Glass Temperature of Polymer Ring Systems

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ABSTRACT: The glass temperatures of polymer ring systems are predicted from first principles and then compared to four sets of experimental data. In all four cases the glass temperatures rise with decreasing molecular weight as predicted by the theory. The glass transition is assumed to occur when the configurational entropy reaches a critically small value as the temperature is lowered. An attempt is made to keep the large number of parameters to a minimum by (1) estimating the number of flexible bonds per monomer through knowledge of chemical structure, (2) estimating the number of beads per monomer through considerations of volume, (3) estimating the intermolecular (hole) energy by means of the thermal expansion coefficient $\Delta\alpha$, and (4) fixing the lattice coordination number at the same value ($z = 4$) for all materials. The stiffness parameter $\Delta\epsilon$ is determined by a fitting to the infinite molecular weight glass temperature. With these constraints the fit to data is only qualitative. Although the theory is compared to experimental data only for glass temperature vs molecular weight, approximate formulas are obtained for ring glass temperature variation with plasticizer and with blend composition when at least one of the two blend components is a ring.

Introduction

In a previous paper[1] the entropy theory of glasses was used to predict the glass temperature of polymer rings. It was predicted that the T_g of rings rises steeply as the molecular weight is lowered while the T_g of linear polymers decreases steeply as the molecular weight is lowered. These surprising predictions were in accord with the data of Clarson et al. for poly(dimethylsiloxane).[2] Since that time, more data have appeared so that we now have four systems with which to compare with the theory (see the figures of this paper). The poly(2-vinylpyridine) studied by Hogen-Esch and Toreki[3] has steep variations in T_g for both rings and linear polymers (see Figure 1). Clarson's data for poly(phenylmethylsiloxane)[4] shows only a slight rise and then a decrease in the T_g of the rings as MW is lowered while the linear chains behave normally (see Figure 2). Data of Hogen-Esch[5] on polystyrene are much like those of P2VP. If we accept these data at face value, we must ask whether the entropy theory can accommodate the diversity of behavior displayed by the four sets of data. Figure 5, which displays theoretical predictions of glass temperature vs molecular weight for various ratios of intermolecular hole energy to intramolecular stiffness energy $E_h/\Delta\epsilon$, shows that the linear chain variations fall into a fairly narrow band while the rings have a much more diverse variation of T_g with molecular weight. We have some curves with steep variations and some with very weak maxima just as do the experimental data. So, in a general way we explain the qualitative observation that there is much more variation in the behavior of ring glass temperatures than linear glass temperatures.

However, in order to predict T_g more accurately for these systems, we need a more careful treatment of the configurational entropy on which the prediction of the glass temperature of rings is based. There are two components to this entropy. One is the number of configurations of an individual ring, and the other is the packing entropy arising from the competition of these rings for the same space. In this paper we make some progress toward this goal by giving improved formulas for the number of ways to pack molecules against each other, but the problem of calculating the number of configurations of an individual ring remains largely unsolved. Another goal of this paper is to compare the theory to experiment with the choice of a reasonable set of parameters. We will not try to fit the experimental curves quantitatively. Rather, we want to demonstrate that the Gibbs–Di Marzio entropy theory provides the correct physical picture for the glass transition and does so consistently for both linear and ring polymers. Therefore, the values for our parameters are most determined from accommodating the chemistry of the system rather than mathematically best fitting the curves. As a result, both the parameter values and the agreement with experimental data are qualitative. The final goal is to predict the glass temperature of various ring systems such as (1) ring–ring blend and ring–linear blend systems, (2) copolymeric rings, and (3) ring systems that are plasticized. These three classes of systems require only simple modifications of the existing treatments of their linear counterparts. Indeed, as will become apparent in this work, the equations of state for rings are virtually the same as those for linear polymers. All we need do to obtain the equations of state for rings from those for linear polymers is account for the difference between the entropy of an isolated ring and an isolated polymer and realize that the site fraction for rings is slightly different from that for linear polymers. This means that for every prediction made for linear systems we have a corresponding prediction for ring systems. We shall give first-order treatments in this work (see eqs 14 and 15), but more accurate treatments are easily obtained.

In the Theory section we discuss and expand the derivation of the two equations of state given in ref 1. The monomer is pictured as occupying b connected sites on a lattice, with rotations being allowed about γ of the bonds connecting the b beads. Also, formulas for blends composed of ring-plus-ring or ring-plus-linear molecules are given. In the Comparison to Experiment section we attempt to fit to the four sets of experimental data. The fits are qualitative rather than quantitative. In the Discussion section we give five approaches that could lead to improved predictions for ring glass temperatures.

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Appendix A relates the number of distinct ways to place an N-step ring polymer on a lattice to the number of distinct returns to the origin of an N-step random walk. The first quantity is needed for the Flory–Huggins counting procedure for flexible rings, but it is the second quantity that is evaluated in the literature. It is observed that no predictions exist in the literature for the number of configurations of semiflexible rings.

