Macromolecules 1990, *23*, 5326-5334

Glass Transition in Polymers: Freezing of Rotational Oscillations

Giuseppe Allegra,[*,†] **Fabio Bignotti,**[†,‡] **Luciano Gargani,**[§] **and Michele Cociani**[∥,⊥]

Dipartimento di Chimica, Politecnico di Milano, Piazza L. da Vinci, 32, 20133 Milano, Italy, ENICHEM-ELASTOMERI, Via Maritano, 26, 20097 San Donato Milanese, Italy, and Dipartimento di Chimica Fisica Applicata, Politecnico di Milano, Piazza L. da Vinci, 32, 20133 Milano, Italy

Received January 4, 1990; Revised Manuscript Received May 7, 1990

ABSTRACT: A nonlattice model based on space-filling criteria is adopted to investigate the glass transition in polymers. In qualitative agreement with Gibbs and DiMarzio, in the glass phase the chains are considered to assume a single rotational isomeric state. The temperature T_2 at which the entropies of the amorphous and of the glass phase are equal is taken as the lower limit of the glass transition temperature for slow experiments. Unlike Gibbs and DiMarzio, rotational oscillations are allowed in both phases, under the assumptions that all the bond lengths are equal and that each side group is represented by a single conformer. Calculations performed on high molecular weight polyethylene, iso- and syndiotactic polypropylene, atactic polystyrene, *cis*-1,4-polybutadiene, and *cis*-1,4-polyisoprene indicate that a substantial reduction of the average rotational oscillation around single bonds takes place upon lowering the temperature at T_2; at this temperature the root-mean-square angle of oscillation appears to be very closely the same for all the polymers investigated (~8°), suggesting a sort of universal behavior at the glass transition.

1. Introduction

Lattice models were extensively used to investigate phase transitions occurring in amorphous polymers upon decreasing temperature; here we refer particularly to the early, fundamental studies by Flory[1] and Gibbs and DiMarzio.[2] While Flory suggests that the transition should result in an ordered state of parallel chains (either liquid crystalline or truly crystalline),[1] Gibbs and DiMarzio, although basically following the same statistical criteria, assume that if the configurational entropy of the system vanishes at a temperature T_2, the polymer changes to a so-called glassy state. Here the actual configuration of the chains is statistically no different from the amorphous state, but the multiplicity may be considered as equal to unity, so that no alternative configuration exists and the system is frozen. Accordingly, T_2 is identified with the lower limit of the glass transition temperature, T_G, which in turn may be reached in principle with very slow experiments. It must be stressed that Flory's and Gibbs and DiMarzio's viewpoints are not intrinsically conflicting. In fact, as already suggested by the latter authors,[2] suppose either that the polymer is structurally unable to achieve a parallel-chain-ordered arrangement, as is the case with an atactic vinyl polymer, or that it may be supercooled to a metastable temperature range where the permitted chain motions are so slow as to make any transformation to an ordered state virtually impossible; in both cases the glass transition at T_2 may be regarded as an equilibrium process, in the (practically attainable) limit of very slow experiments. For the sake of simplicity, throughout this paper we shall identify T_2 with T_G, in the implicit assumption that the latter temperature is always obtained from sufficiently slow experiments.

In the present study, Gibbs and DiMarzio's original viewpoint is extended and generalized. Backbone oscillations around the rotational minima are explicitly considered both above and below the limiting transition temperature T_2. It will be shown that evidence from six well-known hydrocarbon polymers indicates that such oscillations suffer a discontinuous decrease upon cooling of the amorphous polymer at T_2, as was already suggested by Roe and Tonelli on the basis of a specific heat investigation.[3,4] At the present stage, the theory requires that the side groups have a single conformation and that the chain bonds all be of the same length; besides, all the chains are considered to have the same molecular weight. The theory applies to homopolymers with nonequivalent backbone atoms within the monomeric unit, as well as to copolymers with any statistical composition, provided no phase demixing takes place.

2. Space-Filling Model

Let us consider a monodisperse system of ν homopolymer chains ($\nu \gg 1$), each comprising N skeletal atoms, that is $N - 1$ skeletal bonds ($N \gg 1$), at temperature T. The polymer pervades a volume V with a volume fraction ($1 - v_0$), defined as follows. Let $\bar{V}$ be the average volume per chain atom, including the side groups, for the densest state of the polymer (e.g., the crystalline state if it exists at temperature T). Then v_0 will be given by

$$v_0 = 1 - \nu N \bar{V}/V \tag{1}$$

and will be considered as the free volume fraction in the bulk polymer or the (free volume + solvent) fraction if solvent is present.

Our objective will be to evaluate the number of states, Ω, accessible to the polymer system—or, equivalently, its entropy $S = k_B \ln \Omega$—considering both the intramolecular degrees of freedom of the chains and the statistical restrictions inherent with the requirement of space filling. To distinguish the present nonlattice approach from the classical lattice theories, we shall characterize it as the "space-filling model". In the following we shall accept Flory's random-coil hypothesis for the multichain system[1] both above and below T_G (or T_2). Since this hypothesis implies that the packing forces do not modify the chain configurational statistics, it will make it possible for us to factorize the partition function of the system into conformational, positional-orientational, and packing contributions, as will be seen.

[†] Dipartimento di Chimica, Politecnico di Milano.
[‡] Present address: Viale Libertà, 78, 25081 Bedizzole, Italy.
[§] ENICHEM-ELASTOMERI.
[∥] Dipartimento di Chimica Fisica Applicata, Politecnico di Milano.
[⊥] Present address: Via E. Toti, 44, 20090 S, Maurizio al Lambro, Italy.

0024-9297/90/2223-5326$02.50/0

We shall first evaluate the total number, $\Omega_N{}^\circ$, of chain configurational states, irrespective of both packing exclusion and orientation of the chains within the system. Since we want to account for oscillatory fluctuations around the rotational minima, we cannot extract $\Omega_N{}^\circ$ from a lattice model[1,2] nor from the chain partition function in the usual rotational isomeric state (ris) approximation.[5] A full evaluation of the configurational integral, such as may be obtained in the "all skeletal rotations", or asr scheme,[6-10] should be carried out, after the correlation energy over neighboring rotational angles is obtained from an adequate analysis of the intramolecular interactions. However, in this first investigation of the subject we shall adopt the simple assumption that the energy within each rotational minimum may be separated into contributions each due to a single rotational angle, which enables the free energy term for rotational fluctuations to be separately obtained. A more substantial difficulty lies in the absence of a precise definition of the cell volume in the space of configurations, within classical mechanics, which introduces an undetermined factor in the evaluation of $\Omega_N{}^\circ$. The difficulty will be circumvented as follows. We shall assume that at sufficiently low temperatures, because of the increased chain rigidity coupled with packing constraints, each chain is forced to occupy a single rotational isomeric state, belonging to the same ensemble of disordered conformations predominating in the amorphous state. In other words, each skeletal rotational angle is restricted within a single potential energy minimum. This assumption amounts to a definition of the glassy state, with thermodynamics properties of its own. It also suggests a natural way to evaluate $\Omega_N{}^\circ(T{>}T_2)$. Let us suppose $\omega_N{}^\circ(T)$ is the unnormalized number of chain configurations, obtained by assigning an arbitrary, fixed value to the cell volume. We shall define as $\Omega_N{}^\circ(T{>}T_2)$ the ratio $\omega_N{}^\circ(T{>}T_2)/\omega_N{}^\circ(T_2)$. More specifically, let us label as Z_N and $Z_N{}'$ the chain configurational partition function for the amorphous state ($T > T_2$) and the glassy state ($T \leqslant T$), respectively. The chain entropy above T_2 will be

