# Glass Temperature of Ethylene/Propylene Copolymers: An Application of the Pseudostereochemical Equilibrium Approach

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ABSTRACT: The glass-transition temperature of ethylene/propylene statistical copolymers is evaluated by using the pseudostereochemical equilibrium approach; i.e., the partition function of a copolymer chain with interactions between neighboring conformations is formally obtained from a fictitious homopolymer wherein the two comonomer units are in equilibrium, with proper conformational constraints to produce the existing amounts of unit pairs. The resulting formalism enables us to avoid the difficult task of evaluating the geometrical average of the partition functions of different chains. The Gibbs−DiMarzio theory is extended to off-lattice models with any stereochemical structure; the rotational-isomeric-state entropy is supplemented with the contribution from fluctuations of the bond rotation angles around their energy minima. Allowing for rotational fluctuations in the glassy state enables one to account for a larger-than-crystalline entropy through the rms fluctuation angle, treated as an adjustable parameter. Although additional experimental data are awaited, the observed trend of $T_g$ vs composition for propylene-rich copolymers is correctly reproduced. It is predicted that copolymers tending to alternation ($r_E r_P \sim 0$) should have a $T_g$ lower by more than 20 °C than those with unit blocks ($r_E r_P > 1$), in qualitative agreement with what is observed for vinylidene fluoride/hexafluoropropene copolymers.

## Introduction

The glass transition of ordinary liquids is still a widely debated issue. Although the experimentally determined glass temperature $T_g$ turns out to depend on the rate of the experiment, it is generally agreed that a well-defined temperature may be obtained in the limit of an infinitely slow rate.[1] At the glass temperature we apparently have a second-order transition, as shown, e.g., by the discontinuity in the coefficient of thermal expansion; however, the transition appears to be a path-dependent process, as in the glass we have a multitude of states (or "glasses") that cannot interconvert, thereby making the system nonergodic. As a result of an interesting simulation study on a system of $N$ hard spheres, Speedy[2] shows that there are about $\exp(0.2N)$ distinct glasses, the related entropy being thermodynamically ineffective although it may be formally evaluated from the configuration integral. An observation pointing to an analogous conclusion was recently made by Di Marzio and Yang[3] who suggested that the glassy temperature should be defined as the temperature at which the percolation limit of glasslike local structures coexisting with liquidlike "pockets" is reached; as a consequence, the entropy at the glassy temperature is larger than zero.

Specifically for the polymer field, Gibbs and DiMarzio[1] proposed long ago a simple theoretical approach by which the configurational integral of an ensemble of unperturbed chains, with energy interactions between neighboring units, is evaluated. The chains are placed on a regular lattice, and a mean-field probability factor smaller than unity is applied to each chain atom to account for packing prohibition. Although in subsequent papers[3,9] DiMarzio subjected the issue to additional, careful analysis, the original theory was not basically modified: The glass transition temperature is obtained by assuming that the entropy of the melt reduces to zero; i.e., it equals that of the pure crystal, the existence of distinct glasses being neglected as an approximation. More recently, one of us[4] extended Gibbs−DiMarzio's original idea to a general chain model, so that the lattice constraints are overcome, and all possible bond and rotation angles are accounted for. Besides, through application of the pseudostereochemical equilibrium approach, involving the introduction of Lagrangian multipliers within the chain partition function,[5,6] all possible statistical distributions of comonomer unit pairs may be considered. It should also be remarked that, unlike Gibbs−DiMarzio, in our approach the chain entropy is evaluated by accounting for angular fluctuations of the skeletal rotations, or librations, both in the melt and in the glass; the root-mean-square libration angle at the glass temperature is taken as a free parameter, derived from the best fit with glass temperature data from slow experiments.[4] As a result, the chain entropy is effectively evaluated over the continuum of the rotational states; for this reason the glass temperature evaluated with our approach will be denoted as $\bar{T}_g$, to stress the difference from the usual zero-entropy transition temperature $T_2$.

Following these ideas,[4−6] in the present paper we shall evaluate the temperature $\bar{T}_g$ of ethylene/propylene copolymers with a varying composition of comonomer unit pairs. A major motivation to this work lies in the practical interest of predicting the glass temperature of rubberlike copolymers, to determine the optimal composition and statistical distribution of the units, as well as the best temperature range both for polymer processing and for the actual use of the rubber samples. As we shall see, the value of $\bar{T}_g$ is significantly influenced by the unit *pair* concentration, which implies

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a serious warning about easy rules based on copolymer composition, such as the Flory−Fox equation.[7] We notice in this respect that, with the use of modern catalytic systems based on metallocenes, it is now possible to modify the reactivity ratios, thus permitting us to change the pair distribution while keeping the same overall monomer unit composition.[8] Our interest being mainly focused on the influence upon $\bar{T}_g$ of the interconnected compositional and conformational properties of the chains, in the following we shall ignore some aspects correlated with volume expansion across the glass transition, discussed in particular by DiMarzio and Dowell.[9]

In the next section the general theoretical procedure will be outlined, while in a following section the matrix algorithm to evaluate the partition function will be discussed. Then we shall address numerical application to ethylene/propylene copolymers, and the results will be discussed in the last section in the light of the main theoretical aspects.

## General Theoretical Outline

To obtain the configurational entropy $S$ of the amorphous polymer system, we shall follow the mean-field approach that ignores any configurational correlation among packing chains.[1] Accordingly, $S$ is given by the sum of three terms: (i) the entropy $S_0$ due to the ensemble of polymer chains, regarded as both unperturbed and noninteracting with one another, (ii) the entropy $S_W$ associated with the different translation and rotation placements of the chains, and (iii) the negative entropy $S_P$ arising from interchain space overlap. We have

$$S = S_0 + S_W + S_P \tag{1}$$

Denoting by $S^*$ the librational entropy in the glass, at $T = \bar{T}_g$, we shall write

$$S = S^* \tag{2}$$

and the evaluation of $S^*$ shall be recalled in the following. We note that in Gibbs−DiMarzio's theory the critical temperature $T_2$ is obtained from eq 2 after putting $S^* = 0$.

