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# Forced Gelation in an Off-Stoichiometric Copolymerization of $A_2$ and $B_3$ Monomers

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**Summary**: A step-growth alternating copolymerization of monomers $A_2$ and $B_3$ was studied by an off-lattice Monte-Carlo simulation. In the random systems, i.e. with no substitution effect, the polymerization leads to gel formation provided the molar ratio of monomers is not very far from the stoichiometric one ($A_2$: $B_3 \approx 3$: 2) and the reaction is carried out in one batch. A substantial deviation from the stoichiometric ratio may halt gelation altogether, even at conversions of the minority functional groups approaching unity. We demonstrate that in these non-gelling off-stoichiometric systems, one can force the system to gel, after all, without altering the kinetics or diffusion parameters of the reaction. The clue is to carry out the reaction in steps.

**Keywords:** computer modeling; copolymerization; gelation

## Introduction

Over 70 years ago, Staudinger[1] demonstrated the insolubility and the infusibility of polymers prepared from monomers of functionality exceeding 2. Some years later, Flory[2] and Stockmayer[3] explained the molecular nature of branching and gelation using statistical arguments. The statistical methods of modeling the polymerization processes involving multifunctional monomers were further developed in the 1960s and 1970s by Gordon,[4,5] Miller and Macosko,[6,7] Dušek[8,9] and others.[10] These methods were very efficient in describing the evolution of polymerization. Although the statistical methods were intrinsically limited to acyclic systems, they were also successfully used to describe gelling systems. The reason was that, in step-growth polymerization, the proportion of cycle-containing molecules was usually negligibly small up to the gel point conversion.

An alternative method of modeling the polymerization processes became the kinetic analysis,[11] consisting of solving a system of, usually nonlinear, differential Equations describing the rates at which individual species appear in and disappear from the system. An example provides the use of the Smoluchowski coagulation equation,[12,13] in fact used for the first time by Stockmayer[14] for modeling the polymerization of an *f*-functional monomer. Stockmayer demonstrated that the size distribution of acyclic species calculated using the Smoluchowski Equation was identical with that obtained using statistical arguments.

Nonequivalence of statistical and kinetic methods of modeling was shown by Kuchanov and Povolotskaya[15] for a system with varying reactivities of substrates. Later, Spouge[16] and Faliagas[17] clarified that the statistical models, in fact, generate equilibrium distributions, whereas the kinetic methods are more suitable for modeling the systems with kinetically controlled reaction steps.

Both the statistical and the kinetic models of polymerization processes, called the classical, or Flory-Stockmayer, theory, failed in rigorously treating the formation of intramolecular cycle closing links. As

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Flory and Stockmayer well understood, these kinds of links were inevitably formed in real polymerization systems.

Computer simulations represent alternative methods of modeling. Most of these methods are usually based on the same assumptions as those adopted by Flory and Stockmayer and are simply chemical experiments carried out in computer memory. These assumptions were the applicability of the law of mass action (known in physics as the mean-field approximation) and the independence of the reactivity of the functional groups on the size of the molecules on to which they were attached (Flory's principle).[2]

Stauffer was the first to introduce percolation methods.[18] Unfortunately, most of the assumptions made in the first percolation experiments were hard to accept by chemists studying real polymerization systems. Much preferred became the off-lattice models.[19–24] The most theoretically studied gelling system was the model of step-growth homopolymeri-zation of an $\mathbf{A}_f$ monomer ($f = 3, 4,..$).[17,25–27] Another widely studied system was the one comprising $\mathbf{A}_f$ and $\mathbf{B}_g$ (or R$\mathbf{A}_f$ and R'$\mathbf{B}_g$) monomers ($f > 1, g > 2$), which is more relevant to real systems (**A** and **B** denote the kinds of functional groups that are capable to react with each other, e.g. carboxylic (**A**) and amino (**B**) groups, or isocyanate (**A**) and hydroxyl (**B**) groups). Among them, the simplest system was the $\mathbf{A}_2 + \mathbf{B}_3$ one.[28–31] Recently, most of the work has focused on applying the latter systems to prepare hyperbranched polymers rather than gels.[26,32,33] Of interest is to modify the polymerization procedure in order to obtain a product of as highly branched molecular structure as possible. By simple modifications of the polymerization procedure, such as the slow introduction of one or both reagents into the reactor,[27,34,35] an improvement of the attainable conversion (delayed gelation), a reduction of the molecular size distribution or an increase of the branching degree were observed. Another modification of the polymerization procedure was to dilute the system to halt its gelation.[36,37] Dilution of the system indeed substantially delays gelation due to extensive cyclization.

