Intramolecular Interactions as the Source of Sequence Distribution–Glass Transition Effects and Dilute Solution Properties of Styrene–Methyl Methacrylate Copolymers

Alan E. Tonelli

Bell Laboratories, Murray Hill, New Jersey 07974. *Received November 30, 1976*

ABSTRACT: Conformational energies are estimated for the dyads composed of two styrene (S) units, two methyl methacrylate (MMA) units, and neighboring S and MMA units which constitute the homo- and copolymers of styrene and methyl methacrylate. These dyad energies are used to evaluate the isolated chain conformational energies and entropies of S, MMA, and S–MMA homo- and copolymers, through adoption of the rotational isomeric state model of polymer chains and utilization of matrix multiplication techniques convenient for calculating conformationally averaged chain properties. Independent of sequence distribution and stereoregularity the conformational entropies calculated for S–MMA copolymers are found to exceed the weighted sum of S and MMA homopolymer entropies indicating an increase in equilibrium chain flexibility for the S–MMA copolymers. The increase in conformational freedom found here for the copolymers can explain the observations of Beevers that the glass transition temperatures (T_g) of S–MMA copolymers are lower than the T_g's of the constituent homopolymers. Calculated copolymer conformational energies are found to equal or exceed the weighted sum of the homopolymer energies consistent with the observations of Stockmayer et al. on the dilute solution behavior of S–MMA copolymers which indicate repulsive intramolecular S–MMA interactions.

It has recently been demonstrated[1-4] that the sequence distribution–glass transition effects observed in many copolymer systems[5] can be rationalized in terms of the equilibrium intramolecular (intrachain) flexibilities of these copolymers as characterized by their conformational entropies. Copolymers with entropies greater (smaller) than the weighted sum of the constituent homopolymer entropies are expected to show glass transition temperatures, T_g, lower (higher) than those predicted by bulk additive relations such as the Fox equation.[6]

The sequence distribution–T_g effects expected, based on the calculated conformational entropies, were borne out[1-4] for the styrene–acrylonitrile, α-methylstyrene–acrylonitrile, vinylidene chloride–methyl acrylate, vinyl chloride–methyl acrylate, vinylidene chloride–vinyl chloride, and vinyl chloride–vinyl acetate copolymer systems, where positive, negative, and no deviations from Fox-like bulk additive behavior are displayed by one or another of these copolymers.

In the case of the styrene (S)–methyl methacrylate (MMA) copolymer system not only have the sequence distribution–T_g effects been determined,[7] but Stockmayer et al.[8] have studied the dilute solution properties of S–MMA which lead to a characterization of the nature of the intramolecular interactions between S and MMA units in the copolymer chains. For these reasons we describe here calculations of the conformational entropy and energy of isolated S–MMA copolymer chains as a function of sequence distribution and stereoregularity in an effort to determine whether or not the above-mentioned solid-state behavior and dilute solution properties of this copolymer system can be understood on the molecular level.

Description of Calculations

Conformational entropies and energies are obtained in the usual way[9,10] from the configurational partition functions of the polymer chains.

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

$$E = \frac{RT^2}{z}\left(\frac{\mathrm{d}z}{\mathrm{d}t}\right) \tag{2}$$

The configurational partition function is evaluated through adoption of the rotational isomeric state (RIS) model[11] of polymer chains and utilization of convenient matrix multiplication techniques.[12] For a polymer chain of n backbone bonds

$$z = J^* \prod_{i=2}^{n-1} (U_i) J \tag{3}$$

where J^* and J are the $1 \times \nu$ and $\nu \times 1$ vectors

$$J^* = [10000\ldots0];\ J = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} \tag{4}$$

and U_i is the $\nu \times \nu$ statistical weight matrix for bond i

$$U_i = \begin{array}{c|ccc} \phi_{i-1} \backslash \phi_i & \alpha & \beta & \gamma \\ \hline \alpha & \mu_{\alpha\alpha} & \mu_{\alpha\beta} & \mu_{\alpha\gamma} \\ \beta & \mu_{\beta\alpha} & \mu_{\beta\beta} & \mu_{\beta\gamma} \\ \gamma & \mu_{\gamma\alpha} & \mu_{\gamma\beta} & \mu_{\gamma\gamma} \end{array} \tag{5}$$

U_i consists of Boltzmann factors $\mu_{\alpha\beta;i} = \exp(-E_{\alpha\beta;i}/RT)$ of the pairwise dependent backbone conformational energies $E_{\alpha\beta;i} = E(\phi_{i-1} = \alpha,\ \phi_i = \beta)$.