We shall now exploit the well-documented notion that the unperturbed state is an adequate representation of the polymer chain in a molten sample.[10] We define by $\lambda$ the effective partition function per chain bond evaluated within the rotational isomeric state (ris) scheme[11] and by $\psi$ the Boltzmann integral accounting for the libration of a chain bond around each rotational energy minimum at $T = \bar{T}_g$. With $\lambda_0 = \lambda\psi$ the overall bond partition function, $Z_N^0 = \lambda_0^N$ is the configurational partition function of each isolated, unperturbed chain with $N$ bonds. Approximating each energy minimum well with a quadratic potential and denoting as $U_0$ the energy barrier between the minima, we get[4]

$$\psi = \frac{2}{3}\sqrt{\frac{\pi k_B T}{U_0}} \tag{3}$$

The unperturbed contribution to the entropy is

$$S_0 = nk_B\frac{\mathrm{d}[T\ln(Z_N^0)]}{\mathrm{d}T} = nNk_B\frac{\mathrm{d}[T\ln(\lambda\psi)]}{\mathrm{d}T} \tag{4}$$

Proceeding now to the two remaining contributions to the entropy, namely the translational-orientational and the packing contributions, in the limit of very large $N$ we have for $n$ chains[4]

$$S_W \approx nk_B \ln N; \qquad S_P = -nNk_B\left(1 + \frac{\nu_0}{1-\nu_0}\ln\nu_0\right) \tag{5}$$

$\nu_0$ and $(1 - \nu_0)$ respectively being the free volume fraction and the volume fraction occupied by the polymer ($\nu_0 = 0$ for the ideal crystalline state). In agreement with currently accepted results, we shall take $\nu_0 = 0.025$.[12]

As anticipated, the entropy $S^*$ will be obtained on the assumption that in the glassy state the chains are only allowed to perform limited librational motions around their single bonds, in addition to the vibrational motions permitted in the amorphous phase.[4] We note that the present classical approach essentially addresses the continuum of the rotational states; therefore we are not permitted to assume $S^* = 0$, e.g., as in the Gibbs−DiMarzio theory based on discrete chain states,[1] unless we suitably define the angular "size" of a single state. The librations make all the atoms fluctuate around their mean positions by about the same mean-square displacement. With $\langle\Delta^2\rangle$ the mean-square libration angle, from the configurational integral the entropy $S^*$ is

$$S^* = nNk_B\ln(\psi_0); \qquad \psi_0 = (2\pi\langle\Delta^2\rangle)^{1/2} \tag{6}$$

where $n$ is the number of identical chains and $N$ is the number of chain atoms (and bonds) of equal length, both numbers being very large. It should be stressed that in the glass the average rotation angle around a given bond need not correspond to a local energy minimum.

From eqs 1−4, the glass temperature $\bar{T}_g$, is defined by

$$\left.\frac{\mathrm{d}[T\ln(\lambda\psi/\psi_0)]}{\mathrm{d}T}\right|_{T=\bar{T}_g} + \frac{\ln N}{N} - \left(1 + \frac{\nu_0}{1-\nu_0}\ln\nu_0\right) = 0 \tag{7}$$

where the first term is $(S_0 - S^*)/nNk_B$ evaluated at $\bar{T}_g$, and the term with ln $N$ may be neglected for large $N$.

In the following section we shall evaluate the ris partition function per chain bond $\lambda$ as a function of temperature for binary statistical copolymers. Numerical application to obtain the glass temperature $\bar{T}_g$ of ethylene/propylene copolymers will then be discussed.

## Partition Function of an Unperturbed Statistical Copolymer with Fixed Amounts of Unit Pairs

*General Formulation.* By definition, intramolecular interactions within an unperturbed chain need not be considered beyond atom pairs separated by a few chemical bonds. Therefore, in the ris approximation, we express the configurational partition function of a chain with $N$ skeletal bonds ($N \gg 1$) as the trace of a sequential product of correlation matrices whose size increases with the degree of conformational correlation (i.e., the largest number of chemical bonds between interacting atoms). Otherwise said, the problem is of the Markoffian type, with an appropriate order. In a homopolymer chain, wherein all the monomeric units are structurally equivalent, the matrices undergoing repeated multiplication are all identical (=**U**, e.g.). If the chain is long enough, the resulting partition function

$Z$ may be equated to the largest eigenvalue $\bar{\lambda}$ of the correlation matrix $\mathbf{U}$ raised to the power equal to the number of monomer units $\nu = N/m$ (here $m$ is the number of chain bonds per unit). Accordingly, we may write, for an infinitely long, ringlike chain,[13]

$$Z = \text{trace}(\mathbf{U}^{\nu}) \cong \bar{\lambda}^{\nu}; \qquad \nu = N/m; \quad \bar{\lambda} = \text{largest eigenvalue of } \mathbf{U} \tag{8}$$

In case the linear macromolecule consists of a copolymer chain with $\nu$ comonomer units, the correlation matrices $\mathbf{U_1}$, $\mathbf{U_2}$, ..., $\mathbf{U}_\nu$ are not identical among themselves, and in general we have

