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Kinetics of formation of hyperbranched polymers

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Abstract. Kinetic aspects of formation of hyperbranched polymers by three-dimensional polymerisation, polycondensation, cyclotrimerisation, self-condensing vinyl polymerisation and proton transfer ionic polymerisation are considered. The last two mechanisms bear some features of polycondensation. The kinetic features of the polymerisation processes and their effect on the topological structure of hyperbranched polymers are discussed. Particular attention is paid to the dependence of critical conversion (gel point) on the kinetic conditions. Taking into account this dependence, the methods for shifting the gel point to higher degrees of conversion are analysed. Possible approaches to characterisation of the topological structures of hyperbranched polymers are discussed. The bibliography includes 177 references.

I. Introduction

Progress in nanotechnology [1] requires the design of novel materials including polymers with unique properties, such as enhanced absorption capacity, the ability to sorb and stabilise inorganic and organic molecules (*e.g.*, metal nanoclusters), compatibility with media of diferent polarity, viscosity (low viscosity of corresponding solutions), *etc*. Most of these requirements are met by dendrimers.[2–4] However, multistage synthesis of these systems, which involves a sequential growth of generations from a core or the addition of dendritic molecules formed using the same pattern to the core makes the production more expensive and thus precludes wide use of such polymers. Therefore, a relatively new field of polymer science, namely, research on the formation, properties and fields of application of hyperbranched polymers (HBPs) has been developed recently. In contrast to dendrimers, HBPs can be synthesised by conventional methods of polymer chemistry and technology including polycondensation of AB_n ($n \geqslant 2$) monomers, three-dimensional polymerisation and cyclotrimerisation of dialkynes and diisocyanates. Due to relatively simple synthetic procedure HBPs are at least competitive with dendrimers.

Information on the methods of synthesis, topological structure (and methods for its analysis) and practical application of HBPs is available in reviews.[5–17] Particularly thorough are the reviews[5–7] by Korolev, who analysed publications reported up to the year 2005. However, the kinetic aspects of HBP structure formation have been poorly studied so far. Indeed, specific features of stepwise synthesis allow the topological structure of regular dendrimers to be completely described using the number of generations and the functionality of structural units. However, this procedure is inapplicable to HBPs, becuse their formation is essentially stochastic and therefore the structure of HBPs should be described with allowance for the (i) presence of structural units of different functionality and (ii) distributions over structural parameters, which are governed by the kinetic features of HBP formation.

It has been stated[5] that structural (topological) characterisation is insufficient to define the notion 'hyperbranched polymers' and that a complete definition requires the use of particular properties of polymers, that is, solubility and compatibility, low viscosity and ability to sorb atoms and molecules (see above). We believe that there is no need for using the properties. If the topological structure is defined as the structure, in which the number of branching points is comparable with the degree of polymerisation at a restricted number of rings, the corresponding properties will manifest themselves naturally.

Indeed, an increase in the number of branching points is accompanied by a decrease in the ratio of the hydrodynamic

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radius of the macromolecular coil to its molecular mass and in the exponent in the dependence of the intrinsic viscosity on the molecular mass;[18] *i.e.*, the fractal dimension decreases and 'transition from polymeric to colloidal behaviour occurs'.[19] At the same time intense cyclisation causes the formation of microgel in the branched macromolecule (*e.g*, as in radical 3D polymerisation).[7, 20] Typical of gel is microsyneresis; therefore, high sorption capacity of gel cannot be considered.

Having considered possible methods of synthesis of HBPs, Korolev and Bubnova[5] proposed to distinguish between the following types of reactions:

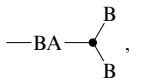
— stepwise polyaddition (polycondensation);
— 3D radical polymerisation; and
— 'living' polymerisation.

Their classification was substantiated by considering synthetic methods of control of processes and we agree with this treatment. However, this is not a kinetic approach. In addition, polycyclotrimerisation of diynes and diisocyanates and their copolytrimerisation with correspodning monomers are left out of consideration. These processes can be treated as polycondensation; however, three rather than two reactants are formally involved in each event. This requires a particular procedure for analysing the kinetic features.[21]

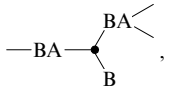
In this review we present a kinetic treatment of the formation of the topological structure of HBPs.

The topological structure of dendrimers is completely defined by the number of generations and the functionality of stuctural units. Characterisation of the structure of HBPs requires taking account of at least three types of units:

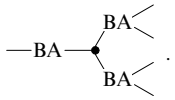
terminal units of different functionality



linear



and branching



From this point on, the letters t, l and d denote the total numbers of terminal, linear and branching units, respectively; and the letters T, D and L denote the percentages (proportions) of these units in the molecule. This example refers to a polymer based on the AB_2 monomer provided that only the reaction A + B is allowed in the course of polymerisation.

It was proposed[22] to use the Frechet parameter (FB), that is, the ratio of the number of branching points to the total number of structural units as a quanitative characteristic of the topological structure. Yet another parameter introduced[23] for characterisation of the topological structure of HBPs is the parameter DB (Degree of Branching), which equals the ratio of the actual number (r) of growth directions, along which new branches grow (chain branching propagation), to the maximum possible number of growth directions

$$\mathrm{DB} = \frac{r}{r_{\max}}.$$

Here DB is the so-called Frey parameter (branching parameter) equal to the number of branches issuing from the linear structure, namely, DB = 0 for a linear polymer, DB = 1 at one branch, *etc*.

It has been shown[23] that for polymers based on AB_2 monomer one has

$$\mathrm{DB} = \frac{2D}{2D + L}. \qquad (1)$$

For a polymer based on AB_m monomer one has

$$D = \sum_{i=2}^{m} (i-1)d_i,$$

$$L = \sum d_1, \quad T = \sum d_0,$$

where d_i is the proportion of points wrom which i branches issue. In this case the Frey parameter equals[23]

$$\mathrm{DB} = \left[m \sum_{i=2}^{m} (i-1)d_i\right]\left[(m-1)\sum_{i=1}^{m} i d_i\right]^{-1}. \qquad (2)$$

When HBPs are synthesised by cyclotrimerisation and polymerisation, the functionality of the branching site usually equals two and the parameter DB is calculated using expression (1).

