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# Ring-Size Distribution in the Depolymerization of Poly(butylene Terephthalate)

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ABSTRACT: Poly(butylene terephthalate) (PBT) was depolymerized in refluxing *o*-dichlorobenzene using stannoxane catalysts to produce good yields of cyclic oligomers. We have studied how the ring size distribution varies as a function of the starting concentration of monomer units. Over a concentration range of 0.05 to 0.2 M, there is little change in the ring size distribution. This result suggests that the depolymerizations were performed above the critical monomer concentration. Application of a recent model by Mandolini (an adaptation of the Jacobson−Stockmayer model) for thermodynamically controlled cyclizations contradicts the experimental results by suggesting that the experiments were run *below* the critical monomer concentration. It appears that Mandolini's model may not be appropriate, in its present form, for depolymerizations. We further studied the experimental data using RIS modeling in which the probability of zero end-to-end distance for linear oligomers was used to calculate macrocyclization equilibrium constants. Reasonable agreement was observed between calculated and experimental data with greater deviation for smaller ring sizes, as might be expected. Incorporation of the width of the distribution and skewness into the calculation depressed the macrocyclization values.

## Introduction

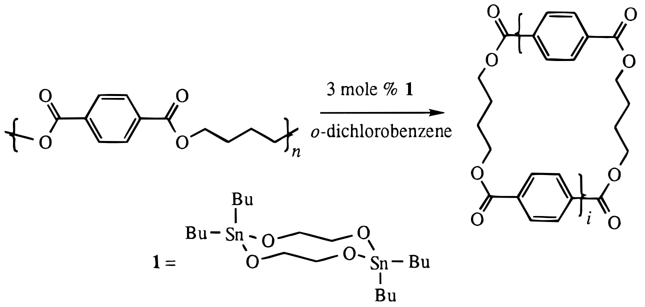
Cyclic or ring molecules occur in a wide range of polymers, particularly those prepared by step-growth polymerization.[1] Macrocyclization can be governed by relative rates of competing processes (kinetic control) or the equilibrium parameters of the system (thermodynamic control). We are particularly interested in cyclic oligomers of aromatic polyesters. Cyclic oligomers have been isolated and studied for poly(ethylene terephthalate) (PET)[2] and poly(butylene terephthalate) (PBT).[3]

Recently, Brunelle and co-workers developed procedures for the preparation of cyclic esters in high yield. One route is based on the amine-catalyzed condensation reaction of terephthaloyl or isophthaloyl chloride with diols.[4,5] The reactions are carried out under pseudo-high-dilution conditions. The yield of the cyclic oligomers is strongly dependent on the structure of the amine catalyst, with the highest yields of cyclics obtained with the sterically unhindered amines such as quinuclidine. The ring-size distribution (which is controlled by the relative rates of intermolecular vs intramolecular ester bond formation) is kinetically controlled.

By definition, in a kinetically controlled reaction, the cyclic oligomers are unreactive to the system once they are formed. According to the statistical treatment of chain molecules, the concentration of cyclics obtained in these reactions should be proportional to the $-^3/_2$ power of their size: $[C_i] \approx i^{-3/2}$; where $C_i$ is the concentration of cyclic oligomers with *i* repeat units.[6,7] This statistical treatment assumes strainless rings and Gaussian chain statistics. A theoretical model of cyclization under kinetic control has been developed by Mandolini and co-workers.[8,9]

Another method for the preparation of cyclic esters is by depolymerization of linear polymer (ring-chain equilibrium). Brunelle and co-workers[10] have optimized the depolymerization process for PBT (Scheme 1) by the development of active tin catalysts. A typical depolymerization is performed by heating a mixture of linear PBT and 3 mol % cyclic stannoxane-**1** in *o*-dichlorobenzene at reflux for 1 h. Residual linear polymer precipitates from solution upon cooling. The yield of cyclics ranged from 42% when the starting polymer concentration was 0.3 M up to 96% when the starting concentration was 0.05 M.

