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Highly-branched off-stoichiometric functional polymers as polymer networks precursors

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Affectionatelly dedicated to Professor J.E. Mark on the occasion of his 70th birthday.

Abstract

Formation of highly-branched off-stoichiometric polymers from $A_x + B_y$ monomers has been described theoretically using a statistical branching theory in which the irreversibility of bond formation was respected. The critical molar ratio (CMR) of A to B groups, i.e., such excess of groups of one type beyond which the system does not gel and only soluble highly-branched polymers are formed, was calculated. CMR depends on the functionality of the components and on the reactivity of functional groups involved in formation of bonds. For an increasing excess of A groups over B groups, soluble A-functional polymers of decreasing molecular weight are formed. When monofunctional monomer is added, the number-average molecular weights and degrees of polymerization as well as the number of functional groups per molecule remain relatively low even at the CMR when the gel point is reached. When one A group in the A3 monomer has higher reactivity than the remaining two and also in B2 where the reactivities of B groups are different, the value of CMR decreases from 2 towards 1.5, which is the limiting case. Important is that with increasing differences in reactivity the range of molecular weights can be extended and the polydispersity can be suppressed. Functional highly-branched polymers of reasonable molecular weight and polydispersity can be obtained, which in their application can compete with conventional hyperbranched polymers. The use of the information obtained in this description of crosslinking of the highly-branched off-stoichiometric polymers is outlined.

Keywords: Functional polymer; Hyperbranched polymer; Polydispersity

1. Introduction

Polymer networks are prepared from precursors, i.e. compounds carrying functional groups capable of bond formation. Their functionality or functionality distribution must be such that the system gels and a network is formed. Some of the precursors are simple chemical compounds, some others are specially designed functional structures (oligomers), and yet others are mixtures of compounds of varying functionality and molecular weight [1]. Low-molecular-weight functional copolymers or hyperbranched functional polymers obtained from AB_f monomers can serve as examples of such polydisperse precursors.

For alternating $A_{fA} + B_{fB}$ systems (groups A and B give bonds A–B), the earliest gelation and maximum crosslink density is obtained in stoichiometric systems. That in off-stoichiometric systems the gel point is shifted to higher conversions of the minority groups has been recognized since the derivation of the gelling condition [2]. However, this phenomenon was employed much later in experimental and theoretical studies as well as in practical applications. Some producers of two-component epoxy-amine adhesives used empirically the pre-reaction of a polyamine in large excess with a diepoxide to increase the viscosity of the amine hardener and to lower its vapor pressure. Later on, the off-stoichiometry effect was used in epoxy-amine and polyol-polyisocyanate systems to control the crosslink density [3–10]. The critical molar ratio (CMR) of A:B or B:A groups was defined [3] as the molar ratio at which gelation took place at full conversion of minority groups and beyond which the gel point could not be reached at all and only soluble branched polymers were formed. The CMR

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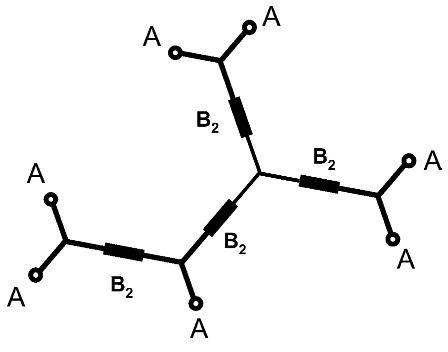
values can be obtained experimentally very easily. These values were discussed in terms of reactivity of functional groups and intensity of cyclization reactions. For instance, the shift of CMR of diepoxide-diamine systems could be explained by the differences in reactivity of primary and secondary amino groups in aliphatic and aromatic curing agents [5,11].

The increasing interest in off-stoichiometric highly-branched polyfunctional polymers in recent years [12–29] has been induced by the development of hyperbranched polymers synthesized by A + B → AB polymerization of AB_f or BA_f monomers. Here, we will be using the abbreviation BA_f (e.g., BA_2) to keep correspondence with the A3–B2 systems. The structures of the highly-branched polymers obtained by $A_{fA}+B_{fB}$ reaction and classical hyperbranched polymers prepared from BA_f monomers are basically not different. Scheme 1 shows one of the distributions of functional highly-branched molecules obtained from A3 to B2 monomers bearing unreacted A groups.

The generally lower price of starting components of X_f type compared to BA_f monomers and the wide range of variation of architecture of group-bearing scaffold X makes the off-stoichiometric highly-branched polymers especially attractive. There is, however, a distinct difference between the two classes: The hyperbranched systems bearing only one focal group do not gel unless side reactions interfere, but the system $A_{fA}+B_{fB}$ does gel in the window of molar ratios of functional groups below the critical values, $(r_A)_{crit}$ or $(r_B)_{crit}$. This is, however, not the only difference. As we shall see later, there is a distinct difference in the dependence of weight-average molecular weight or polydispersity on the number average molecular weight.

Several chemically different off-stoichiometric highly-branched polymers have been investigated so far. The main emphasis of experimental as well as theoretical studies was concentrated on the degree of branching (DB); the key quantity used for classical BA_f hyperbranched polymers that determines compactness of the molecules. Important predictions about the effect of group reactivity and polymerization regime on DB were made recently [21] using kinetic method originally developed for the study of DB of classical hyperbranched polymers [30,31].



Scheme 1.

In this contribution, we have focused on structure of the off-stoichiometric highly-branched molecules designed for their application as polymer networks precursors. We have investigated theoretically the gelation limits and development of molecular weight and functionality averages as a function of initial composition and functional groups reactivity. The use of information obtained for description of the network formation process is also discussed.

2. Modeling of formation of highly-branched off-stoichiometric polymers

For modeling of generation of branched structures, the statistical theory of branching processes based on cascade substitution and employing the formalism of probability generating functions were used. This approach has been applied to a variety of systems and branching problems before (cf., e.g., Refs. [1,3–10]). In its ring-free version, this approach does not consider formation of cycles before the gel point, but does take into account uncorrelated circuit closing beyond the gel point. The statistical approach is rigorously applicable to systems without long-range stochastic correlations and also, as was proved experimentally, for many kinetically controlled systems, where the stochastic correlations are not too strong (e.g., epoxide or polyurethane networks [5,10]). Furthermore, the formalism give easy access to various averages and the relations are pre-prepared for the description of a crosslinking process when these highly-branched functional polymers are further crosslinked (cf., e.g., Ref. [32]). Here, we will be considering primarily non-reacting systems, with only one type of group, the other being completely consumed. However, the treatment and the relations derived below allow for characterization of 'live' systems containing both unreacted groups A and B.

The plan for the analysis of formation and distributions of the off-stoichiometric highly-branched functional polymers is as follows:

1. To calculate the gelation limits in terms of critical molar ratios (CMR) of A to B groups.
2. To calculate the dependence of number- and weight-average molecular weights and, possibly, first and second moments of functionality distributions as a function of initial molar ratios of A to B groups beyond CMR and to compare the correlations between polydispersity and number-average molecular weight or conversion of functional groups.

Here, we have analyzed the A3 + A1–B2 systems with equal reactivity of all A and all B groups, respectively, and A3 − B2 systems with groups of different reactivity. The derivation of the respective equations is explained in the Appendix A.

The structure of A3 + A1 − B2 systems was analyzed in detail in the post gel region in terms of sol fraction, dangling chains, and elastically active network chains [33]. In the Appendix A, the system A3+A1−B2 is described by Eqs. (A1)–(A21).

The boundary between gelling systems and region of branched polymers is determined by the critical value of the molar ratio of A:B functional groups, r_A, i.e., by $(r_A)_{crit} = ([A]_0/[B]_0)_{crit}$ (Eq. (A6))

$$(r_A)_{crit} = x_{Af}(f_A - 1) \tag{1}$$

where f_A is the functionality of Af monomer ($f_A = 3$ in our case), x_{Af} is the fraction of groups of the Af monomer in mixture with the A1 monomer.

The number-average molecular weight of the highly-branched polymer was calculated by Eq. (A8)

$$M_n = \frac{n_{A1}M_{A1} + n_{Af}M_{Af} + n_{B2}M_{B2}}{1 - 2\alpha_B n_{B2}} \tag{2}$$

where n_{A1}, n_{Af}, n_{B2} are molar fractions of components indicated, and M_{A1}, M_{Af}, M_{B2} their molecular weights. The molar fractions, n, can be expressed through molar ratio r_A and x_{Af} or ratio of groups A in mono- (s_{A1}) and polyfunctional (s_{Af}) component, respectively, as is shown in the Appendix A. When the reaction goes to completion, as is usually the case, the conversion of B-groups, α_B, reaches unity.

The weight-average molecular weight is given by Eq. (A13), which, after substitution for the values of derivatives of u gives for $\alpha_B = 1$ ($\alpha_A = 1/r_A$) the relation

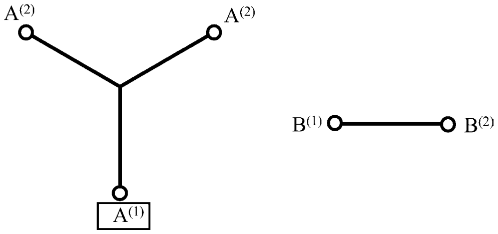
$$\begin{aligned} M_w = {} & m_{A1}M_{A1} + m_{Af}\left[M_{Af} + \frac{f_A(M_{B2} + M_A)}{1 - x_{Af}(f_A - 1)/r_A}\right] \\ & + m_{B2}\left[M_{B2} + \frac{2[M_A + M_{B2}x_{Af}(f_A - 1)/r_A}{1 - x_{Af}(f_A - 1)/r_A}\right] \end{aligned} \tag{3}$$

where $m_{A1} = n_{A1}M_{A1}/S$, $m_{Af} = n_{Af}M_{Af}/S$, $m_{B2} = 1 - m_{A1} - m_{Af}$; $S = n_{A1}M_{A1} + n_{Af}M_{Af} + n_{B2}M_{B2}$ are mass fractions of the components. The first-moment and second-moment average functionalities of the highly-branched polymer are given by the following relations (cf. Eqs. (A16)–(A21))

$$\langle f_A \rangle_1 = \frac{(1 - 1/r_A)(f_A n_{Af} + n_{A1})}{1 - 2n_{B2}} \tag{4}$$

$$\begin{aligned} \langle f_A \rangle_2 = {} & n_{Af}f_A\left[1 - \frac{1}{r_A} + \frac{x_{Af}(f_A - 1)(1 - 1/r_A) + 1}{r_A(1 - x_{Af}(f_A - 1)/r_A)}\right] \\ & + n_{A1}\left(1 - \frac{1}{r_A}\right) \\ & + 2n_{B2}\frac{x_{Af}(f_A - 1)(1 - 1/r_A) + 1}{1 - x_{Af}(f_A - 1)/r_A} \end{aligned} \tag{5}$$

A+B polyfunctional systems with groups of different reactivity have higher potential to offer highly-branched polymers of increased molecular weight and functionality.



Scheme 2.

Of the wide variety of combinations of reactivity differences, we have investigated the case, where the A3 molecule has one group of higher reactivity than the remaining two and also the two B groups in B2 component have different reactivity (Scheme 2).

For instance, the $A^{(1)}$ group is (much) more reactive than the other two $A^{(2)}$ groups and the same is valid for groups $B^{(1)}$ and $B^{(2)}$. Such situation arises in the case when two functional groups of different reactivity are involved such as the amine and hydroxy groups in diethanolamine or diisopropylamine [22]. Also, a number diisocyanates have groups of different reactivity.

Such A3−B2 system treated in Section A.2 of the Appendix A is theoretically more complex than the relatively simple A1+A3−B2. The simplicity of the latter system is in the randomness of the reaction (equal and independent reactivity of functional groups). It has been shown that the solution obtained by application of statistical theory is identical with the results of exact kinetic theory (cf., e.g., [34,35]). In our case, it is easy to distinguish between conversions of different functional groups existing in the system. However, the bond assemblage procedure must guarantee the irreversibility of formation of bonds of the given type. We have used an approach based on first-order irreversible Markovian process where the (eight) transition probabilities are calculated from fractions of dyads of reacted groups (four dyads). The transition probabilities (Eq. (A33)) are functions of overall reaction conversion and are obtained by numerical solution of a system of differential equations for reacted groups dyads. This is described in the Appendix A by Eqs. (A31)–(A32). The transition probabilities are then used in the branching process (Eqs. (A22)–(A30)). The basic *pgf* is described by Eq. (A22)

$$\begin{aligned} F_{0n}(\mathbf{Z}, \mathbf{z}) = {} & n_A Z_A^{M_A}[(1 - \alpha_{A1})Z_{A1unr} + \alpha_{A1}\xi_{1B}] \\ & \times[(1 - \alpha_{A2})Z_{A2unr} + \alpha_{A2}\xi_{2B}]^2 + n_B Z_B^{M_B}[(1 - \alpha_{B1}) \\ & \times Z_{B1unr} + \alpha_{B1}\xi_{1A}][(1 - \alpha_{B2})Z_{B2unr} + \alpha_{B2}\xi_{2A}] \end{aligned} \tag{6}$$

$$\xi_{1A} = p_{A1B1}z_{A1B1} + p_{A1B2}z_{A1B2} \quad \xi_{2A} = p_{A2B1}z_{A2B1} + p_{A2B2}z_{A2B2}$$
$$\xi_{1B} = p_{B1A1}z_{B1A1} + p_{B1A2}z_{B1A2} \quad \xi_{2A} = p_{B2A1}z_{B2A1} + p_{B2A2}z_{B2A2}$$

Eight types of (oriented) bonds are described by the vector $\mathbf{z} = (z_{A1B1}, z_{A1B2}, z_{A2B1}, z_{A2B2}, z_{B1A1}, z_{B1A2}, z_{B2A1}, z_{B2A2})$, which corresponds to the same number of *pgf*'s $\mathbf{F}=(F_{A1B1},F_{A1B2},F_{A2B1},F_{A2B2},F_{B1A1},F_{B1A2},F_{B2A1},F_{B2A2})$ (Eq. (A23)). The gel point condition is determined by 8×8 determinant (Eqs. (A24) and (A25)). Because two components participate in the structure build-up, the weight-average molecular weight is calculated by differentiating the weight-fraction generating function with respect to *pgf* variables Z_A and Z_B that identify the property of the building unit (here, its molecular weight). Thus, M_w is determined by 16 values of derivatives, which are determined by 16 linear equations (A30). Due to extensive degree of degeneration, the arithmetic relations are of reasonable complexity.