Theory

We have evaluated the partition function for rings by first solving the linear chain problem and then accounting for those differences that arise because of the rings. For linear chains the P–V–T and entropy equations of state are given by[6]

$$\ln (V_0^{(z-2)/2}/S_0^{z/2}) - zE_\mathrm{h}S_x^{\,2}/2kT - PC/kT = 0 \qquad (1)$$

$$S/kxN_x = \frac{z-2}{2}\ln\frac{V_0}{S_0} + \frac{N_0}{xN_x}\ln (V_0^{(z-2)/2}/S_0^{z/2}) + \frac{\ln ([(z-2)x+2](z-1)/2)}{x} + \frac{x-3}{x} \times [f\ln (z'-2) - (1-f)\ln (1-f) - f\ln f] \qquad (2)$$

Here N_x is the number of linear polymer chains of x segments, N_0 the number of holes, and $V_0 = 1 - V_x$ is the volume fraction of holes. z is the coordination number of the lattice onto which we imagine that each configuration of the molecule can be placed while z' is the coordination number associated with the molecule.[1] In the isomeric state model there are $z' - 2$ upper wells into which a bond can be placed and one lower well. We will use $z' = 4$ throughout. f, which is the fraction of bonds flexed out of their low-energy configuration, is given by $f = (z'-2)\exp(-\Delta\epsilon/kT)/[1 + (z'-2)\exp(-\Delta\epsilon/kT)]$ where $\Delta\epsilon$ is the energy difference between the one low-energy well and the $z'-2$ upper wells. E_h is the hole energy ($zE_\mathrm{h}/2$ is the energy required to form one hole). P is the pressure and C is the volume associated with one site. $S_0 = 1 - S_x$ is the Huggins surface-site fraction and is given by

$$S_0 = zN_0/[zN_0 + ((z-2)x+2)N_x] \qquad \text{linear chains} \qquad (3)$$

The thermodynamic transition temperature T_2 which we associate with the glass temperature T_g occurs when the configurational entropy reaches a critically small value. We have used $S_\mathrm{c} = 0$ and identified T_2 with T_g as in our previous papers for ease of discussion, but the relationship between T_2 and T_g and the critical value of S_c are important problems in their own right.

Equations 1 and 2 use the surface-site fraction appropriate to linear chains and therefore are, strictly speaking, not applicable to rings. They can be cast into a more general form suitable for discussion of rings by use of eq 10.09.6 of the work by Guggenheim.[7]

$$\ln (V_0^{\phi}/S_0^{\psi}) - zE_\mathrm{h}S_x^{\,2}/2kT - PC/kT = 0 \qquad (1\mathrm{A})$$

$$S/kxN_x = \phi\ln\frac{V_0}{S_0} + \frac{N_0}{xN_x}\ln (V_0^{\phi}/S_0^{\psi}) + \frac{\ln (xz(z-1)V_0/\sigma_\mathrm{g}S_0V_x)}{x} + \frac{x-3}{x} \times [f\ln (z'-2) - (1-f)\ln (1-f) - f\ln f] \qquad (2\mathrm{A})$$

where

$$\phi = (\theta-1)/(x-\theta), \quad \psi = (x-1)/(x-\theta) \qquad (3\mathrm{A})$$

θ is the number of neighbors to a polymer molecule divided by the coordination number z. For linear chains $\theta = [(z-2)x+2]/z$, so that $\phi = (\theta-1)/(x-\theta) = (z-2)/2$ and $\psi = (x-1)/(x-\theta) = z/2$. This shows that eqs 1 and 1A are identical and eqs 2 and 2A are identical except for the coefficients of the $1/x$ terms, which are identical only for small V_0. In our original derivation of eq 2 from the partition function, we were concerned with small V_0 only, but retaining all the terms would have resulted in eq 2A. For linear chains the symmetry factor σ_g is equal to 2. With these substitutions, the two sets of equations, eqs 1 and 2 and eqs 1A and 2A, are very little different from each other.

We use Huggins counting statistics (which are basically equivalent to Miller, Orr, Guggenheim, and Bethe statistics)[8] because they are a significant improvement over Flory statistics. For $z = \infty$ the Huggins and Flory counting statistics are the same, but for small z they are very different.[7]

There are several changes that occur in adapting these equations to rings. The first change that occurs is that the number of neighbors to a ring is now $(z-2)x$ rather than $(z-2)x+2$, which is appropriate for the linear chain. This means that $\theta = (z-2)x/z$ so that

$$\phi = (z-2)/2 - z/2x, \quad \psi = z(x-1)/2x$$

$$S_0 = 1 - S_x = zN_0/[zN_0 + (z-2)xN_x], \quad x > 2, \quad \text{rings} \qquad (4)$$

However, the main difference between rings and linear polymers is that the number of configurations of a ring is much smaller than those of a linear chain. We now seek to account for this difference and derive an equation for rings analogous to eq 2A. Because of the decoupling of holes and flexes, there is no effect on eq 1A other than that arising from the substitutions afforded by eq 4. If the number of configurations of a linear chain is $(z-1)^n$ where n is the number of steps, then we would expect to have $(z-1)^n/(2\pi n/3)^{3/2}$ ring configurations. This is the Jacobson–Stockmayer expression, which arises from the Gaussian approximation for the probability of the ends of a random-walk chain being separated by a distance r.

$$P(r) = \exp(-3r^2/2nl^2)/(2\pi nl^2/3)^{3/2} \qquad (5)$$

This expression is not expected be accurate for small n, so that we would need the exact results of Rappaport[9] or Domb[10] for n below about 10. The problem is compounded further because the chains are semiflexible. For the simple isomeric state model with nearest-neighbor energies we can write the partition function of one linear molecule as

$$q = (1 + (z'-2)\exp(-\Delta\epsilon/kT))^{x-3} = \sum\frac{(x-3)!((z'-2)\exp(-\Delta\epsilon/kT))^{f(x-2)}}{((1-f)(x-3))!(f(x-3))!} \qquad (6)$$