In this work, we study the opposite. We show that in a random, off-stoichiometric $\mathbf{A}_2 + \mathbf{B}_3$ system at the molar ratio that normally produces branched polymer and does not gel up to the full conversion of the minority component, modification of the polymerization procedure may cause the system to gel.

## The Model

Off-lattice Monte-Carlo simulations of an $\mathbf{A}_2 + \mathbf{B}_3$ copolymerization system were carried out. No specific system was considered. The method used shared essentially all its assumptions regarding the mechanism of polymerization with the classical Flory-Stockmayer theory. The smallest element was the unit that was converted by reactions with other units. The comonomers $\mathbf{A}_2$ and $\mathbf{B}_3$ reacted via their functional groups **A** and **B**. Each reaction step changed the composition of the system.

The reaction space created in computer memory had no specific shape or size and the monomers $\mathbf{A}_2$ and $\mathbf{B}_3$ were randomly embedded into it, without any specific coordinates. No possible diffusion effects were taken into account.

The functional groups **A** and **B** pointed to react were selected at random. The rate of reaction for each pair of groups was taken the same. Unlike in the Flory-Stockmayer theory, no restriction on the reaction between a pair of groups belonging to the same molecule were imposed. Hence, intramolecular reactions were also allowed, but these were not specifically labeled. The algorithm used could account for the effect of substitution of units, i.e. the dependence of group reactivity on the unit substitution degree. In the present work, however, no substitution effects were considered.

The novelty of this model compared to the classical ones is that the availability of monomers was limited. The copolymerization process was divided into several steps.

In the first step, the whole amount of one of the monomers was reacted with a portion of the second one. After reaching a predetermined conversion, the next portion of the second monomer was added and the copolymerization was continued. The procedure was continued for every next portion of the monomer. The amount of monomer added depended on the initial molar ratio of monomers and was the same in each step. Also the conversion degree at which the next portion was added was the same for each stage of polymerization.

The conversion degree was defined as the fraction of reacted functional groups in the minority monomer. Two parameters were used to follow the conversion degree. The first was related to the current size of the system in the particular stage of the process. This parameter was used to control the extent of polymerization at a certain stage. It was labeled as $p_A$ or $p_B$, depending on which monomer was the minority one (for a stoichiometric mixture $p_A = p_B$).

The other parameter, $p$, was defined in the same way, but it was related to the whole system. This was a convenient normalizing parameter, suitable for comparing different copolymerization runs. The other molecular parameters were also renormalized to the final size of the system.

## Results and Discussion

The process of copolymerization of a monomer $\mathbf{A}_2$ with a monomer $\mathbf{B}_3$ carried out at the stoichiometric molar ratio of functional groups ($\mathbf{A}_2$: $\mathbf{B}_3 = 3{:}\ 2$) leads to gelation, unless a strong substitution effect exists. At a moderately modified molar ratio of the monomers, gelation also occurs, except that the gel point (conversion at the incipient of gelation) is shifted.[28]

A significant deviation from stoichiometry of functional groups may halt gelation altogether. Under these conditions, a hyperbranched polymer can be obtained. In these cases, by using multistage polymerization, one can improve the branching degree of the hyperbranched polymers. This will be demonstrated later in this section.

In order to obtain polymers of reasonably high molecular weight, the molar ratio $\mathbf{A}_2$: $\mathbf{B}_3$ should be kept within the range of 3:1 to 1:2. Otherwise, mostly small molecules are formed with groups of the minority monomer substituted by a single shell of the majority one and the substantial fraction of the latter left unreacted. In systems with a large excess of one of the monomers, gelation does not occur[28]. The system can, however, be forced to gel by using the multistage process of introducing the majority monomer. At the beginning of the polymerization, the molar ratio of the functional groups is different from the final one. This leads to formation of a gel at a certain stage of the process. It appears that the system can be forced to gel not just at the molar ratio close to, but also far from the stoichiometric one. The condition for gelation appears because, at the initial stages of the reaction, molecules are formed that have, at their outer shells, a substantial amount of minority monomer units. The majority monomer added in the next stage acts then as a cross-linking agent.