$$S_N{}^\circ = k_B \frac{\mathrm{d}}{\mathrm{d}T}(T \ln Z_N) \tag{2}$$

whereas at $T = T_2$ we have

$$S_{N2}{}^\circ = k_B \frac{\mathrm{d}}{\mathrm{d}T}(T \ln Z_N{}')_{T=T_2} \tag{3}$$

the zero suffix meaning again that the isolated chain is being considered, irrespective of packing effects. From the previous definition, considering that the entropy must be proportional to the number of chain bonds, the multiplicity of chain configurations, $\Omega_N{}^\circ$, is

$$\Omega_N{}^\circ = \exp(S_N{}^\circ/k_B)/\exp(S_{N2}{}^\circ/k_B) = [\exp(\Delta s^\circ/k_B)]^{N-1} \tag{4}$$

where

$$\Delta s^\circ = (S_N{}^\circ - S_{N2}{}^\circ)/(N-1) \tag{5}$$

The total number of configurations of all the ν chains, regardless of packing effects as well as of rigid-body chain translations and rotations, will be

$$\Omega^\circ = (\Omega_N{}^\circ)^\nu \tag{6}$$

The effective number of configurations, Ω, of our system will be obtained from Ω° after multiplication by two further factors, P and W, defined as follows.

(i) P is the probability that the random placement of the chains in the total available volume will not be forbidden by packing exclusion; it will be conveniently denoted as the packing factor. We shall consider an ideal process of stepwise introduction of the νN chain atoms, together with their side groups, in the volume V. It is assumed that all the chain bonds are equal and that the side groups are rigidly connected to the main chain. Together with its side groups, the general chain atom pervades a volume V_k ($1 \leqslant k \leqslant \nu N$), which need not be equal to any other $V_{k'}$ with $k' \neq k$. At the introduction of the kth atom into the total volume V, the empty volume fraction is

$$f_k = 1 - (V_1 + V_2 + \dots + V_{k-1})/V \tag{7}$$

and, within the classical mean-field approach, the probability P_k that no steric conflict arises may be taken as

$$P_k = (f_k)^{V_k/V^*} \tag{8}$$

Here V^* is a suitable unit volume, to be regarded as a space portion that may be either completely empty or completely full, with a probability uncorrelated with that of the surrounding space. Postponing determination of V^*, we put

$$V^* = \alpha \bar{V} \tag{9}$$

where the dimensionless quantity α may be reasonably expected to be around unity. The total probability, P, of a sterically permitted space configuration is

$$P = \prod_{k=1}^{\nu N} P_k \tag{10}$$

or when we introduce the logarithm and remember eqs 7–9

$$\ln P = \sum_{k=1}^{\nu N} \frac{V_k}{\alpha \bar{V}} \ln\,[1 - (V_1 + V_2 + \dots + V_{k-1})/V] \tag{11}$$

We shall introduce the variable $z(k)$, defined as

$$z(k) = (V_1 + V_2 \dots + V_{k-1})/V \tag{12}$$

whose general increment is

$$\Delta z(k) = z(k+1) - z(k) = V_k/V \tag{13}$$

Considering that $\Delta z(k)$ is very small compared with unity, so that $z(k)$ changes continuously with k, we may evaluate the sum in eq 11 as an integral. Considering that (see eq 1)

$$z(\nu N) = (V_1 + V_2 + \dots + V_{\nu N})/V = \nu N \bar{V}/V = 1 - v_0 \tag{14}$$

eq 11 reduces to

$$\ln P = \frac{\nu N}{\alpha(1 - v_0)} \int_0^{1-v_0} \ln\,(1 - z)\,\mathrm{d}z = \frac{\nu N}{\alpha}\left(1 + \frac{v_0}{1 - v_0} \ln v_0\right) \tag{15}$$

In principle, $\alpha = V^*/\bar{V}$ might depend on the distribution of the volumes V_k around their average $\bar{V}$ and even, in a subtler way, on their sequential order within the chains. However, we shall assume that the steric factor P' of any sufficiently long chain portion depends solely on the number of the chain atoms and on the fractional volume occupied altogether, no matter how different the volumes associated with the individual chain atoms are. We note incidentally that, aside from intuitive arguments, this assumption is consistent with the widely accepted additivity of the volumes of the molecular fragments.[11] As a direct consequence, α may be regarded as a universal constant; in section 4 we shall see that it is to be equated with unity on account of consistency with lattice statistics.

We stress that the previous statistical derivation rests on the implicit assumption that all the chain bonds have the same length; as an extreme negative example, it is easy to see that if some chain bonds were reduced to a zero length, their number should be subtracted from νN in eq 15. In the following we shall consider single and double carbon-to-carbon chain bonds as having effectively the same length ($d_{\mathrm{C-C}} = 1.54$ Å, $d_{\mathrm{C=C}} = 1.35$ Å).

(ii) W is the positional and orientational factor, that is, the number of ways to place one end of all the ν chains. In turn, this process consists of the placement of the first atom plus the orientation of the intrinsic Cartesian framework of the first bond.[1,2] When r is defined as the possible orientations of this framework, the number of ways, W_i, to place the first end of the ith chain ($1 \leqslant i \leqslant \nu$) is given by r times the number of average volumes $\bar{V}$ remaining empty at this stage;[1] that is

$$W_i = r[\mathcal{N} - (i-1)N] \tag{16}$$

where (see eq 1)

$$\mathcal{N} = V/\bar{V} = \nu N/(1 - v_0) \tag{17}$$

The overall factor W is

$$W = \prod_{i=1}^{\nu} W_i/\nu! \tag{18}$$

where the factorial implies that the sequential order among the chains may be permuted in all possible ways. It should be stressed that, apart from the arbitrary choice of the placement of the first few atoms of each chain, no further freedom is to be allowed, since the chain is assumed to be in one of its Ω_N° intramolecular configurations. Using Stirling's approximation for ln (ν!) and changing again the sums of logarithms into integrals, we get

$$\ln W = \nu\left[\ln (Nr) - \ln (1 - v_0) - \frac{v_0}{1 - v_0} \ln v_0\right] \tag{19}$$

The total number, Ω, of configurational states of the system is given by

$$\ln \Omega = \ln \Omega^\circ + \ln P + \ln W \tag{20}$$

where the terms in the right-hand side are given by eqs 4, 6, 15, and 19. As a result, the overall configurational entropy, S, is

$$S = k_{\mathrm{B}} \ln \Omega = k_{\mathrm{B}}\nu\left\{(N-1)\left[\Delta s^\circ/k_{\mathrm{B}} - \frac{1}{\alpha}\left(1 + \frac{v_0}{1 - v_0}\ln v_0\right)\right] + \ln N + \left[\ln r - \frac{1}{\alpha} - \ln (1 - v_0) - \left(1 + \frac{1}{\alpha}\right)\frac{v_0}{1 - v_0}\ln v_0\right]\right\} \tag{21}$$

Note that $P < 1$, so that $k_{\mathrm{B}} \ln P$ is a *negative contribution* to the entropy.

3. A Second-Order Transition

From eq 21 we obtain the critical temperature, T_2, by putting $S = 0$. This amounts to saying that at $T = T_2$ the system is restricted to a single state, wherein each chain is in a single rotational isomeric configuration with suitable fluctuations; the average amount of the fluctuations will be dealt with in section 6 and is reflected to the actual value of Δs°. It should be noted that if a chain has wider fluctuations than those permitted at $T = T_2$, its configurational multiplicity Ω_N° (see eq 4) is larger than unity even if it were hypothetically restricted to a single rotational isomeric state; in fact, the fluctuations would inevitably bring most of the chain atoms into different unit volumes, thus giving rise to more than one effective configurational state. Note also that we have $S < 0$ for $T < T_2$, because the fluctuations become smaller than those at T_2. Needless to say, negative entropy values are only possible because S is actually obtained as an entropy difference.