The summation variable is the number of flexes in the chain. The flex-dependent term (that multiplying $(x-3)/x$) in eq 2A arises from the individual chain partition function q. To evaluate q for a ring, there are two approaches. The approach used in a previous paper was to use the expression

$$P(r) = \exp(-3r^2/2\langle r^2\rangle)/(2\pi\langle r^2\rangle/3)^{3/2} \qquad (7)$$

with an expression for $\langle r^2\rangle$ that is $\Delta\epsilon$ dependent. However, eq 6 suggests a different route. We write

$$q_\mathrm{r} = \sum\frac{(x-2)!((z'-2)\exp(-\Delta\epsilon/kT))^{f(x-2)}}{((1-f)(x-2))!(f(x-2))!(2\pi(x-2)/3f)^{3/2}} \qquad (8)$$

We use $x-2$ rather than $x-3$ because for a ring the number of bonds is equal to the number of monomer units; for a linear chain the number of bonds is 1 less. To arrive at the additional term in the denominator, we must first modify eq 5 so that it is applicable to a semiflexible chain. Assume that at each place that a flex has occurred we have a swivel. There is free rotation at the swivel but nowhere else. Therefore, $f(x-2)$ is the number of steps in the walk, and l/f is now the average length of the step. The quantity $[(x-2)][l^2]$ in eq 5 (use $n = x-2$) transforms to $[f(x-2)][(l/f)^2] = (x-2)/f$ where the length of the bond l is set equal to 1. There are four corrections to this term which we have ignored. (1) There are actually $f(x-2)+1$ steps in the walk. (2) In the Gaussian expression for the probability we need to use the average of the square (of the number of steps), not the square of the average. This is a core result of the central limit theorem $\langle (l/f)^2 \rangle = 2\langle (l/f) \rangle^2$. (3) There is not a perfect swivel at each flex but rather $z'-2$ nontrans angles. This correction is material dependent. Improving it would mean that we need to abandon the nearest-neighbor assumption on the energies. This would be a major undertaking. (4) The probability is actually $P(r)$ multiplied by a volume element, which we take to be l^3. When we go to fn flexes per molecule rather than n, does the volume element change? If we had used $(l')^3 = (l/f)^3$ rather than l^3, then this would bring the f within the $^3/_2$ power term of eq 8 from the denominator to the numerator. Obviously the form of S is sensitive to these considerations, as is also $T_g\,(x)$.

Another assumption has to do with the use of $x-3$ rather than $x-6$ in eq 6. In the previous work we argued for $x-6$ as a possible alternative to $x-3$ since forming a six-membered ring results in very few conformations. A certain number of flexes is required simply to form the ring. Our intuition now is that $x-3$ is the better value. When we include the factor of 2 in the variance of step length, then eq 8 is modified to

$$q_r = \sum \frac{(x-3)!((z'-2)\exp(-\Delta\epsilon/kT))^{f(x-3)}}{((1-f)(x-3))!(f(x-3))!(4\pi(x-3)/3f)^{3/2}} \quad (9)$$

If we ask for that value of f that minimizes the free energy or maximizes the partition function, we obtain

$$f = A/[A + \exp(-3/2f(x-3))], \quad A = (z'-2) \times \exp(-\Delta\epsilon/kT) \quad (10)$$

which is to be compared to $f = A/[A+1]$ for linear chains. Using for the entropy the relation $S = -\partial F/\partial T$ and remembering that $\partial F/\partial f = 0$, we obtain for rings

$$S_r/kxN_x = \phi \ln \frac{V_0}{S_0} + \frac{N_0}{xN_x} \ln (V_0{}^{\phi}/S^{\psi}) + \frac{\ln (xz(z-1)V_0/\sigma_g S_0 V_x)}{x} + \frac{x-3}{x}[f \ln (z'-2) - (1-f)\ln(1-f) - f\ln f] - \frac{3}{2x}\ln\frac{4\pi(x-3)}{3f} \quad (11)$$

which is to be compared with eq 2 for linear chains. Notice that for large molecular weight, x, the equations for rings are the same as those for linear chains.

The glass temperature of rings is always greater than that of linear chains because as eq 11 shows that the configurational entropy of rings is always less than that of the corresponding linear system. But the statement is of general validity because the configurational entropy of a ring is always less than that of a linear polymer. The glass temperature of a large ring system approaches that of a linear system as x approaches infinity. Again, our equations show this, but the statement is of general validity because the configurational entropy of a large ring approaches that of a linear polymer.

The picture behind our equations is that of a polymer consisting of x beads, one bead per monomer, each one of which fits onto a tetrahedral or diamond lattice. Let us now generalize this to a polymer consisting of b beads per monomer and γ flexible bonds per monomer. A bond connects two beads. It is considered to be flexible if the chemistry is such that rotation about the bond is allowed *and* if rotation results in a distinguishable shape. The beads can be in the side group as well as in the backbone. For carbon-based polymers, the bead size is that of a CH_2 group and the number of beads per monomer is the volume of the monomer divided by the volume of the CH_2 group. The number of beads per monomer unit, b, can be estimated from the paper by Bunn, which gives volumes of various chemical subgroups.[11] The value of γ is easily obtained from a rudimentary knowledge of chemical structure. The monomer is now pictured as an object occupying b connected sites on the lattice, with rotations being allowed about γ of the bonds connecting the b beads. A real monomer is not so accommodating. b is seldom an integer, and the angles are sometimes not tetrahedral, so the monomer does not fit onto the lattice (any lattice). Yet, it is the best we can do. We know from past experience that the use of beads and flexes gives good results in spite of the aforementioned limitations.