Clearly, the parameter DB is suitable for characterisation of molecules of particular structure or systems comprised of identical molecules. This quantity cannot be used to describe systems containing molecules having different structures. It should be emphasised again that characterisation of the topological structure of HBPs requires the inclusion of distributions over structural parameters, because the formation of HBPs is essentially statistical in character.[24]

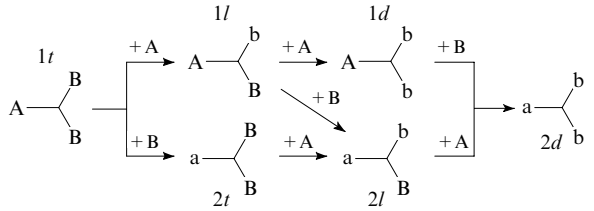
II. Polycondensation

Flory[25] was the first who theoretically considered polycondensation of AB_m monomers using methods of probability theory and showed that in this case the gel point is unreachable but the width of the molecular mass distribution (MMD) increases infinitely if $\alpha_A \to 1$, where α_A is the conversion of groups A. A kinetic approach with inclusion of substitution effect † was for the first time used in Ref. 22. A limiting case for manifestation of the substitution effect was considered in Ref. 26. Considering 3,5-bis(trimethylsilyloxy)benzoyl chloride as reactive monomer, the authors analysed the situation where the reaction of one group causes changes in reactivities of two other groups.

Polycondensation of AB_2 monomers can be characterised by twelve kinetic constants. Possible reactions and notations of reactants 1 and 2 of the types t, l, d (according to Kuchanov,[27] they are called 'monads') are presented in Scheme 1 (upper-case symbols denote the reacting groups and lower-case symbols denote the reacted groups).

† The first-spell substitution effect means (see, *e.g*., Ref. 9) a change in the reactivity of functional groups of a polyfunctional molecule upon reaction of one functional group.

Scheme 1



Each reaction results in corresponding dyads; determination of their concentrations was the main goal of study.[26] Of course, the kinetics of these processes and the overall consumption of functional groups are determined by the matrix of kinetic constants

$$K = \begin{vmatrix} k_{1t1t} & k_{1l1t} & k_{2t1t} & k_{2l1t} \\ k_{1t1l} & k_{1l1l} & k_{2t1l} & k_{2l1l} \\ k_{1t1d} & k_{1l1d} & k_{2t1d} & k_{2l1d} \end{vmatrix}.$$

The subscripts denote the reacting monads.

The authors of Ref. 28 have solved an inverse problem. They determined the most probable values of the kinetic constants (calculated with respect to k_{1t1t}) by analysing the ^{13}C NMR experimental data on changes in the monad concentrations (Fig. 1, open and filled circles, triangles and squares) in the course of reaction

$$K = \begin{vmatrix} 1.00 & 1.18 & 0.68 & 1.28 \\ 1.01 & 1.17 & 0.54 & 1.21 \\ 1.01 & 1.14 & 0.64 & 1.25 \end{vmatrix}. \quad (2a)$$

In this case, DB = 0.606.

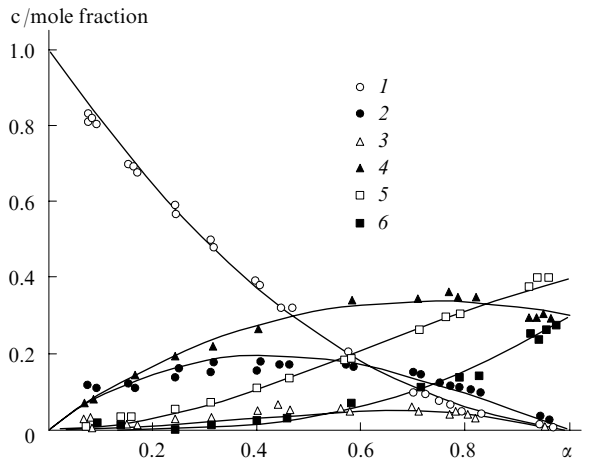


Figure 1. Relative concentrations of monads (see Scheme 1) plotted *vs.* conversion in polycondensation of 3,5-bis(trimethylsilyloxy)-benzoyl chloride.[27]
Monads: 1*t* (*1*), 1*l* (*2*), 1*d* (*3*), 2*t* (*4*), 2*l* (*5*) and 2*d* (*6*). The curves were calculated using the matrix of kinetic constants (2a).

Clearly, this is a rare case. Usually, the chemical structure of monomers is such that the case in point is the substitution effect with respect to groups B. The overall kinetic scheme of the process is as follows:[24, 29]

$$\mathrm{R}(l_1,t_1) + \mathrm{R}(l_2,t_2) \xrightarrow{k_1} \mathrm{R}(l_1 + l_2 + 1,\ t_1 + t_2 - 1),\ \text{reaction with } t \quad (3)$$
$$\xrightarrow{k_2} \mathrm{R}(l_1 + l_2 - 1,\ t_1 + t_2),\ \text{reaction with } l.$$

The set of kinetic constants can be represented in the form:

$$K = \begin{vmatrix} k_1 & k_2 & k_1 & k_2 \\ k_2 & k_2 & k_2 & k_2 \\ k_1 & k_2 & k_1 & k_2 \end{vmatrix}.$$

where the subscripts 1 and 2 characterise the substitution effect.

Scheme (3) leads to an infinite system of equations.‡

$$\frac{\mathrm{d}R(0,1)}{\mathrm{d}\tau} = -R(0,1)(2k_1N + k_2L + 2k_1T), \quad (4)$$

$$\frac{\mathrm{d}R(l,t)}{\mathrm{d}\tau} = -R(l,t)\Big[k_2L + 2k_1T + R(2k_1t + k_2l)\Big] +$$
$$+ 2k_1 \sum_{l_1=0}^{l} \sum_{t_1=1}^{t} R(l_1,t_1)\Big[(t - t_1 + 1)R(l - l_1 - 1, t - t_1 + 1)\Big] +$$
$$+ k_2 \sum_{l_1=0}^{l} \sum_{t_1=1}^{t} R(l_1,t_1)\Big[(l - l_1 + 1)R(l - l_1 + 1, t - t_1)\Big],$$

where τ is time; the initial conditions are as follows: $R(0,1) = N_0$ is the total number of molecules at the beginning of the process and $R(l,t) = 0$ for l and $t = 1, 2, \ldots$. From this point on we use the following notations:

$$N = \sum_{l,t} R(l,t), \quad L = \sum_{l,t} lR(l,t), \quad T = \sum_{l,t} tR(l,t).$$

where N is the total concentration of molecules containing the l- and t-type units whose proportions are L and T, respectively.

