

Conformational Source of Comonomer Sequence-Dependent Copolymer Glass-Transition Temperatures

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Abstract: This brief review addresses the source of the dependence of copolymer glass transition temperatures (T_{gpS}) on their comonomer sequences. Here we show that a comparison of the conformational entropies obtained from the Rotational Isomeric State (RIS) conformational models of the poly-A and poly-B homopolymers and their resultant poly-A/B co-polymers, i.e., $\Delta S_{conf} = (X_A S_A + X_B S_B) - S_{A/B}$ (X = comonomer fraction), can be used to predict/understand the T_{gpS} of copolymers. For copolymers with $\Delta S_{conf} \sim 0$, we expect their T_{gpS} to follow Fox behavior and to depend only on copolymer composition, because of the similar conformational flexibilities of the A and B homo- and A/B-copolymers. When the conformational entropy ΔS_{conf} is negative the A/B copolymer is assumed more flexible than the weighted sum of polymer-A and polymer-B conformational entropies, resulting in T_{gpS} that are lower than expected from the Fox equation. Conversely, a positive ΔS_{conf} suggests the copolymer's lower flexibility, resulting in higher T_{gpS} than expected from the Fox relation. We use the successful comparison of the observed dependence of numerous copolymer T_{gpS} to demonstrate the validity of using their calculated RIS conformational entropies to predict their comonomer sequence dependencies.

Keywords: Comonomer Sequence; Conformational Entropy; Copolymer; Fox equation; Glass-Transition Temperature; Rotational Isomeric State.

1. Introduction

We have correlated/predicted the comonomer sequence dependence observed for copolymer glass-transition temperatures (T_{gpS}). The conformational entropies obtained from the realistic Rotational Isomeric State (RIS) conformational models [1] of the poly-A and poly-B homopolymers and their resultant poly-A/B co-polymers, i.e., $\Delta S_{conf} = (X_A S_A + X_B S_B) - S_{A/B}$ (X = comonomer fraction) were found to be consistent with observed T_{gpS} , which can be described by $1/T_{gp} = W_A P_{AA}/T_{gAA} + (W_A P_{AB} + W_B P_{BA})/T_{gAB} + W_B P_{BB}/T_{gBB}$ (W and P are the weight fractions and diad probabilities of comonomers) as described by Johnston [2]. Copolymers with $\Delta S_{conf} \sim 0$, were expected to exhibit T_{gpS} that follow Fox behavior $1/T_{gp} = W_A/T_{gA} + W_B/T_{gB}$ and depend only on copolymer composition [3–5], because of the similar conformational flexibilities of the A,B homo- and copolymers. Negative calculated conformational entropies ΔS_{conf} for A/B copolymers are assumed to indicate that they are more flexible than the weighted sum of polymer-A and polymer-B conformational entropies, resulting in T_{gpS} that are described by the Johnston equation [2] and are lower than expected from the Fox equation. On the other hand, positive ΔS_{conf} s stem from weighted sums of homopolymer conformational entropies that are greater than that of the

copolymer, resulting in the latter's lower flexibility and higher T_{gps} than expected from the Fox relation.

The detailed experimental and calculational results of our intramolecular conformational approach to predicting the comonomer sequence dependence of copolymers can be found in references [6–12]. Here we will summarize only the predicted T_{gps} of poly (vinyl chloride) (VC)/poly(methyl acrylate) (MA) [7], poly (vinylidene chloride) (VDC)/MA [7], polystyrene (S)/poly(*p*-bromostyrene) (pBrS) [11] and amorphous aliphatic 3,4/6,6 polyesters [12] made from propane and hexane diols, and succinic and adipic acids. These are compared with their observed glass-transition temperatures to see if they are consistent with and show the same observed comonomer sequence dependencies.

2. Representative Scenarios

2.1. VC/MA and VDC/MA Copolymers

In Figure 1 we present the T_{gps} observed [13] for different composition of VC/MA (a) and VDC/MA (b) copolymers, while the conformational entropies ΔS_{conf} s calculated [7] for VDC/MA are shown in part (c). Experimentally it is clear that, while VC/MA copolymer T_{gps} depend only on comonomer composition and follow the Fox equation, the VDC/MA copolymer T_{gps} depend on comonomer sequence, as well as on comonomer compositions, with T_{gps} observed well above those predicted by the Fox relation.

