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A Comparative Study on Barton's and Johnston's Equations for Copolymer Glass Transition Temperature

Hidematsu Suzuki and Takeaki Miyamoto

The equations of Barton and of Johnston, which can predict the sequence-distribution dependence of copolymer glass transition T_g, are revealed to hold some algebraic relationships between the T_g of equimolar random copolymer, the T_g of alternating copolymer, and some kind of the average of the T_g's of the two homopolymers. With use of these relationships and the literature data of 25 copolymer systems, the two equations are compared with each other. Although the predictions of the two equations are rather similar and are seen to be in reasonable accord with all the random copolymer data analyzed, it is found that in certain systems, the predictions greatly differ for alternating copolymers.

KEY WORDS: Glass transition/ Random copolymer/ Alternating copolymer/ Sequence distribution/ Run number/

INTRODUCTION

In order to describe the sequence-distribution dependence of glass transition temperature of copolymers, there have been reported two equations: Barton's[1] and Johnston's.[2] Those two equations, proposed in the same time span yet independently, have been taken as logical extensions, respectively, of the equations of DiMarzio and Gibbs[3] and of Fox.[4] Although they have different theoretical bases, i.e., the configurational entropy and the free volume, the two equations work almost evenly for the copolymer systems the authors analyzed in each publication. For certain systems, however, there must appear some significant differences in prediction between the two equations. Such possible differences have not been examined yet in detail.

In the preceding paper,[5] some algebraic characteristics of the Barton equations has been demonstrated. Those allow us, with minimum experimental results, to predict the whole variation of copolymer glass transition with sequence distribution. Similarly it may be possible to figure out characteristics of the Johnston equation. Those characteristics must provide us with a clue helpful for a comparative study on the two equations. The present paper describes first the intrinsic features of the two equations, followed by the comparison between the two predictions with use of the literature data of glass transition and copolymerization kinetics of 25 copolymer systems. For all random copolymers examined, the predictions of the two equations are rather similar and are seen to be in reasonable accord with experimental data. Accordingly, it is hardly expected to differentiate the two equations with random copolymer data only. It is suggested that crucial examinations could be successful by comparing the data of

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alternating copolymers with the predictions, because, in certain systems, the predictions differ greatly.

EQUATIONS OF BARTON AND OF JOHNSTON

New Expressions

In a copolymer chain composed of two monomer units A and B with mole fractions m_A and m_B, there are four different dyad sequences: AA, BB, AB, and BA. As the last two sequences have an equivalent linkage, the number of different linkages in the copolymer chain becomes three. Since those linkages have generally different stiffness energy of rotation, we have to differentiate between the contributions to the glass transition temperature of the three linkages. This has been called the dyad model. Barton's and Johnston's equations, both being based on this model, have been derived, respectively, as

$$T_g = m_A P_{AA} T_{gAA} + m_B P_{BB} T_{gBB} + (m_A P_{AB} + m_B P_{BA}) T_{gAB} \qquad \text{(B)} \quad (1)$$

and

$$1/T_g = W_A P_{AA}/T_{gAA} + W_B P_{BB}/T_{gBB} + (W_A P_{BB} + W_B P_{BA})/T_{gAB} \quad \text{(J)} \quad (2)$$

Here, T_g is the glass transition temperature of a compolymer *with composition and sequence distribution* specified by the values of products mPs or WPs; W is the weight fraction; P_{IJ} and T_{gIJ} are, respectively, the probability of, and the glass transition temperature referred to, the IJ dyad sequence. In the concrete, P_{AB} implies the probability that a given A monomer has a B monomer on its right. Accordingly, the product of $m_A P_{AA}$ is equal to the mole fraction of the AB dyad sequence, m_{AB}; similarly, $m_B P_{BB} = m_{BB}$, $m_A P_{AB} = m_{AB}$ and $m_B P_{BA} = m_{BA}$. The original form of Barton's equation does not include $m_I P_{IJ}$'s, but is written as eq 1 for better comparison with Johnston's equation. T_{gAA} and T_{gBB} are equal, respectively, to the T_g's of the homopolymers of A and B, and T_{gAB} is the T_g of the corresponding alternating copolymer. Equation 1 has a structure simple to understand. On the other hand, eq 2 may be considered in such a way that each W/T_g term similar to that of the Fox equation is multiplied by a corresponding weight of P, followed by summation.

Only implicitly, both equations in the original form describe the sequence-distribution dependence of copolymer glass transition temperature. So as to express the dependence explicitly, the run number R introduced by Harwood and Ritchey[6] can be used. That is defined as the average number of monomer sequences (runs) occurring in a copolymer per 100 monomer units. With use of the Harwood-Ritchey expressions for P_{IJ}'s or more directly from the relations between m_{IJ} and R,[5,6] it has been shown that Barton's equation may be rewritten as[5]

$$T_g = m_A T_{gAA} + m_B T_{gBB} + (R/100)(T_{gAB} - \bar{T}_g) \qquad (3)$$

with

$$\bar{T}_g = (T_{gAA} + T_{gBB})/2$$

(298)

or

$$T_g = m_A T_{gAA} + m_B T_{gBB} + (R/R^*)[T_g(R^*) - \overline{T}_g] \qquad (4)$$

Here, R^* is the R value of an equimolar random copolymer and is equal to the maximum value of R attainable in conventional copolymerization. So $T_g(R^*)$ ($=$ $T_g(m_A=0.5)$) is an observable. Obviously, T_g is best represented by 3-dimensional plots against m_A and R. For ordinary purposes, however, a plot of T_g against R is preferable: equations 3 and 4 imply that on such a plot, the three points of T_g, $T_g(R^*)$ and T_{gAB} are on the same straight line.[5] This line is the locus of an arithmetic mean of the glass transition temperatures of two random copolymers, $T_g(m_A)$ and $T_g(m_A'=1-m_A)$. It is because the variation of R with m_A is symmetrical with respect to a line of $m_A=0.5$, and those two random copolymers are characterized by a fixed value of R. In other words, the straight line represents the T_g's of hypothetical equimolar copolymers with varying degrees of sequence distributions.