3. Results and discussion

It is obvious that in the ideal A3−B2 system the critical molar ratios $(r_A)_{crit}=2$(excess of A groups) or $(r_A)_{crit}=1/2$(excess of B groups). Addition of a monofunctional compound shifts the critical molar ratio from 2 to lower values and eventually the system stops gelling at molar ratios equal to one. The dependence of $(r_A)_{crit}$ vs. x_{Af} is shown in Fig. 1

The system stops gelling when the numbers of A-groups (not molecules) of mono- and trifunctional components are equal. Addition of monofunctional components makes the system 'safer' against possible gelation but, as we shall see, other properties important for network formation are also affected. It can be seen that the number-average molecular weights remain rather low even at the onset of gelation when the weight-average molecular weight diverges (Fig. 2).

However, the molecular weights of such precursors of 1200–1400 corresponding to number-average degree of polymerization of about 4 are still in the range interesting for certain applications. Better insight into the problem shows Fig. 3 and the functionality averages shown in Fig. 4. Products with reasonable polydispersity and molecular weight are obtained when the modification with A1 is small ($s_{A1}=0.05$, 0.1)

The number-average functionality has reasonable values of about 3 for modification with 10–20% monofunctional component. At higher fractions of the monofuctional component, the molecular weight as well as the number-average functionality decreases with decreasing r_A and a non-negligible amount of zero-functional molecules is produced. Using the Af monomer of higher f_A does not help much because one has to work with higher excess of A

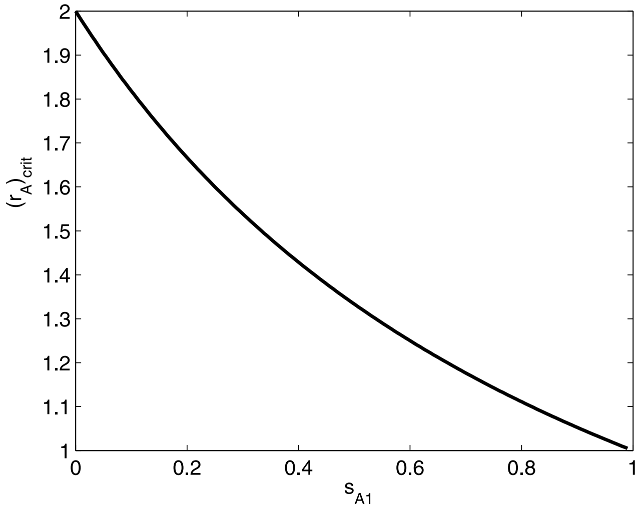


Fig. 1. A3+A1−B2 equireactive systems: dependence of critical molar ratio $(r_A)_{crit}$ on the ratio of A groups of monofunctional component (N_{A1}) to groups of the f_A-functional component (f_AN_{Af}), $s_{A1}=N_{A1}/f_AN_{Af}$.

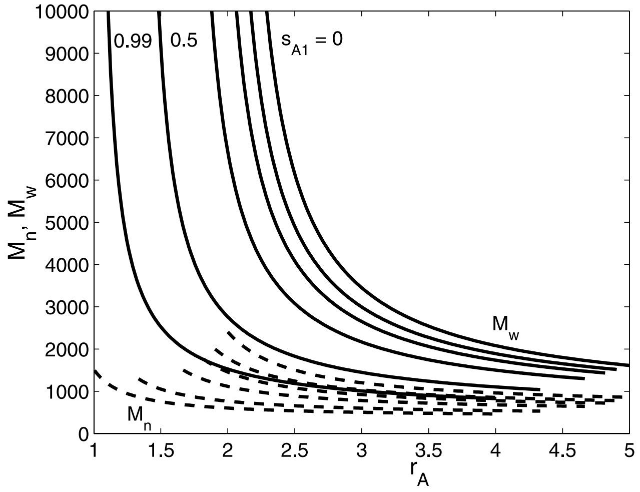


Fig. 2. A3+A1−B2 equireactive systems: dependence of the number-average (dashed line) and weight-average (full line) molecular weight on the ratio of A to B groups, r_A; for various contents of the monofunctional component s_{A1} (=0, 0.05, 0.1, 0.2, 0.5, 0.99 from right to left) ($M_{A1}=300$, $M_{A3}=600$, $M_{B2}=400$).

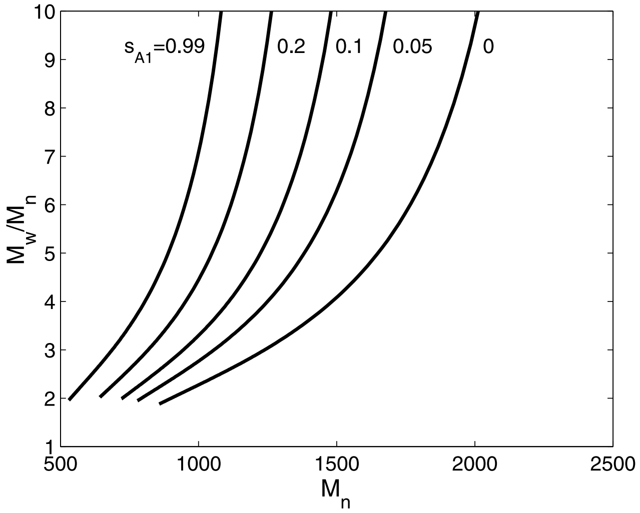


Fig. 3. A3+A1 and B2 equireactive systems: interdependence of polydispersity ($PD=M_w/M_n$) and M_n for the molar ratios of the groups of monofunctional to trifunctional monomers, s_{A1} indicated; ($M_{A1}=300$, $M_{A3}=600$, $M_{B2}=400$).

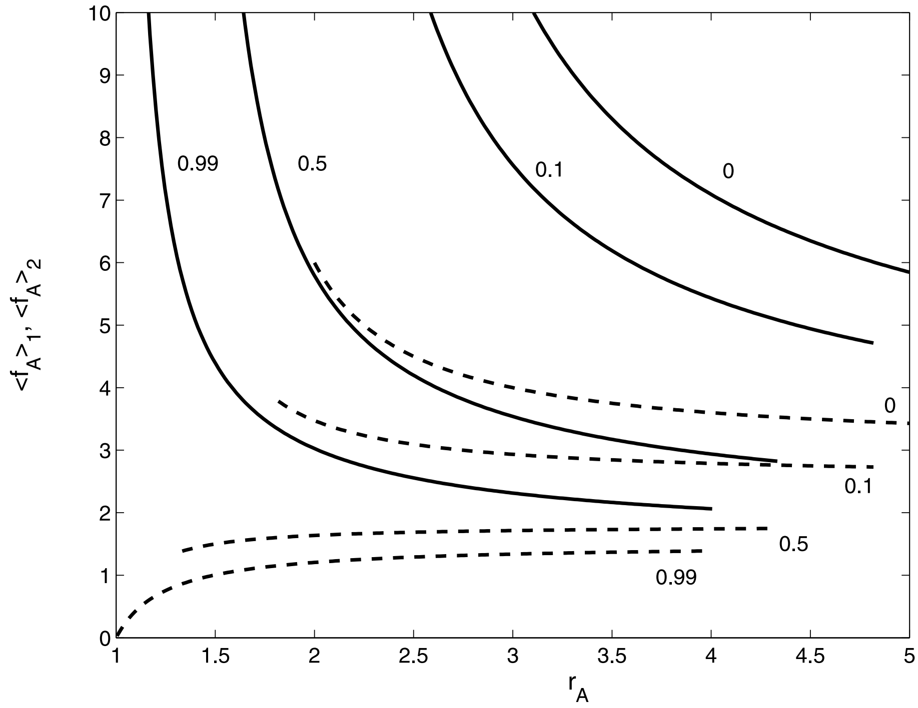


Fig. 4. A3 + A1 and B2 system: functionality averages $\langle f_A \rangle_1$ (dashed) and $\langle f_A \rangle_2$ in dependence on the ratio of A to B groups, r_A, for different ratios of groups of monofunctional to trifunctional monomers, s_{A1} (0, 0.1, 0.5, 0.99 indicated).

groups to get the same polydispersity. The values of M_n for the same polydispersity are even smaller.

Summarizing, highly-branched A-functional polymers from polyfunctional A–B monomers with equireactive groups have only a limited application value. The main disadvantage is a relatively low number-average molecular weight at a composition at which M_w starts growing rapidly and approaching the gel point. However, about 60–70% potential bonds in the system can be preformed and M_n can increase by a factor of 3–5. This can be technologically

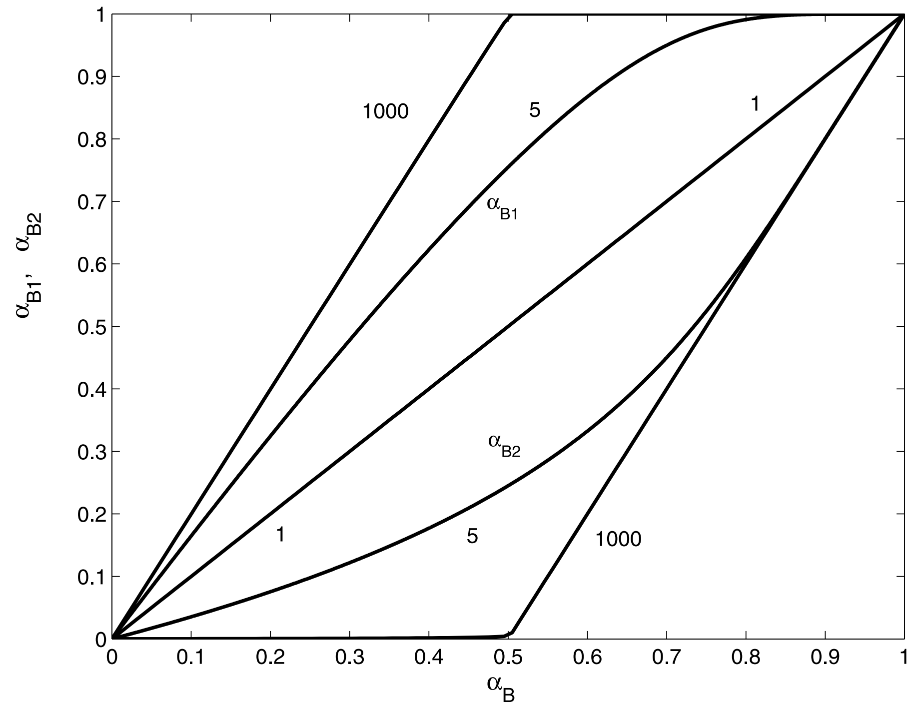


Fig. 5. Dependence of conversions of groups $B^{(1)}$ and $B^{(2)}$ on overall conversion of B groups for values of reactivity ratios $\kappa_A^+ = \kappa_B^+$ indicated.

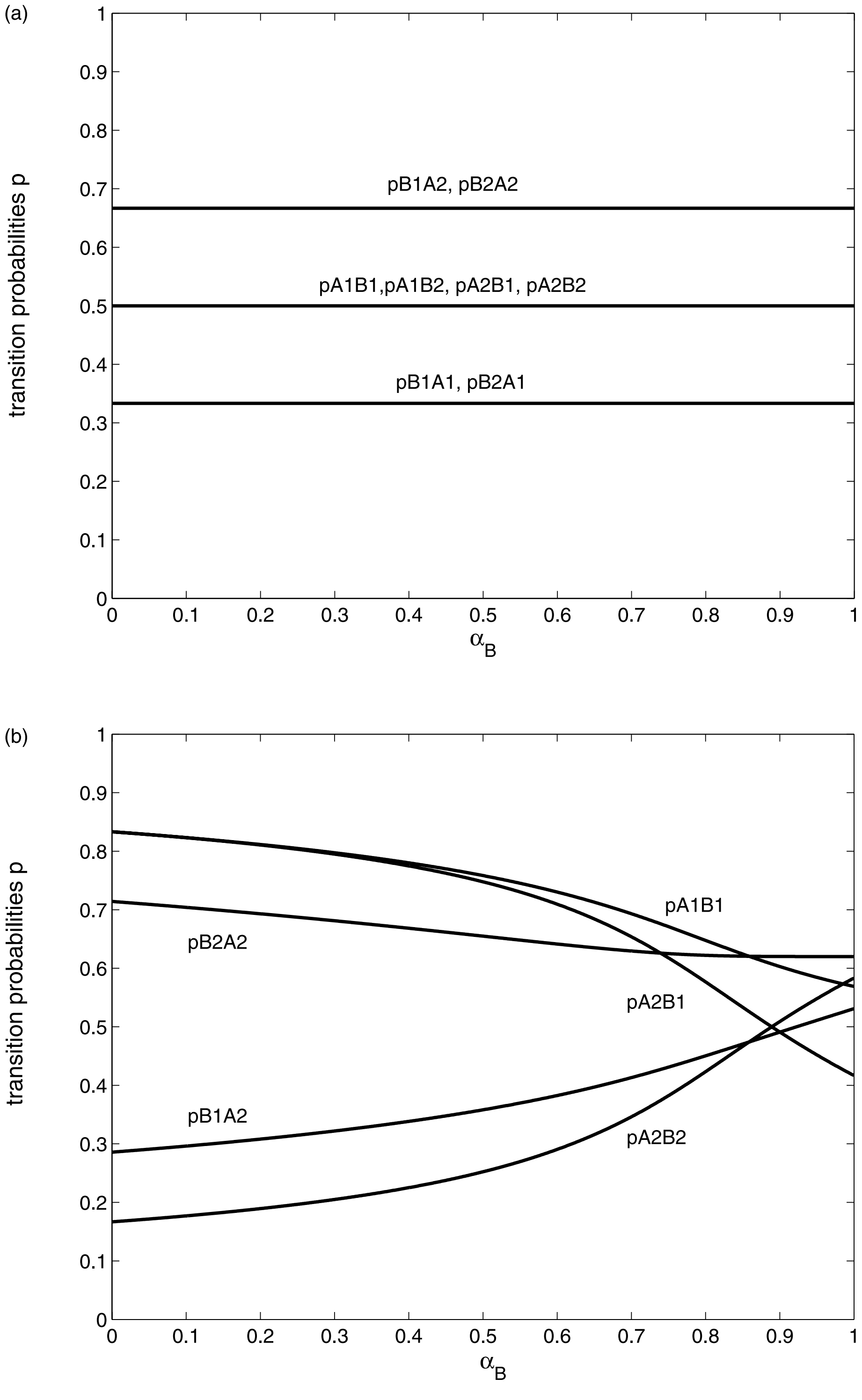


Fig. 6. (a)–(c) Dependence of selected transition probabilities for bonds $p_{\mathrm{X}i\mathrm{Y}j}$ extending from group Xi to group Yj ($p_{\mathrm{X}i\mathrm{Y}1}+p_{\mathrm{X}i\mathrm{Y}2}=1$) for the following values of $\kappa_{\mathrm{A}}^{+}=\kappa_{\mathrm{B}}^{+}$: 6A 1, 6B 5, 6C 1000.

