Copolymer Glass Transition:
Isotactic Poly(Methyl/Ethyl Methacrylate)
as a Random Copolymer

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A mathematical characteristic of Johnston's equation for copolymer T_g (the glass transition temperature) is fully disclosed. This characteristic has been used to analyze the T_g data of the isotactic poly (methyl/ethyl methacrylate)s prepared by random placement of the ester groups. It is shown that these polymers can be treated as a random copolymer characterized by monomer reactivity ratios of unity and the T_g value of the corrspoonding alternating copolymer is predicted to be about 38 K lower than the mean of the homopolymer T_gs.

INTRODUCTION

The glass transition temperatures of most statistical copolymers are known to deviate from linear relations such as the Fox equation[1]

$$1/T_g = W_A/T_{gA} + W_B/T_{gB} \qquad (1)$$

Here, T_g is the glass transition temperature of a copolymer formed from two monomers A and B with weight fractions W_A and W_B, and T_{gA} and T_{gB} are, respectively, the T_g values of the homopolymers of A and B. On the contrary, the glass transition temperatures of certain compatible block copolymers have been reported to fit these linear relations[2]. These two findings show that copolymer T_gs depend on the arrangement of monomers as well as the composition.

The first factor to be taken into account on the monomer arrangement or sequence distribution is the diad. In a given AB copolymer, there are four different diad sequences: AA, BB, AB and BA. The relative numbers of these diad sequences should be considered when attempting to make predictions of copolymer T_gs. Such an extension of the Fox equation has been carried out by Johnsotn:[3]

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

Here, P_{IJ} is the probability that a given monomer I has the other monomer J on its right and T_{gAA}, T_{gBB} and T_{gAB} are, respectively, the T_gs of the homopolymers

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of A and B, and of the corresponding strictly alternating copolymer.

A similar extension of another type of the linear relation[4] has been proposed by Barton:[5]

$$T_g = m_{AA}T_{gAA} + m_{BB}T_{gBB} + (m_{AB} + m_{BA})T_{gAB} \qquad (3)$$

where, m_{IJ} is the mole fraction of diad sequence IJ, being equal to $m_I P_{IJ}$, the product of the mole fraction of monomer I and the probability of diad sequence IJ. The T_g in eq 2 and 3 is the glass transition temperature of a copolymer *with composition and sequence distribution* specified by the values of P_{IJ} or m_{IJ}. The above two equations have been known to be capable of reproducing the T_g-composition behavior of most statistical copolymers and of predicting the unknown T_{gAB} value of the corresponding alternating copolymer.[3,5] In a previous publication,[6] both equations were compared with each other using literature data. Those comparisons were carried out quantitatively and successfully, for the mathematical characteristics which the equations implicitly hold were fully utilized in data analysis.

Those useful characteristics have been disclosed for the first time for Barton's equation, but only suggested for Johnston's.[7] In this paper, the characteristic of the latter, eq 2, will be first described and proved in the following section. Secondly, these two copolymer T_g equations will be applied to the literature data of the isotactic poly(methyl/ethyl methacrylate)s prepared by random re-esterification of isotactic poly(methacrylic acid). The T_{gAB} value of the corresponding alternating copolymer will be predicted with the two equations.

CHARACTERISTIC OF JOHNSTON'S EQUATION

Johnston's equation as expressed by eq 2 is neat but rather awkward. This is because the probabilities P_{IJ}s hide a certain inherent and simple mathematical characteristic of the equation. With the proper term for a quantitative measure of sequence distribution, the equation could be put into forms well suited to use. The expressions below have already been derived in the previous publication.[6]

$$1/T_g = W_A/T_{gAA} + W_B/T_{gBB} + (R/200\bar{M})[(M_A + M_B)/T_{gAB}$$
$$- M_A/T_{gAA} - M_B/T_{gBB}] \qquad (4)$$

with

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

or

$$1/T_g = W_A/T_{gAA} + W_B/T_{gBB} + (R/R^*)[1/T_g(R^*) - W_A^*/T_{gAA}$$
$$- W_B^*/T_{gBB}] \qquad (5)$$

with

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

Here, M_I is the formula weight of monomer I and R is the Harwood-Ritchey run number.[8] The latter is defined as the average number of both A and B mon-

omer sequences (runs) occurring in a copolymer per 100 monomer units. The basic character of R and its relation to P_{IJ}s can be found in the literature.[7,8] So, the minimum knowledge, necessary to extract the mathematical characteristic of eq 4 and 5, of the run number will be stated below.