**Scheme 1**



The subject of this paper is to closely examine the results of PBT depolymerization with a particular interest in gaining mechanistic insight into factors controlling ring-size distribution. Depolymerization reactions and ring-chain equilibrium reactions that form cyclic oligomers are often under thermodynamic control. In contrast to kinetically controlled reactions, cyclic oligomers formed under thermodynamic control are continually reactive, undergoing ring-opening and ring formation throughout the reaction period. The distribution of cyclic oligomers is determined by the relative thermodynamic stability of each species. Cyclic formation can occur by backbiting of the chain end onto an interior carbonyl or by reaction of the internal ether oxygens with other carbonyl groups. Models have been developed which describe the yields and distributions

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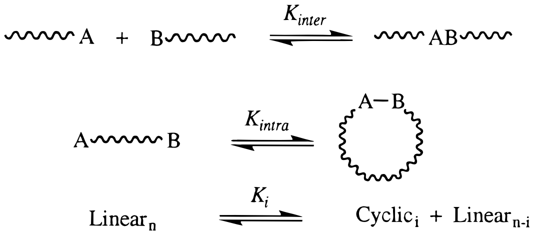
**Scheme 2. Reaction Equilibria in Mandolini's Model**



of cyclic oligomers formed under such conditions. These models usually assume strainless rings and Gaussian statistics for the end-to-end distance of the acyclic chain. In addition, all reactive sites in the molecule (carbonyl group in polyesters) must have equal reactivity.

We have chosen two approaches for understanding the experimental results. The first is a general theory of macrocyclization equilibria proposed in 1950 by Jacobson and Stockmayer[11] as adapted by Mandolini.[12] The second approach involves modeling of cyclic oligomer distributions using rotational isomeric state (RIS) theory.

## Background

Jacobson and Stockmayer's theory[11] of macrocyclization equilibria provided a framework to describe cyclic populations in equilibrium reactions of linear polymers in concentrated solutions.[1,7] Mandolini and co-workers[8] adapted this theory to deal specifically with reactions done under more dilute conditions where the original theory predicts that only cyclic oligomers will be obtained. Mandolini defines an equilibrium effective molarity for a cyclic with $i$ repeat units (EM$_i$) as the ratio of the intramolecular equilibrium constant to the intermolecular equilibrium constant, defined in eq 1 for the reactions depicted in Scheme 2.

$$\mathrm{EM}_i = \frac{K_{(\mathrm{intra})i}}{K_{(\mathrm{inter})i}} \qquad (1)$$

These EM$_i$ values have the meaning of the concentrations of cyclic species extrapolated to infinite monomer concentration. Mandolini showed that the concentration of each cyclic species is related to its effective molarity by eq 2. It can also be shown than $x$ is equal

$$[C_i] = \mathrm{EM}_i x^i \qquad (2)$$

to the fraction of reacted end groups in the acyclic portion of the polymer. Thus, $x$ can be readily calculated from the molecular weight of any residual polymer.

Jacobson and Stockmayer[11] proposed a quantity called the molar cyclization equilibrium constant, $K_i$, which refers to the overall ring-chain equilibrium process (last line, Scheme 2). This equilibrium constant is numerically equivalent to the effective molarity defined by Mandolini. Jacobson and Stockmayer found that this equilibrium constant varied inversely with the $-^5/_2$ power of the cyclic size, $i$, as shown in eq 3 (where $B$ is

$$K_i = \mathrm{EM}_i = Bi^{-5/2} \qquad (3)$$

the effective molarity that the monocyclic ring would have if it were strainless). By considering mass balance, Mandolini derived an expression relating effective molarity values, intermolecular equilibrium constant and the initial monomer concentration, $[M_1]_o$. When the extent of reaction, $x$, equals 1, the theory predicts a cutoff point called the critical monomer concentration, $[M_1]_o$*, given by eq 4. The cyclic fraction can only

$$[M_1]_o{}^* = 2.612B - \sum_{i=1}^{f\text{-}1} (Bi^{-3/2} - i\mathrm{EM}_i) \qquad (4)$$

contain a limited amount of monomer units, and this limit when $x$ approaches 1 is the critical monomer concentration.

