Conditional Monte Carlo Sampling To Find Branching Architectures of Polymers from Radical Polymerizations with Transfer to Polymer

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ABSTRACT: A new algorithm is described that predicts branching architectures of polymers from radical polymerization with transfer to polymer and termination by disproportionation only in a continuously stirred tank reactor (CSTR). An existing full Monte Carlo (MC) method[1−3] generates architectures of molecules with varying overall numbers of monomer units (or chain length), *n*, and numbers of branch points, *N*. The new algorithm is a conditional MC method that generates molecules of given specific *n* and *N*. Both methods employ primary polymers as the linear building blocks of branched molecules. The time order of primary polymer coupling, being determined by the residence time distribution of primary polymers, turns out to be crucial for the architectures. A new and elegant recursive scheme rigorously calculates the primary polymer lengths in coupling order directly from the overall chain length/number of branch points distributions (CLD/DBD), $P(n,N)$, without explicitly dealing with primary polymer residence times. This proved assumptions made in earlier algorithms[4,5] to be erroneous. Primary polymer length and branching density distributions as well as radius of gyration contraction factors from full and conditional MC show excellent agreement. Statistically representative samples of architectures for given *n* and *N* are thus generated in a fast manner. As an application example, a comparison is made to the contraction factor as predicted by an old relation by Zimm and Stockmeyer.[6] It is concluded that the heterogeneous branching of the present chemical case leads to stronger contraction than the homogeneous branching case described by the latter authors.

Introduction

The prediction of branching architectures of polymers with long branches is of high importance since a number of interesting qualities are based on these characteristics. Rheological behavior of such polymer's melts[7,8] and the radius of gyration reduction[9] as compared to linear polymers with the same molecular weight are a few issues strongly associated with branching structure. One of the earliest modeling studies of this issue, performed by Zimm and Stockmeyer,[6] resulted in the famous relation named after these authors describing the size reduction just mentioned—a relation that even nowadays is still used in polymer characterization. More recently, a range of new rheological models have been proposed being directly based on branching architectures, like the "pom-pom" model from the group of McLeish.[7,8] Both radical polymerization of ethylene, where branching is caused by transfer to polymer and catalyzed ethylene polymerization, where long branches are formed by insertion of chains with unsaturated chain ends, have received considerable attention.[4,5,8−11] This study will be devoted to radical polymerization in a continuous stirred tank reactor (CSTR) with disproportionation as the only termination mechanism.

This problem of predicting branching architectures for this particular polymerization has been solved for the first time by Tobita,[1−3] using the concept of primary polymers and a sophisticated Monte Carlo sampling procedure, hereafter called full Monte Carlo sampling. However, this method does not allow to generate molecules of specified molecular weight and number of branch points. Hence, the fact that large molecules with many branch points have low concentrations in reality is reflected in full Monte Carlo sampling by an equally scarce production of such molecules. This hampers a fast statistical evaluation of the properties, like radius of gyration reduction, of just these most interesting large molecules, which despite their low concentration are decisive for the overall product properties. For this reason we have set ourselves to design a new procedure of predicting architectures, which does allow the generation of molecules of specified weight and number of branch points. This method, to be called conditional Monte Carlo sampling, will be described in this article, and its results will be compared to full MC.

The idea of a conditional MC method for a radical polymerization system has been addressed by us previously,[4,5,9] but the solutions proposed until now have always contained certain simplifying assumptions as regards the length (distribution) of primary polymers. Now, for the first time we were able to develop a rigorous solution, completely free of such simplifying assumptions. The crucial part of the new algorithm consists of a rigorous manner to find the proper growth order of primary polymers in a molecule and their specific different length distributions. By comparing the results of the conditional MC method to that of full MC, we were indeed able to confirm the exact agreement between the two.

Obviously, the conditional method requires the a priori knowledge of the concentration distribution of molecular weight and number of branch points. Several methods to find this 2-dimensional solution have been discussed by us in previous work[14] and will here be referred to. In this relative simple case of radical polymerization with transfer to polymer and disproportionation termination only, we have shown that a rigorous solution is easily attainable.

This article is structured as follows. First, we describe the conditional Monte Carlo algorithm: coupling procedure of primary polymers and how to find the primary polymer lengths in coupling order. Before going to the architectures, we introduce means to analyze the lengths and the branching density distributions on pps in coupling order. Then, we describe a statistical-mechanical method to find the radius of gyration (contraction factor) from the graph theoretical representation of architectures generated by either full or conditional MC.

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Table 1. Reaction and Population Balance Equations

Initiator dissociation	$I_2 \xrightarrow{k_d} 2I$
Initiation	$I + M \xrightarrow{k_i} R_{1,0}$
Propagation	$R_{n,N} + M \xrightarrow{k_p} R_{n+1,N}$
Termination by disproportionation	$R_{n,N} + R_{k,K} \xrightarrow{k_{td}} P_{n,N} + P_{k,K}$
Transfer to polymer	$R_{n,N} + P_{k,K} \xrightarrow{k_{tp}m} P_{n,N} + R_{k,K+1}$
Population balance living chains: $\frac{dR_{n,N}}{dt} = k_p M(-R_{n,N} + R_{n-1,N}) - k_{td}\lambda_0 R_{n,N} + k_{tp}(-\mu_1 R_{n,N} + \lambda_0 n P_{n,N-1}) - \frac{1}{\tau} R_{n,N}$	
Population balance dead chains: $\frac{dP_{n,N}}{dt} = k_{td}\lambda_0 R_{n,N} + k_{tp}(\mu_1 R_{n,N} - \lambda_0 n P_{n,N}) - \frac{1}{\tau} P_{n,N}$	
n, k chain length; N, K number of branch points per chain	

Finally, we present results concerning pp length and density distributions and contraction factors from both algorithms and draw conclusions.