(viscosity adjustment, lowering of shrinkage) and environmentally (lowering of VOC and toxic emissions) important.

The A3−B2 systems offer much more versatility when adjusting the groups reactivity. The system investigated here can be denoted as $\mathrm{A}_1^{(1)}\mathrm{A}_2^{(2)}-\mathrm{B}_1^{(1)}\mathrm{B}_1^{(2)}$ where the bracketed superscript denotes the group type and the subscript as usual the number of groups. Since, at this point, no correlation was made with experimental systems, further simplifications have been adopted to demonstrate the reactivity difference effect. Namely, the reactivity of groups (1) was assumed to be higher or equal than that of groups (2)

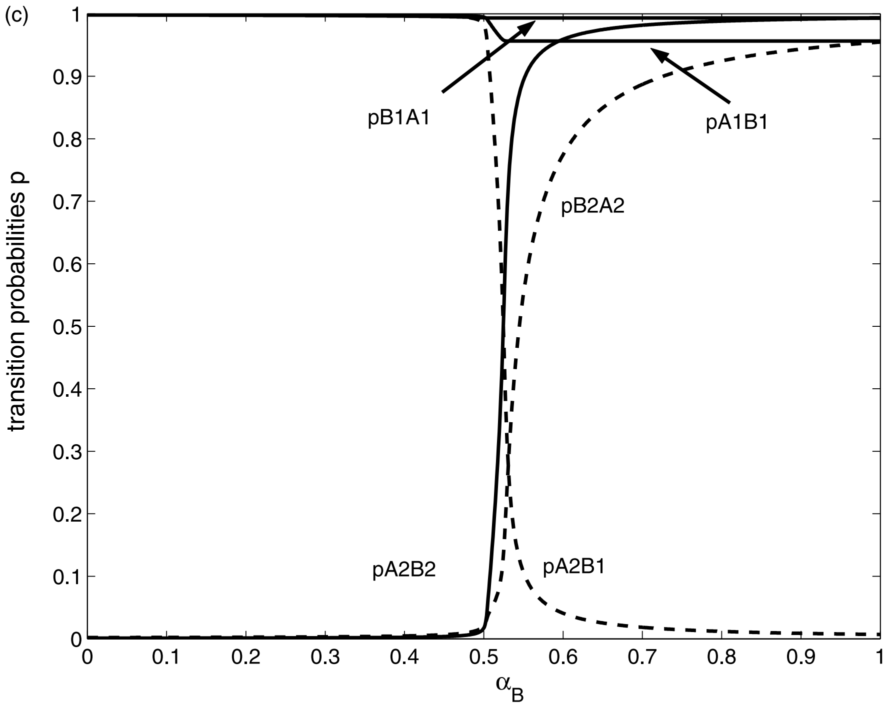


Fig. 6 (*continued*)

and, furthermore, the increase in reactivity of groups A was assumed to be the same as that of groups B. There is, however, no obstacle to investigate the effect of any combinations of rate constant ratios κ_A^+ and κ_B^+.

Three levels of differences in reactivity of $A^{(1)}$ relative to $A^{(2)}$ (rate constants ratio κ_A^+) and $B^{(1)}$ relative to $B^{(2)}$ (κ_B^+) will be discussed: $\kappa_A^+ = \kappa_B^+ = 1$ (equal reactivity, random case), $\kappa_A^+ = \kappa_B^+ = 5$ (moderate reactivity difference) and $\kappa_A^+ = \kappa_B^+ = 1000$ (very strong reactivity difference). Fig. 5 shows the conversions of $B^{(1)}$ and $B^{(2)}$ groups.

For equal reactivity, the conversions are equal, for $\kappa_A^+ = \kappa_B^+ = 5$ the deviations from randomness is well expressed and for $\kappa_A^+ = \kappa_B^+ = 1000$, initially only the more reactive group reacts, and the less reactive starts reacting only after the first one has been consumed.

The changes of transition probabilities for bonds as functions of the degree structure build-up enable us to understand the role of reactivity differences on passage from gelling to non-gelling systems (Fig. 6(a)–(c)).

For the random case, all transition probabilities extending from A to B groups are equal to ½, for the B groups those extending to $A^{(2)}$ groups are larger by a factor of 2 than those extending to $A^{(1)}$ groups (values 2/3 and 1/3) because the concentration of $A^{(2)}$ groups is twice as large. As the reactivity differences increase, B1→A1 and A1→B1 bonds (i.e. dyads A1B1) (cf., Appendix A), are formed initially almost exclusively followed by almost exclusive formation of A2B2 and B2A2 bonds. Still, to the end of the reaction a few percent of $A^{(1)}$ groups reacted with $B^{(2)}$ groups because at that time $B^{(1)}$ groups had been practically consumed. This fact will explain later the slow convergence of the $(r_A)_{crit}$ to the value of 1.5 characteristic of classical hyperbranched polymers.

The dependence of CMR, $(r_A)_{crit}$, on the reactivity ratios is displayed in Fig. 7. It is seen that for the reactivity ratio about 5, the CMC decreases initially more steeply and the decrease slows down after κ_A^+ and κ_B^+ reach the value of about 10. For the highest values of κ_A^+ and κ_B^+ examined (1000), $(r_A)_{crit}$, still has not reached the limiting value of $(r_A)_{crit} = 1.5$, for the reasons discussed above and it would need another decade to approach it closely. When the excess of A groups increases beyond the critical value, the molecular weight averages decrease as is seen in Fig. 8

The maximum achievable number-average molecular weight delimited by the dotted lines increases from about 1.2×10^3 for $\kappa_A^+ = \kappa_B^+ = 1$, to 2×10^3 for $\kappa_A^+ = \kappa_B^+ = 5$ and to 9×10^3 for $\kappa_A^+ = \kappa_B^+ = 1000$. This corresponds to degree of polymerization of about 7, 12 and 50. For practical application, the polydispersity should not exceed a certain limit (e.g., M_w/M_n should not exceed the value 3–4, cf. Fig. 9), which corresponds to degrees of polymerization of 5–25.

The simulation also shows the molecular weights build up for a certain value of molar ratio, r_A. From Fig. 10, one can see that the molecular weight remains low until the very end of the reaction when the increase is getting steep. Here, the value of r_A is equal to $(r_A)_{crit}$ and M_w and polydispersity diverge always at α_B equal to 1. At $r_A > (r_A)_{crit}$, M_w does not diverge at all. When the increase of polydispersity during structure build-up is plotted against M_n (Fig. 11) and the initial portion is enlarged, one can observe for $\kappa_A^+ = \kappa_B^+ =$

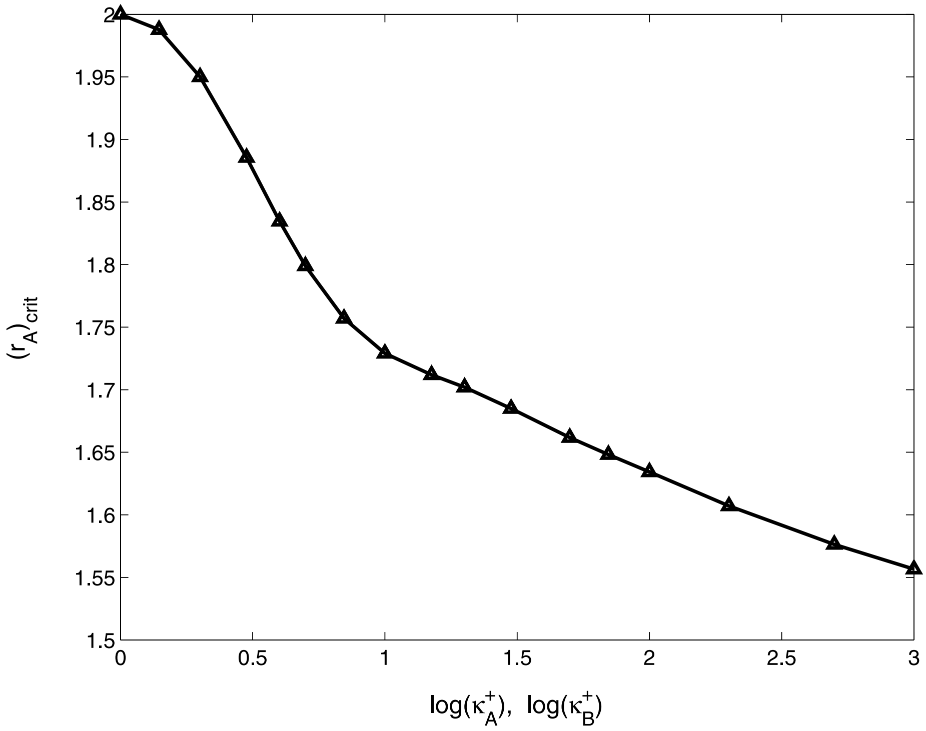


Fig. 7. Dependence of the critical molar ratio (CMR), $(r_A)_{crit}$, for polyaddition of the $A_1^{(1)}A_2^{(2)}$ and $B_1^{(1)}B_1^{(2)}$ components on the reactivity ratios of $A^{(1)}$ to $A^{(2)}$, κ_A^+, and $B^{(1)}$ to $B^{(2)}$, κ_B^+ groups, $\kappa_A^+ = \kappa_B^+$.

1000 a strange phenomenon (Fig. 11(a,b)) that the polydispersity after passage through a small maximum decreases to a value that is smaller than the initial value and approaches 1.

This can be explained by in situ formation of a compound A3−B2 from 1 molecule of monomer $A_1^{(1)}A_2^{(2)}$ and 1 molecule of $B_1^{(1)}B_1^{(2)}$. Closer inspection shows, however, that the compound is not fully pure (polydispersity index about

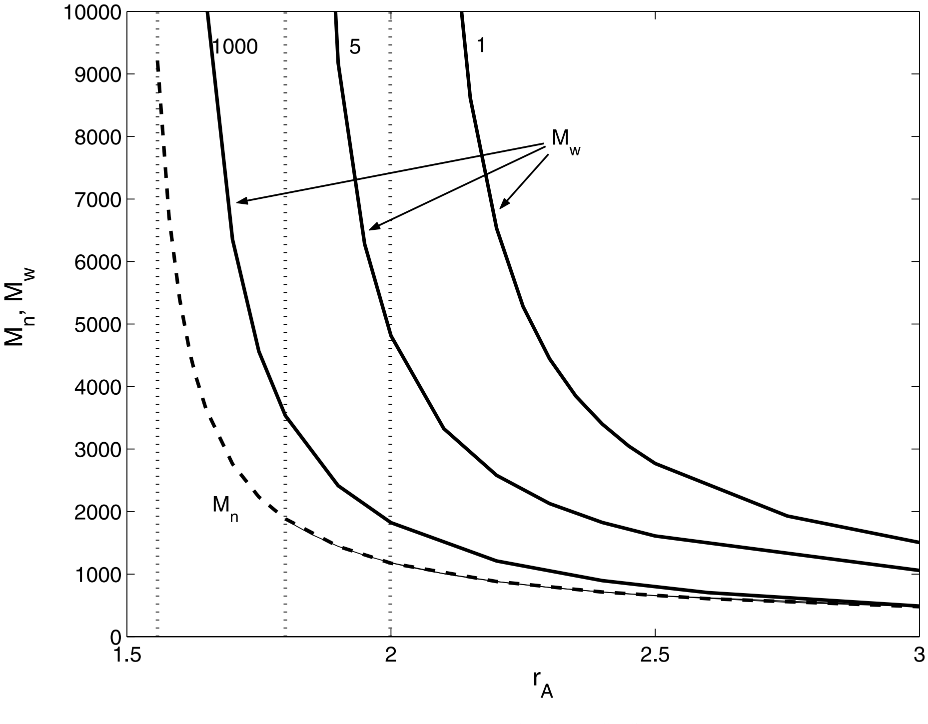


Fig. 8. Dependence of the number- and weight-average molecular weights of the $A_1^{(1)}A_2^{(2)}-B_1^{(1)}B_1^{(2)}$ polymer on the molar ratio of A:B groups, r_A, reactivity ratios of $A^{(1)}$ to $A^{(2)}$, κ_A^+, and $B^{(1)}$ to $B^{(2)}$, κ_B^+ groups indicated, $\kappa_A^+ = \kappa_B^+$; molecular weight of the components A and B, $M_A = 129$, $M_B = 222$.

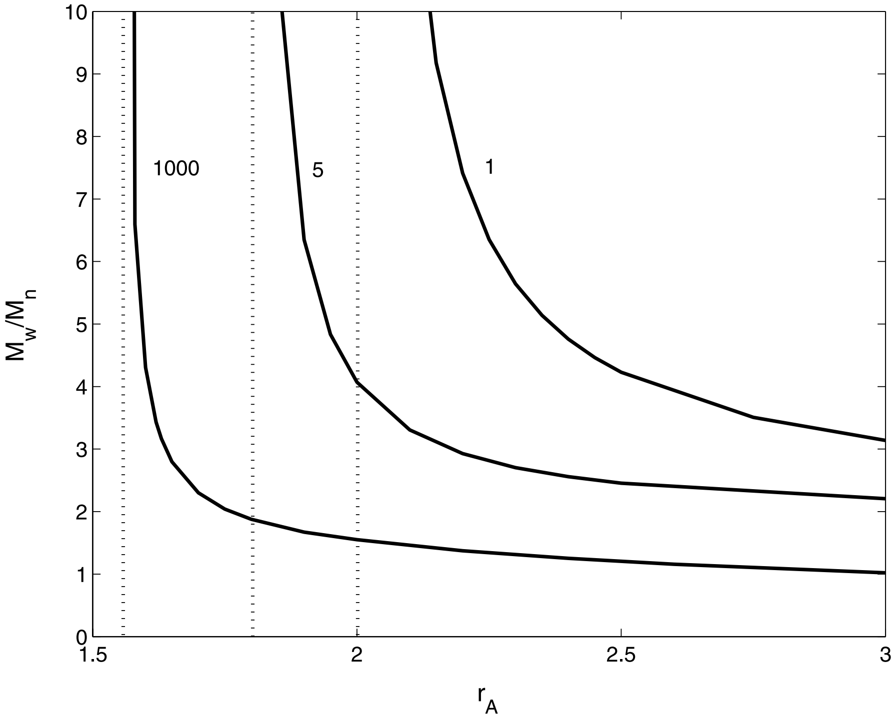


Fig. 9. Dependence of polydispersity index of the $A_1^{(1)}A_2^{(2)}-B_1^{(1)}B_1^{(2)}$ polymer on the molar ratio of A:B groups, r_A, reactivity ratios of $A^{(1)}$ to $A^{(2)}$, κ_A^+, and $B^{(1)}$ to $B^{(2)}$, κ_B^+ groups indicated, $\kappa_A^+=\kappa_B^+$; molecular weight of the components A and B, $M_A=129$, $M_B=222$.

