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Influence of polymerization procedure on polymer topology and other structural properties in highly branched polymers obtained by $A_2 + B_3$ approach

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Abstract

Computational studies were carried out to investigate the influence of polymerization procedure on the topology and various macromolecular characteristics of the highly branched polymers formed by the reaction of A_2 and B_3 type monomers through step-growth polymerization reactions. The influence of three different polymerization procedures on the properties of the polymers formed was investigated, namely, (i) slow addition of A_2 over B_3, (ii) slow addition of B_3 over A_2, and (iii) mixed $A_2 + B_3$. Topology, degree of branching, number and weight average molecular weights, and polydispersity index of the polymers were determined using Monte Carlo simulations, assuming different levels of cyclization ratios during the reactions. Interestingly model polymers obtained by the slow addition of B_3 over A_2 produced much higher degree of branching or truly hyperbranched polymers, when compared with the other two methods, which mainly resulted in linear growth with slight branching.

Keywords: Highly branched polymers; Branching; Monte Carlo simulations

1. Introduction

Preparation of highly branched or hyperbranched polymers through the step-growth polymerization reactions of A_2 and B_3 type monomers has been extensively investigated for over two decades. Commercial availability of a very large number of A_2 and B_3 type monomers has made the preparation of various highly branched polymeric systems, such as polyesters, polyamides, polyurethanes, polyethers, polysulfones, polyphenylenes, poly(ether ketones), polycarbonates and many others, possible. A number of excellent review articles on both the synthetic procedures and the theoretical treatment of these systems are available in the literature [1–11]. Conventionally during step-growth polymerization reactions both monomers are mixed (at desired stoichiometric ratios) at the beginning of the reaction and allowed to react under chosen experimental conditions (solvent, temperature, catalyst). For linear polymers very high conversions are needed in order to obtain high molecular weight polymers. On the other hand in $A_2 + B_3$ polymerizations the system reaches the gel point at a certain conversion, which can be predicted by using the theory of Flory [12,13]. Therefore, it is necessary to stop the polymerization before the gel point in order to obtain soluble and processible, highly branched polymers. As we have recently demonstrated [14,15], it is possible to delay or even prevent gelation by conducting the $A_2 + B_3$ polymerization reactions in very dilute solutions. It is well known that in very dilute solutions the "cage effect", which may effectively prevent intermolecular reactions and promote intramolecular reactions, plays an important role on the structure of the products formed. Kricheldorf has been investigating the cyclization reactions in linear step-growth polymerization reactions. His results also clearly show the presence of cyclization reactions in

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step-growth or polycondensation reactions under various conditions [8].

Another interesting variable which also influences the gel point is the procedure followed during the polymerization of A_2 and B_3 type monomers. In this case, three different scenarios are possible. These are: (i) mixing both monomers ($A_2 + B_3$) at the beginning of the reaction and letting them react, which is the conventional method, (ii) slow addition of A_2 onto B_3, and (iii) slow addition of B_3 over A_2. Theoretical conversions at gel points for these three scenarios are provided in Table 1.

For conventional $A_2 + B_3$ reactions, assuming an initially equimolar mixture (i.e. equal number of A_2 and B_3 monomers) gelation is expected to take place at 86.6% conversion, with respect to A groups [12]. When A_2 is added over B_3 slowly, the gel point will be at 75.0% A group conversion [15]. In this work we show that in B_3 over A_2 addition, gelation will be at 50.0% conversion with respect to A groups. These differences on the gel point conversion values clearly indicate major differences between the branching topologies or chain architectures of the oligomeric intermediates and the polymers formed. The aim of controlled $A_2 + B_3$ polymerization is the preparation of ‘‘truly hyperbranched’’ polymers. Since the gel point is reached at the lowest conversion in the slow addition of B_3 over A_2 polymerization method compared to the others, the topology of the intermediates formed should have the ‘‘highest’’ degree of branching.

Interestingly, although detailed studies on many theoretical and experimental aspects of $A_2 + B_3$ polymerizations have been investigated, there are no detailed reports available on the influence of polymerization method on the topology of the polymers formed. A brief report was recently published by Fossum and Czupik on the influence of reaction procedure on various properties of aromatic poly(ether sulfones) obtained by the $A_2 + B_3$ approach [16]. In our earlier publications [14,15,17] we reported the influence of the concentration of the reaction medium on the gel point, degree of branching and polymer properties for reactions where oligomeric A_2 was added slowly onto B_3. In this study we report the results of our modeling studies on the influence of polymerization method and cyclization rate on the topology, degree of branching, number and weight average molecular weight, and polydispersity index of the polymers formed. We also compute the gel point conversion predicted by Flory’s critical branching coefficient, and show that this is consistent with the gelation conversions seen in the Monte Carlo simulations in the cyclization-free case.

Table 1
Influence of polymerization method used on the theoretical gel point conversions for equimolar $A_2 + B_3$ polymerizations conducted in bulk

Polymerization method	A_2 conversion at gel point (%)	B_3 conversion at gel point (%)	Stoichiometry at gel point (A_2/B_3)
$A_2 + B_3$ (mixed together)	86.6	57.7	1:1
A_2 added slowly over B_3	75.0[a]	50.0	3:4
B_3 added slowly over A_2	50.0	33.3[a]	3:1

[a] Denotes equivalent conversion, including monomers not yet added to the reaction system.

2. Procedure for Monte Carlo simulation

Modeling studies on the formation of highly branched polymers as a function of (i) the polymerization procedure employed and (ii) the conversion of A groups were performed using Kinetic Monte Carlo (KMC) simulations. Monte Carlo simulations provide a conceptually simple modeling framework in which concentrations and reactivities of monomers can be related to the resulting hyperbranched polymer structure. These reactivity models and assumptions originate from the work of Flory [12,13] and Stockmayer [18,19]. Flory’s theory was derived and is useful to predict the gelation in conventional one-pot (cyclization-free) reactions, where all the reactants are mixed (usually in stoichiometric amounts) and reacted. In this study our main aim is not to test Flory’s theory but to predict gel points for reactions where different polymerization procedures are used. In fact our interest in predicting the gel point is mainly to avoid gelation for the preparation of highly branched polymers, which have become important during the last decade. By running Monte Carlo simulations, one is not restricted to kinetic models that have exact or series solutions. This increased flexibility enables the use and exploration of a wider range of kinetic models and assumptions. Each simulation proceeds by one individual reaction step at a time. At each step, either a monomer is added to the system or else an A—B reaction is executed. The selection probabilities are computed according to the Kinetic Monte Carlo algorithm in which the probability of selecting an individual event is proportional to its reaction rate [20]. The specific event to be performed is selected using a random number, and then time is incremented with a random number, based on a Poisson distribution of the time for the next reaction. In the current study Kinetic Monte Carlo simulations were employed assuming three different polymerization methods. These are:

(i) $A_2 + B_3$ mixed and reacted in one-pot,
(ii) A_2 slowly added on B_3 and
(iii) B_3 slowly added on A_2.

