Modeling Ring–Chain Equilibria in Ring-Opening Polymerization of Cycloolefins

Zhong-Ren Chen, Jerome P. Claverie, Robert H. Grubbs, and Julia A. Kornfield*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received August 18, 1994; Revised Manuscript Received January 23, 1995®

ABSTRACT: A combined computational and theoretical method is developed to predict the equilibrium ring–chain distribution of the products of ring-opening metathesis polymerization (ROMP). In ring–chain equilibria, the free energy change of the reaction includes an entropic cost associated with forming cyclic rather than linear products and an enthalpic cost if ring strain is significant (i.e., for small rings). The entropy change is determined using statistical mechanics (based on the Jacobson–Stockmayer theory). The enthalpy change is computed with a Monte Carlo configurational search using molecular mechanics (MM3). Using the resulting equilibrium constants, the calculated distribution of cyclic and linear products is in good agreement with experiment. To characterize the polymerizability of cycloolefins, we compute the critical concentration $[\mathrm{M}]_{\mathrm{c},\infty}$, defined as the total monomer lost to cyclic products.

1. Introduction

In the ring-opening metathesis polymerization (ROMP) of cycloolefins, the products generally consist of cyclic oligomers and linear polymers, since the catalyst is active enough to produce "back-biting" reactions.[1–6] In the ROMP of cyclooctene, Höcker *et al.*[6] showed that there are no polymers formed until the monomer concentration exceeds 0.21 mol/L, which is much higher than the equilibrium monomer concentration $[\mathrm{M}]_\mathrm{e}$ of 0.002 mol/L.[7] Since $[\mathrm{M}]_\mathrm{e}$ provided such a poor indicator of polymerizability in this case, he proposed the concept of a critical concentration $[\mathrm{M}]_\mathrm{c}$, defined as the total amount of monomer per unit volume that forms cyclic products at ring–chain equilibrium. If the initial monomer concentration is less than $[\mathrm{M}]_\mathrm{c}$, only cyclics and linear oligomers are formed. After exceeding $[\mathrm{M}]_\mathrm{c}$, the equilibrium cyclics concentration is almost constant, and linear polymers begin to appear. Thus, $[\mathrm{M}]_\mathrm{c}$ characterizes the polymerizability of a given monomer. The critical concentrations of some cycloolefins have been determined experimentally,[6–11] but theoretical predictions of $[\mathrm{M}]_\mathrm{c}$ are lacking.

Jacobson and Stockmayer[12] developed a theory of ring–chain equilibria in 1950, based on consideration of the set of reaction equilibria

$$\mathrm{P}_{i+j} \rightleftharpoons \mathrm{P}_j + \mathrm{C}_i \qquad (1)$$

where P_j and P_{i+j} are linear polymer chains of degree of polymerization j and $i + j$, respectively, and C_i is a cyclic oligomer of degree of polymerization i. The "J–S theory" includes four assumptions: (1) all rings are strainless and there is no heat of cyclization, (2) the end-to-end distances of linear chains obey Gaussian statistics, (3) the probability of ring formation is governed by the fraction of all configurations for which the ends coincide, and (4) the reactivity of each terminal functional group is independent of chain length. It follows from the first assumption that only the entropic term contributes to the equilibrium constant. There are two contributions to the entropy change: a positive one due to the dissociation of one molecule into two and a negative one due to the decreased number of configurations on going from a linear chain to a linear and a cyclic product. The reduction in configurational entropy increases with ring size i but is independent of j. Thus, the equilibrium constant for reaction (1) depends only on i and is given by

$$K_i = \left(\frac{3}{2\pi\langle r_i^2\rangle_0}\right)^{3/2} \frac{1}{N_\mathrm{A}\sigma_{R_i}} \qquad (2)$$

where $\langle r_i^2\rangle_0$ is the mean-squared end-to-end distance of a random flight chain of i units, N_A is Avogadro's number, and σ_{R_i} is the symmetry number that eliminates overcounting of indistinguishable configurations (for cyclics $\sigma_{R_i} = 2i$).[12] Since $\langle r_i^2\rangle_0 \propto i$ for a random-flight chain, K_i falls off with increasing ring size as $i^{-5/2}$.

While this scaling is in accord with experimental observations, the J–S theory requires an accurate value of $\langle r_i^2\rangle_0$ in order to predict K_i. This need has been addressed by using the rotational isomeric state model (RIS) to calculate the end-to-end distances of chain molecules.[11,13] The results of the "JS–RIS model" for K_i agree very well with the experimental data for macrocyclics (more than 30–40 backbone atoms). However, the predicted values of K_i for smaller cyclics are still too high (Figure 3).

Two approaches have been taken to remedy the failure of the model for small cyclics: (1) avoiding the Gaussian chain approximation,[5,14] and (2) accounting for geometrical constraints imposed by the bond angle at the joining atom (FSM model).[14] In relation to the impact of the Gaussian chain approximation, Suter *et al.* found that a more detailed accounting of the distribution of end-to-end distances provides little improvement in predicting K_i even for small i.[5,11,14] On the other hand, accounting for directional correlation strongly reduces the number of configurations of small cyclics, causing K_i to decrease strongly for small i. While this qualitatively shifts the equilibrium away from small rings, as observed in experiment, they reported no results for rings smaller than approximately 25 backbone atoms.

Both of these approaches attempt to better describe the loss of configurational freedom on forming small rings—primarily an entropic effect. In the context of

---

* Correspondence to: Chemical Engineering 210-41, California Institute of Technology, Pasadena, CA 91125.

® Abstract published in *Advance ACS Abstracts,* March 15, 1995.

0024-9297/95/2228-2147$09.00/0

the JS–RIS model, enthalpic effects enter only through the relative energy levels of the conformers. However, there are a few facts that suggest that the discrepancy between the JS–RIS model and experiment has a strong enthalpic origin.

First, experiments show that $[M]_e$ depends significantly on temperature (e.g., for cyclopentene, it increases 120% from 273 to 303 K,[9] whereas the JS–RIS model would predict an increase of only about 6%).

Second, ring size strongly affects the value of $[M]_e$ for various small cyclic monomers. This effect is readily seen by considering the relative magnitudes of the equilibrium constants for reactions involving the monomer $K_1^{(\nu)}$, where ν denotes the number of backbone atoms in the cycloolefin monomer. For cyclobutene, cyclohexene, and cyclooctene, experimental results show that $K_1^{(4)}/K_1^{(6)} \approx 0$ and $K_1^{(6)}/K_1^{(8)} \approx 5000$. However, if the basic reasoning of the FSM model is applied to these cases, it leads to $K_1^{(4)}/K_1^{(6)} \approx 4.5$ (much too large) and $K_1^{(6)}/K_1^{(8)} \approx 2.2$ (much too small).[15] The inability to polymerize cyclohexene is attributed to lack of ring strain; conversely, it is the relatively higher ring strain in the four- and eight-membered rings that drives the equilibria away from these small cyclics—an enthalpic effect.

