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A Method of Controlling Dispersity by Monomer Feeding Protocol and Forced Gelation in Nongelling Step-Growth Branched Polymerization Systems

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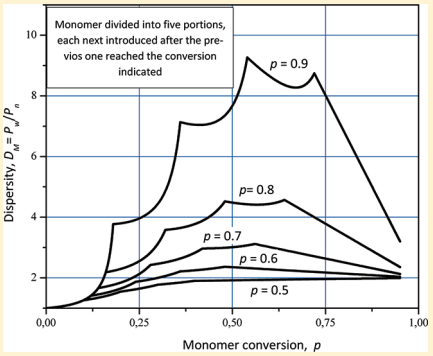
ABSTRACT: Changes in dispersity of step-growth linear polymer were calculated for systems where monomer was added to polymerization reactor in portions, each after the previous ones reached certain conversion or after predetermined time. For step-growth branching polymerization involving di- and trifunctional monomers used in the ratios that do not lead to gelation it was shown that the monomer mixtures can be forced to gel, when they are introduced to the reactor in several portions.



INTRODUCTION

While considering methods of reducing dispersity in step hyperbranched polymerization of a monomer system $AB_f + B_g$, where A and B are the functional groups reacting with each other and f and g are the monomer functionalities,[1,2] we have confirmed[3] that by adding monomer AB_f to the polymerizing system in portions, one can substantially reduce the dispersity of the resulting polymer, expressed as the ratio of the weight to number-average degree of polymerization.[4]

Therefore, it seemed interesting for us to know how the dispersity will change in other types of step polymerization, such as in the homopolymerization of a two-functional monomer or in a more common linear copolymerization of two monomers. In order to stay close to hyperbranched polymers[5] we also studied nonstoichiometric mixtures of A_3 and B_2 monomers. Obviously, these latter systems produce gel, when used in proportions of functional groups not too distant from the stoichiometric ones.

In the first part of the paper we deal with a model linear step polymerization using a single monomer. Not very many polymers are produced in this way (see, e.g., ref 6), a good example being the second stage of the synthesis of poly(ethylene terephthalate). Then, the diester of terephthalic acid and ethylene glycol is condensed in the presence of catalyst with removal of the excess of ethylene glycol. Exactly in the same way behave stoichiometric mixtures of bifunctional monomers, such as the mixture (salt) of adipic acid and hexamethylenediamine, which, upon polymerization, yields nylon-6,6. The problem with the first example (PET) is that polyesterification is an equilibrium process, whereas in the model we apply, the individual reaction steps in polycondensation are considered irreversible. The nonstoichiometric mixture of two monomers will be considered in a forthcoming paper.

The second part of the paper deals with nonstoichiometric mixtures of trifunctional and bifunctional monomers ($A_3 + B_2$) at the concentration ratio just outside that leading to gelation. It was Flory,[7] who showed first that the stoichiometric mixture $A_3 + B_2$ undergo gelation when the conversion of either type of groups (i.e., A or B) reaches $(1/2)^{1/2} \approx 0{,}7071$ and increases in terms of conversion of minority groups as the concentration ratio A/B (or B/A) deviates from unity. When the concentration of minority groups falls below the half of the majority ones, the gel cannot form. The conditions under which the branching systems do not gel were analyzed by Dušek et.al.[8] As one of us (JBL), however, have already demonstrated,[9] in some cases, nonstoichiometric mixtures of composition beyond the gelation region can be forced to gel, after all.

In the following section we present the mathematical tools used for modeling the polymerization processes. These are simplified kinetic models of homopolymerization of a bifunctional monomer[10] and of copolymerization of a system consisting of $A_3 + B_2$ monomers.[11] The latter model takes into account changes in reactivity of functional groups in the form of the so-called first shell substitution effect.[12]

THE MODELS

Linear Polymerization. In the reaction of step polymerization of a single monomer, the reaction system consists of a mixture of macromolecules P_i of polymerization degree i = 1, 2, ... By dealing with the degree of polymerization, rather than with molecular weight, we can neglect the presence of any side

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product. Thus, the reaction reads

$$P_i + P_j \xrightarrow{k} P_{i+j}$$

where k is the rate constant independent of i and j. For this idealized polymerization reaction the size distribution of polymer molecules is described by the Smoluchowski coagulation equation,[10,13] which is in fact the infinite set of rate equations:

$$\frac{dc_i}{dt} = \frac{1}{2}\sum_{j=1}^{i=j} C_j C_{i-j} - C\sum_{j}^{\infty} Cj \tag{1}$$

with C_j being the concentration of macromolecules of polymerization degree j, conveniently expressed as the number of these molecules divided by the total number of units in the system (=the number of P_1 at zero time, τ). The rate constant is adsorbed into time units ($t = \tau k$).

