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A simple model of hyperbranched polymerisation involving AB_2 and B_f core monomers and methods of narrowing the molecular size distribution

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Summary

A simple kinetic model of modelling hyperbranched polymerisation involving AB_2 and B_f core monomers is developed and analytical solutions of the model are presented. The number- and weight- average polymerisation degrees can be calculated using the model as functions of polymerisation time or conversion degree. Application of the model is tested for predicting the broadness of molecular size distribution of the hyperbranched polymers obtained by varying the procedures of feeding AB_2 monomer to polymerisation reactor.

Introduction

In the polymerisation processes involving an AB_2 (or ARB_2) [1] monomer, where A and B are functional groups reacting with each other (R stands for an organic moiety), the molecular size distribution of the resulting polymer is extremely broad, particularly at a high conversion degree of minority A groups. The macromolecules are highly branched, but their structure, unlike in the case of dendrimers, is far from being uniform.

Theoretical models describing an ideal condensation polymerisation of the system AB_2 and B_2 core monomer were described in several papers [2-7]. For the purpose of our studies of hyperbranched polyesters prepared from aromatic monomers, first used by Voit et al. [8-10], namely from the system consisting of 4,4-bis(4′-hydroxyphenyl)-pentanoic acid (AB_2 monomer) and various polyols as B_f monomers, we have also developed a simple kinetic model to analyse the evolution of the molecular size distribution with the progress of polymerisation. This model was recently described [11], but its practical application was limited to the system with a B_2 monomer only (such as Bisphenol A). In fact it was used to analyse the effect of a technical procedure of carrying out the polymerisation on the broadness of the molecular size distribution of the resulting polymer. We have confirmed that in the presence of core monomers the polydispersity of the polymer product, i.e. the ratio of the weight- to

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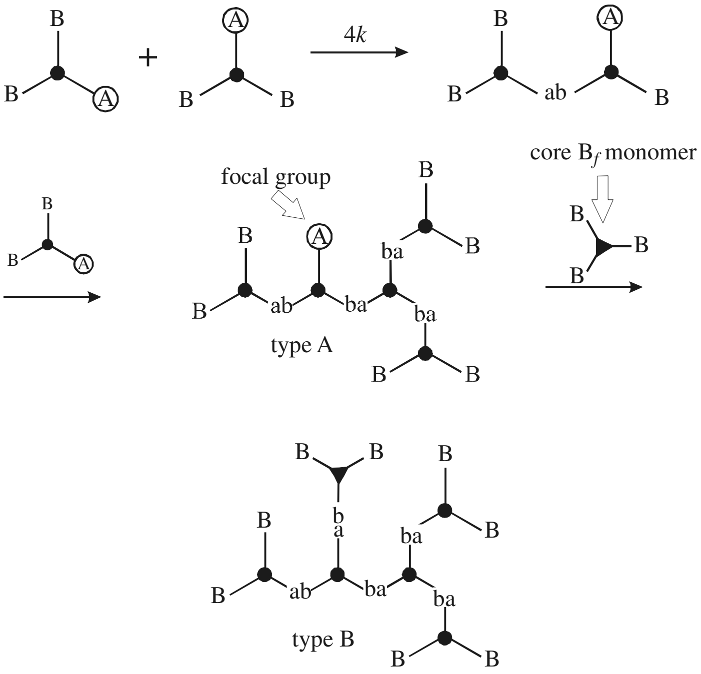
number-average polymerisation degree was substantially reduced. Introducing AB_2 monomer to B_2 monomer in several portions could further reduce the width of distribution. We also proved in calculations that extraction of unreacted monomer from polymer product can make the molecular size distribution still narrower [11].
All these results were obtained by solving (numerically) appropriate sets of differential equations. Identical results were obtained from Monte Carlo calculations, which were essentially virtual polymerisation experiments carried out in computer memory with no spatial correlations imposed.
In this paper we use the same simple kinetic model, extended, however, to core monomers of arbitrary functionality, f. The set of differential equations needed to calculate the number- and weight-average polymerisation degrees are solved analytically. This facilitates modelling and makes it mathematically rigorous.

The model

The system is shown in Scheme 1.



Scheme 1. Polymerisation of an AB_2 monomer with B_3 core monomer.