Thus, we believe that the reason previous researchers fell short in predicting K_i for small rings is that they neglected ring strain. In fact, if a ring has less than 20–30 backbone atoms, there generally exists a strain energy, that can significantly affect ring–chain equilibrium constants. Therefore, the entropic contribution to the change in free energy in reaction (1) must be augmented by determining the enthalpic contribution. Molecular mechanics, although empirical, provides a computational tool to determine the enthalpic contribution.[16,17] Since molecular mechanics with the MM3 force field has been shown to accurately compute heats of formation for hydrocarbons,[17–19] we employ this method to calculate the ring strain for small cyclic olefins. Then we calculate equilibrium constants of each ring–chain equilibrium reaction. Together with the knowledge of the molecular weight distribution of the linear chains, we are able to calculate the distribution of all species (cyclic and linear), from which we evaluate $[M]_c$.

2. Theory and Methods

In order to analyze the contributions to the changes of enthalpy and entropy during these reactions, equilibrium (1) can be viewed as two hypothetical reactions

$$P_{i+j} \rightleftharpoons P_i + P_j \tag{3}$$

$$P_i \rightleftharpoons C_i \tag{4}$$

There is no change in bond energy during reaction (1), i.e., the same number of bonds are formed in reaction (4) as are destroyed in reaction (3). Therefore, the enthalpy change for reaction (3) is recovered in reaction (4) except for the strain energy of the cyclic product, which depends only on its size, i. The entropy term, however, has contributions from both reactions (3) and (4).

2.1. Calculation of the Entropic Term. Following the Jacobson–Stockmayer theory, we evaluate the entropy change of reaction (1), considered as the hypothetical reactions (3) and (4). The entropy change in reaction (3) is positive due to the increase in center of mass freedom. It is evaluated by considering the chain units on each side of the bond to be broken: before the bond breaks, these segments are restricted to lie within a small distance from one other, but after the bond breaks, they may be at any distance from one another, limited only by the sample volume. The entropy change of reaction (4) is negative, since the number of configurations available to the cyclic C_i is a small subset of those available to the linear chain P_i. The ratio of the number of configurations for C_i relative to P_i is simply the probability of P_i closing on itself. The net change in entropy per mole associated with reactions (3) and (4) is

$$\Delta S_i = R \ln\left[\frac{1}{2iN_A}\left(\frac{3}{2\pi\langle r_i^2\rangle}\right)^{3/2}\right] \tag{5}$$

where $\langle r_i^2\rangle$ can be treated by RIS theory or equivalently by introducing the characteristic ratio of an i-mer, which is defined as $c(i) = \langle r_i^2\rangle/ivl^2$, where l is the bond length.[13]

2.2. Calculation of the Enthalpic Term. In ring–chain equilibria the enthalpic change is due only to the strain energy, since the bond energy is unchanged in reaction (1) and intermolecular interactions are barely changed. To evaluate the ring strain, the difference between the heats of formation of corresponding cyclic and linear chains, there are three possible approaches: ab initio, semiempirical, and molecular mechanics calculations. The essence of the present problem is to compute the strain energy of a series of cyclic compounds (monomer, dimer, etc.). Ring strain becomes negligible only for molecules that contain 100 atoms or more. Ab initio calculations are prohibitive for such large molecules. Semiempirical approaches are generally better suited to calculate structure rather than accurate energetics of molecules. Molecular mechanics, on the other hand, can provide reasonably accurate differences in heats of formation with computations that can readily be performed on available workstations, even for the large molecules of interest here.

Within the context of molecular mechanics, numerous choices of force fields are available that successfully predict the configurations of molecules (e.g., AMBER, OPLS, MM3). Here, we choose the MM3 force field, since it has been shown to provide accurate heats of formation and ring strain for hydrocarbons.[17–19] Within molecular mechanics, the heat of formation is calculated as the sum of the energies of the covalent bonds, perturbed by distortion of bond lengths, bond angles, and torsional angles about bonds. In the molecular mechanics literature, the first is termed the "bond-energy", (BE), and all of the rest are grouped together and termed "steric energy" (SE), which can be computed from the specific force field. For molecules having many possible configurations, SE is usually evaluated as that of the minimum energy configuration; this can be improved upon by performing a Boltzmann-weighted average over all configurations.

For sufficiently small molecules (fewer than 12 backbone atoms), all of the conformers (local minima) were realized for both linear and cyclic molecules. In these cases we evaluated SE using both a Boltzmann-weighted average and the minimum energy conformation. In turn, the ring strain ($SE_{C_i}-SE_{P_i}$) was evaluated based on each approach. The two results for the strain energy were found to agree to within 1%. For larger molecules (more than 25 backbone atoms), it was not practical to enumerate all possible conformers of the

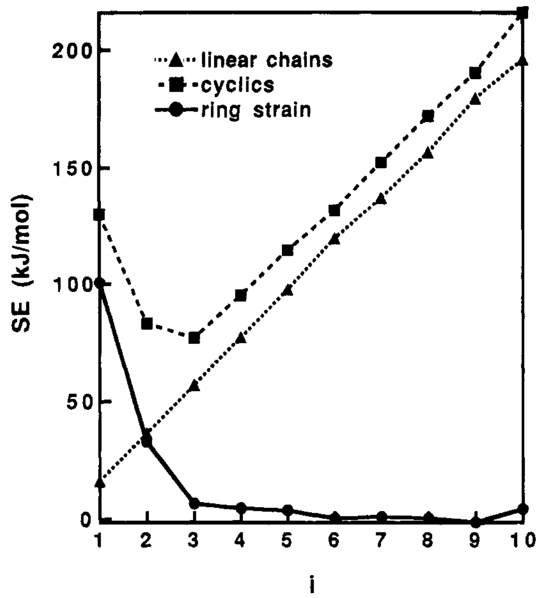

Figure 1. Steric energy of cyclic and linear *i*-mers and ring strain of cyclic *i*-mers formed from ROMP of cyclobutene. The precise choice of end groups has no effect on the overall change in free energy of reaction (1); the results shown here are for a linear *i*-mer constructed by adding one hydrogen each on the two ends of an opened cyclic monomer and subsequent linear chains constructed by inserting one repeat unit.

molecule, and the Boltzmann-weighted average could not be determined. Therefore, for large molecules we adopted the usual practice of using SE determined for the lowest energy conformer found in a Monte Carlo search (greater than 10 000 realizations).