The equations are easily modified to accommodate these ideas. First, x in the argument of the logarithm of the last term in the entropy for rings (eq 11) is replaced by the number of beads in the backbone. This is different from xb, which is the sum of the number of beads in the backbone and in side groups. For vinyl polymers this would be twice the degree of polymerization (DP). These considerations arise from the fact that only the configurations of backbone beads are restricted by forcing a linear chain into a ring. Second, all other x are replaced by b times the degree of polymerization. This is because the size of a lattice site in our lattice model is now the size of a bead. Third, the quantity γ/b multiplies $(x-3)/x$. This is because the number of flexible bonds per molecule is essentially γ times the degree of polymerization x.

Our treatment assumes that each of the γ flexible bonds has the same energy and the same z. What happens if the energies are very different? This question has been answered by plotting the f-dependent part of eq 2 as a function of $\Delta\epsilon/kT$. We obtain a straight line for a wide range of $\Delta\epsilon/kT$. This means that if we use an average bond energy weighted according to the fraction of bonds of each type, then the entropy and T_g are unchanged. On the other hand, if the $\Delta\epsilon_i/kT$ are very different from one another (greater than a factor of 2, say), we would have to replace the f-dependent part of eq 2 by a sum

$$f \ln (z'-2) - (1-f)\ln(1-f) - f\ln f \rightarrow \sum \gamma_i [f_i \ln (z'-2) - (1-f_i)\ln(1-f_i) - f_i \ln f_i] \quad (12)$$

$$f_i = (z'-2)\exp(-\Delta\epsilon_i/kT)/[1 + (z'-2)\exp(-\Delta\epsilon_i/kT)] \quad (13)$$

Here γ_i is the fraction of the bonds that are of type i. We will use the average energy approximation throughout.

The range of possible experiments on ring systems is as great as the range of experiments on linear systems. This means, for example, that we can measure the glass temperature on a ring system as a function of the plasticizer content, pressure, blend composition, and copolymer composition, as well as molecular weight. Also we can do

Table I

	PS	P2VP	PDS	PPMS
z'	4	4	4	4
z	4	4	4	4
flex no.	3	3	2	3
b	5.5	5.5	3.5 (3.0)	5 (5.5)
T_g, K	373	373	150	245
α ($\times 10^4$)[a]	2.9	2.9	6.9	(4.5)
E_h/kB, K	444.7	444.7	181.6	290.1
$\Delta\epsilon/k_B$, K	147.58	539.68	106.33 (197.48)	241.06 (103.67)
$E_h/\Delta\epsilon$	3.01	0.824	1.707 (0.91)	1.2 (2.8)

[a] $\Delta\alpha$ for PS is the same value as in ref 13. $\Delta\alpha$ for P2VP was chosen to be the same as that for PS. $\Delta\alpha$ for PDS is from ref 16. $\Delta\alpha$ for PPMS was obtained by use of the Simha–Boyer relation[17] $\Delta\alpha T_g = 0.113$.

mixtures of rings and linear polymers. The generalizations of eqs 1 and 11 to these cases are straightforward and can easily be derived by the reader. One simply calculates the relevant configurational entropy and equates it to zero. The works of Guggenheim[7] and of Miller[8] can be used for mixtures of rings and linear chains. One must be careful to use different θ's for different species (they use the symbol q_i for our θ_i). We give two examples. Equation 11 gives the glass temperature of a ring polymer plasticized by its own monomer if N_0 is interpreted as the number of plasticizer molecules. Simultaneous treatment of holes and plasticizer is straightforward. The second example is the formula for the glass temperature of a copolymer or of a blend in terms of the homopolymer glass temperatures. We can derive that

$$T_g = B_l T_{gl} + B_r T_{gr} \tag{14}$$

where B_i is the bond fraction of species i.

Let us consider the case of a mixture of rings and linear polymers since we will have reason to use the results in the Discussion section. If as an approximation we have $T_{gl}(x) = T_g(\infty) - A_l/x_l$ for pure linear chains and $T_{gr}(x) = T_g(\infty) + A_r/x_r$ for pure rings, then for a mixture we would expect from eq 14

$$T_g(x) = T_g(\infty) - B_l A_l/x_l + B_r A_r/x_r \tag{15}$$

for mixtures, where B_i is the bond fraction of species i.

Comparison to Experiment

We must first determine the values of the coordination number z, the number of flexes per monomer γ, the number of beads per monomer b, the hole energy E_h, and the stiffness energy $\Delta\epsilon$ for each of the four materials. Table I lists our best a priori estimate. Havlicheck has studied the question of the value of z and concludes that $z = 4$ is an optimal value.[12] We shall use $z = 4$ for most of our calculations. The original Gibbs–Di Marzio[13] paper uses two z's: an isomeric state coordination number describing rotation about tetrahedral bonds ($z' = 4$) and an intermolecular coordination number z (the lattice coordination number), which is between 4 and 12.

The values of the hole energy, E_h, and the stiffness energy, $\Delta\epsilon$, are determined from the experimental values of $\Delta\alpha$, the break in the thermal expansion coefficient for an infinite molecular weight sample, and from $T_g(\infty)$. $\Delta\alpha$ can be obtained from eq 1 or eq 1A by differentiation and is not a function of $\Delta\epsilon$. It is used to obtain E_h. $\Delta\epsilon$ is then obtained from the entropy equation eq 2 or eq 2A. See ref 13 for details.