Putting $S = 0$ in eq 21 implies that, although we have two different functions $S_1(T{>}T_2)$ and $S_2(T{\leqslant}T_2)$ for the amorphous and for the glassy state, respectively, they become equal in the limit $T \rightarrow T_2$, so that we do not have a first-order transition. However, we have, in general

$$C_{\mathrm{P}}(T_2^{\,+}) = T_2\left(\frac{\mathrm{d}S_1(T{>}T_2)}{\mathrm{d}T}\right)_{T\rightarrow T_2} \neq C_{\mathrm{P}}(T_2^{\,-}) = T_2\left(\frac{\mathrm{d}S_2(T{\leqslant}T_2)}{\mathrm{d}T}\right)_{T=T_2} \tag{22}$$

where $C_{\mathrm{P}}(T)$ stands for the heat capacity at constant pressure. We conclude that, within the present space-filling model, at $T = T_2$ we have a second-order transition, in analogy with the lattice model of Gibbs and DiMarzio.[2]

4. Comparison with Previous Results

Equation 21 may be compared with the lattice results obtained both by Flory[1] and by Gibbs and DiMarzio.[2] For the last two authors, at $T \leqslant T_2$ the system is assumed to have a single accessible configuration,[2] so that $S_N^\circ(T{\leqslant}T_2) = 0$. As a consequence, from eq 5 we have $\Delta s^\circ(T{\leqslant}T_2) = S_N^\circ(T)/(N-1)$. Since the partition function may be written as $Z_N = \lambda^{N-1}$ and $S_N^\circ = k_{\mathrm{B}}(\mathrm{d}/\mathrm{d}T)$ $(T \ln Z_N)$, we have

$$\Delta s^\circ = k_{\mathrm{B}}\left(\ln \lambda + T\frac{\mathrm{d} \ln \lambda}{\mathrm{d}T}\right) \tag{23}$$

Although not stated explicitly, the same conclusion is applicable to Flory's theory. In this case the term ΔG_{M} [see eq 3 and following equations of ref 1] represents the free energy difference between an initial state, consisting of the pure solvent and of the pure polymer in a perfectly ordered arrangement of parallel chains with a rodlike configuration and a final state wherein disordering of the chains and their mixing with the solvent has occurred. This quantity may be written as $\Delta H_{\mathrm{M}} - T\Delta S_{\mathrm{M}}$; in turn, ΔS_{M} is to be equated with $S = k_{\mathrm{B}} \ln \Omega$, whereas in our formalism ΔH_{M} may be expressed as

$$\Delta H_{\mathrm{M}} = k_{\mathrm{B}}T\nu N[T\mathrm{d} \ln \lambda/\mathrm{d}T + \chi v_0] \tag{24}$$

χ being the well-known Flory interaction parameter.[12] The first term in square brackets stands for the conformational energy change of the polymer with respect to the initial, reference state; the second term accounts for the solvent–polymer interaction after mixing, the free volume being disregarded in this approach. Remembering eq 23, using the following expression of the configurational partition function per chain bond λ, appropriate to the cubic lattice model

$$\lambda = 1 + (z - 2) \exp(-\epsilon/k_{\mathrm{B}}T) \tag{25}$$

where z is the lattice coordination number and ϵ is the energy of a nonextended conformation of two consecutive bonds, we see that all the N-dependent terms of S in eq 21 are correctly reproduced by eqs 4–6 of ref 1.

Concerning Gibbs–DiMarzio's approach, we shall limit again our analysis to the N-dependent contribution, assuming $N \gg 1$. With the previous notation, eq 20 of ref

2 may be written as

$$S = k_B \ln \Omega = k_B \nu \left\{ (N-1) \left[\ln \lambda + T \frac{d \ln \lambda}{dT} + z/2 \left(\frac{1}{1-\upsilon_0} - \frac{2}{z} \right) \times \ln \left(1 - \frac{2}{z}(1-\upsilon_0) \right) - \frac{\upsilon_0}{1-\upsilon_0} \ln \upsilon_0 \right] + \ln N \right\} \quad (26)$$

where z is again the lattice coordination number and according to Gibbs–DiMarzio's notation λ is expressed as

$$\lambda = \exp(-\epsilon_1/k_B T) + (z-2)\exp(-\epsilon_2/k_B T) \quad (27)$$

ϵ_1 and ϵ_2 being the energy of the extended and nonextended conformations of three consecutive bonds, respectively (e.g., they are the trans and gauche conformational states on a diamond lattice with $z = 4$). Comparison with eqs 15 and 21 shows that in the Gibbs–DiMarzio lattice approach the packing factor P is given by ($N \gg 1$)

$$\ln P = \nu N \left\{ \left[\frac{z}{2(1-\upsilon_0)} - 1 \right] \ln \left[1 - \frac{2}{z}(1-\upsilon_0) \right] - \frac{\upsilon_0}{1-\upsilon_0} \ln \upsilon_0 \right\} = \nu N \left\{ \left[-1 + \frac{1}{z}(1-\upsilon_0) + \frac{2}{3z^2}(1-\upsilon_0)^2 + \ldots \right] - \frac{\upsilon_0}{1-\upsilon_0} \ln \upsilon_0 \right\} \quad (28)$$

The final expression in square brackets decreases toward -1 with increasing z; for example, taking $\upsilon_0 = 0$, it is -0.69, -0.81, -0.86, and -0.91 for $z = 4$ (diamond lattice), 6 (cubic lattice), 8 (centered cubic lattice), and 12 (face-centered cubic lattice), respectively, with no higher z-values existing for regular lattices with equivalent bonds. Within our space-filling model any space direction is permitted in principle to any chain bond, which may suggest to us to set $z \to \infty$ as a sort of analytic continuation from the previous succession. [Note that the limit $z \to \infty$ is suggested for eq 28 but *not* for eq 27. In the latter case, z is not to be regarded as the coordination number of the lattice but rather $z - 1$ is the number of possible rotational states around each bond, which is always finite and small in the rotational isomeric state approximation, e.g.] Identification of eq 28, $z \to \infty$, with eq 15 leads to $\alpha = 1$, which henceforth will be our unique choice. In other words, the basic unit volume V^* that may be regarded as filled or empty independently of the surrounding space appears to coincide with the average volume per chain atom, $\bar{V}$. As an additional remark, we point out that uniformity of all bond lengths is also implied by the comparison of the lattice results with those deriving from the space-filling model.

5. Effective Configurational Degrees of Freedom in the Vicinity of the Glass Temperature

We have shown that eq 21, with $\alpha = 1$, applies to both homo- and copolymers, provided the chains are all both of the same length and of the same statistical composition. With decreasing temperature the configurational entropy S is also decreasing, mostly because of the intramolecular entropy difference per chain bond $\Delta s°$ (see eq 5); at a sufficiently low temperature T_2, S will vanish and we have $\Omega = 1$. Although each chain rotational angle has a limited oscillation around the minimum energy well where it is confined, this only permits the chain atoms to fluctuate around their mean positions. The suppression of rotational transitions from gauche to trans states, e.g., implies that the long chains cannot slip past one another; accordingly, at $T = T_2$ the polymer becomes effectively unable to undergo any significant strain and we may identify T_2 with the lower limit of the glass transition temperature, T_G, for slow experiments. Although eq 21 is only valid for $T \geq T_2$ (cf. eqs 2–5), it is easy to show that Ω would decrease to values smaller than 1 at $T < T_2$, because of the narrowing of the rotational oscillations.

