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Sequence Distribution–Glass Transition Effects in Copolymers of Vinyl Chloride and Vinylidene Chloride with Methyl Acrylate

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ABSTRACT: The conformational entropies of copolymer chains are calculated through utilization of semiempirical potential energy functions and adoption of the rotational isomeric state model of polymers. It is assumed that the glass transition temperature, T_{gp}, is inversely related to the intramolecular, equilibrium flexibility of a copolymer chain as manifested by its conformational entropy. If, for example, the conformational entropy of a 50:50 copolymer of A and B monomer units is larger (smaller) than half the sum of the entropies of the two homopolymer chains (poly-A and poly-B), then the copolymer T_{gp} should be lower (higher) than that predicted by bulk additive relations such as the Fox equation. This approach is applied to the vinyl copolymers of vinyl chloride and vinylidene chloride with methyl acrylate, where the stereoregularity of each copolymer is explicitly considered, and correctly predicts the observed deviations from the Fox relation when they occur. 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 be characterized by estimating the resultant conformational entropy.

It has recently been suggested[1] that the frequently observed[2–7] sequence distribution dependent deviations of the glass transition temperatures T_{gp} of copolymers away from the values predicted by simple bulk additive relations, such as the Fox equation[8] $[1/T_{gp} = (W_A/T_{gA}) + (W_B/T_{gB})$, 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], may have their origins in specific intrachain interactions. The conformational entropy was calculated and employed as a measure of the equilibrium flexibility of a copolymer chain, and an inverse relation between T_{gp} and copolymer flexibility was assumed. If, for example, the conformational entropy of a 50:50 copolymer of A and B monomer units is larger (smaller) than half the sum of the entropies of the two homopolymer chains (poly-A and poly-B), then the copolymer T_{gp} is expected to be lower (higher) than that predicted by bulk additive relations such as the Fox equation.

This approach was applied[1] to the copolymers of styrene and α-methylstyrene with acrylonitrile and was successful in predicting the sequence distribution dependent deviations from the Fox equation observed[2,4,7] for these two copolymers. In the present work we extend the previously proposed[1] correlation of conformational entropy with T_{gp} to the copolymers of vinyl chloride (VC) and vinylidene chloride (VDC) with methyl acrylate (MA).

Calculation of Homo- and Copolymer Chain Entropies

Adoption of the rotational isomeric state (RIS) model[9] of polymer chains permits the utilization of matrix multiplication methods[10] to evaluate the conformational entropy[11] S of a polymer chain of n bonds

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

$$z = J^* \left[\prod_{i=2}^{n-1} U_i\right] J \qquad (2)$$

$$J^* = [100\ldots0](1 \times \nu);\ J = \begin{bmatrix}1\\1\\1\\ \vdots\\1\end{bmatrix}(\nu \times 1) \qquad (3)$$

where the $\nu \times \nu$ (ν rotational states assumed about each backbone bond) statistical weight matrix for bond i

