Ring–Chain Equilibrium in Reversibly Associated Polymer Solutions: Monte Carlo Simulations

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ABSTRACT: Living polymers formed by reversible association of spacers (oligomers) terminated by one donor and one acceptor group at the ends are studied by means of Monte Carlo simulations (using the bond-fluctuation model). To account for the different chemical nature of the associating groups and spacers, we considered three cases of flexible, semiflexible, and rigid polymers. Rigid polymers have both intrinsic rigidity of spacers and rigidity (entropic penalty) imparted by end groups association. Semiflexible polymers possess only the latter, and flexible polymers do not have any type of rigidity. We have studied the average degree of association for all types of polymers as a function of concentration and spacer length and compared the results with a simple analytical model. We found that above some crossover concentration the association behaviors of all chains follow the same pattern, well-described by the analytical model and depending mainly on the number density of donor/acceptor groups. Below the crossover concentration, the association is governed by the individual characteristics of spacers and differs for chains of different rigidity and chain length. Defined in this way the crossover concentration, $c_r$, is a measure of the ring-to-chain transition: below $c_r$, ring formation is most favorable, while above $c_r$, linear chain formation dominates. We found that the rigidity (entropic penalty) imparted by end group association defines the behavior above the $c_r$: the total degree of association of semiflexible chains is much smaller than that for flexible chains of the same concentration and practically coincides with that for rigid chains (despite different spacer rigidity). The crossover concentration, $c_r$, is a function of spacer length and strongly differs for chains of different rigidity: $c_r^{flex} > c_r^{semi} > c_r^{flex}$. The rigidity of the spacer has a much stronger impact on $c_r$ compared to the end group rigidity imparted by association.

1. Introduction

Recent progress in supramolecular chemistry has made available a new class of polymers based on noncovalent interactions that combine the properties of traditional synthetic polymers with the versatility of biomolecules. Various arrays for multiple hydrogen bonding have been developed that allow tuning the strength of association without losing its reversible character. These reversibly associating arrays can be used for the modification of traditional polymers to create materials with new properties. Such reversibly associating polymers are able to change their degree of polymerization in response to chemical parameters (solvent, pH) or physical parameters (temperature, flow fields). Their responsiveness means that they may find application in the general area of “smart materials” or in devices that effect energy, electron, or ion exchange.

So far the experimental observations concerning head-to-tail self-assembly of reversibly associated polymers (RAP) schematically shown in Figure 1 have been analyzed in the framework of classic condensation polymerization theory (CPT). This theory is based on the Jacobson–Stockmayer (JS) approach, which makes the following assumptions: (1) reactivity of each functional group is independent of chain length, (2) chains obey Gaussian statistics, and (3) rings are strainless, that is, the penalty for ring formation is purely entropic. It was also assumed that the molecular size distribution for linear chains is the same as that in ring-free case. The extent of reaction, $p$, is considered to be an input parameter of the model. As noted in the original JS model and by many later researchers, the fraction of rings (in equilibrium with chains) is overestimated by the JS model. Some of the reasons are (1) failure of Gaussian density distribution, (2) the neglect of the geometrical constraints for ring closure (orientational factor), and (3) the neglect of ring strain. The first two factors have been addressed by Flory, Suter, and co-workers. They have approximated the density distribution by a simple correction to the Gaussian distribution (the first Hermitian correction term) or alternatively by a Monte Carlo (MC) procedure to count* Corresponding author: e-mail eed@po.cwru.edu.
the number of chains for which both ends are situated inside of a small sphere. They also have accounted for the geometrical constraints for ring closure which can be calculated either by exact matrix generation methods or by Monte Carlo techniques (using rotational-isomeric-state model, RIS). The third factor, ring strain, has been considered relatively recently. Erololani and co-workers have introduced an additional coefficient to account for small ring strain, whereas Chen and co-authors have employed molecular mechanics computer simulations to account for the enthalpic penalty for ring closure. One of the phenomena, which has been noted by all the researches, is the ring-to-chain transition, which is a true phase transition only for the case of full conversion, i.e., $p \rightarrow 1$. In this limit there is a certain polymer concentration, below which only rings exist and above which both rings and chains are present.

Besides the computer simulations devoted to the estimation of a single ring closure penalties, a series of extensive on and off-lattice MC simulations of the system of many associating monomers have been performed by Wittmer, Landau, and co-workers. In their simulations monomers were modeled as beads with two spins (bond pointers) for reversible bond formation. A reversible bond could be formed or broken only from monomers separated by a certain distance, whereas orientation of the spins was of no concern. There was no distinction between donors and acceptors, but only binary reversible interactions have been considered. The results of these simulations for the average chain length, radius of gyration, and molecular weight distributions have been found to be in good agreement with theoretical predictions for wormlike micelles. When formation of rings has been allowed, it was found that most of the rings are of the smallest allowed size and since the molecular weight distribution for chains still satisfies the same scaling laws as in the ring-free case it was concluded that in general ring presence does not change the properties of the chains formed. It has also been noticed that at low polymer concentration the ring fraction can exceed the chain fraction.

In view of the new classes of noncovalent associations, there are several new aspects of RAP which are not typical of classic condensation polymerization. First, having chemically different spacers and end groups create much larger variety in the properties of reversibly associated materials than anticipated by classic CPT. For instance, using different arrays for hydrogen bonding, the materials obtained may have different orientational specificity for end group association even if they have a similar enthalpic gain for association. Physically this implies that the sections of the resulting chains adjacent to associated end groups have to maintain some particular orientation with respect to each other to ensure the association. In other words, segments adjacent to end groups may become effectively more rigid. The intrinsic rigidity of spacers can vary as well. These factors will evidently influence the association behavior. Classic CPT does not provide solutions for this case as normally it deals with the “averaged” rigidity of polymers, whereas computer simulations have accounted for rigidity (associated with a particular chemical structure) only in the single chain simulations devoted to estimating the penalty for ring closure. Applying spin–lattice simulations (Potts-like model), Landau and Milchev have accounted for rigidity to some extent by allowing a 90° bend of a living chain of beads. To address the influence of the different types of rigidity on association, we will consider in this paper three types of associated polymers: flexible polymers, having flexible spacers and end groups; semiflexible polymers, having flexible spacer and rigid end groups (when they are associated); and rigid polymers, having both spacer and end groups rigid. Comparing semiflexible and flexible polymers we will study the effect of rigidity (entropic loss) imparted by end group association, whereas comparing semiflexible and rigid polymers with similar rigidity of end groups we will analyze the influence of the intrinsic rigidity of spacers on association behavior. In all cases we will consider oligomers (spacers) terminated by one donor and one acceptor group. We will apply Monte Carlo simulations using the bond-fluctuation model and consider self-avoiding walks in 3 dimensions (3d) for polymer solutions of varying concentration. The results of the computer modeling will correspond to good solvent conditions. We will also apply a simple analytical model to compare with MC results.