The value of γ for each of the four polymers is calculated as follows. There are 2 rotatable bonds per monomer in the backbone. The methyl groups in the siloxane are rotatable, but the three configurations per methyl are indistinguishable. So, for poly(dimethylsiloxane), $\gamma = 2$. The phenyl groups are also rotatable. If there are two minima 180° apart, then they are not distinguishable. However, if the phenyl group spends much time at angles other than 180°, then we should count it as flexible. There is another consideration. If there is rotation of phenyl rings below the glass temperature, then we should not count it since it would not show up in the configurational entropy difference ΔS_c, which is set equal to zero to determine the glass temperature. These considerations make it difficult to decide whether γ is 2 or 3 for these systems. We shall suppose that below the glass temperature there is no rotation other than possible 180° flips so that $\gamma = 3$ for polystyrene and for poly(phenylmethylsiloxane). Finally, the side group in poly(2-vinylpyridine) being asymmetric has twice as many rotational states as a phenyl group. Thus, the effective value of γ for the vinylpyridine should be larger than 3. Alternatively, we can add Ln 2 per monomer to the entropy above T_g and retain $\gamma = 3$. The theoretical curves are calculated by adding Ln 2 per monomer to the entropy. Thus the extent to which the T_g curves for PS and P2VP differ is purely an entropy effect. There is a difference of about the right magnitude in the experimental results. This is a gratifying result. See Figure 1.

Using 21.8 cm^3/mol for $-CH_2-$ and 89.9 cm^3/mol for a phenyl group, we calculate $b = 5.5$ for polystyrene by dividing the monomer volume by 21.8 cm^3/mol. Poly(vinylpyridine) is given the same value since its density is only 6% higher and its monomer weight is only 3% lower than polystyrene. Our estimate of b for poly(dimethylsiloxane) is 3.5 (3), and for poly(phenylmethylsiloxane) $b = 5$ (5.5).

Using these values of z, E_h, $\Delta\epsilon$, γ, and b, we compare the predictions of theory with the four sets of experimental data in Figures 1–3. This procedure is the most stringent because our only use of the T_g vs DP data was to fit it to $T_g(\infty)$. Both curves then are predicted without any additional parameters. An alternate procedure would be to adjust the parameters to best fit the $T_g(x)$ curve for linear polymers. Then, only the fit to the ring polymers would be a no-parameter fit.

The first observation is that, for the same molecular weight, experimental glass temperatures for rings are always larger than those for linear polymers. The second observation is that the two curves converge to the same horizontal asymptote, $T_g(\infty)$, for large molecular weight. The theory predicts both of these observations on quite general grounds. See the Theory section.

Figure 1 compares theory to experiment for polystyrene and for poly(2-vinylpyridine). Theory and experiment agree well for linear poly(vinylpyridine), while for ring poly(vinylpyridine) the theory predicts T_g's that are larger than experimental values. Linear polystyrene behaves in much the same manner as linear P2VP, although there is a slight horizontal shift in their glass temperatures. According to our theory, this horizontal shift arises solely from an entropy effect. Due to rotation of the pyridine side group, there are twice as many distinguishable states per monomer as in polystyrene. A 180° rotation of a pyridene ring is distinguishable from 0°, but for a benzene ring the two states are indistinguishable. Thus, the entropy per monomer is increased by Ln 2 for P2VP. It is gratifying that the experiments are in the right direction and of the right magnitude. However, more experiments testing this effect in other systems are needed before we can claim to

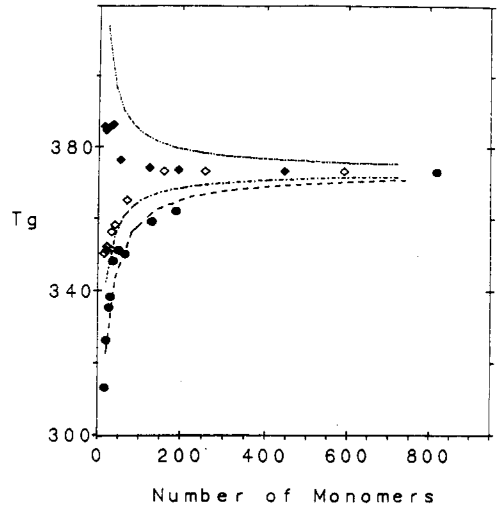


Figure 1. Theoretical and experimental glass temperatures of poly(2-vinylpyridine) and of polystyrene. The open diamonds are experimental T_g values for linear P2VP, and the filled diamonds are the experimental values for rings of P2VP. The middle and the uppermost curves are the corresponding theoretical curves. The curves were fit to a glass temperature of 373 K at infinite molecular weight. There are no other parameters (see text). Similarly, the filled circles are experimental values for linear polystyrene, and the bottommost curve is the theoretical prediction. Because the two materials are so similar we would expect their T_g behavior to be very similar as they are. The small difference can be ascribed to P2VP having twice as many distinguishable rotational states for its phenyl ring as does the benzene ring of PS (see text).