The following should be noted. The initial monomer should be treated as a t-unit and the monomers with one and two reacted groups B as l- and d-units.[23] Here, the relation

$$T = D + 1$$

and the initial condition

$$R(0,1) = N_0$$

are valid. However, yet another approach is possible.§ The initial monomer is not considered as a unit. The monomer with one reacted group B is treated as a t-unit containing two functional groups, A and B, and the monomer with two reacted groups B is an l-unit with a free functional group A. In this case one has

$$T = D$$

and the initial condition

$$R(0,0) = N_0$$

is valid. The authors of Refs 24 and 29 used the first approach.

‡ Hereafter the concentrations of corresponding reactants in the kinetic equations are given in italic.

§ This was noticed by G V Malkov (Institute of Problems of Chemical Physics, Russian Academy of Sciences).

In this connection, mention may be made of the following. Usually, theoretical analysis of polycondensation processes involves consideration of low-molecular-mass products, in particular, monomers and dimers, in general context of polymer chains. However, in the case of HBPs the situation is different. Namely, since molecules of low-molecular-mass compounds cannot have branched units, they should be excluded from the overall set of branched oligomers and polymers. However, we have failed to find any example of this approach in the literature.

It is convenient to solve the system (4) using the generating function

$$\Phi(s,p) = \sum_{l,t} s^l p^t R(l,t),$$

where arbitrary variables s and p correspond to the l- and t-units, respectively. Thus, by a simple substitution, the infinite system (4) is replaced by the following partial differential equation:

$$\frac{\partial\Phi(s,p)}{\partial\tau} = -\Phi(s,p)(2k_1T + k_2L) - \\ -N\left(2k_1p\Phi_p + k_2s\Phi_s\right) + \Phi(s,p)(2k_1s\,\Phi_p + k_2\Phi_s), \quad (5)$$

where

$$\Phi_s \equiv \frac{\partial\Phi(s,p)}{\partial s},$$

$$\Phi_p \equiv \frac{\partial\Phi(s,p)}{\partial p}.$$

This equation cannot be solved, especially with arbitrary values of the kinetic constants k_1 and k_2. Therefore, it is accepted that

$$\Phi(1,1) = N,$$

$$\Phi_s(1,1) = L,$$

$$\Phi_p(1,1) = T,$$

$$\Phi_{ss} \equiv \frac{\partial^2\Phi(1,1)}{\partial s^2} = \sum_{l,t} l^2R(l,t) - L,$$

$$\Phi_{sp} \equiv \frac{\partial^2\Phi(1,1)}{\partial s\partial p} = \sum_{l,t} ltR(l,t),$$

$$\Phi_{pp} \equiv \frac{\partial^2\Phi(1,1)}{\partial p^2} = \sum_{l,t} t^2R(l,t) - T,$$

and then by successive differentiation with respect to s and p followed by equalisation to unity one gets the system of equations for moment generating function

$$\frac{\mathrm{d}N}{\mathrm{d}\tau} = -N(2k_1T + k_2L), \quad (6)$$

$$\frac{\mathrm{d}L}{\mathrm{d}\tau} = -k_2LN + 2k_1TN,$$

$$\frac{\mathrm{d}T}{\mathrm{d}\tau} = -2k_1TN,$$

$$\frac{\mathrm{d}\Phi_{ss}}{\mathrm{d}t} = -2k_2\Phi_{ss}N + 4k_1\Phi_{sp}N + 2L\left(2k_1T + 2k_1\Phi_{ps} + k_2\Phi_{ss}\right),$$

$$\frac{\mathrm{d}\Phi_{sp}}{\mathrm{d}\tau} = -(2k_1 + k_2)\Phi_{sp}N + 2k_1\Phi_{pp}N + T\left(2k_1\Phi_{sp} + k_2\Phi_{ss}\right) + \\ + L\left(2k_1\Phi_{pp} + k_2\Phi_{sp}\right) + 2k_1T^2,$$

$$\frac{\mathrm{d}\Phi_{pp}}{\mathrm{d}\tau} = -4k_1\Phi_{pp}N + 2T\left(2k_1\Phi_{pp} + k_2\Phi_{sp}\right)$$

with the initial values $N = N_0$, $L = 0$, $T = N_0$, $\Phi_{ss} = 0$, $\Phi_{sp} = 0$, $\Phi_{pp} = 0$.

Structural features of HBPs are included using relationships between the numbers of different-type units

$$d = t - 1, \quad (7)$$

$$m = d + l + t = 2t + l - 1,$$

where m is the total number of units in the molecule. Therefore, if $R(l,t)$ is the concentration of molecules of a particular structure (having a given number of linear and terminal units), with allowance for relations (7) for the average proportions of corresponding units one gets the expressions

$$\overline{L}_\mathrm{n} = \frac{1}{N}\sum_{l,t} lR(l,t) = \frac{\Phi_s(1,1)}{\Phi(1,1)}$$

$$\overline{T}_\mathrm{n} = \frac{1}{N}\sum_{l,t} tR(l,t) = \frac{\Phi_p(1,1)}{\Phi(1,1)},$$

$$\overline{D}_\mathrm{n} = \frac{1}{N}\sum_{l,t} (t-1)R(l,t) = \overline{T}_\mathrm{n} - 1.$$

The number-average degree of polymerisation is given by

$$\overline{P}_\mathrm{n} = \frac{1}{N}\sum_{l,t} (2t + l - 1)R(l,t) = 2\overline{T}_\mathrm{n} + \overline{L}_\mathrm{n} - 1.$$