Another aspect, which has a somewhat different meaning for reversibly associated polymers compared to polymers obtained in condensation polymerization, is the ring-to-chain transition. For truly reversible polymers the limit of full conversion, $p \rightarrow 1$, implies an infinite energy of association, $\Delta E_{\text{hb}} \rightarrow \infty$, that can hardly be reached. In condensation polymerization reactions the potential barrier for back (depolymerization) reaction is often much larger than for the forward reaction. This creates a kinetic imbalance between the polymerization and depolymerization reactions. As a result, dilution of the polymerized material does not necessarily result in the decrease of the average molecular weight and hence the degree of conversion. This is one of the reasons for the classic CPT to operate in the terms of extent of reaction, $p$ (instead of e.g. concentration). For truly reversibly associated polymers the degree of association $p$ is directly related to the concentration $c$ (and temperature) and may considerably deviate from $p = 1$ (as long as $\Delta E_{\text{hb}}$ is finite). Although the ring-to-chain transition is a true phase transition only for $p = 1$, for any finite energy of association still there is some crossover point, $c_\text{cr}$, below which the association proceeds mainly by ring formation and above which the chain formation dominates. Defining $c_\text{cr}$ in the infinite energy limit does not provide a relevant measure for the crossover concentration in RAP, and the lower the degree of association, $p$, the worse the estimate will be. Therefore, it would be useful to obtain some criteria to estimate such a point as a function of association strength (enthalpy and entropy) and spacer characteristics (such as length, rigidity, and so on). In this paper we will study the influence of spacer length on the crossover concentration associated with the ring-to-chain transition for flexible chains using MC simulations. We will also analyze the influence of the spacers and end groups rigidity on the crossover concentration. We will use our simple analytical model to suggest a simple criteria for the crossover point. We expect temperature, strength of association, and volume interactions in general to be other factors influencing the ring-to-chain transition and that the physical signature of the transition can be seen in the viscosity (as anticipated in ref 20) or in other dynamic properties.
This paper is arranged in the following way. In the next two sections we will discuss the computer simulation and analytical models employed to obtain the results discussed below. In the Results section we will first discuss association behavior and the ring-to-chain transition for the flexible chains with different spacer length. Then we will analyze the influence of chain rigidity on the association behavior and ring-to-chain transition. The degree of association for chains and rings formed from polymers of different rigidity (flexible, semiflexible, and rigid) will be considered as a function of concentration and spacer length. We will also compare our results with a simple analytical model for reversibly associated polymers, suggesting a simple criteria to define the crossover point. The molecular weight distribution for rings will be analyzed as well. Our findings will be summarized in the Conclusions section.

2. Simulation Model

We model solutions of reversibly associated polymers using Monte Carlo simulations. In the framework of the bond-fluctuation model (BFM), we will consider self-avoiding walks on a 3-dimensional periodic cubic lattice of volume \( V = L^3 \). In most of the calculations, the lattice size is \( L = 64a \) (where \( a \) is the size of a cell) unless otherwise specified. To ensure that chains do not cross each other, there are two conditions to be satisfied:

First, the distance between nearest-neighbor monomers connected in one chain, i.e., bond length, \( l \), should be one of the following: \( l/a = 2, \sqrt{3}, \sqrt{6}, 3, \) or \( \sqrt{10} \). Second, the distance between any two monomers should not be smaller than the minimal bond length (which is \( 2a \) in the present case). This gives us a total of 108 possible nearest neighbors and their corresponding bond vectors. Because the minimum distance between monomers is \( l = 2a \), the maximum number of monomers that can be placed on the lattice is \( V/8 \), such that each monomer effectively occupies at least 8 lattice sites.

Our simulations start with placing \( \ldots \) oligomers (spacers) in lattice box. Each of these oligomers consists of \( N \) monomer units linked in a linear chain through permanent (covalent) bonds. The ends of a spacer are functionalized with one donor and one acceptor group, which are counted as part of \( N \) monomers of the spacer. The size of donor and acceptor groups in this study is assumed to be the same as the size of a regular monomer. A donor group is capable of forming a single hydrogen bond with an acceptor group. Each such association lowers the energy of the system by the association energy \( \Delta E_{\text{hb}} \).

For each MC run, we start with an ordered configuration of the system where all the oligomers are lined up in a regular way. Following the standard BFM procedure, the configuration of the system is updated by randomly choosing one monomer and attempting to move it to a randomly chosen nearest-neighboring site. The move is accepted if it does not violate both of the space constraints described above. A reversible bond between donor and acceptor is treated as a regular bond in all the moving attempts. If the selected monomer is not a donor, then the moving attempt is completed and next monomer is selected. If it is a donor, then besides the moving attempt, we update its reversible bonding configuration as following: After the moving attempt, the previously existed hydrogen bond (if any) is assumed to be broken. All nearest-neighbor sites (separated from the donor by one of the bonding distances described above) are checked for possible (free) acceptors for hydrogen bonding. To each available acceptor (if any) is assigned the probability \( C e^{\Delta E_{\text{hb}}} \) to form a hydrogen bond with the donor (where \( C = (1 + N_a e^{\Delta E_{\text{hb}}})^{-1} \) is the normalization constant and \( N_a \) is the number of acceptors at the bonding distance from the donor), and the probability not to form a hydrogen bond is \( C \). In the present simulation, we allow the distance between donor and acceptor group participating in hydrogen bonding to vary in the same range as that of a chemical bond and the probability to form a bond is assumed to be independent of this distance. This is a simplified picture which, however, is consistent with the overall generality of the model. For an acceptor, we choose not to update the hydrogen-bonding configuration after a moving attempt. The final equilibrium states of the systems will not be affected by this choice. We note that this procedure of updating of hydrogen bonding differs from that applied by Wittmer, Landau, and co-workers. In general, formation of hydrogen bonds can be a cooperative process; i.e., formation of one bond can change the local chain conformation to make it easy for other bonds to be formed, as it would likely be in the case of hydrogen-bonding arrays. Since we consider a single bond formation at the chain ends, there is no origin for such cooperativity, so this factor will not be counted in our procedure.

