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Glass Transition Temperatures of Compatible Block Copolymers

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The purpose of the present note is to suggest an interpretation of compatible block copolymer glass transition temperatures (T_g) within the framework of T_g theories, based on a diad model, for common random copolymers. By diad model we mean adopting diad monomer sequences as a unit for describing the sequence distribution of a given copolymer.[1] The theories due to Barton[2] and to Johnston[3] are known empirically to be adequate for predicting the random copolymer T_g values.[4-7] These theories have recently been shown to be capable of predicting, with minimum data, alternating copolymer T_g values as well.[8,9] This is natural because the alternating copolymer is merely one of the equimolar copolymers whose sequence distribution may be characterized with the Harwood–Ritchey run number, R, of 100.[10] Similarly, these theories must be able to predict the T_g values of di- and multiblock copolymers having R values close to zero. The definition and characteristics of R can be seen in the literature.[8,10]

New formulations of the copolymer T_g equations of Barton and of Johnston have been derived previously.[8,9] Those for the Barton equation are as follows:

$$T_g = m_A T_{gAA} + m_B T_{gBB} + (R/100)(T_{gAB} - \bar{T}_g) \qquad (1)$$

with

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

$$T_g = m_A T_{gAA} + m_B T_{gBB} + (R/R^*)[T_g(R^*) - \bar{T}_g] \qquad (2)$$

Here, T_g is the glass transition temperature of a copolymer composed of monomers A and B, having composition and sequence distribution specified by the values of m and R, respectively. T_{gAA} and T_{gBB} are the T_g values of the homopolymers of A and B, respectively, and T_{gAB} is the T_g values of the corresponding strictly alternating copolymer; m_A is taken, as before,[8] as the mole fraction of monomer A. R^* is the maximum value of R expected for the equimolar random copolymer.[10] The above expressions show the dependence of copolymer T_g on composition (m) and sequence distribution (R). Accordingly, a three-dimensional plot would be well suited to represent the T_g values, an example of which is schematically illustrated in Figure 1.

The usual plot of T_g against m_B may be considered a projection of the predicted curve on the T_g–m_B plane. Another projection of it on the R–m_B plane shows the variation of R with composition. The third projection of it on the T_g–R plane has been recommended as the one to use, because certain mathematical characteristics of the Barton equation become apparent.[8] On a plot of T_g against R, three points of $\bar{T}_g$, $T_g(R^*)$, and T_{gAB} are on a straight line, and this line may be considered a locus of the T_g values of hypothetical equimolar copolymers with varying degrees of sequence distribution. This has been confirmed in part in a previous paper[8] by use of literature data.[11]

Similarly, the line connecting T_{gAA} and T_{gBB} may be considered a locus of the T_g values of compatible (di)block copolymers with varying degrees of composition and a sequence distribution of $R = 0$. A line parallel to this but shifted to $R = R'$ could be a locus of the T_g values of compatible multiblock copolymers with a fixed sequence distribution of R' and composition varying in a range specified by the two random copolymers having the corresponding sequence distribution. These deductions will be compared with the literature data for compatible block copolymers.

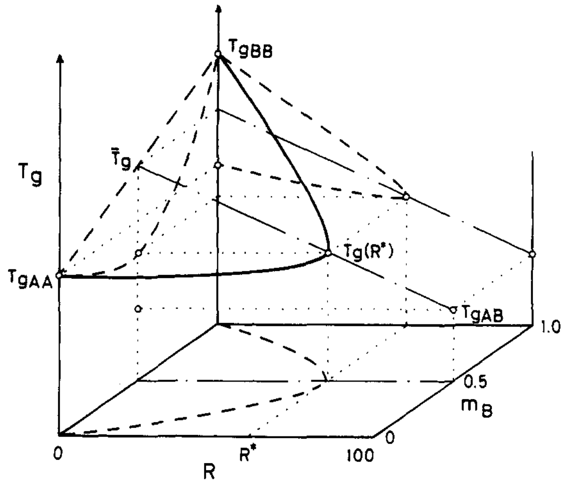

Figure 1. Three-dimensional representation of the prediction of the Barton equation for random copolymer T_g.