The mass-average values of structural parameters are determined from the expressions:

$$\overline{L}_\mathrm{w} = \frac{\sum_{l,t} l^2R(l,t)}{\sum_{l,t} lR(l,t)} = \frac{\Phi_{ss}(1,1)}{\Phi_s(1,1)} + 1,$$

$$\overline{T}_\mathrm{w} = \frac{\sum_{l,t} t^2R(l,t)}{\sum_{l,t} tR(l,t)} = \frac{\Phi_{pp}(1,1)}{\Phi_p(1,1)} + 1,$$

$$\overline{D}_\mathrm{w} = \frac{\sum_{l,t} t^2R(l,t) - 2\sum_{l,t} tR(l,t) + N}{\sum_{l,t} tR(l,t) - N} = \\ = \frac{\Phi_{pp}(1,1) - 2\Phi_p(1,1) + \Phi(1,1)}{2\Phi_p(1,1) + \Phi_s(1,1) - \Phi(1,1)},$$

$$\overline{P}_w = \frac{4\sum_{l,t} t^2 R(l,t) + 4\sum_{l,t} ltR(l,t)}{2\sum_{l,t} tR(l,t) + \sum_{l,t} lR(l,t) - N} +$$

$$+ \frac{\sum_{l,t} l^2 R(l,t) + N - 4T - 2L}{2\sum_{l,t} tR(l,t) + \sum_{l,t} lR(l,t) - N} =$$

$$= \frac{4\Phi_{pp}(1,1) + 4\Phi_{sp}(1,1) + \Phi_{ss}(1,1) - \Phi_s(1,1) + \Phi(1,1)}{2\Phi_p(1,1) + \Phi_s(1,1) - \Phi(1,1)}.$$

The conversion of groups B is

$$\alpha_B = \frac{\alpha_A}{2}.$$

For the number of chains one has

$$\frac{N}{N_0} = 1 - \alpha_A.$$

Therefore, the number-average degree of polymerisation

$$\overline{P}_n = (1 - 2\alpha_B)^{-1}$$

is independent of kinetic conditions. At the same time the mass-average degree of polymerisation and, correspondingly, the width of the MMD

$$\gamma = \frac{\overline{P}_w}{\overline{P}_n}$$

are strongly dependent on the ratio of the kinetic constants k_1 and k_2 (Fig. 2). At low k_2 (reaction of mostly terminal functional groups; negative substitution effect), the width of the MMD increases at low conversions, $\gamma \to 2$ (discontinuation in the range from 1.9 to 2 in the plot). Note that the degree of polymerisation is also about 2. At higher k_2 values (sufficiently high reactivity of functional groups in *l*-units; positive substitution effect or no effect), the parameter γ markedly increases only at high degrees of conversion.

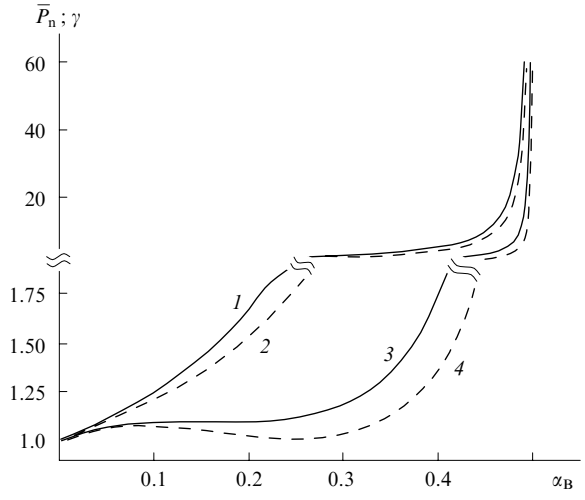


Figure 2. Changes in MMD parameters in the course of reaction.[24]
$\overline{P}_n$ (*1*) and $\overline{P}_w\overline{P}_n$ at $k_2/k_1 = 10$ (*2*), 1 (*3*) and 0.1 (*4*).

The total and relative (divided by N_0) concentrations of terminal units in the system decrease with conversion; the smaller the k_2/k_1 ratio the more pronounced the decrease (Fig. 3). Otherwise, the overall content of *t*-units in the system is rather high even when the reaction is completed. The ratio k_2/k_1 affects the character of accumulation of *l*-units, namely, their concentration almost linearly increases with conversion at small ratio k_2/k_1 and quite rapidly reaches a limiting value and then decreases to some extent at high ratio k_2/k_1.

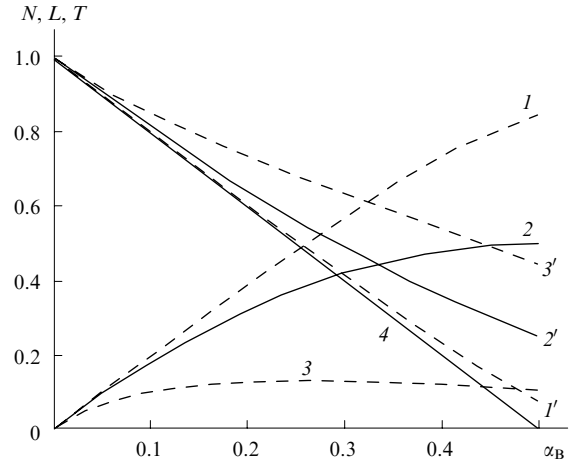


Figure 3. Parameters *N*, *L* and *T* plotted *vs*. conversion in the course of polycondensation of AB_2 monomers.[24]
L (*1*–*3*), *T* (*1′*–*3′*) and *N* (*4*). All numerical values are given per initial number of monomer molecules N_0; $k_2/k_1 = 0.1$ (*1*, *1′*), 1 (*2*, *2′*) and 10 (*3*, *3′*).

Since

$$D = T - N,$$

at small k_2/k_1 ratio the total concentration of *d*-units is low and increases with an increase in the ratio of the rate constants for the second and first addition (see Fig. 3).

Using the data presented in Fig. 3 and relation (1), one can calculate the parameter DB. The DB(α_B) plots are shown in Fig. 4. At positive substitution effect, the para-

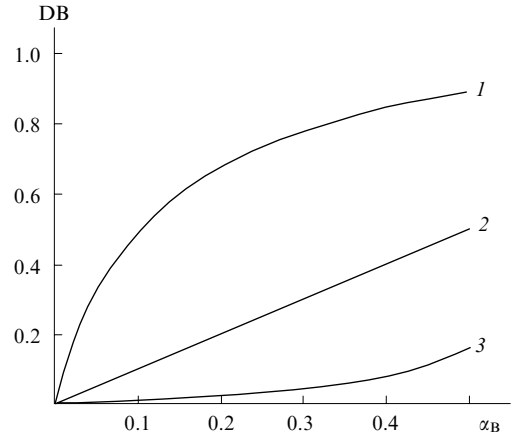


Figure 4. Changes in the parameter DB in the course of polycondensation of AB_2 monomers.[24]
$k_2/k_1 = 10$ (*1*), 1 (*2*) and 0.1 (*3*).

meter DB takes large values, whereas at small k_2/k_1 ratios its values are also small. With respect to this parameter, at $k_2/k_1 > 1$ HBPs can be compared with dendrimers, for which DB = 1; however, the differences between HBPs and dendrimers are significant owing to broad molecular mass distributions and structural parameter distributions for HBPs.