$$Z = \text{trace}(\mathbf{U_1 U_2 ... U}_\nu) \tag{9}$$

If the comonomer sequence obeys some periodic rule, it is possible to express $Z$ as the appropriate power of the eigenvalue of the matrix product over the repeating pattern. In the case of a statistical distribution, such a possibility does not exist, in general. In this instance, a Markoffian distribution of an appropriate order is usually regarded as adequate; we recall that a zero-order law corresponds to the random, or Bernoullian distribution, a first-order law to a random distribution of properly connected unit pairs, etc. Evaluation of the corresponding partition function, sometimes referred to as the copolymer problem, has proved to be a difficult task, since it implies evaluation of the *geometrical* average over the partition functions of chains with different structures. Lehman and McTague first gave a formally exact solution to the problem in terms of a system of functional equations,[14] although their solution is not in closed form as it requires an iterative numerical procedure. Lifson and Allegra[15] and subsequently Allegra[5,6] proposed two approximate matrix approaches formally analogous to that followed in the homopolymer case. In particular, the second approach is based on the assumption that the copolymer partition function may be equated to that of an imaginary homopolymer chain whose ideal monomer units are in a dynamic equilibrium among the whole set of the different conformational states attainable by the real comonomer units. [We remark that such an ideal model is utterly unrealistic because, in an ethylene/butadiene copolymer, for instance, it formally assumes that a 1,4-enchained butadiene unit (spanning 4 skeletal bonds) may dynamically convert to an ethylene unit (spanning two skeletal bonds) and vice versa.] A suitable multiplicity factor must be applied to account for the unique distribution of the comonomer units existing in each real copolymer chain. Assuming a first-order Markoffian distribution, a different Lagrangian multiplier must be applied to the statistical weights pertaining to each different comonomer pair, to adjust the occurrence probability of that pair to the value desired; in general, for a copolymer with $p$ different types of comonomer units, a total of $p(p-1)$ multipliers are needed, corresponding to the number of independent occurrence probabilities of unit pairs. Eventually, the resulting partition function will be "cleared of" these multipliers. It is important to remark that this procedure selects the partition function terms corresponding to the appropriate amounts of comonomer pairs from the overall partition function, including all possible amounts of such pairs.[16] We notice that the partition function obtained after such a selection describes an ensemble of copolymer chains that is not necessarily first-order Markoffian. Otherwise said, the probability of triples, quadruples, etc. may depart from that expected from a random allocation of pairs requiring, as an example, $x_{ABC} = x_{AB}x_{BC}/x_A$, where $x_{AB...}$ is the fractional probability of (AB...). This result, deriving from the noncommutation property of matrices, may in principle be corrected by adjusting the triples' probabilities—instead of the pairs'—to the real values, and so on; the procedure requires introduction of an appropriate set of different multipliers pertaining to different triples and involves the use of a more expanded matrix algorithm.[5]

Let us consider the procedure for a binary (A, B) copolymer. We assume that the degree of conformational energy correlation does not extend beyond first neighboring comonomer units. Let $\mathbf{U}_{AA}$, $\mathbf{U}_{AB}$, $\mathbf{U}_{BA}$, $\mathbf{U}_{BB}$ be the matrices carrying the statistical weights of the conformational states belonging to the four unit pairs, within the framework of the (ris) scheme. Specifically, the $(i, j)$ element of the general matrix $\mathbf{U}_{XY}$ (X, Y = A, B) carries the statistical weight of the local conformation having the X unit in the $i$th state and the Y unit in the $j$th state:

$$\mathbf{U}_{XY} = ||\exp[-E_{XY}(i,j)/k_B T]|| \tag{10}$$

$E_{XY}(i,j)$ being the conformational energy, $T$ the absolute temperature, and $k_B$ the Boltzmann constant. As will be seen in the following examples, the $(i, j)$ state may also apply to a *collection* of conformations, sometimes only differing for the orientation of side groups, in which case $E_{XY}(i,j)$ is to be regarded as a free energy. Also, sometimes the number of different states may just reduce to one on both comonomer units of the pair, in which case $\mathbf{U}_{XY}$ reduces to a scalar quantity. Let us now define the supermatrix (X, Y = A, B)

$$\mathbf{W}_0 = \begin{vmatrix} \mathbf{U}_{AA} & \mathbf{U}_{AB} \\ \mathbf{U}_{BA} & \mathbf{U}_{BB} \end{vmatrix} \tag{11}$$

which may be regarded as the correlation matrix of the (imaginary) homopolymer chain in dynamic equilibrium between the A and the B comonomer units. With $\Lambda_0$ the largest eigenvalue of $\mathbf{W}_0$, the partition function $\bar{Z}$ of this imaginary chain with $\nu$ monomer units is

$$\bar{Z} = \text{trace}(\mathbf{W}_0)^{\nu} \cong \Lambda_0^{\nu} \tag{12}$$

and the probability of any sequence $x^0_{XYZ...}$ may be easily evaluated by matrix algebra. In general, the pair probabilities $x^0_{XY}$ will differ from the expected values, so that the introduction of two Lagrangian constraints is required. A convenient representation turns out to be

$$\mathbf{W}^* = \begin{vmatrix} \sigma\mathbf{U}_{AA} & (1-\sigma)\mathbf{U}_{AB} \\ (1-\tau)\mathbf{U}_{BA} & \tau\mathbf{U}_{BB} \end{vmatrix} \tag{13}$$

where the two limits ($\sigma = \tau = 1$) and ($\sigma = \tau = 0$) respectively correspond to the collection of the pure homopolymers (...AAAA... and ...BBBB...) and to the alternating copolymer (...ABAB...). Indicating with $\mathbf{a}_r$ and $\mathbf{a}_c^T$ respectively the row and the column normalized eigenvectors relative to the largest eigenvalue $\lambda^*$ of the matrix $\mathbf{W}^*$ the pair probabilities $x_{AA}$ and $x_{BB}$ are given by

$$x_{AA} = \mathbf{a}_r \begin{vmatrix} \sigma\mathbf{U}_{AA} & \mathbf{0} \\ 0 & \mathbf{0} \end{vmatrix} \mathbf{a}_c{}^T/\lambda^*;$$

$$x_{BB} = \mathbf{a}_r \begin{vmatrix} \mathbf{0} & \mathbf{0} \\ 0 & \tau\mathbf{U}_{BB} \end{vmatrix} \mathbf{a}_c{}^T/\lambda^* \quad (14)$$

