# Possible Molecular Origin of Sequence Distribution–Glass Transition Effects in Copolymers

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ABSTRACT: The conformational entropies of the various dyads, *i.e.*, A–A, B–B, and A–B or B–A, present in a copolymer of monomer units A and B are calculated through the utilization of semiempirical potential energy functions. It is assumed that the glass transition temperature, $T_g$, is inversely related to the intramolecular equilibrium flexibility of a polymer chain as manifested by its conformational entropy. If the conformational entropy of A–B or B–A dyads is larger (smaller) than half the sum of the entropies of A–A plus B–B dyads, then the $T_g$ of the copolymer should be lower (higher) than that predicted by additive relations such as the Fox equation. This approach has been applied to the alternating vinyl copolymer composed of styrene (S) and acrylonitrile (AN) monomer units, where the stereoregularity (syndiotactic and isotactic) of the various dyads was explicitly considered. Based on the calculated conformational entropies of the S–S, AN–AN, and S–AN dyads of various stereoregularity, in addition to the total conformational entropies of various copolymer chains estimated through adoption of the rotational isomeric state model, the following conclusions, which are supported by experimental data in the literature, may be drawn: (1) $T_g$ for the isotactic (syndiotactic) copolymers should be higher (lower) than $T_g$ (Fox), and (2) the $T_g$'s of the regularly alternating isotactic (syndiotactic) copolymers should be higher (lower) than the $T_g$'s of the random copolymers with the same overall monomer composition. It therefore appears that the sequence distribution $T_g$ effects observed in many copolymers may have an intramolecular origin in the form of specific molecular interactions between adjacent monomer units, which can at least be qualitatively characterized by estimating the resultant conformational entropy.

Copolymer glass transition temperatures $T_{gp}$ are usually predicted by additive relations such as the Fox equation[1]

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

where $W_A$ and $W_B$ and $T_{gA}$ and $T_{gB}$ are the weight fractions of the comonomer units A and B and the glass transition temperatures of their homopolymers, respectively. However, for many copolymers[2–7] this simple bulk additive relation fails, and it becomes necessary to account for the sequence distribution[2,7] of A and B monomer units, in addition to the overall composition of comonomer units as given by $W_A$ or $W_B$. Such deviations from the bulk additive behavior predicted by the Fox equation imply specific intramolecular (intrachain) interactions which both affect the glass transition temperature of copolymers and depend on the precise sequence of monomer units in the copolymer.

In an attempt to substantiate and define the intramolecular source(s) of such sequence distribution–$T_{gp}$ effects the conformational entropies of the various dyads in a styrene (S)–acrylonitrile(AN) copolymer were estimated, with the hope that the sequence distribution-dependent equilibrium chain flexibilities, as characterized by the conformational entropies, would correlate with copolymer glass transition temperatures. Estimation of the conformational entropies is made possible by employing semiempirical potential functions to calculate the energies of various dyad conformations.

Figure 1 presents a schematic representation of those portions of the copolymer chain considered in the conformational energy calculations. The polymer chain segment in Figure 1a includes all atoms whose distances of separation depend upon the two backbone rotation angles $\varphi_1$ and $\varphi_2$ flanked by asymmetric centers. The distances between the atoms in Figure 1b depend on the backbone rotations $\varphi_3$ and $\varphi_4$ flanking a single asymmetric center.

The conformational energies of these two chain segments were calculated through use of a 6–12 plus coulombic potential to account for the nonbonded van der Waals and electrostatic interactions. In addition, the three-fold inherent resistance to rotation about the backbone C–C bonds was included with a barrier[8] of 3.0 kcal/mol. The potential constants of Brant, *et al.*,[9,10] were used and those characterizing the interactions of the nitrile group were estimated in the usual fashion.[10] Partial charges were assigned to the asymmetric carbon atom and the carbon atom of the phenyl group attached to it and to the C and N atoms of the nitrile group based on the bond dipole moments given by Minkin, *et al.*[11] Dielectric constants[12] of 2.5, 6.5, and 4.5 were used to evaluate the electrostatic interactions in S–S, AN–AN, and S–AN or AN–S dyads, respectively.

Rotation in 30° increments about the backbone bonds was permitted, while the phenyl groups were allowed to deviate[13,14] ±30° in 10° increments about the position where the plane of the phenyl ring bisects the valence angle at the asymmetric carbon atom to which it is attached. The carbon and hydrogen atoms in the meta and para positions of the phenyl group were not considered[14] in the intramolecular interactions.