For a given degree of polymerization, linear molecules have many more accessible configurations than cyclics. Thus, the Monte Carlo search rapidly becomes extremely time-consuming with increasing linear chain length. Fortunately, one expects that the incremental energy associated with adding a repeat unit should eventually become a constant. Indeed, we find that SE_{P_i} increases linearly with degree of polymerization over the range of *i* for which the calculations were feasibile, i.e., *i* up to 8 or 9 for cyclobutene (Figure 1). The increment in SE_{P_i} per repeat unit is denoted SE_0; for example, $\mathrm{SE}_0 = 20.3$ kJ/mol for linear chains of cyclobutene (Figure 1). In calculations of the ring strain, the SE for a linear *i*-mer is evaluated as $i\cdot\mathrm{SE}_0$.

For cyclic molecules that are sufficiently large, we find that the steric energy increases linearly with the degree of polymerization (Figure 1). This indicates that the rings are large enough to be strain free, since ring strain generally decreases with ring size. Indeed, in the linear regime, the incremental SE per repeat unit is the same as that observed for the linear chains. In contrast, for small rings, SE_{C_i} can even decrease with increasing ring size *i*, as in the case of cyclobutene monomer (Figure 1). This is attributed to the decrease in ring strain.

To compute the ring strain, we first calculate the difference between the steric energy of the cyclic *i*-mer and that of the linear *i*-mer. However, it is obvious that this difference becomes constant for large *i* (Figure 1). This offset should not be included in the ring strain. Previous researchers have attributed this offset to the difference in torsional degrees of freedom between cyclic and linear molecules.[19] The value of the offset in energy between SE_{C_i} and $i\cdot\mathrm{SE}_0$ for large *i* (9.4 kJ/mol) is indeed equal in magnitude to the ΔTOR term proposed by Allinger *et al.* for hydrocarbons.[19] Thus, we calculate the strain energy as

$$\Delta H_i = (\mathrm{SE}_{C_i} - i\cdot\mathrm{SE}_0) + \Delta\mathrm{TOR} \qquad (6)$$

where SE_{C_i} is the steric energy of *i*-meric cyclics and $\Delta\mathrm{TOR} = -9.4$ kJ/mol.

2.3. Ring–Chain Equilibrium Calculation. To calculate ring–chain equilibria, we need to know the K_i and the molecular weight distribution for linear chains. The equilibrium constants are calculated from the change in free energy of reaction (1), with the entropy change given by eq 5 and the enthalpy change given by eq 6,

$$\ln K_i = -\frac{\Delta H_i}{RT} + \ln\left[\frac{1}{2iN_A}\left(\frac{3}{2\pi\langle r_i^2\rangle}\right)^{3/2}\right] \qquad (7)$$

The molecular weight distribution of the linear chains is the most-probable distribution under the equal reactivity assumption[20]

$$[\mathrm{P}_i] = \frac{[\mathrm{I}+\mathrm{X}]_0}{1+p}\left(\frac{p}{1+p}\right)^i \qquad (8)$$

where p is the average degree of polymerization and $[\mathrm{I} + \mathrm{X}]_0$ is the concentration of the initiator and chain transfer agent. For this distribution of linear chains, the equilibrium condition gives the distribution of cyclics

$$[\mathrm{C}_i] = K_i\left(\frac{p}{1+p}\right)^i \qquad (9)$$

The average degree of polymerization of the linear chains is

$$p = \frac{[\mathrm{M}]_0 - [\mathrm{M}]_c}{[\mathrm{I}+\mathrm{X}]_0} \qquad (10)$$

where the critical concentration is the sum of all monomers lost to cyclic products

$$[\mathrm{M}]_c = \sum i[\mathrm{C}_i] \qquad (11)$$

Equations 7–11 completely determine $[\mathrm{P}_i]$, $[\mathrm{C}_i]$, and $[\mathrm{M}]_c$. With this information, we determine the distribution of cyclic and linear products for a given initial monomer concentration $[\mathrm{M}]_0$ and concentration of initiator and chain transfer agent $[\mathrm{I} + \mathrm{X}]_0$ (i.e., number of linear chains).

2.4. Computational Methods. We performed the computations on Silicon Graphics IRIS-4D1-4.0.5 and Sun workstations. The programs applied were *InsightII*, *Discover*, and *Polymer* by Biosym Technologies, Inc., and *Macromodel* by Columbia University. Statistical weights of rotational isomers, bond lengths, and bond angles for polyethylene and polybutadiene are taken from the literature[13,21] and are used in calculating the characteristic ratio *c*(*i*) for polycycloolefins. The mean-square end-to-end distance and characteristic ratio of chain molecules are determined by a Monte Carlo/RIS calculation. The MM3 force field is used for the Monte Carlo configurational search and steric energy calculations.

3. Results and Discussion

3.1. Effect of Ring Strain on Equilibrium Constants.

To evaluate the equilibrium constants K_i using

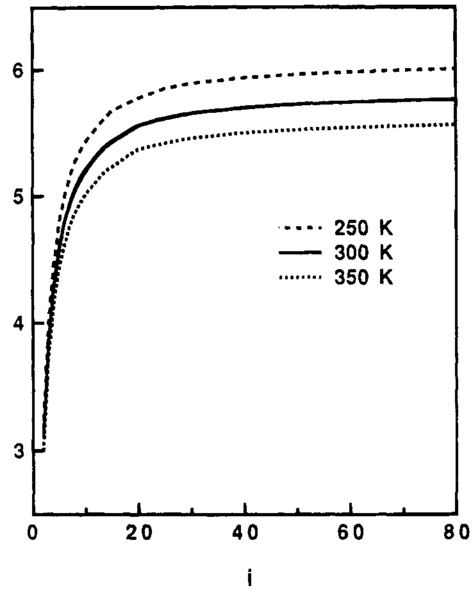

Figure 2. Characteristic ratio *c*(*i*) as a function of temperature for linear *i*-mers of *all-trans*-polycyclobutene.

eq 7, we must compute the ring strain ΔH_i using molecular mechanics and the characteristic ratio $c(i)$ using rotational isomeric state theory.