Figure 5 shows the changes in the average proportion of reactive linear and terminal units in macromolecules in the course of polycondensation. At low k_2, the *l*-units are accumulated faster, whereas the proportion of *t*-units remains of the order of one unit per molecule until deepest conversions. Of course, the reverse is observed at high k_2, namely, relatively slow accumulation of *l*-units owing to their consumption and faster accumulation of *t*-units in the structure of macromolecules.

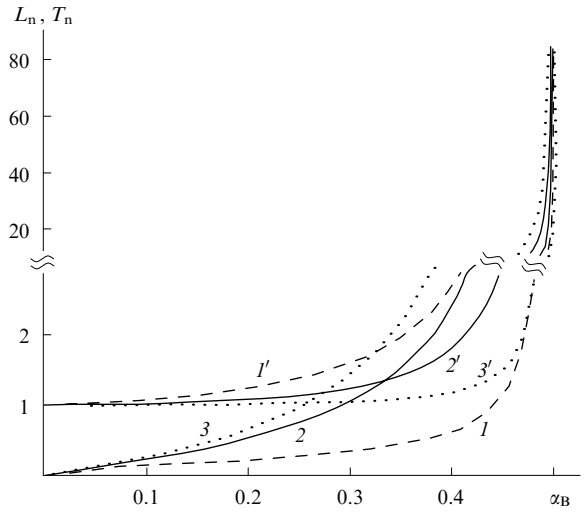


Figure 5. Changes in structural characteristics of macromolecules in the course of polycondensation of AB_2 monomers.[24]
Linear units (L_n) (*1*–*3*) and terminal units (T_n) (*1′*–*3′*).
k_2/k_1 = 10 (*1*, *1′*), 1 (*2*, *2′*) and 0.1 (*3*, *3′*).

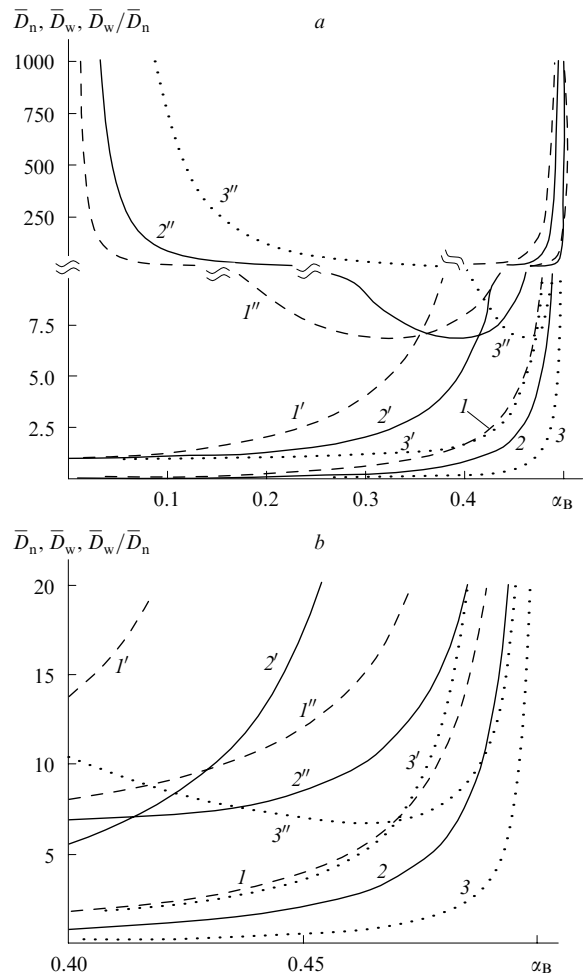


Figure 6. Changes in characteristics of branching of macromolecules in the course of polycondensation of AB_2 monomers at $0 < \alpha_B < 0.5$ (*a*) and $0.40 < \alpha_B < 0.5$ (*b*).[24]
$\bar{D}_n$ (*1*–*3*), $\bar{D}_w$ (*1′*–*3′*) and $\bar{D}_w/\bar{D}_n$ (*1″*–*3″*); k_2/k_1 = 10 (*1*, *1′*, *1″*), 1 (*2*, *2′*, *2″*) and 0.1 (*3*, *3′*, *3″*).

The number-average degree of branching $\bar{D}_n$ slightly increases with conversion, especially at low k_2 (Fig. 6). At the same time the width of the $\bar{D}_w/\bar{D}_n$ distribution varies over a wider range. Noteworthy is an unusual, but quite explainable shape of the dependence of this parameter on conversion, which passes through an extremum. Indeed, $\alpha \to 0$ $\bar{D}_n \to 0$ and $\bar{D}_w \to 1$ at $\alpha \to 0$. The minimum value is $\bar{D}_w/\bar{D}_n \approx 6.8$ and depends only slightly on the ratio of the kinetic constants (in the third decimal digit). But the minimum on the conversion axis is markedly shifted towards larger α_B values as k_2 decreases.

Möller and co-workers[30] seem to be the first who posed the problem of the distribution functions of structural parameters (they compared the mass-average values of the Frechet and Frey branching parameters), although based on the probabilistic approach.

It is the broad molecular mass and branching degree distributions that underlie the search for specific techniques for carrying out polycondensation. In particular, it was proposed to use small additives of the B_f co-monomer (f = 2, 3, ...), which plays the role of the core unit. One of the first publications in this field is devoted to the synthesis of polyester in bulk reaction between 2,2-bis(hydroxymethyl)propionic acid and 2-(hydroxymethyl)-2-ethylpropane-1,3-diol.[31] The molecular mass distribution of the polymer spanned the range from 1200 to 44 300 and the degree of branching was about 80% (^{13}C NMR spectroscopy data). This and other methods used to decrease the polydispersity index, such as $A_2 + B_3$ co-polycondensation of monomers (oligomers) and gradual feed of reactants, have been documented[32–36] (see ¶) and substantiated from the kinetic point of view.[37–41]

The system of equations (4) for the $AB_2 + B_f$ mixture ($f \leqslant 30$) was solved[37,38] assuming equal kinetic constants k_1 and k_2. It was found that the dependence of the polydispersity index on conversion $\gamma(\alpha_A)$ passes through a maximum and decreases towards the limiting yield (Fig. 7). As the functionality f increases, the limiting value γ_{lim} decreases and, depending on the concentration of the core monomer B_f, it can approach a unity (Fig. 7 *b*).