Hydrogen bonding is a directionally specific interaction, and in reality the possibility of its formation depends on mutual orientation of donor and acceptor groups. For absolutely flexible polymers, we omit this limitation, and the energies of all chemical and hydrogen bonds will be totally independent of the positions of the connected monomers. In such a case, each free acceptor has equal probability to form a hydrogen bond with the nearest-neighbor donor, so that the one to form the bond is simply chosen randomly (a similar assumption was made in ref 21). Besides flexible polymers, we will consider the following two cases to study the influence of rigidity imparted by hydrogen bonding and the rigidity imparted by spacer. In what follows, we will call semiflexible polymers those with flexible spacers and rigid end groups. In this case, there will be a penalty for bending a hydrogen bond (or changing bond angles that involve the hydrogen bond) but no penalty for regular bonds within a spacer segment. This case corresponds to experimentally relevant situations when modification of oligomers by bulky end groups for multiple hydrogen bonding will evidently require a particular orientation of the end groups for the association to occur. We also consider the case when the rigidity of spacers is the same as that of end groups, and there is a similar penalty for bending of both. We will refer to this case as rigid polymers below. Comparing flexible and semiflexible polymers will show the difference in association imparted by the rigidity of end group complexes, i.e., entropic loss for association. These two cases illustrate the situations when flexible spacers are terminated by a single association group (flexible poly-
mers) or by an array for multiple hydrogen bonding ( semiflexible polymers). In both cases, the energetic gain per hydrogen bond association may be the same, but entropic loss is very different. Comparing semiflexible and rigid polymers allows us to illuminate the influence of the rigidity of spacers. These two cases correspond to the situations when flexible and rigid spacers are terminated by similar end groups. In the first case, rigidity is imparted by end groups only ( semiflexible polymers), and in the latter one, the rigidity is produced by both the spacer and end group ( rigid polymers).

To account for the difference in rigidity, we modify our MC simulation procedure in the following way. If a spacer is flexible, then a moving attempt for monomers of the spacer is similar to the case of totally flexible chain described above. If a spacer is rigid, then in each moving attempt, after checking for the space limitations mentioned above, we calculate the total energy change caused by the monomer movement. Then, the success of the moving attempt is calculated through the Metropolis algorithm. The energy change is calculated by both the spacer and end group ( rigid polymers), and in the latter one, the rigidity is produced by end groups only ( semiflexible polymers). In both cases, the energetic gain per hydrogen bond association may be the same, but entropic loss is very different.

For averaging, we use only the configurations from the second half of the entire MC interval; i.e., for the 2nth MC time step, we average over the configurations in the MC time interval 2n–1 < t ≤ 2n. This helps us to reduce the influence of initial conditions on the final results.

3. Analytical Model

To describe analytically reversibly head-to-tail associated polymers, we apply the model that has been first suggested for associating networks and has been successfully applied by one of the authors for the description of competing hydrogen bonding in aqueous solutions of poly (ethylene oxide) (PEO). According to this model, the free energy ( density) for solutions of associating polymers can be written in the form

\[ F = F_{\text{ref}} + F_{\text{int}} + F_{\text{ass}} \]  

where \( F_{\text{ref}} \) is the reference free energy and \( F_{\text{int}} \) and \( F_{\text{ass}} \) are the interaction free energy and the association free energy, respectively.

The association free energy, \( F_{\text{ass}} \), is the part of the free energy due to PEO–water and water–water hydrogen bonding:

\[ F_{\text{int}} = \chi \Phi (1 - \Phi) \]  

where \( \Phi \) is the volume fraction of polymer, \( v \) is the reference volume (the volume of a cell in the Flory–Huggins model), and \( v_p \) is the volume per monomer unit of polymer.

The interaction free energy, \( F_{\text{int}} \), describes the (volume) interactions between monomers ( apart from hydrogen bonding):

\[ F_{\text{int}} = \frac{\Phi v}{Nv_p} \ln \left( \frac{\Phi}{N_{\text{le}}(1 - \Phi)} \right) + \left( 1 - \Phi \right) \ln \left( \frac{1 - \Phi}{e} \right) \]

where \( \Phi \) is the volume fraction of polymer, \( v \) is the reference volume (the volume of a cell in the Flory–Huggins model), and \( v_p \) is the volume per monomer unit of polymer.

The association free energy, \( F_{\text{ass}} \), is the part of the free energy due to PEO–water and water–water hydrogen bonding:

\[ F_{\text{ass}} = \frac{-v}{v} \ln Z_{\text{ass}} \]

where \( Z_{\text{ass}} \) is the following partition function

\[ Z_{\text{ass}} = P_{\text{comb}} W \exp \left( \frac{\Delta E_{\text{hb}}}{kT} n_{\text{hb}} \right) \]  

The combinatorial factor, \( P_{\text{comb}} \), describes the number of ways to form \( n_{\text{hb}} \) hydrogen bonds. The probability that donor and acceptor groups can be found in the vicinity of each other and with the correct orientations ( with respect to each other) for formation of hydrogen bonds, \( W \), is given by

\[ W = \left( \frac{v_{\text{hb}}}{V} \right)^{n_{\text{hb}}} \]  

where \( v_{\text{hb}} \) is the characteristic volume per hydrogen bond ( volume where the acceptor can be situated for a chosen donor). At the moment, we will describe \( W \) in a somewhat generalized way, whereas, later, we will assign its different parts to the particular physical effects.