whereas the corresponding chain partition function is

$$Z^* \cong (\lambda^*)^\nu \quad (15)$$

Equations 14 represent the connection between the multipliers $\sigma$ and $\tau$ and the probabilities $x_{AA}$ and $x_{BB}$ and suggest a straightforward numerical evaluation of the probabilities from the multipliers, rather than vice versa. An important remark is in order in this connection: Since the elements of the matrices $\mathbf{U}_{XY}$ are obviously temperature-dependent, so are the multipliers $\sigma$ and $\tau$ required to produce constant values of the probabilities. Once the multipliers are determined for a given pair probabilities, simple matrix algebra enables us to get the probabilities of longer comonomer sequences. In particular, for the triples we get

$$x_{AAA} = \mathbf{a}_r \begin{vmatrix} \dfrac{\sigma\mathbf{U}_{AA}}{\tau^*} & \mathbf{0} \\ 0 & \mathbf{0} \end{vmatrix}^2 \mathbf{a}_c{}^T$$

$$x_{AAB} = \mathbf{a}_r \begin{vmatrix} \dfrac{\sigma\mathbf{U}_{AA}}{\tau^*} & \mathbf{0} \\ 0 & \mathbf{0} \end{vmatrix} \begin{vmatrix} \mathbf{0} & \dfrac{(1-\sigma)\mathbf{U}_{AB}}{\tau^*} \\ \mathbf{0} & \mathbf{0} \end{vmatrix} \mathbf{a}_c{}^T \quad (16)$$

etc. Comparing the resulting figures of $x_{XYZ}$ with the first-order Markoffian values $x_{XY}x_{YZ}/x_Y$ provides us with a measure of the discrepancy between the monomer unit statistics within the ideal homopolymer and that within the Markoffian copolymer. As found in our previous experience, also in the present case the resulting probabilities differ from the Markoffian values by less than $10^{-2}$ in relative terms, so that we conclude that our model represents an accurate description of the first-order Markoffian ethylene/propylene copolymers.

In analogy with eq 12, the (ris) partition function of the ideal homopolymer with a large number $\nu$ of monomer units and with the Boltzmann weights reported in the matrix $\mathbf{W}^*$, is given by $(\lambda^*)^\nu$. To obtain the partition function of the real copolymer we must suppress from this result two "unphysical" contributions deriving from the algorithm, namely, (i) the factor $\Pi$, equal to the number of permutations of the unit pairs in the ideal homopolymer, and (ii) the factor $\Sigma$, representing the product of all the multipliers. We have

$$\Pi^{-1} = \left( \frac{\mathbf{x}_{AA}^{x_{AA}} \mathbf{x}_{BB}^{x_{BB}} \mathbf{x}_{AB}^{x_{AB}} \mathbf{x}_{BA}^{x_{BA}}}{\mathbf{x}_A^{x_A} \mathbf{x}_B^{x_B}} \right)^\nu;$$

$$\Sigma = [\sigma^{x_{AA}}(1-\sigma)^{x_{AB}}(1-\tau)^{x_{BA}}\tau^{x_{BB}}]^\nu \quad (17)$$

and the "clean" partition function $Z$ turns out to be

$$Z = Z^*/(\Pi\Sigma) = \bar{\lambda}^\nu \quad (18)$$

the last equality being analogous with eq 8. Connection between the average partition functions per comonomer unit and per chain bond, respectively, $\bar{\lambda}$ and $\lambda$, is established through the equality ($\nu$ comonomer units, $N$ chain bonds)

$$\bar{\lambda}^\nu = \lambda^N, \quad (19)$$

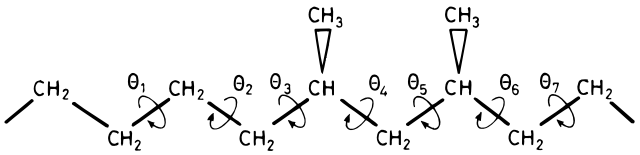


**Figure 1.** Schematic drawing of an ethylene/propylene copolymer chain. Rotation angles around chain bonds with different placements are shown; see text.

which yields the quantity $\lambda$ appearing in eq 7. To implement this equation we need to evaluate $\mathrm{d}\ln\lambda/\mathrm{d}T$, which in turn makes it necessary to take into account the temperature dependence of $\sigma$ and $\tau$. Considering $T$, $\sigma$, and $\tau$ as three independent variables, from $\mathrm{d}x_{AA}/\mathrm{d}T = \mathrm{d}x_{BB}/\mathrm{d}T = 0$ we have

$$\mathbf{M} \cdot \begin{vmatrix} \dfrac{\partial\sigma}{\partial T} \\ \dfrac{\partial\tau}{\partial T} \end{vmatrix} = -\begin{vmatrix} \dfrac{\partial x_{AA}}{\partial T} \\ \dfrac{\partial x_{BB}}{\partial T} \end{vmatrix}$$

where

$$\mathbf{M} = \begin{vmatrix} \dfrac{\partial x_{AA}}{\partial\sigma} & \dfrac{\partial x_{AA}}{\partial\tau} \\ \dfrac{\partial x_{BB}}{\partial\sigma} & \dfrac{\partial x_{BB}}{\partial\tau} \end{vmatrix} \quad (20)$$

From

$$\frac{\mathrm{d}\ln\lambda}{\mathrm{d}T} = \frac{\partial\ln\lambda}{\partial T} + \begin{vmatrix} \dfrac{\partial\ln\lambda}{\partial\sigma} & \dfrac{\partial\ln\lambda}{\partial\tau} \end{vmatrix} \begin{vmatrix} \dfrac{\partial\sigma}{\partial T} \\ \dfrac{\partial\tau}{\partial T} \end{vmatrix}$$

and from eq 20 we get

$$\frac{\mathrm{d}\ln\lambda}{\mathrm{d}T} = \frac{\partial\ln\lambda}{\partial T} - \begin{vmatrix} \dfrac{\partial\ln\lambda}{\partial\sigma} & \dfrac{\partial\ln\lambda}{\partial\tau} \end{vmatrix} \cdot \mathbf{M}^{-1} \cdot \begin{vmatrix} \dfrac{\partial x_{AA}}{\partial T} \\ \dfrac{\partial x_{BB}}{\partial T} \end{vmatrix} \quad (21)$$

a quantity that may be obtained after numerical evaluation of the partial derivatives as incremental ratios of $\lambda$, $x_{AA}$, and $x_{BB}$ over $T$, $\sigma$, and $\tau$ (see eqs 20 and 21).