Calculation of a critical monomer concentration details numerically a general phenomenon known by organic chemists. Since chain extension is a second-order process and cyclization is first order, there is a concentration below which cyclization is favored over chain extension. When the initial monomer concentration is below the critical monomer concentration, the system will ultimately result in cyclic species only. Reactions above the critical monomer concentration will contain a mixture of cyclic and linear species. In addition, reactions carried out below the critical monomer concentration show a change in the distribution of cyclic oligomers as the starting concentration varies. Above the critical monomer concentration, the yield and distribution of cyclic oligomers is fixed, and any excess monomer leads only to acyclic materials.

Mandolini demonstrated his theory in two ways. The first was treatment of a hypothetical hydrocarbon chain. In this case, he found the cutoff behavior of a critical monomer concentration only at high values($10^5$ M$^{-1}$) of $K_{\mathrm{inter}}$. The second application of the theory was to cyclooligomerization of $\beta$-propiolactone. By combining eqs 2 and 3, eq 5 is obtained. Even though theory

$$[C_i] = B\, i^{-\gamma} x^i \qquad (5)$$

predicts $^5/_2$ for $\gamma$, it was used as a fitting parameter by Mandolini and co-workers. A plot of log [$C_i$] vs log $i$ yields a straight line when rings are strainless and can be fit using eq 5. Only when $x = 1$ are the slope and intercept equal to $\gamma$ and $B$. A nonlinear least-squares analysis of the propiolactone data was used to obtain $x$, $\gamma$, and $B$. With these, $K_{\mathrm{inter}}$ and $[M_1]_o$* were calculated, and the system was described in complete detail.

One of the goals of this work is to assess the utility of Mandolini's approach to the depolymerization of PBT. We fit experimental data on ring-size distributions as a function of starting polymer concentration and judge the reasonableness of the outcome. To further help us in our analysis of the experimental data, we employ RIS theory to study ring-size distributions for PBT oligomers.

## Results and Discussion

**Analysis of PBT Depolymerization Using Mandolini's Model.** Depolymerizations were carried out in *o*-dichlorobenzene using 3.0 mol % (based on monomer repeat unit) of cyclic stannoxane-**1** (see Scheme 1) according to a previously reported method.[10] Depolymerization reactions were carried out over a range of concentrations from 0.05 to 0.2 M (based on monomer units). The data are plotted in Figure 1 as the log $C_i$ (concentration of cyclic species $i$ at equilibrium) vs log $i$ (cyclic size). The data in Figure 1 represent cyclic yields for dimer through heptamer.

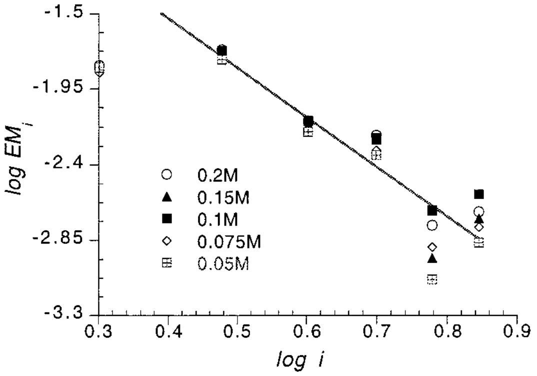


**Figure 1.** Plot of log $[EM]_i$ vs log $i$, for the depolymerization of PBT (in *o*-dichlorobenzene using 3.0 mol % cyclic stannoxane-**1**) at different initial concentrations of PBT repeat unit. The line represents a linear least-squares fit of the experimental data for $i = 3-7$; slope $= -2.9 \pm 0.1$. The concentrations were measured at ambient temperature, not at the temperature of the depolymerization reaction which is 180 °C.

Inspection prompts two observations. If the dimer is ignored (a reasonable assumption since it is the oligomer which is most likely to include a contribution from ring strain), then the slope of the best straight line through the points is $-2.9 \pm 0.1$. Given the scatter in the data, this slope is close to the $-2.5$ value predicted by a statistical treatment of reactions under thermodynamic control. Therefore, it is reasonable to compare Mandolini's model for a thermodynamically controlled process.