In all studies, the total number of A_2 and B_3 monomers is equal (or B groups are in excess), and we use N to refer to this system size. However, in methods (ii) and (iii) it should be noted that not all monomers are added to the system until the end of the simulation, such that the instantaneous stoichiometry of the reaction is changing as the polymerization proceeds. In fact this is one of the novelties described in this study compared to conventional one-pot approach where stoichiometry is fixed.

During all calculations we assume that the reactivities of all A and B groups are the same, i.e. no steric effects or molecular weight effects are included. Degree of branching (DB) of the final products was determined by using the formula

DB = (D + T)/(D + L + T), where D, L, and T indicate dendritic, linear, and terminal units in the system.

We first present the results of very small simulations for illustrative purposes, where 30 A_2 and 30 B_3 molecules were reacted in bulk. In these simulations it is assumed that no cyclization reactions took place in the system. Then we employ much larger simulations (10,000 A_2 and 10,000 B_3 molecules) to make predictions relevant for comparison with bulk experiments, including various levels of the cycle formation rate. Other system sizes were also considered, and the results for $N = 5000$ were the same as for $N = 10{,}000$.

Cyclization is an important factor in step-growth reactions leading to the formation of linear or highly branched macromolecules [8,21–23]. In the larger simulations presented here cyclization was taken into account in a similar manner as described in our previous study [15]. In that study the dilution of the system was varied to study cyclization. Dilution suppresses the overall rate of intermolecular reactions, thereby enhancing the overall extent of intramolecular cycle forming reactions. Here we use the same approach for modeling cycle formation, using the parameter $\gamma = k_c/(k_{nc}N)$ to represent the ratio of the rates of cycle forming (k_c) and non-cycle forming (k_{nc}) reaction rate constants. The term N is required in the denominator because cycle formation is a first order reaction, while intermolecular reactions are second order in system size. As a result, the predictions for any constant value of γ will be independent of the system size N. At each step in the simulation, the total number of possible cycle forming reactions and non-cycle forming reactions is counted and tabulated. The overall reaction rate and selection probability for each of the two reaction types are then proportional to its reaction rate constant k, multiplied by the number of possible reactions in the system.

In the large scale KMC simulations presented here, the number of A_2 and B_3 molecules (N) is taken as 10,000 each. Average molecular weights of A_2 and B_3 were assumed to be 1000 and 300 g/mol, respectively, which are typical for oligomers and monomers used in hyperbranched systems. The cyclization ratio (γ) is varied from $\gamma = 0$ (no cyclization) to $\gamma = 0.25$ (extensive cyclization), and 10 runs are averaged for each case.

3. Results and discussion

Preparation of highly branched polymers through the reactions of A_2 and B_3 type monomers has received widespread attention both from academic and from industrial research groups. Very detailed work has been performed on understanding both the experimental aspects and theoretical modeling of these systems. Most of the research efforts (both in experimental and in theoretical studies) have been focused on the influence of variables such as (i) reaction stoichiometry, (ii) reactivity differences, (iii) cyclization, (iv) percent conversion, (v) dilution and others [24–32] on the structure and properties of highly branched polymers formed. Interestingly, there has been very limited experimental effort on the investigation of the effect of reaction procedure on the highly branched polymers formed and their properties [15–17]. A small number of papers on theoretical treatment of network formation by multistage processes (e.g. prepreg formation) are also available [33–37].

3.1. Calculation of gel point conversions for different polymerization methods

During these modeling studies three different polymerization methods for the preparation of highly branched polymers using A_2 and B_3 type monomers are discussed. These are: (i) $A_2 + B_3$ mixed and reacted in one-pot, (ii) A_2 slowly added on B_3, and (iii) B_3 slowly added on A_2. The theoretical conversion values at the gel points for these three scenarios are provided in Table 1. These results assume bulk reactions and no cyclization.

The analysis of Flory invokes the branching coefficient α to quantify conditions under which gelation is possible [13]. The branching coefficient is defined as the probability that a B group is reacted with an A_2 oligomer that has reacted with another B group. For tri-functional branching units, the critical value of α is 1/2 after which it may be possible for an infinite polymer network to form. Reaching this critical value of the branching coefficient is not a sufficient condition to guarantee gelation, but it has proven to be a useful metric for predicting the gel point conversions.

In the case of $A_2 + B_3$ polymerization, a "one-pot" reaction is the most common situation, and Flory [13] predicts a critical value of $\alpha = 1/2$ at an A_2 conversion of 0.866, when the concentrations of A_2 and B_3 are equal. In a previous study, we compared this case to the slow addition of A_2 into B_3, where the critical value of α occurs at 50% B_3 conversion, such that 75% of the A_2 monomers have been added to the system [15]. (In this study we will refer to this as an equivalent A_2 conversion of 75%.) Since each A_2 is assumed to react completely before another is added, each A_2 in the system connects two B groups to each other. Therefore, at an A_2 conversion of 0.75, 75% of the total A_2 has been added to the system. At this point, the B_3 conversion is 0.50, so the branching coefficient is also 0.50.

In this paper we now also consider the branching coefficient for the slow addition of B_3 onto A_2 and show that the A_2 conversion is 0.50 at $\alpha = 1/2$. At an A_2 conversion of 0.50, the total number of A_2 in the system will be three times the number of B_3, again using the "slow addition" assumption that each B_3 fully reacts before another B_3 is added. Since every A group has equal reactivity in our model, the fraction of fully reacted A_2 is 0.25, as is the number of completely unreacted A_2. The remaining A_2 oligomers have only one A group reacted. At an A_2 conversion of 0.50, 75% of the total A_2 present in the system is in the polymer and one-third of those are fully reacted and connect two B groups to each other. Thus, for every 100 A_2 considered, there are 100 B groups in the system and there are 25 A_2 oligomers connecting them. Consequently, 50 of these B groups are connected to other B groups through an A_2 oligomer, so the branching coefficient α is 0.50 at an A_2 conversion of 0.50.

