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NOTE

Glass Transition Temperatures of Styrene/4-BrStyrene Copolymers with Variable Co-Monomer Compositions and Sequence Distributions

Alan E. Tonelli,*[†] Young K. Jhon,[‡,§] and Jan Genzer[§]

[†]*Fiber & Polymer Science Program, North Carolina State University, Campus Box 8301, Raleigh, North Carolina 27695-8301,* [‡]*Chemical Sciences Division, Army Research Office, RTP, North Carolina 27709-2211, and* [§]*Chemical & Biomolecular Engineering, North Carolina State University, Campus Box 7905, Raleigh, North Carolina 27695-7905*

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With the obvious exceptions of phase segregated "blocky" copolymers, the glass transition temperatures, T_{gp}, of homogeneous copolymers either depend exclusively on their chemical composition,[1] as described in eq 1, or may additionally depend on the sequence distribution of their comonomers,[2] as given by eq 2:

$$(1/T_{gp}) = (W_A/T_{gA}) + (W_B/T_{gB}) \tag{1}$$

$$(1/T_{gp}) = [W_A P_{AA}/T_{gAA}] + [(W_A P_{AB} + W_B P_{BA})/T_{gAB}] + [W_B P_{BB}/T_{gBB}] \tag{2}$$

In both equations W_A and W_B are the weight fractions of comonomer units A and B. In eq 1 T_{gA} and T_{gB} are the glass transition temperatures of homopolymers poly-A and poly-B, and in eq 2 P_{AA}, $P_{AB} = P_{BA}$, P_{BB} and T_{gAA}, T_{gAB}, T_{gBB} are the probabilities/populations of and glass-transitions temperatures contributed by each distinct comonomer diad.

Figure 1 illustrates both behaviors, as observed in methacrylate (MA) copolymers with vinyl chloride (VC) and vinylidene chloride (VDC).[3] While VC−MA copolymers follow the weight-additive relation (eq 1) of Fox et al.,[1] VDC−MA copolymers deviate strongly, with observed T_{gp}s far above those given by the Fox equation, even though the T_gs of PMA and PVDC homopolymers are nearly identical. This is particularly evident when comparing the T_{gp}s of random and regularly alternating VDC−MA copolymers, each having the same overall 50:50 molar composition. The 50:50 random VDC−MA copolymer has a T_{gp} some 35 °C above that predicted by the Fox relation (eq 1), while the regularly alternating sample's T_{gp} is an additional 15 °C higher than that of the 50:50 random copolymer. The contrasting T_{gp} behavior evidenced by VC−MA and VDC−MA copolymers was previously suggested to be the consequence of the conformational flexibilities of their individual copolymer chains.[4−6]

There we put forward the following relationship to describe the deviation between the glass-transition temperatures observed for copolymers T_{gp}(obs) and those predicted by the Fox

Relation (eq 1), T_{gp}(Fox), dependent solely upon the overall weight-average chemical composition of comonomers:

$$T_{gp}(\mathrm{obs}) - T_{gp}(\mathrm{Fox}) \propto \Delta S_{conf} \tag{3}$$

where $\Delta S_{conf} = (X_A\, S_A + X_B S_B) - S_{A/B}$, X_A and X_B are the mole fractions of A and B comonomer units and S_A, S_B, and $S_{A/B}$ are the conformational entropies of the poly-A and poly-B homopolymers and the A/B copolymers. As seen in Figure 1 and Table 1 below, ΔS_{conf}s calculated for VC−MA copolymers are ≈0, independent of both comonomer composition and comonomer sequence distribution. In contrast, ΔS_{conf}s calculated for VDC−MA copolymers are substantially >0, with magnitudes dependent on both comonomer compositions and comonomer sequence distributions.

For example, while the conformational entropies calculated[5] for atactic 50:50 VC−MA, PVC, and PMA are closely similar (0.741, 0.740, and 0.725, respectively), those calculated for atactic 50:50 VDC−MA, PVDC, and atactic PMA are (0.579, 0.754, and 0.732, respectively). Thus, $\Delta S_{conf} = (X_A S_A + X_B S_B)$ - $S_{A/B} \approx 0$ for VC−MA and >0 for VDC/MA copolymers. Furthermore, a comparison of the conformational entropies calculated for atactic 50:50 random and regularly alternating VDC−MA copolymers (0.579 vs 0.412) makes it apparent why ΔS_{conf} and T_{gp} for regularly alternating VDC−MA are both greater than those of 50:50 random VDC−MA.