## Numerical Application to Ethylene/Propylene Copolymers

In the following we shall closely follow the procedure suggested by Mark in a configurational study of ethylene/propylene copolymers.[17] Energy correlation between skeletal rotations is regarded as effectively limited to first neighbors and is algebraically represented by a matrix $\mathbf{U}$ (henceforth denoted as a *pair matrix*) whose $(i, j)$ site contains the Boltzmann weight pertaining to the combination of the $i$th rotation state around one bond and the $j$th state around the bond following along the chain sequence. Since each comonomer unit spans two skeletal bonds, e.g., say the $n$th and the $(n+1)$th bonds, the corresponding matrix $\mathbf{U}_{XY}$ appearing in eqs 11 and 13 is a product of two pair matrices, the first one referring to the bond pair $(n, n+1)$, the second to the pair $(n+1, n+2)$ (see Figure 1, $n$ even). The rotational states around each bond, as defined with respect to the chain skeleton, are trans, gauche$^+$, and gauche$^-$, or T, G$^+$, and G$^-$, respectively.

The propylene sequences are regarded as isotactic; i.e., only D propylene units are present, using Mark's notation; this is reflected indeed in the actual microstructure of ethylene/propylene copolymers obtained with several metallocene-based catalysts.[18] [In this regard we remark that the $T_g$ values of isotactic, syndiotactic, and atactic polypropylene are currently reported to be within 10 °C,[19] which supports the assumption that our results should be generally applicable to copolymers with different microstructures.] Identifying henceforth the comonomer units A and B with ethylene (E) and propylene (P), respectively, we have[17]

$$\mathbf{U}_{AA} = \mathbf{U}_E \cdot \mathbf{U}_E; \qquad \mathbf{U}_E = \begin{vmatrix} 1 & \tau/\eta & \tau/\eta \\ 1 & \tau/\eta & \tau\omega/\eta \\ 1 & \tau\omega/\eta & \tau/\eta \end{vmatrix}$$

$$\mathbf{U}_{AB} = \mathbf{U}_{EP} \cdot \mathbf{U}_P;$$

$$\mathbf{U}_{EP} = \begin{vmatrix} \eta & \tau & 1 \\ \eta & \tau\omega & \omega \\ \eta\omega & \tau\omega & 1 \end{vmatrix}; \qquad \mathbf{U}_P = \begin{vmatrix} \eta & 1 & \tau \\ \eta & 1 & \tau\omega \\ \eta & \omega & \tau \end{vmatrix}$$

$$\mathbf{U}_{BA} = \mathbf{U}_{PE} \cdot \mathbf{U}_E; \qquad \mathbf{U}_{PE} = \begin{vmatrix} \eta/\tau & \omega & 1 \\ \eta/\tau & 1 & \omega \\ \eta/\tau & \omega & \omega \end{vmatrix}$$

$$\mathbf{U}_{BB} = \mathbf{U}_{PP} \cdot \mathbf{U}_P; \qquad \mathbf{U}_{PP} = \begin{vmatrix} \eta\omega & \tau\omega & 1 \\ \eta & \tau\omega & \omega \\ \eta\omega & \tau\omega^2 & \omega \end{vmatrix} \quad (22)$$

The Boltzmann weights $\eta$, $\tau$, and $\omega$ are defined as

$$\eta = \exp(-E_\eta/k_B T); \qquad \tau = \exp(-E_\tau/k_B T); \qquad \omega = \exp(-E_\omega/k_B T)$$

$$E_\eta = 0 \text{ kcal/mol}; \; E_\tau = 0.5 \text{ kcal/mol}; \; E_\omega = 1.6 \text{ kcal/mol} \quad (23)$$

in analogy with the data chosen by Mark,[17] with the exception of $E_\omega$, which is taken within the range suggested by Suter and Flory[20] for a similar investigation.

Figure 2 shows typical plots of the reduced entropy per chain bond $(S_0 - S^*)/nNk_B$ (see eqs 4 and 6) for the homopolymers PE and i-PP, with the graphical solution of eq 7 yielding $\bar{T}_g$. The results of $\bar{T}_g$ for copolymers of different pair compositions, given in terms of the pair fractions $x_{EE}$ and $x_{PP}$, are given in Figure 3. The remaining pair fractions, the comonomer fractions, and the conditional probabilities $p_{XY}$ (X, Y = E , P) are given by

$$x_{EP} = x_{PE} = \frac{1 - x_{AA} - x_{BB}}{2}; \qquad x_E = \frac{1 + x_{EE} - x_{PP}}{2}; \qquad x_P = \frac{1 - x_{EE} + x_{PP}}{2}$$

$$p_{XY} = x_{XY}/x_X \text{ (X, Y = E, P)} \quad (24)$$

Figure 4 shows the same results as in Figure 3 under the form of plots of $\bar{T}_g$ vs $x_E$, for different values of the

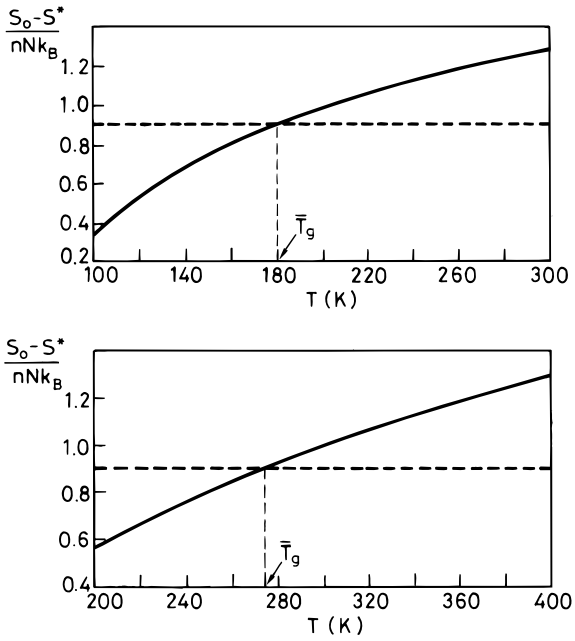


**Figure 2.** Plot showing the reduced entropy per chain bond $(S_0 - S^*)/nNk_B$ (see eqs 4 and 6) vs temperature for polyethylene (above) and polypropylene (below) homopolymers. The glass transition for slow experiments corresponds to the temperature $\bar{T}_g$ at which $(S_0 - S^*)/nNk_B$ equals $\{1 + [\nu_0/(1 - \nu_0)] \ln \nu_0\}$ (see eq 7, $N \to \infty$).