Architectures Generation by Conditional Monte Carlo Sampling

The conditional Monte Carlo algorithm is based on the chemistry of the radical polymerization system as briefly summarized in the reaction and population balance equations of Table 1. The solution of the balance equations, for instance by the direct solution method as described in previous work,[14] is supposed to have provided us with the two-dimensional chain length/number of branch points (degree of branching) distribution (CLD/DBD), $P(n,N)$. This then is the starting point for the conditional MC algorithm.

Coupling of Primary Polymers. Like the full MC procedure by Tobita,[1−3] our algorithm employs linear primary polymers (pp, plural pps) as the branched molecules constituting elements. A molecule with n monomer units and N branch points hence consists of $N + 1$ primary polymer with a total length of n. The length distribution of these $N + 1$ pps, $n_1...n_{N+1}$ ($n = \sum_{i=1}^{N+1} n_i$), in combination with the prescribed coupling order, from 1 to $N + 1$, will be addressed in the next section. Here, first we discuss the coupling procedure as depicted in Figure 1. In the first branching "round" pp2 is attached to pp1 on an arbitrary unit along its length, so pp1 always receives at least one branch point. In the second round pp3 is attached to the structure formed by pps 1 and 2. We assume that the probability of a pp of receiving a branch point is proportional to its length.

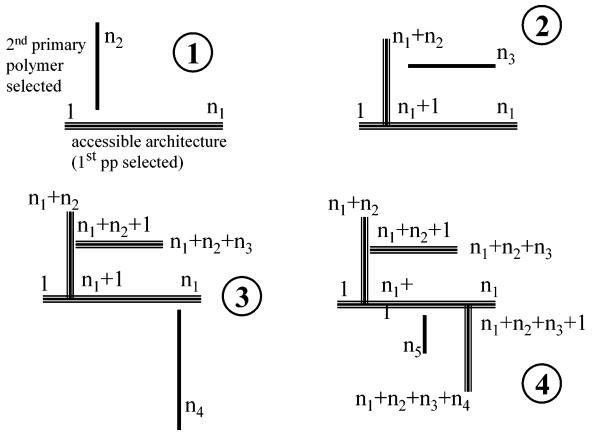

Figure 1. Conditional Monte Carlo sampling procedure.

Table 2. Kinetic and Simulation Data

	symbol	value	unity
dissociation	k_d	0.5	s^{-1}
propagation	k_p	5000	$m^3\,kmol^{-1}\,s^{-1}$
disproportionation termination	k_{td}	10^7	$m^3\,kmol^{-1}\,s^{-1}$
transfer to polymer	k_{tp}	1.5	$m^3\,kmol^{-1}\,s^{-1}$
average residence time CSTR	τ	30	s
feed monomer concentration	M_f	16.75	kmol m^{-3}
feed initiator concentration	$I_{2,f}$	$5\ 10^{-3}$	kmol m^{-3}
monomer concentration	M	9.107	kmol m^{-3}
macroradical concentration	λ_0	5.588×10^{-6}	kmol m^{-3}
incorporated monomer concentration	μ_1	7.643	kmol m^{-3}

Table 3. Full Monte Carlo Simulation Parameters

MC simulation parameter	formula	value
number average chain length	$\bar{n}$ (eq 3)	677
average branching density	$\bar{\rho} = k_{tp}\mu_1\tau$	2.51×10^{-4}
branching probability	$P_b = k_{tp}\lambda_0/(k_{tp} + k_{td})\lambda_0 + k_{tp}\mu_1$	0.170

Thus, the probability that pp1 also gets a branch point in the second round equals $n_1/(n_1 + n_2)$. The attachment point is determined by random sampling of a number of the range $[1...n_1 + n_2]$. Obviously, pp2 does not take part in the first round, only in the second, while pp1 takes part in both. The algorithm repeats itself by N rounds in total, so the last pp, number $N + 1$, does not receive any branch point. Evidently, the order number assigned to a pp is strongly determining its probability of receiving branch points. The order number of a pp turns out to be dependent on its length, which will be discussed in the next section. The result of this algorithm is one possible architecture given this set of pp lengths.

Finding pp Lengths and Coupling Order. The length distribution of all primary polymers in a CSTR at steady state has been shown[1−3] to obey a Flory distribution

$$p_F(n) = (1 - 1/\bar{n})^{(n-1)}/\bar{n} \tag{1}$$

around the average pp length $\bar{n}$. This average can be derived by applying a moment's approach to the population balance of (living) primary polymers based on the kinetic conditions given in Tables 1−3:

$$\frac{dR_n}{dt} = k_p MI\delta(n-1) + k_p M(-R_n + R_{n-1}) - k_{td}\lambda_0 R_n - k_{tp}\mu_1 R_n - \frac{1}{\tau}R_n \tag{2}$$

Multiplying this by n and subsequent summation over n, while realizing that $\bar{n} = \sum_{n=1}^{\infty} nR_n / \sum_{n=1}^{\infty} R_n$, we find

$$\bar{n} = \frac{k_p MI + k_{tp}\mu_1\lambda_0 + k_p M\lambda_0}{\lambda_0(k_{tp}\mu_1 + k_{td}\lambda_0 + 1/\tau)} \tag{3}$$

In the full Monte Carlo procedure primary polymer lengths are sampled from this distribution. Their residence time is sampled from a residence time distribution. No further condition is imposed on pp coupling order and length, as they are resulting from the procedure. In the conditional Monte Carlo procedure, we have to ensure that the prespecified number of $N + 1$ primary polymers of the molecule add up to the specified total length of n. Furthermore, the issue of coupling order—rather than

specifying residence times—has to be addressed as shown in the description of the architectures synthesis method. In our earliest work on this topic[4,5] we assumed all pps to have a Flory distribution around the same average per molecule. Later on,[9] we have argued that pps coming earlier in coupling order are longer on average. At present, we found a rigorous, but elegant, solution to the pp length/coupling order problem.