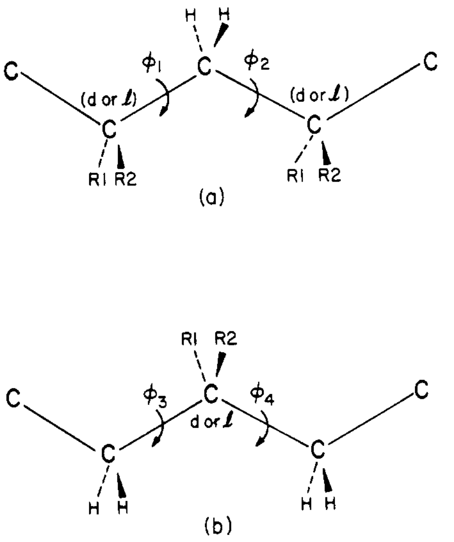


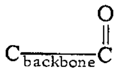
Figure 1. (a) Portion of a VC-MA (R1 ≡ H, R2 ≡ Cl or C(=O)OCH$_3$) or VDC-MA (R1 ≡ R2 ≡ Cl or R1 ≡ H, R2 ≡ C(=O)OCH$_3$) chain whose conformation depends only on the backbone rotations φ_1,φ_2 flanking a methylene group. (b) Portion of a VC-MA (R1 ≡ H, R2 ≡ Cl or C(=O)OCH$_3$) or VDC-MA (R1 ≡ R2 ≡ Cl or R1 ≡ H, R2 ≡ C(=O)OCH$_3$) chain whose conformation depends only on the backbone rotations φ_3,φ_4 flanking a substituted carbon atom.

$$U_i = \begin{array}{c|ccc} & & \varphi_i & \\ \varphi_{i-1} & \alpha & \beta & \gamma \\ \hline \alpha & u_{\alpha\alpha} & u_{\alpha\beta} & u_{\alpha\gamma} \\ \beta & u_{\beta\alpha} & u_{\beta\beta} & u_{\beta\gamma} \\ \gamma & u_{\gamma\alpha} & u_{\gamma\beta} & u_{\gamma\gamma} \end{array} \tag{4}$$

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

The conformational energies were estimated through application of approximate potential energy functions including a 6-12 plus coulombic potential to account for the nonbonded van der Waals and electrostatic interactions and a threefold inherent resistance to rotation about backbone C-C bonds with a 3.0 kcal/mol barrier.[12] Potential constants employed by Brant et al.[13-15] were used and those appropriate to interactions involving the chlorine atom were estimated in the usual fashion.[14,16] Based on the bond dipole moments given by Minkin et al.,[17] partial charges were assigned to the chlorines and the carbon atoms to which they are attached [in VC $\delta_{\mathrm{Cl}} = -0.22$, $\delta_{\mathrm{C}} = +0.22$, and for VDC $\delta_{\mathrm{C}} = +0.3$, $\delta_{\mathrm{Cl}} = -0.15$]. Dielectric constants[18] of 3.0, 4.0, and 5.0 were used to mediate the electrostatic interactions in the VC-VC or VDC-VDC, VC-MA or VDC-MA, and MA-MA dyads, respectively (see Figure 1).

Presented in Figure 1 are those portions of the copolymer chains considered in the conformational energy calculations. The chain segment in Figure 1a includes all atoms whose distances of separation depend on one or both of the backbone rotation angles φ_1 and φ_2 flanking a methylene group, while the distances between the atoms in Figure 1b depend on the backbone rotations φ_3 and φ_4 flanking a substituted carbon atom. Rotations about the backbone bonds and about the methyl acrylate



$$\mathrm{C_{backbone}}\text{—}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}$$

bond were permitted in 30° increments, while the ester bond in MA was fixed in the trans conformation.[15] The geometries (bond lengths and valence angles) employed by Brant et al.,[15] by Mark,[19] and by Matsuo and Stockmayer[20] were adopted for the MA, VC, and VDC[21] portions of the copolymer chains, respectively.

Table I
Conformational Entropies of VC-MA Copolymer Chains of 500 Backbone Bonds

Mol % MA	Stereoregularity^a	Sequence distribution	S,^{b} eu/mol of backbone bonds
0	S		0.845
0	I		0.900
0	A		0.740^c
50	S	Regularly alternating	0.768
50	I	Regularly alternating	0.854
50	A	Random	0.741^c
100	S		0.560
100	I		1.015
100	A		0.725^c

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

Table II
Conformational Entropies of VDC-MA Copolymer Chains of 500 Backbone Bonds

Mol % MA	Stereoregularity^a	Sequence distribution	S,^{b} eu/mol of backbone bonds
0			0.754
20	A	Random	0.636^c
40	A	Random	0.579^c
50	A	Random	0.579^c
50	A	Regularly alternating	0.412^c
50	S	Regularly alternating	0.404
50	I	Regularly alternating	0.420
60	A	Random	0.591^c
80	A	Random	0.641^c
100	S		0.569
100	A		0.732
100	I		1.012

[a] S ≡ syndiotactic, I ≡ isotactic, A ≡ atactic. [b] Calculated at $T = 5°$. [c] Average of 10 Monte Carlo generated chains, where the mean deviation from the average entropy is ca. 1-2%.