Ring strain energy is significant for small rings of up to about 20 backbone atoms (with the exception of cyclohexene). Based on experimental heats of combustion, there is almost no strain energy for cyclics with more than 30–40 backbone atoms.[22] Indeed, we find that, as the number of backbone atoms exceeds 20 (i = 5 for cyclobutene), the slopes of SE versus i for both cyclics and linear chains are almost the same (dashed curves, Figure 1). The ring strain ΔH_i (eq 6) decreases with increasing ring size; e.g., for cyclobutene, ΔH_i is nearly zero for $i \approx 6$, i.e., 24 back-bond atoms (solid curve, Figure 1).

The characteristic ratio $c(i)$ of the linear molecules increases with the degree of polymerization and reaches a constant c_∞ (Figure 2). For the homologous series of cyclobutene, cyclohexene, cyclooctene, cyclodecene, and cyclododecene, the c_∞ values at 300 K are 5.8, 6.5, 7.0, 7.2, and 7.3, respectively, for the *all-trans* polymers. With decreasing unsaturation, c_∞ tends toward the value for polyethylene, which extrapolates to 7.8 at 300 K. For polyolefins the characteristic ratio for the *trans* conformation is larger than *cis*. For example, *all-cis*-polycyclobutene has c_∞ = 4.9 at 300 K, approximately 20% lower than the value for *all-trans*-polycyclobutene. The values of c_∞ computed for *all-trans*- and *all-cis*-polycyclobutene are in good agreement with the literature values.[21] As temperature increases, $c(i)$ decreases (Figure 2), since the difference in energy between trans and gauche conformers becomes less important.

Using the computation results for ΔH_i and $c(i)$, we evaluate K_i. The resulting values of K_i agree well with experimental data for cyclobutene, even for small i (Figure 3). This success is in contrast to the JS theory, which captures the scaling behavior of K_i for large i, or the JS–RIS model, which captures the values of K_i only for large i (Figure 3). In the JS theory, K_i is evaluated using eq 2 with $\langle r_i^2 \rangle = ivl^2$; the JS–RIS model, uses eq 2 with $\langle r_i^2 \rangle = c_\infty ivl^2$; in the present model, K_i is evaluated using eq 7 with $\langle r_i^2 \rangle = c(i)\, ivl^2$ and ΔH_i evaluated as described in section 2.2.

3.2. Equilibrium Cyclics Distribution for Cycloolefins.

We choose cyclobutene, cyclooctene, and cyclododecene to test our model for the ring–chain equlibrium of cycloolefins, since experimental results are available for comparison. The total cyclic concentration increases with initial monomer concentration $[M]_0$ and ultimately reaches a constant that is defined as the critical concentration $[M]_c$ (Figures 4 and 5). The importance of correctly predicting ring–chain equilibrium constants of small rings becomes obvious when determining $[M]_c$, because small deviations of K_i (e.g., see JS–RIS model in Figure 3) cause large errors in $[M]_c$ (Figure 4). For example, our model leads to $[M]_c$ = 0.45 mol/L for cyclobutene, in good accord with experimental observations,[11] whereas the JS–RIS model gives 1.8 mol/L; the JS theory gives 13.8 mol/L (Figure 4). For cyclooctene, we find $[M]_c$ = 0.21 mol/L (Figures 5 and 6), in agreement with the experimental value of ap-

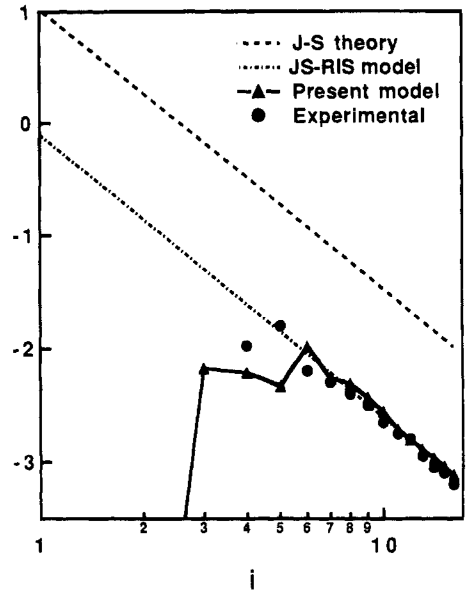

Figure 3. Ring–chain equilibrium constants K_i for the reactions that form cyclic *i*-mers of cyclobutene: comparison of three different models at 300 K in a θ solvent.

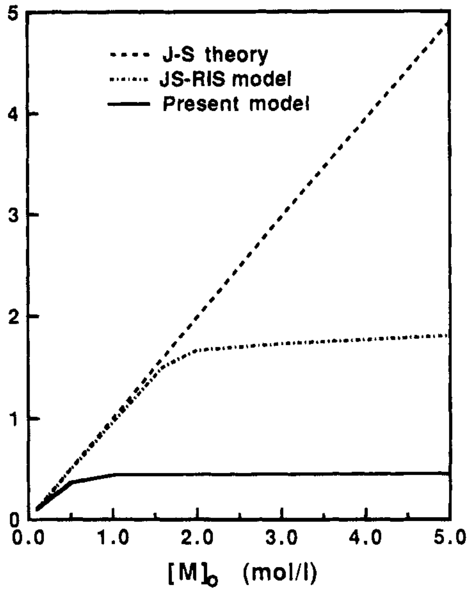

Figure 4. Effect of initial monomer concentration on total cyclic concentration at equilibrium: comparison of three different models for cyclobutene at 300 K in a θ solvent, with $[M]_0/[I + X]_0 = 200$. Total cyclic concentration is in terms of the amount of monomer incorporated in cyclics $\sum i[C_i]$.

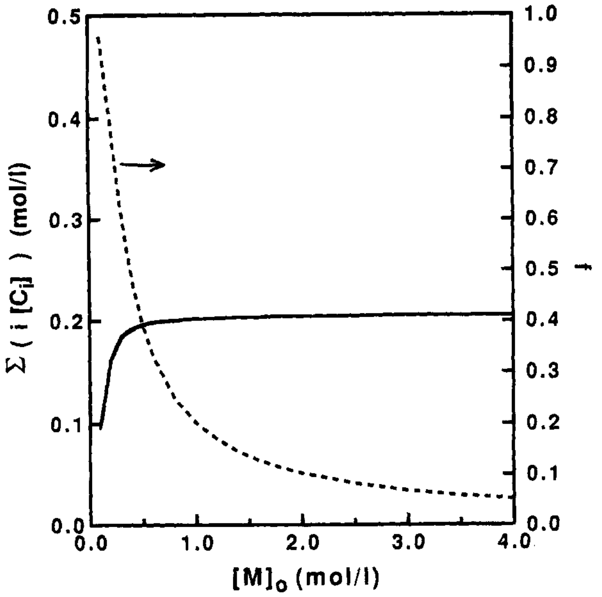

Figure 5. Fraction of cyclics (dashed curve, right axis) and total cyclic concentration (solid curve, left axis) as a function of initial monomer concentration: calculated by the present model for cyclooctene at 300 K in a θ solvent, with $[M]_0/[I + X]_0 = 200$. As $[M]_0$ increases, the amount of monomer that forms cyclics reaches a constant at $[M]_c = 0.21$ mol/L.