The starting point for the argument following is the overall chain length/number of branch points concentration distribution $P(n,N)$, which we calculated from the kinetic conditions and population balances as listed in Tables 1−3. In previous work[14] we have explained how a rigorous solution of this two-dimensional distribution $P(n,N)$ is generated for the case of a CSTR at steady state. Now the main fact underlying our argument is the following statement: under the kinetic conditions specified earlier, molecules of length n and $N + 1$ branch points are exclusively created from shorter molecules with N branch points by a transfer to polymer step and a consecutive growth step. In the first step from a dead chain of n,N a living chain of the same length and $N + 1$ branch points (zero arm length at the Nth branch point) is created with probability p_1:

$$p_1(n,N+1) \sim nP(n,N) \tag{4}$$

In p_1 it is multiplied by n since any of the n units of the molecule can undergo this step. The second step is growth of a new arm by propagation at the Nth branch point to a certain length m until termination. The probability, p_2, of creating an arm length m obeys the Flory distribution (the same as the one sampled from in the full MC algorithm), eq 1:

$$p_2(m) \sim p_F(m) \tag{5}$$

The probability of thus creating a dead molecule of total length $n + m$ and $N + 1$ branches is simply the product of these two probabilities, since length m is independent of length n. Hence, for the conditional probability that a dead chain is created from a dead chain of n,N and subsequent growth of an arm of length m we can write

$$p(n+m,N+1|n,N) \sim nP(n,N)\, p_F(m) \tag{6}$$

Now, following this argument, we state that a molecule of n,N can be created from *any* molecule with $N - 1$ branch points of (shorter) length $n - m$ undergoing transfer to polymer and subsequent growth of an arm with the complementary length m. According to eq 6, the probability of the various combinations is proportional to $(n - m)P(n - m,N - 1)p_F(m)$. Hence, given the length n of the original molecule with N branch points, the probability distribution of arm length m, which is the Nth primary polymer in the coupling order, $q(n,m,N)$, obeys the following probability distribution function (PDF):

$$q(n,m,N) = \frac{p_F(m)P(n-m,N-1)(n-m)}{\sum_{m=1}^{n-1} p_F(m)P(n-m,N-1)(n-m)} \tag{7}$$

In the algorithm a length m is sampled from the PDF $q(n,m,N)$, which then specifies both the lengths of the Nth pp and the structure with $N - 1$ branch points, $n' = n - m$. The algorithm further repeats itself by realizing that this particular structure of length n' and $N - 1$ branch points has grown from a molecule with $N - 2$ branch points and the $(N - 1)$th pp. This proceeds until $N - 1 = 0$, which last turn produces the lengths of the first and the second primary polymer. Thus, a collection of lengths of all primary polymers is obtained in growth order. It is precisely *this* set of pp lengths in *this* order that we employ as the pps in proper order in the coupling procedure described before. This then completes the whole conditional MC architectures synthesis procedure.

The argument given above forms the heart of our new conditional MC method. In its present form it applies to a CSTR at steady state with transfer to polymer and disproportionation termination. It is, however, extendable to other reactor systems and more elaborate kinetics. In the case of a (semi)batch reactor both the 2D-distribution $P(n,N)$ and the Flory distribution $p_F(m)$ change with time and so does the PDF, eq 7. Hence, then sampling should take place from a varying PDF. In the case of termination by recombination molecules of n,N are created by transfer to polymer from molecules of $n-m,N-1$ *and* by recombination of pairs of (smaller) living polymers of $n-m,N-M$ and m,M, respectively. The algorithm then at each step should decide whether a last event was a transfer or recombination step, while in case of the latter the characteristics of the two smaller molecules have to be sampled.

Analyzing pp Length and Branching Density Distributions

Obviously, we want to compare the architectures resulting from the new conditional MC procedure to those from the established full MC algorithm. However, the two methods can already be compared without actually addressing architectures in an explicit manner. In this part we focus on pp length and branching (density) in relation to their coupling order. Extracting such information from the full MC method can only proceed by generating statistically representative samples of molecules. Coupling order is found by recording the residence times of the primary polymers and ranking their lengths accordingly. Note on this point an interesting difference between the full and conditional MC methods: the latter does not explicitly deal with residence times, while the former does so. The underlying idea of the conditional MC method (in fact its coupling procedure) is that once their coupling order is known the pp residence times are of no importance anymore. On the other hand, the results of the conditional MC method most closely related to residence time, being the branching densities on pps, should be consistent with those of the full MC algorithm. This then motivates to make an explicit comparison of branching densities from the two methods, next to directly comparing coupling orders.

In the first part of this section we analzye and compare pp lengths and in the second part branching densities. Most ideally, comparisons should be made of samples of molecular architectures with identical total length, n, and number of branches, N. However, finding statistically representative samples of exactly the specified n and N by full MC sampling is practically impossible at larger values of. Hence, we decided to perform comparisons for samples of specified N and lengths distributed according to the concentration distribution of molecules with N branch points. Here, we choose the weight fraction distribution $P(n,N)n$ since the full MC method also generates weight fraction distributed samples of molecules.