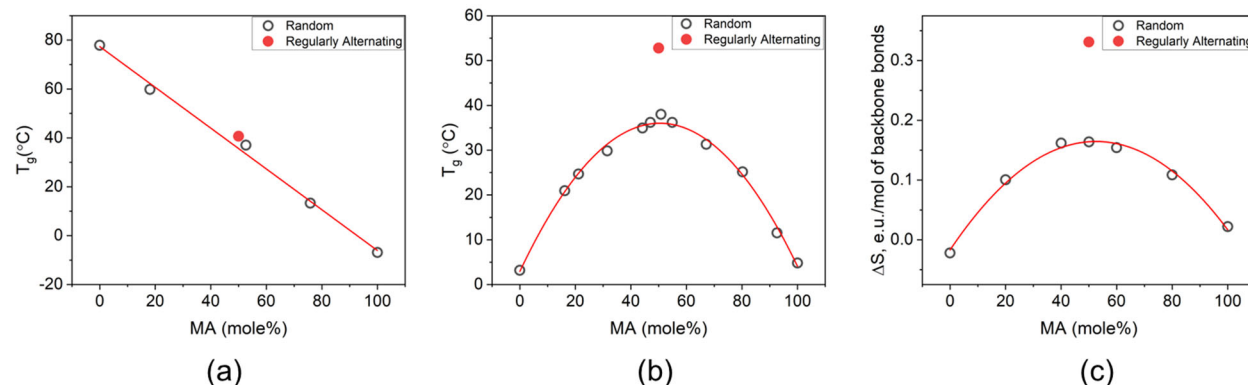


Figure 1. Glass-transition temperature comonomer composition behaviors of VC/MA (a) and VDC/MA (b) copolymers [13], and (c) $\Delta S_{\text{conf}} = (X_{\text{VDC}}S_{\text{VDC}} + X_{\text{MA}}S_{\text{MA}} - S_{\text{VDC/MA}})$ calculated [7] for (o) random and (●) regularly alternating VDC/MA copolymers as a function of comonomer composition.

From a comparison in Table 1 of the conformational entropies calculated for VDC and MA homopolymers and the VDC/MA copolymer it can be seen that the calculated ΔS_{conf} s are positive, so the VDC/MA copolymer conformational entropies are lower than those of the weighted sum of VDC and MA homopolymer conformational entropies as plotted in Figure 1(c). As a consequence, the T_{gps} are elevated above those predicted by the Fox relation. In addition, for the same composition (50:50), the T_{gps} and ΔS_{conf} s for the regularly alternating sample are higher than those of the random sample.

Table 1. Calculated Conformational Entropies of VDC-MA Copolymer Chains [7].

Mole % MA	Stereoregularity	Sequence Distribution	S , e.u./mol of backbone bonds
0	-	-	0.754
20	<i>Atactic</i>	<i>Random</i>	0.636
40	<i>Atactic</i>	<i>Random</i>	0.579
50	<i>Atactic</i>	<i>Random</i>	0.579
50	Atactic	Regularly Alternating	0.412
50	Syndiotactic	Regularly Alternating	0.404
50	Isotactic	Regularly Alternating	0.420
60	<i>Atactic</i>	<i>Random</i>	0.591
80	<i>Atactic</i>	<i>Random</i>	0.641
100	Syndiotactic	-	0.569
100	<i>Atactic</i>	-	0.732
100	Isotactic	-	1.012

This is to be contrasted with the T_{gPS} observed in Figure 1(a) [13] and the ΔS_{confS} calculated in Table 2 for the atactic VC-MA copolymers [7]. The observed VC/MA T_{gPS} follow the Fox relation and only depend on comonomer content. This is supported by the calculated conformational entropies of the atactic VC and MA homopolymers and their atactic 50:50 random and regularly alternating copolymers, respectively, which are closely similar to each other and to that of their resultant copolymer. This means that the calculated ΔS_{confS} are close to zero, indicating little deviation from their Fox behavior as observed in Figure 1(a).

Table 2. Calculated Conformational Entropies of VC-MA Copolymer Chains [7].

Mole% MA	Stereo-regularity	Sequence distribution	S , e.u./mol of backbone bonds
0	Syndiotactic	-	0.845
0	Isotactic	-	0.900
0	Atactic	-	0.740
50	Syndiotactic	Regularly alternating	0.768
50	Isotactic	Regularly alternating	0.854
50	Atactic	Random	0.741
100	Syndiotactic	-	0.560
100	Isotactic	-	1.015
100	Atactic	-	0.725

2.2. S/pBrS Copolymer [11]

We characterized the structures and behaviors of S/pBrS copolymers made by brominating atactic polystyrene and by controlled ATRP and RAFT co-polymerization [14–18]. In Figure 2 we present the glass-transition temperatures measured for random and random-blocky comonomer sequences as a function of comonomer composition [11]. The random and random-blocky S/pBrS copolymers were made via bromination of uncontrolled free-radical polymerized atactic- (a-)

polystyrene in good and poor solvents, where the a-PS chains are relatively expanded and contracted, and produce random and random-blocky comonomer sequences [10]. Their T_{gPS} are nearly independent of comonomer sequence, and instead evidence Fox behavior with dependence solely upon comonomer composition.