The approach embodied in eq 3, which relates comonomer sequence dependent deviations from strictly comonomer composition dependent T_{gp}(Fox) to the comonomer sequence dependent conformational flexibilities of copolymers, as gauged by their ΔS_{conf}s, was also successfully applied to rationalize the comonomer sequence dependent T_gs observed for copolymers of S and α-methyl-S with acrylonitrile and methyl methacrylate.[4,6]

In the present work, we extend this correlation to poly(styrene-*co*-4-bromostyrene) (PBr$_x$S) copolymers, where x is the mole fraction of 4-BrS units, principally because the conformational characteristics/RIS models of S and 4-BrS homopolymers and PBr$_x$S copolymers are expected to be closely similar due to the large distances between 4-Br in the side-chain and the atoms of the backbone. This is demonstrated by the ^{13}C NMR spectra recorded for PS and two PBr$_{0.6}$S copolymers[7] that are shown in Figure 2. Unlike the resonances of the side-chain phenyl carbons, the resonance frequencies of the backbone methine and methylene carbons show no dependence on whether they belong to a S or a 4-BrS repeat unit. Consequently, ^{13}C NMR can only be employed to determine the chemical compositions and not the sequence distributions of comonomers in S/4-BrS copolymers.

Control of the comonomer sequences in PBr$_x$S copolymers was attempted by brominating PS in solvents of different quality to form both random (r) and somewhat blocky (b) copolymers with the same overall comonomer compositions.[7] Specifically, 1-chlorodecane (CD), 1-chloroundecane (CUD), and 1-chlorododecane (CDD), with Θ-temperatures for PS of 6.6, 32.8, and 58.6 °C, respectively, were employed. PSs brominated at 33 °C in CD, CUD, and CDD to the same levels were expected to produce PBr$_x$S copolymers with increasingly blocky comonomer sequences,

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*Corresponding author. E-mail: alan_tonelli@ncsu.edu.

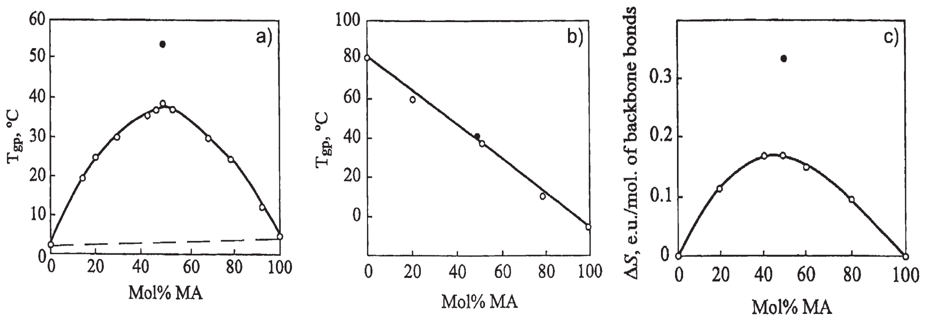

Figure 1. Glass-transition temperature comonomer composition behaviors of VDC−MA (a) and VC−MA (b) copolymers:[3] (o) random; (●) alternating. (c) $\Delta S = (X_{VDC}S_{VDC} + X_{MA}S_{MA}) - S_{VDC/MA}$ calculated[5] as a function of comonomer composition: (o) random; (●) alternating.