Similar results were obtained[39] using the method of moment-generating function.

¶ More detailed information on the studies carrried out using these methods of HBP synthesis including inductrial methods, can be found in the references cited above, especially, in review 5.

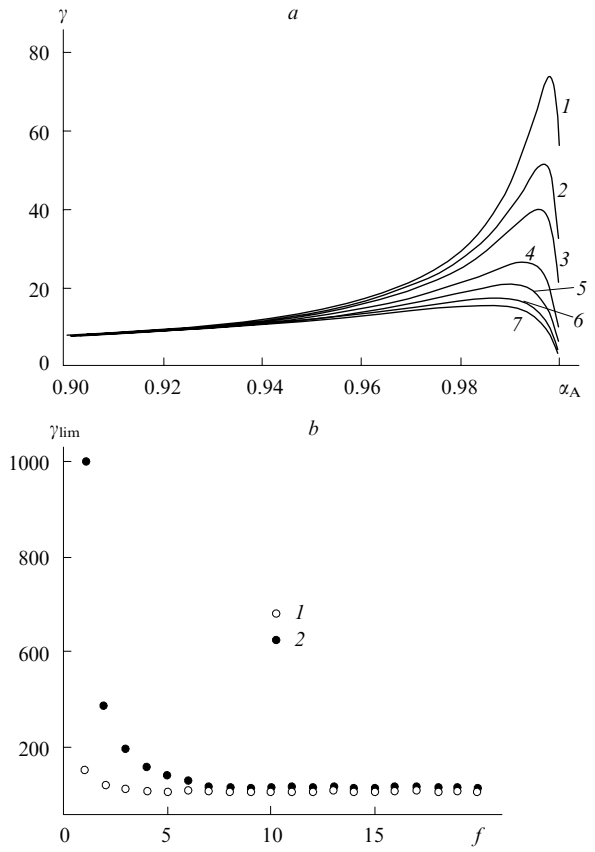


Figure 7. Changes in polydispersity index (γ) in the course of polycondensation of $AB_2 + B_f$ system (*a*) and the limiting polydispersity index (γ_{lim}) plotted *vs.* core unit functionality (f) (*b*).[38]
(*a*) $\lambda = [B_f]/[AB_2] = 10^{-3}$; f = 6 (*1*), 8 (*2*), 10 (*3*), 15 (*4*), 20 (*5*), 25 (*6*), 30 (*7*); (*b*) $\lambda = 10^{-2}$ (*1*), 10^{-3} (*2*).

Cheng and Wang[40] considered the case $AB_2 + C_3$ where the monomer and the core bear different functional groups.

$$\sim A + B \sim \xrightarrow{k_{AB}} \sim a-b \sim ,$$

$$\sim A + C \sim \xrightarrow{k_{AC}} \sim a-c \sim ,$$

$$\frac{k_{AC}}{k_{AB}} = \beta \neq 1.$$

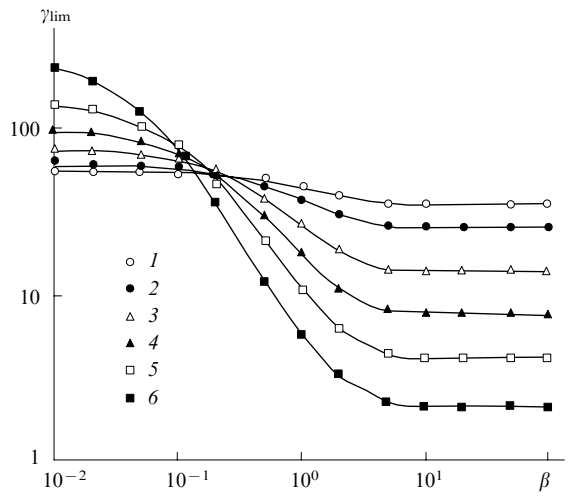


Figure 8. Limiting polydispersity index of HBP plotted *vs.* relative concentration of core unit λ and its relative reactivity $\beta = k_{AC}/k_{AB}$.[40]
$\lambda = [C_3]/[AB_2] = 0.001$ (*1*), 0.002 (*2*), 0.005 (*3*), 0.01 (*4*), 0.02 (*5*), 0.05 (*6*).

The kinetic equations were solved by the method of moment-generating function (see above).

The results of calculations presented in Fig. 8 illustrate the effect of the concentration of the core units and the relative reactivity of groups C on the limiting value γ_{lim}. As β increases, the polydispersity index decreases; the higher the concentration of groups C the more pronounced the decrease. At the same time the effect of concentration causes γ_{lim} to increase at $\beta \ll 1$.

The substitution effect[41] in the system $AB_2 + B_3$ was also studied by the method of moment-generating function. It was assumed that the kinetic constants will change significantly, namely, the reaction of the first group B causes the reactivities of the other groups to enhance (positive effect) or decrease (negative effect) by an order of magnitude; the reaction of the second group B caused them to change by an additional order of magnitude. Analysis of the data presented in Fig. 9 showed that the substitution effect influences the width of the MMD of the polymer formed. In the case of positive effect (see Fig. 9 *a*) the polydispersity index sharply increases with conversion, the concentration of the core unit being almost insignificant. At negative effect (see