1.03) and this is the reason for the fact that the limiting value of $(r_A)_{crit}=1.5$ has not yet been reached for $\kappa_A^+=\kappa_B^+=1000$.

In Fig. 12, the plot of polydispersity index vs. M_n is used for comparison of off-stoichiometric highly-branched polymers with classical BA_2 hyperbranched polymer, for which the molecular weight of the hyperbranched monomer is equal to the sum of molecular weights of A3 + B2. Fig. 12 shows that off-stoichiometric A3 + B2 polymers with strong differences in reactivity of functional groups A are fully equivalent to hyperbranched polymers in the range of molecular weights up to approximately 10,000 ($P_n\approx 50$–60 based on A3 and B2 monomers or $P_n\approx 25$–30 based on BA_2 monomer).

The difference compared to Fig. 11 is that Fig. 11 describes the evolution of M_n and M_w for $r_A=(r_A)_{crit}$ as a

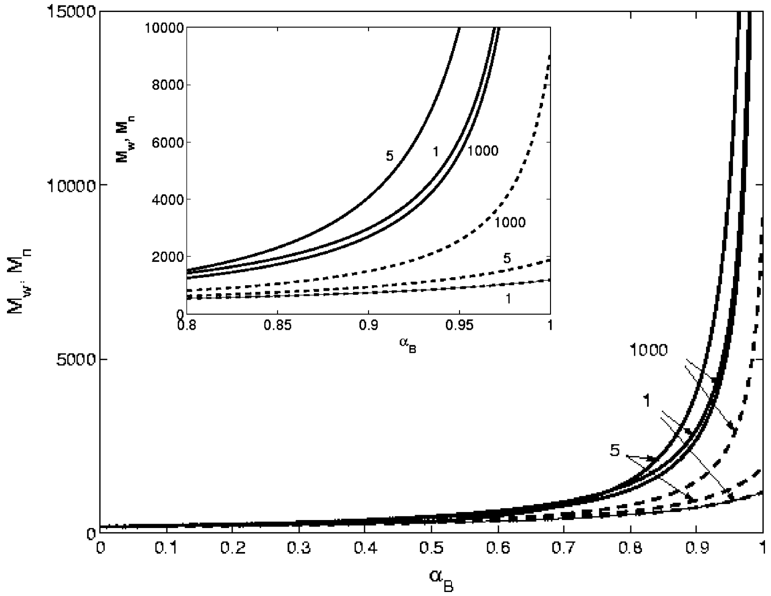


Fig. 10. Dependence of polydispersity index of the $A_1^{(1)}A_2^{(2)}-B_1^{(1)}B_1^{(2)}$ polymer on conversion of B groups for reactivity ratios of $A^{(1)}$ to $A^{(2)}$, κ_A^+, and $B^{(1)}$ to $B^{(2)}$, κ_B^+ groups indicated, $\kappa_A^+=\kappa_B^+$; molecular weight of the components A and B, $M_A=129$, $M_B=222$.

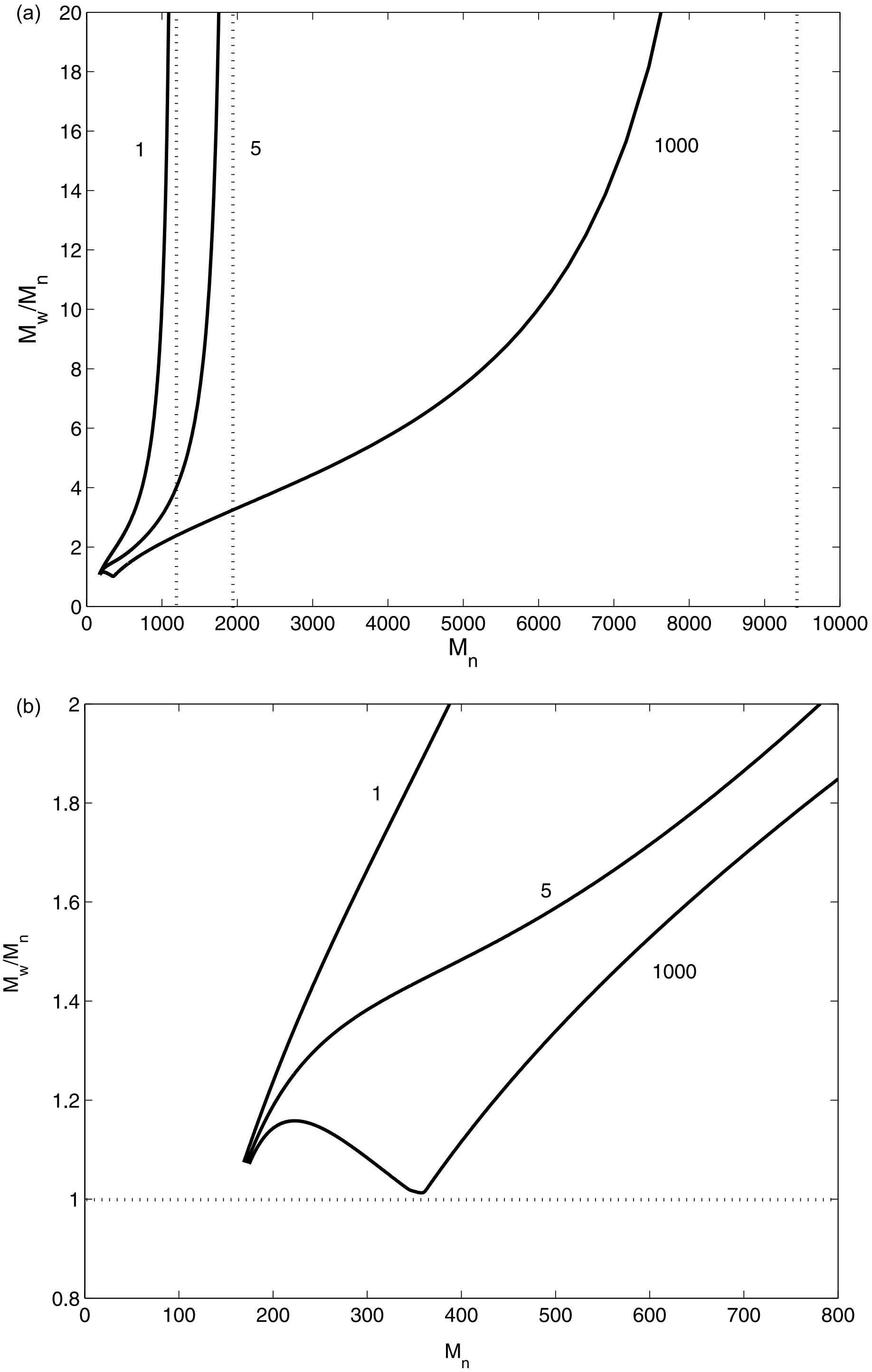


Fig. 11. (a) Interdependence of polydispersity index of the $A_1^{(1)}A_2^{(2)}-B_1^{(1)}B_1^{(2)}$ polymer and M_n during polymer formation for reactivity ratios of $A^{(1)}$ to $A^{(2)}$, κ_A^+, and $B^{(1)}$ to $B^{(2)}$, κ_B^+ groups indicated, $\kappa_A^+=\kappa_B^+$; molecular weight of the components A and B, $M_A=129$, $M_B=222$; (b) Enlarged part of the figure.

function of conversion α_B, whereas in Fig. 12 the dependences correspond to various values of r_A for $\alpha_B=1$. We see again the characteristic initial decrease of the polydispersity index caused by the initial formation of the A3 + B2 ‘compound’. The polydispersity of the off-stoichiometric polymer for $\kappa_A^+=\kappa_B^+=1000$ is even lower than the polydispersity of the hyperbranched polymer. This feature can be explained by the fact that the molecular weight of hyperbranched monomer increases by BA_2 increments whereas in the A3 − B2 case molecules like $(A3)_2B2$, or $(A3)_3(B2)_2$ also exist. Morover, the minimum polydispersity in the A3 − B2 case is reached for molecular weight, which is somewhat higher than the molecular weight of the BA_2 unit.

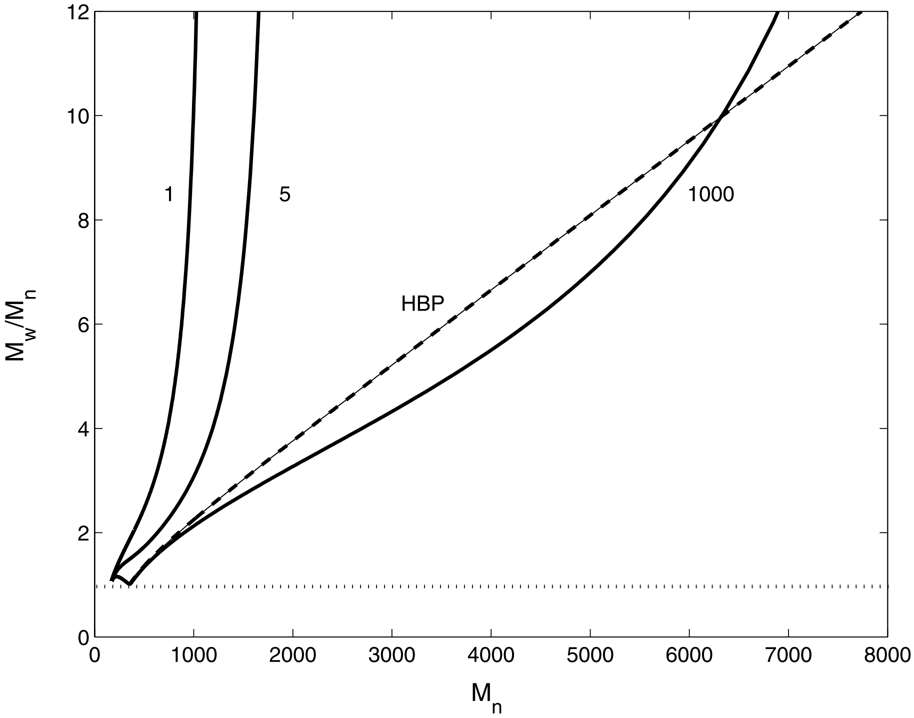


Fig. 12. Interdependence of polydispersity index of the $A_1^{(1)}A_2^{(2)}-B_1^{(1)}B_1^{(2)}$ polymer and M_n obtained for various values of r_A (cf. Fig. 10) and comparison with the same dependence for the random hyperbranched polymers obtained from BA_2 monomer. Reactivity ratios of $A^{(1)}$ to $A^{(2)}$, κ_A^+, and $B^{(1)}$ to $B^{(2)}$, κ_B^+ groups indicated, $\kappa_A^+=\kappa_B^+$; molecular weight of the components A and B, $M_A=129$, $M_B=222$.

4. Conclusions

The formation of highly-branched off-stoichiometric polymers from A_x+B_y monomers has been described by the theory of branching processes in which the irreversibility of bond formation was respected. This treatment offers prediction of the critical molar ratio (CMR), $(r_A)_{crit}=[A]_0/[B]_0$, beyond which the system does not gel and only soluble highly-branched polymers are formed. The value of CMR depends first of all on functionality of the components and also on the reactivity of functional groups involved in formation of bonds. For the ideal $A3-B2$ system, the CMR for the A:B groups, $(r_A)_{crit}$, is equal to 2. For an increasing excess of A groups over B groups, soluble A-functional polymers of decreasing molecular weight are formed. If $(r_A)_{crit}$ is lower than 2, the system gels and non-extractable crosslinked polymer is present. The value of CMR can be lowered by addition of a monofunctional monomer or using A3 and B2 monomers with groups of different reactivity. The effect of modification of the functionality of the A component was demonstrated by the $A3+A1-B2$ system in which a monofunctional component A1 was added to the trifunctional component A3. The excess of A groups characterized by $(r_A)_{crit}$ decreased from 2 to 1 (i.e., $[A]_0=[B]_0$)) when the fraction of A groups of A1 was equal to that of A3 ($n_{A1}=3n_{A3}$). The number-average molecular weights and degrees of polymerization as well as the number of functional groups per molecule remain relatively low even at CMR when the gel point is reached. Therefore, the applications are limited by this factor.

A system denoted as $A_1^{(1)}A_2^{(2)}-B_1^{(1)}B_1^{(2)}$, in which groups $A^{(1)}\equiv A1$ are more reactive than groups $A^{(2)}\equiv A2$ and the same holds for $B^{(1)}\equiv B1$ vs. $B^{(2)}\equiv B2$ groups, was investigated in detail. The relative reactivity of A1 to A2 group and B1 to B2 group varied in the range of $\kappa=1$–1000. With increasing differences in reactivity (increasing κ), the $A1-B1$ and $A2-B2$ become increasingly dominant over the $A1-B2$ and $A2-B1$ bonds and CMR decreases from 2 to 1.5. However, even for $\kappa=1000$, $(r_A)_{crit}=1.55$ and the convergence to the value of 1.50 is slow. Important is that with increasing differences in reactivity the polydispersity can be suppressed. The functional highly-branched polymers obtained in the range of $\kappa\geq 10$ have M_n of several thousands Daltons and in their application can compete with conventional hyperbranched polymers.