Length Distributions of pps. We employ the PDF eq 7 to find pp lengths to find the length distributions per pp for a statistical representative number of molecules of given N and n sampled from $P(n,N)n$, from which then the average length of pps can be calculated. Although generation of such samples in this way proceeds in a straightforward and fast manner, it is

also possible to infer pp length distributions from overall concentration distributions for branched molecules, $P(n,N)$, and single pps, $p_F(n)$, in a direct way, using a recursive procedure. We realize that the PDF of eq 7 determines (a) the length distribution of the $(N+1)$th pp added for given original total length n, $q(n,m,N)$, and (b) the distribution for the complementary length $n-m$ of the existing molecule with $N-1$ branch points, $Q(n,n-m,N-1)$. We see that such distributions may be constructed for each length n of the original molecule. Overall length distributions of added arms and existing molecules for a whole distribution of original chain lengths as given by $P(n,N)$ then follow by multiplying the fraction distributions for each n with $P(n,N)$ and taking the summation over n. In formula, for the added arms

$$q(m,N) = \sum_{n=1}^{\infty} P(n,N)\, q(n,m,N) \tag{8}$$

and for the existing molecules with N primary polymers

$$Q(n-m,N-1) = \sum_{n=1}^{\infty} P(n,N)\, q(n,m,N) \tag{9}$$

It should be noticed that $q(m,N)$ differs from the Flory distribution, while $Q(n-m,N-1)$ differs from the original concentration distribution $P(n,N-1)$. The $Q(n-m,N-1)$ really only describes the distribution of the added lengths of the first N pps in molecules counting $N+1$ pps in total. The length distributions of the pps earlier in coupling order, N_S, and the parts of the molecule comprising the first N_S-1 pps are further recursively inferred from the previously obtained $Q(m,N_S)$ and recursion relations similar to eqs 7−9:

$$q(n,m,N_S) = \frac{p_F(m)P(n-m,N_S-1)(n-m)}{\sum_{m=1}^{n-1} p_F(m)P(n-m,N_S-1)(n-m)} \tag{7a}$$

$$q(m,N_S) = \sum_{n=1}^{\infty} Q(n,N_S)\, q(n,m,N_S) \tag{8a}$$

$$Q(n-m,N_S-1) = \sum_{n=1}^{\infty} Q(n,N_S)\, q(n,m,N_S) \tag{9a}$$

The procedure starts with $N_S = N$ and $Q(n-m,N_S) = P(n-m,N)$, while it ends after $Q(n-m,1)$ has been computed from eq 9a. This enables to directly and rigorously compute pp length distributions from the given overall concentration distribution $P(n,N)$ and the single pp Flory distribution.

The pp lengths distributions thus obtained can be used to compare with those extracted from the full MC simulations, as will be shown in the Results section. However, we must realize that for one molecule the length distribution of one pp in the coupling order depends on the lengths of all other (N) pps in the molecule. This implies, for instance, that arbitrary sampling lengths from the $N+1$ distributions as derived above does not return the original overall length distribution $P(n,N)$. It also means that we cannot simply infer branching density distributions on pps from the generated length distributions. Instead, these have to be calculated from the sets of pp lengths as sampled for each molecule individually. How to perform this will be the topic of the next paragraph.

Branching Density on pps. Here, it is our purpose to show how part of the conditional MC algorithm is employed to directly analyze the probability of pps to receive branch points, without actually making architectures. The direct branching analysis is based on the coupling algorithm explained above, and it proceeds as follows. We denote the probability of pp i of getting one branch point in the jth sampling round by $r(i,j,1)$. For each individual molecule with pp set n_i, obtained by the sampling procedure described before, the probability per pp is given by

$$r(i,j,1) = n_i/\sum_{i=1}^{j} n_i; \quad j = i{:}N-1 \tag{10}$$

The probability that a pp will not get a branch point simply equals

$$r(i,j,0) = 1 - r(i,j,1) \tag{11}$$

Note here that pp i only participates in rounds $j = i{:}\ N-1$. The probability of pp i of having received k branch points after the rounds j it has been participating in is developed in a recursive manner

$$R(i,j,k) = \sum_{m=0}^{k-l} R(i,j-1,l)\, r(i,j,m); \quad l = k-1{:}k \tag{12}$$

starting with

$$R(i,i,k) = r(i,i,k); \quad k = 0,1 \tag{13}$$

Equation 12 expresses the fact that k branch points on a pp after j rounds can be realized by two different situations. One is that this pp has already k branch points after $j-1$ rounds in combination with the fact that it receives zero in the jth round. The other is that after $j-1$ it has $k-1$ branch points, while one is added in round j. Condition eq 13 again originates from the fact that pp i starts participating in round i. The number of branch points probability distribution $R(i,k)$ finally follows as the result of eq 12 after all rounds realized: $R(i,N-1,k)$. Given the length of each pp from $R(i,k)$ the distribution of branching density (or probability of a monomer unit in a pp of being a branch point), $p_i(\rho) = R(i,k)k/n_i$, can be found.

The average branching density or probability of a monomer unit in a pp of being a branch point, $\bar{\rho}_i$, can be calculated from $R(i,k)$ and the pp lengths. It can also directly be obtained by realizing that the subsequent rounds add to the average in the following evident way. For instance, for pp1 we have $\bar{\rho}_1 = 1/n_1 + 1/(n_1+n_2) + \ldots + 1/(n_1+\ldots+n_7)$, for pp2, $\bar{\rho}_2 = 1/(n_1+n_2) + \ldots + 1/(n_1+\ldots+n_7)$, etc., in general:

$$\bar{\rho}_i = \sum_{j=i}^{N-1} \left(\frac{1}{\sum_{k=1}^{j} n_k} \right) \tag{14}$$

Figure 2 shows an example of branch point distributions on various pps in a molecule of specified pp lengths. The inset shows the average of the branching densities of the same case.