The statistical weights $u_{\alpha\beta}$ were evaluated from the conformational energies corresponding to the three staggered backbone rotational states ($\nu = 3$), trans ($\varphi = 0°$) and gauche ± ($\varphi = \pm 120°$). Temperatures of 40° [$\approx \frac{1}{2}(T_{\mathrm{gVC}} + T_{\mathrm{gMA}})$] and 5° ($\approx T_{\mathrm{gVDC}} \approx T_{\mathrm{gMA}}$) were used to calculate the statistical weights for the VC-MA and VDC-MA copolymers, respectively.

Monte Carlo methods were used to generate VC-MA and VDC-MA copolymers with various sequence distributions and stereoregularities. Additionally, the entropies of regularly alternating VC-MA and VDC-MA copolymers were calculated.

Results and Discussion

Conformational entropies calculated for VC-MA and VDC-MA copolymers with varying comonomer compositions, sequence distributions, and stereoregularities are presented in Tables I and II for chains of 500 backbone bonds. Figures 2 and 3 present the T_{gp} monomer composition data of Hirooka and Kato[7] for VC-MA and VDC-MA

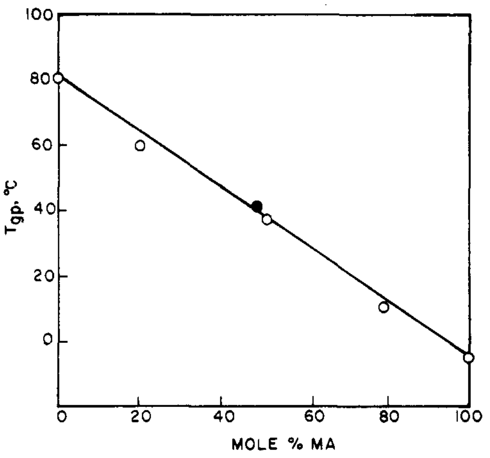


Figure 2. Glass transition temperature monomer composition behavior of VC–MA copolymers (Hirooka and Kato[7]): (○) random; (●) regularly alternating.

copolymers with random and regularly alternating sequence distributions. Three observations may be drawn from the data in Figures 2 and 3: (i) VC–MA copolymers obey the Fox equation, (ii) VDC–MA copolymers exhibit large positive deviations from the bulk additive behavior predicted by the Fox equation, and (iii) regularly alternating VDC–MA copolymer deviates further from the Fox equation than a 50:50 random copolymer. Each of these observations can be rationalized in terms of the calculated conformational entropies if an inverse relation between T_{gp} and copolymer conformational entropy is assumed.[1]

From Table I it is apparent that for a 50:50 VC–MA copolymer $S_{VC-MA} \approx \frac{1}{2}(S_{VC} + S_{MA})$ independent of both sequence distribution (random or regularly alternating) and stereoregularity. The flexibilities of VC–MA copolymer chains, as characterized by their conformational entropies, clearly do not depend on sequence distribution, but depend only on overall composition in agreement with the Fox equation and the data[7] in Figure 2.

VDC–MA copolymers, on the other hand, have calculated conformational entropies smaller than the weighted sums of the entropies of their constituent homopolymers (see Table II) over the entire ranges of monomer composition, sequence distribution, and stereoregularity. We therefore expect and observe[7] (see Figure 3) positive deviations from the bulk additive behavior predicted by the Fox equation. This correlation is further illustrated by comparing the data in Figure 3 with the monomer composition dependent entropy differences ΔS [$\Delta S = X_{MA}S_{MA} + (1 - X_{MA})S_{VDC} - S_{VDC-MA}$, where X_{MA} is the mole fraction of MA] (see Figure 4). Just as the T_{gp} of regularly alternating VDC–MA exceeds the T_{gp} of a 50:50 random copolymer, $\Delta S_{(\text{regularly alternating})} > \Delta S_{(50:50\ \text{random})}$.