**Table I**
**Dyad Conformational Entropies**

| Dyad | Stereo-regularity[a] | $S$,[b] eu/mol of dyad |
|---|---|---|
| S–S | S | 3.434 |
| S–S | I | 4.013 |
| AN–AN | S | 3.981 |
| AN–AN | I | 4.006 |
| S–AN or AN–S | S | 3.897 |
| S–AN or AN–S | I | 3.647 |

[a] I ≡ isotactic; S ≡ syndiotactic. [b] Calculated at 100° = $T_g(\mathrm{S}) \approx T_g(\mathrm{AN})$

The dyad conformational entropies were estimated from the conformational energies according[10] to

$$S = R \ln z + \frac{RT}{z}\left(\frac{\mathrm{d}z}{\mathrm{d}T}\right) \tag{1}$$

$$z = z_{\text{dyad}} = \sum_{(\varphi_1, \varphi_2)} \exp\{-E(\varphi_1, \varphi_2)/RT\} \tag{2}$$

and are presented in Table I for the various dyads as a function of stereoregularity.[15] Adoption of the rotational isomeric state (RIS) model[16] of polymer chains together with the calculated dyad conformational energies permits

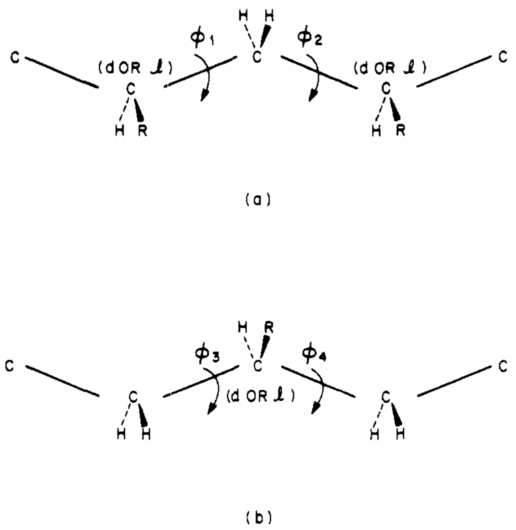

**Figure 1.** (a) Portion of S–AN chain (R ≡ $C_6H_5$ or C ≡ N) whose conformation depends only on the backbone rotations $\varphi_1,\varphi_2$ flanked by asymmetric centers. (b) Portion of S–AN chain whose conformation depends only on the backbone rotations $\varphi_3,\varphi_4$ flanking an asymmetric center.

evaluation of the conformational entropies of copolymer chains of various sequence distribution and stereoregularity. Statistical weight matrices **U**′ and **U**″, corresponding to the pairs of rotations in Figures 1b and 1a, respectively, are constructed from the Boltzmann factors of the calculated conformational energies. As an example, for the dyad flanked by asymmetric centers (Figure 1a)

$$\mathbf{U}'' = \begin{array}{c|ccc} & & \varphi_2 & \\ \varphi_1 & t & g^+ & g^- \\ \hline t & u_{tt} & u_{tg^+} & u_{tg^-} \\ g^+ & u_{g^+t} & u_{g^+g^+} & u_{g^+g^-} \\ g^- & u_{g^-t} & u_{g^-g^+} & u_{g^-g^-} \end{array} \tag{3}$$

where

$$u_{\alpha\beta} = \exp[-E(\varphi_1 = \alpha, \varphi_2 = \beta)/RT] \tag{4}$$

and $\alpha,\beta = t,g^+,g^-$ ($\varphi_{1,2} = 0, 120, 240°$). Matrix multiplication methods described by Flory[17] are used to obtain the partition function $z_{\mathrm{chain}}$ ($z = z_{\mathrm{chain}}$ in eq 1) needed to evaluate the conformational entropy of the copolymer chain, from the statistical weight matrices. The conformational entropies evaluated for all isotactic and all syndiotactic S–AN copolymer chains of 500 bonds using the RIS scheme and the matrix multiplication methods are presented in Table II.