From a qualitative point of view, we may distinguish three different temperature ranges, with decreasing temperature (see eq 21; ν, $N \gg 1$, $\alpha = 1$).

(i) At a sufficiently large T ($> T_2$), the first term within square brackets in eq 21 is positive; consequently, $\ln \Omega$ is of the order $\nu(N-1)$, or $\Omega = C^{\nu(N-1)}$, $C > 1$. This implies that each chain bond does contribute to the total number of states with a factor larger than unity; i.e., some rotational freedom is permitted to each bond, although restricted by packing effects.

(ii) At a lower T, although higher than T_2, the first term in square brackets of eq 21 vanishes. Consequently, we have $\ln \Omega = \nu[\ln N + \ln C]$, or $\Omega = (CN)^\nu$, C being a suitable positive constant. In words, each chain contributes to the total number of states with its own factor; however, this increases very slowly with the chain length, N. Qualitatively, once the location of the chain center of mass is chosen, the chain configuration is nearly fully determined by packing requirements. The situation is somehow reminiscent of the so-called "reptation" model; this states that under suitable circumstances the chains may only slide along their tubular boundaries, in which case their configuration is mostly dictated by the coordinate of their center of mass along the tube axis.[13,14] It should be stressed, however, that the existing number of chain configurations cannot be directly translated into a number of effective dynamical degrees of freedom.

(iii) If $T = T_2$, we have $S = k_B \ln \Omega = 0$ from eq 21, so that we have a single accessible state according to our model. Actually, intuition suggests that there must exist a multitude of such states in the glass phase, since they are configurationally disordered and derive from freezing-in of the amorphous states. This multiplicity of states at $T \leq T_2$ is not accounted for by the theoretical model because no correlation among packing chains is being taken into account; as a consequence, the calculated number of existing states is unduly restricted. The only possible conclusion is that the chain configurations in the glass phase represent a *coarse mapping* of the amorphous configurations. In other words, the result $\Omega = 1$ obtained at T_2 from eq 21 should be read: Ω is very small in the real system, so that a single configurational state in the glass phase coarsely corresponds to many (i.e., of order $C^{\nu N}$) states in the amorphous phase. As a consequence, the glass states are widely separated in phase space and changing from one to another involves a complex, coordinated motion of very many chains, with an effective free-energy barrier tending to infinity.

6. Application of the Theory to Some Representative Hydrocarbon Polymers

In the following we shall discuss some numerical results obtained by us for a few significant hydrocarbon polymers, namely (1) polyethylene, or PE, (2) isotactic polypropylene, or iPP, (3) syndiotactic polypropylene, or sPP, (4) atactic polystyrene, or PS, (5) *cis*-1,4-polybutadiene, or cPB, and (6) *cis*-1,4-polyisoprene, or cPIP. Note that, unlike the other cases, PS was really considered as a statistical copolymer consisting of disordered sequences of *d* and *l* units with opposite stereochemical configuration. This section will be preceded by a theoretical introduction on the calculation of the unperturbed partition function, Z_N (see eqs 2 and 3) for polymers and copolymers.

Let us first state a few simplifying definitions and assumptions. First, we point out that the requirement of uniformity of all the skeletal bond lengths is obeyed at least approximately in all cases, as already mentioned in section 2i). Concerning the second requirement of the theory, namely the existence of a single conformer for each side group, we recall that in the case of PS Yoon, Sundararajan, and Flory did in fact prove that the phenyl ring may only assume a single orientation, within narrow limits, with respect to the backbone bonds, for all the local chain conformations.[15] Likewise, the side methyl groups of PP, PB, and PIP may be expected to undergo a limited oscillation of the favored rotation angle around the C–CH$_3$ bond. The chain bonds will be subdivided in two groups represented by the rotationally flexible and by the rotationally rigid bonds, respectively, corresponding to the single and to the double bonds in this context. In turn, all the energy minima pertaining to the rotational states around flexible chain bonds lie within energy wells having an identical shape, and, although pairwise energy correlation between minima of neighboring bonds is considered,[16,17] rotational correlation within each minimum is neglected. We shall assume the general chain with $N - 1$ skeletal bonds to be part of a superchain with a periodic configuration;[18-20] in other words, disregarding changes of bond lengths and angles, the general configuration of the superchain is fully specified by the periodic sequence of skeletal rotation angles ($\theta_1\theta_2...\theta_{N-1}\theta_1\theta_2...\theta_{N-1}\theta_1\theta_2...$). It is also customary to denote this approximation as the "ringlike closure", which, however, implies the unnecessary constraint of geometrical bending to meet the chain ends. The chain configurational energy may be represented as

$$E(\theta_1,\theta_2...\theta_{N-1}) = E_1(\theta_1,\theta_2) + E_2(\theta_2,\theta_3) + ... + E_{N-1}(\theta_{N-1},\theta_1) \tag{29}$$

where the general contribution is given by

$$E_k(\theta_k,\theta_{k+1}) = E_{i_ki_{k+1}} + \frac{1}{2}U_0[1 - \cos 3(\theta_k - \bar{\theta}_{i_k})] \tag{30}$$

In eq 30 $E_{i_ki_{k+1}}$ is the energy at the minimum specified by the angles $(\bar{\theta}_{i_k},\bar{\theta}_{i_{k+1}})$, closest to the actual rotation angles (θ_k,θ_{k+1}). Here we assume that the kth skeletal bond is a single bond and that the potential barrier U_0 is the same throughout the chain; if we are in the presence of a double bond, the angle θ_k is regarded as fixed and the U_0-dependent term is missing. It should be stressed that, although we use a 3-fold-like potential as a common practice, the minimum energy angles $\bar{\theta}_i$ need not be exactly trans and gauche. Also, the actual value of U_0 is important in that it describes the *shape* and *width* of the energy function around the minima, where the vast majority of the chain conformations lie, but it will not be effectively regarded as an energy barrier in this context, kinetic considerations being absent. From eqs 29 and 30, the chain configurational partition function may be written as

$$Z_N = \sum_{i_1}\sum_{i_2}...\sum_{i_{N-1}}\exp[-E_{i_1i_2}/k_BT] \times \exp[-E_{i_2i_3}/k_BT]...\exp[-E_{i_{N-1}i_1}/k_BT] \times \prod_{k=1}^{N-1}{}^* \int_{\bar{\theta}_k-\pi/3}^{\bar{\theta}_k+\pi/3}\exp\left\{\frac{-U_0}{2k_BT}[1 - \cos 3(\theta_k - \bar{\theta}_k)]\right\} d\theta_k = Z_{N(\text{ris})}Q^* \tag{31}$$

where the general index i_k runs over all the rotational energy minima around the kth bond. In the last equality the result is factorized into two terms, the former (i.e., the multiple sum) being the usual partition function in the ris approximation and the latter being the oscillation contribution, i.e., the product of integrals denoted as Q^*. Actually, the asterisks on both $\prod^*$ and Q^* (see eq 31) are meant to indicate that only the single bonds are capable of undergoing significant torsional oscillations around the energy minima; the double bonds will be regarded as completely rigid, with no significant error, and contribute a factor of 1 to Q^*. Indicating the fraction of the chain single bonds with g, we have from eq 31

$$Q^* = \left\{\exp[-U_0/2k_BT]\frac{2\pi}{3}I_0[U_0/2k_BT]\right\}^{g(N-1)} \tag{32}$$

where $I_0(x)$ is the modified Bessel function of order zero. For most temperatures of interest we may assume $U_0 \gg k_BT$, so that in eq 31 the cosines may be replaced by their series development truncated at the square power terms and the integrals may be extended from $-\infty$ to $+\infty$. We get

$$Q^* \simeq [\Psi(T)]^{g(N-1)}; \quad \Psi(T) = \int_{-\infty}^{+\infty}\exp\left[-\frac{9U_0}{4k_BT}(\theta - \bar{\theta})^2\right] d\theta = \frac{2}{3}(\pi k_BT/U_0)^{1/2} \tag{33}$$

(Note that with our polymers the fraction g of chain single bonds is different from 1 only for cPB and cPIP, in which case $g = {}^3/_4$.)