Similarly, Johnston's equation may be expressed as

$$1/T_g = W_A T_{gAA} + W_B/T_{gBB} + (R/200\overline{M})[(M_A+M_B)/T_{gAB}$$
$$- M_A/T_{gBB} - M_B/T_{gBB}] \qquad (5)$$

with

$$\overline{M} = m_A M_A + m_B M_B$$

or

$$1/T_g = W_A/T_{gAA} + W_B/T_{gBB} + (R/R^*)[1/T_g(R^*)$$
$$- W_A^*/T_{gAA} - W_B^*/T_{gBB}] \qquad (6)$$

with

$$W_I^* = M_I/(M_A+M_B); \qquad I = A \text{ or } B$$

where M stands for the formula weight of monomer. Equation 6 is derived by eliminating T_{gAB} from eq 5 at $R=R^*$ and eq 5 itself. These equations suggest the existence of a straight line similar to that Barton's equation implicitly contains. On a plot of $1/T_g$ against R, the three points, $(W_A^*/T_{gAA} + W_B^*/T_{gBB})_{R=0}$, $1/T_g(R^*)$ and $1/T_{gAB}$ allow us to draw such a straight line. This can be regarced as the locus of $1/T_g$ of hypothetical equimolar copolymers with varying degrees of sequence distributions. This line divides two $1/T_g$'s of random copolymers having a given value of R but different compositions in the ratio of formula weights of monomers A and B. On a plot of T_g against R, however, the line mentioned above deviates from the linearity, the degree of which mainly depends on the location of T_{gAB} relataive to those of T_{gAA} and T_{gBB}. Besides, the ratio of formula weights in which the line divides the two T_g's of random copolymers can be no longer seen on this type of plot. A choice of the plots is totally arbitrary, but only for the simplicity, plots of T_g against R will be used below for comparing the two equations with experiments.

Possible Differences

For easy understanding, the predictions and characteristics of Barton's and John-ston's equations are illustrated in Fig. 1. In addition, the data of acrylonitrile/buta-diene (AN/BD) copolymers by Furukawa and Nishioka[7] are plotted in the same figure. Both T_g and R have been determined experimentally by these authors. Alternatively, the run number may be estimated indirectly from the equation[5]

$$R = 400 \ m_A m_B / [1 + \{1 + 4 \ m_A m_B (r_A r_B - 1)\}^{1/2}] \tag{7}$$

where $r_A r_B$ is the product of the monomer reactivity ratios in copolymerization.[8] Since the T_{gAB} value of this copolymer system has been reported, eqs 3 and 5 were used to draw the predictions. Unless it is known, eqs 4 and 6 will do for the same purpose. That means a change of the reference point, yielding different values for the T_{gAB} predicted.

Prior to assessing those equations with experimental data, it could be sensible to remark the differences in prediction between Barton's and Johnston's equations. One of the differences is obviously that between the curves predicted. In addition, two others can be seen in Fig. 1: the differences between the points at $R=0$ and R^*. The $T_g(R=0)$'s as obtained by extension of the respective line $T_g(R^*) - T_{gAB}$ back to the ordinate are the glass transition temperatures of an equimolar (di-)block copolymer. For copolymer systems like acrylonitrile/butadiene whose ratio of M_A/T_{gAA} to M_B/T_{gBB} differs greatly, a big difference appear between the $T_g(R=0)$'s predicted. This temperature is attractive for comparison with experiment, but one should be aware of the heavy restriction that the two kinds of blocks be compatible. Otherwise, the two-phase structure could be formed by segregation of each other block, presenting two distinct glass transition temperatures identical to those of the homopolymers.[9] The other is the difference between the $T_g(R^*)$'s predicted. This difference is, however, relatively minor and also such a case is actually rare that T_{gAB} is known but $T_g(R^*)$ is not. All things considered, a practically important difference seems to be that between the T_{gAB}'s predicted, as will be illustrated below, when the corresponding $T_g(R^*)$ is used as reference point.

