{aa} or T_{bb} to find the value which gives the best linear fit to the experimental data.

These are two special cases which simplify equation (4):-

(a) When $T_{ab} = (T_{aa} + T_{bb})/2$ and $\alpha_{aa} = \alpha_{bb}$ it can be shown that equation (4) simplifies to the DiMarzio and Gibbs form, equation (2).

(b) When $r_a = r_b = 1$, n_{aa} and n_{bb} are related simply to n_a by the expressions $n_{aa} = n_a^2$ and $n_{bb} = (1 - n_a)^2$. If also $\alpha_{aa} = \alpha_{bb}$, substitution in equation (4) gives the equation:

$$T_G = n_a^2\,T_{aa} + n_b^2\,T_{bb} + 2n_a n_b\,T_{ab} \quad . \qquad (11)$$

This equation was also reported by Ellerstein[9] and is discussed further in section 4.2.

3 RESULTS OF THE APPLICATION OF THE PROPOSED RELATIONSHIP TO EXPERIMENTAL DATA

3.1 Method of calculation

In general, the copolymerisation reactivity ratios are taken from the tabulation of Mark et al[14] and the T_Gs and the reactivity ratios correspond to copolymers prepared under similar experimental conditions.

The general procedure for calculating the parameters in equation (10) is as follows. From the reactivity ratios, values of n_a are calculated from equation (8) for a range of values of $n_A = X/(1 + X)$ between 0 and 1, where n_A is the mole fraction of monomer A in the monomer feed. The values of n_A corresponding to the experimental n_a values are read from a plot of n_A versus n_a, and the corresponding values of X are tabulated. Then n_{aa}, n_{bb}, and $n_{ab} + n_{ba}$, corresponding to experimental n_a are calculated from equations (6), (7), and (9). The values of n'_{ij} are calculated from n_{ij} and α_{ij} using equation (5), and finally T_{ab} is determined graphically using the method described in section 2.2. Values used for r_a, r_b, α_{ij}, T_{aa} and T_{bb} are given in Table 1, which also summarises the results obtained. Any departures from this general method are discussed as they occur.

3.2 Styrene/butadiene copolymers

The T_G-composition data of Wood[5] are given in Fig.1, as a plot of T_G in °C versus the mole fraction of styrene in the copolymer (n_a), for copolymers prepared at 5° and 50°C, respectively. In both cases a straight line between the two homopolymer T_Gs (at n_a = 0 and 1.0) adequately fits the data. This is a simple case where α_{aa} and α_{bb} and where equation (2), corresponding to the straight lines, describes the data. It follows that $T_{ab} = (T_{aa} + T_{bb})/2$.

3.3 Acrylonitrile/methyl methacrylate copolymers

The plot of T_G versus n_b, from the data of Beevers and White[15], exhibits a minimum in T_G, as shown in Fig.2. The variations of the mole fractions of the diad sequences in the copolymer, n_{aa}, n_{bb}, $n_{ab} + n_{ba}$, which correspond to the experimental values of n_a or n_b, are shown in Fig.3. It can be seen that $n_{ab} + n_{ba}$ reaches a maximum in the same region of copolymer composition as is associated with a minimum in T_G. The data are plotted in the form of equation (10) in Fig.4, for $T_{aa} = T_{bb}$ = 105°C [16].

The values reported for the T_G of polyacrylonitrile[16] (T_{aa}) vary over the wide range 52° to 180°C. T_G depends on the molecular weight and the microstructure (branching, stereo-regularity etc.), which in turn depend on the polymerization method. A study of the variation in T_G with molecular weight of polyacrylonitrile prepared by free-radical polymerization in solution[15] yielded, by extrapolation, a T_G of 100°C at infinite molecular weight. Dilatometric measurements on solutions of high molecular weight polyacrylonitrile gave an extrapolated value of 104°C for the pure polymer[17]. This latter value agrees well with results obtained by extrapolating data for various acrylonitrile copolymers to the 100% acrylonitrile level. In this manner, Illers[11], Howard[18] and Reding et al[19] obtained values of 106°, 110°, and 106°C, for copolymers with methyl acrylate, vinyl acetate, and vinyl chloride, respectively.

It is of interest to see how the results vary with values for T_{aa} other than 105°C. The calculations were repeated for a range of T_{aa} values between 100° and 120°C. A measure of the precision of a least squares fit of the data to equation (10) is the sum of the squares of the deviations between observed and calculated T_G. Accordingly Fig.5 is a plot of $\Sigma\Delta^2$ against T_{aa}, for equation (10), where $\Delta = T_G$(observed) $- T_G$ (calculated). The plot shows a minimum in $\Sigma\Delta^2$ for $T_{aa} = 108$°C, and the errors are small in the range $T_{aa} = 105°$ to 111°C, but they increase steeply on either side of this range. A value for the T_G of polyacrylonitrile of 108 ±3°C is therefore the best result obtainable from these data by extrapolation using equation (10), and this is in good agreement with some of the reported values discussed previously. The variation of T_{ab} with the assumed value for T_{aa}, according to equation (10), is shown in Fig.6, and for $T_{aa} = 108$ ±3°C, $T_{ab} = 70.1$ ±1.4°C. The curve drawn through the experimental data in Fig.3 is calculated from equation (4) for $T_{aa} = 108°$, $T_{bb} = 105°$, and $T_{ab} = 70$°C.

3.4 Acrylonitrile/vinyl chloride copolymers

The T_Gs were determined from low frequency dynamic mechanical loss measurements by Reding et al[19]. Fig.7, which is the plot of observed T_G versus n_a, shows a curvature below the "ideal" linear plot. Since both monomer repeating units contain three groups, $n'_{ij} = n_{ij}$, and equation (10) can be plotted in terms of n_{ij}. The best least squares fit of the data to equation (10) is obtained for $T_{aa} = 105$°C, as in Fig.8, and the variation of $\Sigma\Delta^2$ with T_{aa} is shown in Fig.9. The value for the T_G of polyacrylonitrile, 105°C, is in good agreement with the estimate of 108 ±3°C from the acrylonitrile/methyl methacrylate copolymer data, and the corresponding value of T_{ab} is 88.5°C. The curve drawn in Fig.7 is calculated from equation (4) for $T_{aa} = 105°$ and $T_{ab} = 88.5$°C.

3.5 Vinylidene chloride/methyl acrylate copolymers

This system shows a pronounced maximum in T_G with composition as shown in Fig.10. The T_Gs were determined refractometrically, by Illers[11] at a cooling rate of 0.5°C/min and by Powell and Elgood[20] at a heating rate of 0.2°C/min. Since the reactivity ratios[14] are $r_a = r_b = 1$, this is an example of the special case where $n_{aa} = n_a^2$ and $n_{bb} = (1 - n_a)^2$. Fig.11 is the plot of the data in the form of equation (10). The least squares line shown is of slope $T_{ab} = 357.5$°K, and the theoretical curve predicted by equation (4) for this value is shown in Fig.10.

3.6 Vinylidene chloride/ethyl acrylate copolymers

This is another system which exhibits a maximum in the T_G versus composition plot, as shown in Fig.12. The copolymer T_Gs were determined[20] as described above. Although reactivity ratios have not been reported for this system, they are estimated from the Alfrey-Price[21] Q-e values, given in the tabulation of Young[22], to be $r_a = 0.40$, $r_b = 2.44$. The plot of the data according to equation (10) is shown in Fig.13. The least squares line shown is of slope $T_{ab} = 345.4$°K, and the corresponding theoretical curve from equation (4) is shown in Fig.12.

3.7 Styrene/methyl acrylate copolymers

The experimental data of J. nckel and Herwig[23] are shown on a T_G-composition plot in Fig.14. The T_Gs were determined refractometrically by cooling from above T_G at a rate of 0.5°C/min, and this probably accounts for the rather low value found for the T_G of 100% polystyrene (fast cooling tends to underestimate, and fast heating tends to overestimate, T_G). When the T_G of polystyrene has been determined in a rising temperature experiment at slow heating rates, a value of 100°C has been reported by several workers[16]. The plot of the data in the form of equation (10) provides Fig.15. The least squares slope is $T_{ab} = 58.3$°C and the corresponding theoretical curve from equation (4) is shown in Fig.14.

3.8 Styrene/butyl acrylate copolymers

The experimental T_G-composition data (refractometric, cooling rate 0.5°C/min) of Illers[11] are plotted in Fig.16 and the data are plotted in the form of equation (10) in Fig.17. The least squares slope is $T_{ab} = 291.0$°K and the corresponding theoretical curve from equation (4) is shown in Fig.16.

3.9 Styrene/acrylic acid copolymers

The experimental T_G-composition data of Illers[11] are plotted in Fig.18. Various values, between 80° and 106°C, have been reported[16] for the T_G of polyacrylic acid (T_{bb}). The exact determination is very difficult because traces of moisture have a plasticizing effect, and thermal degradation occurs in the glass transition temperature region[11]. By extrapolation of the present copolymer data using the Gordon-Taylor equation[3], Illers estimated[11] T_{bb} to be 166°C. Taking his value of $T_{aa} = 90°C$, and assuming various values for T_{bb} between 100° and 200°C, a series of plots of the data in the form of equation (10) have been obtained. The plot of $\Sigma\Delta^2$ (see section 3.3) against T_{bb} is shown in Fig.19, and the minimum error is obtained when $T_{bb} = 140°C$. Equation (10), with $T_{bb} = 140°C$, is plotted in Fig.20 and the least squares slope is $T_{ab} = 154.9°C$. The corresponding theoretical curve from equation (4) is shown in Fig.18. The extrapolated value of 140°C for T_{bb} is considerably lower than Iller's estimate of 166°C, but both of these values are significantly higher than the previously reported values[16]. However, the Gordon-Taylor equation, which Illers used in his extrapolation, cannot predict a maximum in the variation of T_G with composition, whereas the theoretical curve in Fig.18 is of this type.

3.10 Styrene/methyl methacrylate copolymers

The experimental (refractometric) T_G-composition data of Beevers[10] are shown in Fig.21 and the plot of the data in the form of equation (10) is shown in Fig.22. The least squares slope is $T_{ab} = 89.7°C$, and the corresponding theoretical curve from equation (4) is shown in Fig.21.

Although the experimental data are rather widely scattered about the theoretical curve in Fig.21, it can be seen that nearly all the data lie within the envelope formed by the theoretical curves for $T_{ab} = 85°$ and $95°$, respectively, so that $T_{ab} = 90 \pm 5°C$.

3.11 Methyl methacrylate/methyl acrylate copolymers

The refractometric T_G data of Illers[11] are given in Fig.23 and the usual computations allow the data to be plotted in the form of equation (10) in Fig.24. The least squares slope is $T_{ab} = 93.3°C$, and inserting this value in equation (4) gives the theoretical curve shown in Fig.23.

3.12 Vinyl chloride/vinyl acetate copolymers

The experimental data of Reding et al[19] are given in Fig.25. The T_Gs were determined by low frequency mechanical loss measurements. Fig.26 is a plot of the data in the form of equation (10), and the least squares slope is $T_{ab} = 34.0^{o}C$. The corresponding theoretical curve from equation (4) is shown in Fig.25.

4 DISCUSSION

4.1 Summary of results

The T_G-composition data for all of the eleven copolymer systems examined conform to the proposed theory, and provide the results summarised in Table 1. The calculated values of T_{ab} may be compared with the corresponding value of $(T_{aa} + T_{bb})/2$. All of the systems showing a positive deviation from linearity or a maximum in the T_G versus overall composition plots conform to the condition $T_{ab} > (T_{aa} + T_{bb})/2$. Conversely, with the exception of styrene/butyl acrylate copolymers, all of the systems exhibiting negative deviation or a minimum conform to the condition $T_{ab} < (T_{aa} + T_{bb})/2$. In the case of styrene/butyl acrylate copolymers $T_{ab} - (T_{aa} + T_{bb})/2 = 1.5^{o}K$, which is very small, and it would be advantageous to obtain further experimental data to establish whether or not this system is a genuine exception.

4.2 Comparisons with other theories

Three other equations have been proposed by Kanig[7], Dyvik et al[8], and Ellerstein[9] to describe the variation of copolymer T_G with composition and these are also capable of describing the occurrence of a maximum or a minimum value in T_G.

As shown in section 2.2, the equation proposed by Ellerstein to account for the effect of A-B interactions in copolymer T_G is identical to equation (11) which is the special case of equation (10) when $r_a = r_b = 1$ and $\alpha_{aa} = \alpha_{bb}$. Ellerstein did not give a derivation of the equation nor examples of its application to experimental data and it would seem that this equation is only applicable when these special conditions are fulfilled. When however $r_a = r_b = 1$ but $\alpha_{aa} \neq \alpha_{bb}$, the terms of equation (11) should be weighted to allow for the effects of the numbers of groups in the diad sequences. In this way a good fit is obtained to the experimental data for the vinylidene chloride/methyl acrylate system (section 3.5).

To explain the occurrence of curvature or maxima or minima in plots of T_G versus weight-fractional composition Dyvik et al[8] proposed the empirical equation

$$T_G = W_a T_a + W_b T_b - \psi W_a W_b \qquad (12)$$

where T_G refers to the copolymer, T_a and T_b are the T_Gs of the corresponding homopolymers, W_a and W_b are the weight fractions of A and B in the copolymer, and ψ = 4 times the deviation of the data from the straight line connecting T_a and T_b in the plot of T_G versus weight-fractional copolymer composition. It was shown that equation (12) described the data for five copolymer systems exhibiting negative curvature in the T_G versus W_b plots, and two systems exhibiting minima. It was suggested that the equation could also describe data which exhibited positive curvature or maxima; in these cases ψ would be a negative constant. This equation does not give a very satisfactory fit to the experimental data for vinylidene chloride/methyl acrylate copolymers, and it is difficult to see specific relations between the interaction parameter, ψ, and the molecular structure of the copolymer.

The theory of Kanig[7] was discussed briefly in section 2.1. This theory is based on a thermodynamic model of a copolymer treated as a mixture of molecules and voids, and after introducing several simplifying assumptions the following equation is derived:

$$(T_G - T_{bb})/\phi_{f_a} = K_1 \phi_{f_a} + K_2 \quad , \qquad (13)$$

where

$$\phi_{f_a} = (W_a \delta_a) \Big/ (W_a \delta_a + W_b \delta_b) \quad . \qquad (14)$$

In these equations K_1 and K_2 are both constants for a given comonomer pair and functions of A^*_{ij}, the work to produce "1 mole of holes" by separating ij associations; W_a and W_b are the weight-fractional copolymer compositions.

The terms δ_a and δ_b are the differences between the coefficients of cubical expansion above and below the T_G for homopolymers of A and B, respectively. A random distribution of A and B units in the copolymer is assumed, and it follows that the theory predicts a constant T_G for copolymers of constant overall composition but of varying degrees of alternation. Thus polystyrene, and an alternating, or a random, copolymer containing equal proportions of ethylene and 1,2 diphenylethylene would all have the same T_G, a prediction which does not seem likely for reasons given in section 4.3.

Illers[11] found that the experimental data for styrene/acrylic acid and styrene/butyl acrylate, could not be satisfactorily fitted to equation (13). This Report has demonstrated however that the data for these two systems can be satisfactorily fitted to the proposed theory (equation (10)); the remaining nine copolymer systems give good fits to both equation (10) and equation (13).