We assume the rate constant of the reaction between an A and any B group to be the same. For the reaction between molecules the rate constant has to be multiplied by the stoichiometry coefficient (see Scheme 1), which is the number of ways the reaction can take place. In the presence of B_f monomer, the system splits into two subsystems. The first consists of molecules with exactly one A (focal) group each. The other one consists of molecules without any unreacted A group, but containing exactly one unit from B_f monomer. The subsystems are referred to as ‘type A’ and ‘type B’ molecules, respectively. Note that an A-type molecule built of i units has $(i + 1)$ B groups, while B-type molecule contains $(i + f - 1)$ B groups (i includes the core unit). The rate equations for A- and B-type molecules in the polymerisation process are:

$$\frac{\mathrm{d}[i]_{\mathrm{A}}}{\mathrm{d}\tau} = \tfrac{1}{2}\sum_{l=1}^{i-1}(i+2)[i-l]_{\mathrm{A}}[l]_{\mathrm{A}} - [i]_{\mathrm{A}}\sum_{l=1}^{\infty}(i+1+l+1)[l]_{\mathrm{A}} - [i]_{\mathrm{A}}\sum_{l=1}^{\infty}(l+f-1)[l]_{\mathrm{B}} \qquad \mathbf{(1)}$$

and

$$\frac{\mathrm{d}[i]_{\mathrm{B}}}{\mathrm{d}\tau} = \sum_{l=1}^{i-1}(l+f-1)[i-l]_{\mathrm{A}}[l]_{\mathrm{B}} - (i+f-1)[i]_{\mathrm{B}}\sum_{l=1}^{\infty}[l]_{\mathrm{A}} \qquad \mathbf{(2)}$$

where $\tau = k \cdot t$; $[i]_{\mathrm{A}}$ and $[i]_{\mathrm{B}}$ are the concentrations of A- and B-type molecules consisting of i units (referred to as i-mers), respectively. The concentrations are conveniently expressed as the number-weight fractions. Thus, $[i]_{\mathrm{A}}$ is the number of all molecules of type A containing i units divided by the total number of units in the system.

The distribution of i-mer concentrations at a given stage of polymerisation can be expressed in terms of counting functions resembling the probability characteristic functions [12]:

$$G(\tau, x) = \sum_{i=1}^{\infty}[i]_{\mathrm{A}}\mathrm{e}^{ix} \qquad \mathbf{(3)}$$

and

$$g(\tau, x) = \sum_{i=1}^{\infty}[i]_{\mathrm{B}}\mathrm{e}^{ix} \qquad \mathbf{(4)}$$

where $|x| \le 1$ is a dummy variable of no physical meaning. Moments of the distributions are easily available by successive differentiation of (3) and (4) with respect to x followed by putting $x = 0$. Obviously, the concentrations are functions of the scaled polymerisation time τ.

The reason for introducing the characteristic functions G and g is that the rate equations (1) and (2) can be expressed in terms of these functions and some of its moments. The reader may wish to verify by comparing the terms of appropriate summations that when Eq. (1) is multiplied by $\exp(ix)$ for each i and then the left- and right-hand sides are summed for all i's ($i = 1, 2, \ldots$), one obtains:

$$\frac{\partial G}{\partial \tau} = \left(\frac{\partial G}{\partial x} + G\right)(G - G_0) - \left[G_x + G_0 + g_x + (f-1)g_0\right]G \qquad \mathbf{(5)}$$

Similarly, Eq. (2) can be transformed in the same manner to:

$$\frac{\partial g}{\partial \tau} = \left(\frac{\partial g}{\partial x} + (f-1)g\right)(G - G_0) \qquad \mathbf{(6)}$$

The functions G_0 and g_0 are the zero-th moments of the molecular size distribution, while G_x and g_x are the first moments defined by the equations:

$$G_0 = G_0(\tau) = G(\tau, 0) = \sum_{i=1}^{\infty}[i]_{\mathrm{A}} \qquad \mathbf{(7a)}$$

$$g_0 = \sum_{i=1}^{\infty}[i]_{\mathrm{B}} \qquad \mathbf{(7b)}$$

$$G_x = G_x(\tau) \equiv \left.\frac{\partial G}{\partial x}\right|_{x=0} = \sum_{i=1}^{\infty} i[i]_\mathrm{A} \tag{7c}$$

$$g_x \equiv \left.\frac{\partial g}{\partial x}\right|_{x=0} = \sum_{i=1}^{\infty} i[i]_\mathrm{B} \tag{7d}$$

Equations (5) and (6) describe the time evolution of the entire size distribution of hyperbranched molecules of type A and B, respectively.