Concerning the factor $Z_{N(\text{ris})}$ of eq 31, we concisely recall how to evaluate it through the largest eigenvalue method, both in the homopolymer and in the copolymer case, disregarding henceforth the irrelevant difference between $N - 1$ and N ($N \gg 1$).

Let $\text{-(}A_1A_2\text{–}...\text{–}A_m\text{)-}_{N/m}$ be a homopolymer chain comprising N/m monomeric units, each with m nonequivalent skeletal bonds (i.e., with m nonequivalent atoms). Within the first monomeric unit we shall label as the 1 bond (A_m–A_1), as the 2 bond A_1–A_2..., as the m bond (A_{m-1}–A_m). We shall denote as $\mathbf{U}^{(1)}$ the matrix carrying as its element (i_1,i_2) the statistical weight $\exp(-E_{i_1i_2}/k_BT)$, i_1 and i_2 being the indices of the general rotational minimum around bonds 1 and 2, respectively; see eq 31. An analogous definition applies to $\mathbf{U}^{(2)}$ for the rotational angles around bonds 2 and 3, ... up to $\mathbf{U}^{(m)}$ for the rotational angles around bonds $m - 1$ and m. If double bonds exist along the chain, each of them will be regarded as having a single (cis or trans) rotational state. In general, the statistical weight $\exp(-E_{i_ki_{k+1}}/k_BT)$ is the element (i_ki_{k+1}) of the matrix $\mathbf{U}^{(k)}$ if $k \leq m$; otherwise, it belongs to the matrix $\mathbf{U}^{(k \bmod m)}$. From eq 31 we have ($N/m \gg 1$)

$$Z_{N(\text{ris})} = \text{Tr}\,\{\mathbf{U}^{(1)}\cdot\mathbf{U}^{(2)}...\mathbf{U}^{(m)}\cdot\mathbf{U}^{(1)}\cdot\mathbf{U}^{(2)}...\mathbf{U}^{(m)}...\mathbf{U}^{(m)}\} = \text{Tr}\,(\mathbf{U})^{N/m} \simeq (\lambda_m)^{N/m} \tag{34}$$

where

$$\mathbf{U} = \mathbf{U}^{(1)}\cdot\mathbf{U}^{(2)}...\mathbf{U}^{(m)} \tag{35}$$

and λ_m is the largest eigenvalue of $\mathbf{U}$. It is convenient to write eq 34 in the form

$$Z_{N(\text{ris})} = \lambda^N \tag{36}$$

$$\lambda = (\lambda_m)^{1/m} \tag{37}$$

where λ is the effective ris partition function per skeletal bond. In our model examples, homopolymers PE, iPP, sPP, cPB, and cPIP have m = 1, 2, 2, 4, and 4, respectively; PS is considered a statistical copolymer of stereochemically opposite monomeric units d and l[21-23] and will be considered shortly. In the case of the diene polymers cPS and cPIP, the chain double bonds may not be considered in building up the correlation matrices, by introducing longer virtual bonds;[24] however, in this context it is expedient to retain the present formalism, which considers skeletal bonds of approximately equal length, as required by the theory.

In the case of an atactic polymer like PS, the evaluation of λ will be carried out through the pseudostereochemical equilibrium approach for copolymers with d and l units.[9,10,22,23] In view of the symmetry equivalence of these units, $f_{dd} = f_{ll} = f_{\mathrm{m}}$ is the only parameter required for the chain statistical description, f_{xy} meaning the frequency of occurrence (or unconditional probability) of the (x, y) pair; m stands for meso pair or meso diad. Correspondingly, $f_{\mathrm{r}} = 1 - f_{\mathrm{m}}$ is the frequency of *racemic* diads (dl) or ld).[9] The correlation matrix **U** may be cast in the form

$$\mathbf{U} = \begin{bmatrix} \sigma\mathbf{U}_{\mathrm{m}} & \mathbf{U}_{\mathrm{r}} \\ \mathbf{U}_{\mathrm{r}} & \sigma\mathbf{U}_{\mathrm{m}} \end{bmatrix} \tag{38}$$

where $\mathbf{U}_{\mathrm{m}} = \mathbf{U}_{\mathrm{m}}'\cdot\mathbf{U}_1'$, $\mathbf{U}_{\mathrm{r}} = \mathbf{U}_{\mathrm{r}}'\cdot\mathbf{U}_1'$ in the language of Flory and co-workers.[15,25] Application of this algorithm implies that the chain is formally regarded as a homopolymer whose monomeric units are capable of undergoing ($d \rightleftharpoons l$) stereochemical equilibration, and the multiplier σ is necessary to set f_{m} at the value required. If λ^* is the largest eigenvalue of **U** and **a** and $\mathbf{b}^{\mathrm{T}}$ are its left- and right-handed eigenvectors, respectively, we have

$$f_{\mathrm{m}} = \frac{\sigma}{\lambda^*}\mathbf{a}\begin{bmatrix} \mathbf{U}_{\mathrm{m}} & \mathbf{0} \\ \mathbf{0} & \mathbf{U}_{\mathrm{m}} \end{bmatrix}\mathbf{b}^{\mathrm{T}} \tag{39}$$

The effective value of λ is given by[9,22]

$$\ln \lambda = [\ln \lambda^* - f_{\mathrm{m}} \ln \sigma + f_{\mathrm{m}} \ln f_{\mathrm{m}} + (1 - f_{\mathrm{m}}) \ln (1 - f_{\mathrm{m}})]/2 \tag{40}$$

since the number of chain bonds per monomeric unit is 2 in the present case. Adopting this algorithm, one of us proved, in the case of both atactic polypropylene[9,21] and atactic polystyrene,[23] that the statistical distribution of the d and l units implied by the model was very close to first-order Markovnikovian, i.e., Bernoullian in terms of the diads. Should such a distribution be imposed more strictly, a suitable matrix expansion could be adopted.[26] In this connection, we point out that Flory and co-workers[27,28] used a similar matrix algorithm to obtain a different result. Namely, by putting $\sigma = 1$, they derived the partition function of a stereochemically equilibrated poly-α-olefin chain, polystyrene[15] or polypropylene[25] as examples, such as it may be obtained through the use of appropriate epimerization catalysts. From eqs 2, 31, 33, 36, and 37 the unperturbed chain entropy is

$$S_N{}^\circ = k_{\mathrm{B}}\frac{\mathrm{d}}{\mathrm{d}T}[T \ln Z_N] = k_{\mathrm{B}}N\{\ln \lambda + T\,\mathrm{d} \ln \lambda/\mathrm{d}T + g \ln [e^{1/2}\Psi(T)]\} \tag{41}$$

Concerning the chain partition function at $T \leqslant T_2$, namely Z_N', see eq 3, we shall consider two alternative hypotheses: (i) although no skeletal rotation may overcome the barriers around the energy minimum where it is entrapped, its contribution $\Psi(T)$ to the partition function factor Q^* is still given by the second part of eq 33; (ii) as a result of the packing forces hindering chain motion, at $T = T_2$ a discontinuous decrease of the mean-square oscillation around the minima takes place. In other words, unlike in case (i), in case (ii) at $T = T_2$ we have a sudden jump of the *effective* rotational barrier U_0 to a value $U_0' > U_0$ such that (see eq 33)

$$\Delta' = \langle(\theta - \bar{\theta})^2\rangle_{T=T_2}{}^{1/2} = (2k_{\mathrm{B}}T_2/9U_0')^{1/2} < \Delta = (2k_{\mathrm{B}}T_2/9U_0)^{1/2} \tag{42}$$

where Δ' is the actual root-mean-square value of the rotational oscillation, whereas Δ is the value that we would expect if no discontinuity existed, as in case (i). Determination of U_0' will not be discussed at this point.