The following observations[18] are drawn from the calculated results presented in Tables I and II: (1) for isotactic copolymer chains, $S_{\mathrm{S,AN}} < \frac{1}{2}(S_{\mathrm{S,S}} + S_{\mathrm{AN,AN}})$; (2) for syndiotactic copolymer chains, $S_{\mathrm{S,AN}} > \frac{1}{2}(S_{\mathrm{S,S}} + S_{\mathrm{AN,AN}})$; and (3) for isotactic (syndiotactic) copolymers $S_{\mathrm{Random}} > S_{\mathrm{Regular}}$ ($S_{\mathrm{Random}} < S_{\mathrm{Regular}}$). Direct identification of conformational entropy with equilibrium chain flexibility leads one to conclude that isotactic (syndiotactic) S–AN dyads are less (more) flexible than the weighted average of isotactic (syndiotactic) S–S and AN–AN dyads. In addition, the calculated conformational entropies indicate that regularly alternating isotactic (syndiotactic) S–AN copolymers are less (more) flexible than the corresponding random copolymers with the same overall comonomer composition.

Experimental studies[2,4,7] of the glass transition behavior of S–AN copolymers have led to the following observations: (1) copolymers polymerized at low temperatures, which presumably favor syndiotactic dyad placements, have $T_{\mathrm{gp}}$'s $< T_{\mathrm{g}}$ (Fox); (2) copolymers polymerized at high temperatures, which presumably favor isotactic dyad placements, have $T_{\mathrm{gp}}$'s $> T_{\mathrm{g}}$ (Fox); and (3) regularly alternating copolymers have higher $T_{\mathrm{gp}}$'s than the corresponding random copolymers with the same overall monomer composition when both are prepared at high temperatures (isotactic dyad placements). Each of these experimental observations can be rationalized[19] on the basis of equilibrium chain flexibility, as manifested by the calculated conformational entropies, if the glass transition temperature is assumed to be inversely related to the intramolecular chain flexibility or conformational entropy.

### Table II
### Conformational Entropies of S-AN Copolymers Obtained from RIS Method

| Copolymer sequence distribution | $F_{\mathrm{S}}$[a] | Stereo-regularity[b] | $S$,[c] eu/mol of backbone bond |
|---|---|---|---|
| Regular | 0 | I | 1.323 |
| Regularly alternating | 50 | I | 1.137 |
| Random[d] | 50 | I | 1.148 |
| Regular | 100 | I | 1.015 |
| Regular | 0 | S | 1.381 |
| Regularly alternating | 50 | S | 1.225 |
| Random[d] | 50 | S | 1.198 |
| Regular | 100 | S | 1.006 |

[a] $F_{\mathrm{S}}$ ≡ mole fraction of styrene units. [b] I ≡ isotactic; S ≡ syndiotactic. [c] Calculated at $100° = T_{\mathrm{g}}(\mathrm{S}) \approx T_{\mathrm{g}}(\mathrm{AN})$. [d] Average of ten Monte Carlo generated chains, where the mean deviation for each chain is ±0.5% from the average.

Dyad and chain conformational entropies have also been calculated for α-methylstyrene (α-S)–acrylonitrile and α-methylstyrene–methylmethacrylate (MMA) copolymers, which show respectively negative deviations from and agreement with the Fox relation in their glass transition behavior.[4,7] Only syndiotactic dyad placements were considered and led to $S_{\alpha\text{-S,AN}} > \frac{1}{2}(S_{\alpha\text{-S},\alpha\text{-S}} + S_{\mathrm{AN,AN}})$ and $S_{\alpha\text{-S,MMA}} < \frac{1}{2}(S_{\alpha\text{-S},\alpha\text{-S}} + S_{\mathrm{MMA,MMA}})$. The calculated entropies are consistent with the glass transition temperatures observed for α-S–AN copolymers, which are lower than those predicted by the Fox relation, but predict $T_{\mathrm{gp}}$'s for α-S–MMA copolymers to be higher than those observed, which are correctly predicted by the Fox relation. However, it must be mentioned that only syndiotactic dyad placements were considered, and it is well known[20] that the glass transition temperatures of disubstituted vinyl homopolymers like poly-MMA are very sensitive to stereoregularity. Consequently, in those copolymers containing two disubstituted vinyl monomers, sequence distribution–$T_{\mathrm{gp}}$ effects may be overwhelmed and masked by stereochemical effects.

In any event, the successful correlation[21] of glass transition temperatures with sequence distribution and stereoregularity in terms of the equilibrium chain flexibility (conformational entropy) of the S–AN copolymers discussed in this preliminary report is sufficiently encouraging to warrant further investigation. As a result, we are initiating a program to prepare and carefully characterize the sequence distribution, stereoregularity, and $T_{\mathrm{gp}}$'s of a series of S–AN copolymers for the purpose of subjecting to more stringent comparisons with experiment the idea that an inverse relationship exists between the $T_{\mathrm{gp}}$ and the equilibrium flexibility of a copolymer chain.