The tentative correlation between the chain flexibilities, as monitored by copolymer chain conformational entropy, and deviations in copolymer T_{gp}'s away from the bulk additive behavior predicted by the Fox equation, which was proposed[1] previously on the basis of the predicted and observed[2,4,7] glass transition–sequence distribution behavior in styrene–acrylonitrile and α-methylstyrene–acrylonitrile copolymers, receives further support from the present study of VC–MA and VDC–MA copolymers. It appears that the sequence distribution dependent deviations away from the bulk additive T_{gp} monomer composition behavior predicted by the Fox equation have an intramolecular (intrachain) origin in the form of specific molecular interactions between neighboring monomer units. Furthermore, these intrachain interactions, as characterized by the resultant conformational entropy, can be used to correlate the equilibrium flexibility and the glass transition behavior[22] of a copolymer.

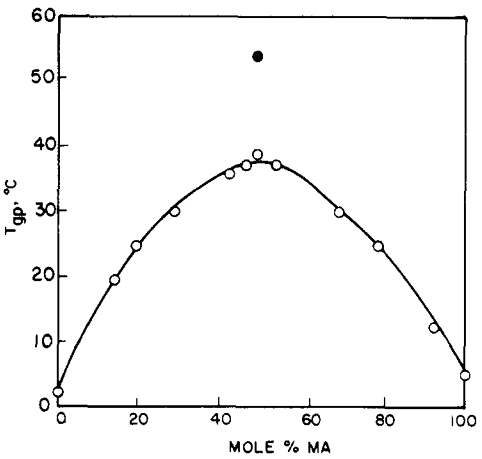


Figure 3. Glass transition temperature monomer composition behavior of VDC–MA copolymers (Hirooka and Kato[7]); (○) random; (●) regularly alternating.

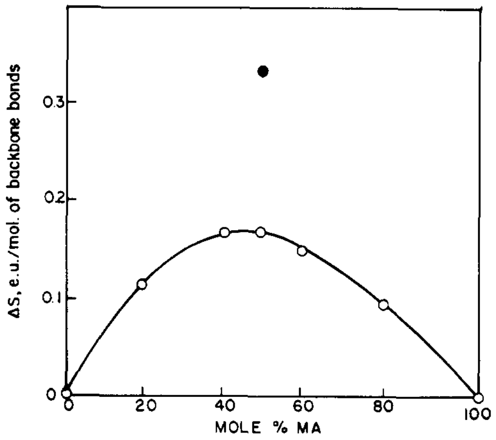


Figure 4. $\Delta S \equiv [X_{MA}S_{MA} + (1 - X_{MA})S_{VDC}] - S_{VDC-MA}$ calculated at 5° as a function of monomer composition: (○) random; (●) regularly alternating.

Finally it is worth mentioning that other statistical properties[23] of copolymer chains, such as the mean-square dimensions and dipole moments, vary with composition and sequence distribution in a manner similar to that exhibited by T_{gp}.

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Liquid Crystalline Type Order in Polydiethylsiloxane

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ABSTRACT: Polydiethylsiloxane has been demonstrated via calorimetric, dielectric, NMR, and X-ray techniques to exist in a two-phase structure for approximately 20° above its crystalline melting point, 270°K. One phase is amorphous and the other partially ordered. Analogies are drawn between polymer and liquid crystal morphology and behavior. The properties of the partially ordered phase are stable and intermediate between the amorphous and crystalline states suggesting that the term viscous crystalline is more descriptive of this phase.