In either case, for $T \leqslant T_2$ we shall follow the previous formalism, except that $Z_{N(\mathrm{ris})}$ will be identified with a single term of the sum given in eq 31, since each bond is restricted to a single rotational minimum in this temperature range.

(i) $T \leqslant T_2$; $U_0' = U_0$.

$$Z_N' = \exp[-(E_{i_1i_2} + ...)/k_{\mathrm{B}}T]\left[\frac{2}{3}(\pi k_{\mathrm{B}}T/U_0)^{1/2}\right]^{gN}$$

$$S_{N2}{}^\circ = k_{\mathrm{B}}\frac{\mathrm{d}}{\mathrm{d}T}[T \ln Z_N']_{T=T_2} = k_{\mathrm{B}}gN \ln \left[\frac{2}{3}(\pi e k_{\mathrm{N}}T_2/U_0)^{1/2}\right] \tag{43i}$$

(ii) $T \leqslant T_2$; $U_0' > U_0$. Equation 43i still holds, U_0 being replaced by U_0'. From eq 42 we have

$$S_{N2}{}^\circ \cong k_{\mathrm{B}}gN \ln [(2\pi e)^{1/2}\Delta'] \tag{43ii}$$

According to eqs 5, 41, and 43, the intramolecular entropy difference per chain bond $\Delta s^\circ = (S_N{}^\circ - S_{N2}{}^\circ)/(N - 1)$ is, in either case, $(N - 1 \simeq N)$

$$\Delta s^\circ = k_{\mathrm{B}}\left[\ln \lambda + T\frac{\mathrm{d} \ln \lambda}{\mathrm{d}T} + \frac{1}{2}g \ln \frac{T}{T_2}\right] \tag{44i}$$

$$\Delta s^\circ = k_{\mathrm{B}}\left[\ln \lambda + \frac{\mathrm{d} \ln \lambda}{\mathrm{d}T} + \frac{1}{2}g \ln \frac{2k_{\mathrm{B}}T}{9U_0\Delta'^2}\right] \tag{44ii}$$

From eq 21 with $\alpha = 1$, putting $S = 0$ to determine T_2, in the limits $\nu \to \infty$ and $N \to \infty$, we have

$$\lim_{\nu,N\to\infty} [S/k_{\mathrm{B}}(N - 1)] = \Delta s^\circ/k_{\mathrm{B}} - 1 - \frac{v_0}{1 - v_0} \ln v_0 = 0 \tag{45}$$

where Δs° is given by either one of eqs 44i or 44ii; $T = T_2$, depending on which model is chosen. We shall consider the alternative assumptions (i) and (ii) separately, with the aim of reproducing the experimental values of T_{G}, henceforth identified with T_2, of the six amorphous polymers under consideration (see Table I) after a suitable choice of U_0 and of Δ' for each of them.

Concerning the experimental T_{G}'s, we chose 180 K for PE both as an average of data reported by several authors[29] and as a suitably extrapolated figure from the T_{G}'s of ethylene–propylene copolymers with different compositions.[30] The data for iPP, sPP, cPB, and cPIP were taken from ref 29, and that for PS, from ref 30.

Values of λ in the rotational isomeric state (ris) approach were obtained following conformational and statistical analyses described elsewhere for PE,[20] iPP and sPP,[25] PS,[15,23] cPB,[24] and cPIP.[24] For both iso- and syndiotactic polypropylene, the sets of conformational parameters labeled as A–C in ref 25 were used, set A being the one that gives the best agreement between stereochemical-equilibration experimental results and energy calculations.[25] In the PS case the frequency of the meso diads was adjusted to the value $f_{\mathrm{m}} = 0.41$, corresponding to $\sigma = 1$ at $T = 300$ K in the matrix **U** (see eq 38), all the other parameters being given by ref 15, eqs 7–9, $E_{\omega''} = 2.2$ kcal/mol, $E_\eta = 0.38$ kcal/mol.

(i) Unrestricted Oscillation within Rotational Minima at T_{G}. Values of v_0 satisfying eq 45 for $T = T_{\mathrm{G}}$ $(= T_2)$ are reported in Table I, 3rd column; the intramolecular entropy difference per chain bond, Δs°, is given by eq 44i extrapolated at $T = T_2$. The resulting figures appear to be inconsistent among themselves, and, especially, much too large in comparison with common

Table I
Assumption (i) Implying Unrestricted Oscillation within Rotational Minima at T_G (Values of v_0 Deduced from Equations 44i and 45; $T_2 = T_G$) and Assumption (ii) Implying Restricted Oscillation at T_G (Values of the Barrier U_0 and of the Root-Mean-Square Oscillation, Δ, Just above T_G Evaluated from Equations 42, 44ii, and 45 for a Fixed Rms Oscillation at T_G (i.e., $\Delta' = 7.8°$))[a]

			U_0 (calc), kcal/mol, ($\Delta' = 7.8°$, assumption (ii)[b])			$\Delta = (2k_BT_G/9U_0)$, deg		
polym	T_G (exptl), K	v_0 (calc, assumption(i))	set A[25]	set B[25]	set C[25]	set A	set B	set C
PE	180[29,30]	0.12		3.0[19]			9.3	
iPP	265[29]	0.21	2.8	3.0	2.7	11.7	11.3	11.9
sPP	265[29]	0.21	2.8	3.0	2.6	11.7	11.3	12.2
PS	373[30]	0.36		3.5[24]			12.4	
cPB	171[29]	0.18		1.9[23]			11.3	
cPIP	200[29]	0.19		2.2[23]			11.5	

[a] The temperature T_G is identified with the transition temperature T_2 throughout. [b] The function ln $\lambda(T)$, see eq 44ii, was evaluated from the papers referenced in columns 4–6. With assumption (ii) v_0 is equal to 0.025.

sense expectation. If v_0 is identified with the free volume of the phenomenological theory (sometimes under the symbol f_g),[31,32] it is worth reminding in this connection that the value of v_0 at T_G is found to be in the vicinity of 0.025 for most known materials,[32] i.e., about 1 decade less than reported in Table I under the present assumptions.