The second observation from Figure 1 is that the yield of cyclic does not change in a systematic way with starting concentration. The yield of cyclic would be expected to be independent of starting concentration above the critical monomer concentration, $[M_1]_0$*.

The first step taken to understand the distribution of cyclics was to try to fit the results using Mandolini's model. Since the data indicated that reactions were done above $[M_1]_0$*, the first set of calculations was done assuming this was the case. Using this assumption, effective molarity values for each ring size, $EM_i$, can be obtained directly from their final concentrations in the reactions. First, the degree of polymerization of the remaining polymer was calculated from its molecular weight. Then, $EM_i$ values were calculated from eq 2. From $EM_i$ values, a value for $B$ was calculated as 0.31 M, and the critical monomer concentration was calculated using eq 4, where $f$[13] is the degree of polymerization of the first strainless ring, taken as 3 for this reaction. Details of the calculations are reported by Hubbard.[14] Surprisingly, the *calculated* critical monomer concentration was 0.42 M, which was well above any of the depolymerization concentrations. This result would predict that different starting concentrations below this value (like those used in the depolymerization) would result in variable ring size distributions, *which was not observed*. There was concern that the inconsistency might have resulted due to an invalid assumption that reactions were carried out above the critical monomer concentration. For the next calculation, no assumptions were made about the data, and effective molarity values were calculated by nonlinear least-squares fitting of eq 5. Calculations were carried out by fitting each data set to the equation, and calculating $B$ as the average obtained from the seven data sets. Our technique was verified by reproducing Mandolini's calculations for propiolactone oligomerization within error. The dimer was treated in two ways. In the first, it was assumed that the dimer was not strained, so $f$ was set at 2. For the second calculation, the dimer was assumed to be strained, so $f$ was set at 3, and a value for $EM_2$ was estimated at 0.015 M from the average final concentration of dimer in the various runs. Values calculated for the critical monomer concentration ranged from 0.5 to 0.6 M, depending on the dimer treatment. *The contradiction between the experimental data and the predicted results still exists.*

There are several possible reasons for this lack of fit. First, Mandolini's model assumes strainless rings. This assumption is not likely for the smaller rings. If we assume that the experimental data for cyclic yields is not flawed and the assumption of strainless and Gaussian rings is correct, there are still two possibilities why Mandolini's model cannot explain the data. The first would be that the reaction is not under thermodynamic control. However, this is not consistent with the $-2.9$ dependence of cyclic yields on ring size (Figure 1). Another possibility is that Mandolini's model is not appropriate for depolymerizations. Given the last possibility, we turned to an alternative method for examining the ring-size distribution in PBT depolymerization. The next section discusses our results using RIS modeling.

**Rotational Isomeric State (RIS) Modeling of PBT Cyclization.** Although there is scatter in the data depicted in Figure 1, the Jacobson−Stockmayer model[11] provides a reasonable rationalization for the trend of $C_i$ with $i$ for $i > 2$, in the sense that the straight line with slope $\approx -5/2$ reproduces the general trend of the data in this Figure. Here we seek an understanding of the origin of the intercept of this straight line (or, equivalently stated, of the size of $C_i$ at a particular value of $i$, rather than merely being content with the dependence of $C_i$ on $i$) as well as a rationalization for the strong deviation of $C_2$ from the linear extrapolation of the best straight line defined with $C_3$−$C_7$.

Effective molarity values consist of contributions from enthalpy and entropy.[15] The enthalpic contribution is related to ring strain energy of the cyclic being formed, and for strainless rings is zero. The entropic component for macrocyclization in the unperturbed state, as in the bulk polymer, can be calculated using the RIS model if $i$ is large enough so that the ring is free of strain.[16] This requirement is not met with the cyclic dimer. The crystal structure shows that the two benzene rings in the cyclic dimer are bent to a small extent into boat-shaped structures, which convincingly shows that intramolecular strain is present.[17] In absence of any information in the literature on the presence or absence of strain in the larger rings, data for all rings with $i >$ 2 will be plotted along with the results from the theoretical analysis.