Determination of Radius of Gyration Contraction. A molecular property directly related to branching architecture is the radius of gyration, especially its contraction as a consequence of branchedness. Here, we will only deal with the square radius of gyration $\langle s^2 \rangle$ as expressed in monomeric size units. It is calculated using a statistical-mechanical model developed by

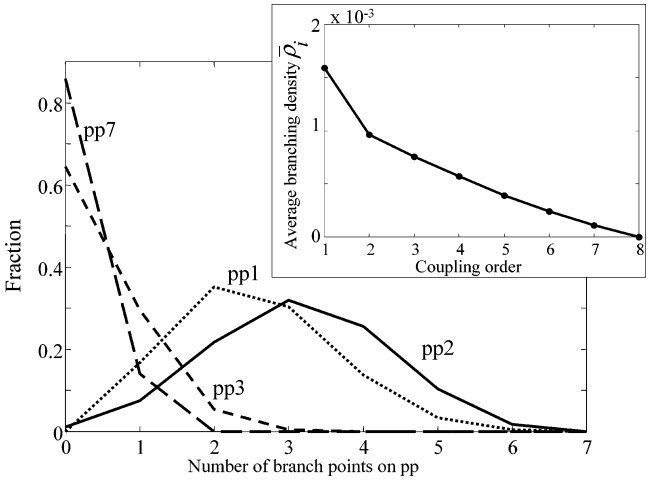

Figure 2. Number of branch points distributions on primary polymers and average branching densities for a molecule of total length $n = 9003$ and $N = 7$ branch points. Lengths of the pps are, in coupling order, $[n_1...n_8] = [1589, 3233, 555, 189, 1137, 992, 1267, 41]$.

Eichinger.[15] This model takes as input the architecture represented in terms of graph theory, the Kirchhoff matrix, **K**, which is derived from the incidence matrix, **C**:[4]

$$\langle s^2 \rangle = n^{-1} \mathrm{Tr}(\Lambda_{n-1}{}^{-1}) \tag{15}$$

Here, n is the number of monomer units and $\mathrm{Tr}(\Lambda_{n-1}{}^{-1})$ denotes the trace of $\Lambda_{n-1}{}^{-1}$ being the matrix with $n - 1$ reciprocals of the eigenvalues of the Kirchhoff matrix **K**. The full $n \times n$ sized matrix **K** is calculated from

$$\mathbf{K} = \mathbf{C}\boldsymbol{\nu}\mathbf{C}^{\mathrm{T}} \tag{16}$$

where $\mathbf{C}^{\mathrm{T}}$ is the transpose of **C** (size; $(n) \times (n - 1)$) and $\boldsymbol{\nu}$ is a vector of length $(n - 1)$ related to the size of monomer units. In previous work[4] we discussed various ways of "coarse graining" to reduce the computational effort to find the smallest eigenvalues of matrices having sizes of over 1 million. We here apply intermediate levels of coarse graining, varying from weak for small N to strong for large N, where it turns out to be less critical.[5] The contraction factor, g, finally is found as the ratio between the radii of the branched molecule and that of a linear molecule with the same number of monomer units, the latter being calculated under the same levels of coarse graining:

$$g = \langle s^2 \rangle_{\mathrm{br}} / \langle s^2 \rangle_{\mathrm{lin}} \tag{17}$$

It is customary to analyze branched molecules in terms of combs or Cayley trees. What we observe is that the smallest radii are associated with the most Cayley treelike molecules and the largest radii for the most comblike ones. In the Results section we will compare contraction factors for samples of molecules from the full and conditional Monte Carlo methods. Furthermore, we compare our results to those predicted by an expression derived already 50 years ago by Zimm and Stockmeyer,[6] which is however still employed when dealing with branchedness in size exclusion chromatography. The expression reads

$$g(N) = \frac{\langle s^2 \rangle_{\mathrm{br}}}{\langle s^2 \rangle_{\mathrm{l}}} = \frac{3}{(f-1)N+3}\left[1 + \sum_{j=1}^{N}(f-1)^j \prod_{m=0}^{N} \left\{\frac{N-m}{(f-1)N+2-m}\right\}\right] \tag{18}$$

where N is the number of branch points and f is the functionality of the branched polymer, here $f = 3$.

Results

Reaction equations, population balances, and kinetic and simulation data for both full and conditional MC algorithms are listed in Tables 1−3. All results have been obtained using this data set. The essential part of the full MC algorithm was implemented according to the original description published by Tobita.[1−3] However, to analyze the characteristics of the individual primary polymers in coupling order and to obtain the explicit graph theoretical description of the generated molecules, we had to add new features to the algorithm. We also observed that a considerable amount of extra computation time was associated with these extra features.

Averages and distributions of pp lengths for $N = 7$ and 30 branch points are shown in Figures 3 and 4, both from full MC and recursive PDF approach (eqs 7a−9a). Agreement for the case of $N = 7$ is seen to be almost perfect—the large full MC sample (29 000 molecules) features practically no scatter. Much more scatter is seen in the $N = 30$ sample of only 127 molecules. These differences in sample size are directly explainable from the weight fraction distribution of all molecules over number of branch points, in which proportion full MC generates molecules. Both the $N = 7$ and the $N = 30$ samples are taken from an overall population of more than 6 million, with weight fractions 4.76×10^{-3} for $N = 7$ and 2.43×10^{-5} for $N = 30$. This took the algorithm, including the above-mentioned extra features, around 1 week on a 1.5 GHz PC. Note that realizing equally little scatter in the $N = 30$ case as in the $N = 7$ case would require a total sample of more than 1 billion molecules, the time equivalent of several years. Obviously, the rigorous solutions from the recursive PDF approach do not suffer from a limited sample size. As regards primary polymer lengths these results convince us that the full MC and our recursive PDF approach describe the same chemical system.