The Smoluchowski coagulation equation[13] was first applied for kinetic modeling of polymerization by Stockmayer.[14] Then, it was used many times for analysis of both polymerization[10,15,16] and cross-linking processes.[17] A more general analysis of aggregation processes by using the Smoluchowski equation was published in a series of papers by a Dutch group.[18−21]

It is not difficult to see that by multiplying both sides of the Smoluchowski eq 1 by x^i where x is a dummy variable ($|x| \leq 1$) and summing up for all i, one obtains the single partial rate equation:

$$\frac{\partial H}{\partial t} = \frac{1}{2}H^2 - HM_0 \tag{2}$$

where

$$H(x,t) = \sum_{i=1}^{\infty} C_i(t)x^i \tag{3}$$

is the polynomial representation of the entire size distribution in the polymerization system, and M_0 is the zeroth moment of the distribution:

$$M_0 = \sum_{i=1}^{\infty} C_i(t) = H(1,t) \tag{4}$$

The number-average degree of polymerization, P_n, equal, by definition, the ratio of the number of monomeric units to number of molecules, is simply

$$P_n = 1/M_0 \tag{5}$$

In this approach, the first moment of the distribution is independent of time and equals 1.

The second moment

$$M_2(t) = \sum_{i=1}^{\infty} i^2 C_i(t) \tag{6}$$

is available as the combination of derivatives of H with respect to x with then x put to 1:

$$M_2 = \left.\frac{\partial^2 H}{\partial x^2}\right|_{x=1} + \left.\frac{\partial H}{\partial x}\right|_{x=1} \tag{7}$$

Formally, the weight-average degree of polymerization is the ratio of the second to first moment of distribution: $P_w = M_2/M_1$. Hence, in this case: $P_w = M_2$.

Finally, the dispersity in the system is defined as follows:[4]

$$D_M = \frac{P_w}{P_n} = M_0 M_2 \tag{8}$$

The time dependence of the moments of distribution are given by successive differentiation of eq 2 followed by setting $x = 1$. Thus

$$\frac{dM_0}{dt} = \left.\frac{\partial H}{\partial t}\right|_{x=1} = -\frac{1}{2}M_0^2 \tag{9}$$

The general solution of 9 is

$$M_0 = \frac{2M_0(t_0)}{(t-t_0)M_0(t_0) + 2} \tag{10}$$

and the first moment

$$\frac{dM_1}{dt} = \left.\frac{\partial^2 H}{\partial t \partial x}\right|_{x=1} = 0 \tag{11}$$

and hence $M_1 = 1$, as mentioned above.

Finally, the second moment

$$\frac{dM_2}{dt} = \left.\frac{\partial^3 H}{\partial t \partial x^2}\right|_{x=1} = M_1^2 = 1 \tag{12}$$

is given by the general solution

$$M_2(t) = t - t_0 + M_2(t_0) \tag{13}$$

Note that both P_n (=$1/M_0$) and P_w are linear functions of time.

When polymerization is carried out in one batch, $t_0 = 0$ and both M_0 (t_0) = M_2 (t_0) = 1. Then

$$M_0(t) = \frac{2}{t+2}; \quad M_2(t) = t + 1 \quad \text{and}$$
$$D_M = \frac{t}{t+2} + 1 \tag{14}$$

It is not difficult to see that the conversion degree of functional groups in the polymerization is simply:

$$p = 1 - M_0 = \frac{t}{t+2}$$

Step Copolymerization of A_3 + B_2 Monomers. Both the kinetic and statistical models of this polymerization, taking into account the first shell substitution effect are described in ref 11.

The Smoluchowski-type master equation reads

$$\frac{\partial H}{\partial t} = \left(axX + by\frac{\partial H}{\partial x} + \frac{\partial H}{\partial y}\right)\left(czY + \frac{\partial H}{\partial y}\right) - (X + H_x + H_y)\left(Y + cz\frac{\partial H}{\partial y}\right) - (Y + H_z)\left(X + ax\frac{\partial H}{\partial x} + by\frac{\partial H}{\partial y}\right) \tag{15}$$

where

$$H_\omega = \left(\frac{\partial H}{\partial \omega}\right)_{x=1/a;y=1/b;z=1/c}; \quad \omega = x,y,z \tag{16}$$

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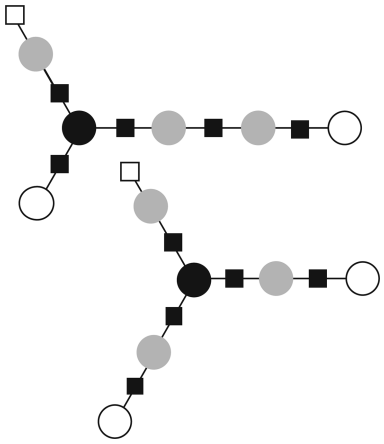

Figure 1. Two isomeric {2,3,1}-molecules sharing the same set of *i*, *j*, *k* parameters in eq 17. For an acyclic molecule the set of the three parameters defines the size *n* (degree of polymerization) of the molecule:[11] $n = 4i + 2j + 3k - 5$.