In deriving his equation, Kanig assumed a random distribution of A and B units in the copolymer, so that the numbers of AA, BB, and AB (or BA) interactions are only dependent on the overall concentrations of A and B units. Kanig's treatment corresponds to the case of the present theory when $r_a = r_b = 1$, so that the occurrence of aa, bb, ab, and ba sequences are all equally probable. When this last assumption is made, together with the condition that $\alpha_{aa} = \alpha_{bb}$, it has been shown that the equation of Ellerstein[9], equation (11), appears as a special case of equation (10). It is therefore pertinent to relate equation (11) (Ellerstein) to equation (13) (Kanig). Equation (11) can be written as follows:

$$(T_G - T_{bb}) \big/ n_a = A_1 n_a + A_2 \quad , \qquad (15)$$

where $A_1 = T_{aa} + T_{bb} - 2T_{ab}$ and $A_2 = 2(T_{ab} - T_{bb})$, and this equation is of the same algebraic form as equation (13). Furthermore there is a striking similarity between the constants A_1 and K_1, and A_2 and K_2, since[7] in equation (13) $K_1 = k(A^*_{aa} + A^*_{bb} - 2A^*_{ab})$ and $-k_2 = 2k(A^*_{ab} - A^*_{bb})$, where k is a function of the ratio of "hole volume" to free volume, which is a constant for any given polymer[7]. The terms A^*_{ij} and T_{ij} are thus combined in exactly the same form within the constants A_1 and K_1, and A_2 and K_2, respectively. The parameters n_a and ϕ_{f_a} and equations (13) and (15) are related by the expression

$$[(1/n_a) - 1] \Big/ [(1/\phi_{f_a}) - 1] = M_a \delta_a / M_b \delta_b \quad , \qquad (16)$$

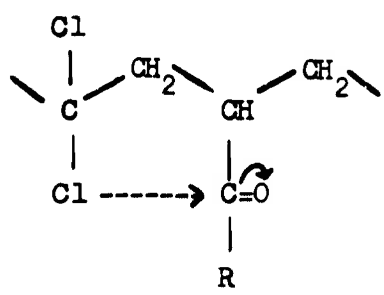
where M_a and M_b are the molecular weights of monomers A and B. When $M_a \Delta\alpha_a = M_b \Delta\alpha_b$, $n_a = \phi_{f_a}$, making equations (13) and (15) formally identical, which is the case for the methyl methacrylate/methyl acrylate copolymer system. For the other copolymer systems under discussion the value of $M_a \delta_a / M_b \delta_b$ varies between 0.6 and 2.8, and for these systems the Kanig and Ellerstein equations are inter-related by the more complex form of equation (16). Equations (13) and (15) would also be identical if $n_a/\phi_{f_a} = (K_1/A_1)^{\frac{1}{2}} = K_2/A_2$.

4.3 The influence of chemical structure on the T_Gs of copolymers

The relative extents to which intermolecular and intramolecular forces determine the T_G of a polymer or copolymer is still not clearly defined: the DiMarzio and Gibbs[2] copolymer theory emphasises the role of intramolecular forces, particularly chain stiffness, while that of Kanig[7] places more weight on the role of intermolecular forces.

It is possible in some cases to see qualitative reasons why the T_G of a copolymer system should exhibit a maximum or a minimum value if the chemical structures of the relevant pairs of repeating units are considered in terms of the possible interplay of steric and electronic interactions, as in the following examples.

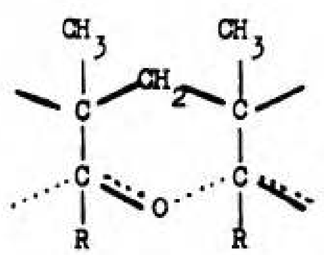
The maximum observed in T_G with composition for vinylidene chloride/methyl acrylate and vinylidene chloride/ethyl acrylate copolymers can be partly explained by assuming an intramolecular electronic interaction in the ab unit:



R = $CH_3 \cdot O-$
or $CH_3 \cdot CH_2 \cdot O-$

Interaction between the electronegative chlorine and the ester carbonyl group would tend to inhibit rotation of the main-chain segments. This interaction would reinforce the effect of steric hindrance caused by the proximity of the chloro and ester substituents.

The [illegible] in T_G observed in styrene/methyl methacrylate copolymers can be explained in similar terms. In the aa sequence steric hindrance is likely due to the proximity of the pendant phenyl rings, while in the bb sequence intramolecular interaction to form a pseudo-ring conformation is possible:



R = CH_3·O–

Both of these interactions are likely to be absent in the ab sequence, where the phenyl groups are spaced apart by methoxy carbonyl groups, thus conferring greater ease of rotation about the main chain.

This type of qualitative approach could be useful in predicting whether a given copolymer system is likely to exhibit positive or negative curvature in the T_G versus composition plot.

The results show that a pair of stiff homopolymers can often be flexibilised by the alternating spacing conferred by copolymerization, and when this is so the minimum T_G will be obtained at the maximum degree of alternation; this may be a useful concept in the design of new elastomers. It seems unlikely, however, that chains already flexible in homopolymer form (low T_G) could themselves be greatly reduced in T_G on copolymerization.

5 CONCLUSIONS

A simple relationship is proposed (equation (10)) between T_G and the mole fractions of the repeating unit diad sequences in a copolymer. When the reactivity ratios are known, the relationship also gives T_G as a function of overall copolymer composition. There is good agreement between theory and experimental data for all of the eleven copolymer systems examined including those exhibiting a maximum or a minimum in T_G with respect to the corresponding homopolymer T_Gs. Furthermore, the data for two systems which did not fit the Kanig theory[11], namely, styrene/acrylic acid and styrene/methyl methacrylate copolymers, agree well with the proposed relationship.

The copolymer equations of DiMarzio and Gibbs[2] and Ellerstein[9] are special cases of the proposed relationship; the Ellerstein and the Kanig[7] equation are closely related in form.

When one of the homopolymer T_Gs (i.e. T_{aa} or T_{bb}) is unknown it may be estimated by finding the value which gives the best fit of the data to equation (10). In this way the T_G of polyacrylonitrile is estimated to be 378° and 381°K, from the data for copolymers with vinyl chloride and methyl methacrylate, respectively. From the data for styrene/acrylic acid copolymers, the T_G of polyacrylic acid is estimated to be 413°K.

A knowledge of the factors which determine the values of the parameter T_{ab} would enable quantitative predictions to be made of copolymer T_G from the homopolymer T_Gs and the copolymerisation reactivity ratios. At present, however, it is only possible to discuss the factors governing T_{ab} in qualitative terms. Very much more data will be required before quantitative correlations may be made between T_{ab} and the molecular structure of the ab unit.

Appendix A

CALCULATION OF THE FRACTIONS OF DIAD SEQUENCES IN A COPOLYMER

(see section 2.2)

The mole fraction of an ij sequence is given by

$$n_{ij} = n_i \; P_{ij} \quad , \qquad \text{(A-1)}$$

where n_i is the mole fraction of i units in the copolymer and P_{ij} is the probability of forming an ij sequence. For example, $n_{aa} = n_a \; P_{aa}$. Now an aa sequence can only be formed from the reaction of monomer A with a chain ending in a radical $A^{\bullet}$, but there is a competing reaction $A^{\bullet} + B$ to give an ab sequence, so that P_{aa} is given by

$$P_{aa} = k_{aa} \, [A^{\bullet}][A] \Big/ (k_{aa} \, [A^{\bullet}][A] + k_{ab} \, [A^{\bullet}][B]) \quad , \qquad \text{(A-2)}$$

where k_{aa} is the rate constant for the propagation reaction $A^{\bullet} + A$, and k_{ab} is the rate constant for $A^{\bullet} + B$. Although this treatment is given in terms of free-radical intermediates, the same method can be applied to ionic copolymerization if the propagation reactions are of the same simple bimolecular type.

Equation (A-2) can be rearranged to give

$$P_{aa} = r_a \, X \Big/ (r_a \, X + 1) \quad , \qquad \text{(A-3)}$$

where $r_a = k_{aa}/k_{ab}$, and $X = [A]/[B]$ the ratio of the concentrations of the comonomers in the monomer feed.

The conventional copolymer composition equation[24-26] may be written as

$$n = (r_a \, X + 1) \Big/ [(r_b/X) + 1] \quad , \qquad \text{(A-4)}$$

where n = [a]/[b], the ratio of the concentrations of a and b units combined in the copolymer at low conversions. From equation (A-4) it follows that

$$n_a = (r_a X + 1) \Big/ [r_a X + (r_b/X) + 2] \quad . \qquad \text{(A-5)}$$

Combining equations (A-3) and (A-5) according to equation (A-1) gives equation (6) of section 2.2:

$$n_{aa} = r_a X \Big/ [r_a X + (r_b/X) + 2] \quad . \qquad \text{(A-6)}$$

In a similar manner the expressions for n_{bb} and n_{ab} may be derived.

It should be noted that these derivations neglect any penultimate group effects and apply to low conversion copolymers.

Table 1

SUMMARY OF RESULTS

Monomer A	Monomer B	r_a	r_b	α_{aa}	α_{ab}	α_{bb}	T_{aa} (°K)	T_{bb} (°K)	$\frac{T_{aa} + T_{bb}}{2}$ (°K)	T_{ab} (°K)	Shape of T_G-composition plot	Expt. data ref.
Styrene	Butadiene	-	-	6	6	6	373	195[1] 188[2]	284 280.5	284 280.5	Linear	5
Acrylonitrile	Methyl methacrylate	0.15	1.20	6	9	12	381[3]	378	379.5	343	Min[4]	15,16
Acrylonitrile	Vinyl chloride	3.6	0.05	6	6	6	378[3]	353	366	361.5	-ve[5]	19
Vinylidene chloride	Methyl acrylate	1.0	1.0	8	9	10	254	279	266.5	375.5	Max[6]	11,16, 20
Vinylidene chloride	Ethyl acrylate	0.40	2.44	8	10	12	254	249	251.5	354	Max	16,20
Styrene	Methyl acrylate	0.75	0.18	6	8	10	364	279	321.5	331	+ve[7]	22
Styrene	Butyl acrylate	0.76	0.15	6	11	16	363	216	289.5	291	-ve	11
Styrene	Acrylic acid	0.15	0.25	6	7	8	363	413[3]	388	428	Max	11
Styrene	Methyl methacrylate	0.48	0.46	6	9	12	372	368	370	363	Min	10
Methyl methacrylate	Methyl acrylate	0.3	1.5	12	11	10	376	278	327	366	+ve	11
Vinyl chloride	Vinyl acetate	1.35	0.65	6	8	10	353	303	328	307	-ve	19

Notes

1. Copolymerization at 5°C
2. Copolymerization at 50°C
3. By extrapolation to give best fit to equation (10)
4. Exhibits a minimum in T_G
5. Exhibits negative curvature below "ideal" linear plot
6. Exhibits a maximum in T_G
7. Exhibits positive curvature