The relations derived using the statistical branching theory have implicitly built-in the information on the unreacted functional groups and can be further used for description of crosslinking of these off-stoichiometric polymers with a crosslinking monomer (component C) by which A–C bonds are formed. For example, equations (A2) and (A22) contain the *pgf* variables Z_{Aunr}, and Z_{A1unr} and Z_{A1unr}, respectively. When these polymers are randomly crosslinked, the transformation to be made is of the type

$$Z_{Aunr}\rightarrow(1-\alpha_{AC})Z_{Aunr}+\alpha_{AC}z_{AC}$$

where α_{AC} is the degree of conversion of A groups into A–C bonds and z_{AC} is the *pgf* variable identifying A→C bonds. The treatment can be further refined if A groups of different reactivity are present in the highly-branched off-stoichiometric polymer.

Acknowledgements

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Appendix A. Derivation of relations for critical molar ratios and molecular weight and functionality averages

A.1. Af+A1−B2 system with equal and independent reactivity of functional groups

The basic information on units, bonds and unreacted functional groups is contained in the probability generating function $F_{0n}(\mathbf{z},\mathbf{Z})$

$$\begin{aligned} F_{0n}(\mathbf{z},\mathbf{Z}) &= n_{A1}Z_{A1}^{X_{A1}}[(1-\alpha_A)Z_{Aunr}+\alpha_A z_B] \\ &\quad + n_{Af}Z_{Af}^{X_{Af}}[(1-\alpha_A)Z_{Aunr}+\alpha_A z_B]^{f_A} \\ &\quad + n_{B2}Z_{B2}^{X_{B2}}[(1-\alpha_B)Z_{Bunr}+\alpha_B z_A)^2 \end{aligned} \tag{A1}$$

where n_{A1}, n_{Af}, n_{B2} are molar fractions of components A1, Af and B2, respectively. The variables of the *pgf*'s $Z_{A1}^{X_{A1}}$, Z_{Aunr}, z_B (for A1) count, respectively, a property of the unit (e.g. molecular weight of A1), number of unreacted functional groups A, and number of bonds extending from A to B units; z_A is associated with bonds extending from B to A units, and α_A and α_B are conversions of A and B groups, respectively.

The molar fractions $\mathbf{n}$ can be expressed through the fraction of the A-groups of monofunctional component x_{A1} or the ratio s_{A1} as follows:

$$n_{A1}=\frac{N_{A1}}{N_{A1}+N_{Af}+N_{B2}},\quad n_{Af}=\frac{N_{Af}}{N_{A1}+N_{Af}+N_{B2}},$$

$$n_{B2}=1-n_{A1}-n_{Af},\quad x_{A1}=\frac{N_{A1}}{N_{A1}+f_AN_{Af}},$$

$$x_{Af}=\frac{f_AN_{Af}}{N_{A1}+f_AN_{Af}},\quad s_{A1}=\frac{N_{A1}}{f_AN_{Af}},\quad s_{Af}=\frac{f_AN_{Af}}{N_{A1}},$$

$$r_A=\frac{N_{A1}+f_AN_{Af}}{2N_{B2}}$$

where N are number of moles of components. For instance, expressing n through x and r_A gives

$$\begin{aligned} n_{A1} &= \frac{2f_Ar_Ax_{A1}}{2r_A(f_Ax_{A1}+x_{Af})+f_A}, \\ n_{Af} &= \frac{2r_Ax_{Af}}{2r_A(f_Ax_{A1}+x_{Af})+f_A},\quad n_{B2}=1-n_{A1}-n_{Af}, \\ x_{A1} &= \frac{n_{A1}}{n_{A1}+f_An_{Af}},\quad x_{Af}=1-x_{A1} \end{aligned} \tag{A2}$$

The *pgf* for additional bonds extending from units already bound to another unit (in the preceding generation) is obtained by differentiation, as shown in Eqs. (A3) and (A4)

$$\begin{aligned} F_A(z_B,\mathbf{Z}) &= \frac{\partial F_{0n}(\mathbf{z},\mathbf{Z})}{\partial z_B}\times N_A \\ &= x_{A1}Z_{A1}^{X_{A1}}+x_{Af}Z_{Af}^{X_{Af}}[(1-\alpha_A)Z_{Aunr}+\alpha_A z_B]^{f_A-1} \end{aligned} \tag{A3}$$

$$F_B(z_B,\mathbf{Z})=\frac{\partial F_{0n}(\mathbf{z},\mathbf{Z})}{\partial z_A}\times N_B=Z_{B2}^{X_{B2}}[(1-\alpha_B)Z_{Bunr}+\alpha_B z_A]^2 \tag{A4}$$

where N_A and N_B are normalizers, so that $F_A(1,\mathbf{1})=F_A(1,\mathbf{1})=1$; x_{A1} and x_{Af} are molar fractions of A groups in component A1 and Af, respectively.

The gel point is determined only by structure connectivity and molecular weight and number of unreacted groups are irrelevant, i.e., $Z_{A1}^{X_{A1}}=Z_{Aunr}=1$. For formation of an infinite path of bonds, the average number of bonds extending from a unit on generation i to units in generation $i+1$ ($i>0$) must be equal to 1

$$\begin{aligned} \left[\frac{\partial F_A(1,z_B)}{\partial z_B}\frac{\partial F_B(1,z_A)}{\partial z_A}\right]_{z_A=z_B=1} &\equiv F_A^BF_A^B \\ = x_{Af}(f_A-1)\alpha_A\alpha_B &= 1 \end{aligned} \tag{A5}$$

where F_A^B and F_A^B are shorthand notations for the values of derivatives on the left-hand side of Eq. (A5).

For excess of A groups, the critical molar ratio $(r_A)_{crit}=([A_0]/[B_0])_{crit}=((f_An_{Af}+n_{A1})/2n_{B2})_{crit}$ is obtained from the condition $\alpha_B=1$

$$(r_A)_{crit}=x_{Af}(f_A-1) \tag{A6}$$

From this equation, one can find that the critical value of x_{Af}, fraction of A groups of the polyfunctional component, $(x_{Af})_{crit}$, when r_A drops to 1

$$(x_{Af})_{crit}=1/(f_A-1) \tag{A7}$$

This is the lowest possible content of the polyfunctional monomer in mixture with the monofunctional one at which the system can gel. For $f_A=3$, $(x_{Af})_{crit}=1/2$ and $(s_{Af})_{crit}=1$.

A.1.1. Molecular weight averages

The number-average molecular weight of the highly-branched polymer is given by the weights of the building units per molecule. The number of molecules is given by the number of building units minus the number of bonds. The number of bonds is given by the value of derivatives of the function $F_{0n}(\mathbf{z},\mathbf{Z})$; $N_{\text{bonds}} = (\partial F_{0n}/\partial z_{\text{A}})_{z_{\text{A}}=z_{\text{B}}=1} = (\partial F_{0n}/\partial z_{\text{B}})_{z_{\text{A}}=z_{\text{B}}=1} = (n_{\text{A1}} + f_{\text{A}} n_{\text{A}f})\alpha_{\text{A}} = 2n_{\text{B2}}\alpha_{\text{B}}$,

$$M_{\text{n}} = \frac{n_{\text{A1}}M_{\text{A1}} + f_{\text{A}}n_{\text{Af}}M_{\text{Af}} + n_{\text{B2}}M_{\text{B2}}}{1 - 2n_{\text{B2}}\alpha_{\text{B}}} \tag{A8}$$

The weight-average molecular weight is derived from the weight fraction generating function, $W(\mathbf{Z}(\mathbf{u}))$, in which the distribution of degrees of polymerization is implicitly generated through recursive equations of variable $\mathbf{u}$. Note that $\mathbf{u}$ is a function of *pgf* variables bearing information on the structural units, $Z_{\text{A}}^{M_{\text{A1}}}, Z_{\text{A}}^{M_{\text{Af}}}, Z_{\text{B}}^{M_{\text{B2}}}$. Thus

$$\begin{aligned} W(\mathbf{Z}(\mathbf{u})) = {} & m_{\text{A1}}Z_{\text{A}}^{M_{\text{A1}}}[1 - \alpha_{\text{A}} + \alpha_{\text{A}}u_{\text{B}}] + \\ & m_{\text{Af}}Z_{\text{A}}^{M_{\text{Af}}}[1 - \alpha_{\text{A}} + \alpha_{\text{A}}u_{\text{B}}]^{f_{\text{A}}} + \\ & m_{\text{B2}}Z_{\text{B}}^{M_{\text{B2}}}[1 - \alpha_{\text{B}} + \alpha_{\text{B}}u_{\text{A}}]^2 \end{aligned} \tag{A9}$$

where m_{A1}, m_{Af}, m_{B2} are mass fractions of initial components

$$m_{\text{A1}} = \frac{n_{\text{A1}}M_{\text{A1}}}{n_{\text{A1}}M_{\text{A1}} + n_{\text{Af}}M_{\text{Af}} + n_{\text{B2}}M_{\text{B2}}},$$

$$m_{\text{Af}} = \frac{n_{\text{Af}}M_{\text{Af}}}{n_{\text{A1}}M_{\text{A1}} + n_{\text{Af}}M_{\text{Af}} + n_{\text{B2}}M_{\text{B2}}},$$

$$m_{\text{B2}} = 1 - m_{\text{A1}} - m_{\text{Af}}$$

and the recursive equations read

$$u_{\text{A}} = Z_{\text{A}}^{M_{\text{A1}}}(1 - x_{\text{Af}}) + Z_{\text{A}}^{M_{\text{Af}}}x_{\text{Af}}[1 - \alpha_A + \alpha_{\text{A}}u_{\text{B}}]^{f_{\text{A}}-1} \tag{A10}$$

$$u_{\text{B}} = Z_{\text{B}}^{M_{\text{B2}}}(1 - \alpha_{\text{B}} + \alpha_{\text{B}}u_{\text{A}}) \tag{A11}$$

Since the molecular weight average is obtained by differentiation of $W(\mathbf{Z}(\mathbf{u}))$

$$M_{\text{w}} = [\partial W(\mathbf{Z}(\mathbf{u}))/\partial Z_{\text{A}} + \partial W(\mathbf{Z}(\mathbf{u}))/\partial Z_{\text{B}}]_{Z=1} \tag{A12}$$

that is

$$\begin{aligned} M_{\text{w}} = {} & m_{\text{A1}}M_{\text{A1}} + +m_{\text{Af}}[M_{\text{Af}} + f_{\text{A}}\alpha_{\text{A}}(u_{\text{B}}^{\text{A}} + u_{\text{B}}^{\text{B}})] \\ & + m_{\text{B2}}[M_{\text{B2}} + 2\alpha_{\text{B}}(u_{\text{A}}^{\text{A}} + u_{\text{A}}^{\text{B}})] \end{aligned} \tag{A13}$$

one has to find the derivatives of u_{A} and u_{B} with respect to Z_{A} and Z_{B}

$$u_{\text{A}}^{\text{B}} \equiv \left[\frac{\partial u_{\text{A}}(\mathbf{Z})}{\partial Z_{\text{A}}}\right]_{Z_{\text{A}}=Z_{\text{B}}=1} \quad \text{etc.}$$

explicitly

$$\begin{aligned} & u_{\text{A}}^{\text{A}} = x_{\text{Af}}[M_{\text{Af}} + (f_{\text{A}} - 1)\alpha_{\text{A}}u_{\text{B}}^{\text{A}}] + (1 - x_{\text{Af}})M_{\text{A1}}, \\ & u_{\text{A}}^{\text{B}} = x_{\text{Af}}(f_{\text{A}} - 1)\alpha_{\text{A}}u_{\text{B}}^{\text{B}}, \quad u_{\text{B}}^{\text{A}} = \alpha_{\text{B}}u_{\text{A}}^{\text{A}}, \quad u_{\text{B}}^{\text{B}} = M_{\text{B2}} + \alpha_{\text{B}}u_{\text{A}}^{\text{B}} \end{aligned} \tag{A14}$$

The solution for the four variables reads

$$\begin{aligned} & u_{\text{A}}^{\text{A}} = \frac{x_{\text{Af}}M_{\text{Af}} + (1 - x_{\text{Af}})M_{\text{A1}}}{1 - D}, \\ & u_{\text{A}}^{\text{B}} = \frac{x_{\text{Af}}(f_{\text{A}} - 1)\alpha_{\text{A}}M_{\text{B2}}}{1 - D} = \frac{\bar{M}_{\text{A}}}{1 - D}, \\ & u_{\text{B}}^{\text{A}} = \frac{\alpha_{\text{B}}[x_{\text{Af}}M_{\text{Af}} + (1 - x_{\text{Af}})M_{\text{A1}}]}{1 - D} = \frac{\alpha_{\text{B}}\bar{M}_{\text{A}}}{1 - D}, \\ & u_{\text{B}}^{\text{B}} = \frac{M_{\text{B2}}}{1 - D}, \quad D = x_{\text{Af}}(f_{\text{A}} - 1)\alpha_{\text{A}}\alpha_{\text{B}} \end{aligned} \tag{A15}$$

Note that for highly-branched off-stoichiometric networks, $\alpha_{\text{B}} = 1$ and $\alpha_{\text{A}} = 1/r_{\text{A}}$.