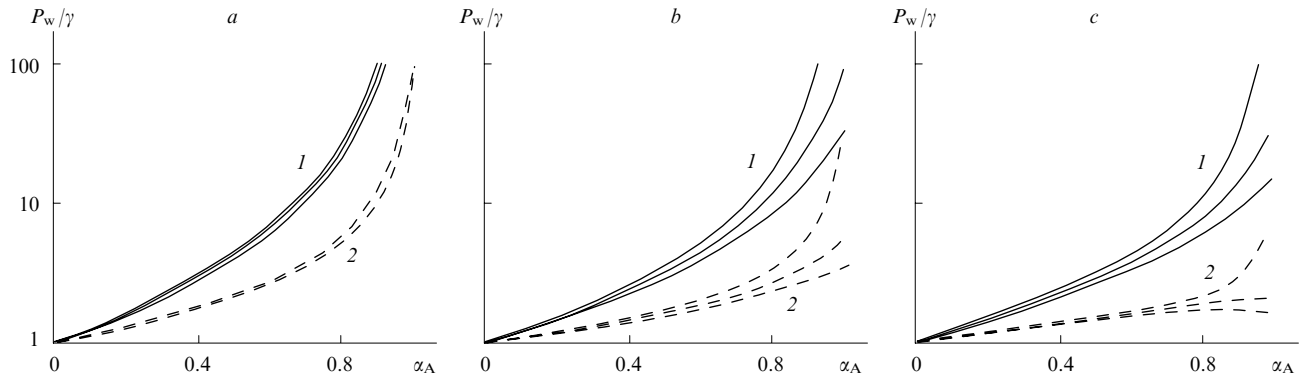


Figure 9. Influence of B_3 core unit and substitution effect on the mass-average degree of polymerisation (*1*) and the polydispersity index (*2*).[41]
Substitution effect: positive (*a*), no effect (*b*) and negative (*c*). For each series of curves from top to bottom: $\lambda = [B_3]/[AB_2] = 0$, 0.05 and 0.1.

Fig. 9 *c*), the parameter γ slightly increases, the higher the B_3 concentration the more pronounced the maximum in the $\gamma(\alpha_A)$ plot.

The influence of the substitution effect on the parameter DB is illustrated in Fig. 10. At positive effect, the DB value appreciably increases with conversion; at negative effect, it remains small. Qualitatively, these results explain the structural features of a widely used industrial HBP 'Boltorn H40'; as shown in Ref. 42, polycondensation is accompanied by negative substitution effect.

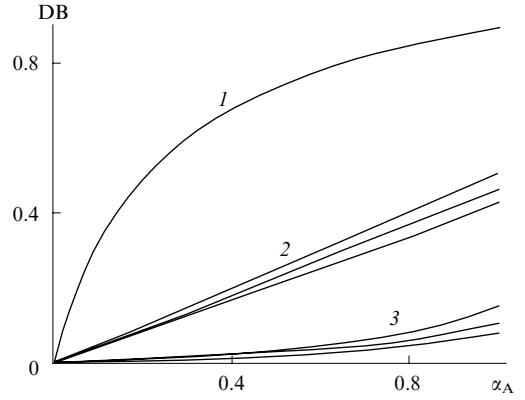


Figure 10. Influence of B_3 core unit and substitution effect on the parameter DB.[41]
Substitution effect: positive (*1*), no effect (*2*) and negative (*3*). For each series of curves from top to bottom: $\lambda = [B_3]/[AB_2] = 0$, 0.05 and 0.1.

Yet another technique for narrowing the MMD is gradual feed of the AB_2 monomer to the reactor, the core monomer (in this case, B_2) being fed with the first portion.[39, 43] It was shown that the efficiency of the technique depends on both the concentration of the core unit and the number of portions. From the data in Fig. 11 it follows that γ_{lim} decreases with an increase in the number of doses. The same result is obtained as the B_2 concentration increases.

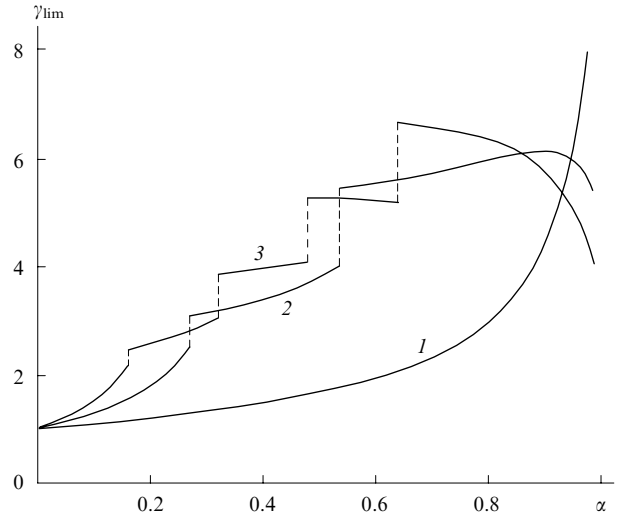


Figure 11. $\gamma_{lim}(\alpha)$ plots illustrating the effect of gradual dosage of AB_2 monomer.[42]
Dosage: single (*1*), triple (*2*) and quintuple (*3*). Conditions: $\alpha_A = 80\%$ and $[B_2] = 5\%$ for each stage.

The corresponding values of the limiting polydispersity index ($\alpha_A \approx 0.95$) at quintuple dosage of the monomer[42] are given below

$[B_2]$ (%)	0	1	5	10	15
γ_{lim}	$\sim 10^7$	20	4	2.6	2.5

These calculations ignored the possibility of cyclisation. At the same time investigations of HBPs based on AB_2, AB_4 and AB_6 siloxysilanes[44] showed that polycondensation is accompanied by intramolecular cyclisation; as a consequence, the molecular mass is limited to a value of $\sim 5000 - 10\,000$ and the polydispersity index equals ~ 2. The presence of rings in HBPs based on dimethyl 5-(ω-hydroxyalkoxy)isophthalates was established by matrix-assisted laser desorption-ionisation time-of-flight mass spectrometry.[45, 46] Noteworthy is a strong dependence of cyclisation on the relative concentration of core units (Fig. 12 *a*). Namely, with no core units the proportion of the cyclised macromolecules reaches 100% and decreases to almost zero as the concentration of the core units increases; this correlates with the decrease in the molecular mass (Fig. 12 *b*).[45]

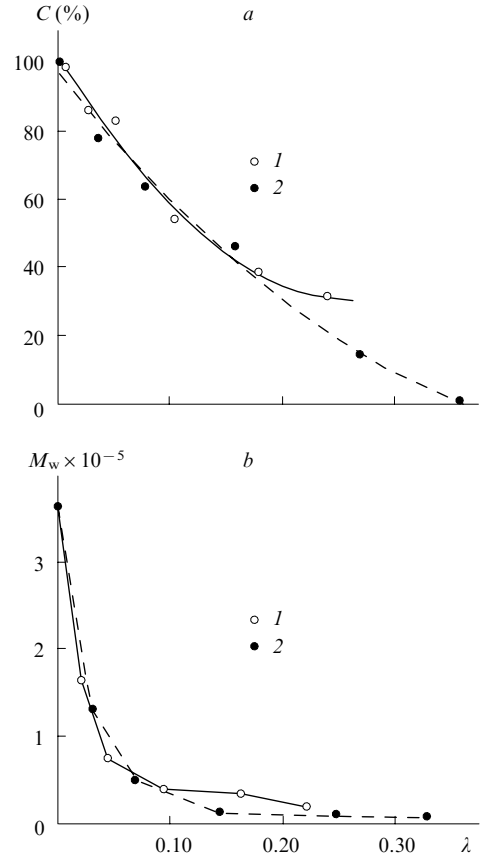


Figure 12. Yield of cyclic products C (*a*) and mass-average molecular mass (*b*) plotted *vs.* relative concentration of the core units B_2 (*1*) and B_3 (*2*).[45]