ANALYSIS OF THE LITERATURE DATA

Systems whose T_{gAB}'s are known

As McEwen and Johnson have listed in their contribution to "Alternating Copo-lymers",[10] there are nine copolymer systems whose T_{gAB}'s are known up to now. One of them is the acrylonitrile/butadiene (AN/BD) system which have already been depicted in Fig. 1. The predictions, as illustrated in the figure, are based on eqs 3 and 5 with the experimental data: 248.2 K for T_{gAB} of the alternating copolymer and 373.2 K and 193.2 K for the T_g's of the corresponding homopolymers. For the calculation of R, use was made of the value of $r_A r_B$, 0.054, estimated from the R values reported by Furukawa and Nishioka. Although the formula weights are almost the same for these monomers ($M_{AN}/M_{BD} = 53.06/54.09$), Johnston's value of $T_g(R=0)$ for a corresponding
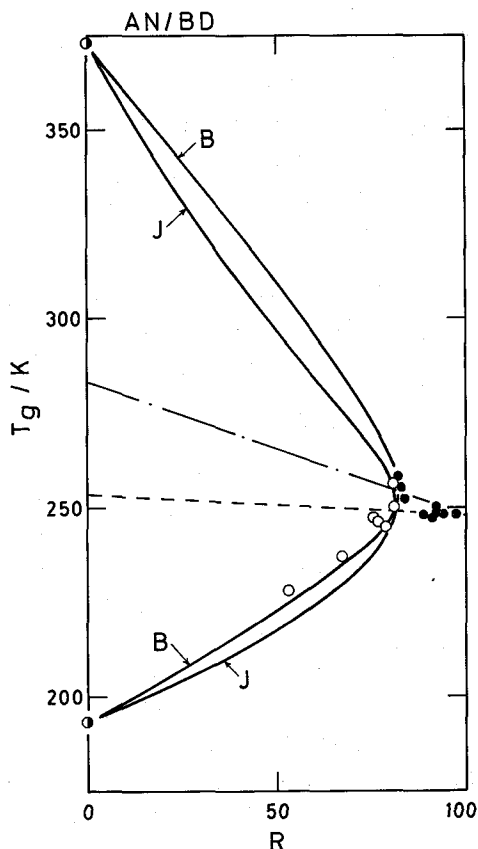
Figure 1. Plot of T_g against R for AN/BD ($\bigcirc$) random, ($\bullet$) alternating copolymers and ($\bigcirc$) the two homopolymers.[7] Solid lines, theoretical predictions of Barton (B) and of Johnston (J). Dash-dot and broken lines, the loci of T_g of hypothetical equimolar copolymers with varying degrees of sequence distribution by Barton and by Johnston, respectively.

hypothetical equimolar (di-)block copolymer is apart from the arithmetic mean $\overline{T}_g$ due to the great difference between T_g's of the homopolymers.

The experimental data presented cover only a limited range of R, but roughly speaking, both equations seem to be in fair accord with the data. In more detail, the data of the random copolymers are seen to conform to Barton's equation better than to Johnston's. As for the data of the equimolar copolymers having sequence distributions slightly deviated from strict alternation, six out of the nine data points are in good agreement with Johnston's prediction illustrated by broken line. Yet, on the whole, it can be seen that those are in better accord with Barton's prediction. Since the values of T_g and R have been obtained experimentally, it may be said that this comparison is considered to be more important than those in the figures below. In the following eight systems, the data of Hirooka and Kato[11] for equimolar random and alternating copolymers are to be plotted. The run numbers are to be estimated from eq 7.

Figure 2a shows the data of Illers,[12] as referred to by Hirooka and Kato, for styrene/methyl methacrylate (S/MMA) copolymers. The predictions were drawn by using eqs 3 and 5 with the T_{gAB} value of 366.1 K and the kinetics data, $r_S/r_{MMA} = 0.520/0.480$. The actual experimental value for T_{gAB} by Hirooka and Kato is 364.2 K,[13] while our own value, though not presented in the figure, is 369.2 K,[13] when that is
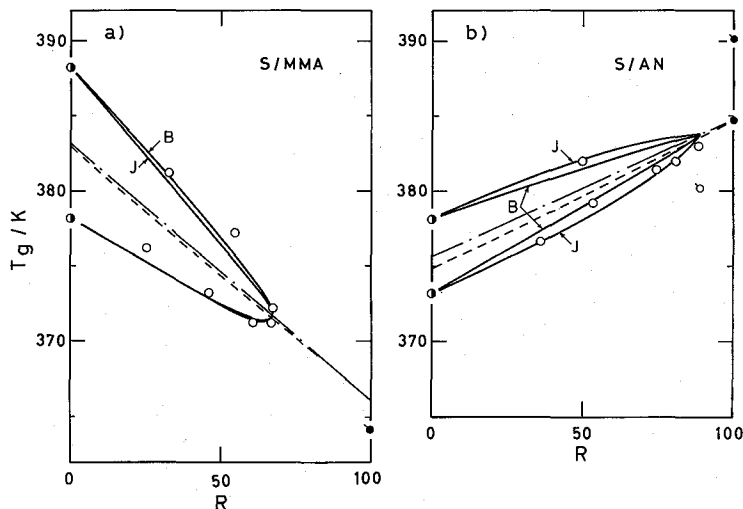
Figure 2 a and b. Plots of T_g against R for (a) S/MMA[12] and (b) S/AN copolymers:[2] data with pip, Hirooka and Kato.[11] For key of each symbol or line, refer to Fig. 1.

determined from the enthalpy curve.[14] The value adopted here was obtained in such a way that an average value of two $T_g(R^*)$ measurements, 371.7 K, was used as reference data in eq 4. Both predictions of Barton and of Johnston do not differ appreciably and are seen to be in reasonable accord with the experimental data. Barton and Johnston analyzed Beevers' data[15] independently to estimate the T_{gAB} value, respectively, as 363.2 ± 5 K (most probably 362.9 K) and as 363.1 K. However, Beevers' data are rather widely scattered and also 4–8 K lower than the data presented, accordingly being withdrawn.