A comprehensive review of the RIS model is available.[18] This model has been successfully used to quantitatively describe macrocyclization equilibrium constants for oligomers in poly(dimethylsiloxane),[19] poly(6-aminocaproamide),[20] and polyolefins.[21] The most extensive comparison between experiment and calculation has been reported for poly(dimethylsiloxane).[19] Good agreement was obtained for oligomers with a degree of polymerization of 15 or higher, where the number of rotatable bonds in the oligomer is 30 or more. The agreement was less satisfactory for smaller oligomers. PBT, with seven rotatable bonds per monomer unit, would require a degree of polymerization of 4−5 to have a number of rotatable bonds comparable with a poly(dimethylsiloxane) with a degree of polymerization of 15. There is a form of the RIS model that allows the incorporation of fluctuations of the torsional angles about their preferred values, in the approximation that these fluctuations at neighboring bonds are independent.[22−24] That form has not been employed here. While it is true that deviations from preferred values undoubtedly occur in small rings, the deviations at neighboring bonds surely would not be independent of one another but would instead be strongly correlated. Therefore, the use of a form that assumes independent fluctuations cannot be justified for the problem at hand.

Cooper and Semlyen[2] applied RIS theory to ring size distributions of PET cyclic oligomers. The calculated values underestimated the experimental values by roughly 40%. The authors suggested that those differences might be related to a failure to obey Gaussian statistics or to correlations in the positions and directions of the PET chain end.

For cyclization to occur, a linear $i$-mer must have an end-to-end distance, $r$, of zero, so that the ends are superimposed on one another. Kuhn[5] derived the probability of an end-to-end distance of zero using a random walk, which leads to Gaussian distribution for large chains. The restriction to a Gaussian distribution can be relaxed by calculating higher even moments of the end-to-end distance.[25] The equations used in the present RIS analysis of the macrocyclization of a single chain of PBT are[26] eqs 6−10. The calculations employ

$$C_i = \frac{W(0)}{\sigma_{\mathrm{ci}} N_{\mathrm{A}}} \tag{6}$$

$$W(0) = \left(\frac{3}{2\pi\langle r^2\rangle_0}\right)^{3/2} h(0) \tag{7}$$

$$h(0) = 1 + 3 \times 5\, g_4 + 3 \times 5 \times 7\, g_6 + \ldots \tag{8}$$

$$g_4 = -\left(\frac{1}{2^3}\right)\left(1 - \frac{3\langle r^4\rangle_0}{5\langle r^2\rangle_0^{\,2}}\right) \tag{9}$$

$$g_6 = -\left(\frac{1}{2^3 \times 3!}\right)\left[3\left(1 - \frac{3\langle r^4\rangle_0}{5\langle r^2\rangle_0^{\,2}}\right) - \left(1 - \frac{3^2\langle r^6\rangle_0}{5 \times 7\,\langle r^2\rangle_0^{\,3}}\right)\right] \tag{10}$$

even moments calculated for unperturbed conditions, as shown by the use of the subscript 0 in $\langle r^2\rangle_0$, $\langle r^4\rangle_0$, and $\langle r^6\rangle_0$. This usage is in conformity with prior usage for other systems,[19−21,26] and with the behavior or linear chains in molecular dynamics simulations.[27]

The denominator in eq 6 is the product of Avogadro's number, $N_{\mathrm{A}}$, and the symmetry number of the ring, $\sigma_{\mathrm{ci}}$. For PBT, the symmetry number is $2i$ because there are two reactive sites per repeat unit.[2] The probability for an end-to-end distance of zero, denoted by $W(0)$, can be evaluated from the RIS model with different levels of approximation. The simplest approximation, using $h(0) = 1$, assumes a Gaussian distribution function with a mean square unperturbed end-to-end distance of $\langle r^2\rangle_0$. If the distribution function has a width different from that defined by a Gaussian distribution function, the influence of the actual width on $C_i$ is introduced via $g_4$. The value of the dimensionless ratio $\langle r^4\rangle_0/\langle r^2\rangle_0^2$, which is a measure of the width of the distribution function for $r^2$, is $^5/_3$ if the distribution function is Gaussian, which recovers $g_4 = 0$ and $h(0) = 1$ in this case. The influence of the skewness of the distribution function for $r^2$ is introduced via $g_6$ which depends on the dimensionless ratio $\langle r^6\rangle_0/\langle r^2\rangle_0^3$, the value of which is 35/9 for a Gaussian distribution. Therefore $g_4 \rightarrow 0$ and $g_6 \rightarrow 0$ as $i \rightarrow \infty$ but $g_4$ and $g_6$ may assume nonzero values when $i$ is small.