The conformational energies required in the construction of the statistical weight matrices are obtained by evaluating the energies of the dyad fragments illustrated in Figure 1. Approximate potential energy functions,[13-15] which were described earlier[1-3] and include a 6–12 plus coulombic potential to account for the nonbonded van der Waals and electrostatic interactions and an inherent threefold resistance to rotation about backbone C–C bonds with a 3.0 kcal/mol barrier,[16] are used in the dyad energy calculations. The potential function constants, dielectric constant, and polymer chain geometry employed in previous copolymer studies[1-3] are also used here.

Rotation in 30° increments is permitted about each of the backbone bonds and about the C–C_6H_6 and C–(C(O)–O–CH_3) side chain bonds, where the ester bond in MMA side chains is fixed in the trans conformation.[15] The statistical weights $\mu_{\alpha\beta}$ are obtained from the conformational energies corresponding to the three staggered backbone rotational states

Table I
Conformational Entropies and Energies of S–MMA Copolymer Chains

Mol % S	Stereo-regularity[a]	Sequence distribution	S, eu/mol of backbone bonds	E, kcal/mol of backbone bonds
0	S		0.510	0.17
0	I		1.457	0.40
25	S	Random	0.871[b]	0.26[b]
50	S	Random	1.086[b]	0.34[b]
50	S	Regularly alternating	1.444	0.39
50	I	Regularly alternating	1.659	0.68
75	S	Random	1.163[b]	0.43[b]
100	S		1.082	0.51
100	I		1.218	0.54

[a] S ≡ syndiotactic; I ≡ isotactic. [b] Average of ten Monte Carlo generated chains, where the mean deviation from the average is ca. 1–2%.

Table II
Difference between Copolymer and the Weighted Sum of Homopolymer Conformational Entropies and Energies for S–MMA Copolymers

X ≡ mol fraction S	Stereo-regularity[a]	Sequence distribution	ΔS, eu/mol of backbone bonds	ΔE, kcal/mol of backbone bonds
0			0	0
0.25	S	Random	0.217	0.01
0.50	S	Random	0.290	0
0.50	S	Regularly alternating	0.648	0.05
0.50	I	Regularly alternating	0.321	0.21
0.75	S	Random	0.223	0.01
1.00			0	0

[a] S ≡ syndiotactic; I ≡ isotactic.

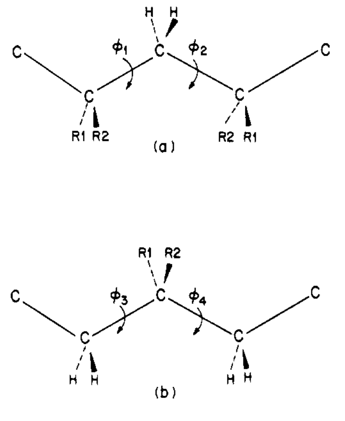

Figure 1. (a) Portion of a S–MMA chain (R1, R2 ≡ H and C_6H_5 or CH_3 and C(O)–O–CH_3) whose conformation depends only upon backbone rotations ϕ_1, ϕ_2 flanking a methylene group. (b) Portion of a S–MMA chain (R1 ≡ H or CH_3, R2 ≡ C_6H_5 or C(O)–O–CH_3) whose conformation depends only on the backbone rotations ϕ_3, ϕ_4 flanking a substituted carbon atom.

($\nu = 3$), trans ($\phi = 0°$) and gauche ± ($\phi = \pm 120°$). Temperatures[17] of 130 and 72 °C [$\simeq \frac{1}{2}(T_g(\text{S}) + T_g(\text{MMA}))$] are employed to calculate the statistical weights of syndiotactic and isotactic homopolymers and copolymers, respectively.