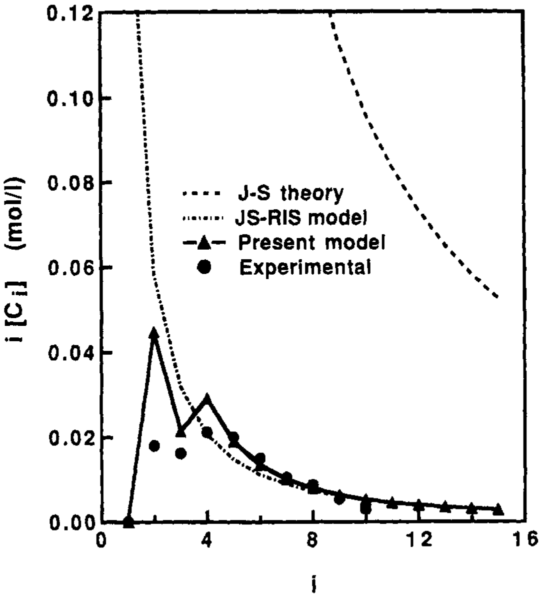

Figure 7. Cyclic distribution, i.e., concentration of cyclic i-mer as a function of size: comparison of three models and experimental results for cyclooctene at 300 K in a θ solvent with $[M]_0/[I + X]_0 = 200$. For the JS theory, when $i = 1, 2, 3$, etc., cyclic concentrations are off scale. Concentration of monomer ($i = 1$), $i[C_i] = 3.1$ mol/L.

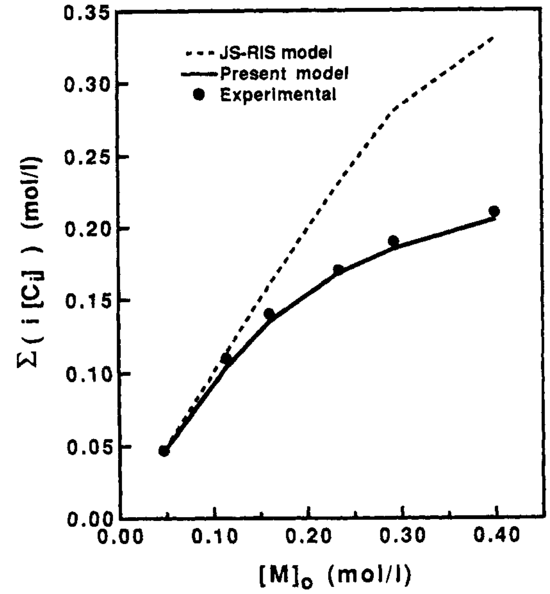

Figure 6. Total cyclic concentration as a function of initial monomer concentration: comparison of the JS–RIS model, the present model, and experimental results for cyclooctene at 300 K in a θ solvent, with $[M]_0/[I + X]_0 = 200$.

proximately 0.2 mol/L.[11] For cyclododecene, we obtain $[M]_c = 0.13$ mol/L.

When $[M]_0$ is lower than $[M]_c$, the majority of products are cyclics (Figure 5), with a small amount of linear oligomers. For example, for cyclooctene with $[M]_0 = 0.23$ mol/L and $[I + X]_0 = 0.0023$ mol/L; if cyclics were not present, the degree of polymerization would be $p \approx 100$. Instead, the ROMP products consist of 0.164 mol/L of monomer in cyclics (71% by weight of the products) and 0.066 mol/L of monomer in linear oligomers with $p \approx 30$. As $[M]_0$ increases, the fraction of cyclic products decreases dramatically (Figure 5). When $[M]_0$ is large enough, the amount of cyclics remains almost constant at $[M]_c$, and all additional monomers contribute to form linear polymers. The effect of $[M]_0$ on the total cyclic concentration predicted by the present model is in good agreement with experiment (Figure 6).[6]

Since the JS–RIS model neglects ring strain, it performs very poorly in predicting the concentration of small rings (Figure 7) and consequently overpredicts $[M]_c$ (Figure 6). The predictions of macrocyclic concentration by the JS–RIS model for rings with more than 60 backbone atoms (e.g., $i \gtrsim 8$ for cyclooctene) are nearly the same as our model. This is because the two models coincide when ring strain vanishes and when $c(i) \to c_\infty$. For cyclics with 30–60 backbone atoms, the error in the JS–RIS model is mild (Figure 7). For example, in the case of cyclododecene, ring strain is significant only for monomers, and thus the JS–RIS model performs well except for the monomer concentration. Nevertheless, even this small deficiency results in a fairly large error (>100%) in predicting $[M]_c$.

The cyclic distribution calculated with the present model agrees quite well with experimental data for polymerization of 4-, 6-, 8-, and 12-membered cyclic olefins (Figures 7 and 8). Due to ring strain there are almost no monomers left at ring–chain equilibrium for 4-, 8-, and 12-membered cyclic olefins (Figures 7 and 8); for cyclobutene, even dimer is hardly present (Figure 8a). In contrast, cyclohexene is free of strain, and there is actually a small enthalpic cost for cyclohexene to form linear molecules or larger cyclics. The equilibrium constant K_1 is so large that $[M]_c$ is estimated as about 7 mol/L, almost the bulk concentration. Since $[M]_c$ is so high, it is not possible to polymerize cyclohexene, and the corresponding polymer spontaneously depolymerizes to monomers and a small amount of cyclic and linear oligomers (Figure 9). This calculated result is in accord with observations that cyclohexene is unpolymerizable: only trace amounts of cyclic oligomers are found even in bulk cyclohexene.[3]

3.3. Effect of Reaction Conditions on Ring–Chain Equilibria.

The effects of monomer concentration, concentrations of initiator and chain transfer agent, solvent quality, and temperature on polymerizability and product distributions are of obvious practical