The analysis for slow B_3 addition onto A_2 and for slow A_2 addition onto B_3 uses the assumption that all A groups have equal reactivity, which is not the case when cycle formation is suppressed or favored. Furthermore, the branching coefficient is only an indicator of when gel formation is possible. Our Monte Carlo simulations are consistent with these predictions, but give additional metrics and consider additional mechanisms, such as varying rates of cycle formation and the prediction of degree of branching.

In Table 1 we also report the stoichiometry of each reaction at the predicted gelation conversion. We also note that at these particular stoichiometries of $A_2/B_3 = 3{:}4$ and 3:1, the analysis of Flory for one-pot reactions predicts that no gelation will be possible [3]. In both cases, the critical value of $\alpha = 1/2$ is achieved at full monomer conversion, indicating that gelation will not be possible at any conversion. Thus, by utilizing slow addition of monomers, it may be possible to achieve altered polymer topology. We investigate this further using the Monte Carlo simulations.

3.2. Monte Carlo simulations on the influence of polymerization procedure on the branching topology

The conventional method for the preparation of highly branched polymers through the step-growth polymerization reactions of A_2 and B_3 type monomers is to mix both monomers at desired concentrations and let them react. Recently, we demonstrated the preparation of highly branched segmented polyurea copolymers by the slow addition of oligomeric A_2 onto B_3 [15,17]. As displayed in Table 1, calculations based on the branching coefficient suggest major differences in the critical A_2 and B_3 conversions at the gel point for three different polymerization methods. For the case where equimolar amounts of each monomer are mixed and reacted, A_2 conversion at the gel point is 86.6%. When A_2 is slowly added on B_3, the critical A_2 conversion at the gel point is reduced to 75%. For the third case, which involves the slow addition of B_3 onto A_2, the conversion of A_2 at the gel point is further reduced to 50%. All of these results qualitatively point out to the fact that in the preparation of highly branched polymers by step-growth polymerization, slow addition of either monomers results in a higher degree of branching in the system, which eventually leads to crosslinking at lower conversions.

3.2.1. Monte Carlo simulations and visualization of 30 A_2 and 30 B_3 molecules

In order to better understand and illustrate the differences between the extent of branching and the topology of the structures formed as a function of the polymerization method, a simple modeling study based on 30 A_2 and 30 B_3 molecules was performed. The results are presented graphically for a single Monte Carlo simulation, which enables visualization of the differences between the polymers formed in the three addition strategies. This small number of molecules allowed us to easily represent and illustrate the topologies of the intermediates and polymers formed in two-dimensional space as a function of conversion.

3.2.1.1. Modeling studies on topology development in HB polymers obtained by mixing and reacting 30 A_2 and 30 B_3 molecules in bulk ($A_2 + B_3$). The conventional synthetic procedure for the preparation of hyperbranched polymers by step-growth polymerization involves mixing both monomers together at desired stoichiometric ratios and reacting them under chosen experimental conditions (solvent, temperature, catalyst). Structures of the molecular species formed, their average chain lengths and length distributions can be determined by using the statistical theory developed by Flory [12,13].

In order to understand the structures formed during the conventional procedure for the preparation of highly branched polymers a simple modeling study was performed where 30 A_2 and 30 B_3 molecules are mixed together and reacted. Fig. 1 displays schematic representations of the structures of the species present in such a reaction system as a function of conversion of the A groups. Fig. 1a and b shows the distribution of products when 16.7 and 33.3% of the A groups have reacted. Both systems consist mainly of monomers and dimers. At 50.0 and 66.7% conversions (Fig. 1c and d) the mixture still mainly consists of monomers, dimers and a few higher molecular weight species. As shown in Fig. 1e, at 76.7% conversion of the A groups, formation of short oligomers containing 5–15 monomer units is observed, some with branched structures. Interestingly, even at this point a substantial amount of monomers and dimers is still present in the system, typical for step-growth polymerization reactions. At 90.0% conversion of the A groups (Fig. 1f) formation of a branched polymer is observed. Topology of the final highly branched polymer formed when all A groups have reacted is shown in Fig. 1g.

3.2.1.2. Modeling studies on topology development in HB polymers obtained by the slow addition of 30 A_2 molecules onto 30 B_3 molecules in bulk (A_2 over B_3). Fig. 2a–f shows the structures of the species formed as A_2 is slowly added into a reactor where 30 B_3 molecules are initially present. When an A_2 monomer is added into the system, a B group is randomly selected from any B_3 present in the system and reacted with one end of an A_2. Each unreacted B group in the system has an equal probability of being selected. After that, the remaining end of the A_2 molecule added is reacted with another B group. Since no cyclization is allowed, each reacted B group belongs to a different B_3 monomer. Fig. 2a and b shows the structures formed after the addition of 5 and 10 A_2 monomers or 16.7 and 33.3% A group conversion, respectively. These systems mainly consist of unreacted B_3 monomers, some trimers and pentamers. After the addition of 20 and 23 A_2 monomers (or 66.7 and 76.7% A group conversion, respectively) there are still a large number of B_3 monomers together with some fairly high molecular weight oligomers (Fig. 2c and d). This is quite different when compared to $A_2 + B_3$ scenario discussed above! When 27 A_2 monomers are added and reacted (90.0% A group conversion) a fairly large polymer is formed