Monte Carlo methods are used to generate S–MMA copolymer chains with random sequence distributions. In addition, the conformational entropy and energy are calculated for the regularly alternating copolymer. Each chain is 500 bonds in length and has either syndiotactic or isotactic stereoregularity, i.e., neighboring C_6H_5 and/or C(O)–O–CH_3 side groups lie on opposite, or the same, sides of the chain backbone, respectively, in the all trans or planar zigzag conformation (see Figure 1).

Results and Discussion

Conformational entropies and energies calculated for S–MMA copolymers of differing monomer composition, sequence distribution, and stereoregularity are presented in Table I along with the entropies and energies calculated for the S and MMA homopolymer chains. The difference between the copolymer entropy (energy) and the weighted sum of homopolymer entropies (energies) $\Delta S(\Delta E)$, e.g.,

$$\Delta S = S_{\text{S-MMA}} - [XS_{\text{S}} + (1 - X)S_{\text{MMA}}] \qquad (6)$$

is presented in Table II.

It is clear that independent of sequence distribution and stereoregularity $\Delta S > 0$, i.e., at equilibrium the S–MMA copolymers are more flexible than the weighted flexibilities of their constituent homopolymers. This would lead to the expectation[1–3] that the T_g's of these copolymers should be lower than predicted by bulk additive relations such as the Fox equation. This expectation is indeed borne out in the work of Beevers[7] who did find the T_g's of S–MMA copolymers to deviate negatively from the Fox equation. In addition the entropy calculated for the regularly alternating copolymer exceeds that obtained for the 50:50 random copolymer. This is consistent with the observations of Hirooka and Kato[19] who find the regularly alternating copolymer to have a T_g 8 °C below the 50:50 random copolymer.

Although the conformational entropies of S–MMA copolymers are larger than the weighted sum of homopolymer entropies, i.e., the number of conformations of comparable energy is greater for the copolymers, the average energies of the copolymer conformations are higher than those of the homopolymers. Thus, as we see in Table II, $\Delta E \geq 0$. This means that on balance the interactions between S and MMA monomer units are repulsive.

Dilute solution studies of S–MMA copolymers by Stockmayer et al.[8] also seem to indicate that the interactions between unlike monomer units are repulsive. They found the interaction parameter χ_1 of the binary S–MMA copolymers to be less than the weighted sum of homopolymer interaction parameters with the same pure solvent. Interpretation of this finding in terms of χ_{AB}, the parameter characterizing the interaction between monomer units A and B in a copolymer chain, leads to the conclusion that the interactions between S and MMA units are repulsive.

In the case of S–MMA copolymers at least, it appears that calculation of isolated chain conformational entropies and energies provides a molecular basis for understanding both the sequence distribution–T_g effects (a solid state property) and the dilute solution behavior of these copolymers.

References and Notes

(1) A. E. Tonelli, *Macromolecules,* **7,** 632 (1974).

(2) A. E. Tonelli, *Macromolecules,* **8,** 544 (1975).

(3) A. E. Tonelli, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.,* **16 (2),** 228 (1975).

(4) A. E. Tonelli, unpublished results.

(5) N. W. Johnston, *J. Macromol. Sci., Rev. Macromol. Chem.,* **14 (2),** 215 (1976).

(6) T. G. Fox, *Bull. Am. Phys. Soc.,* **1,** 123 (1956).

(7) R. B. Beevers, *Trans. Faraday Soc.,* **58,** 1465 (1962).

(8) W. H. Stockmayer, L. D. Moore, Jr., M. Fixman, and B. N. Epstein, *J. Polym. Sci.,* **16,** 517 (1955).

(9) T. L. Hill, "Introduction to Statistical Thermodynamics", Addison-Wesley, Reading, Mass., 1960, Chapter 1.

(10) A. E. Tonelli, *J. Chem. Phys.,* **52,** 4749 (1970).

(11) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains", Interscience, New York, N.Y., 1963.

(12) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969, Chapter III.

(13) D. A. Brant and P. J. Flory, *J. Am. Chem. Soc.,* **87,** 2791 (1965).