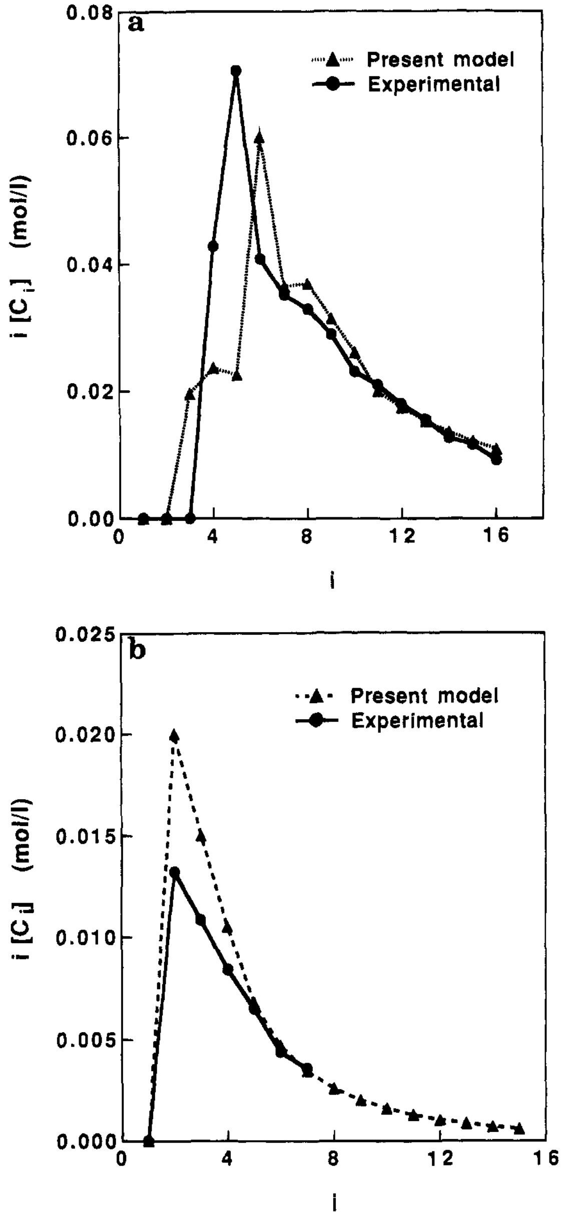

Figure 8. Calculated and observed cyclic distribution at 300 K in a θ solvent, for (a) cyclobutene and (b) cyclododecene at 300 K in a θ solvent, with $[M]_0$ = 1.0 mol/L and $[M]_0/[I + X]_0$ = 200.

interest. For a given monomer, the primary way to control the yield and average molecular weight of linear polymer is by varying the initial monomer concentration $[M]_0$ and the ratio of monomer to catalyst and chain transfer agents $[M]_0/[I + X]_0$. The effect of $[M]_0$ on total cyclic concentration has already been presented above (in section 3.2 and Figures 4–6). Regarding its effect on the distribution of cyclics and linear chains, increasing $[M]_0$ beyond $[M]_c$ hardly changes the distribution of cyclics (Figure 10a), while it increases the yield and length of linear polymer (Figure 10b). Since many applications require polymers with a degree of polymerization larger than 200, synthesis conditions will typically lie in a regime where the cyclic distribution changes very little with $[M]_0$ (Figures 10a and 11a). In this regime the linear chain distribution varies dramatically with increase in $[M]_0/[I + X]_0$ (Figure 11b).

Other conditions of practical importance are temperature and solvent quality. For most cycloolefins (except for cyclohexene), K_i increases with temperature, and thus the equilibrium cyclic concentrations and $[M]_c$ increase. The increase in $[M]_c$ arises predominantly from the decreased significance of the enthalpic (ring strain) contribution and secondarily from the decrease in the end-to-end distances (eq 7). Generally, the effect of temperature on the product distribution is quite mild compared to radical polymerization, for example, because ring strain is small compared to bond energy.

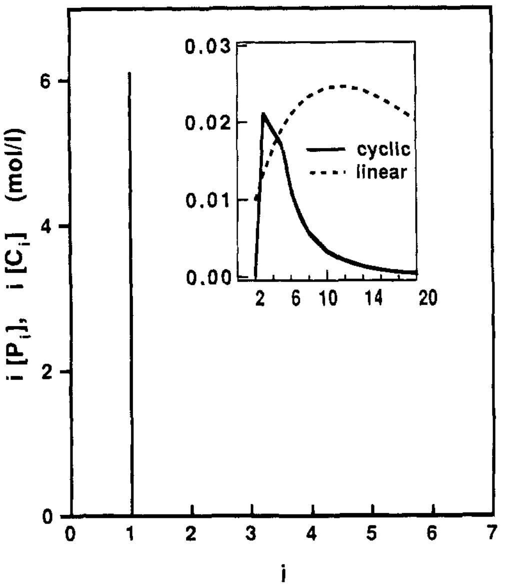

Figure 9. Ring–chain equilibrium of cyclohexene predicted by the present model at 300 K, $[M]_0$ = 7.0 mol/L, with $[M]_0/[I + X]_0$ = 200. Over 90% by weight of species persists as monomer (peak in the main graph), with the trace amounts of linear and cyclic products (inset, expanded scale).

When considering the effect of the solvent, there is almost no enthalpic contribution, since differences in solvation energy between cyclics and linear chains are negligible. Solvent quality can have a significant effect on the entropic term if the polymer solution is dilute and the solvent is good, since the chain becomes expanded and the probability of its ends meeting falls dramatically (scaling approximately as i^{-2} for a linear i-mer).[24,25] In this case, the equilibrium concentration of cyclics and, consequently, $[M]_c$ decreases; and the slope of the lines in Figure 3 becomes nearly −3. This effect has been observed in the polymerization of cyclooctene in heptane and in benzene: fewer cyclics are formed in the better solvent (benzene).[26]

3.4. Definition of Critical Concentration. The value of $[M]_c$ defined so far depends on reaction conditions such as $[M]_0/[I + X]_0$, temperature, and solvent quality. For convenience in comparing different monomers, a number, rather than a function, is preferred to characterize the polymerizability of cycloolefins. Therefore, we define $[M]_{c,\infty}$ as the critical concentration at room temperature, in a θ solvent or concentrated solution, and at infinite degree of polymerization of linear chains p (i.e., large $[M]_0/[I + X]_0$). Thus, $[M]_{c,\infty}$ can serve as a characteristic parameter in determining polymerizability. We obtain $[M]_{c,\infty}$ = 0.23 mol/L for cyclooctene, which is very close to the $[M]_c(p)$ when p is about 200 ($[M]_c(200)$ = 0.21 mol/L). So in practice, if p is greater than 200, we can use $[M]_c \approx [M]_{c,\infty}$.