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Fig. 1

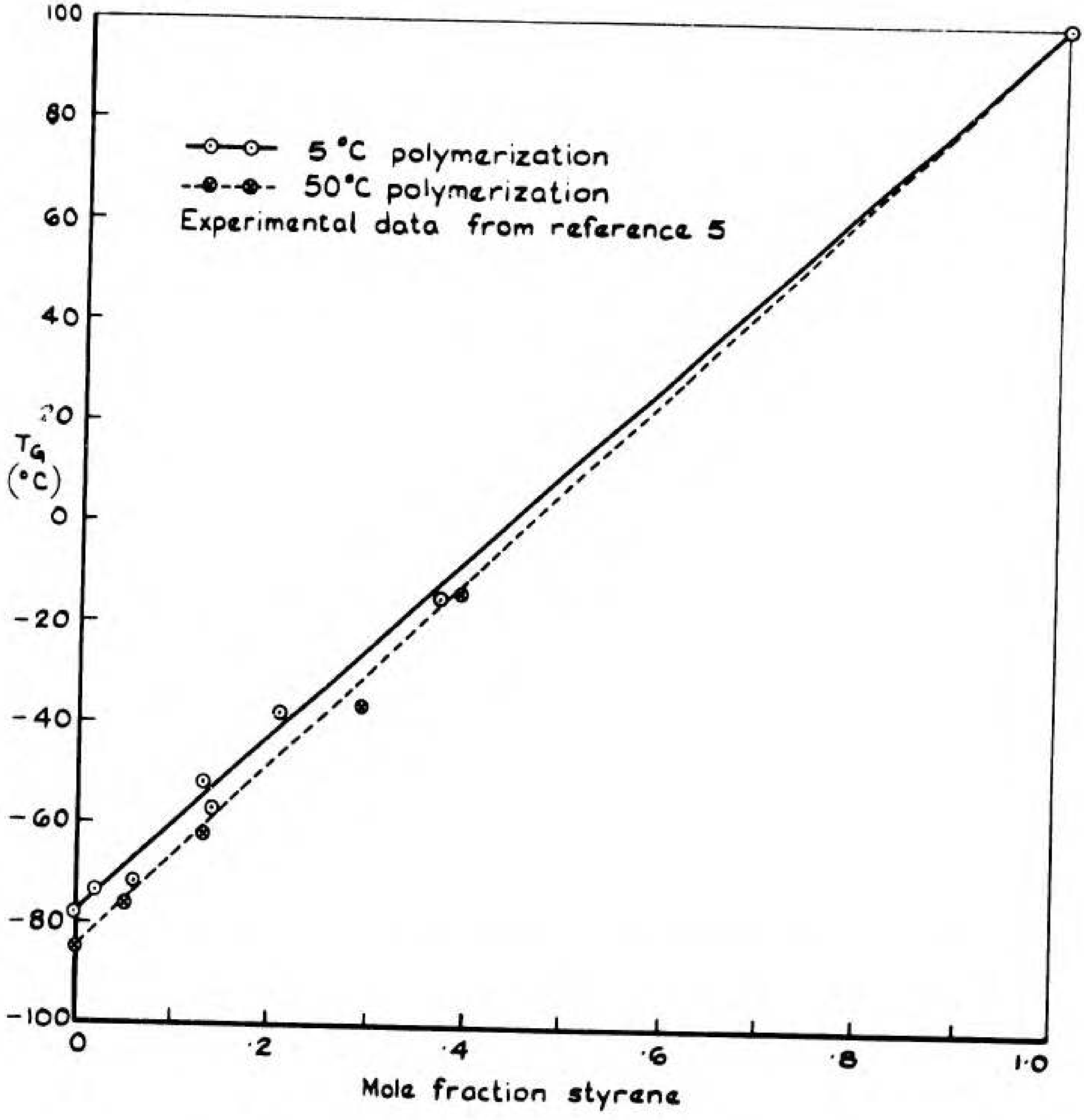

Fig.I Dependence of T_G on composition for styrene/butadiene copolymers

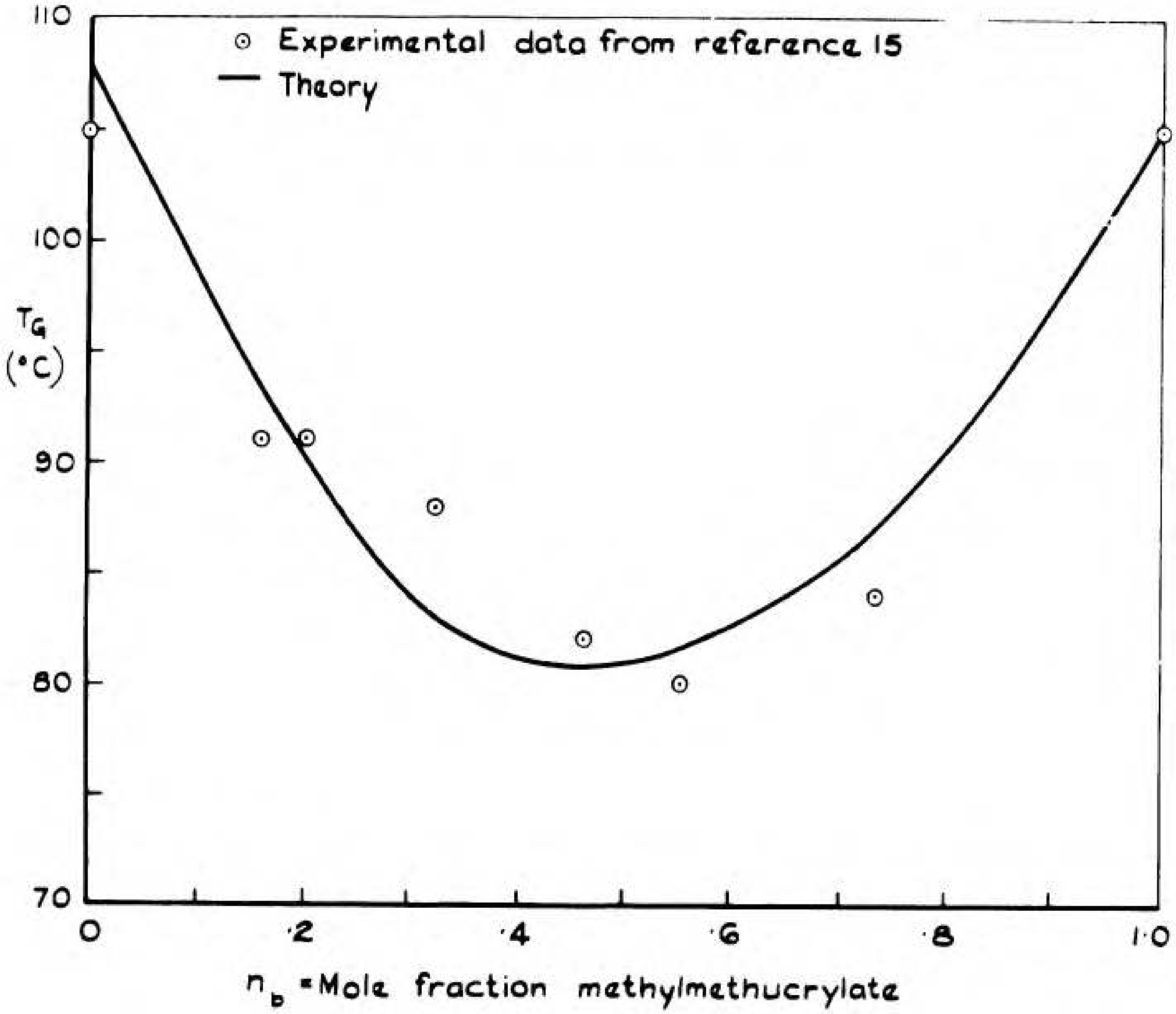

Fig.2 Dependence of T_G on composition for acrylonitrile / methylmethacrylate copolymers

Fig. 3

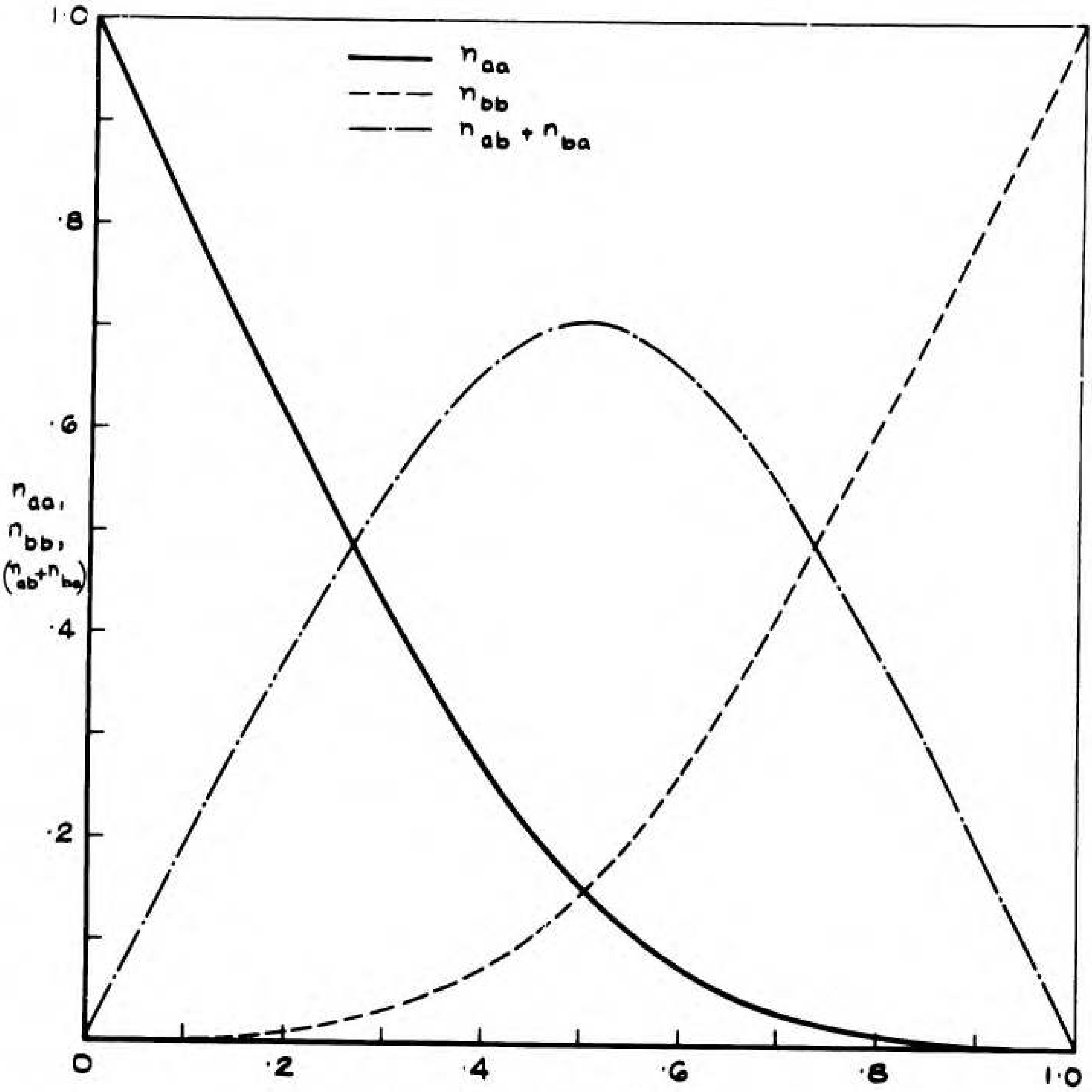

Fig. 3 Calculated sequence distributions for acrylonitrile/methylmethacrylate copolymers

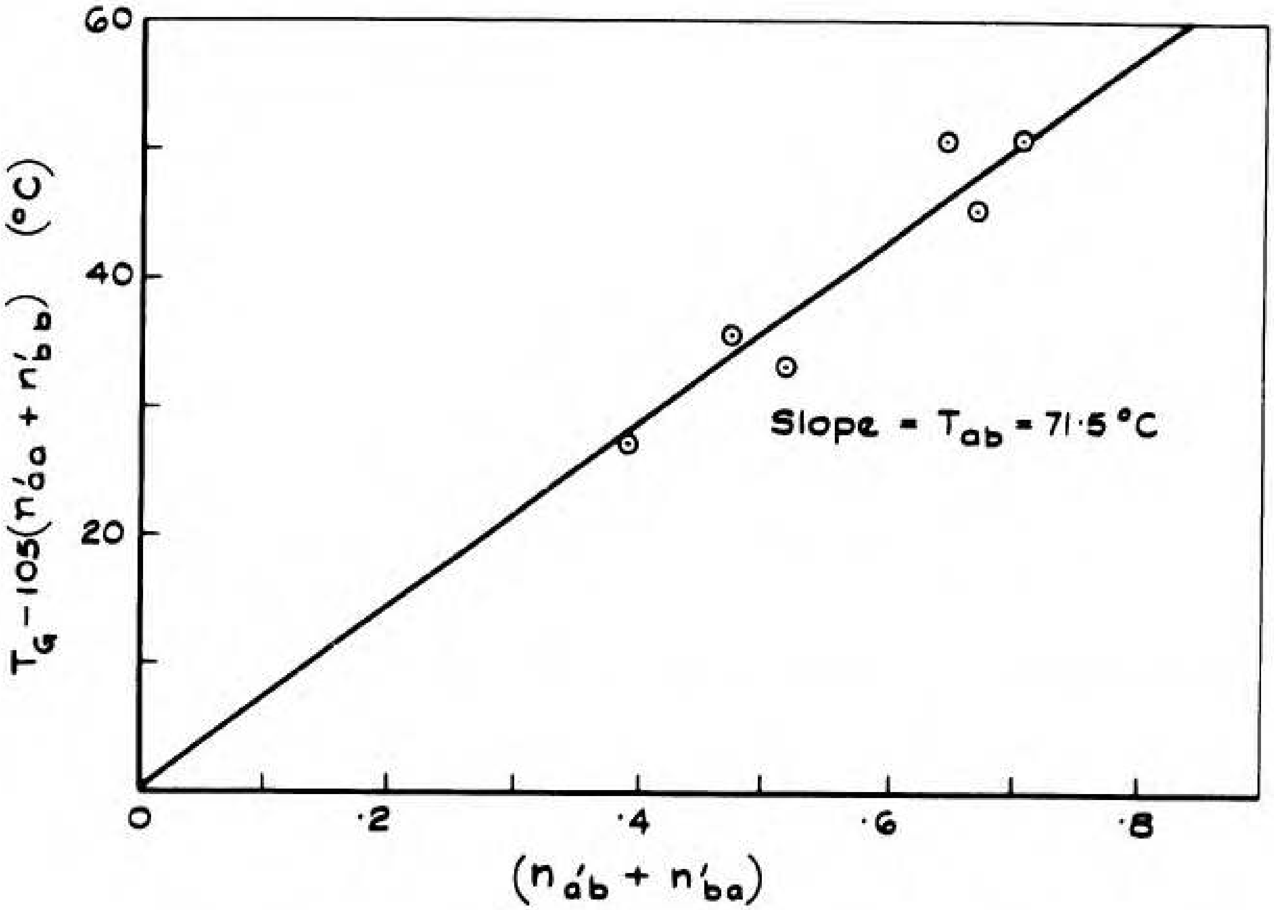

Fig.4 Plot of equation (10) for acrylonitrile/methylmethacrylate copolymers

Fig. 5

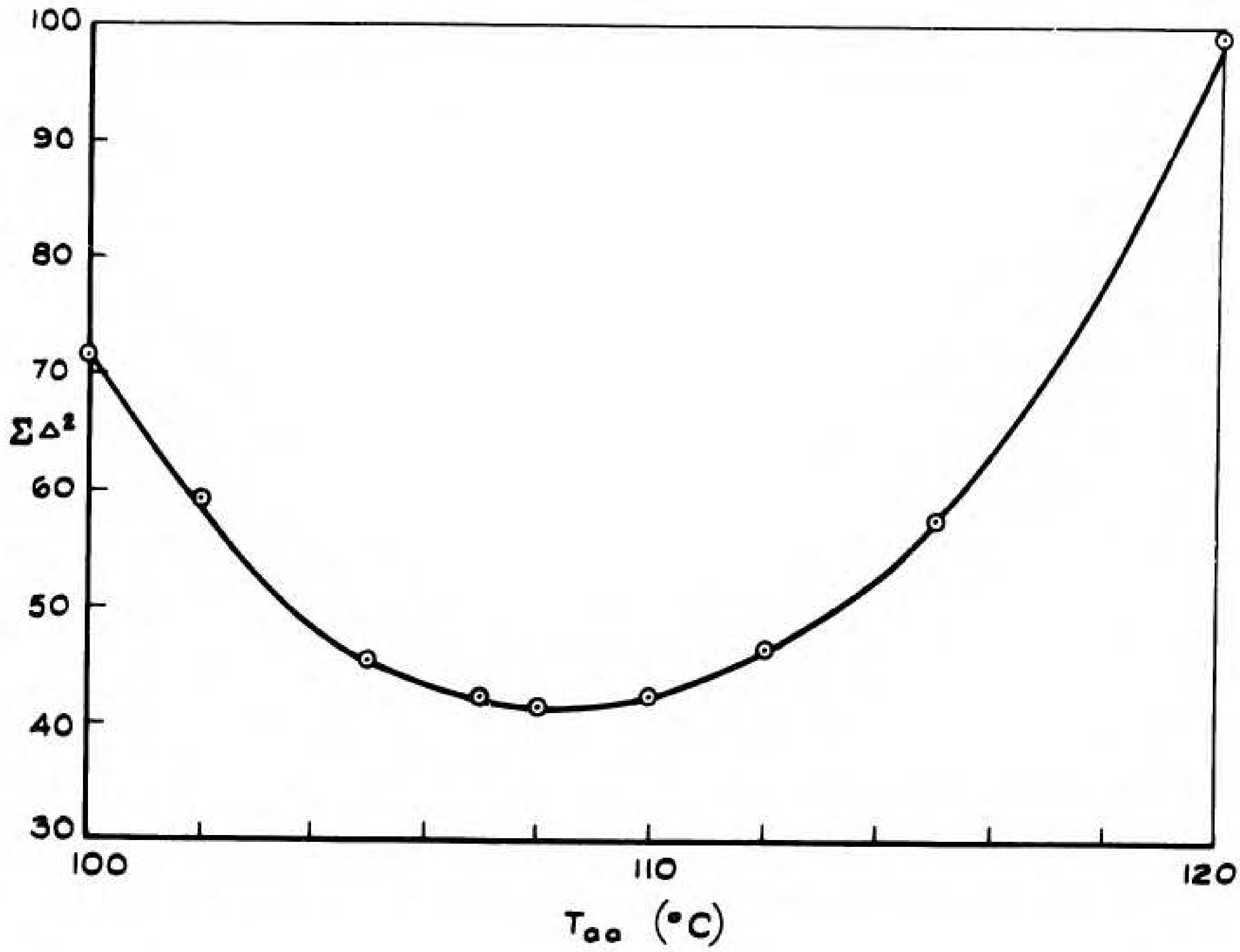

Fig.5 Variation in $\Sigma\Delta^2$ with T_{aa} for acrylonitrile/methylmethacrylate copolymers