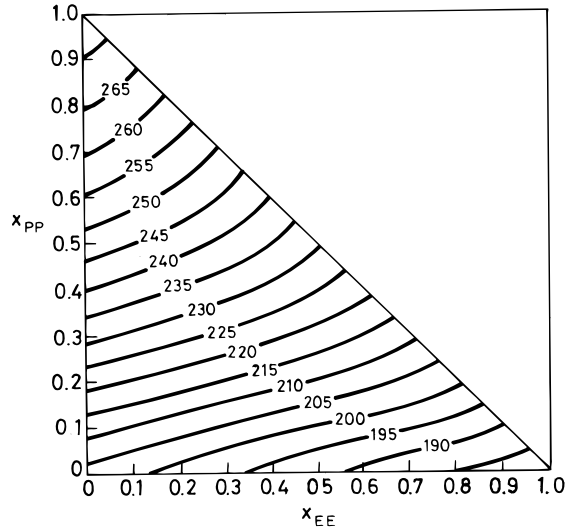


**Figure 3.** Glass temperature $\bar{T}_g$ (K) of ethylene/propylene copolymers with different mole fractions of pairs ($x_{EE}$ , $x_{PP}$) ($x_{EE} + x_{PP} + x_{EP} + x_{PE} = 1$, $x_{EP} = x_{PE}$).

product of the reactivity ratios $r_E r_P$. This product is correlated with the pair fractions by the equation[21]

$$r_E r_P = \frac{4 x_{EE} x_{PP}}{(1 - x_{EE} - x_{PP})^2} \quad (25)$$

A section of Figure 4 is reported in Figure 5 by taking $x_E = x_P = 0.5$ and using the pair fraction $x_{EE} = x_{PP}$ as the coordinate on the abscissa. As it may be seen, $\bar{T}_g$ is markedly lower for copolymers tending to alternation ($r_E r_P \ll 1$, i.e., $x_{EE}$, $x_{PP} \sim 0$) than for random or block copolymers ($r_E r_P \geq 1$, $x_{EE}$, $x_{PP} \sim 0.5$). This result is strictly correlated with the larger conformational freedom allowed to the copolymer chains if the more

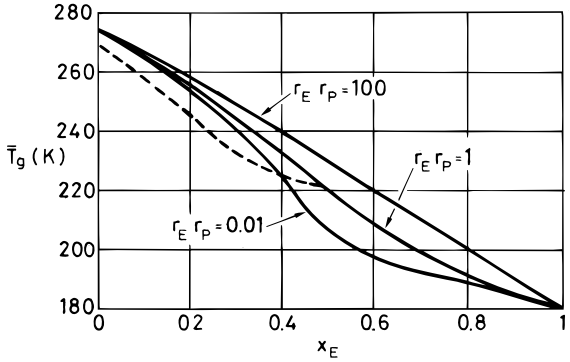


**Figure 4.** Glass temperature $\bar{T}_g$ (K) for ethylene/propylene copolymers. Same results as given in Figure 3, reported as a function of the mole fraction $x_E$ ($x_E + x_P = 1$) for three different values of the product of the reactivity ratios (see eqs 24 and 25). The dashed line is an interpolation of experimental data, as reported in ref 29.

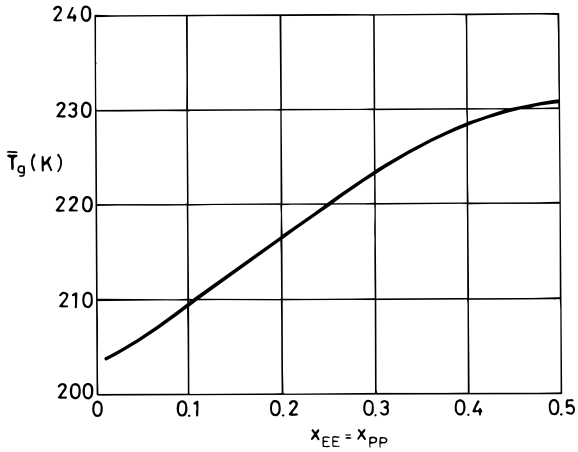


**Figure 5.** Glass temperature $\bar{T}_g$ (K) for ethylene/propylene copolymers. Section of the plot reported in Figure 3, taken through the bisector straight line $x_{EE} = x_{PP}$, corresponding to equimolar fractions $x_E = x_P = 0.5$. If $x_{EE} = x_{PP} = 0$, we have a completely alternating copolymer (i.e., $r_E r_P \rightarrow 0$ in Figure 4), if =0.5 we have a block copolymer ($r_E r_P \rightarrow \infty$).

stereochemically hindered propylene units do not follow themselves.

Closeness of our copolymer model to the first-order Markoffian distribution of the comonomer units was checked by us through numerical evaluation of the pair and of the triple probabilities. In agreement with the case of other copolymer models previously investigated with the same approach,[22,23] the probabilities of the triples $x_{XYZ}$ evaluated for the actual copolymer ensemble according to eq 16 were always close to within $\pm 0.001$ to the Markoffian values $x_{XY}x_{YZ}/x_Y$.