and the polynomial representation of the entire size distribution has the form

$$H(t,x,y,z) = X(t) + Y(t) + \Sigma_i^\infty \Sigma_j^\infty \Sigma_k^\infty C_{ijk}(t)[ax]^i[by]^j[cz]^k \quad (17)$$

where $X(t)$, $Y(t)$, and $C_{ijk}(t)$ are the concentrations of monomer A_3, monomer B_2 and polymer molecules sharing structural parameters *i*, *j*, and *k*, respectively (cf. Figure 1), *x*, *y*, and *z* are dummy variables, and $a = 2k_1/3k_0$, $b = k_2/3k_0$, $c = k'_1/2k'_0$ are the relative rate constants. More precisely, k_0, k_1, and k_2 are the contributions to rate constants for the reaction of functional groups from unsubstituted, mono- and disubstituted A_3 units, respectively, whereas k'_0 and k'_1 are those from the unsubstituted and monosubstituted B_2 units, respectively. The actual rate constants of reactions between units are the products of the respective contributions k_m and k_n' ($m = 0, 1, 2$; $n = 0, 1$) premultiplied by the stoichiometric numbers ($3-m$ and $2-n$). Thus, the rate constant for the reaction between two monomers is $k_{00} = 6k^*k_0k'_0$, between two monosubstituted units is $k_{11} = 2k^*k_1k'_1$, etc., with k^* being the substitution independent part of the rate constant. The product form of the rate constants is consistent with the assumption on the additivity of contributions from units to the activation energy of each individual elementary reaction step.[12] This product form greatly facilitates modeling the substitution effect, i.e. the form of a conversion dependence of the reactivity of functional groups. Only for the random reaction the values of all contributions k_0 through k'_1 are equal and taken to be 1. Since the monomers are considered 'symmetric', the physical significance of, e.g., $k_1 = 10$ is that each of the two functional groups in a monosubstituted A-type unit has the reactivity 10 times higher than that of either group in an unsubstituted A_3 molecule.

The zeroth and second "kinetic" moments of the molecular size distribution are expressed in terms of the combinations of the second and first derivatives of function *H* with respect to *x*, *y*, and *z* calculated at $x = 1/a$, $y = 1/b$, and $z = 1/c$. For evaluating the corresponding "statistical" moments, on the other hand, the first derivatives are sufficient.[11] The derivatives were calculated numerically using commercial software. The formulas used for calculating the moments are presented in Appendix.

Calculation Procedures Used in Modeling Polymerizations Carried out in Steps. For modeling polymerization of bifunctional monomer, the time or conversion dependence of the moments of molecular size distribution and dispersity were calculated using eqs 10, 13, and 14. The total of monomer was conceptually divided into portions of the same or different sizes. The moments were calculated for the first portion up to predetermined time or conversion degree at t_1. Then, the values of M_0 and M_2 were rescaled to accommodate new monomer portion, in the following way. Suppose, the total of monomer consisted of *m* equal portions. As the second portion was the same as the first one, the calculated moments had to be multiplied by $^1/_2$ and extra $^1/_2$ added, representing fresh monomer. The scaled moments were then the initial values in eqs 10 and 13, along with the new starting time, $t_0^{(2)} = t_1$. The moments were then calculated for the second portion, again up to predetermined time or conversion degree. For the $j+1$-th portion ($1 \le j \le m-1$), the moments used as the initial values were scaled according to the equation

$$M_*^{(j+1)}(t_0^{(j+1)}) = M_*^{(j)}\frac{j}{j+1} + \frac{1}{j+1}; \quad * = 0 \text{ or } 2 \quad (18)$$

On the other hand, the final results, shown in the graphs, had to be back scaled to represent the whole system, regardless of the monomer portion considered. Thus, in the system divided into *m* equal portions, the moments calculated for the *j*th portion, had to be recalculated according to the equation

$$M_*^{(j,scal)} = \frac{jM_*^{(j)} + m - j}{m} \quad (19)$$

The moments calculated for the last portion did not require the back scaling.

For the system with portions of sizes linearly increasing, it is not difficult to show that the moments used as initial values in eqs 10 and 13 had to be scaled according to

$$M_*^{(j+1)}(t_0^{(j+1)}) = M_*^{(j)}\frac{S_j}{S_{j+1}} + \frac{S_{j+1} - S_j}{S_{j+1}} \quad (20)$$

with $S_j = \Sigma_i^j i = 1 + 2 + 3 + \cdots + j$, whereas for linearly decreasing sizes of portions

$$M_*^{(j+1)}(t_0^{(j+1)}) = M_*^{(j)}\frac{S_{m-j+1}}{S_{m-j+1} + S_{m-j}} + \frac{S_{m-j}}{S_{m-j+1} + S_{m-j}} \quad (21)$$

The calculations for the systems of monomers $A_3 + B_2$ were carried out in analogous way. All systems were conceptually divided into 2 through 5 equal portions. The set of 12 differential equations for the concentrations of monomers $X(t)$ and $Y(t)$, functions $H_\omega(t)$ and $H_{\omega\varphi}(t)$ ($\omega, \varphi = x, y, z$) supplemented with $H_0(t)$ (cf. Appendix) was solved numerically for an appropriate vector of initial values, which for the first portion had the form: $\mathbf{y}^{T(1)}(t_0) = [X_0, Y_0, H_x^{(1)}, H_y^{(1)}, H_z^{(1)}, H_{xx}^{(1)}, H_{xy}^{(1)}, H_{xz}^{(1)}, H_{yy}^{(1)}, H_{yz}^{(1)}, H_{zz}^{(1)}, H_0^{(1)}]^T = [X_0, Y_0, 0,0,0,0,0,0,0,0,0,1]^T$, where X_0 and Y_0 are the mole fractions of monomers A_3 and B_2, respectively ($X_0 + Y_0 = 1$). For each portion of monomers, the moments were calculated up to a predetermined value of the conversion degree of minority groups. Then, the set of differential equations was solved again