Fig.6

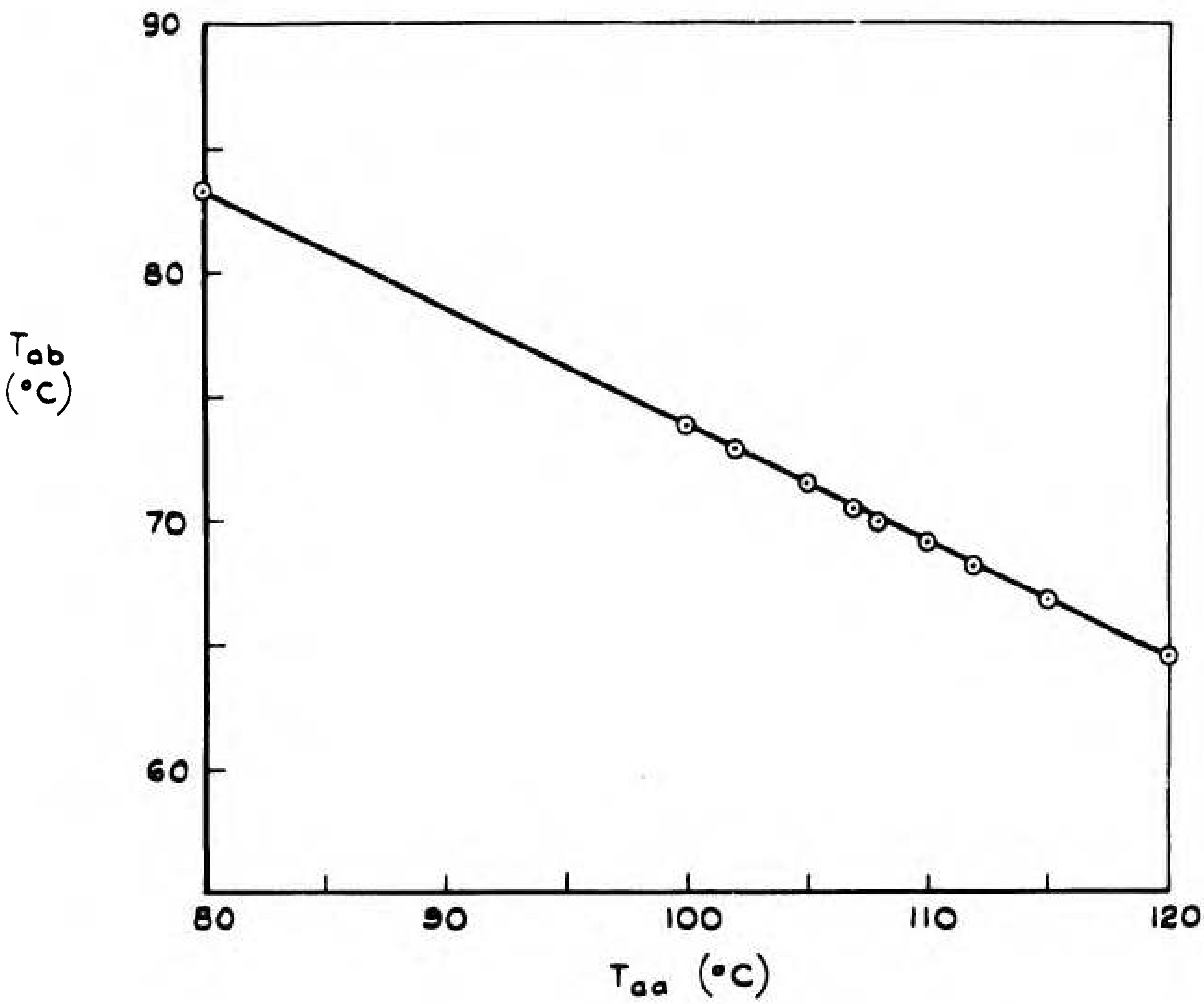

Fig. 6 Dependence of T_{ab} on T_{aa} for acrylonitrile/methylmethacrylate copolymers

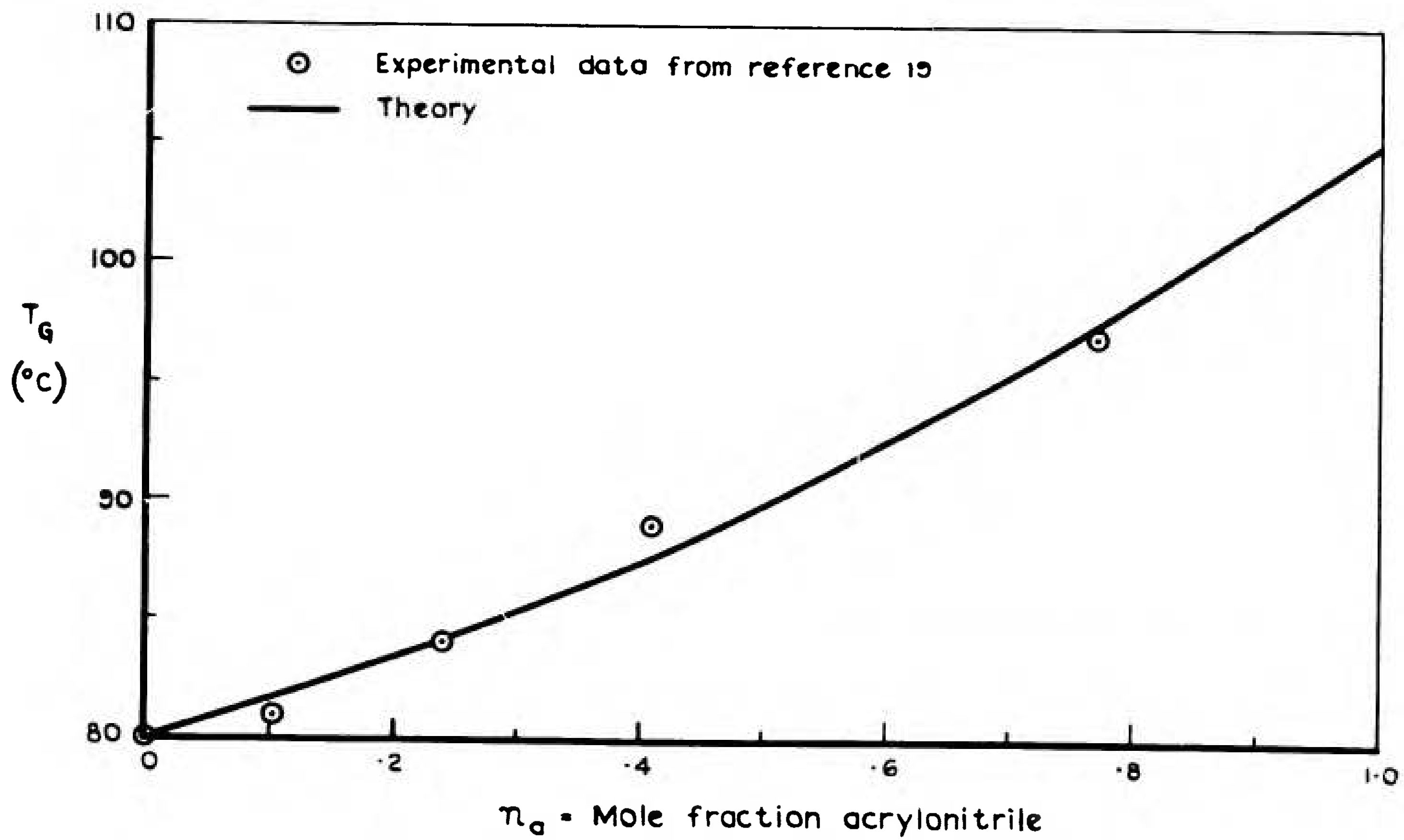

Fig. 7 Dependence of T_G on composition for acrylonitrile / vinyl chloride copolymers

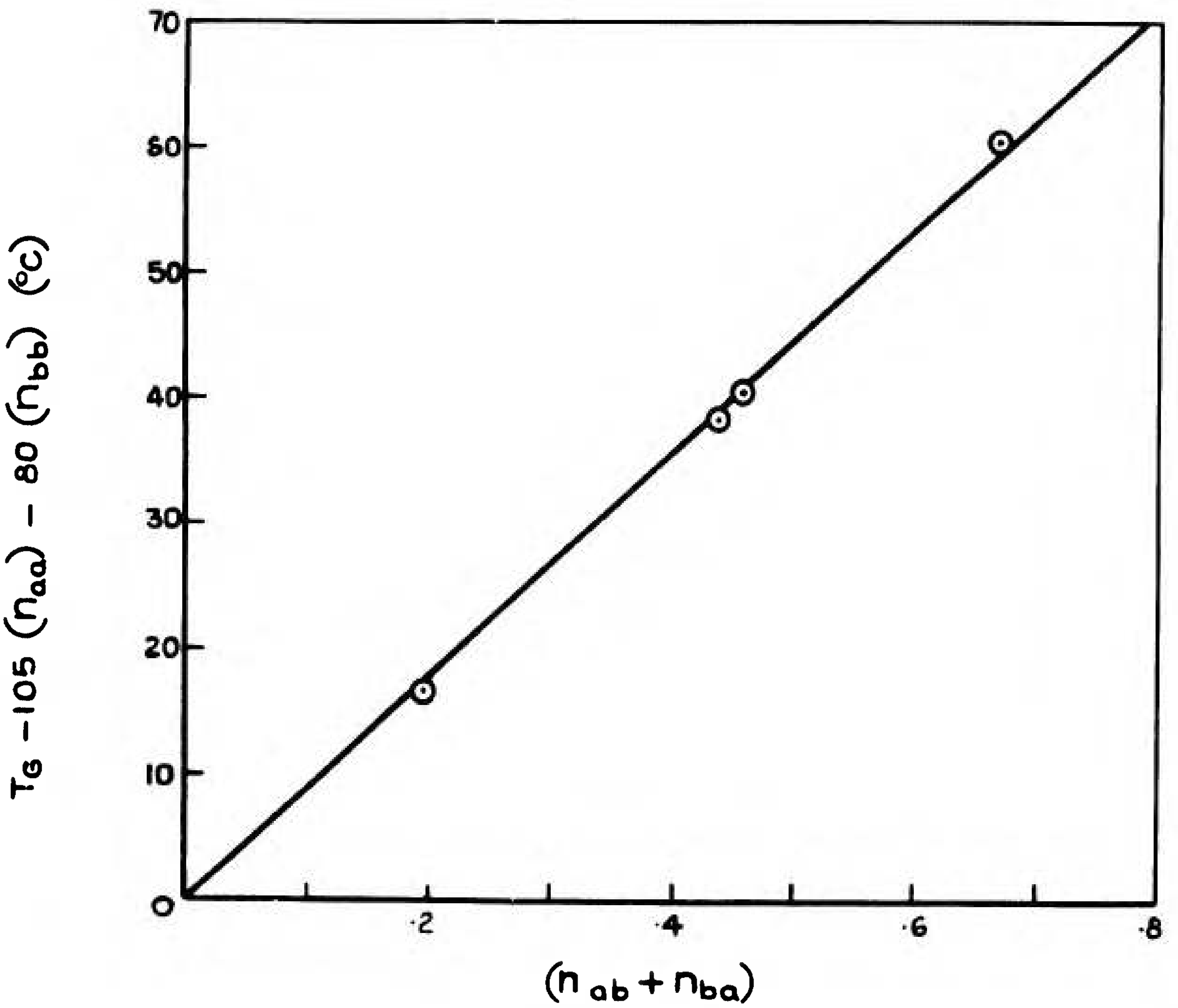

Fig.8 Plot of equation (10) for acrylonitrile/vinyl chloride copolymers

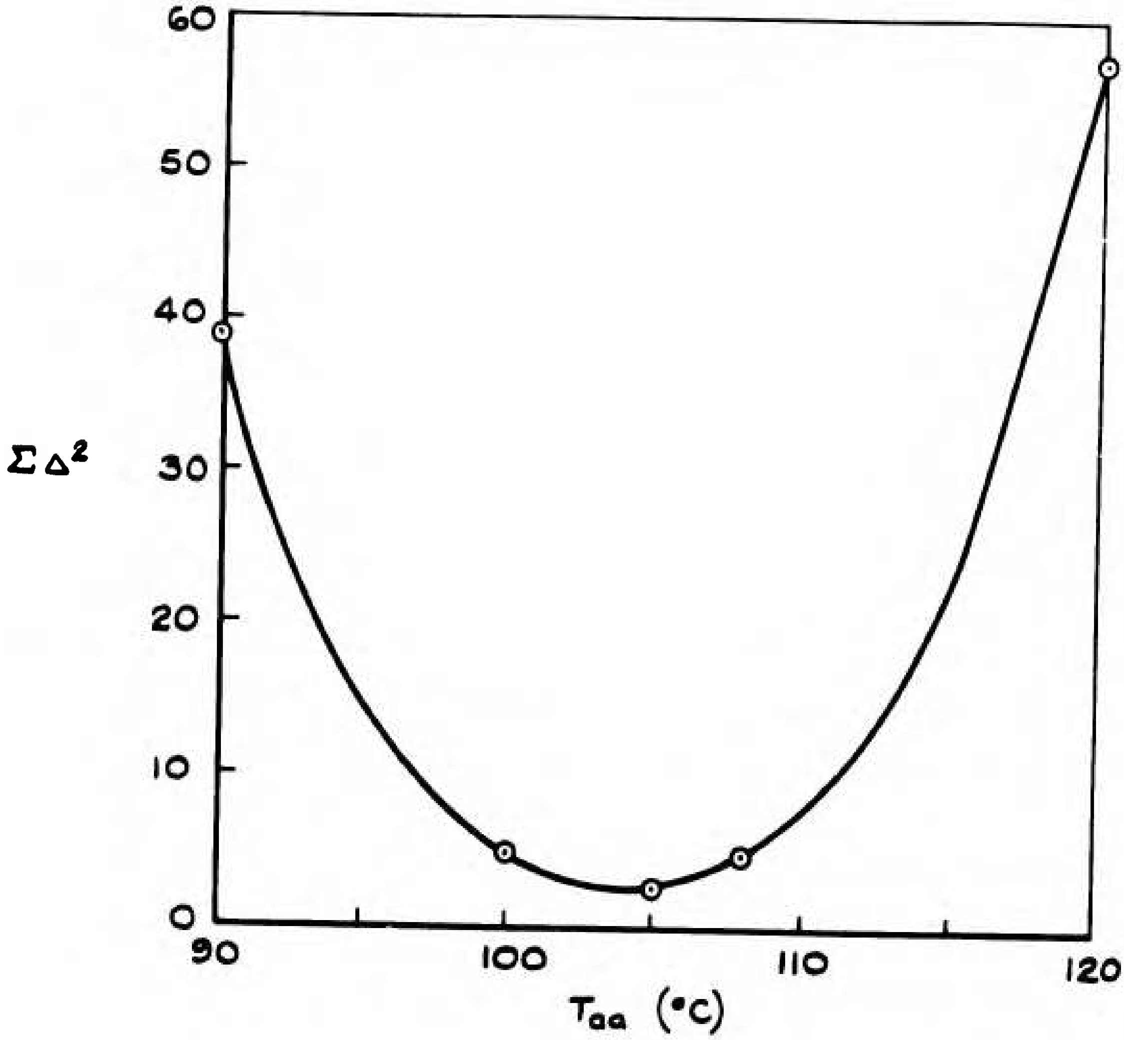

Fig. 9 Variation in $\Sigma\Delta^2$ with T_{aa} for acrylonitrile/methyl methacrylate copolymers