Table I
Characterization Data of Styrene–α-Methylstyrene Multiblock Copolymers by Phalip et al.[14]

$10^{-4}M_n$[a]	$m_{\alpha MS}$	N[b]	R[c]	T_g/K	$m'_{\alpha MS}$[d]	deviation/%
2.4	0.40	5	2.3	406.2	0.380	-5
1.9	0.47	11	6.2	408.2	0.413	-12
7.0	0.60	7	1.1	424.2	0.639	7
2.7	0.74	17	7.2	431.2	0.748	1
2.6	0.83	7	3.1	434.2	0.787	-5

[a] The number-average molecular weight. [b] Total number of blocks. [c] $R = 100N/\mathrm{DP}$; DP = the average degree of polymerization. [d] Estimated from the T_g positions on a plot of T_g against R.

Such data are unfortunately rare in the literature. Nevertheless, to our knowledge, the T_g data for styrene (S)–α-methylstyrene (αMS) block copolymers reported by Phalip et al.[12] and that cited therein[13] seem satisfactory for analysis.[14] Their samples are of the multiblock type; the characterization data of those samples are reproduced in Table I. The T_g data are plotted against $m_{\alpha MS}$ in Figure 2. Two data points for diblock and random copolymers are also included and compared with the theoretical predictions of the Barton equation for the corresponding types of copolymers. For the prediction of the random copolymer T_g, values of R and T_{gAB} (or $T_g(R^*)$) are required. The former was calculated by using the reported values of the monomer reactivity ratio r:[8] $r_S = 1.124$ and $r_{\alpha MS} = 0.627$.[15] By use of the T_g data of S–αMS random copolymers,[15] the latter was estimated to be 406.1 K from the slope, $(\bar{T}_g - T_{gAB})/100$, of a plot of $(m_A T_{gAA} + m_B T_{gBB} - T_g)$ against R.

It can be seen from Figure 2 that the data for both the block and random copolymers are in reasonable accord with each of the lines theoretically predicted. As is clear from this figure, this copolymer system is not predicted to show significant deviation of the random copolymer T_g values from the line connecting the two homopolymer T_g values, i.e., from the simple additivity rule. This may be confirmed in terms of the closeness of the random copolymer T_g to the T_g values of the multiblock

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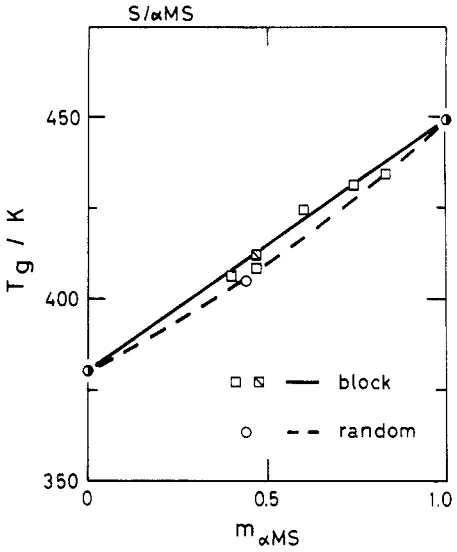

Figure 2. Plots of T_g against $m_{\alpha MS}$ for styrene–α-methylstyrene diblock (▨),[14] multiblock (□),[12] and random (○)[15] copolymers and for the two homopolymers together (◑)[12] with the predictions of the Barton equation for block copolymers with $R = 0$ (—) and for random copolymers (- -).