Figure 2b shows Johnston's data of styrene/acrylonitrile (S/AN) random and alternating copolymers together with two data of Hirooka and Kato. The data of Beevers and White[16] were withdrawn for those are significantly lower than Johnston's. The predictions were drawn by using eqs 3 and 5 with Johnston's data only: 384.7 K for T_{gAB} and 0.41/0.04 for r_S/r_{AN}. Both predictions are rather close to each other, and cannot be expected to assess by experiments. This copolymer system is known to deviate from statistics of the terminal model in the study of reaction kinetics.[17] However, this figure suggests that the dependence of glass transition temperature on sequence distribution is reasonably described by the dyad model principally identical to the terminal model in the copolymerization study.[5]

Figure 2c shows the data of Jenckel and Herwig[18] for styrene/methyl acrylate (S/MA) random copolymers. The predictions drawn are based on eqs 3 and 5 with the data: 337.7 K for T_{gAB} and 0.76/0.19 for r_S/r_{MA}.[11] It can be seen that both predictions hardly differ, and are in accord with the experimental data. Barton analyzed these data of Jenckel and Herwig to get the estimate of 331.5 K for T_{gAB}. This lower value of T_{gAB} could be more correct for this set of random copolymer data, because the experimental methods adopted by the two groups[11,18] are incompatible. Figure 2d shows the data of Hirooka and Kato for vinly choloride/methyl acrylate (VCl/MA)
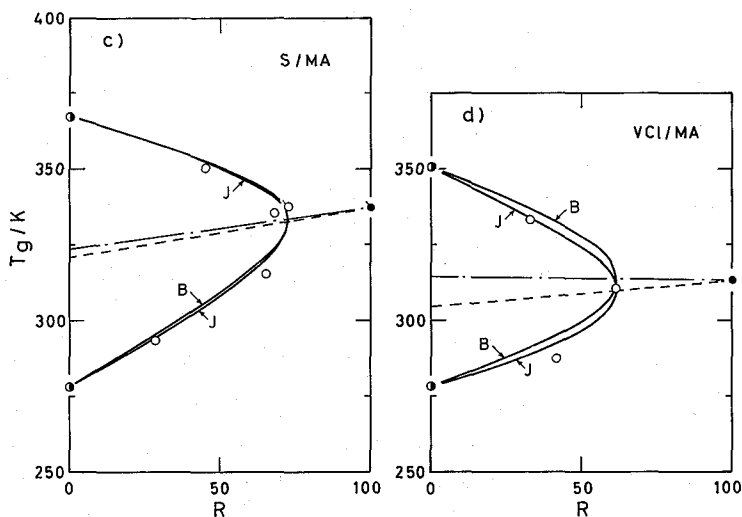
Figure 2 c and d. Plots of T_g against R for (c) S/MA[18] and (d) VCl/MA copolymers:[2] data with pip, Hirooka and Kato.[11] For key of each symbol or line, refer to Fig. 1.

copolymers.   The predictions illustrated are based on eqs 3 and 5 with the data: 313.2 K for T_{gAB} and 0.07/5.6 for r_{VCl}/r_{MA}.   The data shown are seen to be a little favorable to Johnston's equation, but the differences between the two predictions are less than 5 K. We should say there is not much to choose between the two equations.

Figure 2e shows Johnston's data[2] for α-methyl styrene/acrylonitrile (αMS/AN) copolymers.   The data of Hirooka and Kato are also plotted in this figure, but those are systematically lower than Johnston's data.   So the predictions illustrated were calculated with Johnston's data only: 395.2 K for T_{gAB} and 0.17/0.88 for r_{MS}/r_{AN}.   Both equations are seen to describe well the dependence of T_g on sequence distribution for this copolymer system.   Figure 2f shows Reding's data[19] for vinyl chloride/acrylonit-
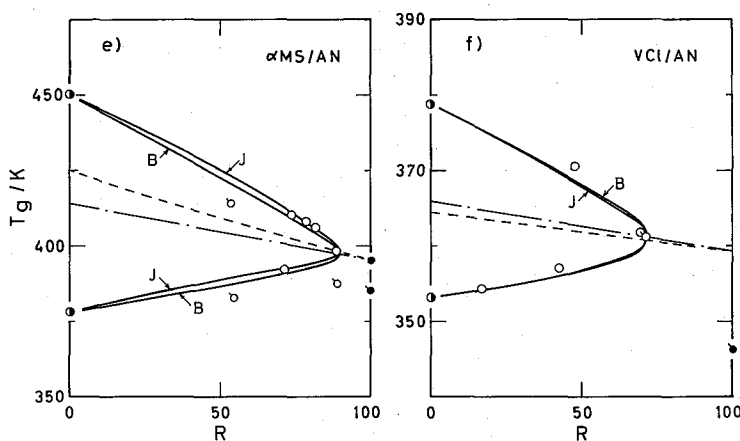

Figure 2 e and f. Plots of T_g against R for (e) αMS/AN[2] and (f) VCl/AN copolymers:[19] data with pip, Hirooka and Kato.[11] For each symbol or line, refer to Fig. 1.

rile (VCl/AN) random copolymers. Since the datum of 346.2 K for T_{gAB} by Hirooka and Kato is not compatible due certainly to the low molecularity of their sample, the T_{gAB} value is estimated from eq 4 with the data: 361.2 K for $T_g(R^*)$ and 0.05/3.2 for r_{VCl}/r_{AN}.[11] Both equations are seen to be actually identical and be in good accord with the experimental data.