The moments of size distribution are available from these equations as sets of ordinary differential equations with respect to time. At $x = 0$ Equations (5) and (6) read:

$$\dot{G}_0 = -[G_x + G_0 + g_x + (f-1)g_0]G_0 \tag{8}$$

and $\dot{g}_0 = 0$, respectively. The latter reflects the fact that the number of molecules of type B is always constant. The upper dot denotes differentiation with respect to time, τ.

By differentiation of (5) and (6) with respect to x followed by setting $x = 0$, one obtains

$$\dot{G}_x = -[g_x + (f-1)g_0]G_x \tag{9}$$

and

$$\dot{g}_x = [g_x + (f-1)g_0]G_x \tag{10}$$

Finally, by differentiating (5) and (6) twice with respect to x we obtain at $x = 0$:

$$\dot{G}_{xx} = 2(G_{xx} + G_x)G_x - [g_x + (f-1)g_0]G_{xx} \tag{11}$$

and

$$\dot{g}_{xx} = 2[g_{xx} + (f-1)g_x]G_x + [g_x + (f-1)g_0]G_{xx} \tag{12}$$

for the second moments of size distribution in populations of A- and B-type molecules, respectively.

The moments are needed to calculate the conversion of A groups, number-, P_n and weight-average polymerisation degree, P_w as well as the dispersity:

$$D_\mathrm{M} = \frac{P_\mathrm{w}}{P_\mathrm{n}} \tag{13}$$

Thus, the conversion of groups A can be calculated from stoichiometric considerations. Let the number of all units in the system be N. Among them there are units from B_f (Ng_0) and from AB_2 [$NG_0(0)$] monomers. The number of all unreacted groups A in the system is NG_0, since only the A-type molecules contain one A group each. The fraction of remaining (unreacted) A group is $G_0/G_0(0)$ and the conversion degree:

$$p = 1 - \frac{G_0}{G_0(0)} \tag{14}$$

The number average polymerisation degree is simply the reciprocal of $G_0 + g_0$ as follows from the definition of concentration units:

$$P_\mathrm{n} = \frac{1}{G_0 + g_0} \tag{15}$$

Again, the proper choice of concentration units provides the useful relationship:

$$G_x + g_x = 1 \tag{16}$$

Finally, the weight-average polymerisation degree in the whole system is given by:

$$P_{\mathrm{w}} = G_{xx} + g_{xx} \tag{17}$$

By substituting Eq. (15) into (8) one obtains:

$$\dot{G}_0 = -[G_0 + 1 + (f-1)g_0]G_0 = -G_0^2 - \gamma G_0 \tag{18}$$

with $\gamma \equiv 1 + (f-1)g_0$, a constant. The solution of this Bernoulli equation is:

$$G_0 = \frac{\gamma}{\left[\dfrac{\gamma}{G_0(0)} + 1\right]\exp(\gamma\tau) - 1} \tag{19}$$

The exponential factor will appear in all solutions, hence the substitution

$$v \equiv \exp(\gamma\tau) \tag{20}$$

is justified and practical [13]

Note, that no explicit value was set as the initial $G_0(0)$ value. This is because the same equation is to be used again and again to describe the process after supplying new portions of monomer. Then the initial value $G_0(0)$ as well as γ would change.

The solutions of Eqs (9) and (10) are equally straightforward after using Eq. (16): These are:

$$G_x = \frac{\gamma}{\left[\dfrac{\gamma}{G_x(0)} - 1\right]v + 1} \tag{21}$$

and $g_x = 1 - G_x$.