3.5. General Approach to Predicting Polymerizability. The model developed here is successful in predicting ring–chain equilibria in ring-opening metathesis polymerization of cycloolefins. Historically, there have been two theoretical treatments of polym-

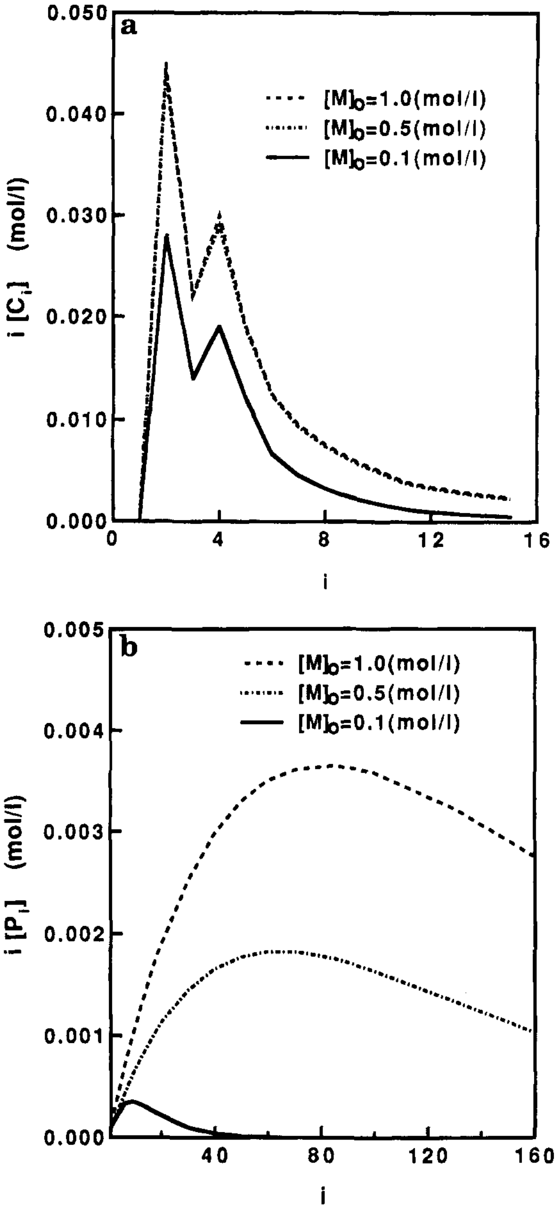

Figure 10. Effect of initial monomer concentration on ring–chain equilibrium of cyclooctene calculated by the present model at 300 K in a θ solvent, with $[M]_0/[I + X]_0 = 200$: distribution of (a) cyclic and (b) linear products. Notice that the distribution of cyclics becomes independent of $[M]_0$ once it is sufficiently large compared to $[M]_c$.

erization thermodynamics. The traditional thermodynamic analysis of Dainton–Ivin *et al.*[7] is based on the free energy changes during the aggregation processes from monomers to polymers. This theory has been applied very successfully to many types of polymerizations, especially to radical-chain polymerization. The concepts of ceiling temperature and equilibrium concentration $[M]_e$ are widely used to describe the polymerizability of monomers. However, Ivin's treatment is not adequate for polymerizations in which cyclic products are formed.

Systems involving both cyclic and linear products have been described separately by the Jacobson–Stockmayer theory and its descendents. These models are not able to predict the polymerizability of cyclic monomers, because (1) the JS theory only succeeds in predicting the scaling of equilibrium constants for large rings, (2) the JS–RIS model does not describe the equilibria involving small rings, and (3) correcting the

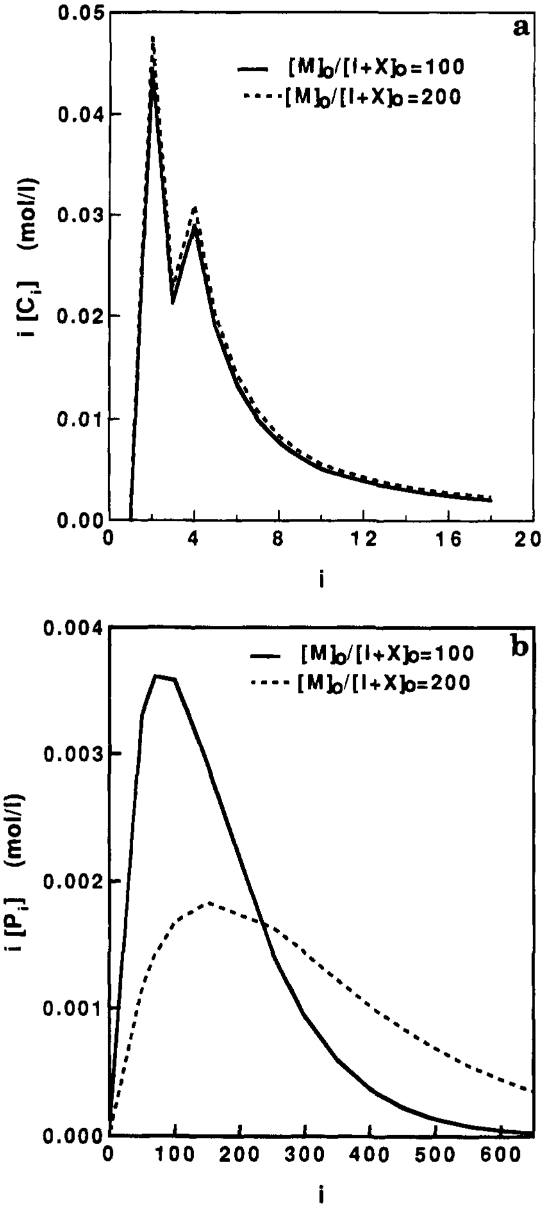

Figure 11. Effect of the ratio of $[M]_0/[I + X]_0$ on ring–chain equilibrium of cyclooctene calculated by the present model at 300 K in a θ solvent with $[M]_0 = 1.0$ mol/L: distribution of (a) cyclic and (b) linear products.

model to account for directional correlation did not provide reasonable results for small cyclics.[11]

The model developed here is the first to account for ring strain and succeeds in quantitatively predicting the critical concentration and equilibrium ring–chain distribution. We define $[M]_{c,\infty}$ as the determining parameter for polymerizability, and we find that this model fills the same role in ring-opening polymerization as Dainton and Ivin's treatment in radical-chain polymerization. Furthermore, when the polymerization mechanism prohibits the formation of cyclics, $[M]_{c,\infty}$ has only the first term, i.e., the equilibrium concentration of monomer $[M]_e$. Thus, we can also use this model to deal with polymerization systems where only cyclic monomer and polymers exist.