Note that both random and random-blocky copolymer T_g s closely follow the additive behavior of the Fox equation, with T_g s that depend only on comonomer composition, but not upon comonomer sequences. For S/pBrS copolymers this is expected, because the conformational characteristics of PS and PpBrS homopolymers and S/pBrS copolymers are virtually identical and depend only on their tacticities [19].

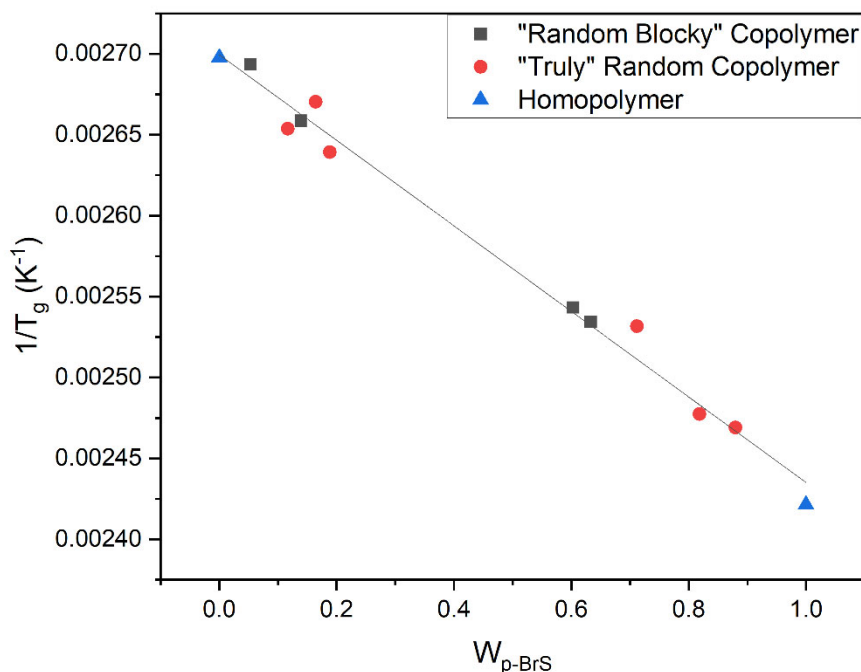


Figure 2. Glass transition temperatures of a-S/pBrS copolymers having random (circle) and random-blocky (square) comonomer sequences [11].

2.3. Amorphous aliphatic 3,4/6,6 co-polyester

In Figure 3(a) the observed T_{gPS} of random 3,4/6,6-aliphatic polyesters are plotted versus their composition (ester bonds/ CH_2 ratio) produced from propane and hexane diols and succinic and adipic acids. There it is seen that their T_{gPS} are linearly related to their compositions, or, in other words, show Fox behavior. This is expected, because the conformations of all $-CH_2-$ sequences separating ester bonds are independent of the conformations of $[-CH_2-]_3$ or $[-CH_2-]_6$ sequences on either side of the rigid planar trans ester bond adjoining them [20,21]. As seen in Figure 3(b), Fox behavior of the aliphatic 3,4/6,6 polyester T_{gp} is also demonstrated by the linear relation of $1/T_{gPS}$ to their calculated conformational entropies (S_{conf}).