Figure 2g shows Haward's data[20] for vinyl acetate/acrylonitrile (VAc/AN) copolymers. The predictions drawn are based on eqs 3 and 5 with the data of Hirooka and Kato: 344.7 K for T_{gAB} and 0.04/5.3 for r_{VAc}/r_{AN}. The agreement between the predictions and the experimental data are rather fair, but the differences between the three data for $T_g(R^*)$ are too large to be acceptable. If the values of $T_g(R^*)$ and T_{gAB} are almost equal, as the data of Hirooka and Kato indicate, those should be close to the value of $\overline{T_g}$, too. This means their values of $T_g(R^*)$ and T_{gAB} might be some 10 K higher than the expected. This difference must be an artifact due to incompatible experimental conditions. Figure 2h shows the data of vinylidene chloride/methyl acrylate (NdCl/MA) copolymers, which were taken from Illers[12] and from Powell and Elgood.[21] The data of Wessling et al.[22] are not shown simply because it is cumbersome to plot more points in the figure. The predictions illustrated are based on eqs 4 and 6 with the data: 312.0 K for $T_g(R^*)$ and 1.0/1.0 for r_{VdCl}/r_{MA}. The adoption of this $T_g(R^*)$ value reproduces Barton's result of analysis, 357.5 K for T_{gAB}. It is seen that both predictions are hardly different for the random copolymers, but significantly different for the alternating one. This is the first case where both predictions of T_g are different more than 10 K at a certain degree of sequence distribution. The T_{gAB} value of Hirooka and Kato, 325.7 K, seems to be too low to be compared with either prediction. Only for the random copolymers, a fair comparison can be seen between theory and experiment.
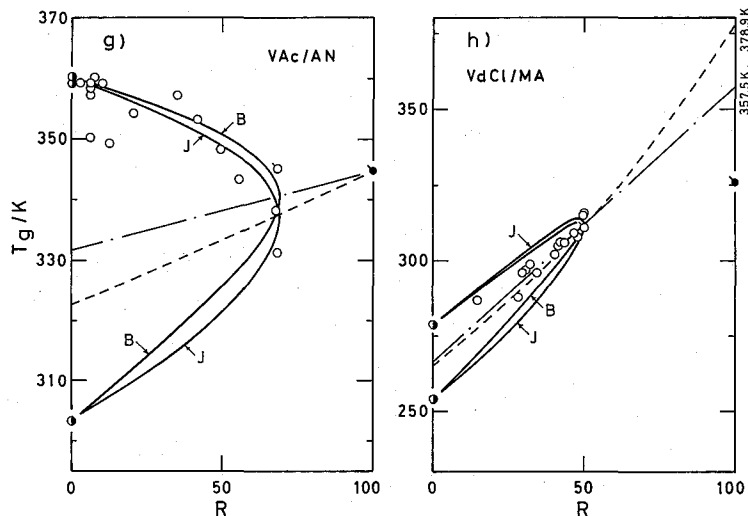

Figure 2 g and h. Plots of T_g against R for (g) VAc/AN[20] and (h) VdCl/MA copolymers:[12,21] data with pip, Hirooka and Kato.[11] For each symbol or line, refer to Fig. 1.

Systems whose T_{gAB}'s are unknown

These systems will be divided into three groups according to the degree of difference between the two predictions, especially for T_{gAB}.

Differences negligible

In Fig. 3, the theoretical predictions for four systems whose differences are negligible over the entire region of sequence distribution. The data of acrylonitrile/methyl methacrylate (AN/MMA) copolymers were taken from Johnston.[2] His values of 0.150/1.20 for r_{AN}/r_{MMA} were used for calculating the run number. Since the T_g's of the corresponding homopolymers are indentical, no loops are drawn as predictions. Although the formula weights of these monomers differ greatly, $M_{AN}/M_{MMA} = 53.05/100.12$, no practical differences between the two predictions appear. Johnston has estimated T_{gAB} to be 352.2 K, which was used for drawing the two lines in the figure. The data of Beevers and White[16] for this system were withdrawn. Their data of the homopolymers are not identical with the presented ones: 371.2 K for polyacrylonitrile is rather low, while 390.1 K for poly(methyl methacrylate) is definitely higher than Johnston's value of 378.2 K. This reminds us of the fact that the microstructure of polymers affects glass transition temperature.[23] Another set of Johnston's data[2] of methyl methacrylate/vinyl chloride (MMA/VCl) copolymers is presented in the same left panel. The predictions drawn are based on his data: 322.8 K for T_{gAB} and 11.2/0.0$_4$ for r_{MMA}/r_{VCL}. The differences between the two predictions are at most 2 K, much smaller than the range of experimental error.
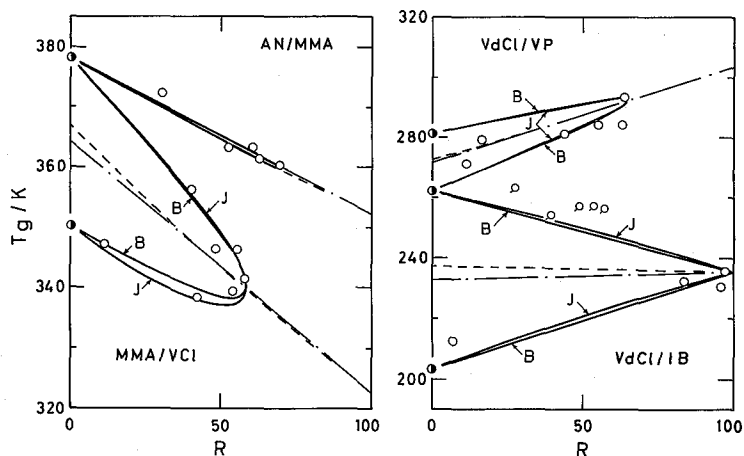

Figure 3. Plots of T_g against R for AN/MMA,[2] MMA/VCl,[2] VdCl/VP,[22] and VdCl/IB copolymers:[22] data with pip, prepared in emulsion. For each symbol or line, refer to Fig. 1.