The fact that some polymers do crystallize has resulted in extensive studies of the supramolecular texture and the mechanism of crystallization. Conventionally, crystallinity has come to be associated with a regular spatial repeat in three dimensions over some long range. However, it has been found that sharp diffraction intensities are observed for spatial repeats in only one or two dimensions.[1] This phenomena occurs in liquid crystals (low molecular weight materials) which may possess order in one or two dimensions. Several polymers have been studied which show one- and two-dimensional order. Stratton[2] concluded from a study of several of these polymers that two-dimensional order could be attributed to a regular lateral packing of linear molecules with no order along the chain direction, and one-dimensional order to longitudinal periodicity with no lateral order.

Recently the synthesis and characterization of poly(*p*-biphenyl acrylate) (PPBA) was reported.[3] Subsequent X-ray[4,5] and calorimetric studies[5] on PPBA, poly(*p*-cyclohexylphenyl acrylate) (PPCPA), and poly(*p*-biphenyl methacrylate) (PPBMA), all of which are atactic, showed PPBA and PPCPA to produce single sharp X-ray peaks, while PPBMA gave an amorphous halo. Annealing increased the intensity of the diffraction peaks of PPBA and PPCPA. DSC data also showed distinct melting over 5° ranges for PPBA and PPCPA while PPBMA showed no distinct melting range. The combined results for PPBA and PPCPA are explained in terms of a high degree of order, yet they are not crystalline in the convential sense, showing long-range order only in one direction. However, when the same thermodynamic considerations applied to semicrystalline polymers are used, "degrees of crystallinity" determined from heats of fusion and specific heat measurements are in good agreement for both polymers although the crystallinity of PPCPA is less than PPBA.

It was concluded that the formation of ribbon-like macromolecules in the solid PPBA is energetically favorable if the substituents are sufficiently long.[5] That is, the lowest free energy is found for molecular conformations in which the side groups are arranged in a plane passing through the main chain.

Despite the dissimilarity of PPBA and PPCPA and because PPCBA contains the flexible cyclohexyl ring, it is reasoned that the mobility of the cyclohexyl ring is severely reduced when bound to the benzene ring and as a result PPCPA is more like PPBA than expected, making the side chains fairly rigid. It has also been demonstrated that the order observed in the copolymerization of the monomers of PPBA and PPCPA is very sensitive to its copolymer partner.

It has also been reported that dilute solutions of methacrylylphenyl polyesters of alkoxy benzoic acids exhibit mesomorphic type order in which side chains form a mobile liquid-crystal structure.[6–9] Cooling of the macromolecules in a thermodynamically poor solvent is accompanied by an improvement in the orientational order of the side groups because of the reduction in polymer–solvent interaction which competes with the interaction between side chains within the polymer molecule. For the poly(phenylmethacrylyl ester of hexyloxybenzoic acid), PEHA, larger absolute birefringence of PEHA solutions than the EHA monomer indicated that larger "intrinsic units" were responsible for the observed birefringence in polymer solutions. There is also a high degree of orientational polar ordering within the structure of these units. Negative birefringence of PEHA solutions is a consequence of the orientation of the dipole molecules of the polymer, and the increase in this effect as the temperature is lowered is a result of the improvement in the intramolecular ordering within the side groups which have a tendency toward the formation of a liquid-crystal phase. Prolonged thermostating of the solutions led to a large positive value of the Kerr constant. This increase in K with time is due to the formation of molecular aggregates with an ordered internal structure whose dimensions increase with time.

Wendorff et al.[10] have also observed a nematic liquid-crystalline type order in 4-acryloxybenzylidene-4^1-ethoxyaniline. All of the systems mentioned above appear to have the following common features: (1) they are composed of fairly stiff shift chains, (2) they are not potentially crystallizable, and (3) they can exist in a single phase exhibiting liquid-crystalline type order. Recent utilization of block co-