The differential rate equation for the weight-average polymerisation degree can be expressed explicitly using (17). Thus, by summing (11) and (12) and using (17) we get:

$$\frac{\mathrm{d}P_{\mathrm{w}}}{\mathrm{d}\tau} = 2\left(P_{\mathrm{w}} + f - 1\right)G_x - 2(f-2)G_x^2 \tag{22}$$

or, by changing variable according to (21):

$$\frac{\mathrm{d}P_{\mathrm{w}}}{\mathrm{d}v} - \frac{2P_{\mathrm{w}}}{v(\alpha v + 1)} = \frac{2(f-1)}{v(\alpha v + 1)} - \frac{2\gamma(f-2)}{v(\alpha v + 1)^2} \tag{23}$$

where $\alpha \equiv \gamma / G_x(0) - 1$

The solution is:

$$P_{\mathrm{w}} = \frac{1}{(\alpha v + 1)^2}\left\{\left[P_{\mathrm{w}}(0)(\alpha + 1)^2 - (f-1)(\gamma - 1 - 2\alpha) + \gamma\right]v^2 + (f-1)(\gamma - 1 - 2\alpha v) - \gamma\right\} \tag{24}$$

Calculation procedure

The calculations aimed at evaluating the effect of functionality f of core monomer B_f and of the procedure of feeding reactor with AB_2 monomer on the average size and distribution of hyperbranched molecules. In all cases the total amount of B_f monomer was introduced into reactor at the beginning of polymerisation process. Three general methods of feeding were tested.

In the one-pot reaction, all monomers were introduced at once. The average size and its distribution depended on the functionality and content of B_f monomer.

The total of AB_2 monomer was divided into several (usually 3 to 5) equal parts. The first part was introduced to the reactor with the core monomer and polymerised up to a predetermined conversion degree of A groups. Then the next portion of AB_2 monomer was introduced. This procedure is referred to as the pseudo-one-pot reaction.

Finally, by starting with the mixture of B_f and AB_2 monomers of molar ratio 1 to f, next portions of AB_2 monomer were introduced in increasing amounts. The amounts were proportional to the numbers of pendant groups B in the successive generations of the corresponding ideal dendrimer that could be obtained from the given monomer system. The feeding method is referred to as 'dendrimeric' one. Two-generation dendrimer illustrating the idea is shown in Fig. 1. Note that the final fraction of B_f in the dendrimeric feeding is fixed for given f and generation number.

The values of G_0, G_x, and P_w were calculated for several values of t (or v) according to Eqs. (19), (20), and (24), respectively, including the time at the final conversion p_k (set to 0.8 or 0.95). In the first run, the initial values were $1 - g_0^{(1)}$ for G_0 and G_x, and 1 for P_w, ($g_0^{(1)}$ was the mol fraction of B_f units in the first step of polymerisation). The functions G_0, G_x, and P_w were then all rescaled in the same way:

$$G_0^{(2)}(0) = G_0^{(1)}(t_{p_k})\frac{N^{(1)}}{N^{(2)}} + 1 - \frac{N^{(1)}}{N^{(2)}} \qquad \mathbf{(25)}$$

The rescaling corresponded to the change of the total number of units from $N^{(1)}$ in the first step, to $N^{(2)}$ in the second, followed by addition of fresh AB_2 monomer in the matching concentration units. The value of g_0 was rescaled (reduced) by just multiplying by $N^{(1)}/N^{(2)}$

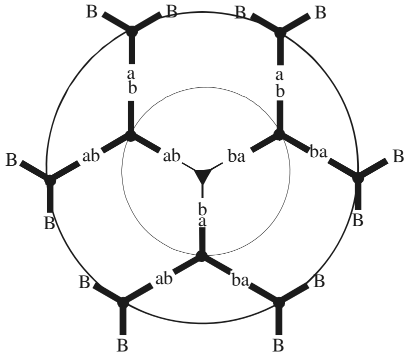


Figure 1. A two-generation dendrimer with trifunctional core unit. The relative numbers of AB_2 monomers added in the successive steps of polymerisation are, in this case, 3, 6,…, $3{\cdot}2^{i-1}$ (i is the number of generation).