Having a closer look at the pp length results, we see primary polymer lengths decreasing with coupling order number, but especially the first pps being considerably longer. As regards distribution shape, we observe that again pp1 deviates most strongly: it turns out to be much narrower, with a polydispersity as low as 1.37 (both $N = 7$ and $N = 30$). Length distributions of pps later in coupling order widen up to Flory distributions (around decreasing averages). This then clearly disproves the assumption of all Flory distributions around the same average that was the basis of our very first approach.[12,13]

Results with respect to branching density are shown in Figures 5 and 6, for the case of $N = 7$ only. The average of the PDF approach is calculated with eq 13, while the recursion eqs 9−14 are employed to find the distributions. This time, the PDF approach does rely on a sampling procedure because of the interdependency of pp lengths, but this is a fast sampling and does not require the construction of the full architectures. The sample of 500 000 took around 1 h computation time on a 1.5 GHz PC. The agreement between the average branching densities from full MC and PDF approach are again excellent. Density distributions from full MC (29 000 molecules) still show

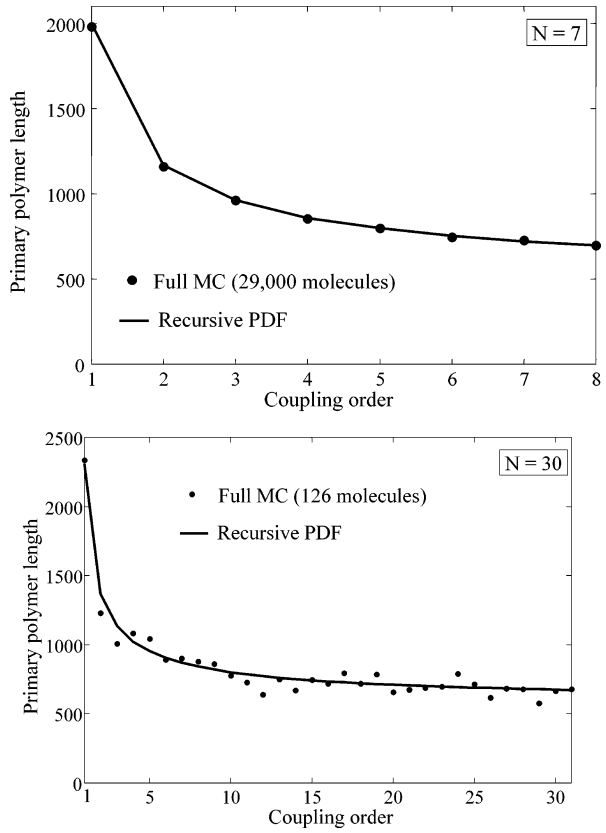

Figure 3. Average primary polymer lengths in coupling order for $N = 7$ and 30 branch points and overall molecular chain lengths n distributed according to the CLD/DBD, $P(n,N)$. Results from full Monte Carlo and recursive PDF (eqs 7a−9a) are compared.

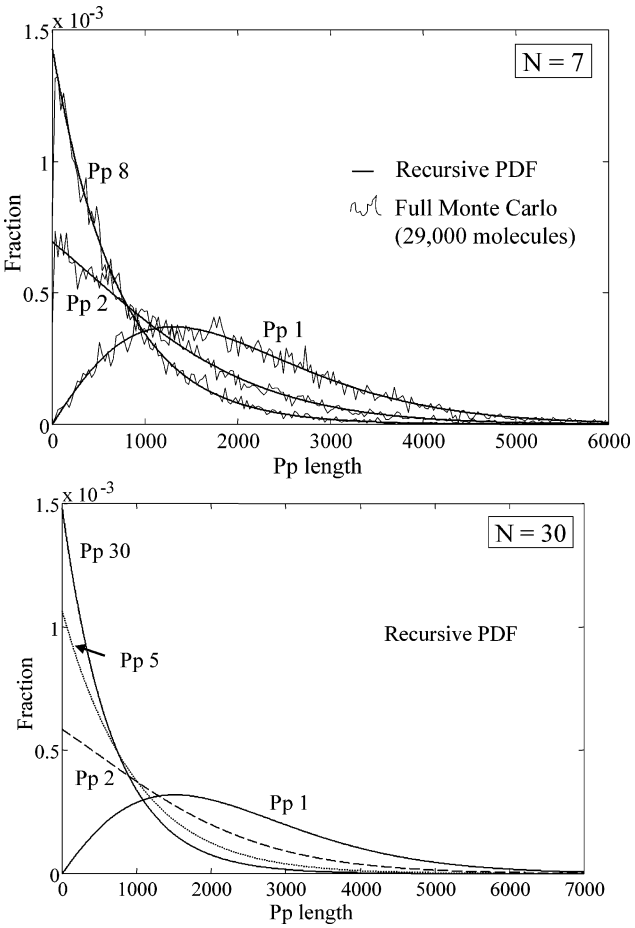

Figure 4. Distributions of primary polymer lengths in coupling order for $N = 7$ and 30 branch points and overall molecular chain lengths n distributed according to the CLD/DBD, $P(n,N)$. Results from full Monte Carlo (only $N = 7$) and recursive PDF (eqs 7a−9a).

considerable scatter, while the 500 000 molecules of the PDF approach lead to almost smooth distributions. However, agreement is satisfactory on this point. Note besides that these distributions are of a peculiar shape. They exclusively represent pps with branch points. It should be realized, however, that one or more pps in a molecule except pp1 may have zero branch points, which leads to a peak at $\rho = 0$ in the distribution graph. Thus, in Figure 6 (see caption) we see that for $N = 7$ a fraction 0.6 of pps of coupling order 4 has zero branch points and a fraction 0.9 for coupling order 7. As regards these fractions, excellent agreement is observed between full MC and PDF approach.

At this point we draw the conclusion that concerning pp lengths and branching densities the difference between the results from full MC and PDF approach can completely be attributed to the limited sample size of the former. The chemistry underlying both approaches appear, however, to be fully equivalent. Note that we state this even before comparing full architectures from both methods, but expect them to also be identical.