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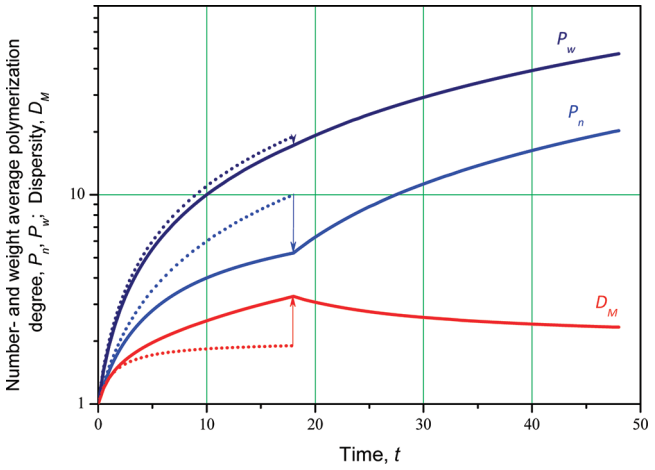

Figure 2. Number and weight-average polymerization degree, P_n, P_w, and dispersity D_M, calculated for the system where 10% of monomer was added to polymerization reactor after 90% of functional groups of the previous monomer portion have reacted. The dotted lines represent the values before scaling to the total amount of monomer.

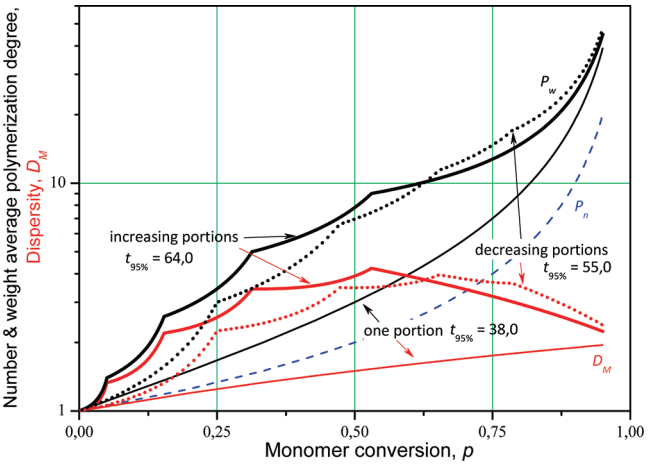

Figure 3. Weight-average polymerization degree, P_w, and dispersity D_M vs conversion calculated for polymerization carried out with monomer added in five linearly increasing (solid line) or linearly decreasing (dotted line) portions. Each next portion was added after 6 time units. The values for one-step reaction are plotted with thin lines. The number-average polymerization degree (thin broken line) is identical for all systems. The times to reach 95% of monomer conversion are also shown.

for new set of initial values. For the second portion of monomers, the new set of initial values was

$$\mathbf{y}^{T(2)}(t_0^{(2)}) = \frac{1}{2}\mathbf{y}^{T(1)}(t_1^{(1)}) + \frac{1}{2}[X_0, Y_0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1]^T \quad (22)$$

In fact the same scaling parameters were used as those given by eq 18, except that the whole vectors were scaled, rather than just moments. On the other hand, the back scaling was applied to the calculated moments. The procedure was stopped before reaching the predetermined conversion when the second moment of size distribution in the system diverged; i.e., within a small time interval the moments increased by several orders of magnitude. The conversion degree at that time was taken as the gel point. In the statistical calculations the gel point was defined as the conversion degree at which denominator in eq A10 in Appendix became zero.

RESULTS AND DISCUSSION

Linear Polymerization. The relationship between the extent of step polymerization and the size distribution of the resulting polymer molecules is well understood since the pioneering works of Flory.[7,22] While starting this work we did not anticipate finding a method of improving step polymerization procedures. We just expected to learn how the size distribution, expressed in terms of the dispersity, would change in the system where monomers were added in portions. And indeed, as will become clear later, the time needed to reach 95% monomer conversion in the model linear polymerization was the shortest when it was carried out just in one batch. Also the dispersity value was then the smallest. On the other hand, in the industrial synthesis of epoxy resins, some brands are 'improved' by adding a portion of both monomers: bisphenol A and epichlorohydrin to the condensation reactor soon before the synthesis is completed.

In Figure 2, the time dependence of the number- and weight-average polymerization degree is shown along with the dispersity for the system where the polymerization reaction was carried out for 18 time units, sufficient to reach 90% conversion of functional