(14) D. A. Brant, W. G. Miller, and P. J. Flory, *J. Mol. Biol.,* **23,** 47 (1967).

(15) D. A. Brant, A. E. Tonelli, and P. J. Flory, *Macromolecules,* **2,** 228 (1969).

(16) D. R. Herschbach, *Proc. Int. Symp. Mol. Struct. Spectrosc.,* 1 (1963).

(17) T_g(S) = 100 °C, T_g[MMA(syndiotactic)] = 160 °C, and T_g[MMA(isotactic)] = 43 °C (see ref 18).

(18) D. W. Van Krevelen, "Properties of Polymers", Elsevier, Amsterdam, 1972, Chapter 7.

(19) M. Hirooka and T. Kato, *J. Polym. Sci., Part B,* **12,** 31 (1974).

Biellipsoidal Model for AB Block Copolymers. Excluded Volume Effect in Isolated Molecules

John Bendler, Karel Šolc,*[1] and William Gobush

Midland Macromolecular Institute, Midland, Michigan 48640.

Received December 9, 1976

ABSTRACT: A new smooth density model is proposed to account for the intramolecular excluded volume effect in dilute solutions of AB block copolymers. Each block is approximated by an ellipsoidal Gaussian segment cloud which is allowed to interact with itself as well as its neighbor. The mean molecular properties, calculated by Monte Carlo method, are the overall mean square radius $\langle S^2 \rangle$, the mean square radii of the two blocks $\langle S_I^2 \rangle$, the mean square distance between the centers of mass of the blocks $\langle G^2 \rangle$, the mean square distances between the joint-segment and the centers of each block $\langle G_I^2 \rangle$ as well as the angle $\langle \theta \rangle$ between these two vectors, and the number of AB contacts N_{AB}. Applied to a homopolymer and to a block copolymer in a theta solvent for its blocks, the model agrees well with previously established theories. More complex cases studied include a block copolymer in a good solvent and a block copolymer in a preferential solvent. The model permits a unified view of both homopolymers and block copolymers. The molecular shape emerging from this model can be characterized as "arrowhead-like." The process of segregation is not unique to block copolymers. It is unlikely that it would result in a linear dumbbell conformation or in a spherically symmetrical core-in-shell conformation. The model is capable of reproducing the intramolecular transition. It is doubtful that AB repulsions increasing from zero alone could bring about a transition between the Gaussian and "segregated" conformations. The essential feature of the transition is a collapse caused by attractive forces, either a volume collapse of one or both blocks or an orientational collapse of the two blocks.

(I) Introduction

Until recently, progress in understanding the dilute solution behavior of block copolymers has been highly unsatisfactory, particularly for the following reasons:

(1) No theoretical basis was available to quantitatively explain the (often anomalous) experimental data. Therefore in many cases their interpretation has been confined to qualitative terms of either "segregated" or "pseudo-Gaussian" conformations which were considered as two distinct extreme cases.[2,3] The former one implies a bipolar geometry, with each block occupying a distinct region of space and almost no contact between the two blocks. Entropy loss in the segregated conformation is compensated for by a reduction in the number of energetically unfavorable heterocontacts A–B. On the other hand, a chain with the pseudo-Gaussian conformation is believed to have virtually the same conformation as a homopolymer, i.e., unaffected by the presence of A–B contacts. It is not surprising that the assumption of the existence of more or less only two distinct conformations then provoked discussions about a possible intramolecular transition from one to the other, in particular since some experimental data do suggest such a behavior.[4–7] It seems obvious that this is an over-simplification of the problem, since in reality the finite polymer chains can assume many other conformations between or beyond these two special cases which should be adequately taken into account. Furthermore, considerable controversy exists regarding the interpretation of data in terms of these two distinct conformations.[8,9]

(2) In the absence of any other theories, interpretations of experimental data have often been based[2a,3a] on the perturbation theory for the radius of gyration of block copolymer molecules worked out by Froelich and Benoit.[10] But it is well known from the homopolymer field[11] that the practical applicability of perturbation theory is severely limited to the very neighborhood of the theta point which, in most block copolymer systems, is far away from the experimental con-