Architectures are compared on the basis of radius of gyration contraction factor (eq 17). Results are shown in Figures 7 and 8 for $N = 7$ and $N = 30$ branch points. The sample average contraction factor of 13 600 molecules from full MC for $N = 7$ is calculated to be 0.6510 vs 0.6514 for the 700 000 molecules from conditional MC. The scatter in the full MC contraction factor fraction distribution is significantly stronger than that in the distribution resulting from conditional MC, but globally the shapes are identical. For $N = 30$ branch points (Figure 8) samples from both techniques are smaller and hence possess more scatter. Both averages (full MC: 0.341; conditional MC: 0.336) and distributions of the contraction factor from the two

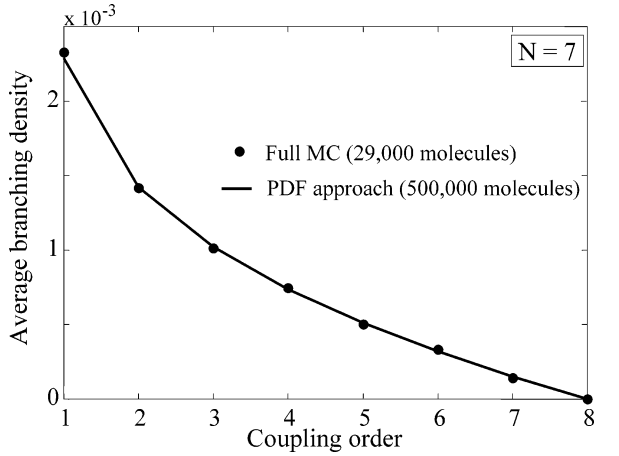

Figure 5. Average branching density (or branching probability of a monomer unit) of primary polymers in coupling order for $N = 7$ branch points and overall molecular chain lengths n distributed according to the CLD/DBD, $P(n,N)$. Comparison between full MC and PDF approach (eq 14).

techniques are still found to be very close. Note that generating the full MC sample and computing its architectures and contraction factors took a few days on a 1.5 GHz PC, whereas creating the samples with conditional MC took several hours. These results now lead us to the conclusion that the algorithms generate identical populations of architectures.

Finally, to illustrate the practical importance of knowing architectures and computing contraction factors, we compare

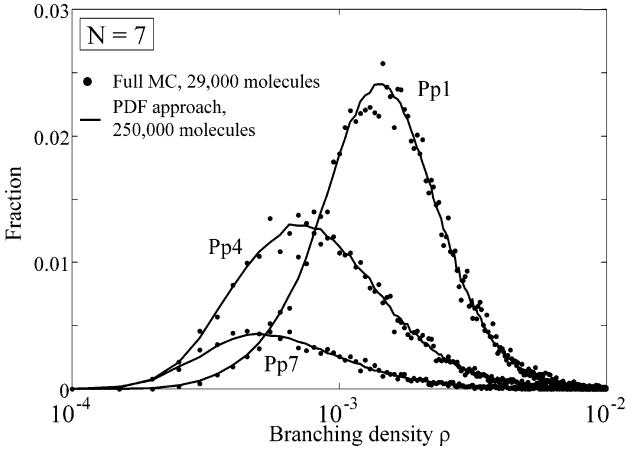

Figure 6. Distributions of branching density of primary polymers in coupling order for $N = 7$ branch points and overall molecular chain lengths n distributed according to the CLD/DBD, $P(n,N)$. Comparison between full MC and PDF approach (eqs 10−13). Peaks at $\rho = 0$ (obviously) not shown, representing fractions of pps with zero branch points: pp1: 0; pp4: 0.601 (full MC), 0.599 (PDF); pp7: 0.900 (full MC), 0.902 (PDF).

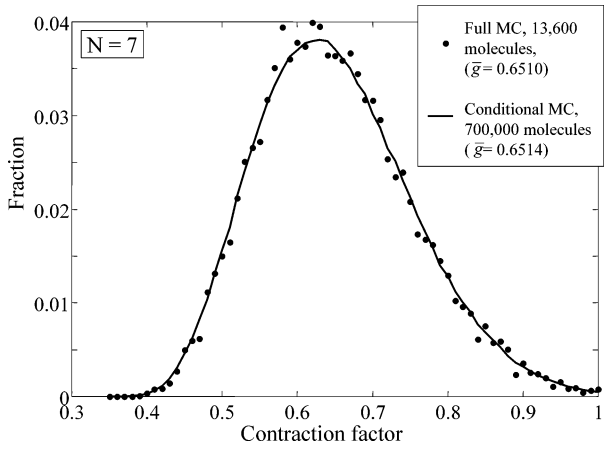

Figure 7. Distribution of radius of gyration contraction factor as calculated (eqs 15−17) for architectures generated by full and conditional MC for $N = 7$ branch points and overall molecular chain lengths n distributed according to the CLD/DBD, $P(n,N)$.

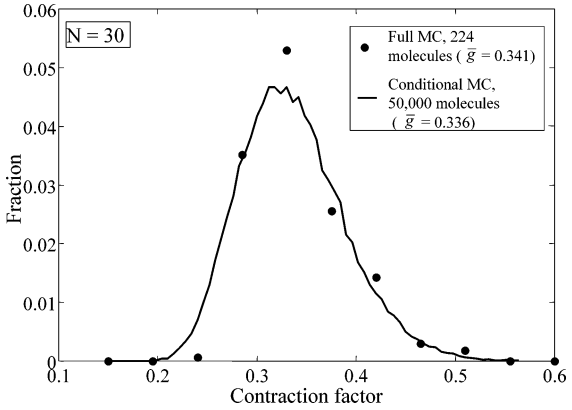

Figure 8. Distribution of radius of gyration contraction factor as calculated (eqs 15−17) for architectures generated by full and conditional MC for $N = 30$ branch points and overall molecular chain lengths n distributed according to the CLD/DBD, $P(n,N)$.

our results to the old work by Zimm and Stockmeyer.[6] Their relationship, eq 18, predicts the contraction factor as a function of number of branch points. It is shown in Figure 9 as compared to what we have found from the conditional MC method.