(ii) Restricted Oscillation within Rotational Minima at T_G. In this case, $v_0 = 0.025$ was *assumed* a priori as the most probable value for the six polymers, and Table I gives the figures of U_0 required to fulfill eqs 44ii and 45; $T = T_G$. Under the further assumption that the root-mean-square amplitude, Δ', of the rotational oscillation at T_G is the same for all the polymers and such as to agree with the frequencly accepted value $U_0 = 3$ kcal/mol of the rotational barrier in polyethylene (about equal to that found in ethane[33]), Table I also reports the resulting figures of U_0 for iPP, sPP, PS, cPB, and cPIP. These values appear to be quite reasonable. In particular, the increase of U_0 for PS ($U_0 \simeq 3.5$ kcal/mol) with respect to PE ($U_0 = 3$ kcal/mol) is roughly equal to that resulting from conformational calculations[15] and should reflect the steric hindrance of the side phenyl groups during the rotations around chain bonds. Conversely, the value of U_0 for iPP and sPP turns out to be either equal to or a little smaller than 3 kcal/mol, depending on the actual parameters used for the ris description of the two polymers.[25] Concerning the two diene polymers, U_0 is found in the vicinity of 2 kcal/mol. Although the intrinsic rotational barrier for single bonds adjacent to double bonds is indeed ~2 kcal/mol,[34] the barrier for C–C bonds between saturated atoms is around 3 kcal/mol. Considering that the arithmetic average of the bond entropy contribution implies geometric average of the rotational barriers, see eq 44ii, the effective U_0 value to be expected for both cPB and cPIP should be approximately $U_0 = [(3)(2)(2)]^{1/3} = 2.3$ kcal/mol, instead of ~2 kcal/mol as given in Table I, with a modest disagreement within the degree of approximation of these preliminary calculations.

As a further consideration on this regard, the slightly larger figure of U_0 (cPIP) than of U_0 (cPB) as resulting from our calculations (2.2 vs 1.9 kcal/mol; see Table I), appears to be qualitatively consistent with the hindering effect of the side methyl groups of 1,4-polyisoprene, which are missing in 1,4-polybutadiene. Table I also gives the figures of the root-mean-square amplitudes of oscillation Δ at $T = T_G^+$, namely just above the transition temperatures, obtained as $(2k_BT_G/9U_0)^{1/2}$ (cf. eq 42; $T_2 = T_G$). On the average, the discontinuous decrease of the oscillation amplitude at T_G, expressed as $(\Delta - \Delta')/\Delta'$, is about 0.5. Figure 1 shows the plots of $\Delta s°/k_B$ vs T for all the polymers, a horizontal dashed line being drawn at the value $\Delta s°/k_B = 0.91$, namely the figure expected for $T = T_G$ (see eq 45, $v_0 = 0.025$). As may be observed, the specific value chosen for v_0 is not very important; even putting $v_0 = 0$, the calculated T_G's would not change by more than a few degrees. In other words, the experimental T_G's would be reproduced after only a small change of U_0 (~0.1 kcal/mol).

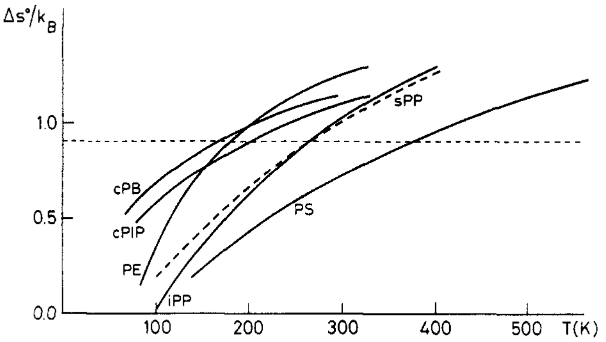

Figure 1. Plot of $\Delta s°/k_B$ vs T for six different hydrocarbon polymers. The entropy difference per chain bond, $\Delta s°$, is defined in eq 5 and is actually evaluated according to eq 44ii, with the parameters given in Table I, corresponding to restricted oscillation around chain bonds. The dashed straight line is equal to $(1 + [v_0/(1 - v_0)] \ln v_0)$ with $v_0 = 0.025$ (see text and eq 45); T_2 is given by the intersection of the dashed line with that giving $\Delta s°/k_B$ for any given polymer.

In conclusion, our calculations, based on currently accepted parameters, indicate that the observed glass transition temperatures of PE, iPP, sPP, PS, cPB, and cPIP (see Table I) agree with the present theoretical approach if each chain single bond is assumed to lie within a single rotational energy minimum at $T = T_G$ and if a sudden decrease of the root-mean-square amplitude of the rotational oscillation takes place at this temperature. More specifically, this oscillation changes from ~10–12° to a value $\Delta' = 7.8°$, which appears to be the same for all the polymers under investigation if currently accepted values of the rotational energy barrier U_0 are considered. Obviously enough, we may reverse the argument: if we assume reasonable values of U_0, we find values of Δ' that are closely similar for the six polymers investigated. Such a uniform bond oscillation at the glass transition might reflect the widely accepted uniformity of the free volume v_0 (=0.025) at T_G.[32] A significant, sharp reduction of the torsional oscillations at T_G was also suggested by Roe and Tonelli[3] on the basis of specific heat measurements for several polymers.

7. Physical Meaning of the Rotational Discontinuity at T_G

A comment on the abrupt decrease $\Delta \rightarrow \Delta'$ of the root-mean-square rotational oscillation at T_G is in order (see Table I). Let us regard Δ' as the largest rms angular oscillation, permitting the chain atoms to fluctuate around their mean positions without disturbing the tight chain packing in a single atomic arrangement, as is allowed at T_G. We may denote the arrangement of one chain in this state as an elementary chain configuration. At T just above T_G, many elementary chain configurations in thermal equilibrium are permitted, and, no matter how small the probability of each of them is, their statistical ensemble produces the root-mean-square value Δ ($>\Delta'$) expected from the Boltzmann distribution. It should be stressed that a single rotational isomeric state with a rms oscillation Δ, actually encompasses *many* elementary chain configurations (in particular, $\Omega_N{}^\circ \gg 1$; see eq 4). Accordingly, any misconception that at T_G the system suffers two distinct discontinuities, i.e., one in the number of ris states and another in the oscillation amplitude, should be dispelled. *Across T_G any chain of the system merely changes from a multitude of elementary configurations to a single one.*

It should be noted that if the whole continuum of chain rotational states is to result from a superposition of elementary configurations, the small oscillations permitted to these configurations should not be centered at the energy minima only. If this were the case, the average chain energy at T just above T_G would be larger than that at $T = T_G$ and we would have a first-order transition, contrary to the implication $S(T = T_2 = T_G)$ $(=\Delta S(T_G)) = 0$, see eq 21 and section 3, and contrary to experimental evidence. We conclude that the present ris approach is an expedient approximation wherein the oscillations are only permitted about the energy minima, although a more accurate physical picture of the elementary states at $T \leqslant T_G$ should regard them as being centered at any rotational angle, according to the Boltzmann distribution, with no substantial change of the theory.

8. Concluding Remarks

In this study the original idea of Gibbs and DiMarzio[2] that the glass transition in polymer systems arises from sudden suppression of most configurational states attainable in the amorphous state is used in an extension of the previous theory[1,2] to a nonlattice model, which allows for rotational oscillations; it may also be extended to the copolymer case. At the present stage of the new theoretical development, the assumptions are made that all the chain bonds have the same length and that the side groups do not possess any configurational freedom. As in Gibbs–DiMarzio's case, at the theoretical second-order transition a single, although disordered, rotational isomeric state (ris) is permitted to all the chains, and the corresponding temperature T_2 is to be regarded as the lower limit of the glass transition temperature for very slow experiments. Unlike for Gibbs and DiMarzio, the configurational entropy decreases continuously for $T < T_2$ in view of the ever smaller amplitude of the rotational oscillations (see eqs 42 and 43), within the classical–mechanical approach. The theory is not fully self-contained in that one statistical parameter, α (see eqs 9, 15, and 21), cannot be assigned a precise value from first principles. Comparing the final result with that derived from the lattice model (cf. eqs 15 and 28) enables us to overcome this ambiguity by establishing $\alpha = 1$. In physical terms, a volume equal to the average volume per chain atom may be regarded as being occupied with a probability independent from the occupation probability of the surrounding space.