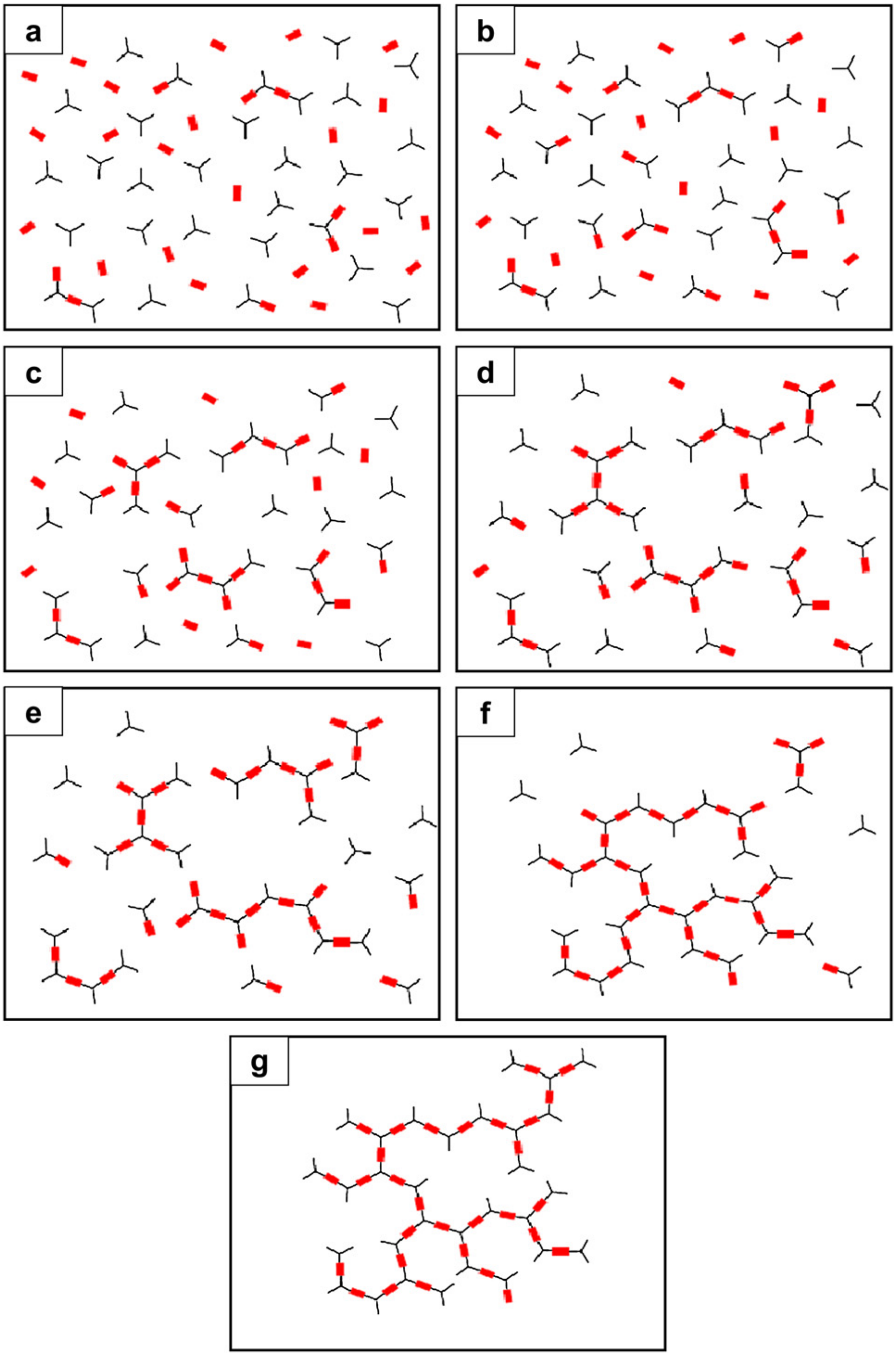

Fig. 1. Schematic representation of structures of the species formed as 30 A_2 and 30 B_3 molecules are mixed and reacted.

(Fig. 2e). Fig. 2f shows the topology of the highly branched polymer obtained after the addition of all 30 A_2 molecules.

3.2.1.3. Modeling studies on topology development in HB polymers obtained by the slow addition of 30 B_3 molecules onto 30 A_2 molecules in bulk (B_3 over A_2). This method is quite different from the former two. Even in the first step, when one B_3 is added into 30 A_2 molecules that are originally present in the reactor, the end groups are capped forming a branched structure. Fig. 3a shows the model reaction mixture after the addition of only 5 B_3 molecules (25% A group conversion). They are all end capped with A_2 molecules and the system consists of 5 branched tetramers and 15 A_2 monomers. After the addition of 10 B_3 monomers (50% A group conversion) several short oligomers are present together with a number of A_2 monomers. Note that 50% A group conversion is the predicted gel point as shown in Table 1. When 2 additional B_3 or a total of 12 B_3 monomers are added into the system and reacted (60% A group conversion), formation of a large and highly branched polymer molecule is observed. This is

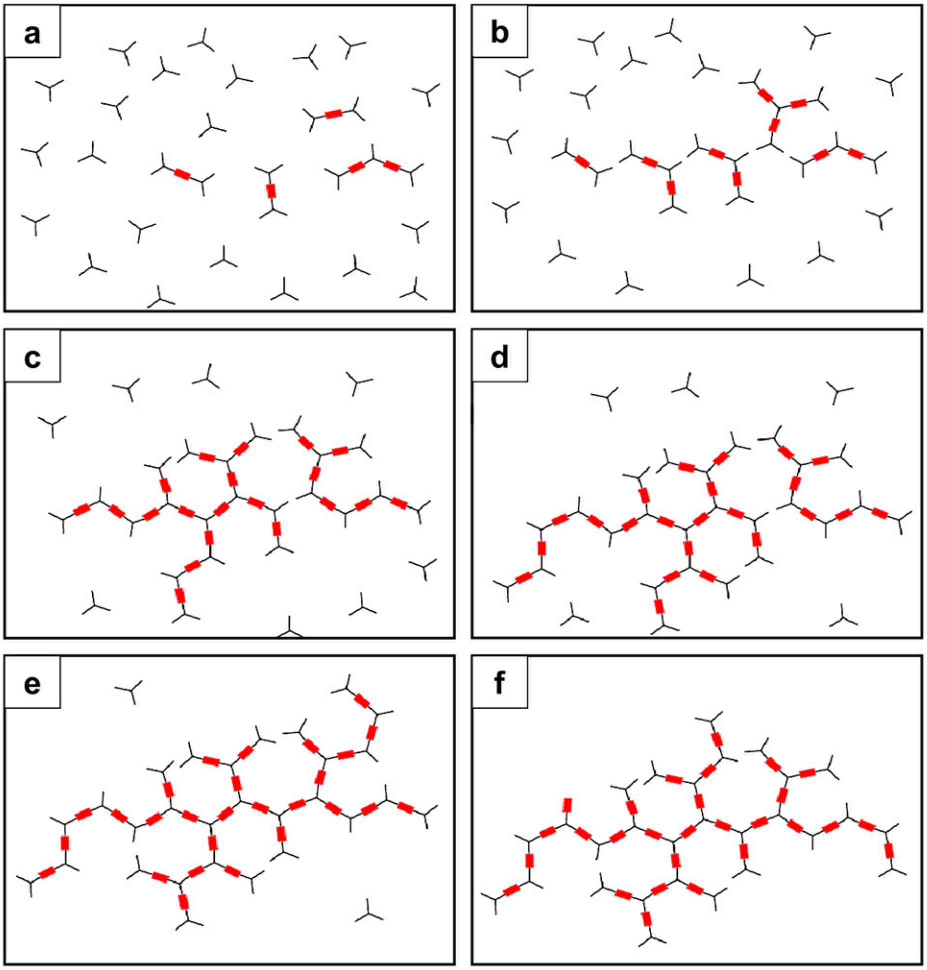

Fig. 2. Schematic representation of structures of the species formed as A_2 is slowly added into a reactor where 30 B_3 molecules are initially present.