## Discussion of the Results

As the temperature is lowered, the molecular motions within any liquidlike substance become progressively hindered because the configurational change of a small part of the system requires the concerted rearrangement of larger and larger surrounding portions of matter. The domain of cooperativity may grow to infinity well above $T = 0$ K,[24] although not necessarily above the temperature of crystallization. In case the crystallization process is frustrated, as, for example, with stereoirregular polymers such as atactic polystyrene obtained from anionic polymerization, we may have a genuine transition to a phase wherein all but the most localized motions (bond and bond angle vibrations, methyl group rotations, ...) are hindered, and we have a stable glass. Although, according to Kauzmann's paradox,[25] the simplest conceivable description of such a state suggests a zero configurational entropy as in a crystal, the prevailing view at present is that in the glass it should be somewhat larger. In the case of the hard-sphere system, Speedy,[2] using inter alia previous results by Woodcock,[26] has shown that the glass may be realized in a number of noninterconverting configurations on the order of $\exp(0.2N)$, $N$ being the number of the spheres, so that the (frozen) entropy of the glass is about 0.2 $k_B$ per sphere. Investigations carried out by Milchev[27] and by Binder and co-workers[28] concur to indicate that the entropy of a polymer glass is larger than expected for the crystalline state. DiMarzio and Yang[3] provide an interesting theoretical suggestion to further support the concept of the glass entropy being larger than zero, in terms of the "percolation of frustration" that may be attained by the system at the glass transition: Although the glasslike regions may not comprise the whole system, they may be so spatially connected among themselves as to reach the percolation limit, with inclusion of liquid "pockets" that increase the effective entropy.

The model implemented in this paper to investigate the glass transition of a polymer system comprises some of the basic features of the Gibbs-DiMarzio theory,[1] with the significant modification that it is not bound to configurations of chains placed on regular lattices.[4] Any chain geometry and structure is encompassed by the model, which explicitly allows for librational oscillations around the chain single bonds. In fact, if we assume that in a glassy polymer the chain atoms may only undergo small displacements from their mean positions, the most important entropy contribution may be identified with the libration fluctuation around the skeletal bonds; both the structural disorder and the significant amount of the free volume in the glassy state[11] should favor this sort of motion, provided the average atomic displacement from the mean positions does not exceed one bond length, roughly speaking. The root-mean-square value of this libration angle for a few hydrocarbon polymers, derived by best-fitting their experimental $T_g$ values, appears to lie within an acceptable range ($\langle\Delta^2\rangle^{1/2} \cong 7.8°$).[4] However, its effective value should be regarded as comprehensive of the physical factors discussed above, which increase the entropy of the glass above the crystalline state level. It may be interesting to notice that, *in the unperturbed chain*, the root-mean-square fluctuation of a skeletal rotation angle around each energy minimum $T$, $G^+$, and $G^-$ ($= \sqrt{2k_BT/9U_0}$, see ref 4, eq 42) is 12.0° and 9.8°, respectively, at 300 and at 200 K, taking $U_0 = 3$ kcal/mol. Therefore, the angular fluctuation of each skeletal rotation of the unperturbed chain around each energy minimum turns out to be larger than the corresponding fluctuation in the glassy state (7.8°). We point out that this result is consistent with our physical picture by which in the glass each skeletal rotation undergoes restricted oscillations around an average value. We also stress that the quoted value of 7.8° derives from a numerical best-fit with experimental glass temperature values of several hydrocarbon polymers,[4] and it should not be unduly extrapolated to other polymers.

When dealing with statistical copolymers, evaluation of the configurational unperturbed partition function is

a nontrivial task on account of the frozen-in statistical distribution of the comonomer units that compounds itself with the statistics of the rotational states with neighbor interactions.[5,6,13−15] A rigorous solution of this problem implies the need to obtain the geometrical average of the partition functions pertaining to the different chains of the statistical ensemble. We made recourse to the approximate pseudostereochemical equilibrium approach suggested by one of us,[5,6] by which a hypothetical homopolymer chain is worked out, its monomers having access to the rotational states of all the comonomer units and its unit-pair composition being properly restricted. The resulting statistical distribution of the comonomer pairs is very close to first-order Markoffian. The entropy contribution resulting from fluctuation of the chain rotation angles is also accounted for, so that the overall chain entropy may be regarded as effectively derived from the full configurational integral.

Rather few reliable experimental data on the glass temperature of ethylene/propylene copolymers are available, to the best of our knowledge. Differential-scanning calorimetry data obtained in the DuPont Laboratories by Baldwin and Ver Strate,[29] are interpolated by the dotted line in Figure 4. It is generally agreed that the onset of crystallization in copolymers with an ethylene content larger than ∼50% tends to alter the results through a pronounced increase of the elastic modulus, which may be the reason for the discrepancy from our calculations at $x_E > 0.4$. At smaller ethylene contents the trend is roughly in agreement with our calculations for a random copolymer (i.e., $r_E r_P = 1$, $r_X$ being the reactivity ratio of the X units), if we allow for a systematic downward temperature shift of the experimental data by ∼5 °C. Our numerical results for ethylene/propylene copolymers show that the resulting $\bar{T}_g$ (to be compared with the experimental $T_g$ from very slow experiments) is lowest for the highest comonomer unit alternation, corresponding to $r_E r_P \rightarrow 0$. Although for ethylene/propylene copolymers direct experimental evidence still appears to be missing, we remark that the analogous vinylidene fluoride/hexafluoropropene copolymers (wherein the HFP comonomer has $r = 0$, so that $r_1 r_2 = 0$) seem indeed to show this behavior,[30] resulting in a glass temperature much lower (by more than 50 °C, see Figure 6) than the value predicted by the Flory−Fox equation:[7]

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \tag{26}$$

We note incidentally that this rule, implying a quasi-straight line through the whole range of compositions in Figures 4 and 6, is well obeyed in the block copolymer case with $r_E r_P \rightarrow \infty$, but is not otherwise. As far as the ethylene/propylene copolymers are concerned, in the random case (i.e., $r_E r_P = 1$) we calculate a decrease of $\bar{T}_g$ larger than 10 °C in the central region of compositions, to become twice as large in the case of a tendency to complete alternation (i.e., $r_E r_P \rightarrow 0$, see Figures 4 and 5).