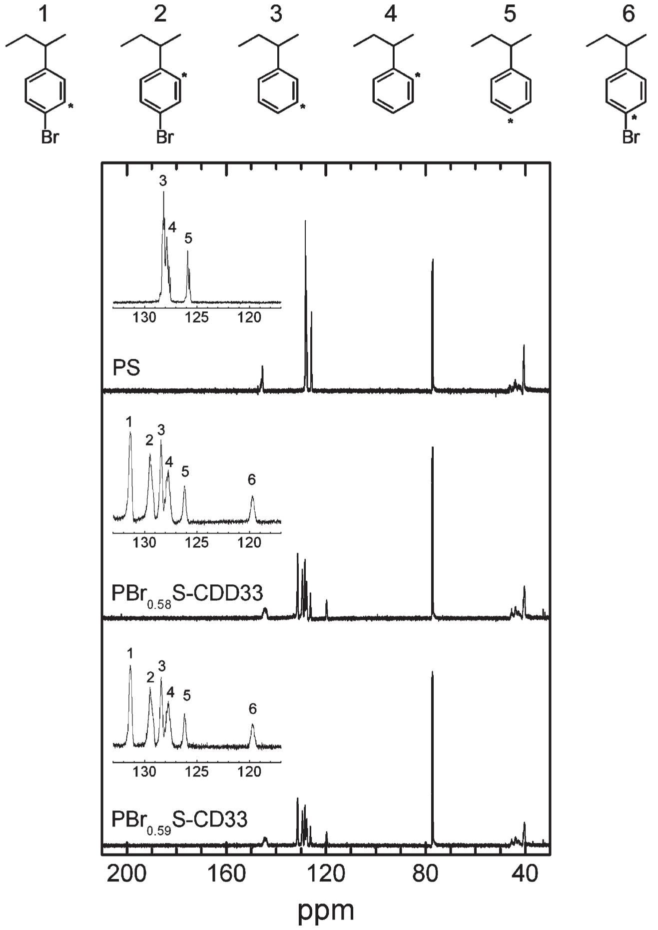

Figure 2. ^{13}C NMR spectra of PS (top), PBr$_{0.58}$S-CDD33 (middle), and PBr$_{0.59}$S-CD33 (bottom); the peak labels in the spectra mark the resonances of phenyl ring carbons in the *ortho*, *meta*, and *para* positions (shown in the upper panel of the figure) in PS and PBr$_x$Ss. The ^{13}C NMR data confirm that the bromination occurred exclusively in the *para* position of the phenyl ring of PS, while the aliphatic part of the PS chain and its ^{13}C NMR spectrum are not affected by the bromination. The mole fraction of 4-BrS in PBr$_x$S can be obtained from the ratios of peaks 1 and 3, 2 and 4, or 6 and 5.

because of the contraction of PS coils produced by the decrease in solvent quality. Since the comonomer sequences of 4-BrS in PBr$_x$S copolymers cannot be determined with ^{13}C NMR, or by any other spectroscopic means, to confirm this expectation, their Kerr constants, as observed by measuring the birefringence produced upon application of a strong electric field to their dilute solutions,[8] were determined.[7] The Kerr constants measured for PBr$_x$S copolymers with the same composition decrease as the blockiness of their comonomer sequences increased, as was anticipated from the Kerr constants estimated for them[7,8] using the RIS conformational model appropriate to PS.[9] On the basis of the assumption that completely random bromination occurred at $T > \Theta$, and comparison with the measured and estimated Kerr constants for 40:60 S:4-BrS copolymers (PBr$_{0.60}$S) brominated at $T \leq \Theta$, suggested that the lengths of their 4-BrS blocks may be in the range of 10−20 consecutive 4-Brs monomer units.

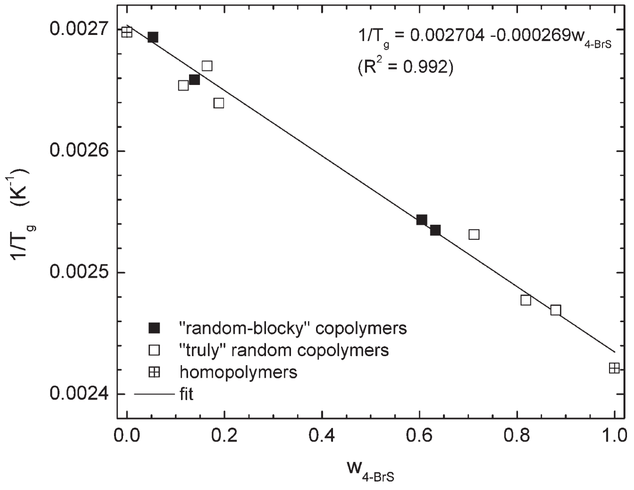

Figure 3. Glass transition temperatures of PBr$_x$S copolymers having random (open symbols) and random-blocky (closed symbols) comonomer sequence distributions.

