

Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

ON THE CORRELATION OF THE GLASS TRANSITION TEMPERATURE OF A COPOLYMER WITH ITS COMONOMER SEQUENCES

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Abstract

The glass transition temperature of a copolymer depends not only on chemical composition but also on its comonomer sequences. This experimental fact is explained by Barton's and Johnston's equations. Their equations, though complicated, become simple, if a suitable parameter is used to describe the comonomer sequences. It is shown that with these new expressions, their equations can be used to understand glass transition temperatures of two additional types of copolymers, compatible multiblock copolymers and homopolymers with various tacticities treated as steric copolymers.

Keywords: comonomer sequence, copolymer, glass transition temperature, homopolymer, tacticity

Introduction

An ultimate objective for polymer scientists is to understand the structure-property relationships of polymers. Here, we will consider a possible correlation of the glass transition temperature (T_g) of a copolymer with its chain structure. This means the sequences of two monomers, A and B, in a given copolymer.

There have been frequent attempts to elucidate the variation in T_g of a copolymer as a function of composition, as is shown in Fig. 1. This figure shows that the T_g of an alternating copolymer does not lie on a line expected for the corresponding statistical copolymers [1]. In other words, there exists a definite difference in T_g between two copolymers with the same composition but different comonomer sequences. This fact reveals a defect in linear equations such as

$$T_g = m_A T_{gA} + m_B T_{gB} \quad (1a)$$

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

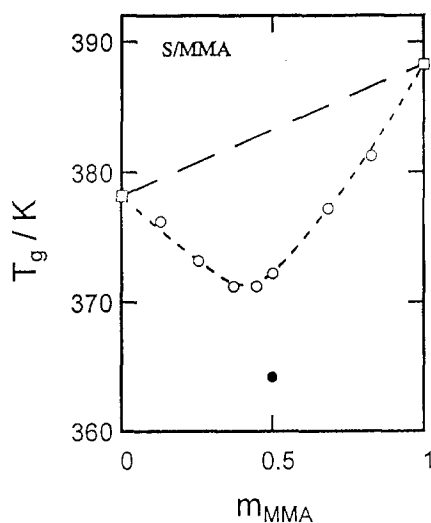


Fig. 1 Plot of T_g vs. m_{MMA} for styrene-methyl methacrylate (S/MMA) statistical (o) and alternating (•) copolymers and the two corresponding homopolymers (□) [1]

Here, T_g and T_{gX} are the glass transition temperatures, respectively, of a given copolymer specified by mole fraction (m) or weight fraction (W) and of a homopolymer of monomer X ($=A$ or B). One can see the necessity of introducing the second variable which describes the comonomer sequences.

More than twenty years ago, nonlinear equations addressing this problem were proposed by Barton [2] and Johnston [3]. Unfortunately, their equations were too complicated for practical use and have been applied only to understand the variation in T_g of statistical copolymers or to estimate the T_g of the alternating copolymer in a given system. However, if a suitable parameter is used to describe the comonomer sequences, their equations become quite simple. Such expressions allow us to gain insights into their equations.

In this article, we will extend their work by exploring the intrinsic characteristics of their equations and applying them to two types of copolymer originally not intended to be covered by their equations: compatible multiblock copolymers and homopolymers with various tacticities treated as steric copolymers.

New expressions and characteristics of Barton's and Johnston's equations

Since a given copolymer is composed of two monomers, the first way for expressing the comonomer sequences is to take the fractions of diads into account. There are three different diads in a copolymer chain, AA, BB and AB ($=BA$),

so long as the direction of the chain is not important. With these diads, Barton and Johnston derived, respectively, the equations for the glass transition temperature of a copolymer as follows

$$T_g = m_A P_{AA} T_{gAA} + m_B P_{BB} T_{gBB} + (m_A P_{AB} + m_B P_{BA}) T_{gAB} \quad (\text{B}) \quad (2a)$$

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

Here, T_g is the glass transition temperature of a copolymer with composition and comonomer sequences specified by the values of products mPs or WPs ; P_{ij} is the probability that a given I monomer is followed by a J monomer; T_{gIJ} is the T_g value of the polymer composed of IJ diads only. That is, the product of $m_A P_{AA}$ is equal to the mole fraction of the AA diad, m_{AA} ; similarly, $m_B P_{BB} = m_{BB}$ and so on. T_{gAA} and T_{gBB} are the T_g s of the respective homopolymers and T_{gAB} is the T_g of the corresponding strictly alternating copolymer.

The parameter m_{IJ} can be defined, after Barton, as the fraction of rotatable bonds in diad IJ . For simplicity, that is taken to be the mole fraction of diad IJ in this article. This means that the number of possible rotatable bonds in A monomer unit is assumed to be the same as that in B monomer unit and the polymerization process produces only rotatable bonds.