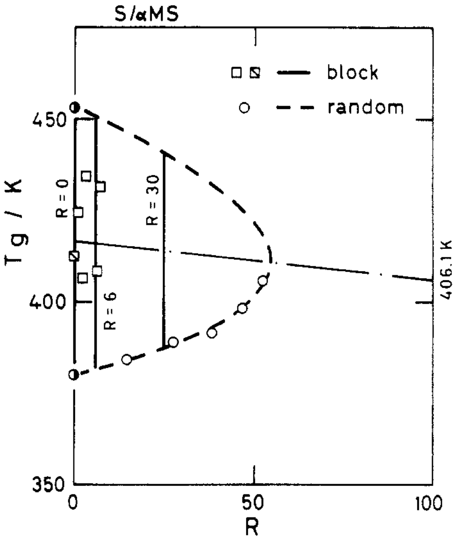

Figure 3. Plots of T_g against R for styrene–α-methylstyrene copolymers together with the predictions of the Barton equation for block copolymers with fixed values (0, 6, and 30) of R (—) and for random copolymers (- -). For each symbol, refer to Figure 2.

copolymers having comparable compositions. This type of plot seems inadequate for investigating possible effects of small differences in sequence distribution on copolymer T_g.

In Figure 3, the copolymer T_g values observed are plotted against the R values calculated for the samples. An equation used for the calculation is given as a footnote of Table I. The T_g values of multiblock copolymers having a fixed sequence distribution are represented by vertical lines with both ends on the T_g curve predicted for the corresponding random copolymers. It is seen on this plot that the multiblock copolymer T_g values occupy a space markedly different from that the random copolymer T_g values do.

The multiblock copolymers analyzed here are different both in composition and sequence distribution. Three data points above the dash-dot line have compositions of $m_{\alpha MS} > 0.5$, while the three others below the line have compositions of $m_{\alpha MS} < 0.5$. The small differences in sequence distribution of the samples are realistically magnified on this plot. Overall, it can be said that the T_g data are neatly mapped on this figure. The degree of validity of such a plot of multiblock copolymer T_g values could be checked from a comparison of the composition estimated from the relative position of a T_g point on the line with the observed one.

Consider a predicted T_g line at the R value of 30, for example. Both ends coincide with the T_g values of random copolymers with compositions of $m_{\alpha MS} = 0.17$ and 0.83, and this line is divided linearly by the difference in the two compositions. Then, the composition of a sample whose T_g point is on the line can be read with such a measure. In fact, however, the composition was calculated in terms of the T_g and $m_{\alpha MS}$ values predicted for the random copolymers having the corresponding sequence distribution. The results are shown in Table I.

It is seen that the $m_{\alpha MS}$ values estimated agree fairly well with the observed ones. Indeed, a deviation as large as 12% is seen in the worst case. Yet it should be noted that the transitions observed in block copolymers are apparently broad, and a 1-deg error in the T_g determination yields a 3% deviation in composition. When these unfavorable conditions are taken into account, it may be said that the analysis and understanding of compatible multiblock copolymer T_g values stated above are practically reasonable.

Other T_g data, determined by Baer[16] and by Hansen and Shen,[17] on S–αMS block copolymers have been reported to be approximately proportional to the content of one component. These findings are seen to furnish additional evidence for the present analysis. So far, use has been made of the new formulations of the Barton equation, but this is only for the sake of convenience. Those of the Johnston equation can also be used for the same purpose, for both equations are known to be equally adequate in most cases: which equation is more adequate is a crucial and yet unsettled question related to the molecular mechanism of the glass transition.

In conclusion, by means of theories based on a diad model, compatible multiblock copolymer T_g values are predicted and understood as well as the ordinary random copolymer T_g values.

Acknowledgment. We are indebted to S. Ross-Murphy, Unilever Research Colworth Laboratory, for reading the manuscript.

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Registry No. (S)(αMS) (block copolymer), 108080-90-6.

Relaxation of Binary Blends of Long and Short Chains: Evidence for Orientational Coupling

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Introduction

Various experimental studies have revealed the existence of local orientational correlations between molecules in a large variety of systems. For example, short-range order has been detected by depolarized Rayleigh scattering and Raman spectroscopy in n-alkane liquids.[1–4] Deuterium magnetic resonance studies have also shown that solvent molecules, even those of nearly spherical shape, as well as oligomers are oriented in deformed networks.[5,6] Free polymer chains dispersed in a deformed network also exhibit a segmental orientation[7] even though their overall dimensions remain isotropic.[8] An abnormally high orientation of a fluorescent molecule, covalently incorporated in a polyisoprene network[9,10] or at the end of a dangling chain,[11] has been detected by fluorescence polarization measurements. The orientational behavior of both rigid[12] and flexible[13] free probe molecules has also been related to the probe geometry.