As discussed in our earlier publication,[7] single composition-dependent T_gs were observed for all of our PBr$_x$S copolymers, regardless of their random or blocky comonomer sequences, and were intermediate to those of PS and P4-BrS homopolymers, as observed in either their neat samples or in their phase-segregated physical mixtures. On the basis of DSC-observed glass-transitions, all our PBr$_x$Ss appear to be homogeneous, single-phase solids regardless of whether their comonomer sequences are random or blocky. Additionally, PBr$_x$S copolymers with the same comonomer compositions, but with distinct random and blocky distributions of comonomer sequences, had closely similar T_gs. This behavior is clearly illustrated in Figure 3 for an expanded set of PBr$_x$S copolymers,[7,10] where only their chemical compositions and not their comonomer sequences are seen to affect their glass-transition temperatures, as indicated by their excellent "fit" to the Fox relation (eq 1). This result further strengthens the previously suggested relationship (cf. Equation 3) between the comonomer sequence dependent (or not) glass-transition temperatures of copolymers and the conformational flexibilities of their individual chains, as characterized by their conformational entropies ΔS_{conf}s. This is particularly relevant for the PBr$_x$S copolymers discussed here, because they all have essentially identical conformational characteristics,[11] leading to internal conformational flexibilities and entropies that are independent of both the composition and sequence distribution of their comonomers.

Table 1. Conformational Entropies of VDC−MA and VC−MA Copolymer Chains of 500 Backbone Bonds

copolymer	mole % of MA	stereoregularity[a]	co-monomer sequence distribution	conformation entropy S (eu/mol of backbone bonds)
VDC−MA	0			0.754[b]
VDC−MA	20	A	random	0.636[b,d]
VDC−MA	40	A	random	0.579[b,d]
VDC−MA	50	A	random	0.579[b,d]
VDC−MA	50	A	alternating	0.412[b,d]
VDC−MA	50	S	alternating	0.404[b]
VDC−MA	50	I	alternating	0.420[b]
VDC−MA	60	A	random	0.591[b,d]
VDC−MA	80	A	random	0.641[b,d]
VDC−MA	100	S		0.569[b]
VDC−MA	100	A		0.732[b]
VDC−MA	100	I		1.012[b]
VC−MA	0	S		0.845[c]
VC−MA	0	I		0.900[c]
VC−MA	0	A		0.740[c,d]
VC−MA	50	S	alternating	0.768[c]
VC−MA	50	I	alternating	0.854[c]
VC−MA	50	A	random	0.741[c,d]
VC−MA	100	S		0.560[c]
VC−MA	100	I		1.015[c]
VC−MA	100	A		0.725[c,d]

[a] A ≡ atactic, I ≡ isotactic, and S ≡ syndiotactic. [b] Calculated at 5 °C. [c] Calculated at 40 °C. [d] Average of 10 Monte Carlo generated chains, where the mean deviation from the average entropy is ≈1−2%.

It may be worth emphasizing that eqs 1 and 2 are not only distinguishable for the bases chosen to describe copolymer T_gs, ie., comonomer composition and comonomer sequence distributions, respectively, but eq 1 is essentially an intermolecular approach, while eq 2 is intramolecular. This was noted recently for eq 1 by Pinal,[13] who also took an intermolecular approach, but for the first time in the form of the entropy of mixing, to correlate the T_gs of polymer blends. Like eq 2 our approach (eq 3) is clearly intramolecular, and its success in describing the comonomer sequence dependence of T_gs in homogeneous copolymers provides the underlying physical/chemical bases for eq 2, i.e., the relative conformational entropies (equilibrium flexibilities) of copolymers and their constituent homopolymers, which may or may not depend on their comonomer sequence distributions. However, it remains to be demonstrated if an intermolecular approach, such as Pinal's (entropy of mixing),[13] can ever predict distinct T_gs for 50:50 random and regularly alternating copolymers, as observed for VDC−MA copolymers[3] (Figure 1c) and reproduced by our intramolecular conformational entropy approach (Figue 1 c).

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