In the right panel of Fig. 3, the data of Wessling et al.[22] for vinylidene chloride (VdCl) copolymers with vinyl propionate (VP) and with isobutylene (IB) are presented. The predictions illustrated are based on eqs 4 and 6 with the data: for the VdCl/VP system, 292.2 K for $T_g(R^*)$ and 0.3 for the product of reactivity ratios, and for the

VdCl/IB system, 235.0 K for $T_g(R^*)$ with $R^*=100$, because the product of reactivity ratios is practically zero. On the whole, the agreement between theory and experiments is fair, but the VdCl/IB copolymers prepared in emulsion are seen to indicate the behavior different from those prepared in bulk. Another example, though not shown in Fig. 3, is the styrene/butadiene (S/BD) system. Wood's data[24] of S/BD random copolymers prepared at 50°C are in good accord with the predictions of Barton and of Johnston, both of which coincide within an error of 0.3 K for the random copolymers, when the following data are used: 188 K for T_{gBD}, 0.5/1.12 for r_S/r_{BD} and 276.5 K for $T_g(R^*)$. For the alternating copolymer, Barton's prediction is 273.5 K, while Johnston's is 274.6 K.

Diffrences less than 10 K

In Fig. 4, comparisons are made for four systems for which the defferences in predictions of the T_{gAB} value are less than 10 K. The data for styrene/acrylinc acid (S/AAc) random copolymers shown in the left panel were taken from Illers.[12] The predictions illustrated are based on eqs 4 and 6 with the data: 421.0 K for $T_g(R^*)$ and 0.07/0.37 for r_S/r_{AAc}. For the T_{gAB} predicted, Barton's value is 424.2 K, while Johnston's is 426.2 K. Even for a highly polar system like this, the reasonable agreements are seen between the two predictions and the data. The data for styrene/butyl acrylate (S/BA) random copolymers were also taken from Illers.[12] For drawing the theoretical predictions, the following data were used: 271.2 K for $T_g(R^*)$ and 0.76/0.15 for r_S/r_{BA}. For the T_{gAB} predicted, Barton's value is 265.0 K, while Johnston's is 273.7 K. Barton has analyzed these data, being based on all the data of random copolymers to obtain the T_{gAB} value of 291 K. This value is considerably higher than the present estimate. For better agreements with the data, Barton's value for T_{gAB} might be preferable to
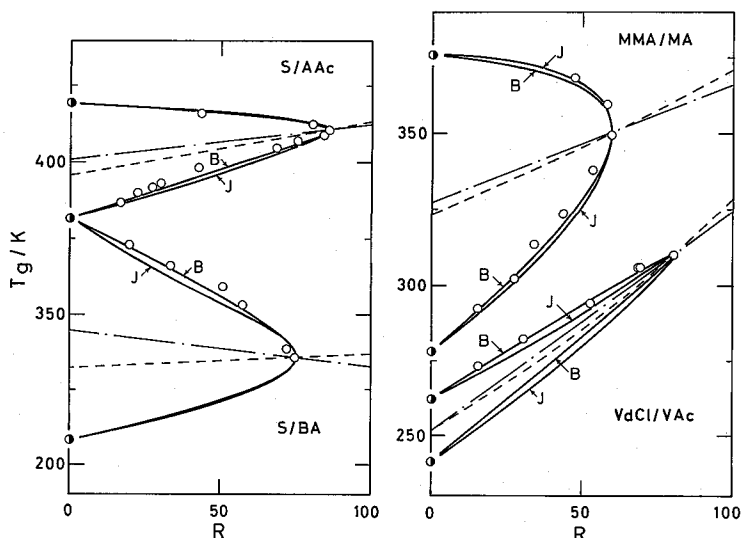

Figure 4. Plots of T_g against R for S/AAc,[12] S/BA,[12] MMA/MA,[12] and VdCl/VAc copolymers.[19] For key of each symbol or line, refer to Fig. 1.

ours, because a single datum, $T_g(R^*)$, for an equimolar random copolymer is taken here as reference point.

In the right panel, the predictions are drawn for the methyl methacrylate/methyl acrylate (MMA/MA) system, the data for which were taken from Illers, again. The data used for predictions are 350.4 K for $T_g(R^*)$ and 0.3/1.5 for r_{MMA}/r_{MA}. For the T_{gAB} predicted, Barton's value is 366.0 K, while Johnston's is 371.2 K. The differences between both predictions for the random copolymers are seen to be much smaller than that for T_{gAB}, 5.2 K. The data of Wessling et al.[22] for vinylidene chloride/vinyl acetate (VdCl/VAc) random copolymers are compared with the predictions, which are based on the data: 317.2 K for $T_g(R^*)$ and 1.35/0.65 for r_{VCl}/r_{VAc}. For the T_{gAB} predicted, Barton's value is 307.0 K, while Johnston's is 312.7 K. Another example, though not shown in this figure, is the vinyl chloride/vinyl acetate (VCl/VAc) system. The data of Reding et al.[19] for VCl/VAc random copolymers are in good accord with the two predictions, both of which coincide within error of 1.3 K for the random copolymers, when the following data are used: 317.2 K for $T_g(R^*)$ and 1.35/0.65 for r_{VC}/r_{VAc}. For the T_{gAB} value, Barton's prediction is 307.0 K, while Johnston's is 312.7 K.