Since a given A monomer must be followed by either A or B, the fraction of AA diads is equal to the fraction of A monomer minus the fraction of AB diads:

$$m_{AA} = m_A - m_{AB} \quad (3a)$$

Similarly

$$m_{BB} = m_B - m_{BA} \quad (3b)$$

We may note that every sequence of monomer A is followed by a sequence of monomer B, and there are, in a copolymer chain long enough, as many A sequences as B sequences. Those two types of sequences are linked by an AB or BA diad. So m_{BA} is equal to m_{AB} . Let us express the number of AB and BA bonds in the copolymer chains as that per 100 monomer units. This is called the run number \bar{R} [4], which is equal to the percentage of sum of AB and BA diads:

$$\bar{R} = 100 (m_{AB} + m_{BA}) = 200 m_{AB} \quad (4)$$

From Eqs 3a and 4, one obtains

$$m_{AA} = m_A - \bar{R}/200 \quad (5)$$

This equation explicitly shows that a diad fraction has information on both composition and comonomer sequences. Substitution of Eq. (5) into Eq. (2a) yields [5, 6]

$$T_g = m_A T_{gAA} + m_B T_{gBB} + (\bar{R}/100)(T_{gAB} - \bar{T}_g) \quad (6a)$$

with

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

Similarly, substitution of Eq. (5) into Eq. (2b) yields [6, 7]

$$\begin{aligned} 1/T_g &= W_A/T_{gAA} + W_B/T_{gBB} + (\bar{R}/200\bar{M}) \\ &\times [(M_A + M_B)/T_{gAB} - M_A/T_{gAA} - M_B/T_{gBB}] \end{aligned} \quad (6b)$$

with

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

Here, M_X ($X=A$ or B) stands for the formula weight of monomer X . The complicated probabilities, P_{ij} s, no longer appear in the equations. The \bar{R} value of a given copolymer can be determined by nuclear magnetic resonance experiments [8] or calculated by

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

where $r_A r_B$ is the product of the monomer reactivity ratios in copolymerization. The \bar{R} value is zero for homopolymers and 100 for alternating copolymers. Those of statistical copolymers vary with composition, having a maximum, \bar{R}^* , at $m_A = 0.5$ for low-conversion products. Those of diblock copolymers are practically zero, for there is only one AB diad in a long chain.

Since the T_{gAB} is often unknown, another expression of Eq. (6a) should be derived. For the T_g of equimolar statistical copolymer, Eq. (6) reads

$$T_g(m_A = 0.5) = \bar{T}_g + (\bar{R}^*/100)(T_{gAB} - \bar{T}_g) \quad (8)$$

Elimination of T_{gAB} from Eqs (6a and 8) yields

$$T_g = m_A T_{gAA} + m_B T_{gBB} + (\bar{R} / \bar{R}^*) [T_g(\bar{R}^*) - \bar{T}_g] \quad (9)$$

An expression of Johnston's equation, similar to Eq. (9) can be seen [6, 7]. These expressions show two facts: (i) the T_g of a copolymer is a function of two independent variables, composition ($m_B = 1 - m_A$) and the number of comonomer

reversals (\bar{R}) and (ii) the \bar{R} -dependent term is separated from the m -dependent ones.

The usual plot of T_g against m_B as in Fig. 1 may be considered to be a projection of the T_g curve in three dimensions onto the T_g - m_B plane. Its projection onto the T_g - \bar{R} plane, yielding a plot like Fig. 2a, is suitable to represent the dependence of T_g on \bar{R} . Moreover, certain mathematical characteristics useful for data analysis may be derived from this type of plot [5]. For Johnston's equation, similar characteristics are found when $1/T_g$ is plotted vs. \bar{R} [6, 7].

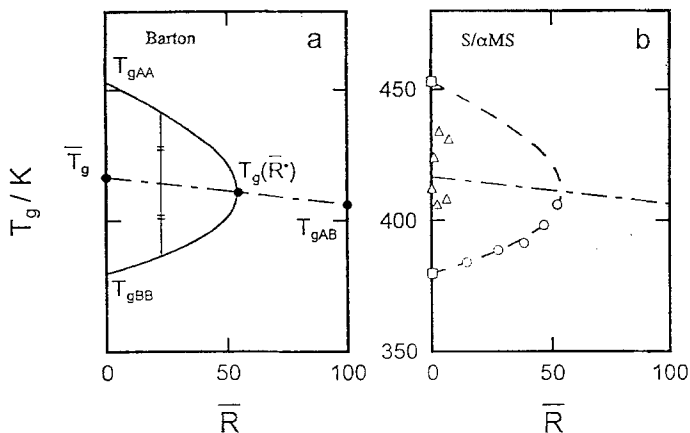


Fig. 2 a) Schematic representation of plot of T_g vs. \bar{R} , showing two characteristics of Eq. (6a); b) Plots of T_g vs. \bar{R} for styrene- α -methylstyrene (S/ α MS) multiblock copolymers together with predictions (---) of Eq. (6a) for statistical (o) copolymers