Here we will not distinguish between the probabilities to find donor–acceptor pairs for chains and rings, whereas, in principle, these two do not have to be the
same. Taking this into account, we obtain for $P_{comb}$

$$P_{comb} = \left( \frac{1}{(1 - n_{hb})^2} \right)^{1/2} \frac{1}{n_{hb}}$$  \hspace{1cm} (8)

Combining all the factors together, we get the expression for total free energy. Minimizing the total free energy with respect to the average degree of hydrogen bonding, $p = n_{hb}/v$ (which is analogous to the extent of reaction in condensation polymerization theory), we get its equilibrium value:

$$p = \exp \left( \frac{\Delta F_{hb}}{kT} \right) (1 - p)^{2 - 1/v}$$  \hspace{1cm} (9)

where $\Delta F_{hb}/kT = \Delta E_{hb}/kT - \Delta S$ is the free energy change upon hydrogen bond formation and $\Delta S = -\ln(v/(v/v))$. For the case of flexible polymers, there is no entropic penalty for hydrogen bond formation and $\Delta S = 0$. For semiflexible and rigid polymers, there is an additional entropic penalty, which, in general, depends on the architectures of hydrogen-bonding arrays.

4. Results

We will start with a consideration of solutions of flexible polymers. For these chains, there is no preference in relative orientations of neighboring bonds, whether they are chemical bonds within spacers or hydrogen bonds.

**Degree of Association.** One of the important characteristics of the polymer system under consideration is the number of hydrogen bonds formed. Besides the overall number of hydrogen bonds, we can also distinguish between the ones belonging to topologically different species: linear chains and rings. For each MC time interval, we count and average separately the number of hydrogen bonds for different species: linear chains and rings. For each MC reaction in condensation polymerization theory, we get its equilibrium value.

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Table 1. Results of Monte Carlo Simulations<sup>a</sup> for Single Flexible Spacer (Oligomer) of Length N in the Absence of Association

<table>
<thead>
<tr>
<th>N</th>
<th>P&lt;sub&gt;0&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>R&lt;sub&gt;g&lt;/sub&gt; &lt;sup&gt;c&lt;/sup&gt;</th>
<th>p(N/V → 0)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.185 × 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>5.190</td>
<td>0.997</td>
</tr>
<tr>
<td>8</td>
<td>2.127 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>12.90</td>
<td>0.984</td>
</tr>
<tr>
<td>16</td>
<td>4.735 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>31.30</td>
<td>0.935</td>
</tr>
<tr>
<td>32</td>
<td>1.210 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>74.83</td>
<td>0.771</td>
</tr>
<tr>
<td>64</td>
<td>2.947 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>175.7</td>
<td>0.473</td>
</tr>
</tbody>
</table>

<sup>a</sup> We use L = 128a in these simulations. <sup>b</sup> P<sub>0</sub> is the probability that two ends of an oligomer are at a bonding distance from each other. <sup>c</sup> R<sub>g</sub> is square radii of gyration for the oligomer, in units of a<sup>2</sup>. <sup>d</sup> p(N/V → 0) is the limiting value of the degree of association calculated from eq 12 for the association energy ΔE<sub>hb</sub> = 8kT.

The values of P<sub>0</sub> and p(N/V → 0) (calculated for ΔE<sub>hb</sub> = 8kT) are shown in Table 1. The values of p(N/V → 0) calculated using eq 12 are also shown in Figure 2 as the short bars on the vertical axis. They are consistent with the extrapolations of the total degree of association, p, and the degree of association for rings f<sub>r</sub>, to the zero-concentration limit for the systems of different spacer lengths. We note that the product P<sub>0</sub>e<sup>ΔE<sub>hb</sub>/kT</sup> defines the fraction of rings compared to the free (unreacted) spacers in the zero-concentration limit. The longer the spacer or the weaker the hydrogen bonding strength, the larger the fraction of free spacers compared to rings.

Crossover Concentration for Ring-to-Chain Transition. As we discussed above, at low concentration, ring formation is dominating, whereas at high concentration hydrogen bonding with chain formation is favorable. The crossover concentration that divides these two different types of behavior can be defined in different ways. In classical CPT model, the ring-to-chain transition is a phase transition in the limit of full conversion p → 1 from the regime where there is no chains at all to the regime with a finite weight fraction of chains. For reversibly associated polymers, the full conversion limit is a relatively unique case (reached only for ΔE<sub>hb</sub> → ∞), and the definition of the transition requires some reconsideration. Despite the fact that for p < 1 the ring-to-chain transition is not a true phase transition, there are still regions of ring and chain dominance, and there must be some transition concentration (or area) signifying the boundary between these regimes. One way to locate this transition is to consider the point where the numbers of hydrogen bonds participating in ring and chain formation are the same, f<sub>r</sub>(c<sub>r</sub>) = f<sub>c</sub>(c<sub>c</sub>). This value is readily available from Figure 2, and we will call it the equal-fraction concentration, c<sub>f</sub>. The spacer length dependence of the equal-fraction concentration is shown in Figure 3. With an increase in spacer length, the equal-fraction concentration considerably decreases. It is reasonable to compare the observed dependence with the behavior of the overlap concentration c<sub>o</sub>, the concentration at which nonassociated spacers start touching each other. To evaluate c<sub>o</sub>, we need to know the radius of gyration R<sub>g</sub> for a single spacer. For this, we perform a direct simulation of a single spacer of length N (in the absence of end group association) and calculate the mean-square radius of gyration

R<sub>g</sub> = \frac{1}{2N} \sum_{i=1}^{N} (r<sub>i</sub> - r<sub>0</sub>)<sup>2</sup>  \tag{13}

where N is the number of monomers and r<sub>i</sub> is the position of the ith monomer on the spacer. The square radius of gyration values for the spacers of different lengths are listed in Table 1. We found in our simulations that R<sub>g</sub> scales as N<sup>-ν</sup>, ν ≈ 0.64, which is slightly larger than found for a polymer chain with excluded volume (a self-avoiding walk).29 This difference is due to relatively short spacer lengths considered here. For longer spacers (N > 50) we recover R<sub>g</sub> ∼ N<sup>0.59</sup>, as expected.