A.1.2. Averages of functionality distribution

To obtain the first- and second-moment average of the number of functional groups per molecule, one proceeds similarly as in the case of molecular weights, but the *pgf* variables Z_{Aunr} and Z_{Bunr} are considered instead of those monitoring the molecular weight. Thus, the function F_{0n} is changed to U_{0n} (Eq. (A16), U = unreacted); as before, z_{A} and z_{B} remain to be variables related to bonds B → A and A → B, respectively. Here. The condition $\alpha_{\text{B}} = 1$ was applied.

$$\begin{aligned} U_{0n}(\mathbf{z},\mathbf{Z}) = {} & n_{\text{A1}}[(1 - \alpha_{\text{A}})Z_{\text{Aunr}} + \alpha_{\text{A}}z_{\text{B}}] + \\ & n_{\text{Af}}[(1 - \alpha_A)Z_{\text{Aunr}} + \alpha_{\text{A}}z_{\text{B}}]^{f_A} + \\ & n_{\text{B2}}[(1 - \alpha_{\text{B}})Z_{\text{Bunr}} + \alpha_{\text{B}}z_{\text{A}}]^2 \\ = {} & n_{\text{A1}}[(1 - \alpha_{\text{A}})Z_{\text{Aunr}} + \alpha_{\text{A}}z_{\text{B}}] + \\ & n_{\text{Af}}[(1 - \alpha_{\text{A}})Z_{\text{Aunr}} + \alpha_{\text{A}}z_{\text{B}}]^{f_{\text{A}}} + n_{\text{B2}}z_{\text{A}}^2 \end{aligned} \tag{A16}$$

Using the same reasoning as in the case of number-average molecular weight and the fact that, one get for $\langle f_{\text{A}}\rangle_1$

$$\langle f_{\text{A}}\rangle_1 = \frac{(1 - \alpha_{\text{A}})(f_{\text{A}}n_{\text{Af}} + n_{\text{A1}})}{1 - 2n_{\text{B2}}} \tag{A17}$$

The second moment average of functionality distribution defined as

$$\langle f_{\text{A}}\rangle_2 = \frac{\sum_{i=1}^{\infty} i^2 a_i}{\sum_{i=1}^{\infty} i a_i}$$

is derived from

$$\begin{aligned} U_2(\mathbf{z},\mathbf{Z}) = {} & n_{\text{A1}}[(1 - \alpha_{\text{A}})Z_{\text{Aunr}} + \alpha_{\text{A}}u_{\text{B}}] + \\ & n_{\text{Af}}[(1 - \alpha_A)Z_{\text{Aunr}} + \alpha_{\text{A}}u_{\text{B}}]^{f_{\text{A}}} + n_{\text{B2}}u_{\text{A}}^2 \end{aligned} \tag{A18}$$

with

$$u_{\text{A}} = x_{\text{A1}} + x_{\text{Af}}[(1 - \alpha_{\text{A}})Z_{\text{Aunr}} + \alpha_{\text{A}}u_{\text{B}}]^{f_{\text{A}}-1}, \quad u_{\text{B}} = u_{\text{A}} \tag{A19}$$

giving

$$u_{\mathrm{A}}^{\mathrm{A}}=\frac{x_{\mathrm{Af}}(f_{\mathrm{A}}-1)(1-\alpha_{\mathrm{A}})}{1-D},\quad u_{\mathrm{A}}^{\mathrm{B}}=\frac{1}{1-D},$$

$$u_{\mathrm{B}}^{\mathrm{A}}=\frac{x_{\mathrm{Af}}(f_{\mathrm{A}}-1)(1-\alpha_{\mathrm{A}})}{1-D},\quad u_{\mathrm{B}}^{\mathrm{B}}=\frac{1}{1-D} \tag{A20}$$

with $D=x_{\mathrm{Af}}(f_{\mathrm{A}}-1)\alpha_{\mathrm{A}}$

Therefore

$$\langle f_{\mathrm{A}}\rangle_2=n_{\mathrm{Af}}f_{\mathrm{A}}[1-\alpha_{\mathrm{A}}+\alpha_{\mathrm{A}}(u_{\mathrm{B}}^{\mathrm{A}}+u_{\mathrm{B}}^{\mathrm{B}})]+ \\ n_{\mathrm{A1}}(1-\alpha_{\mathrm{A}})+2n_{\mathrm{B2}}(u_{\mathrm{A}}^{\mathrm{A}}+u_{\mathrm{A}}^{\mathrm{B}}) \tag{A21}$$

Note that $\alpha_{\mathrm{A}}=1/r_{\mathrm{A}}$.

A.2. A3−B2 system with unequal reactivity of functional groups

We will consider reaction of two monomers A3 ($\mathrm{A}_1^{(1)}\mathrm{A}_2^{(2)}$ and B2 ($\mathrm{B}^{(1)}\mathrm{B}^{(2)}$) having A-groups of different reactivity ($\mathrm{A}^{(1)}\equiv\mathrm{A1}$ and $\mathrm{A}^{(2))}\equiv\mathrm{A2}$) and B-groups of different reactivity ($\mathrm{B}^{(1)}\equiv\mathrm{B1}$ and $\mathrm{B}^{(2)}\equiv\mathrm{B2}$). No substitution effect (change of reactivity as a result of reaction) and no cyclization are considered. The degrees of conversion of functional groups A1 and A2 as well as B1 and B2 into bonds α_{A1}, α_{A2} and α_{B1}, α_{B2}, respectively, are different. Also, the bonds leading from groups A*i* to B*j* and B*j* to A*i* are to be distinguished. The relations will be derived first as functions of conversion of functional groups and then conditions characteristic of highly-branched off-stoichiometric systems ($\alpha_{\mathrm{B}}=1$, $\alpha_{\mathrm{A}}=1/r_{\mathrm{A}}$) will be introduced.

The following bonds connecting the functional groups are considered:

A1 → B1 B1 → A1
A1 → B2 B1 → A2
A2 → B1 B2 → A1
A2 → B2 B2 → A2

This notation will be retained but the arrow will not be displayed, for example, A1B1 means A1 → B1, etc.

The basic probability generating function describing the composition of the system in term of reaction states of building units reads

$$\begin{aligned}F_{0n}(\mathbf{Z},\mathbf{z})={}&n_{\mathrm{A}}Z_{\mathrm{A}}^{M_{\mathrm{A}}}[(1-\alpha_{\mathrm{A1}})Z_{\mathrm{A1unr}}+\alpha_{\mathrm{A1}}\xi_{\mathrm{A1B}}]\\&[(1-\alpha_{\mathrm{A2}})Z_{\mathrm{A2unr}}+\alpha_{\mathrm{A2}}\xi_{\mathrm{A2B}}]^2\\&+n_{\mathrm{B}}Z_{\mathrm{B}}^{M_{\mathrm{B}}}[(1-\alpha_{\mathrm{B1}})Z_{\mathrm{B1unr}}+\alpha_{\mathrm{B1}}\xi_{\mathrm{B1A}}]\\&\times[(1-\alpha_{\mathrm{B2}})Z_{\mathrm{B2unr}}+\alpha_{\mathrm{B2}}\xi_{\mathrm{B2A}}]\end{aligned} \tag{A22}$$

Here, the *pgf* variables $\mathbf{z}$ associated with bonds are replaced by $\boldsymbol{\xi}$ and these are a function of z by which the types of bonds are distinguished, e.g., z_{A1B1}, z_{A2B1},…etc.

$$\xi_{\mathrm{A1B}}=p_{\mathrm{A1B1}}z_{\mathrm{A1B1}}+p_{\mathrm{A1B2}}z_{\mathrm{A1B2}}\quad \xi_{\mathrm{A2B}}=p_{\mathrm{A2B1}}z_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}z_{\mathrm{A2B2}}$$

$$\xi_{\mathrm{B1A}}=p_{\mathrm{B1A1}}z_{\mathrm{B1A1}}+p_{\mathrm{B1A2}}z_{\mathrm{B1A2}}\quad \xi_{\mathrm{B2A}}=p_{\mathrm{B2A1}}z_{\mathrm{B2A1}}+p_{\mathrm{B2A2}}z_{\mathrm{B2A2}}$$

The structure of the equation and the subscripts of variables z show that the succession of units A and B can proceed in various sequences. The variable ξ_{A1B} means that we consider bonds extending from unit A via group A1. This bond can extend to unit B either through group B1 or group B2. The probabilities of these events are given by p_{A1B1} and p_{A1B2}, ($p_{\mathrm{A1B1}}+p_{\mathrm{A1B2}}=1$). Therefore, $p_{\mathrm{X}i\mathrm{Y}j}$ are transition probabilities of a first-order Markov process, i.e. conditional probability given group *i* on X has reacted, it forms a bond with Y via group *j*. The transition probabilities are a function of conversions of the reactive groups and their values are calculated by solving the system of differential equations for dyads as will be shown later.

Because we distinguish eight different types of bonds we have eight *pgf*'s for the number of additional bonds extending from units already bonded by one bond. They are obtained by differentiation of *pgf* (A22)

$$\begin{aligned}F_{\mathrm{B1A1}}(\mathbf{Z},\mathbf{z})&=\frac{\partial F_{0n}(\mathbf{Z},\mathbf{z})}{\partial z_{\mathrm{A1B1}}}\times N_{\mathrm{B1A1}}\\&=Z_{\mathrm{A}}^{M_{\mathrm{A}}}[(1-\alpha_{\mathrm{A2}})Z_{\mathrm{A2unr}}+\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}z_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}z_{\mathrm{A2B2}})]^2\end{aligned} \tag{A23}$$

$$\begin{aligned}F_{\mathrm{B2A1}}(\mathbf{Z},\mathbf{z})&=\frac{\partial F_{0n}(\mathbf{Z},\mathbf{z})}{\partial z_{\mathrm{A1B2}}}\times N_{\mathrm{B2A1}}\\&=Z_{\mathrm{A}}^{M_{\mathrm{A}}}[(1-\alpha_{\mathrm{A2}})Z_{\mathrm{A2unr}}+\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}z_{\mathrm{A2B1}}\\&\quad+p_{\mathrm{A2B2}}z_{\mathrm{A2B2}})]^2\end{aligned}$$

$$\begin{aligned}F_{\mathrm{B1A2}}(\mathbf{Z},\mathbf{z})&=\frac{\partial F_{0n}(\mathbf{Z},\mathbf{z})}{\partial z_{\mathrm{A2B1}}}\times N_{\mathrm{B1A2}}\\&=Z_{\mathrm{A}}^{M_{\mathrm{A}}}\{[(1-\alpha_{\mathrm{A1}})Z_{\mathrm{A1unr}}+\alpha_{\mathrm{A1}}(p_{\mathrm{A1B1}}z_{\mathrm{A1B1}}\\&\quad+p_{\mathrm{A1B2}}z_{\mathrm{A1B2}})][(1-\alpha_{\mathrm{A2}})Z_{\mathrm{A2unr}}\\&\quad+\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}z_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}z_{\mathrm{A2B2}})]\end{aligned}$$

$$\begin{aligned}F_{\mathrm{B2A2}}(\mathbf{Z},\mathbf{z})&=\frac{\partial F_{0n}(\mathbf{Z},\mathbf{z})}{\partial z_{\mathrm{A2B2}}}\times N_{\mathrm{B2A2}}\\&=Z_{\mathrm{A}}^{M_{\mathrm{A}}}\{[(1-\alpha_{\mathrm{A1}})Z_{\mathrm{A1unr}}+\alpha_{\mathrm{A1}}(p_{\mathrm{A1B1}}z_{\mathrm{A1B1}}\\&\quad+p_{\mathrm{A1B2}}z_{\mathrm{A1B2}})][(1-\alpha_{\mathrm{A2}})Z_{\mathrm{A2unr}}\\&\quad+\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}z_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}z_{\mathrm{A2B2}})]\end{aligned}$$

$$\begin{aligned}F_{\mathrm{A1B1}}(\mathbf{Z},\mathbf{z})&=\frac{\partial F_{0n}(\mathbf{Z},\mathbf{z})}{\partial z_{\mathrm{B1A1}}}\times N_{\mathrm{A1B1}}=Z_{\mathrm{B}}^{M_{\mathrm{B}}}[(1-\alpha_{\mathrm{B2}})Z_{\mathrm{A2unr}}\\&\quad+\alpha_{\mathrm{B2}}(p_{\mathrm{B2A1}}z_{\mathrm{B2A1}}+p_{\mathrm{B2A2}}z_{\mathrm{B2A2}})]\end{aligned}$$

$$F_{\mathrm{A2B1}}(\mathbf{Z},\mathbf{z}) = \frac{\partial F_{0n}(\mathbf{Z},\mathbf{z})}{\partial z_{\mathrm{B1A2}}} \times N_{\mathrm{A2B1}} = Z_{\mathrm{B}}^{M_{\mathrm{B}}}[(1-\alpha_{\mathrm{B2}})Z_{\mathrm{A2unr}} + \alpha_{\mathrm{B2}}(p_{\mathrm{B2A1}}z_{\mathrm{B2A1}} + p_{\mathrm{B2A2}}z_{\mathrm{B2A2}})]$$

$$F_{\mathrm{A1B2}}(\mathbf{Z},\mathbf{z}) = \frac{\partial F_{0n}(\mathbf{Z},\mathbf{z})}{\partial z_{\mathrm{B2A1}}} \times N_{\mathrm{A1B2}} = Z_{\mathrm{B}}^{M_{\mathrm{B}}}[(1-\alpha_{\mathrm{B1}})Z_{\mathrm{A1unr}} + \alpha_{\mathrm{B1}}(p_{\mathrm{B1A1}}z_{\mathrm{B1A1}} + p_{\mathrm{B1A2}}z_{\mathrm{B1A2}})]$$

$$F_{\mathrm{A2B2}}(\mathbf{Z},\mathbf{z}) = \frac{\partial F_{0n}(\mathbf{Z},\mathbf{z})}{\partial z_{\mathrm{B2A2}}} \times N_{\mathrm{A2B2}} = Z_{\mathrm{B}}^{M_{\mathrm{B}}}[(1-\alpha_{\mathrm{B1}})Z_{\mathrm{A1unr}} + \alpha_{\mathrm{B1}}(p_{\mathrm{B1A1}}z_{\mathrm{B1A1}} + p_{\mathrm{B1A2}}z_{\mathrm{B1A2}})]$$

$N_{\mathrm{X}i\mathrm{Y}j}$ are normalizers, so that $F_{\mathrm{X}i\mathrm{Y}j}\,(\mathbf{1},\mathbf{1})=1$.