**Table 1. $\langle r^{2p}\rangle_0$, $p$ = 1, 2, 3, for PBT Oligomers at 454 K**

| $i$ | $\langle r^2\rangle_0$, Å$^2$ | $\langle r^4\rangle_0/\langle r^2\rangle_0^2$ | $\langle r^6\rangle_0/\langle r^2\rangle_0^3$ |
|---|---|---|---|
| 3 | 501.9 | 1.337 | 2.129 |
| 4 | 701.3 | 1.408 | 2.43 |
| 5 | 900.0 | 1.455 | 2.65 |
| 6 | 1100 | 1.488 | 2.815 |
| 7 | 1300 | 1.512 | 2.942 |
| 8 | 1500 | 1.531 | 3.043 |
| 9 | 1699 | 1.545 | 3.124 |
| 10 | 1899 | 1.557 | 3.192 |
| : | : | : | : |
| ∞ | 203.7 $i$ | 5/3 | 35/9 |

An RIS model can be used to calculate $\langle r^{2p}\rangle_0$, $p = 1,2,3, \ldots$, as a function of $i$. For this purpose we have adopted the RIS model described by Mendicuti et al.[28] and summarized as entry V065 in the recent compilation of RIS models by Rehahn et al.[29] This model employs three pairwise interdependent rotational isomeric states (trans, gauche$^+$, gauche$^-$) at the five bonds in the sequence O−CH$_2$−CH$_2$−CH$_2$−CH$_2$−O and two equally weighted, independent rotational isomeric states (cis and trans) at the bonds where the ester joins the aromatic ring. The ester bonds themselves are maintained in trans states. The energies of the three nonzero first-order interactions are 0.5 kJ/mol for CH$_2$···CH$_2$, 4.2 kJ/mol for O···CH$_2$, and 0.4 kJ/mol for C*···CH$_2$ where C* denotes the carbonyl carbon atom and its pendant groups. The second-order interaction of CH$_2$ with O is assigned an energy of 0.56 kJ/mol. The second-order interaction of CH$_2$ with C* and its pendant groups is so large that it is taken to be infinite.

When applied to PBT at 300 K, the temperature for which the numerical values of the statistical weights are tabulated by Rehahn et al., this RIS model predicts a dimensionless characteristic ratio of 4.36. This characteristic ratio is defined as the ratio of the actual $\langle r^2\rangle_0$ to the value expected for a freely jointed chain with bonds of the same number, $n$, and length. The macrocyclization experiments were performed at reflux in $o$-dichlorobenzene, which implies an experimental temperature near 454K. Even though the temperature coefficient of the mean square unperturbed dimensions of PBT is small ($\partial \ln \langle r^2\rangle_0/\partial T_\infty$ is calculated to be on the order of $-10^{-4}$ deg$^{-1}$), the temperature of the pertinent experiments is substantially higher than 300 K. Therefore we have used numerical values for the statistical weights calculated as exp $(-E/RT)$ from the interaction energies tabulated by Rehahn et al., using the experimental temperature of 454 K. The nonzero statistical weights obtained by this procedure have values of 0.64, 1.25, 0.57, and 0.54 for $\sigma_1$, $\sigma_2$, $\sigma_3$ and $\omega_2$, respectively. The oligomer used in the calculation of the $\langle r^{2p}\rangle_0$, $p$ = 1,2,3, was terminated by oxygen atoms, with initial bond O−C* and final bond C*−O.