For low-conversion copolymers, the run number is expected to take the maximum value R^* for equimolar copolymers (with $m_A = m_B = 0.5$) and to decrease with the increase of one component (or with a decrease in the other) to nought for the corresponding homopolymers. In general, the R values can be experimentally determined from spectroscopic measurements or theoretically calculated by use of the relation

$$R = 400m_A m_B / [1 + (1 + 4m_A m_B (r_A r_B - 1))^{1/2}] \qquad (6)$$

For the convenience of description, the prediction of Johnston's equation is drawn in Fig. 1 with the data of butyl methacrylate/vinyl chloride (BMA/VCl) statistical copolymer:[3] $T_{gBMA} = 293.3$ K, $T_{gVCl} = 350.2$ K, $r_{BMA} r_{VCl} = 0.68$, $R^* = 54.9$ and $T_g(R^*) = 295.6$ K. Usually and exclusively, the T_gs had been plotted against the monomer composition. As is clear in eq 4 and 5, the T_g is a function of composition (W_A) and sequence distribution (R). Ideally, a three-dimensional plot
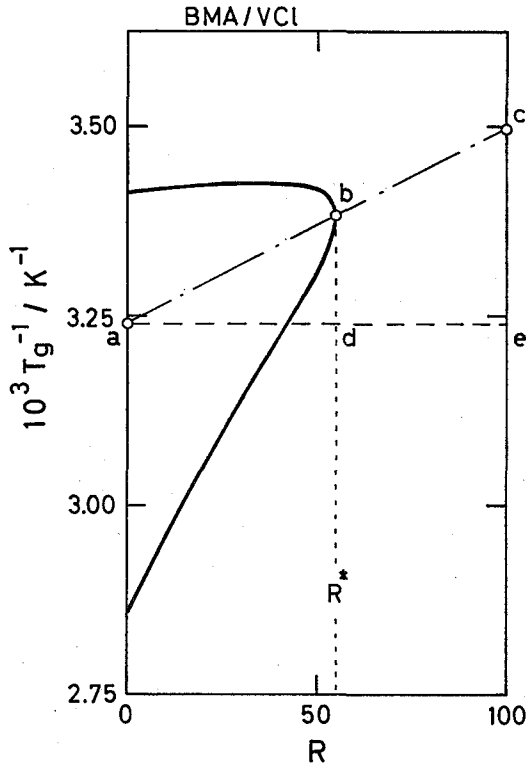

Fig 1. Johnston's prediction, projected onto the T_g^{-1}-R plane, for butyl methacrylate/vinyl chloride (BMA/VCl) copolymers. See the text for Points a to e.

should be made, but here the projection of it onto the $T_g^{-1}-R$ plane is depicted.

Basically, the two expressions, eq 4 and 5, differ in the reference point used: $T_{gAB}(=T_g(R=100))$ is used for it in eq 4, while $T_g(R^*)$ is in eq 5. As is the case with this copolymer system, the T_{gAB} value of the corresponding alternating copolymer is often unknown. For the copolymer systems like this, the second expression, eq 5, is definitely preferable for practical purposes.

The characteristic of Johnston's equation concerns three points on the figure, a, b and c. They are defined as follows: Point a is $(W_A^*/T_{gAA}+W_B^*/T_{gBB})$, the reciprocal of Fox's T_g, Point b is $1/T_g(R^*)$ and Point c is $1/T_{gAB}$. Those three points are on the same straight line, as will be proved below.

In eq 4, we consider a T_g point at $R=R^*$ (i.e., $m_A=0.5$). After simple rearrangements, eq 4 can be expressed as

$$[1/T_g(R^*)-(W_A^*/T_{gAA}+W_B^*/T_{gBB})]$$
$$= (R^*/100)[1/T_{gAB}-(W_A^*/T_{gAA}+W_B^*/T_{gBB})] \qquad (7)$$

The left-hand-side of the above equation is $\overline{bd}$ on the figure, while the corresponding part appearing in the right-hand-side is $\overline{ce}$. What eq 7 means is the proportion, $\overline{bd}/\overline{ce}=R^*/100$. Since $\overline{bd}$ and $\overline{ce}$ are parallel to each other, it can be said that Point b is on the straight line connecting Points a and b.