The theoretical results are applied to six widely known synthetic polymers, namely polyethylene, isotactic and syndiotactic polypropylene, atactic polystyrene, *cis*-1,4-polybutadiene, and *cis*-1,4-polyisoprene. The conformational parameters were taken from previous studies on the chain's properties in unperturbed solution.[15,20,24,25] Atactic polystyrene was treated as a statistical copolymer of *d* and *l*, stereochemically opposite monomeric units, using the pseudostereochemical equilibrium approach, i.e., assuming a hypothetical epimerization equilibration with fixed amounts of *dd*, *dl*, *ld*, and *ll* pairs.[9,10,21–23] It is assumed for simplicity that within any local conformational energy minimum no correlation exists between neighboring rotation angles (see eq 30). However, the approximation might be avoided by recurring to the all-skeletal-rotations (asr) approach,[6–10] based on the Fourier expansion of the statistical weight and resulting in a matrix algorithm formally isomorphic with that associated with the rotational-isomeric-state (ris) scheme.[35] For all the six polymers under investigation, the second-order temperatures, T_2, cannot be reconciled with the experimental T_G's unless we assume that at T_2 a discontinuity exists in the mean-square oscillation around skeletal rotations. In fact (see Table I, case i), the free-volume fraction, v_0, should be attributed unphysically large values if no such discontinuity existed. It is noteworthy that if we assign the same value $\Delta' = 7.8°$ to the rms oscillation at T_G of all the investigated polymers, from the experimental T_G's we derive values of the rotational energy barrier, U_0 (see eq 30) in basic agreement with currently accepted figures (see Table I, case ii). A uniform value of the rotational oscillation Δ' at $T = T_G$ might reflect the existence of similar packing constraints for different polymers at the transition temperature and appears to be consistent with the fairly general value currently assumed for the free volume v_0 (=0.025) at T_G.[32] In particular, the actual figure of Δ' may be interpreted as the limit beyond which the rotational oscillations are incompatible with the existence of a single ris configuration in a tightly packed state. Taking the zero-point root-mean-square oscillation around the C–C bond in gaseous CH_3CHCl_2 (5.6°) and CH_2ClCl_3 (3.5°)[36] as a rough indication of the range wherein the zero-point rms skeletal oscillations of our polymers should lie, we see that they are comparable with, although smaller than, Δ'. This suggests that quantum effects cannot be excluded, although the present classical conclusions should be essentially correct.

In this connection, it is important to remember that Roe and Tonelli[4] already found that the abrupt change in C_p at the glass transition temperature for several polymers cannot be interpreted solely on the basis of the ris contribution to the free energy. They claim that even assuming a complete freezing of the torsional oscillations, the observed ΔC_p values cannot be fully accounted for and suggest that a change in the intermolecular nearest-neighboring coordination at T_G should be considered. In any event, these authors suggest that a significant reduction of the torsional oscillations is likely to take place at T_G.[3] Our results appear to support this suggestion completely. However, it must be mentioned that DiMarzio and Dowell's theory[37] of the vibrational contribution at the glass transition also explains the discontinuity of the specific heat. Although these authors do not predict a discontinuity in vibrational amplitude, they account for the specific heat effect in terms of changes in the characteristic frequencies arising from conformational and free-volume changes, in addition to changes of the force constants with temperature.

Acknowledgment. G.A. acknowledges the financial support of the Progetto Finalizzato Chimica, Consiglio Nazionale delle Ricerche, Italy. Very constructive criticism by the two reviewers of this paper is also acknowledged.

References and Notes

(1) Flory, P. J. *Proc. R. Soc. London, A* **1956**, *234*, 60.
(2) Gibbs, J. H.; DiMarzio, E. A. *J. Chem. Phys.* **1958**, *28*, 373.
(3) Roe, R. J.; Tonelli, A. E. *Macromolecules* **1979**, *12*, 878.
(4) Roe, R. J.; Tonelli, A. E. *Macromolecules* **1978**, *11*, 114.
(5) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(6) Allegra, G.; Immirzi, A. *Makromol. Chem.* **1969**, *124*, 70.
(7) Allegra, G.; Calligaris, M.; Randaccio, L. *Macromolecules* **1973**, *6*, 390.
(8) Allegra, G.; Calligaris, M.; Randaccio, L.; Moraglio, G. *Macromolecules* **1973**, *6*, 397.
(9) Allegra, G.; Brückner, S. *Macromolecules* **1977**, *10*, 106.
(10) Brückner, S.; Malpezzi Giunchi, L.; Allegra, G. *Macromolecules* **1980**, *13*, 42.
(11) Immirzi, A.; Perini, B. *Acta Crystallogr.* **1977**, *A33*, 216.
(12) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(13) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(14) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans.* **1978**, *74*, 1789, 1802, 1818.
(15) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(16) Volkenstein, M. V.; Ptitsyn, O. B. *Dokl. Akad. Nauk SSSR* **1951**, *78*, 657; *Zh. Fiz. Khim.* **1952**, *26*, 1061.
(17) Lifson, S. *J. Chem. Phys.* **1959**, *30*, 964.
(18) Corradini, P.; Allegra, G. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1961**, *30*, 516.
(19) Corradini, P.; Ganis, P.; Oliverio, P. *Atti Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat., Rend.* **1962**, *33*, 320.
(20) Allegra, G. *J. Chem. Phys.* **1978**, *68*, 3600.
(21) Allegra, G. *Makromol. Chem.* **1968**, *117*, 24.
(22) Brückner, S.; Allegra, G.; Gianotti, G.; Moraglio, G. *Eur. Polym. J.* **1974**, *10*, 347.
(23) Allegra, G.; Higgins, J. S.; Ganazzoli, F.; Lucchelli, E.; Brückner, S. *Macromolecules* **1984**, *17*, 1253.
(24) Mark, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 4354.
(25) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.
(26) Allegra, G. *Makromol. Chem.* **1968**, *117*, 12.
(27) Flory, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 1798.
(28) Williams, A. J.; Flory, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 3111.
(29) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975; Chapter III, pp 143–144, and also, for PE, Chapter V, p 16.
(30) Ferry, J. D. *Viscoelastic Properties of Polymers*; 2nd ed.; Wiley: New York, 1970; Table 12-III.
(31) Goldstein, M., Simha, R., Eds. *The Glassy Transition and the Nature of the Glassy State. Ann. N.Y. Acad. Sci.* **1976**, 279.
(32) Eisenberg, A. *Physical Properties of Polymers*; Mark, J. E., Ed.; American Chemical Society: Washington, DC, 1984; Chapter 2, p 55.
(33) Herschbach, D. R. *Bibliography for Hindered Internal Rotation and Microwave Spectroscopy*; Lawrence Radiation Laboratory, University of California: Berkeley, CA, 1962.
(34) Lide, D. R., Jr.; Mann, D. E. *J. Chem. Phys.* **1957**, *27*, 868; *Am. Rev. Phys. Chem.* **1964**, *15*, 225.
(35) Brückner, S. *Macromolecules* **1981**, *14*, 449.
(36) Allen, G.; Fewster, S. *Internal Rotation in Molecules*; Orville-Thomas, W. J., Ed.; Wiley: New York, 1974; Chapter 8, pp 255–283.
(37) DiMarzio, E. A.; Dowell, F. *J. Appl. Phys.* **1979**, *50*, 6061.