Correspondingly, the overlap concentrations c<sub>o</sub> are found as

\[
c<sub>o</sub> = \frac{3N}{4\pi R<sub>g</sub>} ∼ N^{1-3ν} \tag{14}
\]

and plotted in Figure 3 as well. As is shown, the spacer length dependence for c<sub>o</sub> ∼ N<sup>-1.2</sup> follows the same general trend as for c<sub>f</sub> ∼ N<sup>-0.94</sup> even though the former decreases slightly quicker than the latter. Besides the difference in the scaling laws, the absolute values of the overlap concentration c<sub>o</sub> is about 3 times larger than c<sub>f</sub>. The overlap concentration can be considered as the upper boundary for the ring-to-chain transition and can be consulted for a qualitative trend of spacer length.
decreasing spacer number density (start to deviate from the region of chain dominance, the total degrees of association for different spacer lengths converge to the same curve which is described in the framework of the simple analytical model (Figure 2). This implies that association behavior in this region is defined mainly by the number density of donor/acceptor groups and the association strength (eq 9). With a decrease in the spacer number density, the observed degrees of association start to deviate from the mean-field behavior, stabilizing at some level or going through some minimum prior to that. This is the consequence of preferential ring formation at low concentrations, which is not considered in the mean-field model. Therefore, the points where the observed degrees of association start to deviate from the universal curve described by the mean-field model are the crossover points below which ring contribution becomes noticeable. Numerically, to define this point, one can plot the product $pNv_N/([1-p]kT)$ as a function of spacer number density $1/v_N$. The point where the MC data start to increase with decreasing spacer number density (start to deviate from the universal curve) gives us the crossover number density. We followed this method and plot the corresponding crossover concentrations $c_{cr}$ in Figure 3 as a function of spacer length. For short spacer length, $c_{cr}$ coincides (within statistical error) with the equal-fraction concentration $c_s$. For longer spacers, the crossover concentration exceeds $c_s$. We note that for longer spacer length the total degree of association $p$ decreases, and the transition becomes less distinct. This is consistent with the fact that the true phase transition exists only for $p \to 1$, and the closer the degree of association to that point, the more distinct is the signature of the transition. As is seen from Figure 3, the scaling behavior of $c_{cr} \sim N^{-1}$ is very close to that for the overlap concentration $c^* \sim N^{-0.94}$, and similar to $c_s$, the absolute value of $c_{cr}$ is about 3 times smaller than $c^*$. Evidently, the transition from “mainly ring” to “mainly chain” behavior occurs prior to the overlap concentration. The reason is likely to be the gain in free energy due to chain formation which evidently overcomes the translational entropy penalty. We plan to analyze these issues in more detail in our future work by refining our analytical model and considering other parameters influencing the transition in our MC simulations. We note that the definition of the crossover concentration $c_{cr}$ is not as precise as that for the equal-fraction concentration $c_s$. However, it is likely to be more useful in analyzing experimental data because the overall degree of association $p$ can be determined in a variety of ways experimentally, including the spectroscopic signature of hydrogen-bonded end groups.

At concentrations larger than $c_{cr}$, the fraction of chains gradually increases, exceeding that for rings. Figure 4, plotted for spacer length $N = 8$, shows that above $c_{cr}$ the chain concentration increases nearly linearly at almost the same rate as the overall concentration, whereas the concentration of rings increases only slightly. This behavior is in agreement with the recent results for solutions of bifunctional 2-ureido-4(1H)pyrimidinone derivatives. Deconvolution of the $^1H$ NMR spectrum has allowed the determination of the concentration of small rings (dimers) and all other aggregates which have been taken to be linear chains. The experimental results demonstrated an evident saturation of the small-ring formation, signifying the beginning of the linear increase in chain concentration. Above some crossover concentration, the fraction of small rings does not change at all with concentration. Although the fraction of rings presented in Figure 4 increases at much slower rate with concentration increase than chain fraction, it still evidently changes with concentration. The reason for the difference in the results of computer simulations and experimental observations becomes clear from the inset of Figure 4. As is shown, the increase in overall ring concentration is due to formation of rings of higher molecular weights. The concentration of small rings remains nearly unchanged with the concentration increase, in agreement with experimental observations. Rings of larger size reach their optimal (saturation) level at larger polymer concentrations, thereby increasing the overall fraction of rings. The fraction of rings changes as a function of oligomer chain length and chain rigidity, as will be discussed below.

4.1 Influence of Rigidity on Association Behavior and Crossover Concentration. As we discussed above, the use of hydrogen-bonded arrays in end group modification of oligomers results in polymers of complex rigidity. The associating complexes impart additional rigidity to the chains whereas the oligomer spacer between them may remain rather flexible or it may have its own rigidity. In this section, we will analyze the influence of both types of rigidity on the association. We have performed a set of computer simulations for different polymer concentrations and spacer length for semiflexible and rigid polymers, and the results of these simulations are presented below in comparison with the results for the flexible polymers. Comparison of flexible and semiflexible polymers will illuminate the influence of the rigidity (entropy loss) associated with hydrogen-
difference between them is in the rigidity of the spacer, 
paring the semiflexible and rigid polymers, the main
length $p$ of association, $N$ for flexible, semiflexible, and rigid polymers of spacer
denise). Figure 5 shows the total degrees of association
bonded complex formation on the association behavior, whereas comparing semiflexible and rigid polymers will
how this flexibility of the spacer influences the association behavior.

**Association Behavior (Concentration Dependence).** Figure 5 shows the total degrees of association $p$ for flexible, semiflexible, and rigid polymers of spacer length $N = 8$ at the bonding energy $\Delta E_{hb} = 8kT$ as functions of concentration $c = N/V$. As is shown, the rigidity has a dramatic effect on the degree of association: the degree of association for semiflexible polymers is much smaller than that for flexible ones and very close to that for rigid polymers. Comparing to our analytical model, eqs 9 and 11, we can see that in the high concentration region the agreement is rather good. Compared to the value of the fitting parameter $\alpha \approx 16$ for flexible polymers mentioned above, for semiflexible and rigid polymers we get $\alpha \approx 0.3$. This difference in the fitting parameter value and the overall results is not surprising. For semiflexible polymers the spacer remains the same as for flexible polymers, but the end groups are more rigid (when associated); i.e., there is an entropic penalty for hydrogen bond formation. Any deviation from linearity of the (tangential) directors for the segments adjacent to donor and acceptor groups costs some energy for bond bending, as described above. This leads to the decrease in the degree of hydrogen bonding. As we mentioned above, the fitting parameter reflects the entropic penalty for hydrogen bond formation: $\alpha = 2e^{-\Delta S/V}$ or $\Delta S = 3.97$. Comparing the semiflexible and rigid polymers, the main difference between them is in the rigidity of the spacer, and this has little influence on the degree of association at reasonably high concentration. Because of this, it