Differences larger than 10 K

As systems for which the T_{gAB} values predicted have a difference larger than 10 K, six examples can be cited in Figs. 5a to f. Figure 5a shows the two predictions, together with Johnston's data,[2] for the butyl methacrylate/vinyl chloride (BMA/VCl) system. Johnston has analyzed his T_g data by using 13.5/0.05 for r_{BMA}/r_{VCl},[2] to obtain 274.2 K for T_{gAB}. His prediction is reproduced in this figure, and the $T_g(R^*)$ reads 296.5 K. For Barton's prediction, equation 4 with this $T_g(R^*)$ value was used, yielding 285.8 K for T_{gAB}. Although the two predictions don't differ more than 8 K for the
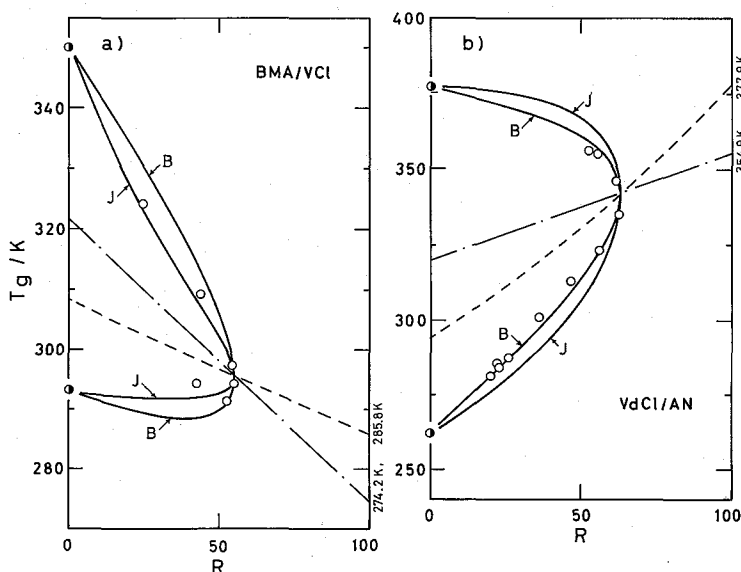

Figure 5 a and b. Plots of T_g against R for (a) BMA/VCl[12] and VdCl/AN cioiktners.[21,22] Fore key of each symbol or line, refer to Fig. 1.

random copolymers, the difference between the T_{gAB} values predicted amounts to 11.6 K. As is shown in Fig. 5b, a much larger difference for T_{gAB}, 23.0 K, can be seen for vinylidene chloride/acrylonitrile (VdCl/AN) copolymers. The experimental data presented were taken from Wessling et al.[22] and from Powell and Elgood.[21] The predictions drawn are based on eqs 4 and 6 with the data: 342.0 K for $T_g(R^*)$ and 0.37/0.91 for r_{VdCl}/r_{AN}. It is seen that these are preferable to Barton's prediction, while the data shown in Fig. 5a are to Johnston's on the contrary.
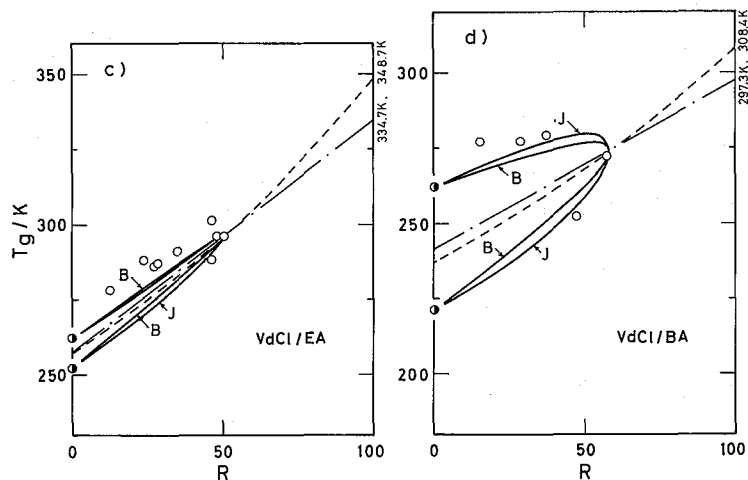

Figure 5 c and d. Plots of T_g against R for VdCl/EA[22] and VdCl/BA copolymers.[22] For key of each symbol or line, refer to Fig. 1.

In Fig. 5c, the two predictions for the system vinylidene chloride/ethyl acrylate (VdCl/EA) are compared together with the data of Wessling et al.[22] Those were calculated from eqs 4 and 6 with the data: 296.2 K for $T_g(R^*)$ and 0.72 for the product $r_{VdCl}r_{EA}$. The difference between the T_{gAB} values predicted is 14.0 K. We find two other sets of data for this system in the literature. The data of Powell and Elgood[21] are analyzed with their data, 299 K for $T_g(R^*)$, yielding 346.0 K/367.7 K for T_{gAB}(Barton)/ T_{gAB}(Johnston). On the other hand, the data of Comyn and Fernadez[25] are analyzed with their data, 308 K for $T_g(R^*)$, yielding 367.6 K/404.6 K for T_{gAB}(Barton)/ T_{gAB}- (Johnston). Although this system seems to be problematic a little, the two prediction for T_{gAB} can be said to differ by at least more than 10 K. Figure 5d shows the comparison of the two predictions for the system vinylidene chloride/butyl acrylate (VdCl/BA), the experimental data for which were taken from Wessling et al.[22] The data used for predictions are 274.2 K for $T_g(R^*)$ and 0.72 for the product $r_{VdCl}r_{BA}$.[22] As is clear from this figure, the predictions are different for the alternating copolymers by a degree much larger than for the random copolymers. The agreements between the predictions and the data for both systems VdCl/EA and VdCl/BA are rather fair on the whole, but obviously more reliable data are desired.