definitely quite different from the behavior of the other two systems discussed, where even at 80% A group conversion, they consisted only of short, linear oligomers. As shown in Fig. 3d, upon the addition of 14 B_3 molecules (70% A group conversion), a highly branched polymer structure is formed and only one A_2 molecule is left. End groups of this structure consist of the A molecules. Fig. 3e shows the structure formed after the addition of 15 B_3 molecules (75% A group conversion). Since no cyclization is assumed in these model studies, addition of the remaining 15 B_3 molecules will react with the A type end groups present and convert them into B_2 type end groups as shown in Fig. 3f. Otherwise the topology does not change.

3.2.1.4. Degree of branching in the HB polymers formed in modeling studies by using three different polymerization methods. Before discussing the degree of branching, it is important to recall that since equal number of A_2 and B_3 molecules is used in the modeling studies, and since the cyclization reactions are ignored, chain ends of all polymers formed are terminated by B groups, except for one. As can be seen in Fig. 1g, the polymer topology formed by mixing and reacting 30 A_2 and B_3 molecules contains 8 dendritic (D) units, 13 linear (L) units and 9 terminal (T) units. The degree of branching (DB) value for this molecule is calculated to be 0.57. Structure obtained by the slow addition of A_2 over B_3 method (Fig. 2f) contains 10 D units, 11 T units and 9 L units, resulting in a DB value of 0.70. On the other hand, the structure formed by the slow addition of B_3 units over A_2 contains 14 D units, 15 T units and 1 L unit. This structure has the highest DB value of 0.97. These results are tabulated in Table 2, for a better comparison.

Results of this very simple modeling study presented in Table 2 clearly demonstrate the very dramatic effect of the polymerization procedure employed on the topology of the highly branched structures formed during the reactions of A_2 and B_3 type monomers. Interestingly, the conventional method, where both monomers are mixed and reacted together, seems to provide the lowest degree of branching. When A_2 is added over B_3 slowly and reacted degree of branching seems to improve slightly. On the other hand and somewhat surprisingly, addition of B_3 over A_2 results in almost a completely branched structure. These modeling results based on very limited number of A_2 and B_3 molecules are also in line with the theoretical gel point values provided in Table 1, which indicates higher branching (or lower A conversion at gelation) for B_3 addition

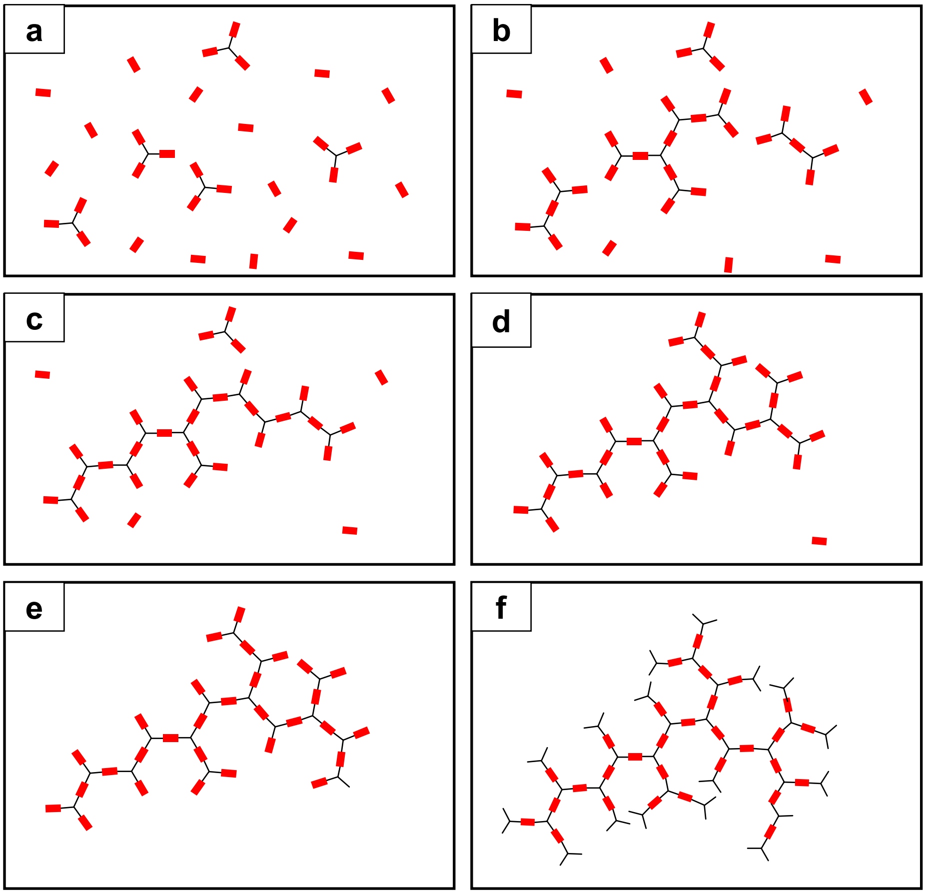

Fig. 3. Schematic representation of structures of the species formed as B_3 is slowly added into a reactor where 30 A_2 molecules are initially present.

over A_2, followed by A_2 over B_2 and A_2+B_2 systems. This study which was based on the model reactions of 30 A_2 and 30 B_3 molecules was followed by a more extensive and realistic study using Kinetic Monte Carlo (KMC) simulations in which 10,000 A_2 and B_3 molecules are used.