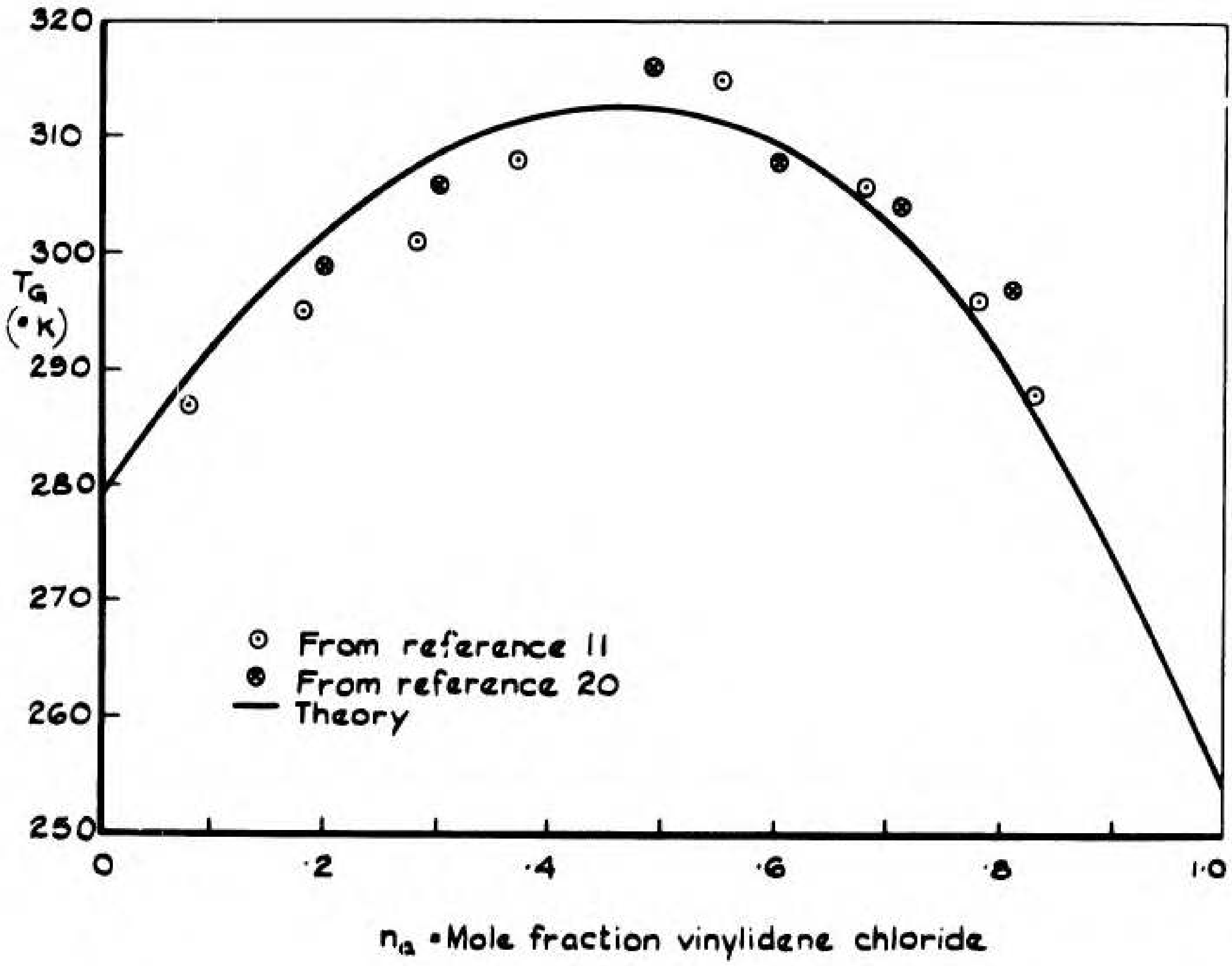

Fig.10 Dependence of T_G on composition for vinylidene chloride/methyl acrylate copolymers

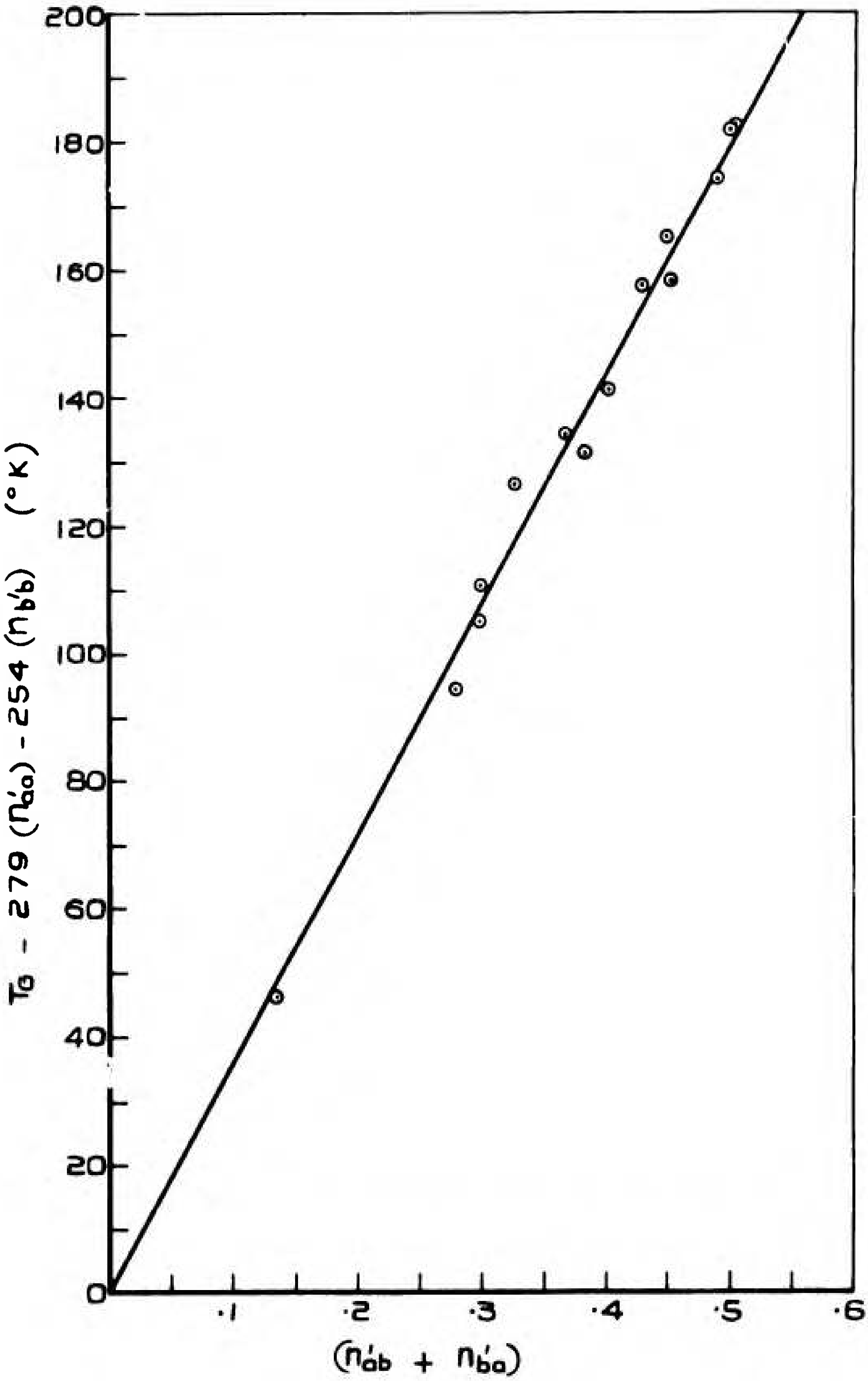

Fig.11 Plot of equation (10) for vinylidene chloride / methyl acrylate copolymers

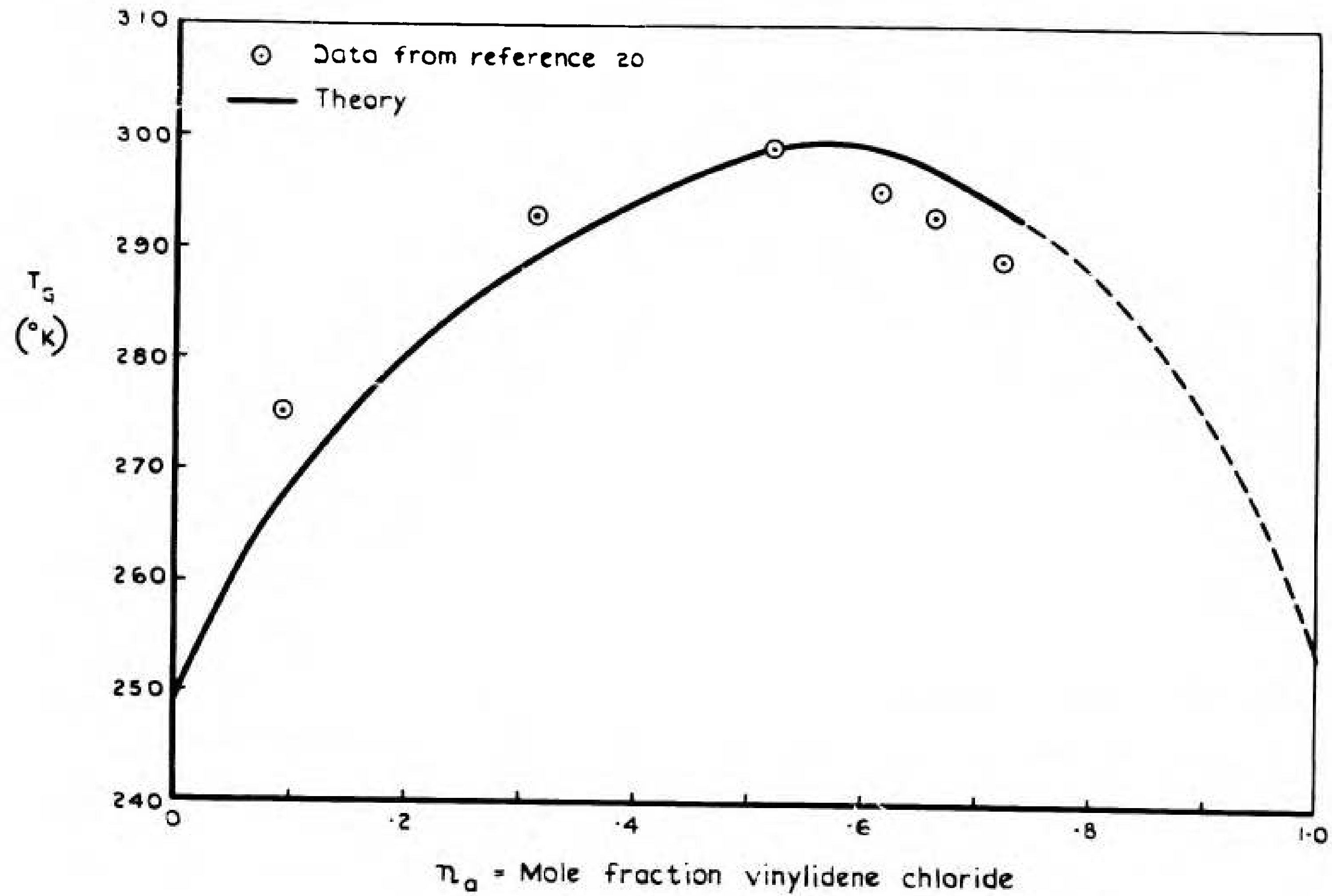

Fig. 12 Dependence of T_G on compostion for vinylidene chloride/ethyl acrylate copolymers