Those of Barton's equation are as follows. (i) The three points, \bar{T}_g , $T_g(\bar{R}^*)$ and T_{gAB} are on the same straight line and (ii) T_g values for two statistical copolymers having a given value of \bar{R} but different compositions deviate by an equal distance from this line. It is clear that the straight line connecting \bar{T}_g and T_{gAB} represents the T_g locus of hypothetical equimolar copolymers with varying degrees of comonomer alternation. The inside of the curve in Fig. 2a is the region for blocklike copolymers: the portion of the ordinate, T_{gAA} to T_{gBB} , may be considered to represent the T_g locus of compatible diblock copolymers with varying degrees of composition. Barton's and Johnston's equations were originally derived for statistical copolymers but actually cover T_g values of (compatible) multiblock copolymers as well.

Data analysis and discussion

Compatible block copolymers

In general, blocks of a given multiblock copolymer are, like two different homopolymer chains, incompatible, forming the two-phase structure and show-

Homopolymers including these triads may be called steric copolymers. Equations 2a and b can be applied to such homopolymers by simply replacing AA with *mm*, i.e., *I* and so on.

$$T_g = IT_{gI} + ST_{gS} + HT_{gH} \quad (10a)$$

$$1/T_g = I/T_{gI} + S/T_{gS} + H/T_{gH} \quad (10b)$$

Here, T_g is the T_g value of homopolymer having the tacticity specified by *I*, *S* and *H*. T_{gK} ($K=I, S$ or H) is the T_g value of pure *K*-tactic form. The mole fraction of *I* triad is written as *I* itself as usual, the sum of *I*, *S* and *H* being unity. It is not necessary to distinguish between weight and mole fractions in this case. With these equations, the dependence of T_g of poly(methyl methacrylate) (PMMA) on tacticity will be considered. Before applying them to T_g data, let us derive new expressions of Eqs (10a and b). Since

$$m = I + H/2 \quad \text{and} \quad r = S + H/2$$

Equations (10a and b) can be written as

$$T_g = (1 - r)T_{gI} + rT_{gS} + H[T_{gH} - (T_{gI} + T_{gS})/2] \quad (11a)$$

$$1/T_g = (1 - r)/T_{gI} + r/T_{gS} + H[1/T_{gH} - (1/T_{gI} + 1/T_{gS})/2] \quad (11b)$$

These expressions correspond, respectively, to Eqs (6a and b). In order to determine the dependence of glass transition temperature on tacticity, plots of T_g vs. r ($=1-m$) have repeatedly been made. Equation 11a implies, however, such a plot cannot be linear: the deviations from the linear relation are always expected due to the third term. As the three T_g s are constant, the deviation is seen to be proportional to the value of *H* in each sample. So it is not sensible to make an ordinary plot of T_g against r .

In Eq. (10) T_g , *I*, *S* and *H* are observables. In addition, both T_{gI} and T_{gS} can be determined, for it is possible to prepare PMMA molecules in almost pure tactic forms. The following values are used below: 315.2 K for T_{gI} and 400.2 K for T_{gS} . So the only unknown is T_{gH} , and T_g value of the heterotactic polymer specified by the sequence of strict alternation of *m* and r . This quantity can be estimated from the plot shown in Fig. 3a. This plot is based on Eq. (10b): the slope of the linear line passing through the origin is the reciprocal of T_{gH} . The used T_g data of various types of PMMAs prepared with various catalysts are listed in Table 1 [15–18]. From this plot, the T_{gH} was estimated to be 400.1 K. Similarly, a plot based on Eq. (10a) yields a value of 390.7 K for T_{gH} .

Now the experimental T_g values can be compared with those calculated by Eq. (10). These are given in the last two columns of Table 1. Good agreement

Table 1 Tacticity data and observed and predicted glass transition temperatures of various types of PMMA samples

Sample	Triads/%		T_g /K		
	<i>I</i>	<i>S</i>	obs.	Eq. (10a)	Eq. (10b)
1*	99	0	315.9	315.9	315.9
2	81	5	336.7	329.7	328.3
3	80	7	336.2	330.7	329.0
4	67	15	344.5	341.2	338.7
5	62	17	340.6	345.1	342.6
6	57	24	350.3	349.6	346.6
7	38	30	364.2	364.2	362.5
8	28	36	372.3	372.2	371.5
9*	7	62	389.9	390.7	392.2
10*	7	62	391.7	390.7	392.2
11*	4	65	397.5	393.2	395.4
12*	0	94	398.8	399.5	400.1
13*	0	94	396.6	399.5	400.1
14*	6	43	388	390.8	395.0
15*	3	65	394	393.9	396.4

* Close to Bernoullian and denoted by solid circles in the figure.