In Figs. 5e and f, comparisons are made again for vinylidene chloride copolymers, respectively, with methyl methacrylate (MMA) and with vinyl chloride (VCl). The
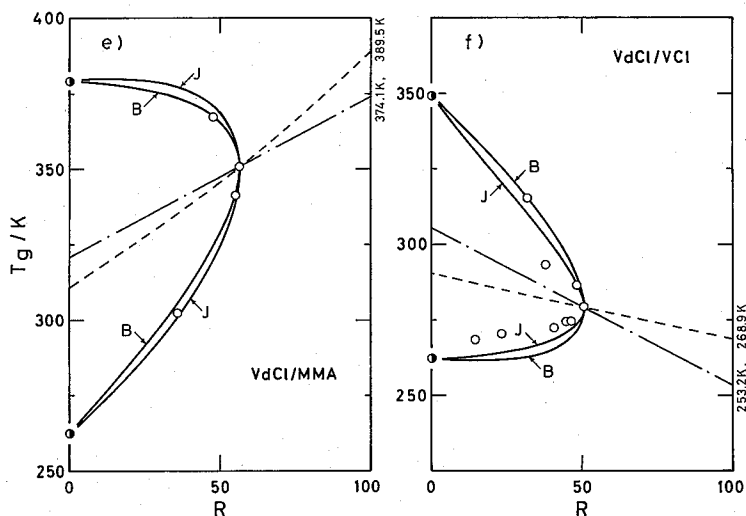
Figure 5 e and f. Plots of T_g against R for (e) VdCl/MMA[22] and VdCl/VCl copolymers.[22] For key of each symbol or line, refer to Fig. 1.

data used for predictions are, for VdCl/MMA copolymers, 350.7 K for $T_g(R^*)$ and 0.24/2.53 for r_{VdCl}/r_{MMA}, and for VdCl/VCl copolymers, 279.2 K for $T_g(R^*)$ and 3.2/0.3 for r_{VdCl}/r_{VCl}.[22] Both predictions don't differ by 5 K at most for the random copolymers, but does differ by more than 15 K for the alternating copolymers. It can be seen that the two equations predict fairly well the sequence-distribution dependence of copolymers glass transition.

DISCUSSION

A common feature of Barton's and Johnston's equations for copolymer glass transition temperature is the fact that, though sometimes misunderstood in the literature,[26] no adjustable parameters are included therein. Usually and exclusively, it is on plots of T_g against overall composition that their equations have been compared with experimental data. However, as the new expressions derived here suggest, plots of T_g (or $1/T_g$) against the run number is much preferable. This is because the simple algebraic relationship holds for the three points, $T_g(R=0)$, $T_g(R^*)$ and $T_{gAB}(R=100)$, e.g., in Barton's equation, on a plot of T_g against R. With use of this algebraic relationship and the data of equaimolar random copolymers, $T_g(R^*)$'s, it is possible to predict the whole T_g variations with sequence distribution for the corresponding random, alternating and even compatible (di-)block copolymers.

Both equations are seen to be in reasonable accord with all the copolymer systems analyzed here except only one T_{gAB} datum shown in Fig. 2h. That includes highly polar systems like styrene/acrylic acid and styrene/butyl acrylate copolymers. We recall Iller's remark that Kanig's theory[27] does not satisfactorily fit to the data of those polar copolymer systems. In addition, there is another strong point in the two equations. As is suggested by the new expressions, it is possible to predict that T_g's of

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hypothetical equimolar copolymers with varying degrees of sequence distribution. This is totally out of the scope of Kanig's theory, for he assumes the random distribution of the two monomers in the copolymers of constant overall composition irrespective of sequence distribution. Earlier theories[28,29] including Kanig's which are capable of describing the occurrence of a maximum or a minimum value of T_g on the conventional plot have critically been discussed by Barton,[1] and have been interrelated to his own equation. On the other hand, some extended theoris[30,31] which appeared after Barton's and Johnston's papers have been discussed in detail in the previous article.[5]

Since they are based on the dyad model, the two equations may be considered to have the common intrinsic limitation: these equations can be applied only to the copolymers in which the concentration of the AB dyad is appreciably high. In other words, these equations could not be applied to block-like copolymers that have both monomer reactivity ratios noticeably larger than unity. This aspect will be treated in a separate paper in conjunction with the block-length distribution and the resulting phase structure. The VdCl/MA copolymer system whose data are shown in Fig. 2h has the monomer reactivity ratios of unity. So these equations can be applicable. Figure 2h shows, however, a big difference in T_{gAB} between theory and experioment. This failure should not be ascribed to theory but to experiments, for example, to the incompatibility of measurements and/or low molecularity of the smaple.

It is not necessarily clear from the figures presented that which of the two equations is more superior to the other. Some systems like vinylidene chloride/acrylonitrile are seen to fit better to Barton's equation, while some other systems like butyl methacrylate/vinyl chloride are to Johnston's. Although the result of Fig. 1 is more favorable to Barton's equation, crucial examinations could be carried out in the systems shown in Figs. 5a to f by measuring T_g of the corresponding alternating copolymers. Such works may be considered to have another significance in the long debating discussion of polymer glass transition theories. Since the two equations are based on different theories, thermodynamic[32] or free-volume,[33] measurements of the T_{gAB}'s of those systems must provide us with a new, promising clue for assessing theoretical models of polymer glass transition.

ACKNOWLEDGMENTS

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