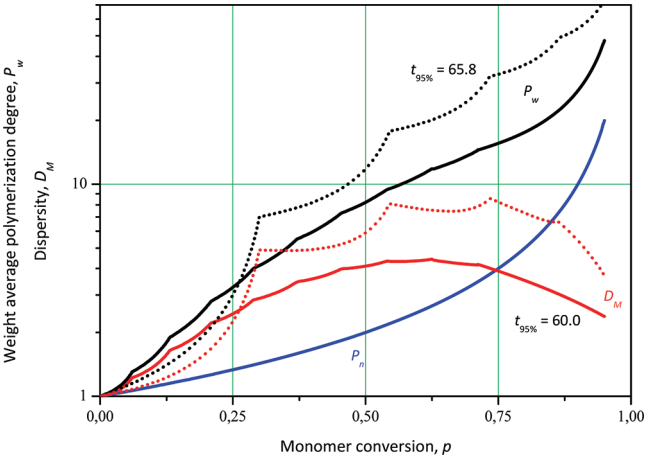

Figure 4. Weight-average polymerization degree and dispersity in two systems where monomer was divided into 10 equal portions and each next was added to the reactor after 3 time units (solid lines). The dotted lines represent the system divided into five portions of linearly decreasing size with each next introduced after 18 time units. In both cases the reaction involving the last portion was carried out up to monomer conversion 0.95. The total times of reactions are shown. As in all cases studied, the number-average polymerization degree depended on conversion in the same way.

groups. Then, extra monomer is added in the amount of 10% of the total. Note that the weight-average polymerization degree grows smoothly (in fact linearly with time) and both the number-average polymerization degree and dispersity have discontinuities. Note, however, that the heavier lines in Figure 2 represent the scaled values, i.e., the values related to the whole system. The nonscaled average degrees of polymerization calculated up to t_1 = 18 and the dispersity values are plotted using dotted lines. They were evaluated as if the reaction were carried out in one step. The values jump as indicated by arrows after fresh monomer has been added.

Similar observations were made with different feeding protocols. In Figures 3 and 4 the results are shown for systems with the

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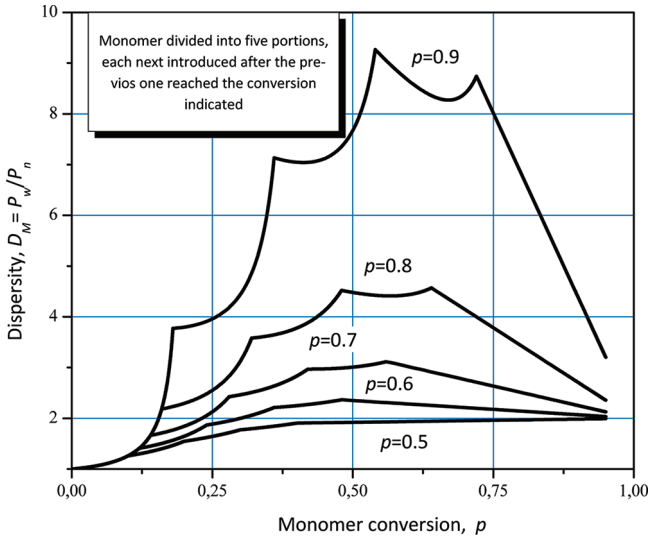

Figure 5. Dispersity ($=P_w/P_n$) of polymers obtained by step polymerization of a bifunctional monomer divided into five equal portions, each next introduced to the reactor after the previous portions reached the indicated value of conversion degree. The polymerization involving the last portion was carried out up to 95% conversion degree.

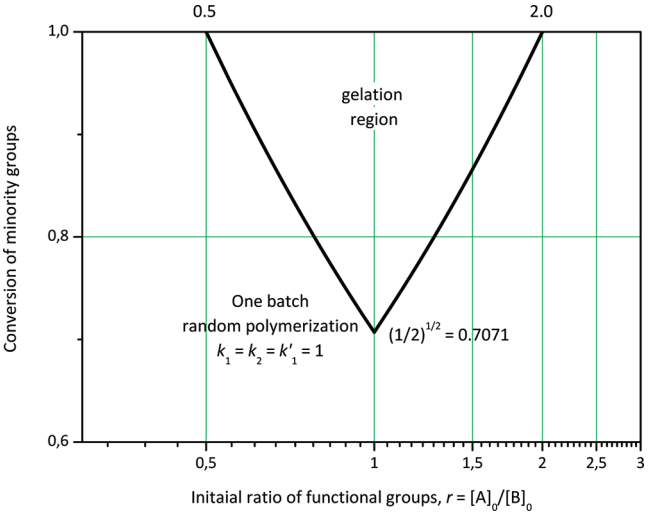

Figure 6. Boarders of gelation region, defining the range of conversion of minority functional groups in the random step polymerization of A3 and B2 monomers, where gel is produced, vs the initial ratio of reacting groups. The smallest conversion at the gel point is at the stoichiometric ratio of functional groups ($r = 1$). Formation of cycle closing links is excluded.

monomer dived into 5 or 10 portions of the same or different sizes each added after a predetermined time, the same in all protocols. After the last portion was added, the polymerization was carried out to reach 95% of monomer conversion. This time is also shown in the figures.

All the plots presented in Figures 3 and 4 look similar. The weight-average polymerization degree quite quickly increases at small conversion to grow more-less steadily at higher conversion. The dispersity, on the other hand, grows rapidly at small conversion, much quicker than in one step reaction, where it linearly changes with conversion ($D_M = 1 + p$). Then, after reaching a maximum, it starts to decrease. Only for the system shown in Figure 5, where each next portion of monomer was introduced after the conversion degree of all previously added monomer reached the value of 0.5, and the fifth step was continued out until $p = 0.95$, the dispersity did not decrease.