The conversion in step (i) was recalculated to be valid in step (i + 1) by noting that

$$\frac{p^{(i+1)}(0)}{p_k} = \frac{N^{(i)}}{N^{(i+1)}}\frac{1-g_0^{(i)}}{1-g_0^{(i+1)}} \qquad \mathbf{(26)}$$

The term on the right-hand-side is the factor by which one has to multiply the conversion degrees of the previous step to express them in the scale of the given polymerisation step. It is worth noting that for the equal amounts of AB_2 monomer in each step, the scaling factors on the right-hand side of (26) for the series are $\frac{1}{2}, \frac{2}{3}, \frac{3}{4}, \frac{4}{5} \cdots$. Hence, carrying polymerisation in 5 steps one has to multiply the conversions in the first step by $\frac{1}{2} \cdot \frac{2}{3} \cdot \frac{3}{4} \cdot \frac{4}{5} = \frac{1}{5}$; those in the second step by $\frac{2}{3} \cdot \frac{3}{4} \cdot \frac{4}{5} = \frac{2}{5}$, etc. In the case of dendrimeric feeding, the corresponding series, is $\frac{1}{3}, \frac{3}{7}, \frac{7}{15}, \frac{15}{31} \cdots$, irrespectively of *f*.

Results and discussion

One-pot reaction

As one can see in Figure 2, the dispersity D_{m}, i.e., the ratio of the weight- P_{w} to number-average P_{n} degree of polymerisation of the hyperbranched polymers obtained in one-pot polymerisation reaches rather high values. It means that the width of the molecular size distribution is very high, particularly at high conversion of minority groups. The dispersity is the higher, the smaller is the proportion of the B_f monomer used and the lower is the functionality *f*.

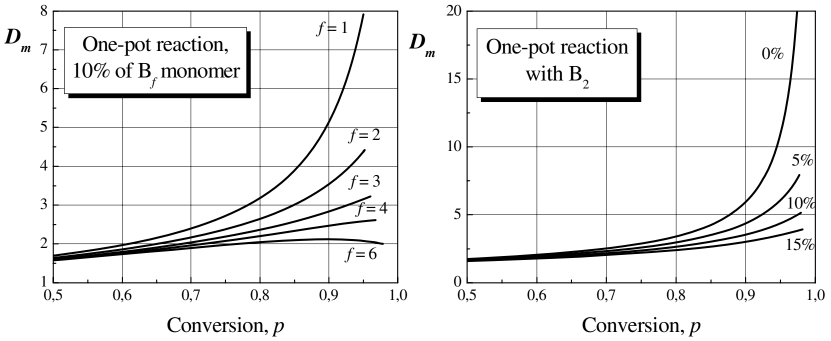


Figure 2. The effect of functionality of the core monomer B_f and of its content on the dispersity of hyperbranched polymers.

As it is easy to deduce [3], the number-average polymerisation degree, unlike the weight-one and hence dispersity, does not depend on the functionality of core monomer, but on its content. Indeed, for one-pot reaction system, $G_0(0) = 1 - g_0$. By combining Eqs (14) and (15) one obtains

$$P_{\mathrm{n}} = \frac{1}{1-(1-g_0)p} \qquad \mathbf{(27)}$$

Another well understood consequence of Eq. (27) is that the maximum attainable number-average polymerisation degree is the reciprocal of the mol fraction of B_f monomer, again, irrespectively of its functionality.

Pseudo-one-pot reaction

By introducing the whole of B_f monomer at once to a polymerisation reactor and AB_2 monomer divided into portions one can achieve a significant reduction of the molecular weight distribution of hyperbranched polymers [11]. The present approach helps to study this case. Two ways of splitting the total of AB_2 monomer are compared in this paper. One method consists of using equal portions of AB_2 monomer as already presented in our previous report [11]. Alternatively, we can study the effect of dividing the total amount of AB_2 monomer into portions of increasing size. The method of dividing AB_2 monomer in dendrimeric way keeps the proportion of B_f monomer fixed, unlike for the pseudo-one-pot system, where any fraction of B_f could be applied.

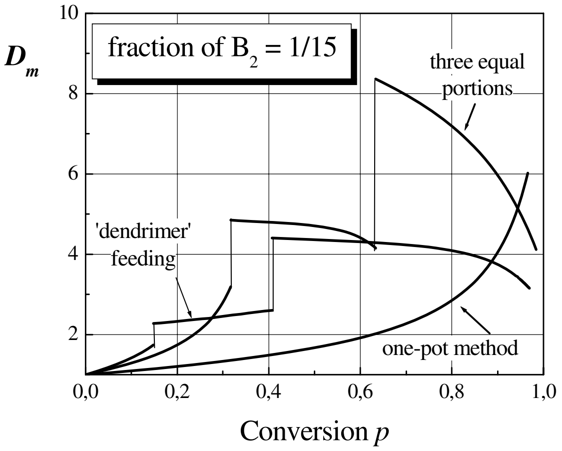


Figure 3. The dispersities of hyperbranched polymers obtained using different monomer feeding procedures. In the pseudo one-pot method, each next portion of AB_2 monomer was introduced after 95 % of A groups of the previous portion had reacted. The vertical tie lines are added to discriminate between the functions.