The possibility that the same kind of interaction might exist in polymer melts has been recently put forward.[14–16] Infrared dichroism measurements on isotopically labeled block copolymers of linear and star polystyrenes have shown a higher orientation of the ends of the arms of the stars relative to that of linear chains.[14] Recent results, obtained by using an infrared dichroism based rheooptical technique,[16] also indicate that in a bimodal blend the relaxation of the short chains after a step–shear was slowed down when the concentration of the long chains was increased. These observations cannot be accounted for by the tube theories,[17–19] even if constraint release effects[20–23] are taken into account. To explain these results, a nematic-like interaction between chain segments in the melt has been proposed. The influence of this interaction on the relaxation dynamics has been theoretically treated independently by Merrill et al.[24] and Doi et al.[25]

The aim of this note is to present further evidence of this orientational coupling between chains in deformed melts and to test the recent theoretical modeling of this phenomenon. To this end, infrared dichroism measurements have been performed on blends of deuterated short PS chains ($M < M_e$) and nondeuterated long PS chains ($M \gg M_e$), where M_e is the molecular weight between entanglements. Such a technique has recently proved to be powerful for the study of the dynamics of relaxing systems.[14,26,27]

Table I
Characteristics of the Different Polymers

material	$10^{-5}M_w$	M_w/M_n
PS160	1.63	1.1
PS1000	11.90	1.4
PSD10	0.10_7	1.07
PSD27	0.27	1.06

Experimental Section

Blends containing 15 wt % deuterated short PS chains in long-chain PS matrices were studied. This composition was chosen to ensure a reasonable accuracy in the dichroism measurements especially for the deuterated species without having concentrations of the short chains which were too high. The characteristics and designation of the short chains and matrices are given in Table I. The mixtures were prepared by dissolving a weighted amount of the individual components in distilled benzene at a total polymer concentration of 6%. The polymer films were prepared according to a well defined procedure.[14,26,28] The glass transition temperature T_g of the resulting films was 108 ± 1 °C. No drop of T_g with respect to the long-chain homopolymer has been detected due to the presence of deuterated short chains.

Films were uniaxially stretched up to a draw ratio $\lambda = 4$, at a constant strain rate of $0.1\ s^{-1}$ and at a temperature of 115 ± 0.4 °C. The films were held at fixed strain and allowed to relax for a given aging time.[28] They were then quickly quenched to room temperature. Short and long times have been reached by varying the stretching temperature and applying time–temperature superposition.[14,28]

The orientation of the PS chains and of the deuterated species was obtained by using a Nicolet 7199 Fourier transform spectrometer, according to a method detailed in the literature.[14,26] The orientation is quantified in terms of the second moment of the orientation distribution function, $\langle P_2(\cos\theta)\rangle = (1/2)\langle 3\cos^2\theta - 1\rangle$, where θ is the angle between the chain axis and the stretching direction. We estimate that our experimental uncertainty is ± 0.005 P_2 units.

The possibility of a phase separation of the samples in this binary isotopic mixture[29] seems unlikely because of the relatively high value of the χ parameter for the single-phase stability ($\chi_s = 3.3 \times 10^{-2}$) due to the combinatorial entropy of the low molecular weight deuterated species. We also do not believe the segregation is due to stretching[30] since the critical draw ratio would be on the order of 30.

Results

Hereafter, the orientation of the long and short chains is reported as a function of the aging time t at 115 °C and expressed in seconds.

The relaxation of both components of the blend PS1000–PSD10 (with a volume fraction of short chains $\phi_s = 0.15$) is presented in Figure 1. The long chains undergo a rapid relaxation at short times $-1 < \log t < 1.5$ and a much slower one at longer times. Their orientation seems to go through a plateau in the time scale $2 < \log t < 4$. The orientation of the short chains is always significantly lower, but their relaxation shows a behavior rather similar to

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