It is interesting that despite the way of introducing monomer into the reaction vessel the number-average polymerization degree changes with conversion always in the same way, thus confirming the validity of the Carothers equation:[23]

$$P_n = 1/(1-p) \qquad (23)$$

The most important conclusion, however, is that the dispersity can be reduced after a portion of fresh monomer is added. In the real polymerization systems, particularly with exothermic reaction steps and side products difficult to remove, some hard to control inhomogeneity in the polymerization reactor may occur. The method of adding the monomer in portions may be considered equivalent to the presence of regions in a polymerization system that differ in the extent of reaction. Should this occur, an efficient method of reducing dispersity in the product seems to be adding an extra portion of fresh monomer at the final part of the process.

Forced Gelation. Explaining the polymerization leading to branched polymer systems and to gelation was another fundamental achievement of Flory in the early days of polymer science.[24] The models of Flory, however, both dealing with the linear[22] and branched systems, use statistical arguments and well describe the polymerization processes in which equilibrium establishes between formation and breaking the bonds linking units.[25] On the other hand, the kinetic models, developed in the 1980s[26,27] are appropriate for polymerization processes with irreversible elementary reaction steps. The distributions calculated by using the two approaches are in fact identical, unless there is a conversion dependent change in the reactivity of functional groups, e.g., in the form of a substitution effect.

The aim of this part of work was to show that in step polymerization leading to branched systems, namely in the polymerization of A_3 and B_2 monomers, gelation may eventually occur, even if the (off-stoichiometric) composition of the monomer mixture does not justify gel formation. The gel point is defined as the conversion degree at which the weight-average polymerization degree diverges.[28,29] The number-average, though, remains finite at the gel point.[24] In the model polymerization of A_3 and B_2 monomers, the other factor affecting the gel point conversion is the initial molar ratio of functional groups, $r = [A]_0/[B]_0$ (cf. ref 7). The range of r values in which gelation occurs in the random polymerization is shown in Figure 6. The model random polymerization is considered, i.e., the process where no cycle-closing links are allowed and all A and B groups react with each other at the same rate, irrespective of the reaction progress. For this idealized systems both statistical and kinetic calculations produce the same results. Very recently the critical molar ratios were determined experimentally for Michael addition networks.[30] These critical ratios determine the boarders of the gelation region for different step-growth branching systems.

The shape and surface area of gelation region changes with the values of the relative reactivities of functional groups. By using eq 15 one can calculate the boarders of gelation region both by using kinetics or statistical approach for different values of the rate constants, k_1, k_2, and k'_1 representing the first shell substitution effect, at which the functional groups react. Except for the random case, shown in Figure 6, the gelation boarders are slightly different when calculated with either of these two methods,

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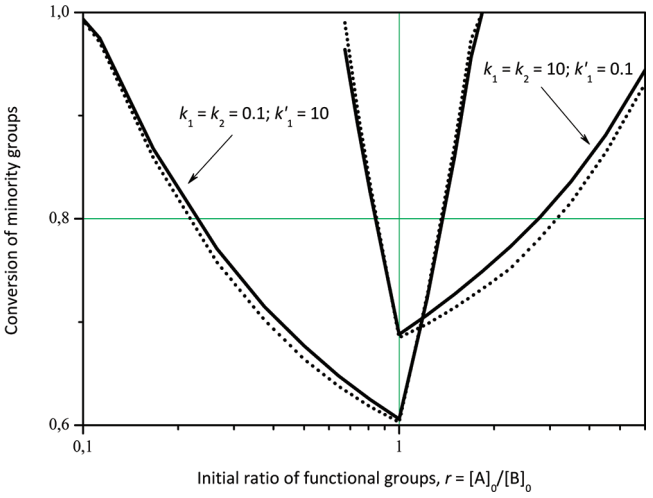

Figure 7. Gelation regions for $A_3 + B_2$ polymerization systems reacting with substitution effect characterized by the sets of relative rate constants, shown in the plot. The solid and dotted lines represent kinetic and statistical calculations, respectively.

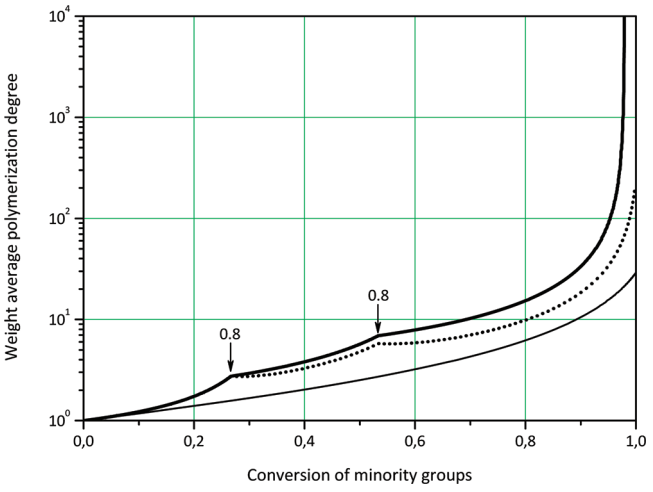

Figure 8. Calculated and scaled for the whole system the weight-average polymerization degree of branched polymer obtained by polymerization of the $A_3 + B_2$ system at nonstoichiometric ratio of functional groups $[A]_0:[B]_0 = 2.25$. The thin line represents calculations for a one batch system. The heavy solid and dotted lines were calculated by using kinetic and statistical approach, respectively, for the system divided into three equal portions, each next introduced after the previous reached the conversion of B groups equal 0.8.

provided the substitution effects are not extremely large (values of the constants not much deviating from unity) cf. Figure 7.