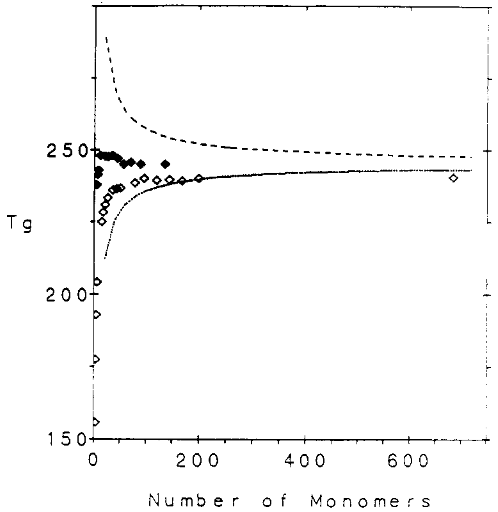


Figure 2. Theoretical and experimental glass temperatures of poly(phenylmethylsiloxane). Upper data and upper curve are for rings; lower data and curve are for linear polymers. The fit is qualitative rather than quantitative. See text for a discussion of the maxima in the experimental ring T_g's.

have observed this pure entropy effect unambiguously.

Figure 2 compares theory to experiment for poly(phenylmethylsiloxane). The rings show a maximum in the experimental T_g curve. The variation in experimental glass temperatures is smaller than that for P2VP and also much smaller than that predicted by the theory. The fit is only qualitative. Although we do not accurately fit the ring data, Figure 5 shows that there are values of the parameters that display a maximum in the $T_g(x)$ curves for rings.

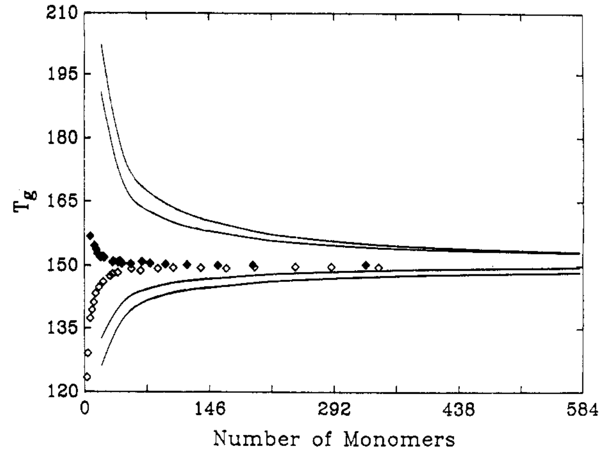


Figure 3. Theoretical and experimental glass temperatures of poly(dimethylsiloxane). The two sets of theoretical curves correspond to b values of 3.5 and 3 (b is the number of beads per monomer). See text. Again, the fit is qualitative rather than quantitative.

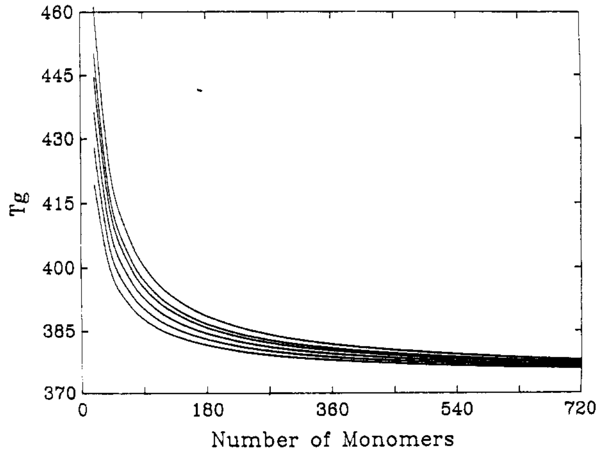


Figure 4. Glass temperature of ring polystyrene when the $^{3}/_{2}$ power of molecular weight in the Gaussian expression for the number of configurations is set equal to δ. The δ values are, starting from the top, $^{3}/_{2}$, $^{4}/_{3}$, $^{5}/_{4}$, $^{9}/_{8}$, 1, and $^{7}/_{8}$. The glass temperature of the rings is sensitively dependent on δ because the number of ring configurations depends on δ.

Figure 3 displays the fit of theory to experiment for poly(dimethylsiloxane). The theoretical variation is much larger than the experimental variation. We have also plotted glass temperatures when the value of b is changed from 3.5 to 3. One could improve the fit further by making b smaller, but this is arbitrary.

It is clear that by choosing the parameters z, z', b, γ, E_h, and $\Delta\epsilon$ arbitrarily a better fit to experiment can be obtained. However, we have used other, more honest, criteria. γ and b were determined from the chemical structure. E_h was determined from the experimental value of the thermal expansion coefficient. The coordination numbers z and z' were not investigated carefully. Instead, we used the common value of $z = z' = 4$ which we chose partly because picking optimal values of z *and* z' would be little more than curve fitting, partly because this is the value we had used in our original papers, and partly because a comprehensive treatment of the glass temperature of many polymers by Havlicheck[12] suggests the value 4. The only parameter of the theory that was fit to glass temperature data was $\Delta\epsilon$.

Having said this, it is still useful to examine the behavior of the T_g vs x curves over the whole range of parameter space. Figure 4–6 attempt this.

Figure 4 displays ring glass temperatures when the exponent in the denominator of the Jacobson–Stockmayer expression is varied from the value $^{3}/_{2}$. We do this because other authors claim different values for the exponent. The effect on the T_g of rings is substantial.