The raw results are presented in Table 1. In the range of $i$ of interest, the dimensionless ratios $\langle r^{2p}\rangle_0/\langle r^2\rangle_0^p$, $p$ = 2, 3, are below their asymptotic limits of 5/3 and 35/9, respectively, as is the case for most chains at small degrees of polymerization. The values of $g_4$ are

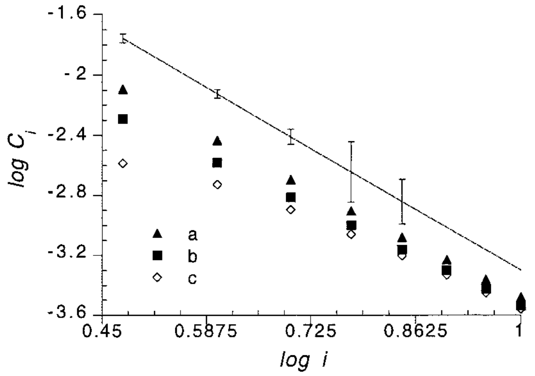


**Figure 2.** Comparison of calculated and experimental macrocyclization equilibrium constants for the dimer through the decamer of PBT at 454K. The vertical bars denote the range of the experimental results, taken from Figure 1. Lines denoted by a, b, and c are calculated from the RIS model using (a) $h(0) = 1$, (b) $h(0) = 1 + 15g_4$, and (c) $h(0) = 1 + 15g_4 + 105g_6$.

negative for the oligomers listed in Table 1, rising from $-0.0247$ at $i = 3$ to $-0.0082$ at $i = 10$. The distribution functions are narrower than a Gaussian distribution, which will tend to depress the values of $K_i$, because cyclization depends on conformations that are located at an extreme of this distribution function. The values of $g_6$ are initially negative ($g_6 = -0.0029$ at $i = 3$) and become less negative as the size of the oligomer increases in Table 1.

The values of $C_i$ calculated in each case from eq 6, but using three different levels of truncation for $h(0)$ in eq 8, are presented in Figure 2 for oligomers from the trimer through the decamer. The calculated $C_i$ are depicted along with the ranges for the experimental $C_i$ taken from Figure 1. In Figure 2, the calculated $C_i$ values are for *o*-dichlorobenzene at 454 K. The experiments were performed at this temperature, but the solutions were cooled to ambient temperature for measurement of the experimental $C_i$. Thus the experimental $C_i$ and calculated $C_i$ in Figure 2 have an inherent difference that arises from the thermal expansion of *o*-dichlorobenzene from ambient temperature to 454 K. If we were to correct the calculated values from 454 K to ambient temperature, the calculated $C_i$ would increase by an amount roughly equivalent to the sizes of the plotted symbols in Figure 2. Incorporation of the width of the distribution (through $g_4$) and its skewness (through $g_6$) decreases the calculated value of $C_i$ for oligomers of this size. The calculation used here would be expected to be more reliable for the larger oligomers, since there is a greater likelihood of being able to describe the distribution function with simple corrections to a Gaussian form. Although the agreement is certainly not exact, the calculated values do provide a convenient rationalization for the general sizes of the macrocyclization equilibrium constants. A sensitivity analysis, performed by incrementing each statistical weight in turn by 0.05, shows that the calculated macrocyclization equilibrium constants are most sensitive to the value of $\omega_2$, which weights the second-order interaction between a methylene group and the ester oxygen atom. The calculated $C_i$ values increase as $\omega_2$ increases (as this second-order interaction becomes less repulsive).

## Conclusions

The experimental ring size distributions for cyclic oligomers of PBT obtained by depolymerization were invariant over the concentration range studied for the process. This invariance was not adequately explained by Manodlini's model for thermodynamically controlled cyclization. However, the concentration of cyclics ($C_i$) as a function of ring size is roughly proportional to $-^5/_2$ which is consistent with a thermodynamically controlled process as described by the Jacobson−Stockmayer model. RIS modeling was used to calculate macrocyclization equilibrium constants as deduced by the probability of a zero end-to-end distance. Reasonable agreement between the calculated and experimental values was obtained with greater deviation observed for smaller ring sizes, as might be expected. Incorporation of the width of the distribution and its skewness into the RIS calculation decreased the values of $C_i$.

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