In computer simulations of gelling systems, the most convenient parameter used for determining the gel point conversion is the weight-average polymerization degree of the sol fraction.[22] The clear maximum in the plot $P_{w,sol}$ vs. conversion determines the gel point. The parameter is evaluated by neglecting the biggest molecule, while calculating the weight-average degree of polymerization, $P_w$, for the whole system. It is worth pointing out that, although the biggest molecule in the system cannot be treated as gel at the early stages of the polymerization, the error of the assumption is negligibly small. The plots of $P_{w,sol}$ vs. $p$ and $P_w$ vs. $p$ for the systems of molar ratio of monomers $\mathbf{A}_2$: $\mathbf{B}_3 = 2{:}\ 3$ are shown in Figures 1 and 2, respectively. The majority monomer was $\mathbf{B}_3$. The process was carried out by introducing the latter in three equal portions, each after the previous portion reacted to conversion $p_A$ shown in

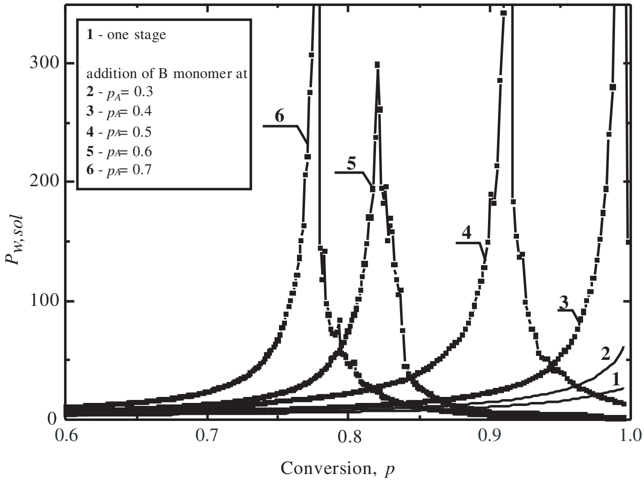

***Figure 1.***

Conversion dependence of the weight average polymerization degree of the sol fraction in the copolymerization of monomers $\mathbf{A}_2$ and $\mathbf{B}_3$ at the molar ratio $\mathbf{A}_2$: $\mathbf{B}_3 = 2: 3$. The polymerization was carried out as a one- or three-stage process. Each next portion of $\mathbf{B}_3$ monomer was introduced to the system after reaching the minority group conversion $p_A$ shown in the insert. The total number of monomers in the system $N = 2\,000\,000$.

the insert. The values are compared to those for the one-step polymerization.

As one can see, for the molar ratio of monomers in question, the system does not gel in a one-stage process or when the second and third portion of monomer $\mathbf{B}_3$ are introduced before the conversion of minority (**A**) groups has reached a value of about 0.4 (curves 1 or 2, respectively). In these cases, the weight-average polymerization degree of the sol fraction is practically the same as the weight-average degree of polymerization for the whole system. Both values monotonically grow with conversion, $p$. The same applies to the polydispersity of the system, expressed as

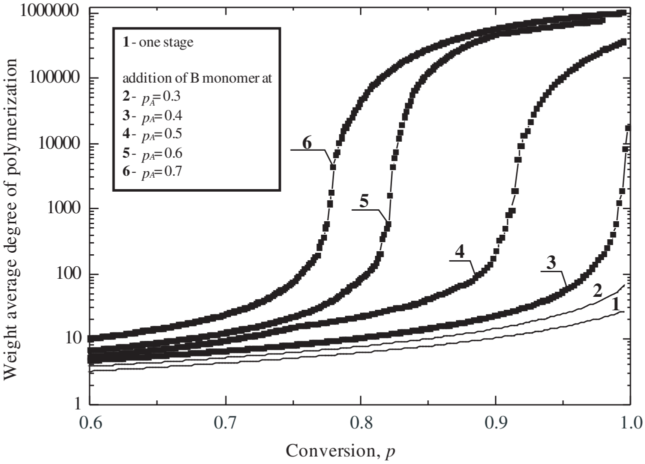

***Figure 2.***

Conversion dependence of the weight-average polymerization degree in the copolymerization of monomers $\mathbf{A}_2$ and $\mathbf{B}_3$ at the molar ratio $\mathbf{A}_2$: $\mathbf{B}_3 = 2: 3$. The polymerization was carried out as a one- or three-stage process. Each next portion of $\mathbf{B}_3$ monomer was introduced to the system after reaching the minority group conversion $p_A$ shown in the insert. The total number of monomers in the system $N = 2\,000\,000$.