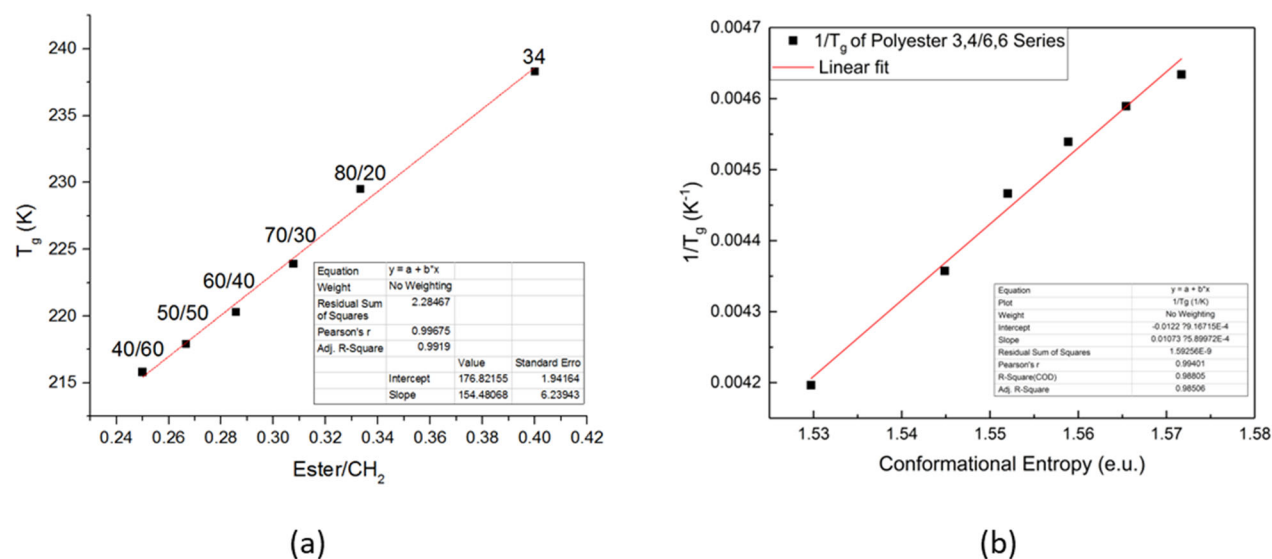


Figure 3. Amorphous aliphatic 3,4/6,6 polyester T_{gp} versus their ester bond/ CH_2 ratio (a) and $1/T_{gps}$ versus conformational entropies S_{conf} (b) (Reprinted with permission from Ref. [12]. Copyright Elsevier 2017).

3. Current Status and Future Perspectives

We have demonstrated that the comonomer dependence of copolymer glass-transition temperatures has an intramolecular origin: the conformational flexibility of their individual chains as evidenced by their conformational entropies S_{conf} s. A recent study has clearly emphasized the relatively higher importance of intra-chain effects as compared to the inter-chain interactions [22]. They went on to categorize monomers into mono-substituted (M), asymmetrical di-substituted (AD), and symmetrical di-substituted (SD) types, and proposed that the origin of the T_{gp} deviations from the linear relationship is the destruction of the special conformational structures, either as rigid or flexible local sequences, by inserting a dissimilar comonomer. Successes were met explaining the negative T_{gp} deviation in copolymers of M-type and AD-type comonomers, and the positive T_{gp} deviation in copolymers of the M-type and SD-type comonomers. However, this simplified approach was unsatisfactory for the more complex binary copolymers, especially AD–SD type copolymers [22]. The most fundamental molecular origin and the source of ΔS_{conf} reside in the pair-wise nearest-neighbor dependent rotational states, which is adequately described by the RIS model regardless of the types of comonomers used. It seems that the two hypothetical scenarios raised by the authors in reference to our approach were both caused by intramolecular backbone conformations, captured in the RIS treatment, as evidenced by the calculated ΔS_{conf} . The authors' scenario B is clearly the effect of replacing –AA– and –BB– intrachain homopolymer sequences by –AB– copolymer sequences. This may lead to ΔS_{conf} s = or < or > 0 and not just to “an excess conformational entropy”, causing the copolymer T_{gps} to be dependent solely on comonomer composition (Fox behavior) or show higher or lower T_{gps} than those linearly related

to their compositions. Thus it is an intrachain conformational effect, as we have previously demonstrated [6–12].

Though not detailed here, it should also be mentioned that the comonomer, as well as the stereosequence, dependencies of several additional copolymers have been rationalized/understood in the same way: *via* correlation with the conformational flexibilities of their individual homo- and co-polymer chains, as evidenced by their RIS conformational entropies ΔS_{conf} [6,8,9]. Negative/positive ΔS_{conf} s were calculated for random syndiotactic (s)/isotactic (i) S/Acrylonitrile (S/AN) copolymers which correlated with their observed T_{gPS} [6]. On the other hand, the ΔS_{conf} s calculated for S/poly(methyl methacrylate) (MMA) copolymers were negative no matter their stereo- or comonomer sequence [9]. This is consistent with observed T_{gPS} that are lower than predicted by the Fox relation. The observed T_{gPS} of both S/AN and S/MMA copolymers are not the result of interchain interactions.

RIS is a generalized conformational approach dependent on the types of comonomers, as each bond pair is explicitly examined and all energy levels are statistically summed along any specific chain connectivities, e.g., any regio-, stereo-, or comonomer-sequence distributions can be explicitly considered. Thus it has great potential in future studies to explain the more peculiar comonomer sequence dependent T_{gp} deviations observed for AD-SD type comonomers [23]. In addition, similar to stereosequence dependence of local conformational geometry and subsequently the dynamics of the glass transition process [24], comonomer sequence dependence of glass transition dynamics of copolymers with tunable chain architectures can be studied in combined experimental and simulation studies which ultimately contribute to the understanding of the molecular bases of polymer glass transition phenomena.

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