**Table 2. Crossover ($c_r$), Equal-Fraction ($c_a$), and Overlap ($c^*$) Concentrations Related to Ring–Chain Transition in Various Types of Reversibly Associated Polymers with Spacer Length $N = 8$ and Association Energy $\Delta E_{hb} = 8kT$**

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>$c_r \times 10^3$</th>
<th>$c_a \times 10^4$</th>
<th>$c^* \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexible</td>
<td>86</td>
<td>88.8</td>
<td>412</td>
</tr>
<tr>
<td>Semiflexible</td>
<td>54</td>
<td>16.5</td>
<td>412</td>
</tr>
<tr>
<td>Rigid</td>
<td>0.85</td>
<td>0.039</td>
<td>124</td>
</tr>
</tbody>
</table>

* The concentrations are calculated in the units of inverse cell volume ($a^{-3}$).

![Figure 5](image55x542 to 295x744)

**Figure 5.** Monte Carlo simulation results for the total degree of association $p$, for flexible (C), semiflexible (O), and rigid (△) polymers as functions of concentration, $c = N/V$, for spacer length $N = 8$ and association energy $\Delta E_{hb} = 8kT$. Lines show the theoretical results calculated using eq 11. The values of fitting parameter $\alpha$ are shown next to the lines. Monte Carlo and theoretical results for flexible chains are the same as in Figure 2 (except here we plot them as a function of concentration, $N/V$, instead of number density, $\rho/N$). Arrows point to the critical concentrations, $c_r$, for flexible and semiflexible polymers. For rigid polymers it is out of the figure scale.

**Figure 6.** Monte Carlo simulation results for the total degree of association $p = f_r + f_c$ (open symbols with solid lines), ring fraction, $f_r$ (crossed symbols with dashed lines), and chain fraction, $f_c$ (black symbols with dotted lines), as functions of polymer concentration (in units of inverse cell volume $a^{-3}$) for flexible (C), semiflexible (O), and rigid (△) polymers (inset) of spacer length $N = 8$ and association energy $\Delta E_{hb} = 8kT$. Vertical dashed lines indicate the equal-fraction concentrations $c_a$. For concentrations lower than $5 \times 10^{-4}$ we use $L = 128a$ or $L = 256a$ for the simulation box size.

comes as no surprise that the observed degrees of association for semiflexible and rigid polymers are nearly the same at high polymer concentrations.

**Crossover Concentration.** While MC results show good agreement with the mean-field theory at high polymer concentration, they start to deviate at low concentration. As discussed above, this is due to the preferable formation of rings at low concentration and can be considered as a signature of the chain-to-ring transition. Following the same procedure as for flexible polymers ($c_{cr}^{flex} \approx 8.6 \times 10^{-3}$), we determined the crossover concentrations for semiflexible $c_{cr}^{semi} \approx 5.4 \times 10^{-3}$ and rigid polymers (with the spacer length $N = 8$ and $\Delta E_{hb} = 8kT$) $c_{cr}^{rigid} \approx 8.5 \times 10^{-3}$ as the points where the total degree of association starts to deviate from the general curve satisfying mean-field model. We note that to avoid statistical errors in dealing with low polymer concentrations ($c < 5 \times 10^{-4}$), the larger box sizes ($L = 128a$ or $L = 256a$) have been used. As we can see from Table 2, the difference in the crossover concentrations for the polymers of various stiffness is considerable. To understand the role of stiffness in ring formation, we plot in Figure 6 the fractions of hydrogen bonds in rings $f_r$ and chains $f_c$ for the three types of polymers.

**Table 2.**
and the concentration where fractions of hydrogen bonds in rings and chains coincide (\(c_{\text{cr}} = 1.65 \times 10^{-3}\)) is lower, too. We note that the entropic loss for hydrogen bond formation for semiflexible chains is larger; i.e., there are fewer possible orientations between donor and acceptor groups to form a hydrogen bond. We have estimated the probability (for \(\Delta E_{\text{hb}} = 0\)) to find end groups in a bonding distance from each other for semiflexible oligomers and found that the ratio between it and that for flexible oligomers, \(P_{0}^{\text{semi}}/P_{0}\), is in the range 0.015–0.025 for different chain lengths. Since the difference between the flexible and semiflexible polymers is in the rigidity imparted by end groups only, it becomes evident that the ratio \(P_{0}^{\text{semi}}/P_{0}\), simply corresponds to the entropic factor \(e^{-\Delta S}\), whose absolute value is consistent with the estimation obtained from Figure 5 (\(e^{-\Delta S} \approx 0.01875\)). This entropic restriction on ring formation for semiflexible polymers results in the smaller overall degree of association and smaller fraction of rings (in the zero concentration limit) compared to flexible polymers. A smaller fraction of rings implies that there are more available free spacers for semiflexible polymers, and the necessary level of free oligomers to start the polymerization process is achieved at lower polymer concentration; i.e., the crossover point lowers for the semiflexible polymers.