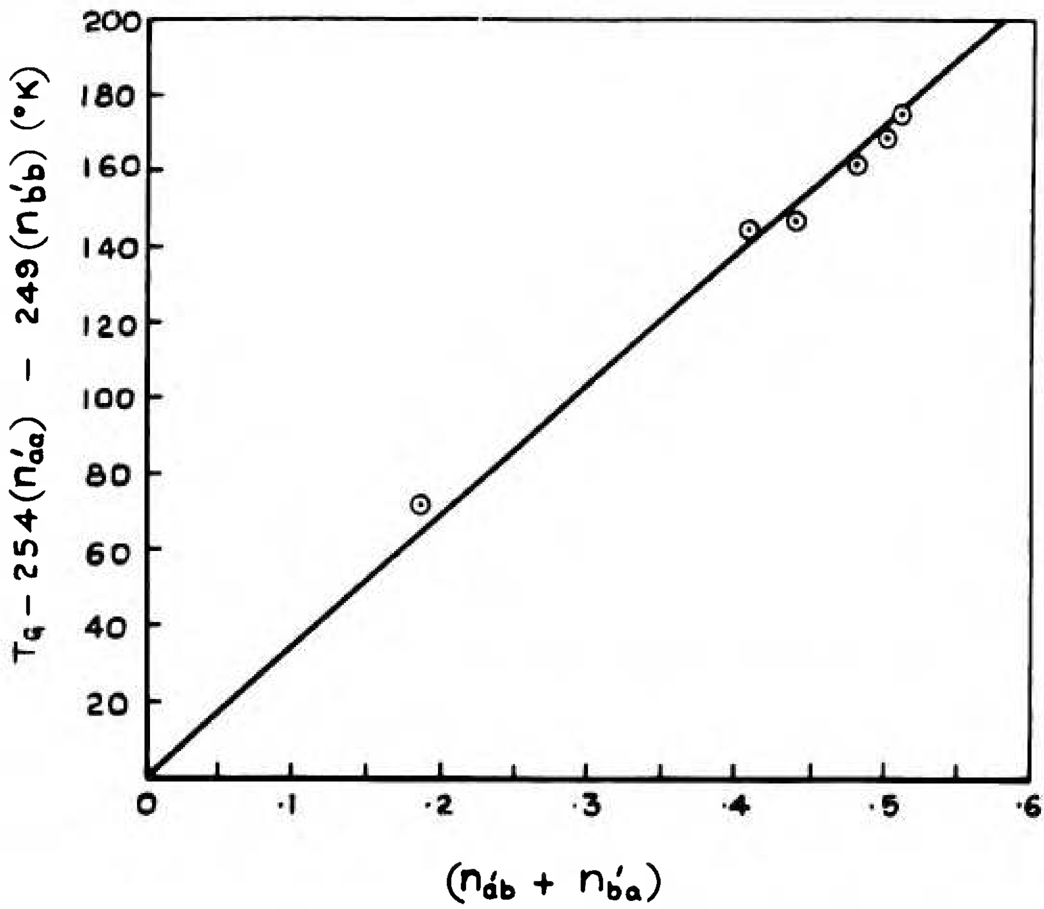

Fig.13 Plot of equation (10) for vinylidene chloride / ethyl acrylate copolymers

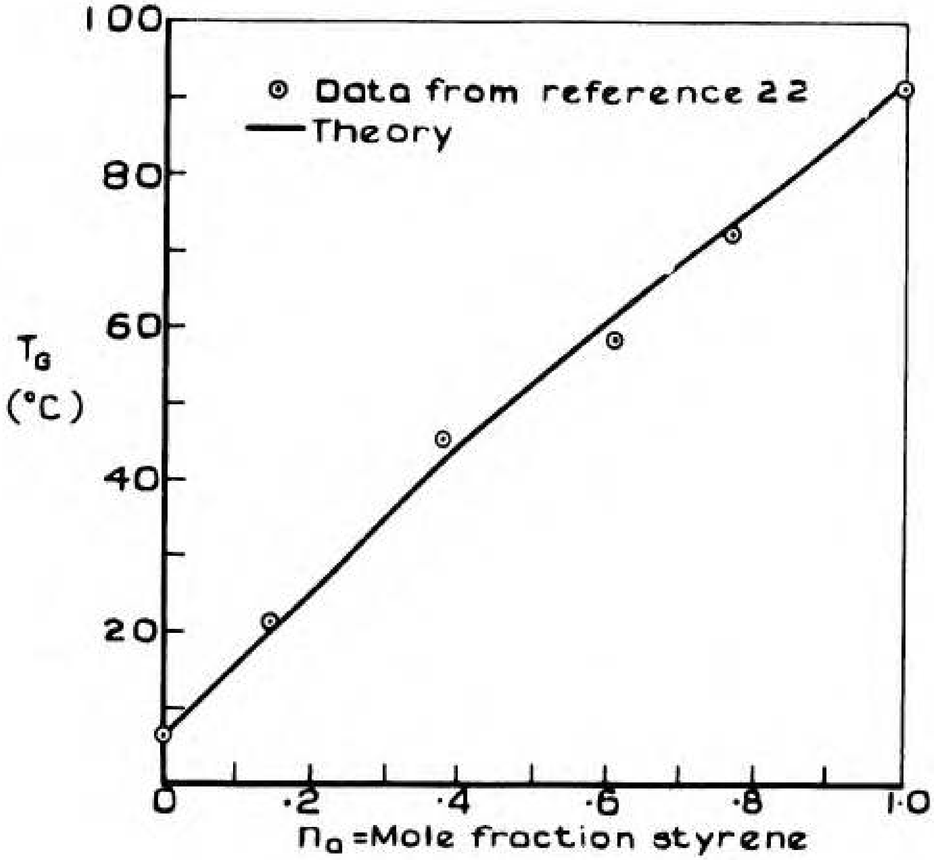

Fig.14 Dependence of T_G on composition for styrene / methyl acrylate copolymers

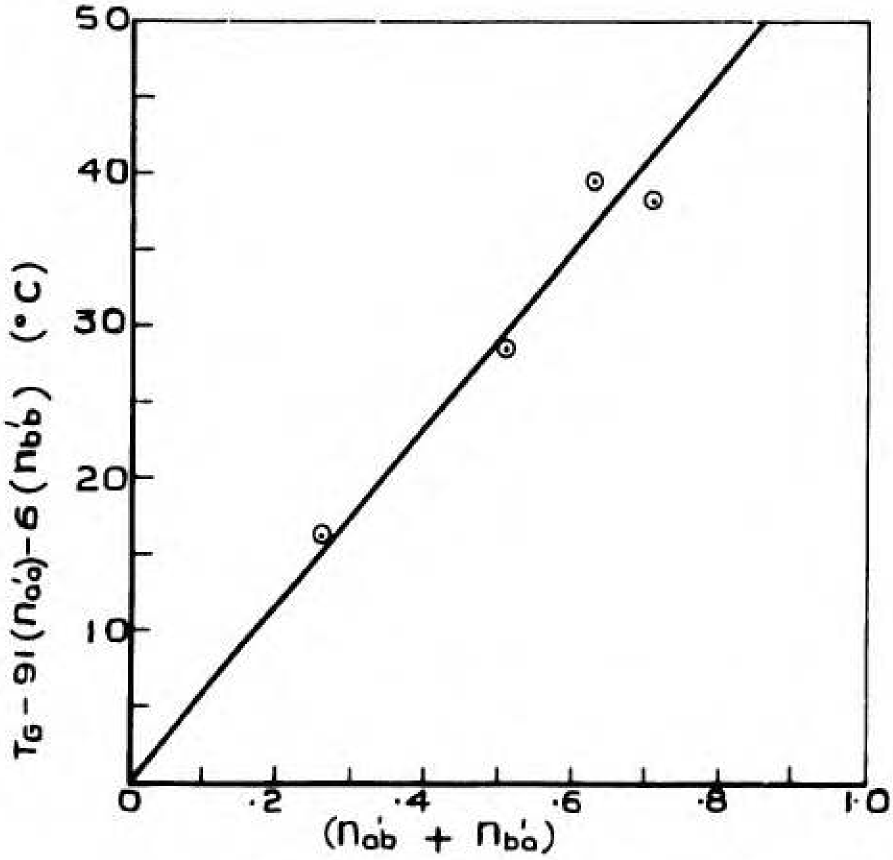

Fig.15 Plot of equation(10) for styrene / methyl acrylate copolymers

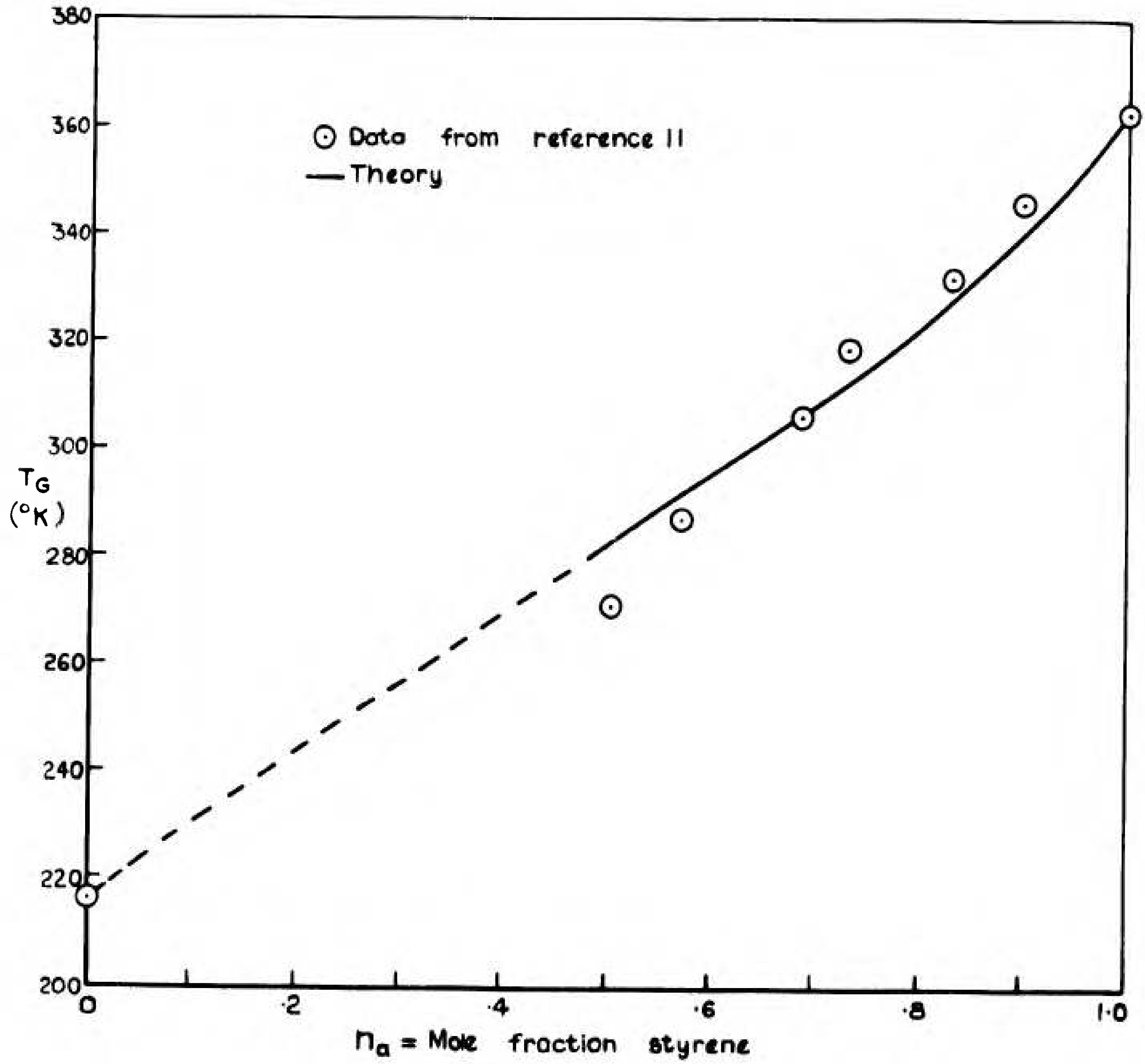

Fig.16 Dependence of T_G on composition for styrene/butyl acrylate copolymers

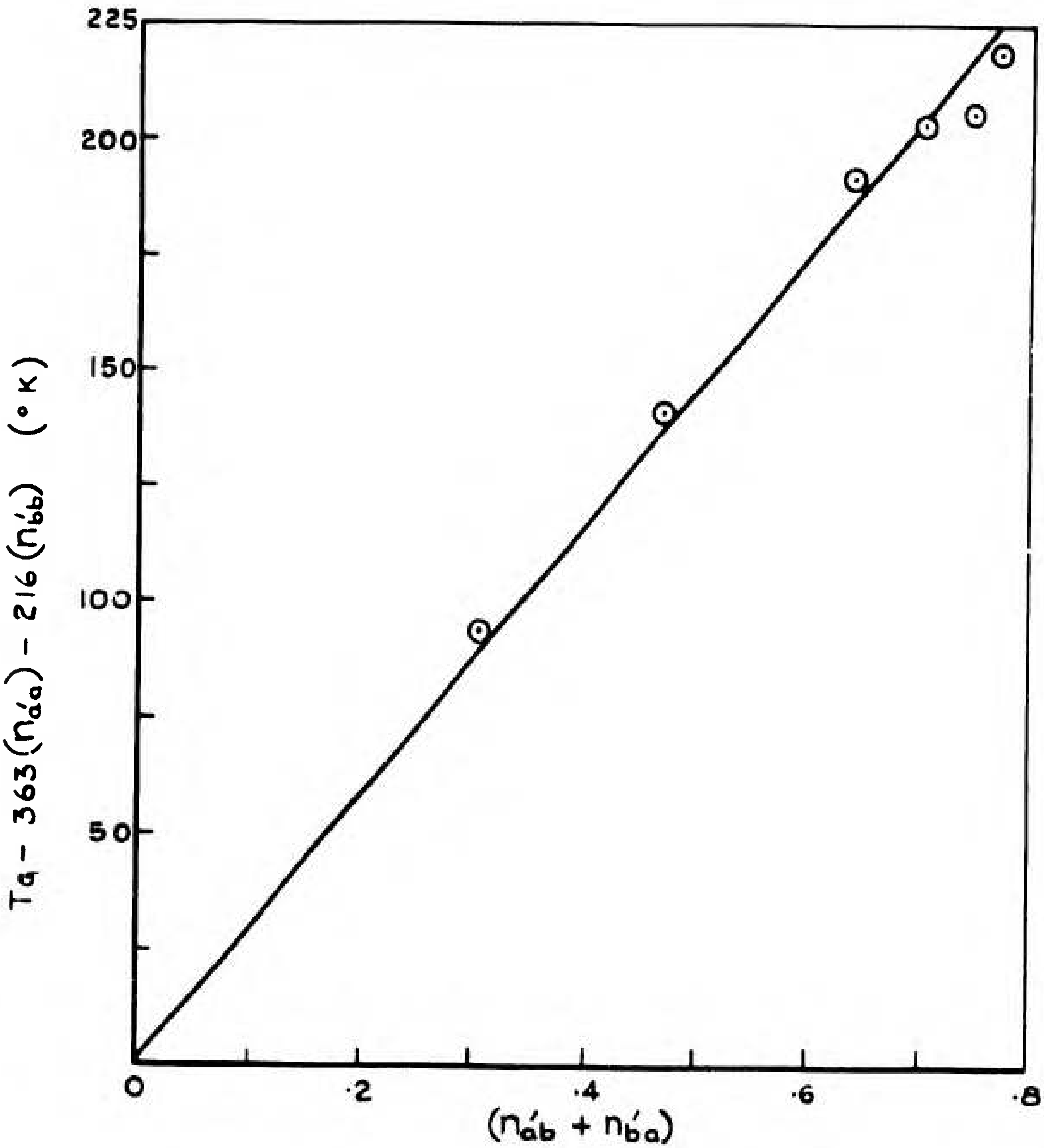