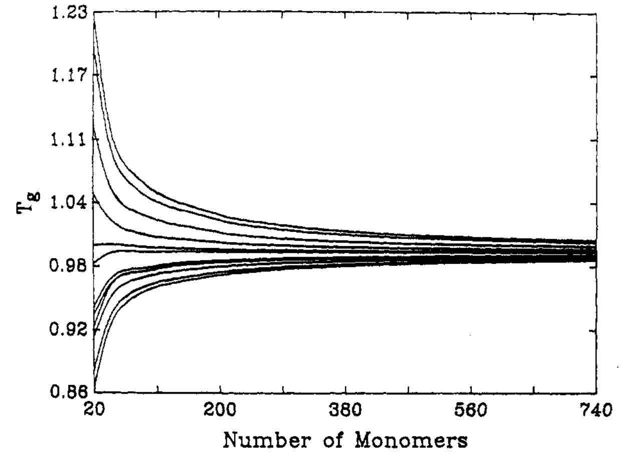


Figure 5. Glass temperature for rings and for linear polymers as a function of the ratio of hole energy to stiffness energy, $E_h/\Delta\epsilon$. Starting from the top, there are seven curves for rings with $E_h/\Delta\epsilon$ values of 3, 2, 1, 0.5, 0.25, 0.2, and 0.1. An interesting feature of these curves is that the fifth and sixth curves display a very shallow maximum and that the seventh curve decreases. Starting from the bottom, there are five curves for linear polymers corresponding to $E_h/\Delta\epsilon$ equal to 3, 2, 1, 0.5, and 0.25. The curves for 0.20 and 0.1 are indistinguishable from the 0.25 curve. There is a wide variation in the ring glass temperature curves compared to the glass temperature curves of linear polymers. This feature seems to be reflected in the experiments.

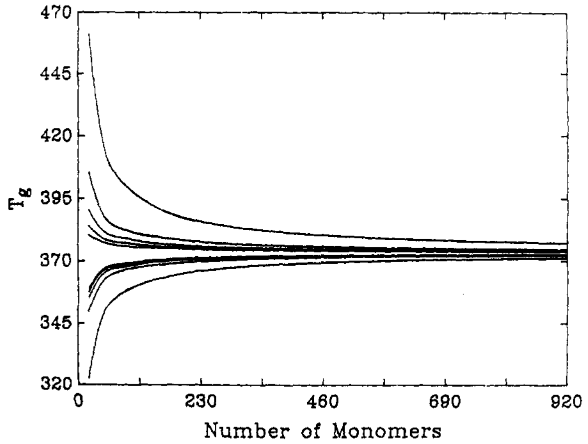


Figure 6. Glass temperature vs molecular weight for various values of the lattice coordination number z (z is set equal to the polymer coordination number z'). z progresses from 4 to 12 in steps of 2 from the two outermost curves to the two innermost curves.

Figure 5 shows $T_g(x)$ variation for different values of the ratio of hole energy to stiffness energy. The curves display a maximum for small $E_h/\Delta\epsilon$. This is important because there are general arguments that show that ring glass temperature must necessarily pass through a maximum as we reduce x. The values of $E_h/\Delta\epsilon$ for which there is a maximum are not physical. We conclude that a better estimate of the number of ring configurations for small x is needed.

Figure 6 shows the $T_g(x)$ variations when the coordination numbers are varied. Obviously a better fit to the data is obtainable.

We conclude from these various curves that (1) our fits to data using a priori estimates of the variables z, z', E_h, $\Delta\epsilon$, γ, and b are qualitative rather than quantitative and that (2) if we are willing to adjust these values and the $-^3/_2$ exponent in eq 5, then quantitative fits can be obtained. The latter conclusion offers the hope that a more accurate calculation of the entropy would give a better fit to data with the a priori estimates of z, z', b, γ, E_h, and $\Delta\epsilon$.

Discussion

In comparing the Theory and experiment it seems that the predictions for rings are always higher than the experimental values. The theoretical value of $T_g(x) - T_g(\infty)$ is perhaps 3 times larger than it should be. There are five possible ways to correct this.

First, the number of configurations of a ring may be different from our estimate. Cates and Deutsch[14] estimate that for an isolated polymer the power of n in the denominator of eq 5 may be as small as 1.2. This means that we should replace the factor $^3/_2$, multiplying the last term of eq 11 by δ where δ can be other than $^3/_2$. In Figure 4 we plot the predicted glass temperature for rings of polystyrene when only δ is varied. The behavior is in the right direction. On the other hand, Caracciolo, Pelissetto, and Sokal[15] estimate $\delta = \alpha_{\text{sing}} - 2 = \mathrm{d}\nu = 1.776$, which would make things worse. The ratio R of the number of linear conformations to ring conformations is

$$R = \mu^N N^{\gamma-1}/\mu^N N^{-\mathrm{d}\nu} = N^{\gamma-1+\mathrm{d}\nu} = N^{-1.94} \qquad (16)$$

One can argue that this number should replace $^3/_2$ if we are calculating the difference in entropies. These results are for completely flexible rings. The ideal situation would be to have an accurate formula for the number of configurations of rings when the fraction of flexed bonds, f, is known. This information does not seem to be available.

Second, even if we know the numbers of ring configurations exactly, we still need an accurate estimate of the packing entropy. It is difficult to know how accurate our $1/x$ term in eq 1 is since we know the configurational entropy to within several percent and the $1/x$ term is only several percent of the total entropy. Obviously more accurate estimates are needed. In this connection it should be noted that the entropy ($S-V-T$) equation of state which we require is always much more difficult to obtain than the $P-V-T$ equation of state.