As shown in Figure 6, in the random process the gel should not form for a monomer mixture at the initial ratio of functional groups exceeding 2.0 (or smaller than 0.5). If, however, the mixture is divided into, say, three equal portions, and each next is added after the previous portions reached certain degree of conversion, the gelation does occur as manifested by divergence of the weight-average polymerization degree. It is illustrated in Figure 8, where the weight-average degree of polymerization is plotted versus conversion of B groups for the system with $[A_3]:[B_2] = 3:2$, i.e. with $r = [A]_0:[B]_0 = 9:4 = 2.25$, beyond the gelation region for the random system.

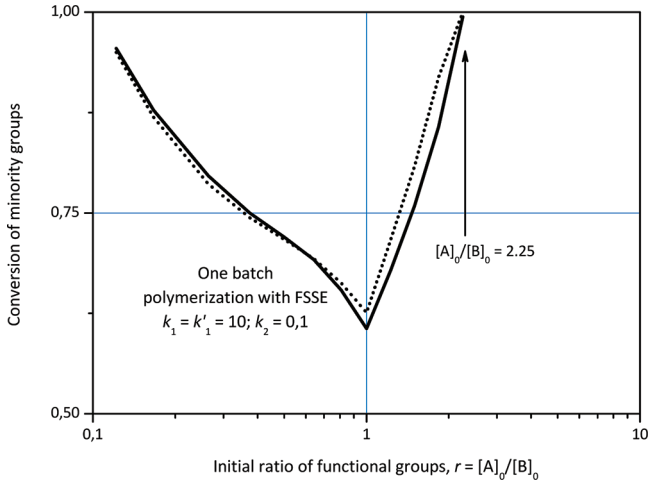

Figure 9. Gelation regions for $A_3 + B_2$ polymerization systems reacting with substitution effect characterized by the sets of relative rate constants, shown. The solid and dotted lines represent kinetic and statistical calculations, respectively.

Table 1. Gel Point Conversions As Calculated Using the Kinetic Method, for the Mixture of A_3 and B_2 Monomers, Reacting with the Set of Relative Rate Constants: $k_1 = k'_1 = 10$; $k_2 = 0.1$, at the Initial Mole Fraction of A Groups Equal to 0.602[a]

	conversion at next feeding				
no. of portions	0.5	0.6	0.7	0.8	0.9
5	0.940	0.884	0.734	-	-
4	0.950	0.909	0.816	-	-
3	0.963	0.937	0.884	0.765	-
2	0.979	0.966	0.943	0.905	0.818

[a] The values in the first row are the conversions of the minority groups (B in this case) at which the next portion of monomers was introduced.

The off-stoichiometric system reacting with FSSE and the set of relative rate constants $k_1 = k'_1 = 10$; $k_2 = 0.1$ (cf. Figure 9) was studied in greater details. The gel points calculated for the systems with the initial monomer ratio $[A3]_0:[B2]_0 \approx 3:2$, more precisely, at mole fraction of A equal to 0.602 and divided into 2, 3, 4, or 5 equal portions are presented in Table 1. The value of 0.602 was chosen as laying just outside the gelation region for the system. As one can see, according to kinetic calculations, the system does gel in all instances of dividing the monomer mixture into portions. The higher was the monomer conversion at the next feed, the lower was the gel point conversion. It can also be clearly seen that into more portion the monomer mixture was divided, the lower was the gel point. In the statistical calculations for the same system, the gel point was predicted at very high conversions only when four or five portions were introduced after the previous ones reached conversion of 0.9. The "statistical" gel points were at 0.988 and 0.977, respectively. Another conclusion is that the kinetic calculations for the system in question predict substantially lower gel point conversions than the statistical ones, although the gelation regions predicted by the two approaches are similar in shape (Figure 9).

The behavior of the nongelling systems divided into portions introduced to the reactor each next after the previous one reached

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certain conversion of minority groups is not difficult to explain. When polymerized in one batch all molecules grow in more-less uniform manner, until nearly all minority groups are consumed. Branched molecules are formed that have no chance to interconnect into a giant molecule. The situation changes when new monomer portion is introduced into the system already containing branched molecules. The bigger is the molecule the higher is the chance of its functional groups to capture fresh monomer. The big and branched molecules grow faster than small and linear ones. This seems to be the main reason for the gelation forced upon the nongelling system by dividing it into portions.

It is interesting that in nonstoichiometric nongelling systems with an excess of bifunctional monomer, gelation could not easily be attained in the similar way. In the system reacting with the set of relative rate constants: $k_1 = k_2 = 10$; $k'_1 = 0.1$, the calculations made for the system with $[A_3]_0$: $[B_2]_0 = 3$: 7 ($r = 0.643$), i.e., just outside its gelation region (cf. Figure 7), did not produced gel in any attempt with monomer mixture divided into equal portions.