From the viewpoint of the numerical results the main message of this paper stands in the prediction that the more the propylene and the ethylene units alternate along the chain sequence, the more the chain entropy increases and the lower the glass temperature turns out to be. In turn, this result is easily understood with the use of the correlation matrices reported in eqs 22; regarding the Boltzmann weight $\omega$ to be roughly zero ($T < 0$ °C), there are only five sequences of rotational states allowed to a PP unit pair, all of which comprise a TG or GT combination, whereas there are 13 of them for either an EP or a PE pair. Analogous, although quantitatively different, considerations apply to the fluorinated copolymers.

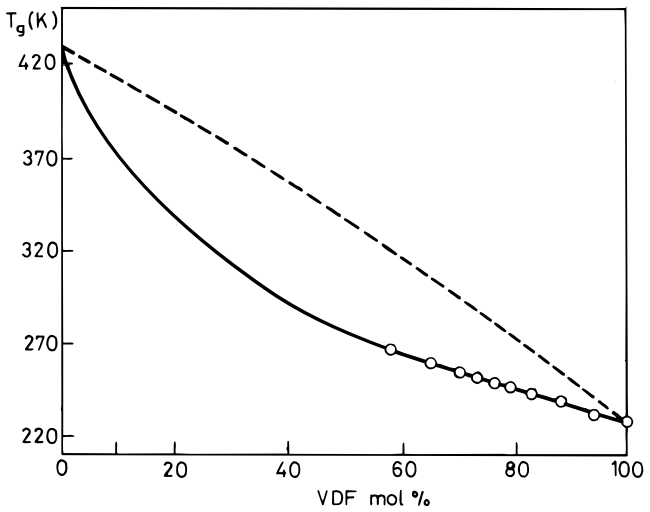


**Figure 6.** Glass transition temperature of vinylidene fluoride (VDF)/hexafluoropropene (HFP) copolymers for various compositions, reported after Bonardelli, Moggi, and Turturro.[30] The open circles are experimental values, the solid line is evaluated from a modification of the Flory−Fox equation accounting for the concentration of the comonomer dyads,[30] and the dashed line is the prediction from the simple Flory−Fox equation.[7]

As an additional comment, we see from Figure 2 that a polyethylene chain has a much larger entropy per chain bond than has a polypropylene chain at the same temperature. This may appear at odds with the former polymer being more expanded than the latter in the unperturbed state (the characteristic ratio $C_\infty$ is ∼6.8 and <5, respectively, for similar temperatures $T$ >100 °C).[10] Therefore, we conclude that a larger *chain expansion* is not necessarily associated with a larger *chain rigidity*.

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## References and Notes

(1) Gibbs, J. H.; DiMarzio, E. A. *J. Chem. Phys.* **1958**, *28*, 373.
(2) Speedy, R. H. *Mol. Phys.* **1993**, *80*, 1105.
(3) Di Marzio, E. A.; Yang, A. J. M. *J. Res. Natl. Inst. Stan. Technol.* **1997**, *102*, 135.
(4) Allegra, G.; Bignotti, F.; Gargani, L.; Cociani, M. *Macromolecules* **1990**, *23*, 3, 5326.
(5) Allegra, G. *J. Polym. Sci., Part C* **1967**, *16*, 2815.
(6) Allegra, G. *Makromol. Chem.* **1968**, *117*, 12; **1968**, *117*, 24.
(7) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
(8) Zambelli, A.; Grassi, A.; Galimberti, M.; Mazzocchi, R.; Piemontesi, F. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 523.
(9) DiMarzio, E. A.; Dowell, F. *J. Appl. Phys.* **1979**, *50*, 6061.
(10) Cotton, J. P.; Farnoux, B.; Jannink, G.; Mons, J.; Picot, C. *C. R. Acad. Sci. (Paris)* **1972**, *275, 3C*, 175. Wignall, J. D.; Ballard, D. G. H.; Schelten, J. *Eur. Polym. J.* **1974**, *10*, 861.
(11) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.

(12) Eisenberg, A. In *Physical Properties of Polymers*, 2nd ed.; Mark J. E.; American Chemical Society: Washington, DC, 1993; p 61.
(13) Lifson, S. *J. Chem. Phys.* **1959**, *30*, 964.
(14) Lehman, G. W.; McTague, J. P. *J. Chem. Phys.* **1966**, *44*, 4567.
(15) Lifson, S.; Allegra, G. *Biopolymers* **1964**, *2*, 65.
(16) Allegra, G. *Chim. Ind.* **1973**, *55*, 485.
(17) Mark, J. E. *J. Chem. Phys.* **1972**, *57*, 2541.
(18) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253.
(19) Quirk, R. P.; Alsamarraie, M. A. A., in *Polymer Handbook*, 3rd ed., Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; Sect. V/27.
(20) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.
(21) Allegra, G.; Marchessault, R. H.; Bloembergen, S. *J. Polym. Sci., Part B* **1992**, *30*, 809.
(22) Brueckner, S.; Allegra, G.; Gianotti, G.; Moraglio, G. *Eur. Polym. J.* **1974**, *10*, 347.
(23) Allegra, G.; Brueckner, S. *Macromolecules* **1977**, *10*, 106.
(24) Matsuoka, S. *J. Res. Natl. Inst. Stan. Technol.* **1997**, *102*, 213.
(25) Kauzmann, W. *Chem. Rev.* **1948**, *43*, 219.
(26) Woodcock, L. V. *Ann. N. Y. Acad. Sci.* **1981**, *371*, 274.
(27) Milchev, A. I. *C. R. Acad. Bulg. Sci.* **1983**, *36*, 1413.
(28) Binder, K. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1381.
(29) Baldwin, F. P.; Ver Strate, G. *Rubber Chem. Technol.* **1972**, *45*, 709.
(30) Bonardelli, P.; Moggi, G.; Turturro, A. *Polymer* **1986**, *27*, 905.

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