Representative results obtained for the two approaches are shown in Figure 3 where the dispersities versus conversion of minority A groups are plotted for the systems with B_2 (mol fraction $g_0 = 1/15$) added at once and AB_2 monomer divided either into three equal portions or into portions of increasing size corresponding to the relative contents of units in a tri-generation dendrimer (‘dendrimer’ feeding). For comparison, the dispersities in the system reacting according the one-pot method are also shown in Figure 3.

The effectiveness of dispersity reduction by using different feeding procedures strongly depends on the conversion of A groups at the moment of introducing the next portion. This is illustrated in Figure 4 where calculated dispersities of hyperbranched polymers are plotted against conversion of A groups for two variations of feeding procedure. Both are the ‘dedrimeric’ pseudo-one methods differing in the conversion at which the next portion of AB_2 monomer is introduced. As one can see in Figure 4 the broadness of molecular size distribution is smaller when the feeding of next portion comes at lower conversion, but at the same time the weight average of the polymer (not shown) is considerably smaller than that for the later feeding version. It is worth noting that the final number-average polymerisation degree is in all cases the same, irrespectively of the feeding procedure.

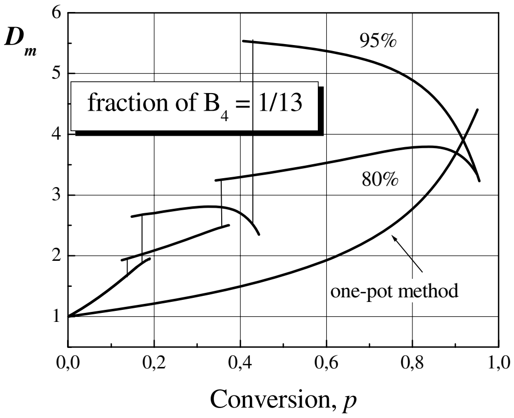


Figure 4. The dispersity of hyperbranched polymer in the three-generation 'dendrimeric' feeding where the next portion was introduced after 80 % or 95 % of conversion of the previous portion of monomer.

Conclusions

By using pseudo-one-pot procedures of feeding AB_2 monomer to B_f core monomer one can significantly reduce the size distribution of hyperbranched polymers prepared by condensation polymerisation. The effect of a certain feeding procedure can easily be estimated by applying the simple mathematical model of this polymerisation presented in this paper.

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References

1. Flory PJ (1952) J Am Chem Soc 74:2718; Flory PJ (1953) Principles of Polymer Chemistry. Cornell Univ Press, Ithaca
2. Radke W, Litvinenko G, Müller AHE (1998) Macromolecules 31:239
3. Yan D, Zhou Z (1999) Macromolecules 32:819
4. Zhou Z, Yan D (2000) Polymer 41:4549
5. Galina H, Lechowicz JB, Walczak M (2002) Macromolecules 35:3161
6. Cheng K-Ch, Don TM, Guo W, Chuang TH (2002) Polymer 43:6315
7. Cheng, K-Ch (2003) Polymer 44:1259
8. Turner SR, Voit B, Mourey TH (1993) Macromolecules 26:4617
9. Turner SR, Walter F, Voit B, Mourey TH (1994) Macromolecules 27:1611
10. Pavlova E, Voit B, Duškova-Smrčková M, Dušek K (2004) Polym Prep (Am Chem Soc, Div Polym Chem) 45:217
11. Galina H, Lechowicz BJ, Walczak M (2005) J Macromol Sci B, Macromol Phys, 44:925
12. Feller W (1968) An Introduction to Probability Theory and its Applications 2. Wiley, New York
13. Ziff RM, Ernst MH, Hendriks EM (1984) J Colloid Interface Sci 100:220