The values of derivatives for $\mathbf{z}=\mathbf{Z}=\mathbf{1}$ are denoted as

$$\left[\frac{\partial F_{\mathrm{B2A1}}(\mathbf{Z},\mathbf{z})}{\partial z_{\mathrm{A2B1}}}\right]_{\mathbf{z}=\mathbf{Z}=1} \equiv F_{\mathrm{B2A1}}^{\mathrm{A2B1}}, \quad \text{etc.}$$

and can be expressed by an 8×8 matrix of derivatives

$$\begin{pmatrix} F_{\mathrm{B1A1}}^{\mathrm{B1A1}} & \cdots & F_{\mathrm{A2B2}}^{\mathrm{B1A1}} \\ \vdots & \ddots & \vdots \\ \vdots & & \vdots \\ F_{\mathrm{B1A1}}^{\mathrm{A2B2}} & \cdots & F_{\mathrm{B2A2}}^{\mathrm{A2B2}} \end{pmatrix}$$

The gel point condition is determined by the equality

$$D_{\mathrm{G}} = \begin{vmatrix} 1-F_{\mathrm{B1A1}}^{\mathrm{B1A1}} & \cdots & \cdots & \cdots & -F_{\mathrm{A2B2}}^{\mathrm{B1A1}} \\ \vdots & \ddots & & & \vdots \\ \vdots & & \ddots & & \vdots \\ \vdots & & & \ddots & \vdots \\ -F_{\mathrm{B1A1}}^{\mathrm{A2B2}} & \cdots & \cdots & \cdots & 1-F_{\mathrm{B2A2}}^{\mathrm{B2A2}} \end{vmatrix} = 0 \qquad \text{(A24)}$$

In this particular case, $D_{\mathrm{G}}=$

$$\begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 & -p_{\mathrm{B1A1}}\alpha_{\mathrm{B1}} & -p_{\mathrm{B1A1}}\alpha_{\mathrm{B1}} \\ 0 & 1 & 0 & 0 & -p_{\mathrm{B2A1}}\alpha_{\mathrm{B2}} & -p_{\mathrm{B2A1}}\alpha_{\mathrm{B2}} & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & -p_{\mathrm{B1A2}}\alpha_{\mathrm{B1}} & -p_{\mathrm{B1A2}}\alpha_{\mathrm{B1}} \\ 0 & 0 & 0 & 1 & -p_{\mathrm{B2A2}}\alpha_{\mathrm{B2}} & -p_{\mathrm{B2A2}}\alpha_{\mathrm{B2}} & 0 & 0 \\ 0 & 0 & -p_{\mathrm{B1A1}}\alpha_{\mathrm{A1}} & -p_{\mathrm{B1A1}}\alpha_{\mathrm{A1}} & 1 & 0 & 0 & 0 \\ -2p_{\mathrm{A2B1}}\alpha_{\mathrm{A2}} & -2p_{\mathrm{A2B1}}\alpha_{\mathrm{A2}} & -p_{\mathrm{A2B1}}\alpha_{\mathrm{A2}} & -p_{\mathrm{A2B1}}\alpha_{\mathrm{A2}} & 0 & 1 & 0 & 0 \\ 0 & 0 & -p_{\mathrm{A1B2}}\alpha_{\mathrm{A1}} & -p_{\mathrm{A1B2}}\alpha_{\mathrm{A1}} & 0 & 0 & 1 & 0 \\ -2p_{\mathrm{A2B2}}\alpha_{\mathrm{A2}} & -2p_{\mathrm{A2B2}}\alpha_{\mathrm{A2}} & -p_{\mathrm{A2B2}}\alpha_{\mathrm{A2}} & -p_{\mathrm{A2B2}}\alpha_{\mathrm{A2}} & 0 & 0 & 0 & 1 \end{vmatrix}$$

Note that pairs of values are the same. This is because the pairs of right-hand sides of the functions $F(\mathbf{z},\mathbf{Z})$ are the same.

The solution of the determinant D_{G} using the Symbolic Toolbox MATLAB® software after rearrangements gives

$$\begin{aligned} D_{\mathrm{G}} = {} & 1 + 2(p_{\mathrm{A1B1}} - p_{\mathrm{A2B1}})(p_{\mathrm{B1A1}} - p_{\mathrm{B2A1}})\alpha_{\mathrm{A1}}\alpha_{\mathrm{A2}}\alpha_{\mathrm{B1}}\alpha_{\mathrm{B2}} \\ & - p_{\mathrm{A2B1}}\alpha_{\mathrm{A2}}\alpha_{\mathrm{B2}}(1 + p_{\mathrm{B2A1}}) \\ & - p_{\mathrm{A2B2}}\alpha_{\mathrm{A2}}\alpha_{\mathrm{B1}}(1 + p_{\mathrm{B1A1}}) - p_{\mathrm{A1B1}}p_{\mathrm{B2A2}}\alpha_{\mathrm{A1}}\alpha_{\mathrm{B2}} \\ & - p_{\mathrm{A1B2}}p_{\mathrm{B1A2}}\alpha_{\mathrm{A1}}\alpha_{\mathrm{B1}} \end{aligned} \qquad \text{(A25)}$$

Molecular weight averages. The number-average molecular weight is obtained by the same reasoning as before; it is equal to the mass per molecule. The number of molecules is given by the number of building units minus number of bonds. The number of half-bonds is obtained by differentiation of $F_{0n}(\mathbf{z},\mathbf{Z})$ with respect to all variables $\mathbf{z}$, putting $\mathbf{z}=\mathbf{Z}=\mathbf{1}$, $F'_{0n}(\mathbf{1},\mathbf{1})$. Thus

$$M_{\mathrm{n}} = \frac{n_{\mathrm{A}}M_{\mathrm{A}} + n_{\mathrm{B}}M_{\mathrm{B}}}{1 - F'_{0n}(\mathbf{1},\mathbf{1})/2} \qquad \text{(A26)}$$

Because the number of half-bonds extending from A units must be equal to that extending from B units (remembering that $p_{\mathrm{X}j\mathrm{Y}1}+p_{\mathrm{X}j\mathrm{Y}2}=1$)

$$M_{\mathrm{n}} = \frac{n_{\mathrm{A}}M_{\mathrm{A}} + n_{\mathrm{B}}M_{\mathrm{B}}}{1 - n_{\mathrm{B}}(\alpha_{\mathrm{B1}} + \alpha_{\mathrm{B2}})} = \frac{n_{\mathrm{A}}M_{\mathrm{A}} + n_{\mathrm{B}}M_{\mathrm{B}}}{1 - 2n_{\mathrm{B}}\alpha_{\mathrm{B}}} \qquad \text{(A27)}$$

where $\alpha_{\mathrm{B}} = (\alpha_{\mathrm{B1}} + \alpha_{\mathrm{B2}})/2$ is the conversion of all B groups.

The weight-average molecular weight is obtained from the generating function $W(\mathbf{Z})$

$$\begin{aligned} W(\mathbf{Z}) = {} & m_{\mathrm{A}}Z_{\mathrm{A}}^{M_{\mathrm{A}}}[1 - \alpha_{\mathrm{A1}} + \alpha_{\mathrm{A1}}(p_{\mathrm{A1B1}}u_{\mathrm{A1B1}} \\ & + p_{\mathrm{A1B2}}u_{\mathrm{A1B2}})]^2[1 - \alpha_{\mathrm{A2}} + \alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}u_{\mathrm{A2B1}} \\ & + p_{\mathrm{A2B2}}u_{\mathrm{A2B2}})] + m_{\mathrm{B}}Z_{\mathrm{B}}^{M_{\mathrm{B}}}[1 - \alpha_{\mathrm{B1}} \\ & + \alpha_{\mathrm{B1}}(p_{\mathrm{B1A1}}u_{\mathrm{B1A1}} + p_{\mathrm{B1A2}}u_{\mathrm{B1A2}})][1 - \alpha_{\mathrm{B2}} \\ & + \alpha_{\mathrm{B2}}(p_{\mathrm{B2A1}}u_{\mathrm{B2A1}} + p_{\mathrm{B2A2}}u_{\mathrm{B2A2}})] \end{aligned} \qquad \text{(A28)}$$

where the components of the vector $u(\mathbf{Z})$ are a function of Z_{A} and Z_{B}. These dependencies are determined by a set of recursive equations

$$\begin{aligned}
u_{\mathrm{B1A1}}(\mathbf{Z}) &= Z_{\mathrm{A}}^{M_{\mathrm{A}}}[1-\alpha_{\mathrm{A2}}+\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}u_{\mathrm{A2B1}}\\
&\qquad +p_{\mathrm{A2B2}}u_{\mathrm{A2B2}})]^2,\\
u_{\mathrm{B2A1}}(\mathbf{Z}) &= Z_{\mathrm{A}}^{M_{\mathrm{A}}}[1-\alpha_{\mathrm{A2}}+\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}u_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}u_{\mathrm{A2B2}})]^2,\\
u_{\mathrm{B1A2}}(\mathbf{Z}) &= Z_{\mathrm{A}}^{M_{\mathrm{A}}}\{[1-\alpha_{\mathrm{A1}}+\alpha_{\mathrm{A1}}(p_{\mathrm{A1B1}}u_{\mathrm{A1B1}}+p_{\mathrm{A1B2}}u_{\mathrm{A1B2}})]\\
&\qquad \times[1-\alpha_{\mathrm{A2}}+\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}u_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}u_{\mathrm{A2B2}})],\\
u_{\mathrm{B2A2}}(\mathbf{Z}) &= Z_{\mathrm{A}}^{M_{\mathrm{A}}}\{[1-\alpha_{\mathrm{A1}}+\alpha_{\mathrm{A1}}(p_{\mathrm{A1B1}}u_{\mathrm{A1B1}}+p_{\mathrm{A1B2}}u_{\mathrm{A1B2}})]\\
&\qquad \times[1-\alpha_{\mathrm{A2}}+\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}u_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}u_{\mathrm{A2B2}})],\\
u_{\mathrm{A1B1}}(\mathbf{Z}) &= Z_{\mathrm{B}}^{M_{\mathrm{B}}}[1-\alpha_{\mathrm{B2}}+\alpha_{\mathrm{B2}}(p_{\mathrm{B2A1}}u_{\mathrm{B2A1}}+p_{\mathrm{B2A2}}u_{\mathrm{B2A2}})],\\
u_{\mathrm{A2B1}}(\mathbf{Z}) &= Z_{\mathrm{B}}^{M_{\mathrm{B}}}[1-\alpha_{\mathrm{B2}}+\alpha_{\mathrm{B2}}(p_{\mathrm{B2A1}}u_{\mathrm{B2A1}}+p_{\mathrm{B2A2}}u_{\mathrm{B2A2}})],\\
u_{\mathrm{A1B2}}(\mathbf{Z}) &= Z_{\mathrm{B}}^{M_{\mathrm{B}}}[1-\alpha_{\mathrm{B1}}+\alpha_{\mathrm{B1}}(p_{\mathrm{B1A1}}u_{\mathrm{B1A1}}+p_{\mathrm{B1A2}}u_{\mathrm{B1A2}})],\\
u_{\mathrm{A2B2}}(\mathbf{Z}) &= Z_{\mathrm{B}}^{M_{\mathrm{B}}}[1-\alpha_{\mathrm{B1}}+\alpha_{\mathrm{B1}}(p_{\mathrm{B1A1}}u_{\mathrm{B1A1}}+p_{\mathrm{B1A2}}u_{\mathrm{B1A2}})]
\end{aligned} \tag{A29}$$

M_{w} is obtained by differentiation with respect to Z_{A} and Z_{B}:

$$\begin{aligned}
M_{\mathrm{w}} &= \left[\frac{\partial W(\mathbf{Z})}{\partial Z_{\mathrm{A}}}+\frac{\partial W(\mathbf{Z})}{\partial Z_{\mathrm{B}}}\right]_{\mathbf{Z}=\mathbf{1}}\\
&= m_{\mathrm{A}}\{M_{\mathrm{A}}+\alpha_{\mathrm{A1}}[p_{\mathrm{A1B1}}(u^{\mathrm{A}}_{\mathrm{A1B1}}+u^{\mathrm{B}}_{\mathrm{A1B1}})\\
&\quad +p_{\mathrm{A1B2}}(u^{\mathrm{A}}_{\mathrm{A1B2}}+u^{\mathrm{B}}_{\mathrm{A1B2}})]\\
&\quad +2\alpha_{\mathrm{A2}}[p_{\mathrm{A2B1}}(u^{\mathrm{A}}_{\mathrm{A2B1}}+u^{\mathrm{B}}_{\mathrm{A2B1}})\\
&\quad +p_{\mathrm{A2B2}}(u^{\mathrm{A}}_{\mathrm{A2B2}}+u^{\mathrm{B}}_{\mathrm{A2B2}})]\}+m_{\mathrm{B}}\{M_{\mathrm{B}}\\
&\quad +\alpha_{\mathrm{B1}}[p_{\mathrm{B1A1}}(u^{\mathrm{A}}_{\mathrm{B1A1}}+u^{\mathrm{B}}_{\mathrm{B1A1}})\\
&\quad +p_{\mathrm{B1A2}}(u^{\mathrm{A}}_{\mathrm{B1A2}}+u^{\mathrm{B}}_{\mathrm{B1A2}})]\\
&\quad +\alpha_{\mathrm{B2}}(p_{\mathrm{B2A1}}(u^{\mathrm{A}}_{\mathrm{B2A1}}+u^{\mathrm{B}}_{\mathrm{B2A1}})\\
&\quad +p_{\mathrm{B2A2}}(u^{\mathrm{A}}_{\mathrm{B2A2}}+u^{\mathrm{B}}_{\mathrm{B2A2}})]\}
\end{aligned} \tag{A29a}$$

Here, the short-hand notations of values of derivatives have the following meaning:

$$u^{\mathrm{A}}_{\mathrm{A1B2}} \equiv \left[\frac{\partial u_{\mathrm{A1B2}}(\mathbf{Z})}{\partial Z_{\mathrm{A}}}\right]_{\mathrm{Z}=\mathbf{1}}, \quad u^{\mathrm{B}}_{\mathrm{A1B2}} \equiv \left[\frac{\partial u_{\mathrm{A1B2}}(\mathbf{Z})}{\partial Z_{\mathrm{B}}}\right]_{\mathrm{Z}=\mathbf{1}}, \quad \text{etc.}$$