As has been mentioned,[6] this line may be considered to represent a locus of $1/T_g$ of the hypothetical equimolar copolymers with varying degrees of sequence distribution. On the other hand, the line connecting the two points, $1/T_{gAA}$ and $1/T_{gBB}$, may be considered a locus of $1/T_g$ of copolymers with $R=0$, i.e., of block copolymers with varying degrees of composition. This prediction could be valid provided that two different blocks of a given block copolymer are compatible. Furthermore, multiblock copolymers with finite values of R may be supposed to have T_g values inside the curve of copolymer T_g predictions. If the formula weights of two monomers are identical, then Line $\overline{ac}$ divides two $1/T_g$ points at a fixed value of R by an equal distance. In general, however, such a simple relation does not hold except Point a: Point a divides the two points, $1/T_{gAA}$ and $1/T_{gBB}$, in the ratio of W_A^* to W_B^*.

ANALYSIS OF THE T_g DATA OF ISOTACTIC POLY (METHYL/ETHYL METHACRYLATE)S

The isotactic poly(methyl/ethyl methacrylate) (EMA/MMA) taken from the literature[9] is not an ordinary statistical copolymer synthesized by copolymerization of the corresponding monomers. It is intended here to demonstrate the copolymer T_g equations of Johnston and of Barton are still applicable to such a polymer system. First, the preparation of the polymer will be reproduced.

The isotactic poly(methyl methacrylate) (>99% isotactic triads) was hydrolyzed using concentrated sulphuric acid and the resulting poly (methacrylic acid) was re-esterified by adding appropriate amounts of ethereal diazomethane and diazoethane to the polymer suspended in benzene. This procedure caused a *random* placement of the ester groups but ensured the same degree of tacticity for the copolymers as
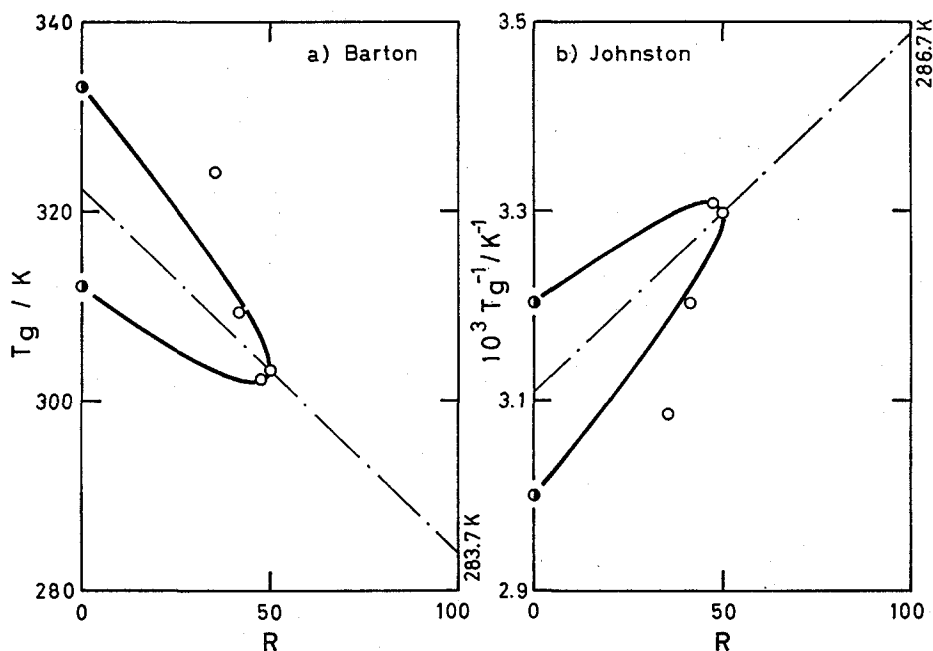
Fig. 2.   Analyses of the T_g data of poly (methyl/ethyl methacrylate) s and estimation of T_{gAB} value of the corresponding alternating copolymer.

for the starting polymer.   Therefore, this polymer could be treated as a typical random copolymer, whose structure is predictable with the reactivity ratios of unity, $r_A = r_B = 1$.   For the polymer samples like this, the run number may be estimated by eq 6 and R^* takes a value of 50.

The T_g data of the samples are plotted in two ways in Fig. 2.   Panel a shows a plot of T_g against R.   This is based on Barton's equation, eq 3, whose expression corresponding to eq 5 reads

$$T_g = m_A T_{gAA} + m_B T_{gBB} + (R/R^*)[T_g(R^*) - T_g] \qquad (8)$$

with

$$T_g = (T_{gAA} + T_{gBB})/2$$

Barton's equation suggests that an extension, to $R = 100$, of a line connecting T_g and $T_g(R^*)$ meets the T_{gAB} of the corresponding alternating copolymer.   On the other hand, panel b shows a plot of $1/T_g$ against R, being based on Johnston's equation. The key data used for making these plots are as follows: $T_{gEMA} = 312.2$ K, $T_{gMMA} = 333.2$ K and $T_g(R^* = 50) = 303.2$ K.