For rigid polymers shown in the inset of Figure 6, the fraction of rings is very small compared to flexible and semiflexible polymers. The reason for that is the entropic limitations for hydrogen bond formation (similar to semiflexible polymers) and the restrictions on ring closure imparted by the rigidity of the spacer. The latter is less important at the high concentration range where the degree of association is defined by the density of donor/acceptor groups and the overall degree of association is similar to semiflexible polymers. However, at low concentrations the rigidity of the spacer becomes the dominant factor in ring formation, as the probability to find end groups in a bonding distance decreases to \(2.5 \times 10^{-4}\) compared to \(2.11 \times 10^{-2}\) for flexible polymers. As a result, the crossover \((c_{\text{cr}}^{\text{rigid}} \approx 8.5 \times 10^{-5})\) and equal-fraction concentration \((c_{\text{eq}}^{\text{rigid}} \approx 3.93 \times 10^{-6})\) for the rigid polymers are much smaller than those for flexible and semiflexible ones (Table 2). For both semiflexible and rigid polymers the equal-fraction concentration is smaller than the crossover concentration (Table 2). This is similar to the behavior observed for longer spacers, for which the degree of association \(p\) is also considerably smaller than 1 at low concentration (Figure 3). Comparing the results for flexible, semiflexible, and rigid polymers presented in Table 2, one can conclude that the influence of the intrinsic rigidity of the spacer on the crossover (or equal-fraction) concentration is considerably stronger than that of the rigidity (entropic factor) imparted by end group association. The main reason for that is the fact that individual properties of the spacer define its capability to form a ring (especially small rings) and small ring formation is the dominant factor defining the association behavior at small concentrations and hence the ring-to-chain transition. Because of this, the ring-to-chain transition never has a universal character unless \(p \rightarrow 1\) (and \(\Delta E_{\text{hb}} \rightarrow \infty\)). We note that for both semiflexible and rigid polymers the fraction of rings in the ring-dominated concentration range is actually smaller than the fraction of free oligomers. Therefore, in the spirit of ref 30 one can say that the ring-to-chain transition in these cases is in fact the transition from the “free oligomers dominated” state to the “chain dominated” state.

As we can see in general, both the rigidity imparted by end group association and by the intrinsic spacer rigidity has considerable influence on the ring-to-chain transition. Whereas there has been no systematic experimental study of the influence of the spacer (or end group) rigidity, recent experimental results obtained for chemically different short spacers imply that there is a strong effect of the spacer quality on the crossover concentration. Fortunately, it is hard to make any further qualitative conclusions based on the data since besides the change in spacer rigidity, chemical modification of the spacers has also influenced the end group association enthalpy and entropy.

As we discussed above, the main difference in the association behavior of chains of different rigidity is in ring formation. To explore in more detail the ring formation, we considered the molecular weight distribution for rings at different concentrations. In Figure 7, we compare molecular weight distribution for rings formed from rigid and semiflexible (inset) polymers. The molecular weight distributions for rings formed by flexible polymers are qualitatively similar to those of semiflexible ones, and we do not present them here. For semiflexible polymers, the fraction of rings of increasing molecular weight steadily decreases. With increasing concentration, the fraction of rings of higher molecular weight increases (and that with smaller molecular weight decreases) and overall distribution becomes broader. The molecular weight distribution for rigid polymers follows the same trend, although the shape of distribution function is somewhat more complicated. The rings of size one (formed from one spacer) are not the most common as in the case of semiflexible polymers, unless the concentration is very low. The reason for that is that rigid spacer has to overcome a considerable penalty to form a loop, and because of that, rings of larger size are more favorable. For very low concentration, formation of any size other than single rings becomes unfavorable due to translational entropy effects.
Figure 8. Monte Carlo simulation results for the total degree of association $p$ as a function of spacer length $N$ for flexible (○), semiflexible (○), and rigid (△) polymers at concentration $c = N/V = 2^{-5}$ (in units of inverse cell volume $a^{-3}$) with an association energy $\Delta E_{hb} = 8kT$. Lines correspond to theoretical results calculated using eq 9. The values for the fitting parameter $\alpha$ shown next to the lines are the same as in Figure 5.

Figure 9. Fraction of hydrogen bonds in rings as a function of spacer length $N$ for flexible, semiflexible, and rigid polymers at fixed polymer concentration $c = N/V = 2^{-5}$ (in units of inverse cell volume $a^{-3}$) and association energy $\Delta E_{hb} = 8kT$, when we considered the concentration dependence (i.e., $\alpha = 16$ for flexible polymers and $\alpha = 0.3$ for semiflexible and rigid ones). This implies that the model describes correctly both concentration and the spacer length dependence, at least for reasonably high polymer concentrations.

4.2. Oligomer Length Dependence. We have also changed the spacer length at the fixed concentration $c = 2^{-5} \approx 0.031$ and energy of association $\Delta E_{hb} = 8kT$ and studied the influence of this factor on the degree of association and other relevant properties. Figure 8 shows the degrees of association for flexible, semiflexible, and rigid polymers as functions of spacer length $N$. As is shown for all cases, the degree of association decreases with an increase of spacer length. This effect is quite natural if we consider the fact that the same polymer concentration can be achieved by having smaller number of longer chains or larger number of shorter ones. Therefore, for longer chains, there are fewer donors and acceptors present in the system, and this leads to the decrease in the degree of association. Similar to the concentration dependence considered above, the degree of association of semiflexible polymers is considerably smaller than of flexible ones and very close to that of rigid polymers. The reason for this is the entropic penalty for hydrogen-bond formation (end group orientation), which is the same for rigid and semiflexible polymers and absent for the flexible polymers. The concentration considered is far from the crossover concentration for all semiflexible and rigid polymers, and as a result, the difference in the intrinsic spacer rigidity of semiflexible and rigid polymers does not show in Figure 8. As previously, we have compared the MC simulation results with predictions of analytical model (eqs 9 and 11). The values of the fitting parameter $\alpha$ for all three cases turn out to be the same as before.
with spacer length increase. The reason for this difference in the behavior of flexible and semiflexible (rigid) chains is in the crossover concentration. As we discussed above, \( c_{cr}^{\text{rigid}} < c_{cr}^{\text{semi}} < c_{cr}^{\text{flex}} \). Therefore, for semiflexible and rigid polymers, the considered concentration \( c \approx 0.031 \) is much higher than \( c_{cr} \), and chain formation dominates ring formation. A slight increase or decease of ring fraction with increase in \( N \) has little impact on chain fraction, and the fraction of hydrogen bonds in chains follows the same pattern as the total degree of association which decreases with an increase of \( N \). For flexible polymers, \( c \approx 0.031 \) is higher than the \( c_{cr} \) for short oligomers \( N = 4 \), comparable with the \( c_{cr} \) for spacers with \( N = 8 \), and somewhat larger than the \( c_{cr} \) for other spacer lengths considered. Below, at and just above the crossover concentration the fraction of chains increases at the expense of rings (Figure 2), and that is what we see in Figure 10. The decrease in ring fraction for flexible polymers (Figure 9) ensures the overall dependence of ring degree of association as shown in Figure 9. The chain molecular weight distribution is very similar for semiflexible and flexible chains (not shown here), except the average molecular weight of flexible chains formed from the same length spacers is higher for flexible chains, as expected on the basis of the higher overall degree of association.