Fig. 17 Plot of equation (10) for styrene/butyl acrylate copolymers

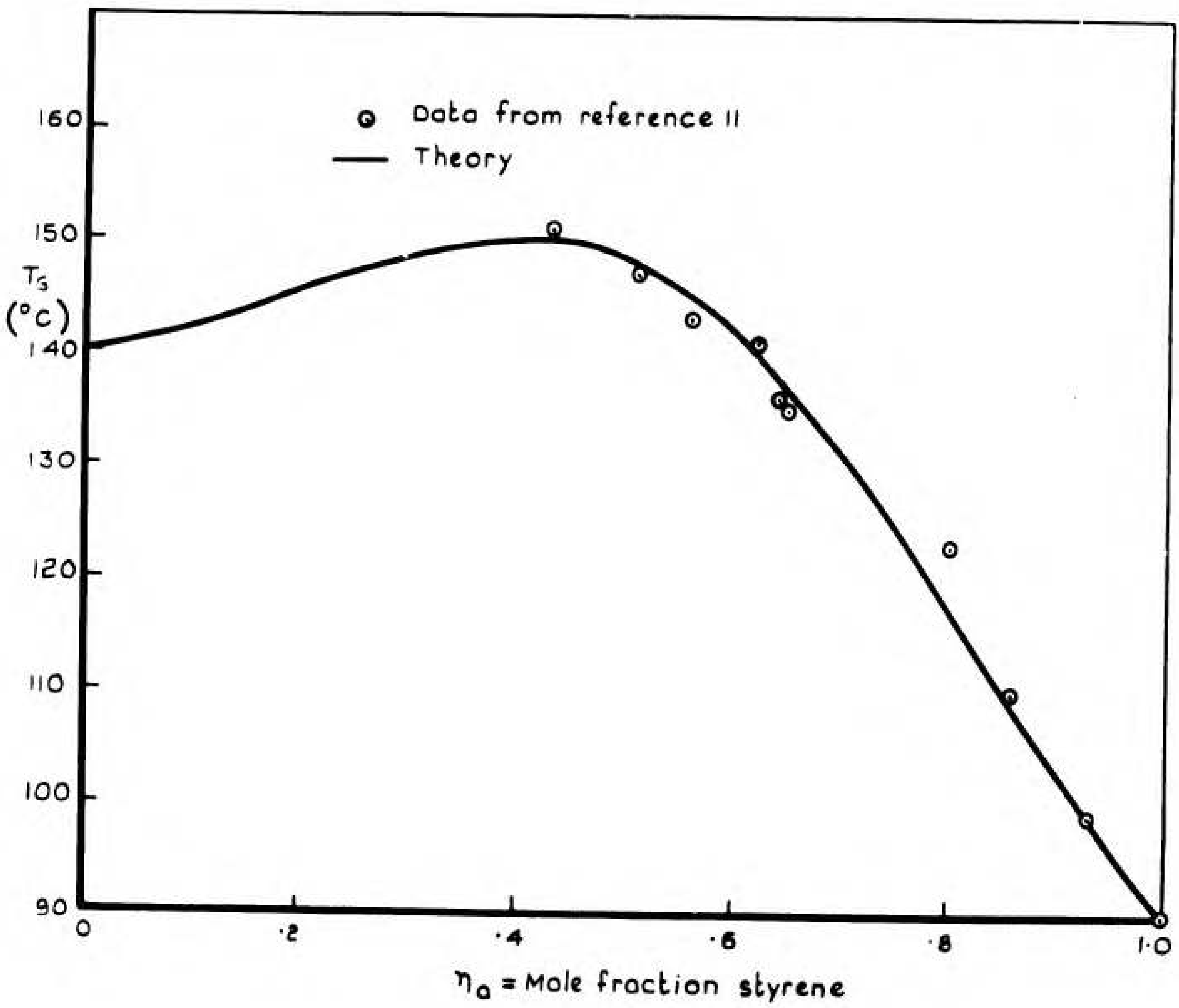

Fig. 18 Dependence of T_G on composition for styrene/acrylic acid copolymers

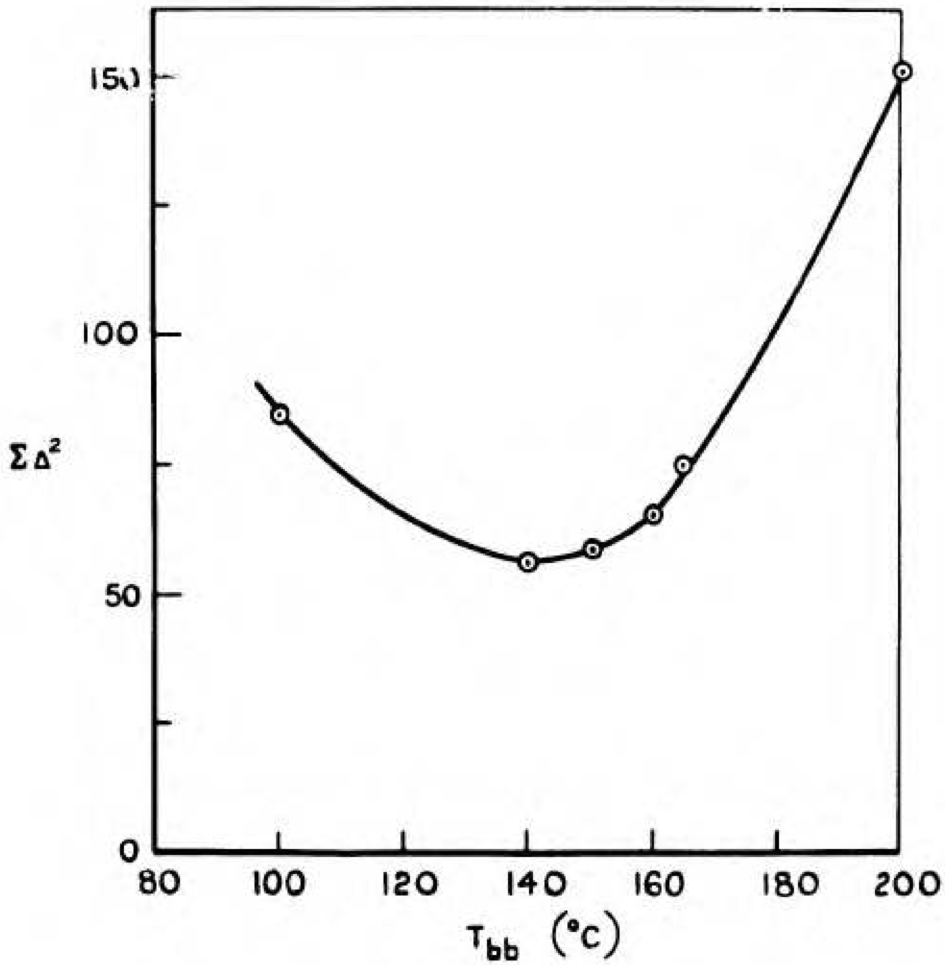

Fig. 19 Variation in $\Sigma\Delta^2$ with T_{bb} for styrene/acrylic acid copolymers

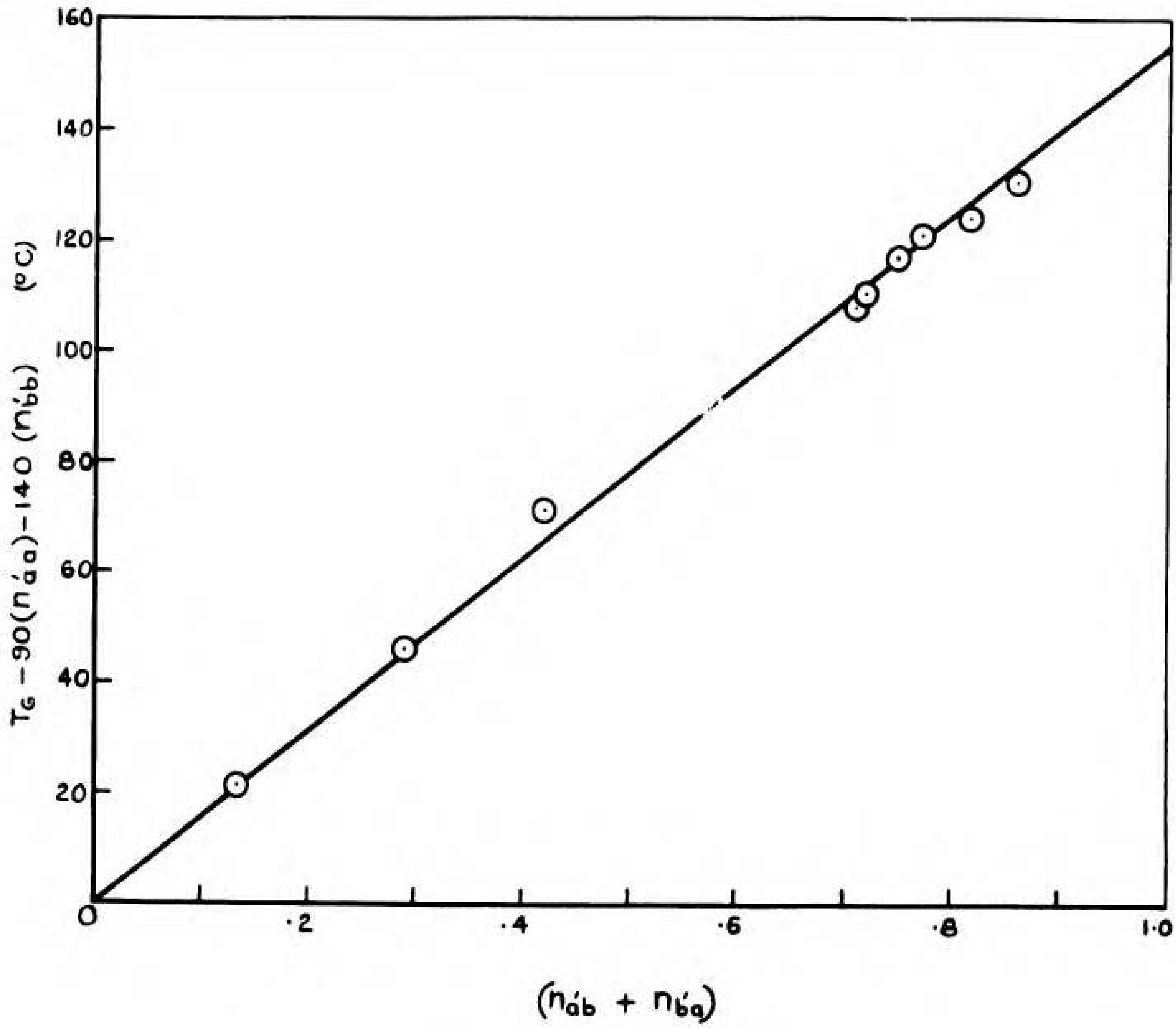

Fig. 20 Plot of equation (10) for styrene/acrylic acid copolymers

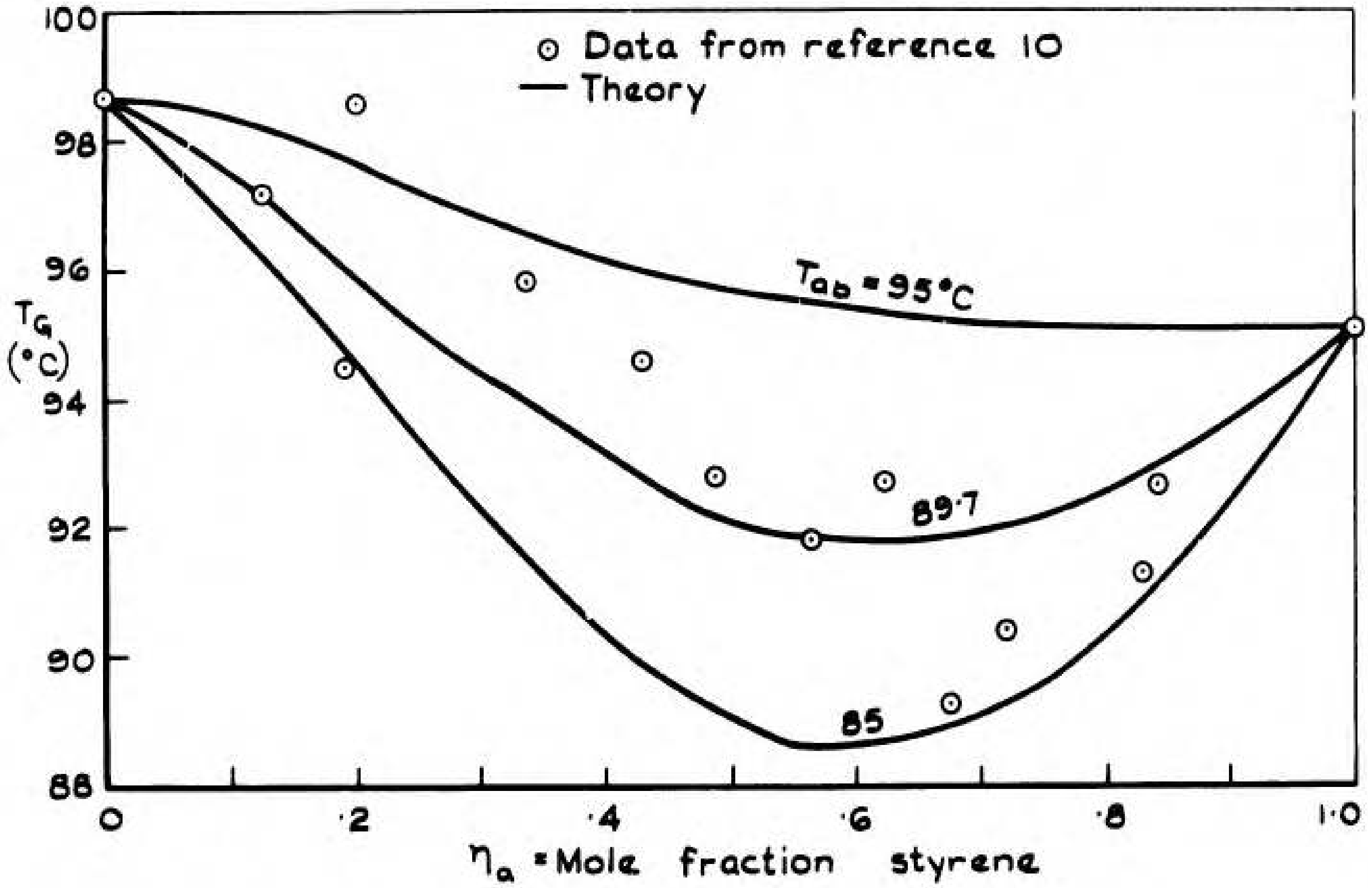

Fig.21 Dependence of T_G on composition for styrene / methylmethacrylate copolymers