Here, the reason might be that the molecules were not sufficiently branched and, hence, large molecules could not capture fresh monomer quicker than smaller ones.

To summarize, the portions of fresh bifunctional monomer added to a polymerization reactor where the same monomer reached already certain degree of conversion, tends to reduce the dispersity expressed in terms of the ratio of polymerization degrees. On the other hand, the nongelling combination of A_3 and B_2 monomers can be forced to gel by dividing it into portions introduced one at a time. It is particularly evident for the mixture with an excess of A_3 monomer. This means that in this case the feeding procedure tends to increase the dispersity of the polymer system indefinitely.

One should bear in mind, however, that possible cycle formation in the polymerization leading to branched systems were disregarded. Hence, particularly for the systems with the gel points calculated at the level of 0.9 or higher, one cannot exclude that due to intramolecular cyclization no gel will be obtained while trying to verify the calculations experimentally.

APPENDIX

The set of 12 ordinary differential equations necessary to evaluate the moments of size distribution of polymer molecules formed by polymerization of $A_3 + B_2$ monomers is derived in the following way.[11] In terms of the notation used in the paper, the equations describing the rate at which monomers vanish from the system are:

$$\frac{dX}{dt} \equiv \dot{X} = -X(Y + c\Sigma_{i,j,k} kC_{i,j,k}) = -X(Y + H_z) \quad (A1)$$

and

$$\dot{Y} = -Y(X + H_x + H_y) \quad (A2)$$

with H_ω; $\omega = x, y, z$ is defined by eq 16.

The ordinary differential equations describing the time evolution of H_ω are available by successive differentiation of eq 15 with respect to the dummy variables, x,y and z followed by setting $x =$. Thus

$$1/a; \quad y = 1/b; \quad z = 1/c$$

$$\dot{H}_x = -a(H_x - X)(Y + H_z) \quad (A3)$$

Table 2. Functions Appearing in Equation A6

ω	φ	$P_{\omega\varphi}$	$Q_{\omega\varphi}$	R_ω	S_ω
x	x	$-2aH_{xx}$	0	$aX + H_{xx} + H_{xy}$	H_{xz}
x	y	$bH_{xx} - (a + b)H_{xy}$	0		
x	z	$-aH_{xz}$	$-cH_{xz}$		
y	y	$2b(H_{xy}-H_{yy})$	0	$bH_x+HX_y+H_{yy}$	H_{yz}
y	z	0	$-cH_{yz}$		
z	z	0	$-2cH_{zz}$	$H_{xz} + H_{yz}$	$cY + H_{zz}$

$$\dot{H}_y = -b(H_y - H_x)(Y + H_z) \quad (A4)$$

$$\dot{H}_z = -c(H_z - Y)(X + H_x + H_y) \quad (A5)$$

Similarly, the functions $H_{\omega\varphi}$; $\omega, \varphi = x, y, z$ become available by solving ordinary differential equations derived by differentiating eq 15 twice with respect to dummy variables and putting $x = 1/a$, $y = 1/b$, and $z = 1/c$. The resulting six formulas are

$$\dot{H}_{\omega\varphi} = P_{\omega\varphi}(Y + H_z) + Q_{\omega\varphi}(X + H_x + H_y) + R_\omega S_\varphi + R_\varphi S_\omega \quad (A6)$$

with the functions P, Q, R, and S presented in Table 2

Finally, by setting $x = 1/a$; $y = 1/b$; $z = 1/c$ directly into eq 15 one gets:

$$\dot{H}_0 = -(Y + H_z)(X + H_x + H_z) \quad (A7)$$

The last equation yields H_0, the value equal to the zeroth moment of distribution. The second moment is calculated following the definition:

$$M_2 = X + Y + \Sigma_{i,j,k}(4i + 2j + 3k - 5)^2 C_{ijk} \quad (A8)$$

since the term in parentheses corresponds to the size of molecules sharing the set of parameters i, j, and k. When raised to the power, the individual terms can be expressed by the functions H_0, H_ω, and $H_{\omega\varphi}$.

The moments of size distribution can alternatively by calculated using the statistical cascade theory. The appropriate equations for the system $A_3 + B_2$ were also derived in.[11] They are expressed in terms of the functions H_0 and H_ω, only. The equations read:

$$M_0 = 1 - \frac{1}{2}(F^B_{0A}X_0 + F^A_{0B}Y_0) \quad (A9)$$

$$M_2 = 1 + \frac{F^B_{0A}(F^A_{1B} + 1)X_0 + F^A_{0B}(F^B_{1A} + 1)Y_0}{1 - F^B_{1A}F^B_{1B}} \quad (A10)$$

The terms appearing in the right-hand-side of A9 and A10 are

$$F^B_{0A}X_0 = 3X_0 - 3X - 2\frac{H_x}{a} - \frac{H_y}{b} \quad (A11)$$

$$F^B_{0A}Y_0 = 2Y_0 - 2Y - \frac{H_z}{c} \quad (A12)$$

$$F^B_{1A} = \frac{4 - 10X - 15H_x - 20H_y}{2 - 5(X - H_x - H_y)} \quad (A13)$$

$$F^A_{1B} = \frac{3 - 5Y - 10Hz}{2 - 5(Y - H_z)} \quad (A14)$$

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