3.2.2. Kinetic Monte Carlo (KMC) simulations on systems containing 10,000 A_2 and 10,000 B_3 molecules

KMC simulations are very useful in investigating the formation of highly branched (HB) polymeric materials under various experimental conditions. Our earlier simulation studies on the formation and properties of HB systems, where A_2 was slowly added onto B_3 (A_2 over B_3), have already been reported [15,17]. These results were in good agreement with experimental observations for polyurea and polyester type HB polymers. In this study we used larger number of A_2 and B_3 monomers (10,000 each) and extended our simulations to include two additional polymerization procedures, which were (A_2+B_3) or "one-pot" approach, where both monomers are mixed and reacted, and (B_3 over A_2), where B_3 was slowly added over A_2. For each reaction procedure calculations were performed at four different cyclization ratios (γ). These were: (i) $\gamma=0$ (no cyclization or ideal case), (ii) $\gamma=0.01$ (very small cyclization), (iii) $\gamma=0.1$ (significant cyclization), and (iv) $\gamma=0.25$ (very high cyclization). We have already demonstrated the effect of the concentration of reaction medium on the extent of cyclization in HB polymers obtained by step-growth polymerizations [15], where as the reaction system got more dilute an increase in the extent of cyclization was observed. At very high dilutions there was no gelation. This was the main rationale for the investigation of different cyclization ratios in these KMC studies, where we investigated the development of the following:

(i) number ($\langle M_n \rangle$) and weight ($\langle M_w \rangle$) average molecular weights,
(ii) polydispersity index (PDI; $\langle M_w \rangle / \langle M_n \rangle$) and
(iii) degree of branching (DB)

as a function of conversion of the A groups. During the KMC studies equimolar amounts of A_2 and B_3 (10,000 molecule of each type) were used. As a result the total number of B end groups was in excess in every case. Average molecular weights of A_2 and B_3 were taken as 1000 and 300 g/mol,

Table 2
Comparison of the degree of branching in model HB polymers obtained by different polymerization methods as shown in Figs. 1g, 2f and 3f

Polymerization method	D units	L units	T units	DB
A_2+B_3 (Fig. 1g)	8	13	9	0.57
A_2 over B_3 (Fig. 2f)	10	9	11	0.70
B_3 over A_2 (Fig. 3f)	14	1	15	0.97

respectively, to mimic our experimental studies which will be discussed separately.

3.2.2.1. KMC results on the influence of the polymerization method on molecular weight development and estimated gel point. As discussed earlier, there is a significant effect of the polymerization method on the extent of reaction (conversion of A or B groups) at the gel point during the preparation of highly branched polymers from A_2 and B_3 monomers. Under ideal conditions, where it is assumed that there is no cyclization in the system, conversion of A groups at the gel point (or gelation) is provided in Table 1. At the gel point, the average molecular weight of the reaction system increases sharply and becomes infinite as the crosslinking takes place. On the other hand in our KMC studies, where there is only finite number of molecules (10,000 A_2 and 10,000 B_3), a sharp increase in the average molecular weight of the system can be considered as a good measure of the starting point of gel formation. To illustrate this point, plots of weight average molecular weight ($\langle M_w \rangle$) of polymers formed against conversion of A groups are reproduced in Fig. 4 as a function of the polymerization method used. These plots are for ideal systems, where it is assumed that there is no cyclization during reactions ($\gamma = 0$).

The plots in Fig. 4 clearly demonstrate the dramatic influence of polymerization method on the development of molecular weight as a function of conversion. We believe that the sharp increase in the weight average molecular weights as shown in Fig. 4 provides a very good indication of the starting point for the gel formation for each method. For this reason the values of A group conversions at the upturn were determined by extrapolation. As clearly seen in Fig. 4, weight average molecular weight of the HB polymer formed starts increasing at much lower A group conversion for the method where B_3 is slowly added on A_2 (ca. 50% A_2 conversion), followed by A_2 over B_3 method (ca. 75% A_2 conversion) and $A_2 + B_3$ method (ca. 87% A_2 conversion). These results are in very good agreement with the theoretical gel point data which are provided in Table 1.

For comparison, plots of number average molecular weight ($\langle M_n \rangle$) of the highly branched polymers formed as a function of A group conversion and method of polymerization are also reproduced in Fig. 5 for the ideal case ($\gamma = 0$ or no cyclization). Although the trend in $\langle M_n \rangle$ development is the same as the trend in $\langle M_w \rangle$, A group conversion values where the sharp upturn starts are much higher in Fig. 5. In general $\langle M_w \rangle$ is more representative of the system as the gel point is approached, since it is much more sensitive to the contribution from the high molecular weight species.

It is well known that the polydispersity index (PDI) or molecular weight distribution ($\langle M_w \rangle / \langle M_n \rangle$) of the highly branched polymers is dramatically higher than that of linear systems. While the PDI values for linear step-growth polymers are around 2, the PDI for HB polymers can be 10 or more [38]. As a result a sudden increase in the PDI during the polymerization of HB polymers can also be considered as a good measure of the approach to gelation. Fig. 6 gives the PDI versus conversion plots as a function of polymerization method employed for the system where $\gamma = 0$.

As shown in Fig. 6, very low PDI values, typical for the oligomerization phases in step-growth polymerizations, suddenly start increasing sharply to very high PDI values. As expected, the polymerization method used has a strong influence on the A group conversion where the sharp rise in PDI starts. Extrapolated values for critical A group conversions as PDI values start rising sharply for different polymerization methods are determined as 50% for B_3 addition on A_2, 74% for A_2 addition on B_3 and 86% for $A_2 + B_3$. Comparative results of the simulations with $N = 30$ and $N = 10{,}000$ are presented in Table 3, together with the theoretical gel point conversion values of A groups for different methods. The small and large simulations give similar results for degree of branching at gelation, suggesting that the structure evolution illustrated in Figs. 1–3 describes the differences between the three addition strategies. Gel point conversion values obtained by KMC simulations from Fig. 4 are also in excellent agreement with the theoretical values provided in Table 1, clearly indicating the power of the KMC approach in predicting experimentally relevant properties.

3.2.2.2. Influence of the extent of cyclization on gelation and the structure and properties of highly branched polymers. As is well described in the literature, during step-growth

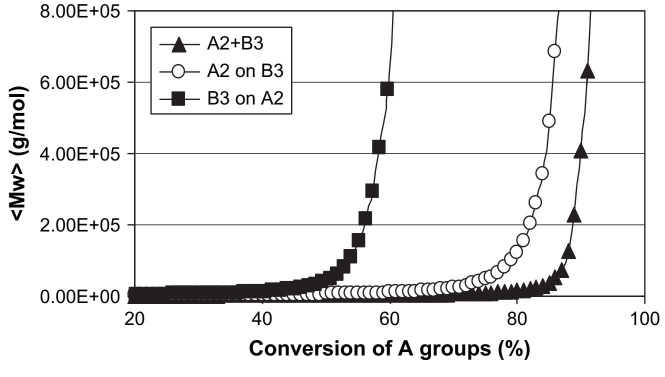

Fig. 4. Influence of the polymerization procedure on the development of weight average molecular weight ($\langle M_w \rangle$) as a function of conversion of A groups ($\gamma = 0$ or no cyclization).