the ratio of the weight- to the number-average polymerization degrees. With a higher conversion of the minority groups, before the second or third portion of monomer $\mathbf{B}_3$ is introduced, the system gels. Gelation was observed already at $p_A = 0.40$. Then, the gelation occurred at a total conversion $p = 0.99$, i.e. at a value hardly accessible in a real experiment.

Each increase of $p_A$ resulted in a shift of gelation towards a lower total conversion. It should be pointed out that the average degrees of polymerization of the polymer present in the system at the moment of introducing the next portion of monomer, $p_A = 0.4$ or $p_A = 0.5$, are relatively low. Despite that, gelation does occur in the third stage of the reaction. This can be interpreted in terms of formation of branched structures undergoing cross-linking much more readily than those formed in the one stage process.

Table 1 summarizes the conversions at which the subsequent portions of monomer $\mathbf{B}_3$ were added and compared with the gel point conversion $p_g$.

The results presented in Table 1 help to verify the logic of changes in the polymerization procedure from single to a multi-stage one. As one can see, at the small conversions at which the next portion of monomer is added, $p_A = 0.4$ or 0.5, the gel point lies above the conversion of the last monomer introduction. Here, the non-stoichiometric system of monomer can be forced to gel, although the system does not gel in the one-stage polymerization process.

**Table 1.**
The renormalized conversion degree, $p$, at which each next portion of majority monomer was introduced to the system. The gel point conversions, $p_g$, are also shown.

| $p_A$ | Conversion degree, $p$, at each introduction of next portion of monomer | | $p_g$ |
|---|---|---|---|
| | Stage 2 | Stage 3 | |
| 0.4 | 0.30 | 0.60 | 0.99 |
| 0.5 | 0.38 | 0.75 | 0.91 |
| 0.6 | 0.45 | 0.90 | 0.82 |
| 0.7 | 0.53 | — | 0.78 |
| 0.95 | 0.71 | — | 0.61 |

In the three-stage system, the conversion at the gel point strongly depends on the stage of reaction at which the subsequent portions of monomer are added.

When the next portion of monomer is added at somewhat higher conversion of minority groups, say, at $p_A = 0.6$, gelation is observed before the last portion of the monomer is introduced. Further increase of the conversion at the first stage, up to $p_A = 0.7$ or to 0.95 leads to the situation where gelation occurs in the second or even first polymerization stage, respectively. Introduction of next portions of monomers do not change the situation, at least for the system studied, which is kinetically controlled, i.e. the elementary reactions are irreversible. The last three variants of carrying out the polymerization process seem not to have practical significance as gelation takes place actually at a different molar ratio of monomers than that considered.

As already mentioned, the systems that do not gel are often used to produce hyperbranched polymers. The extent of ramification in the hyperbranched (macro)-molecules is characterized by the degree of branching devised by Frey.[38] The dependence of the degree of branching on conversion for the system studied in this work ($\mathbf{A}_2$: $\mathbf{B}_3 = 2$: 3) is shown in Figure 3 for the one- and three-stage versions of the polymerization. The three-stage systems differed in the conversion $p_A$ at which the next portions of monomer were introduced. The values are indicated by the curves.

As can be seen in Figure 3, the degree of branching of the polymer molecules takes rather small values. The polymers can hardly be called hyperbranched. One should notice, however, that by dividing the total of $\mathbf{B}_3$ monomer into portions, one can significantly increase the degree of branching as compared with polymers obtained in a one-stage polymerization process. The higher the $p_A$ value, the higher the increase in the degree of branching.