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(18) None of these observations are qualitatively affected by ignoring the electrostatic interactions. The nonbonded steric, or van der Waals, interactions dominate the conformational energy estimates.

(19) *It is clearly not necessary to postulate*[4] *the existence of interactions*, such as are possible between the $\pi$-electron clouds of the phenyl ring and nitrile group, any more exotic in nature than those of the ordinary van der Waals type in order to achieve this qualitative understanding.

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(21) It must be stressed that the proposed correlation between the equilibrium chain flexibility and the $T_{\text{gp}}$'s of copolymers is applicable to the sequence distribution-dependent deviations from the simple bulk additive behavior predicted by the Fox relation, and should not be construed as a means for predicting the absolute value of the glass transition temperature.

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# Calculation of Neutron Diffraction Pattern by Polymer Chains in the Bulk State

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ABSTRACT: The incompressibility of the bulk polymer is assumed in order to calculate the neutron diffraction pattern from labeled polymer chains in a matrix of unlabeled chains. The scattering law obtained is the Fourier transform of the pair correlation function of atoms along the labeled polymer chain. When the scattering vector $\mathbf{q}$ is small relative to the inverse monomer dimensions we find that the chain has a Gaussian configuration in the bulk polymer. In the range of higher values of $q$ the diffraction pattern is associated with the short-range interactions (corresponding to the transfer matrix) which characterize the polymer studied. The neutron diffraction pattern is obtained from a computer experiment using hydrogenous $n$-alkanes in a matrix of deuterated $n$-alkanes in a $q$ range between $10^{-2}$ and 2.5 Å$^{-1}$. The results are discussed in order to obtain experimental evidence about the transfer matrix.

In the discussion of the pair correlation function $p(r)$ of atoms along the chain,[1] three ranges of magnitude of $r$ are usually considered. For large distance $r \sim R$ where $R^2 = \langle R^2 \rangle$ is the mean-squared end-to-end distance, the analysis of $p(r)$ is carried out in terms of the moments of $r$. In the intermediate range $l < r < R$, where $l^2$ is the mean-squared length of a statistical element, $p(r)$ has the characteristic dependence $r^{-\alpha}$, $1 \leq \alpha \leq 2$. In the short correlation distance range $r \leq l$, one expects to find patterns associated with the short-range interactions. There is, however, no analytical form for $p(r)$ in this range.

The ranges of $r$ are naturally transposed into ranges of the momentum transfer $q$, since the Fourier transform of $p(r)$ is the scattering law $S(q)$ for a single chain.

The study of the first two ranges has shown a close relationship between $p(r)$ and the chain environment. This is particularly clear in the case of the molecular mass dependence of the second moment and in the case of the exponant $\alpha$. Similarly, one may expect that the diffraction patterns for $q \geq l^{-1}$ will reflect chain environment, although perhaps for different reasons. The main interest in the study of this range is, however, the detailed nature of the conformation. The analysis should give evidence of conformational differences among chemically different polymers. It should also reveal local modifications due to environment, such as the partial alignment predicted in the amorphous state.

Conformation is an expression of enthalpy and conformational entropy. The latter is calculated from internal rotation potential barriers and nearest neighbor interactions. The result of the calculation is expressed in the form of a "transfer" matrix.[2] Values of the matrix elements are determined by calorimetric measurements. They are consistent with the value of $l$ measured by scattering experiment at $q \leq l^{-1}$. The study of the range $q \geq l^{-1}$ will bring, however, a closed relationship between the observed conformation and the transfer matrix.

There are yet few experimental results in this momentum transfer range. If one considers chains dispersed in a solvent, the contrast between solvent and solute will be too small to be observed, as $q$ increases away from the $q^{-\alpha}$ singularity. The diffraction pattern will mostly reflect the solvent liquid state. Scattering by bulk material yields the polymer diffraction patterns. However, the pair correlation along the chain and the pair correlation between chains are not easily discernible from the intensity momentum transfer dependence.

The possibility of labeling chains by deuteration[3] and the use of high flux neutron sources has suggested experiments which give complementary information with respect to the unlabeled bulk material. These experiments have proven to be very successful in the first two momentum ranges[4] ($q \leq l^{-1}$). We investigate here the condition for the observation of diffraction patterns of labeled chains in the