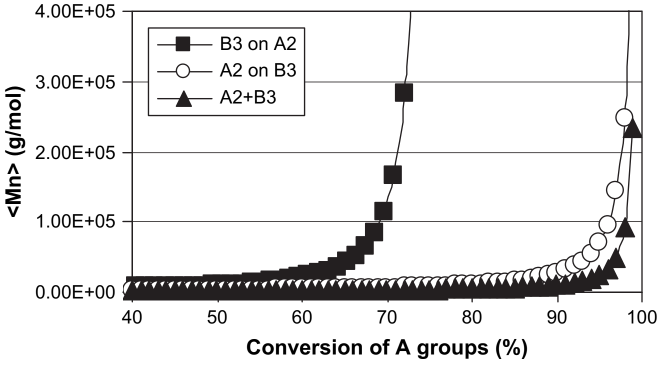

Fig. 5. Influence of the polymerization procedure on the development of number average molecular weight ($\langle M_n \rangle$) as a function of conversion of A groups ($\gamma = 0$ or no cyclization).

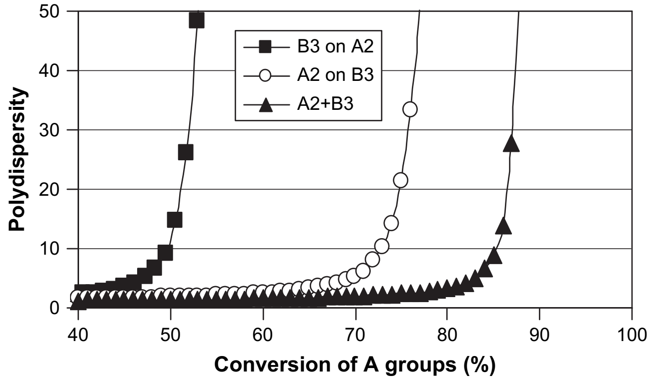

Fig. 6. Influence of the polymerization procedure on the development of polydispersity as a function of conversion of A groups ($\gamma = 0$ or no cyclization).

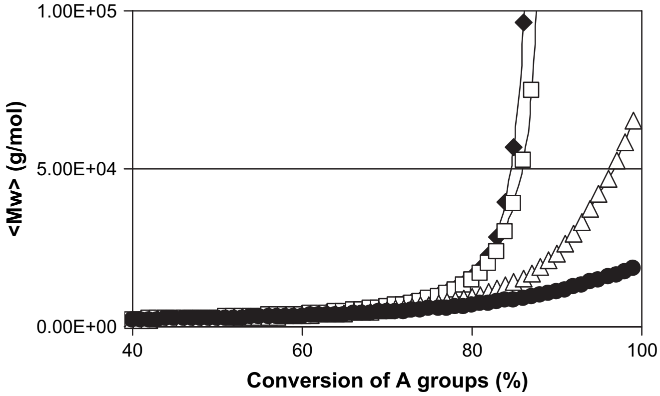

Fig. 7. Development of weight average molecular weight (M_w) as a function of the extent of cyclization for the conventional A_2+B_3 "one-pot" reaction. (◆) $\gamma = 0$, (□) $\gamma = 0.01$, (△) $\gamma = 0.1$ and (•) $\gamma = 0.25$.

polymerization reactions of linear or highly branched polymers, there may be significant amount of cyclization depending on the solvent used, concentration of the reaction medium, temperature and steric effects [8]. Cyclization may have major effects on various structural and physicochemical properties of the polymers formed. During the preparation of highly branched polymers by the $A_2 + B_3$ methodology, cyclization results in lower overall polymer molecular weights, lower polydispersity and a lower number of functional end groups. In $A_2 + B_3$ polymerizations cyclization also affects the molecular weight distribution of the polymer formed and depending on the extent of cyclization gel formation may be retarded or totally prevented. To understand the effect of cyclization on the properties of the polymers formed, KMC simulations were performed at four different cyclization ratios (γ) for every reaction method. These were: $\gamma = 0$ (no cyclization or ideal case), $\gamma = 0.01$ (very small cyclization), $\gamma = 0.1$ (reasonable cyclization), and $\gamma = 0.25$ (very high cyclization).

Fig. 7 gives the development of weight average molecular weight as a function of cyclization for the conventional $A_2 + B_3$ "one-pot" reactions. As expected, the molecular weight growth is very slow until very high conversions, typical for step-growth reactions. Another important observation is the maximum $\langle M_w \rangle$ achieved as a function of the extent of cyclization for the $A_2 + B_3$ or conventional "one-pot" reaction system. As shown in Fig. 7, for $\gamma = 0$ and $\gamma = 0.01$ $\langle M_w \rangle$ starts rising sharply as the gel point is approached and eventually leads to the formation of very high $\langle M_w \rangle$ polymers. On the other hand for high cyclization regimes of $\gamma = 0.1$ and $\gamma = 0.25$, $\langle M_w \rangle$ values obtained are very low. The data provided in Fig. 7 also point out to another important fact that at $\gamma = 0.1$ and $\gamma = 0.25$, most probably no gelation will be observed in the system.

Table 3
Comparative results of simulations with $N = 30$ and $N = 10{,}000$ and the theoretical gel point conversion values of A groups for different methods (no cyclization)

Polymerization strategy	Conversion of A groups at gelation (%)		DB at gel	
	Theoretical	KMC results	$N = 10{,}000$	$N = 30$
$A_2 + B_3$	86.6	87	0.55	0.57
A_2 over B_3	75.0	75	0.60	0.70
B_3 over A_2	50.0	50	1	0.97

As discussed above in Section 3.2.2.1, for the ideal case where $\gamma = 0$ (no cyclization) the critical conversion of A groups at gel point was estimated to be 50% for B_3 over A_2; 75% for A_2 over B_3; and 87% for $A_2 + B_3$ (one-pot) methods. Cyclization is known to retard the gelation and this can clearly be seen in Fig. 8, where $\langle M_w \rangle$ values are plotted against A group conversions for different polymerization methods for $\gamma = 0.01$ scenario. To get an estimate of the critical A group conversions at gel point (for $\gamma = 0.01$ scenario) the curves are extrapolated similar to the approach used in earlier discussions. The results were as follows: 59% for B_3 over A_2; 87% for A_2 over B_3; and 92% for $A_2 + B_3$ (one-pot) methods. It was interesting to observe such large differences in A group conversions at gel point for such a small cyclization ratio of $\gamma = 0.01$, when compared to $\gamma = 0$ (Fig. 4).