4. Conclusion

To accurately predict the equilibrium constants for both macrocyclics and small cyclics, we introduce the ring strain as an enthalpic term and use molecular mechanics to compute its value. Regarding entropic contributions, we use the JS–RIS model. By combining molecular mechanics and statistical mechanics, we have developed a new method that quantitatively predicts the polymerizability of cycloolefins and the distributions of cyclic and linear chain products. The critical concentration $[M]_{c,\infty}$ is the determining parameter to predict the polymerizability of a given monomer at a specified temperature. If the initial monomer concentration exceeds the critical concentration, almost all of the additional monomer contributes to linear products, increasing the yield and average degree of polymerization. For given polymerization conditions, such as initial monomer concentration, ratio of monomer to chain transfer agent and catalyst, temperature, and solvent, the complete product distribution can be computed.

Based on the success of this method in the case of ROMP of cycloolefins, we expect it to work for other types of cyclic monomers, such as heterocyclics, and for other kinds of polymerizations. In reaction conditions that allow the system to approach equilibrium, the model provides guidance in the development of synthetic strategy. For example, when making cyclic species is the goal, low monomer concentrations (close to the critical concentration) are desired to achieve the highest yield of cyclic products.[27,28] In addition, this new model can be applied to analyze polymer degradation by metathesis reactions.[29]

Acknowledgment. We gratefully acknowledge the National Science Foundation for financial support.

References and Notes

(1) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.

(2) Novak, B. M.; Risse, W.; Grubbs, R. H. *Adv. Polym. Sci.* **1992**, *102*, 47.

(3) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983.

(4) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*; John Wiley & Sons: Chichester, U.K., 1985.

(5) Semlyen, J. A. *Cyclic Polymers*; Elsevier Applied Science Ltd.: Barking, U.K., 1986.

(6) (a) Reif, L.; Höcker, H. *Macromolecules* **1984**, *17*, 952. (b) Höcker, H. *J. Mol. Catal.* **1980**, *8*, 202.

(7) Ivin, K. J. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 1.

(8) Scott, K. W. *Adv. Chem. Ser.* **1969**, *91*, 399.

(9) Ofstead, E. A.; Calderon, N. *Makromol. Chem.* **1972**, *154*, 21.

(10) Thorn-Csanyi, E.; Hammer, J.; Pflug, K. P.; Zilles, J. U. *Abstracts, MacroAkron'94, 35th IUPAC International Symposium on Macromolecules*; Akron, OH, 1994; p 241.

(11) Suter, U. W.; Höcker, H. *Makromol. Chem.* **1988**, *189*, 1603.

(12) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 12, 1600.

(13) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Hanser Publishers: Munich, Germany, 1988.

(14) Flory, P. J.; Suter, U. W.; Mutter, M. *J. Am. Chem. Soc.* **1976**, *19*, 5733.

(15) Following JS theory, the entropy change of reaction (1) is the sum of that for reactions (3) and (4):

$$\Delta S_3 = k \ln(V/2v_s) \tag{12}$$

$$\Delta S_4 = k \ln(\mathscr{P}(i,\nu)/i) \tag{13}$$

where V is the volume of the system, v_s is the volume swept out by a bond, i is the number of repeat units in the cyclic product, and $\mathscr{P}(i,\nu)$ is the probability that a linear i-mer has a configuration compatible with cyclization: the ratio of the number of configurations of the ring to that of the corresponding linear molecule. Let $K_i^{(\nu)}$ denote the equilibrium constant for the case of ν bonds per repeat unit: $K_i^{(\nu)} = (v/2v_s)(\mathscr{P}/i)$. For the equilibria involving cycloolefin monomers ($i = 1$) cyclobutene, cyclohexene, and cyclooctene (ν = 4, 6, and 8), the relative magnitudes of the equilibrium constants are $K_1^{(a)}/K_1^{(b)} = \mathscr{P}(1,a)/\mathscr{P}(1,b)$, independent of V and v_s. For cyclobutene there is only one conformation of the ring, but 3^3 rotational isomers of the linear analogue, leading to $\mathscr{P}(1,4) \approx 0.037$. For cyclohexene, there are two conformations of the ring, and 3^5 rotational isomers of the linear analogue, $\mathscr{P}(1,6) \approx 0.0082$. For cyclooctene, there are eight conformations of the ring, and 3^7 rotational isomers of the linear analogue, $\mathscr{P}(1,8) \approx 0.0037$. Based on these values, $K_1^{(4)}/K_1^{(6)} \approx 4.5$ and $K_1^{(6)}/K_1^{(8)} \approx 2.2$. Thus, accounting for directional correlations, which lead to the very small number of configurations for small rings, cannot explain the experimental result that $K_1^{(6)}$ is vastly higher than $K_1^{(4)}$ and $K_1^{(8)}$.

(16) (a) Lipkowitz, K. B.; Boyd, D. B. *Reviews in Computational Chemistry*; VCH: New York, 1994; Vol. 5. (b) Hirst, D. M. *A Computational Approach to Chemistry*; Blackwell: London, 1990.

(17) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(18) (a) Allinger, N. L.; Li, F.; Yan, L. *J. Comput. Chem.* **1990**, *11*, 848. (b) Allinger, N. L.; Li, F.; Yan, L. *J. Comput. Chem.* **1990**, *11*, 868.

(19) (a) Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566. (b) Allinger, N. L.; Yuh, Y. H.; Lii, Jenn-Huei *J. Am. Chem. Soc.* **1989**, *111*, 8551. (c) Allinger, N. L.; Zhu, Z.; Chen, K. *J. Am. Chem. Soc.* **1992**, *114*, 6120.

(20) Flory, P. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.

(21) (a) Mark, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 4354. (b) Mark, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 6829.

(22) (a) Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1985**, *68/69*, 16. (b) Cherednichenko, V. M. *Vysokomol. Soedin.* **1978**, *5*, 1086.

(23) This statement is based on JS theory with Gaussian chains, although it is unlikely that short chains still obey Gaussian statistics. For a general reference, see: Semlyen, J. A. *Cyclic Polymers*; Elsevier Applied Science Ltd.: Barking, U.K., 1986.

(24) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1971.

(25) des Cloizeaux, J. *Phys. Rev. A* **1974**, *10*, 1665.

(26) Höcker, H. *Makromol. Chem.* **1976**, *177*, 1707.

(27) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856.

(28) Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108.

(29) Hummel, K.; Zekoll, H.; Chemelli, R. *Makromol. Chem.* **1987**, *188*, 1075.

MA946002J