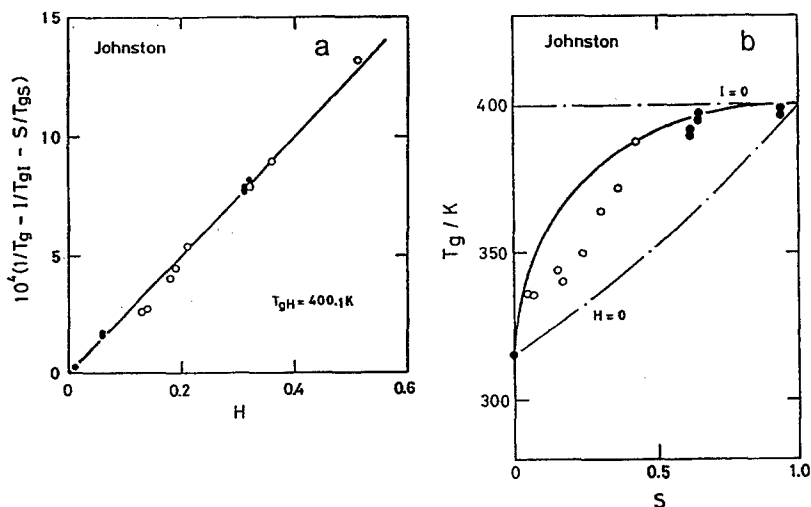


Fig. 3 a) T_{gH} determination based on Eq. (10b) and two T_g values: T_{gI} =315.2 K and T_{gS} =400.2 K. (●) close to Bernoullian and (○) deviated from Bernoullian PMMAs; b) Plot of T_g against S for various types of PMMAs together with theoretical predictions by Eq. (10b) for Bernoullian (—) and stereoblock (---) PMMAs

is seen, with some exceptions, for all the samples, regardless of the differences in preparation. This means that there is a one-to-one correspondence between the T_g of PMMA and a set of its triads. The exceptions are isotactic samples 2 to 5. Since T_{gI} is markedly lower than T_{gS} and T_{gH} and the latter are more or less equal, it is clear that errors in the determination of tacticity have a bigger influence on the T_g values of isotactic samples.

It was understood that Eq. (10) can be applied to describing the dependence of T_g of homopolymers on tacticity. These T_g data are plotted against S in Fig. 3b. Before looking at the experimental points, we will consider theoretical predictions for some cases. A solid line, based on Eq. (10b), is for a simple case of polymerization kinetics, assuming that the configuration of an adding monomer unit is independent of that of the growing chain. These polymers are called Bernoullian, whose triad fractions can be expressed as

$$I = (1 - r)^2, \quad H = 2r(1 - r), \quad S = r^2 \quad (12)$$

Thus, the solid line in Fig. 3b is the T_g locus of Bernoullian PMMAs. Dash-dot lines and the ordinate are the boundaries: $I=0$, $H=0$ and $S=0$. The dash-dot lines for $I=0$ and $H=0$ represent, respectively, the T_g loci of H - S and I - S stereoblock polymers with varying degrees of S . The T_g data of all types of PMMAs must be inside the triangle defined by these three line segments. The data are located in the triangle, but they do not fit a single curve. Filled circles are close to the solid line, while open circles are not.

This is quite natural. A big difference between tactic polymers like PMMAs and ordinary statistical copolymers must be recognized. The comonomer sequences of the latter is governed, as can be seen from Eq. (7), by a single parameter $r_A r_B$. It is impossible, however, to prepare PMMA molecules with various tacticities under specific polymerization kinetics. We recall the finding of Bovey and Tiers that free radical PMMA molecules are Bernoullian but anionic PMMA molecules are not [19]. This figure confirms their finding only in a different way.

In this discussion, we tried to understand the relationship of glass transition temperature of a copolymer with its comonomer sequences. As a theoretical basis, Barton's and Johnston's equations were used. Although they are known to be useful for ordinary copolymers, both equations were found to be applicable to compatible multiblock copolymers and steric copolymers like PMMA, providing further understanding of the T_{gs} of these types of copolymers.

So far, the glass transition was implicitly assumed to be a property determined primarily by intramolecular interactions. And we did not ask why, for instance, T_{gAB} becomes smaller than $T_g(\bar{R}^*)$ in the case shown in Fig. 1. An answer could be found from a consideration based on the actual molecular structure of comonomer sequences. Such conclusions have already been published, for several copolymer systems including tactic PMMAs, by Tonelli [20]. The question of which theory is more valid, Barton's (configurational entropy

theory) or Johnston's (free-volume theory), still remains unsettled, however. This problem is now under intensive investigation by use of the copolymer systems whose T_{gAB} values predicted are markedly different from each other [6].

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