Much more ramified hyperbranched polymers can be obtained by the copolymerization of the $\mathbf{A}_2 + \mathbf{B}_3$ system with molar excess of monomer $\mathbf{A}_2$. This was

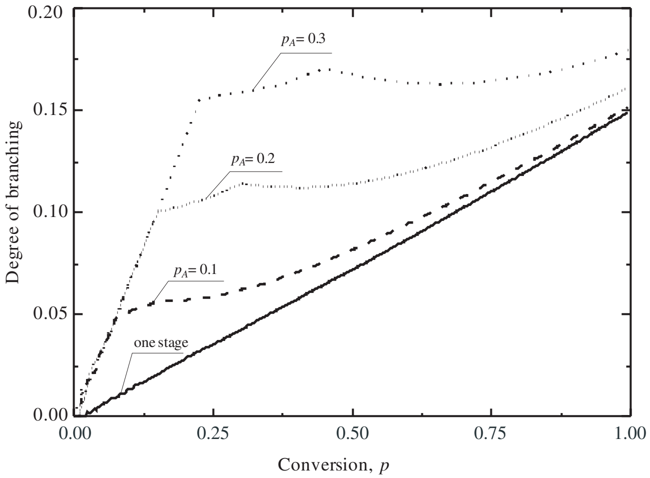

***Figure 3.***
The changes in Frey's degree of branching vs. conversion for the polymerization systems carried out in one or in three stages with each next portion of monomer introduced after the fraction 0.1, 0.2 or 0.3 of functional groups of the minority monomer has reacted. System size: $N = 2\,000\,000$ units.

studied at a molar ratio of monomers $\mathbf{A}_2$: $\mathbf{B}_3 = 3$: 1. In this system, even in the single-stage procedure, one can obtain a polymer with a degree of branching as high as 0.73. Unlike in the systems with excess of $\mathbf{B}_3$ monomer, the degree of branching is not sensitive to the change of the procedure from single to a multistage one.

The other molecular parameters of the products changed in the same directions after switching from a one-stage procedure to a multistage one, despite whether $\mathbf{B}_3$ or $\mathbf{A}_2$ monomer was used in excess. In the case of $\mathbf{A}_2$ excess, gelation was observed already at $p_B = 0.3$. As in the previous cases, the gel point conversion, $p_g$, moved towards the smaller conversion, the higher was the conversion of the next feed, $p_B$. This is illustrated by the data in Table 2 where the renormalized conversions $p$ are listed at which each new portion of excess monomer $\mathbf{A}_2$ was added. The resulting values of gel point $p_g$ are also shown.

From the analysis of both cases, i.e. with **A** and **B** groups used in excess, it follows that in order to exploit the change of the procedure from a one-stage to a three-stage one, the excess monomers should be introduced to the system at relatively small conversion on minority groups, but high enough for the system to gel at the third stage of reaction.

In further simulations, the minority monomer was divided into three portions and was added to the majority component. With this procedure, no gelation was observed at the ratios of monomers that do not lead to gelation in the one-stage process.

The change of the method of carrying out the polymerization from one- to multi-stage was also studied for the systems that gel already in the one-stage procedure. Regardless of which monomer was introduced in portions, the conversion at gela-

***Table 2.***
The renormalized conversion degree, $p$, at which each next portion of majority monomer was introduced to the system. The gel point conversions, $p_g$, are also shown.

| $p_B$ | Conversion degree, $p$, at each introduction of next portion of monomer | | $p_g$ |
|---|---|---|---|
| | Stage 2 | Stage 3 | |
| 0.3 | 0.20 | 0.4 | 0.98 |
| 0.4 | 0.27 | 0.53 | 0.95 |
| 0.5 | 0.33 | 0.67 | 0.91 |
| 0.6 | 0.40 | 0.8 | 0.78 |
| 0.7 | 0.47 | 0.94 | 0.76 |
| 0.8 | 0.53 | — | 0.71 |
| 0.9 | 0.60 | — | 0.58 |

tion was always lower in the multi-stage procedure, than in the straight mixture. Higher was also the polymer dispersity (defined as the ratio $P_w/P_n$). Hence it is hard to foresee any applications of carrying out polymerization processes for gelling systems by modifying them through partitioning a component into portions.

## Conclusion

With the aid of Monte Carlo simulations, we showed that the reaction between multivalent monomers at ratios that would not lead to network formation in a single-batch mode of addition can result in network formation when the majority monomer is added in small portions. An interesting question that needs to be addressed in the future is whether or not the same effect can be observed when both the majority and the minority monomers are added in portions to a common reactor. An experimental verification of the theoretical predictions is in progress for both polyesters and polyamides.

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