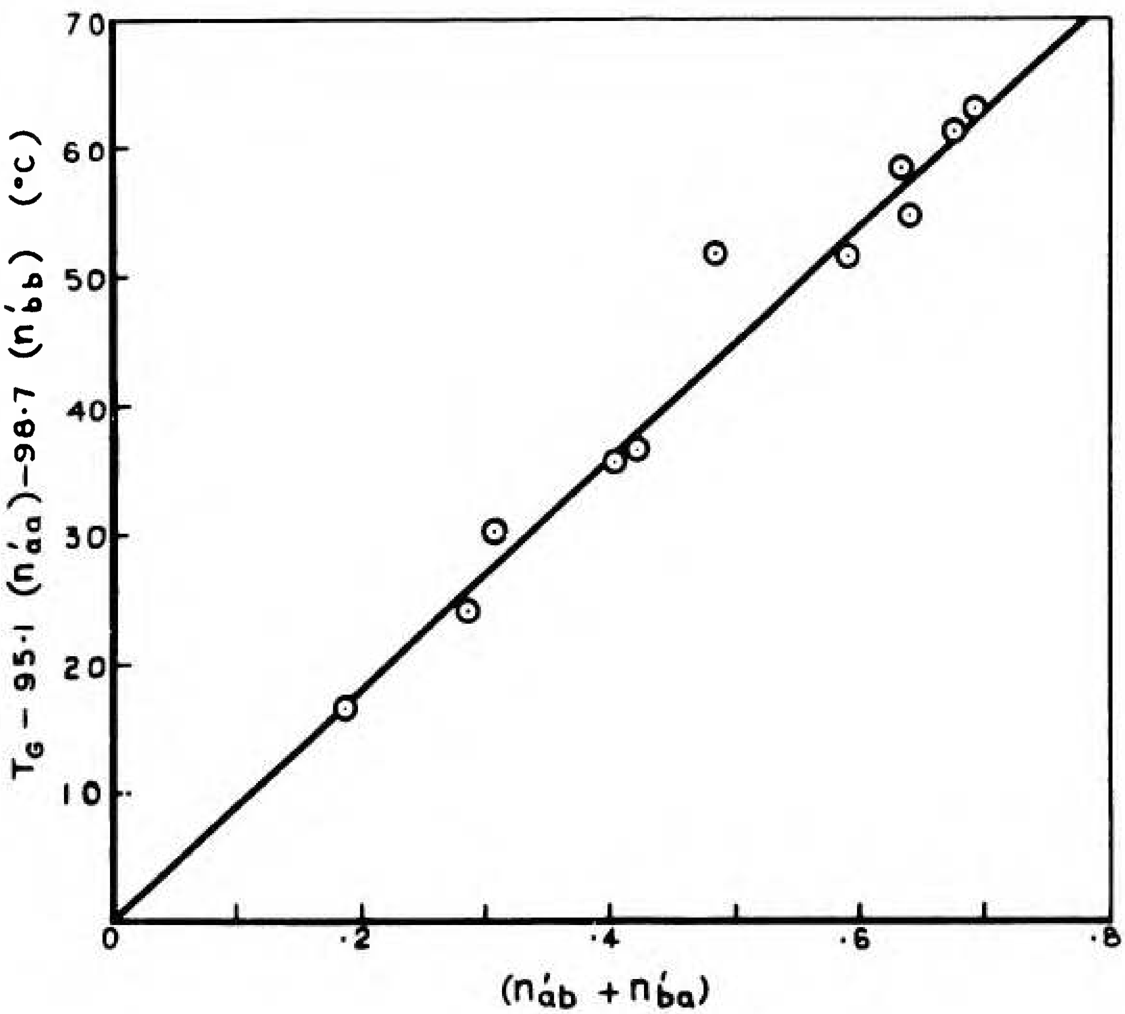

Fig. 22 Plot of equation (10) for styrene / methyl methacrylate copolymers

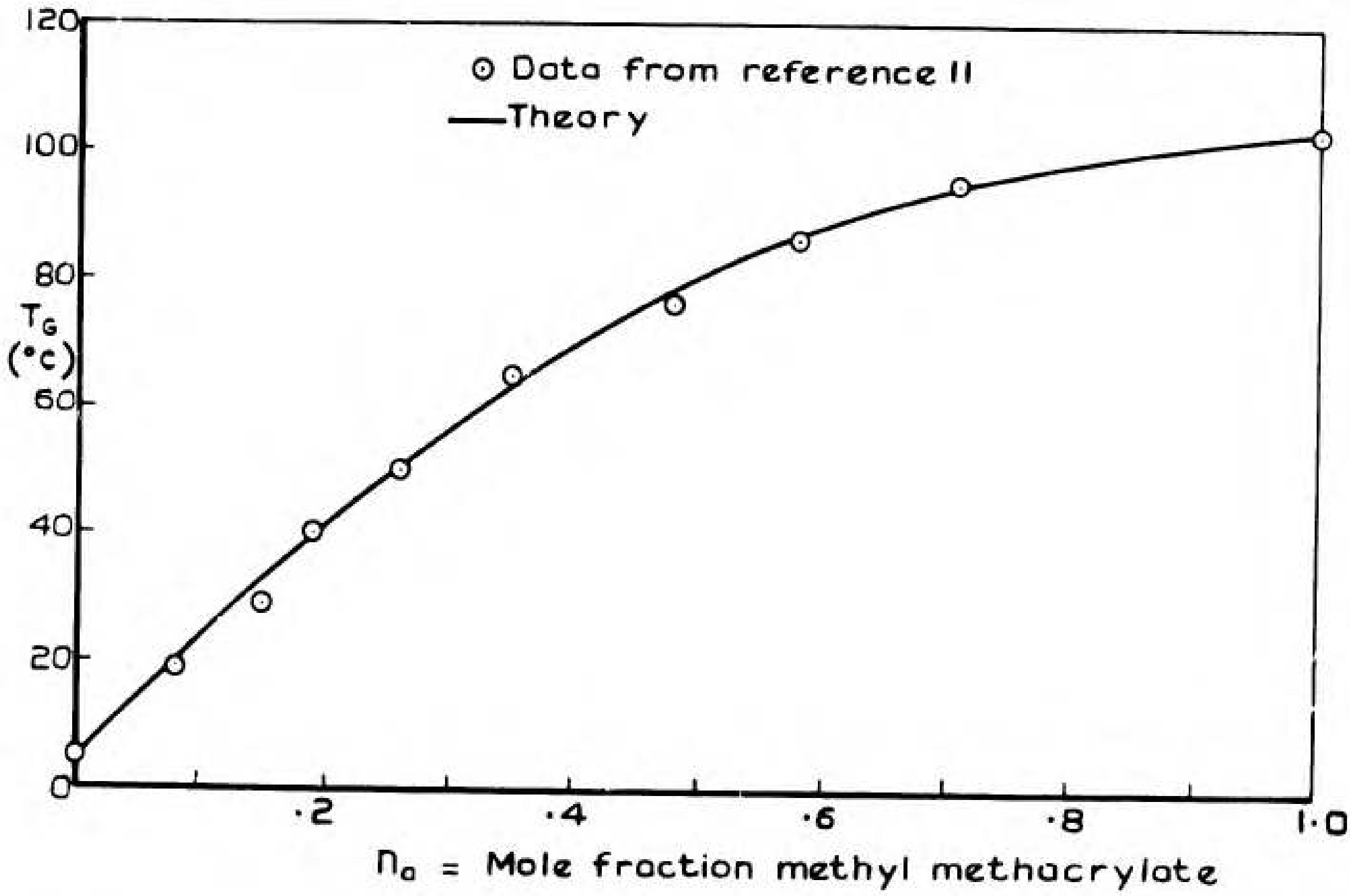

Fig.23 Dependence of T_G on composition for methyl methacrylate / methyl acrylate copolymers

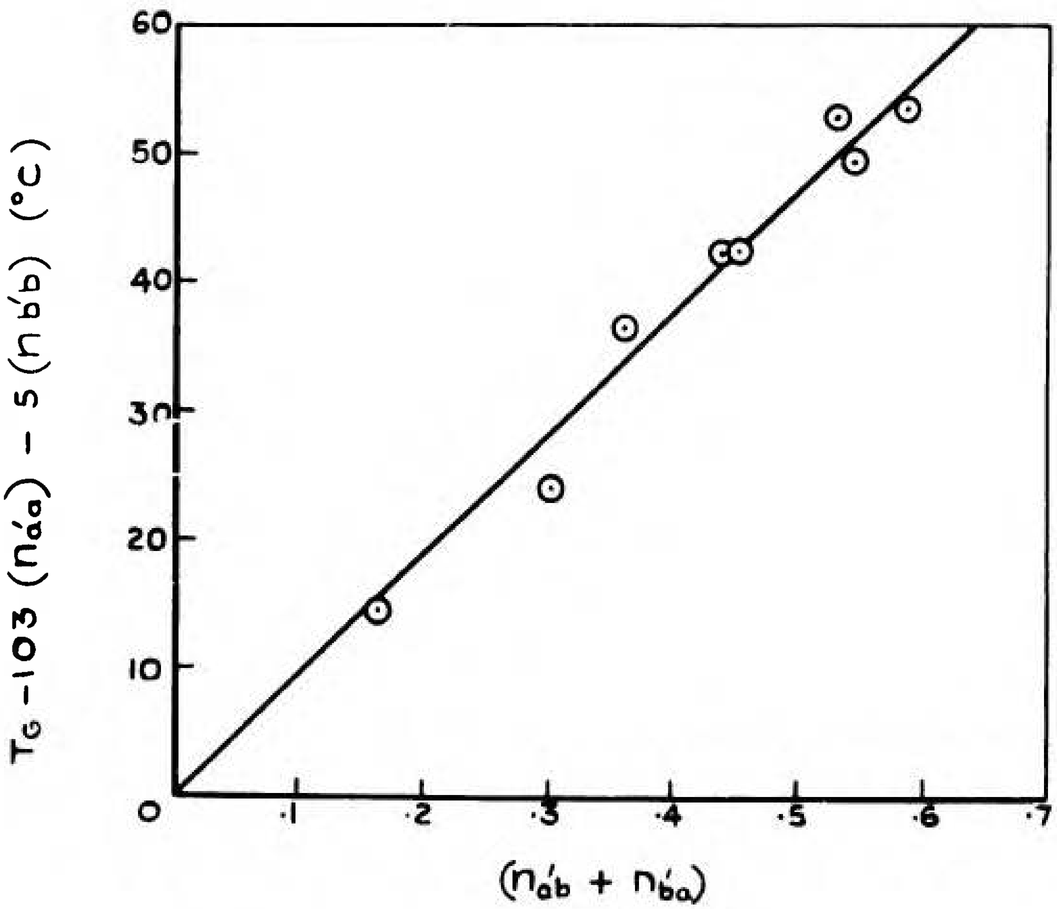

Fig. 24 Plot of equation (IC) for methyl methacrylate / methyl acrylate copolymers

Fig. 25

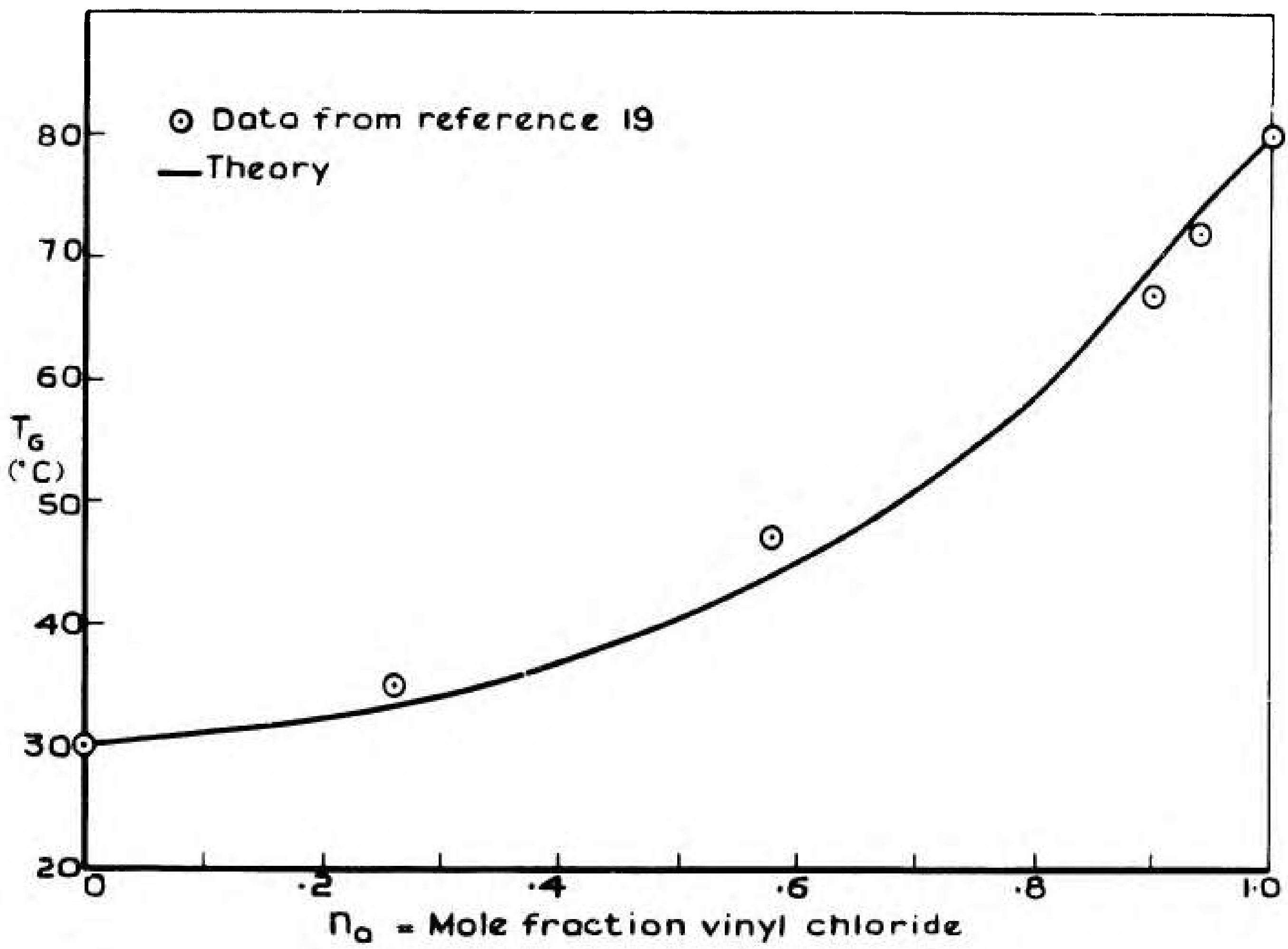

Fig. 25 Dependence of T_G on composition for vinyl chloride / vinyl acetate copolymers

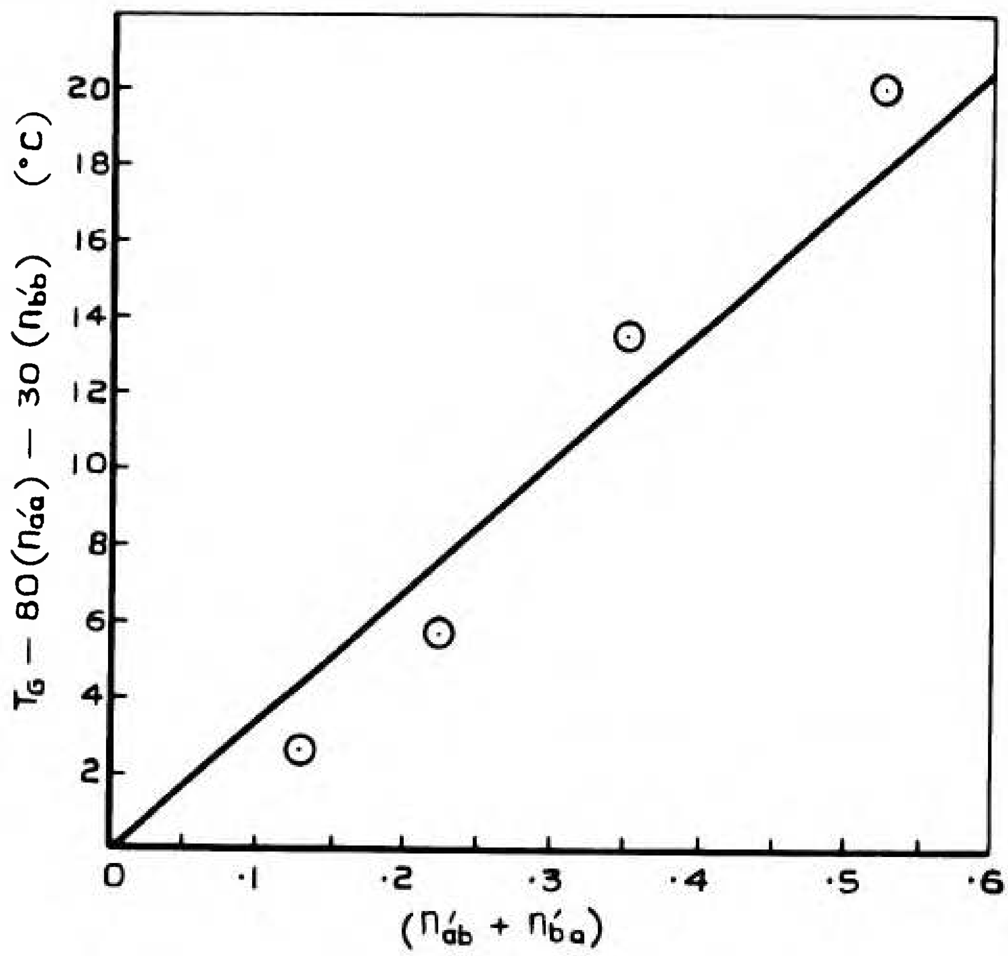

Fig. 26 Plot of equation (10) for vinyl chloride/vinyl acetate copolymers