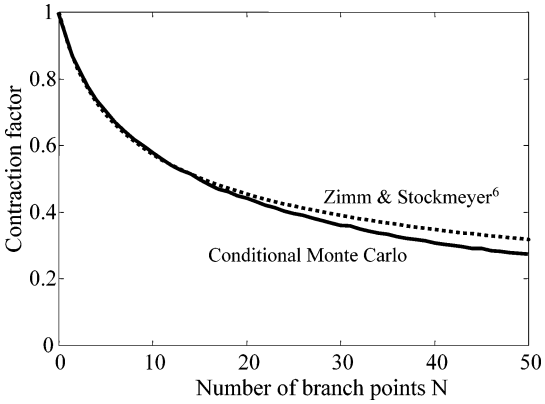

Figure 9. Radius of gyration contraction factor from conditional MC (eqs 15−17) vs number of branch points per molecule (samples of 2000 per N value) as compared to relation by Zimm and Stockmeyer,[6] eq 18. Difference due to condition of homogeneous branching in Zimm and Stockmeyer and heterogeneous branching in the actual chemical system.

At low N fair agreement is observed, but at higher N size contraction as predicted by our algorithm is clearly stronger. This discrepancy must in part or wholly be attributed to differences in underlying assumptions. Zimm and Stockmeyer assumed segments between branch points and "terminal" segments to be Flory distributed around the same average—a homogeneously branched system. Segment lengths in terms of our approach follow from pp lengths, n_i, and numbers of branch points on pps, N_i, as $n_i/(N_i + 1)$. Realizing that branching density $\rho_i = N_i/n_i$, and using the information on averages of length and density as depicted in Figures 3 and 5 for the case of $N = 7$, we computed average segment lengths per pp in coupling order. The overall average being 530, pp1 has the shortest average, 359, pp7 the longest, 697, and all other pps have lengths in between. The segment lengths per pp turn out to be Flory distributed around these (different) averages. In other words, we have heterogeneously branched molecules in this radical polymerization system. Since the contraction factors found by us are lower, we conclude that architectures have a stronger Cayley tree character than the ones of the homogeneous branching system analyzed by Zimm and Stockmeyer.[6]

Conclusion and Discussion

We have proposed a simple and straightforward coupling algorithm for primary polymers forming branched architectures for radical polymerization with transfer to polymer and disproportionation termination in a CSTR. The new conditional Monte Carlo algorithm allows us to create branched molecules given the total number of monomer units and number of branch points of the molecule. In existing full Monte Carlo simulations[1−3] sampling of primary polymer residence times is an esential element, since it determines the time order in which pps are growing on existing ones and hence their coupling order. In the conditional MC method we have introduced a new method of finding the proper length distributions of pps in coupling order directly from the chain length/number of branch points distribution. This works without explicitly dealing with residence times of pps. That conditional MC thus leads to correct results is most clearly proven by showing that the distributions of branch points (densities) on pps of specific pps fully agree with full MC. This has proved assumptions underlying our previous architectural algorithms[4,5] to be both erroneous and unnecessary.

Some of the properties of the molecules made by the two different algorithms could already be compared without actually

generating the architectures. A recursive method was developed which directly generates pp length distributions from CLD/DBD, even without sampling. Branching density distributions could be obtained by another recursive algorithm from sampled sets of primary polymer lengths. In all cases we found excellent agreement between the two methods, although this was hampered by the limited size of the full MC samples due to limiting computation time. This leads to considerably scattered distribution plots, especially for larger numbers of branch points, *N*, the generation of only a few hundreds of these already takes days of simulation time. Note that our conditional MC algorithm does not suffer from this disadvantage. It allows to generate statistically representative samples of architectures of large molecules, that are very rare in practice, in a few hours only at one moderately fast PC.

The final test of the algorithm was performed by comparing radii of gyration contraction factors from complete molecular architectures generated by the two algorithms. These factors were calculated by a statistical-mechanical model using graph theory.[15] Apart from the scatter again in the full MC results we found excellent agreement. Thus, we conclude that the simple and straightforward conditional Monte Carlo algorithm indeed describs the same chemistry as the full MC algorithm. The new method can be used to find architectures for molecules with a given *n* and *N*, provided distributions of these are known, from either full MC or alternative methods.[14]

In this paper we have shown that the conditional MC method provides an equally rigorous solution to the problem of finding architectures as does full MC, but in a computationally more efficient way. However, its validity has until now only been proven for the case of a CSTR at steady state with transfer to polymer and disproportionation termination, while the full MC method already has a wider range of applications. These include batch reactors and other kinetic systems, like recombination termination, terminal double-bond propagation (another source of branching), and random scission.[16,17] As regards the extendability of the conditional MC method to other reactor and kinetic systems in general, it is required that the proper distributions are available. In the present case we need the two-dimensional chain length/number of branch points distribution. For a batch reactor with the same kinetics this distribution should be available as a function of conversion. The extension to recombination termination additionally requires the number of combination points distribution. To this end we have developed a new method to find the three-dimensional chain length/number of branch points/number of combination points distribution.[14] Some aspects of the way a batch reactor and recombination have to be implemented in the conditional MC algorithm have briefly been mentioned in the present paper. Hence, we conclude that several options exist to extend the conditional MC to a wider scope of applications.

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