5. Conclusions

Using MC simulations (self-avoiding walk in the framework of the bond-fluctuation model), we studied the association of spacers (oligomers) via a donor or acceptor group attached to their ends. Considering the experimentally relevant case of spacers of different intrinsic rigidity and different entropic loss (rigidity) imparted by end group association, we studied the following three cases: flexible polymers, semiflexible, and rigid polymers. Flexible polymers contain flexible spacers and exhibit no entropic penalty for end group association. Semiflexible polymers have flexible spacers but also have a rigidity (entropic penalty) enforced by end group association. Finally, rigid polymers have both the intrinsic rigidity of spacers and the rigidity enforced by end groups. To minimize the number of parameters, we choose the same rigidity parameter for the bending of chemical and hydrogen bonds. To be able to distinguish the influence of end group and spacer rigidity, we have also used the same end group rigidity for semiflexible and rigid polymers. Therefore, comparing flexible and semiflexible polymers, we were able to analyze the influence of the rigidity (entropic penalty) imparted by end group association, whereas comparing rigid and semiflexible polymers, we could study the influence of intrinsic rigidity of the spacer on association behavior. MC simulations have allowed us to obtain the total degree of association as well as the fraction of hydrogen bonds in rings and chains. We have studied the influence...
ence of concentration and spacer length on the average degree of association for flexible, semiflexible, and rigid polymers. We found that, with an increase in the initial spacer number density, the overall degree of association for flexible spacers of different lengths increases following the same pattern for concentrations above some crossover polymer fraction (Figure 2). In this region, the average degree of association is well-described by the proposed simple analytical model. Since the model accounts for the generic features of association based on the energy/entropy of association and number density of donor/acceptor groups, it works in the region of preferable chain formation governed by these generic parameters, and any deviation from it implies significant ring contribution (as the model neglects any additional entropic or enthalpic loss associated with the ring formation). Therefore, the concentration where the average degree of association starts to deviate from the universal curve described by the analytical model can be considered as a crossover concentration, \( c_{cr} \). The proposed definition of the ring-to-chain transition point for reversibly associated polymers (RAP) differs from that in classic condensation polymerization model, where the limit of full conversion is considered. The reason is that in RAP with a finite association energy the degree of association strongly changes with concentration, so there is no region where only rings are present and the transition occurs from the “ring-dominated” to “chain-dominated” region. Another way to define the ring-to-chain transition in RAPs is to consider the concentration \( c_r \) where the fractions of hydrogen bonds in chains and rings coincide. The definition of the crossover concentration for reversibly associated polymers \( c_{cr} \) is not as precise as that for the equal-fraction concentration \( c_r \). However, it is likely to be more useful in analyzing experimental data as the overall degree of association \( p \) can be determined in a variety of ways experimentally.

Comparing flexible, semiflexible, and rigid polymers above the corresponding crossover points, we found that the degree of association for semiflexible polymers coincides with rigid ones and is smaller than for flexible polymers (Figure 5). Evidently, the intrinsic rigidity of spacers is not a factor defining the association above the crossover concentration, but the entropic penalty (rigidity) for end group association does influence the degree of association. Therefore, we conclude that above a certain (crossover) concentration, \( c_{cr} \), the degree of association depends mainly on the total number density of donor/acceptor groups as well as energy/entropy of association and is not influenced by individual characteristic of spacers, such as their length or rigidity. In contrast, the crossover concentration \( c_r \) itself strongly depends on the individual characteristics of spacers and changes with spacer length or its rigidity. We found that for flexible polymers \( c_{cr} \) decreases as the spacer length increases (Figure 3), and it also decreases with an increase of either rigidity imparted by end group association or especially with the intrinsic rigidity of spacer (Figures 5 and 6 and Table 2). Thus, the crossover concentration \( c_{cr} \) for semiflexible polymers is several times smaller than that for flexible polymers, and it is nearly 2 orders of magnitude higher than that for rigid ones. It is not surprising that the crossover point depends on the individual characteristics of spacers since below \( c_{cr} \), ring formation dominates and the latter strongly depends on the possibility to find spacer ends in proximity of each other. For semiflexible and rigid polymers, the probability to find spacer ends within a bonding distance is smaller than for flexible polymers, and the total fraction of rings decreases. This is especially the case for rigid polymers, where single spacer rings are not favorable unless the concentration is extremely low. In general, we found that ring concentration slightly increases with concentration, even above the crossover concentration. This increase is due to an increase in the fraction of larger size rings (Figure 4).

Considering the spacer length dependence for flexible, semiflexible, and rigid polymers at fixed concentration, we found that in all cases the degree of association decreases with spacer length, \( N \). The degree of association for semiflexible and rigid polymers coincides with each other, and they are considerably smaller than that for flexible polymers (Figure 8). For semiflexible and rigid polymers, where the concentration was well above the crossover value for all spacer lengths considered, the decrease in the total degree of association arises from the decrease in the fraction of hydrogen bonds in rings, whereas the chain fraction first increases and then stabilizes with increasing \( N \). This change in the chain fraction is due to the vicinity of the crossover concentration for flexible polymers of spacer length \( N = 8 \). Therefore, we expect the spacer length dependence (at fixed concentration) to be different near and far from the crossover point.

We also studied molecular weight distributions for chains and rings and found that it mainly follows the JS model for flexible polymers. For semiflexible and rigid polymers, the JS model is not applicable due to its neglect of the ring strain, and we observed in accordance with the predictions of refs 15, 16, and 18 the shift in the maximum of ring distribution from one to some certain number, depending on spacer length and rigidity.

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References and Notes


(26) In the conventional approach,29 stiffness energy has the form

$$E_{st} = K (\cos \theta - \cos \theta_0)^2$$

with $\theta_0 \neq 0$. Since in the present conditions $\theta_0 = 0$, we use somewhat different form for $E_{st}$ to keep similar asymptotic behavior for small deviations.


(31) In our calculations we have distinguished between long chains wrapped around the periodic box and normal rings (by means of a special computer code calculating the sum of bond vectors along the chain). Calculations obtained using a larger box size ($L = 128a$) have confirmed this delineation.