Third, the glass temperature of rings is a strong function of the ratio of hole energy to stiffness energy, $E_h/\Delta\epsilon$. Figure 5 displays this variation. Unfortunately this variation is not available to us since E_h is fixed by the experimental value of the thermal expansion coefficient and $\Delta\epsilon$ is then determined by the experimental value of the glass temperature at infinite molecular weight. There is some leeway in that the size of a hole may be considerably smaller than that of a lattice site, and in the choice of coordination number z. However, unless these quantities can be determined from other experiments, we would be curve fitting, which we choose not to do. Nonetheless, smaller values of $E_h/\Delta\epsilon$ do result in smaller values of $T_g(x)$ for rings. An interesting feature of Figure 5 is that the curves display a slight maximum for small $E_h/\Delta\epsilon$ which mimics the experimental maximum in the poly(phenylmethylsiloxane) data.

Fourth, the use of a larger value of intermolecular coordination number results in a smaller change of glass temperatures of rings and of linear polymers. Figure 6 displays glass temperatures when only z is varied.

Fifth, in actual experiments, are the rings pure rings, or are they a mixture of rings and linear polymers? As eq 15 shows any admixture of linear chains (of the same degree of polymerization) always lowers the glass temperature. In our fitting we have presumed the ring systems to be pure rings and we see no reason to doubt the experimental data since we have four other ways of explaining the features of ring glass temperatures.

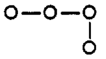
The existence of a mixed ring–linear system suggests an interesting experiment. At a finite molecular weight a blend of linear polymer and ring polymer can be made such that the glass temperature is the same as the glass temperature of a system of infinite (large) molecular weight. We are now ready to do iso-T_g experiments. Is the viscosity of the finite molecular weight system the same as that of the large molecular weight system? Does iso-T_g imply isoviscosity?

One may ask how the glass temperature is predicted to vary when we have topologies other than rings and linear molecules. The glass temperature of cross-linked systems has been given previously and is known to be a strongly increasing function of cross-link density. This leaves stars and comb molecules. On general grounds we predict that stars and combs would have higher glass temperatures than linear systems of the same molecular weight: the configurational entropy of stars and combs is less than that of linear molecules; therefore, the glass temperature is higher. The actual amount of elevation depends on just how much the stiffness energies of the rotatable bonds near the branches are increased. The relevant formulas analogous to eqs 1 and 2 are easily derived.

Appendix: Relationship between the Number of Configurations of a Ring and the Entropy

Accurate estimates of the number of returns to the origin after a random walk of x steps exist for a completely flexible random walk. No comparable statistics exist for the case of semiflexible rings, so we have been forced to use the crude estimate of eq 9. In this appendix we comment on an additional problem. The number of returns to the origin, Λ, is a quantity different from the number of distinguishable shapes, ω, which in turn is different from the number of distinguishable ways to place the ring on a lattice, Ω. Λ is the quantity usually calculated in the literature while Ω is the quantity necessary to the Flory–Huggins calculation of entropy.

Two shapes are distinguishable if they cannot be superposed by translation and rotation. They are indistinguishable if they can. Distinguishability is a mutual property of the two shapes in question *and also* of the space in which they are imbedded. For example, the shapes i and ii are distinguishable in two dimensions and indistinguishable in three dimensions.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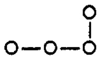
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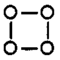
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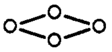
iv


v

If we have a complete set of ω distinguishable shapes the number of distinguishable ways to place one ring on a lattice of N sites is not simply given by $zN\omega$. For example, on a square lattice the object iii can be placed in N ways, the object iv can be placed in $2N$ ways, and the object v can be placed in $4N$ ways. However, if we break the symmetry of the object by coloring one of the monomer units, then there are $4N$ ways to place each object. Ω is not equal to $N\Lambda$. On a square lattice the number of returns to the origin resulting in the object iii is 8. The number of returns resulting in the object iv is 8. The number of returns resulting in the object v is 16. A moment of consideration shows that we cannot transform $N\Lambda$ to Ω by dividing $N\Lambda$ by any number. In the following tables we list values of Λ, ω, and Ω for linear chains and for rings as a function of the number of bonds x (Table II). Thus, our use of $\sigma_g = x$ for rings and $\sigma_g = 2$ for linear chains can only be viewed as an approximation.

Table II

Linear

x	$\Lambda/2$	4ω	Ω/N
1	2	4	2
2	8	12	10
3	32	40	36
4	128	144	138

Rings

x	$\Lambda/2x$	ω	Ω/N
2	1	4	2
4	4.5	20	9
6	33	48	42

Tables of exact values of Λ both for self-reversing and for non-self-reversing walks have been tabulated by Domb.[10] These numbers compare favorably with estimates made from eq 5. To obtain approximate Ω/N from eq 5, we must first divide by x. This is because, given a shape, one can imagine it was generated by starting at any of the x monomer units. To obtain the approximate Ω/N from the tables of Domb, one must divide by an additional factor of 2 because one can generate the same shape by traveling in either of two directions along the chain.

It is easy to show that Ω/N is bounded above by 4ω and below by $\Lambda/2$ ($\Lambda/2x$ for rings). In addition, in the limit of large x

$$\lim_{x\to\infty} \Lambda/2 = \lim_{x\to\infty} 4\omega = \lim_{x\to\infty} \Omega/N, \quad \text{linear chains} \tag{A1}$$

$$\lim_{x\to\infty} \Lambda/2x = \lim_{x\to\infty} 4\omega = \lim_{x\to\infty} \Omega/N, \quad \text{rings} \tag{A2}$$

In deriving these results, one uses the fact that chain shapes with geometrical symmetries become a vanishingly small fraction of the total number of shapes as $x \to \infty$.

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Registry No. Polystyrene, 9003-53-6; poly(2-vinylpyridine), 9003-47-8.