Growth in polymer weight average molecular weight $\langle M_w \rangle$ as a function of the extent of reaction is substantially reduced for higher cyclization ratio of $\gamma = 0.1$. $\langle M_w \rangle$ versus A group conversion plots of KMC simulation results for $\gamma = 0.1$ (10% cyclization) are reproduced in Fig. 9. Curves shown in Fig. 9 are quite different from those given in Fig. 4 ($\gamma = 0$) and Fig. 8 ($\gamma = 0.01$). Firstly, except for the B_3 over A_2 method, no sharp increase in $\langle M_w \rangle$ is observed in Fig. 9.

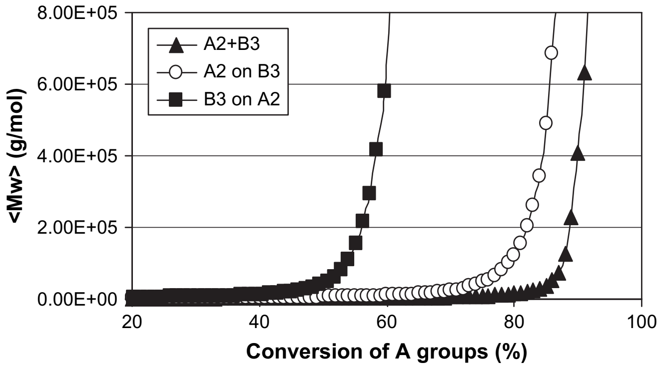

Fig. 8. Change in $\langle M_w \rangle$ as a function of A group conversion for different methods at $\gamma = 0.01$.

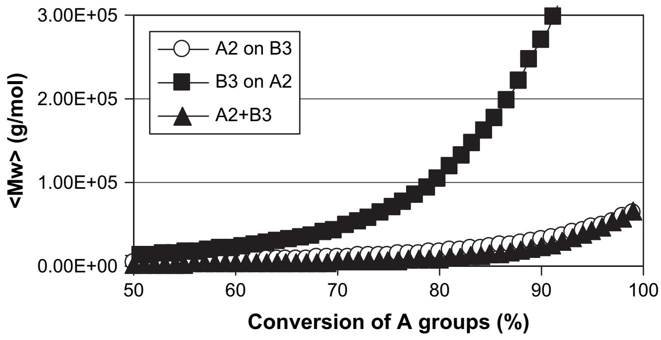

Fig. 9. Change in $\langle M_w \rangle$ as a function of A group conversion for different methods at $\gamma = 0.1$.

Secondly and more importantly, the maximum or ultimate $\langle M_w \rangle$ values obtained by $A_2 + B_3$ and A_2 over B_3 methods are very low. Maximum value of $\langle M_w \rangle$ for B_3 over A_2 method (9.2×10^5 g/mol) is more than an order of magnitude higher than those obtained by A_2 over B_3 (6.3×10^4 g/mol) and $A_2 + B_3$ (one-pot) (6.5×10^4 g/mol) methods. On the other hand similar to the previous results, growth in $\langle M_w \rangle$ for the case of B_3 over A_2 is much faster when compared to the other methods.

Degree of branching (DB) values of polymers at gel point (for $\gamma = 0$ and $\gamma = 0.01$) and at complete reaction (for $\gamma = 0.10$ and $\gamma = 0.25$) obtained by different methods are provided in Table 4. It is interesting to note that for the same polymerization method extent of cyclization does not have a major effect on the DB values of the polymers formed. DB values for $A_2 + B_3$ and A_2 over B_3 systems are between 0.55 and 0.60 and are very similar to each other regardless of the extent of cyclization. These DB values are in fairly good agreement with our results tabulated in Table 2. Another interesting observation is a DB of 1.00 for B_3 over A_2 system regardless of the extent of cyclization. This is easily understandable since any B_3 added onto A_2 will immediately react to form a dendritic unit (or else possibly a terminal unit when cyclization is prohibited at $\gamma = 0$). However, there will not be any formation of linear units.

4. Conclusions

We have demonstrated that during the preparation of highly branched polymers through the polymerization of A_2 and B_3 type monomers, the addition strategy has a very dramatic effect on the polymer structure, topology, molecular weight distribution and gel point conversions. Options for different addition strategies are not typically explored experimentally, but could enable a wider range of hyperbranched polymer topologies and properties. It is not clear which polymerization method is superior, and the method selected may depend on the specific application and desired polymer properties. In the case of slow B_3 addition over A_2, truly hyperbranched polymers are generated, which is a very important finding of this study. However, gelation also occurs at a lower A_2 conversion, which may or may not be undesirable for practical purposes. At gelation, only one-third of the B_3 monomers have been added, so a reaction that is stopped at this point will not have the 1:1 ratio of A_2 to B_3. In fact as it is well known, changing the ratio of A_2 to B_3 provides an additional handle to influence the process, which can be considered along with changing the dilution and the addition strategy. Kinetic Monte Carlo (KMC) simulations provide a powerful tool to explore a wider range of addition strategies than is practical in an experimental setting. Moreover, the KMC simulations allow the modeling of a wider range of phenomena, such as cyclization and modified monomer addition strategies, and the prediction of a wider range of properties, such as degree of branching and extent of cyclization, than is possible with the analytical results of Flory.

Table 4
Degree of branching (DB) values achieved as a function of the extent of cyclization and reaction procedure used during polymerization of A_2 and B_3 monomers

γ	DB		
	$A_2 + B_3$	A_2 over B_3	B_3 over A_2
0	0.55	0.60	1.00
0.01	0.55	0.55	1.00
0.1[a]	0.56	0.56	1.00
0.25[a]	0.57	0.56	1.00

[a] Indicates DB values at complete reaction of A groups.

Cyclization, which is generally overlooked and ignored, is an important factor that influences the structure and properties of highly branched polymers prepared by step-growth polymerization reactions. In this study we have demonstrated the critical effects of the extent of cyclization on the molecular weights, molecular weight distribution and gel point conversions for highly branched polymers obtained from $A_2 + B_3$ systems. Interestingly, simulation results indicate that the extent of cyclization does not affect the degree of branching at gel point substantially.

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