The set of values of derivatives of component of the vector $\mathbf{u}$ is obtained from the vector $\mathbf{u}$ (Eq. (A29)) by solving the set of linear Eq. (A30):

$$\begin{aligned}
u^{\mathrm{A}}_{\mathrm{B1A1}} &= M_{\mathrm{A}}+2\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}u^{\mathrm{A}}_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}u^{\mathrm{A}}_{\mathrm{A2B2}}),\\
u^{\mathrm{B}}_{\mathrm{B1A1}} &= 2\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}u^{\mathrm{B}}_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}u^{\mathrm{B}}_{\mathrm{A2B2}}),\\
u^{\mathrm{A}}_{\mathrm{B2A1}} &= u^{\mathrm{A}}_{\mathrm{B1A1}}, \quad u^{\mathrm{B}}_{\mathrm{B2A1}} = u^{\mathrm{B}}_{\mathrm{B2A1}},\\
u^{\mathrm{A}}_{\mathrm{B1A2}} &= M_{\mathrm{A}}+\alpha_{\mathrm{A1}}(p_{\mathrm{A1B1}}u^{\mathrm{A}}_{\mathrm{A1B1}}+p_{\mathrm{A1B2}}u^{\mathrm{A}}_{\mathrm{A1B2}})\\
&\quad +\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}u^{\mathrm{A}}_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}u^{\mathrm{A}}_{\mathrm{A2B2}}),\\
u^{\mathrm{B}}_{\mathrm{B1A2}} &= \alpha_{\mathrm{A1}}(p_{\mathrm{A1B1}}u^{\mathrm{B}}_{\mathrm{A1B1}}+p_{\mathrm{A1B2}}u^{\mathrm{B}}_{\mathrm{A1B2}})\\
&\quad +\alpha_{\mathrm{A2}}(p_{\mathrm{A2B1}}u^{\mathrm{B}}_{\mathrm{A2B1}}+p_{\mathrm{A2B2}}u^{\mathrm{B}}_{\mathrm{A2B2}}),\\
u^{\mathrm{A}}_{\mathrm{B2A2}} &= u^{\mathrm{A}}_{\mathrm{B1A2}}, \quad u^{\mathrm{B}}_{\mathrm{B2A2}} = u^{\mathrm{B}}_{\mathrm{B1A2}},\\
u^{\mathrm{A}}_{\mathrm{A1B1}} &= \alpha_{\mathrm{B2}}(p_{\mathrm{B2A1}}u^{\mathrm{A}}_{\mathrm{B2A1}}+p_{\mathrm{B2A2}}u^{\mathrm{A}}_{\mathrm{B2A2}}),\\
u^{\mathrm{B}}_{\mathrm{A1B1}} &= M_{\mathrm{B}}+\alpha_{\mathrm{B2}}(p_{\mathrm{B2A1}}u^{\mathrm{B}}_{\mathrm{A2B1}}+p_{\mathrm{B2A2}}u^{\mathrm{B}}_{\mathrm{B2A2}}),\\
u^{\mathrm{A}}_{\mathrm{A2B1}} &= u^{\mathrm{A}}_{\mathrm{A1B1}}, \quad u^{\mathrm{B}}_{\mathrm{A2B1}} = u^{\mathrm{B}}_{\mathrm{A1B1}},\\
u^{\mathrm{A}}_{\mathrm{A1B2}} &= \alpha_{\mathrm{B1}}(p_{\mathrm{B1A1}}u^{\mathrm{A}}_{\mathrm{B1A1}}+p_{\mathrm{B1A2}}u^{\mathrm{A}}_{\mathrm{B1A2}}),\\
u^{\mathrm{B}}_{\mathrm{A1B2}} &= M_{\mathrm{B}}+\alpha_{\mathrm{B2}}(p_{\mathrm{B1A1}}u^{\mathrm{B}}_{\mathrm{A1B1}}+p_{\mathrm{B1A2}}u^{\mathrm{B}}_{\mathrm{A1B2}}),\\
u^{\mathrm{A}}_{\mathrm{A2B2}} &= u^{\mathrm{B}}_{\mathrm{A1B2}}, \quad u^{\mathrm{B}}_{\mathrm{A2B2}} = u^{\mathrm{B}}_{\mathrm{A1B2}}
\end{aligned} \tag{A30}$$

The solution of these 16 linear equations was obtained using MATLAB Symbolic Toolbox®. The expressions for the derivatives were substituted into Eq. (A29a) and M_{w} was calculated.

Transition probabilities. Instead of eight types of bonds in which we distinguish the direction looking through the bonds, there exist only 4 distinguishable bonds differing in their composition irrespective of the bond direction:

A1B1	A1B2
A2B1	A2B2

For kinetically controlled systems controlled by irreversible bond formation, the concentrations of bonds are determined by a system of differential equations and which are a function of reaction variable (time or conversion). Thus,

$$\frac{\mathrm{d[A1B1]}}{\mathrm{d}t} = k_{11}[\mathrm{A1}][\mathrm{B1}] = k_{11}[\mathrm{A1}]_0(1-\alpha_{\mathrm{A1}})[\mathrm{B1}]_0(1-\alpha_{\mathrm{B1}}),$$

$$\frac{\mathrm{d[A1B2]}}{\mathrm{d}t} = k_{12}[\mathrm{A1}][\mathrm{B2}] = k_{12}[\mathrm{A1}]_0(1-\alpha_{\mathrm{A1}})[\mathrm{B2}]_0(1-\alpha_{\mathrm{B2}}),$$

$$\frac{\mathrm{d[A2B1]}}{\mathrm{d}t} = k_{21}[\mathrm{A2}][\mathrm{B1}] = k_{21}[\mathrm{A2}]_0(1-\alpha_{\mathrm{A2}})[\mathrm{B1}]_0(1-\alpha_{\mathrm{B1}}), \tag{A31}$$

$$\frac{\mathrm{d[A2B2]}}{\mathrm{d}t} = k_{22}[\mathrm{A2}][\mathrm{B2}] = k_{22}[\mathrm{A2}]_0(1-\alpha_{\mathrm{A2}})[\mathrm{B2}]_0(1-\alpha_{\mathrm{B2}})$$

and $-\frac{\mathrm{d[A]}}{\mathrm{d}t} = -\left(\frac{\mathrm{d[A1]}}{\mathrm{d}t} + \frac{\mathrm{d[A2]}}{\mathrm{d}t}\right)$

$$= k_{11}[\mathrm{A1}][\mathrm{B1}] + k_{12}[\mathrm{A1}][\mathrm{B2}] + k_{21}[\mathrm{A2}][\mathrm{B1}] + k_{22}[\mathrm{A2}][\mathrm{B2}]$$

The dependence of concentrations of bonds on time t is transformed into the dependence on concentration of all groups A, i.e., dependence on conversion of groups A

$$\frac{\mathrm{d[A1B1]}}{\mathrm{d[A]}} = \times \frac{k_{12}[\mathrm{A1}][\mathrm{B1}]}{k_{11}[\mathrm{A1}][\mathrm{B1}] + k_{12}[\mathrm{A1}][\mathrm{B2}] + k_{21}[\mathrm{A2}][\mathrm{B1}] + k_{22}[\mathrm{A2}][\mathrm{B2}]}; \text{ etc.}$$

This equation can be further transformed factoring out the initial concentration of B group, $[\mathrm{B}]_0$ and considering that that the ratios of the initial concentration of groups $[\mathrm{A1}]_0/[\mathrm{A}]_0 = 1/3$, $[\mathrm{A2}]_0/[\mathrm{A}]_0 = 2/3$, $[\mathrm{B1}]_0/[\mathrm{B}]_0 = 1/2$, $[\mathrm{B2}]_0/[\mathrm{B}]_0 = 1/2$. Thus,

$$\frac{\mathrm{d[A1B1]}}{[\mathrm{B}]_0\mathrm{d}\alpha_{\mathrm{A}}} = \frac{k_{11}(1/6)(1-\alpha_{\mathrm{A1}})(1-\alpha_{\mathrm{B1}})}{S},$$

$$\frac{\mathrm{d[A1B2]}}{[\mathrm{B}]_0\mathrm{d}\alpha_{\mathrm{A}}} = \frac{k_{12}(1/6)(1-\alpha_{\mathrm{A1}})(1-\alpha_{\mathrm{B2}})}{S},$$

$$\frac{\mathrm{d[A2B1]}}{[\mathrm{B}]_0\mathrm{d}\alpha_{\mathrm{A}}} = \frac{k_{21}(1/3)(1-\alpha_{\mathrm{A2}})(1-\alpha_{\mathrm{B1}})}{S}, \tag{A32}$$

$$\frac{\mathrm{d[A2B1]}}{[\mathrm{B}]_0\mathrm{d}\alpha_{\mathrm{A}}} = \frac{k_{22}(1/3)(1-\alpha_{\mathrm{A2}})(1-\alpha_{\mathrm{B2}})}{S}$$

where

$$S = k_{11}(1/6)(1-\alpha_{\mathrm{A1}})(1-\alpha_{\mathrm{B1}}) + k_{12}(1/6)(1-\alpha_{\mathrm{A1}})(1-\alpha_{\mathrm{B2}}) + k_{21}(1/3)(1-\alpha_{\mathrm{A2}})(1-\alpha_{\mathrm{B1}}) + k_{22}(1/3)(1-\alpha_{\mathrm{A2}})(1-\alpha_{\mathrm{B2}})$$

This system of differential equations was solved numerically and the integral values were used for calculation of transition probabilities **p** as a function of conversion of A or B groups:

$$p_{\mathrm{A1B1}} = \frac{[\mathrm{A1B1}]}{[\mathrm{A1B1}] + [\mathrm{A1B2}]},$$

$$p_{\mathrm{A1B2}} = 1 - p_{\mathrm{A1B1}},$$

$$p_{\mathrm{A2B1}} = \frac{[\mathrm{A2B1}]}{[\mathrm{A2B1}] + [\mathrm{A2B2}]},$$

$$p_{\mathrm{A2B2}} = 1 - p_{\mathrm{A2B1}}, \tag{A33}$$

$$p_{\mathrm{B1A1}} = \frac{[\mathrm{A1B1}]}{[\mathrm{A1B1}] + [\mathrm{A2B1}]},$$

$$p_{\mathrm{B1A2}} = 1 - p_{\mathrm{B1A1}},$$

$$p_{\mathrm{B2A1}} = \frac{[\mathrm{A1B2}]}{[\mathrm{A1B2}] + [\mathrm{A2B2}]}, \quad p_{\mathrm{B2B2}} = 1 - p_{\mathrm{B2A1}}$$

A.2.1. Auxiliary interrelations

The relations derived above are functions of conversions of functional groups α_{A1}, α_{A2}, α_{B1}, α_{B2}. They are interdependent and are a function of conversion of all A or B groups, α_{A} and α_{B}. The relations between α_{A1}, α_{A2}, α_{B1}, α_{B2} are determined as follows. The kinetics of consumption of groups A1 and A2 can be described as a function of concentrations of groups A1, A2, B1 and B2

$$-\frac{\mathrm{d[A1]}}{\mathrm{d}t} = k_{11}[\mathrm{A1}][\mathrm{B1}] + k_{12}[\mathrm{A1}][\mathrm{B2}],$$
$$-\frac{\mathrm{d[A2]}}{\mathrm{d}t} = k_{21}[\mathrm{A2}][\mathrm{B1}] + k_{22}[\mathrm{A2}][\mathrm{B2}] \tag{A34}$$

The four rate constants depend on reactivity of groups. In the simplest case of additivity of Gibbs activation energies,

$$k_{11} \propto k_{1\mathrm{A}}k_{1\mathrm{B}} \quad k_{12} \propto k_{1\mathrm{A}}k_{2\mathrm{B}} \quad k_{21} \propto k_{2\mathrm{A}}k_{1\mathrm{B}} \quad k_{22} \propto k_{2\mathrm{A}}k_{2\mathrm{B}}$$

the rate constants are considered to be proportional to the products of rate constants with a reference compound. If the reaction variable is conversion of functional groups, the structure build up is controlled by ratios of rate constants:

$$\frac{k_{11}}{k_{21}} = \frac{k_{12}}{k_{22}} = \frac{k_{1\mathrm{A}}}{k_{2\mathrm{A}}} = \kappa_{\mathrm{A}}^{+} \quad \frac{k_{11}}{k_{21}} = \frac{k_{21}}{k_{22}} = \frac{k_{1\mathrm{B}}}{k_{2\mathrm{B}}} = \kappa_{\mathrm{B}}^{+}$$

Under these conditions, the Eq. (A34) can be transformed to

$$\frac{\mathrm{d[A1]}}{\mathrm{d[A2]}} = \frac{k_{1\mathrm{A}}[\mathrm{A1}]}{k_{2\mathrm{A}}[\mathrm{A2}]} = \kappa_{\mathrm{A}}\frac{[\mathrm{A1}]}{[\mathrm{A2}]} \tag{A35}$$

The solution of this differential equation reads

$$\ln\frac{[\mathrm{A1}]}{[\mathrm{A1}]_0} = \kappa_{\mathrm{A}} \ln\frac{[\mathrm{A2}]}{[\mathrm{A2}]_0} \quad \text{or} \quad 1-\alpha_{\mathrm{A1}} = (1-\alpha_{\mathrm{A2}})^{\kappa_{\mathrm{A}}} \tag{A36}$$

$[\mathrm{A1}]_0$ and $[\mathrm{A2}]_0$ are initial concentrations of reactive groups. Similarly, for α_{B1}, α_{B2}

$$\alpha_{B1} = 1 - (1 - \alpha_{B2})^{\kappa_B} \tag{A37}$$

In transforming Eqs. (A36) and (A37), the following balance equations are employed

$$3\alpha_A = 2\alpha_{A2} + \alpha_{A1}, \quad 2\alpha_B = \alpha_{B1} + \alpha_{B2}$$

The derivation explained above is valid for any value of conversions α_A or α_B. For highly-branched off-stoichiometric functional polymers, $\alpha_B = 1$ and $\alpha_A = 1/r_A$.

A.3. Hyperbranched polymers from BA$_2$ monomer[1]

To characterize the application potential of highly-branched off-stoichiometric polymers, the M_n and M_w values of classical hyperbranched polymers are compared. Although the relations have already been derived in the past, the generating function approach will be briefly explained (cf. Ref. [36] pp. 136–141[2] and Refs. [37] and [38]). If all A groups have the same reactivity, the respective *pgf*'s have the form

$$F_{0n}(Z, \mathbf{z}) = Z^{M_0}[(1 - \alpha_B)Z_{Bunr} + \alpha_B z_{AB}]\\ [(1 - \alpha_A)Z_{Aunr} + \alpha_A z_{BA}]^2 \tag{A39}$$

$$F_{BA}(\mathbf{Z}, \mathbf{z}) = Z^{M_0}[(1 - \alpha_B)Z_{Bunr} + \alpha_B z_{AB}]\\ [(1 - \alpha_A)Z_{Aunr} + \alpha_A z_{BA}] \tag{A40}$$

$$F_{AB}(Z, \mathbf{z}) = Z^{M_0}[(1 - \alpha_A)Z_{Aunr} + \alpha_A z_{BA}]^2 \tag{A41}$$

The same procedure as above using the recursive equation for $\mathbf{u}$ (i.e., $F'_0 \rightarrow M_n$, and $F \rightarrow u \rightarrow W \rightarrow W' \rightarrow M_w$) gives

$$M_n = \frac{M_0}{1 - \alpha_B}, \quad M_w = \frac{M_0(1 - \alpha_B^2/2)}{(1 - \alpha_B)^2} \tag{A42}$$

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[1] Monomers for hyperbranched polymers are usually denoted as AB$_f$; some of us denoted in the past the polyfunctional monomers by the letter A and for hyperbranched case the abbreviation BA$_f$ and we retain this notation here.

[2] The second term of denominator of Eq. (10) of Ref. [36] should read $(1-\alpha_B)^2$ instead of $(1-\alpha_B^2)$.