As can be seen from this figure, the experimental data are in fair agreement with the predictions.   And also, it appears that the T_g value of the isotactic methyl/ethyl methacrylate alternating copolymer could be predicted to be

283.7 K (Barton); 286.7 K (Johnston)

Although they are close to each other, these predicted values do differ because of

(51)

the different theoretical bases used for the two equations. As has been described,[6] it is not clear up to now which equation predicts the copolymer T_gs more correctly. So, the two values obtained are given above without comments.

DISCUSSION

Several pairs of monomers have been known to copolymerize randomly, i.e., to have the monomer reactivity ratios of unity within the experimental error.[10] To our knowledge, however, it is unknown that highly tactic random copolymers and even such alternating copolymers are to be synthesized by copolymerization of monomers. Accordingly, it must be worth analyzing the T_g data of isotactic poly(methyl/ethyl methacrylate)s prepared by the involved procedures and predicting the T_g value of the isotactic MMA/EMA alternating copolymer. The results of analyses as shown in Fig. 2 are seen to be fair on the whole. The T_g value of the corresponding alternating copolymer would be some 38 K lower than the arithmetic mean of the homopolymer T_gs. However, a remark should be made about the operational definition of T_g adopted for collecting those data: the T_g value was read as the temperature observed at the midpoint of the heat capacity transition under the experimental conditions that the samples were quench cooled and haeted at a rate of 20 K min^{-1} on a differential scanning calorimeter.[9] These experimental conditions may cause the observed T_g values to be considerably higher than the true ones.[11] The amounts of such deviations would be estimated by comparing them with the standard T_g data for the two homopolymers[12]: 285 K and 311 K for isotactic poly(ethyl methacrylate) and isotactic poly(methyl methacrylate), respectively.

In general, a polymer chain obtains, at the glass transition temperature (or more correctly, in that region), thermal energy sufficient to surmount the rotational energy barirer due to the neighboring atoms. It can be seen, therefore, that the chain stiffness plays an important role in determining the glass transition temperature. This view does hold for copolymers as well, in which the heterodiads emerge. Accordingly, the relative stiffness of the heterodiad to those of the homodiads could be a key factor for the deviation of T_g from the linear relations such as eq 1 and 3.

As for the present copolymers, the deviation is definitely negative. The T_g value of 303.2 K for the equimolar copolymer is 20 K lower than the arithmetic mean of the homopolymer T_gs. The T_{gAB} values predicted for the copolymer formed only from the heterodiads are much lower than any of the T_gs of their constituent homopolymers. This is similar to the finding on another copolymer system of methyl methacrylate with styrene (S).[13] These phenomena could be understood in such a way that the stiffness of heterodiad AB is less than the mean stiffness of homodiads AA and BB.

Theoretically, this behavior has been interpreted by Tonelli in terms of the conformational entropy as a measure of bond flexibility.[14] The conformational entropies may be estimated by employing semi-empirical potential functions to calculate the energies of various diad conformations· For the S/MMA copolymers having a given stereoregularity and sequence distribution, it has been found that (1)

for either homopolymer, the conformational entropy is larger for isotactic chain than for syndiotactic chain and (2) the conformational entropies of the S/MMA copolymers are larger than the weighted sum of the entropies of the constituent homopolymers. These results confirm that the S/MMA statistical copolymers have T_gs lower than those expected from eq 1 or 3 and the alternating copolymer has the lowest T_g value. The present copolymer system concerns two disubstituted vinyl monomers, but a conjecture similar to that for S/MMA copolymers could be applied to this case as well.

The intermolecular force is, of course, another factor effecting the T_g values. Chain packing, side chain stiffness and bulkiness, dipole interactions, etc. are of importance. However, it is very difficult to ioslate the effects of intermolecular forces from other skeletal factors. Here, we mention only the fact that the two homopolymers are known to be compatible: the blend has a single glass transition temperature intermediate to the T_gs of the pure components.[9] As has been stated in the Introduction, compatible block copolymers have the T_g-composition behavior different from that for the statistical copolymers of the same constituents. This behavior will be investigated and discussed on the same basis for eq 2 and 3 in a subsequent paper.

ACKNOWLEDGEMENT

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