The cyclisation reaction, in which the determining role is played by the macromolecular configurations and conformations, is usually studied using methods of computer simulation.[47] For instance, a Monte Carlo study[48] of

polycondensation of AB_2 and AB_4 revealed an increase in the percentage of ring-containing molecules in proportion to the degree of polymerisation. As the process is completed, all macromolecules have cyclic structures. Table 1 lists the data on the distribution of the rings on the size m_c at polycondensation of AB_2 and AB_4. Due to cyclisation the final values of the average degrees of polymerisation HBP ($\overline{P}_n$ and $\overline{P}_w$) are relatively low.

Table 1. Characteristics of cyclic structures of HBP.[48]

m_c	Proportion of cyclisation product	
	AB_2 (see [a])	AB_4 (see [b])
1	0.786	0.815
2	0.126	0.131
3	0.042	0.034
4	0.019	0.013
5	0.009	0.009

[a] $\overline{P}_n = 10.7$; $\overline{P}_w = 86$. [b] $\overline{P}_n = 7.5$; $\overline{P}_w = 37$.

To substantiate the correctness of the analytical approach, the Monte Carlo method was used.[49] The system (3) was augmented with the reaction of formation of a cyclic molecule as a result of intramolecular interaction between the groups A and B (coefficient $\lambda_c < 1$ included the possibility of cyclisation)

$$\mathrm{R}(l,t) \xrightarrow{\lambda_c k_1} \mathrm{R_c}(l+1, t-1), \text{ reaction with } t$$
$$\mathrm{R}(l,t) \xrightarrow{\lambda_c k_2} \mathrm{R_c}(l-1, t), \text{ reaction with } l. \qquad (8)$$

Clearly, cyclic molecules cannot react with one another due to the absence of groups A, but react with acyclic molecules owing to the presence of groups B. Correspondingly, the system of differential equations (4) was augmented with two equations for two generating functions, one for acyclic and the other for cyclic molecules. Then, like usually, the system of equations for the moments was solved.

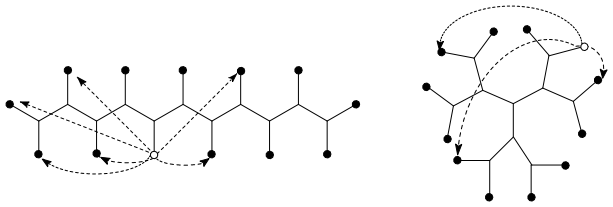
It was found that both methods, analytical calculations and computer simulation on a two-dimensional grid, give more or less consistent results with respect to the yield of cyclic products, but the percentage of these products is very low (at most 10% of the total mass of the polymer) at all kinetic constants used. This contradicts the results obtained in other studies.[45, 46, 48] Probably, the two-dimensional model and kinetic calculations ignoring the configuration effect are equally incorrect.

A combined approach to the solution of the cyclisation problem has been proposed.[50]

First of all, the method of solution to the system of equations (4) using the kinetic (dynamic) Monte Carlo simulation should be mentioned. It was developed by Dušek and co-workers.[51–53] In this case the Monte Carlo steps are time quantified. The rates of all reactions are determined by reactant concentrations (*i.e.*, by the number of reactants divided by the volume of the system) and by the kinetic constants whose values are specified depending on the type of reactant, interacting functional groups and their position in the reactant structures.

For instance, Scheme 2 taken from Ref 50 shows the possibility for monomolecular cyclisation reactions (shown by the arrows) to occur; the rate constant for each reaction is determined by the contour length of the chain between the reacting groups. It is the possibility of specifying particular structures of reactants and reaction products that determines the advantage of the combined technique over traditional methods of solving the equations of chemical kinetics.

Scheme 2



In each step the probability of reaction is 'raffled' in accordance with the hierarchy of events, namely, the type of the reaction, *i.e.*, a monomolecular (cyclisation) or bimolecular (chain propagation) process, is chosen first and then reactants and functional groups are chosen. This choice determines the numerical value of the kinetic constant and, correspondingly, the increment of the corresponding reaction product in the Monte Carlo step, *i.e.*, the reaction rate. Since the solution involves simulation of particular topological structures, the method proposed allows the kinetics of formation of the architecture of the polymer network to be determined. It is also possible to include the substitution effect and the excluded volume effect.

To a first approximation, the cyclisation probability was calculated as the weighted average over two limiting structures, a linear and a globular one (see Scheme 2). The probability (p_c) of formation of a cycle comprised of m_c segments was calculated using the Jacobson–Stockmayer relationship

$$p_c(m_c) \propto m_c^{-3/2}.$$

The rate constant for cyclisation was determined by averaging over all positions of groups B.

The results of calculations can be summarised as follows:

— at a given degree of conversion, the proportion of ring-containing structures increases with the molecular mass and tends to some limiting value;

— the overall proportion of cyclic macromolecules increases with conversion and tends to a limiting value of 100%;

— the degree of cyclisation depends on the flexibility of structural units (*i.e.*, on the smallest ring size).

These conclusions are illustrated in Fig. 13. As can be seen, noticeable accumulation of rings is observed at conversions higher than 90%; the higher the degree of polymerisation the larger the proportion of rings. Almost all smallest molecules contain no rings.

As an example, Table 2 presents the results of calculations and experimental data on the determination of the proportion of cyclic products in polycondensation of 2,2-bis(hydroxymethyl)propionic acid (BHMPA) obtained by matrix-assisted laser desorption-ionisation time-of-flight mass spectrometry. Reasonable agreement between these results is undoubtful.

Yet another kinetic factor affecting the topological structure of HBPs is intramolecular transetherification.[54, 55]

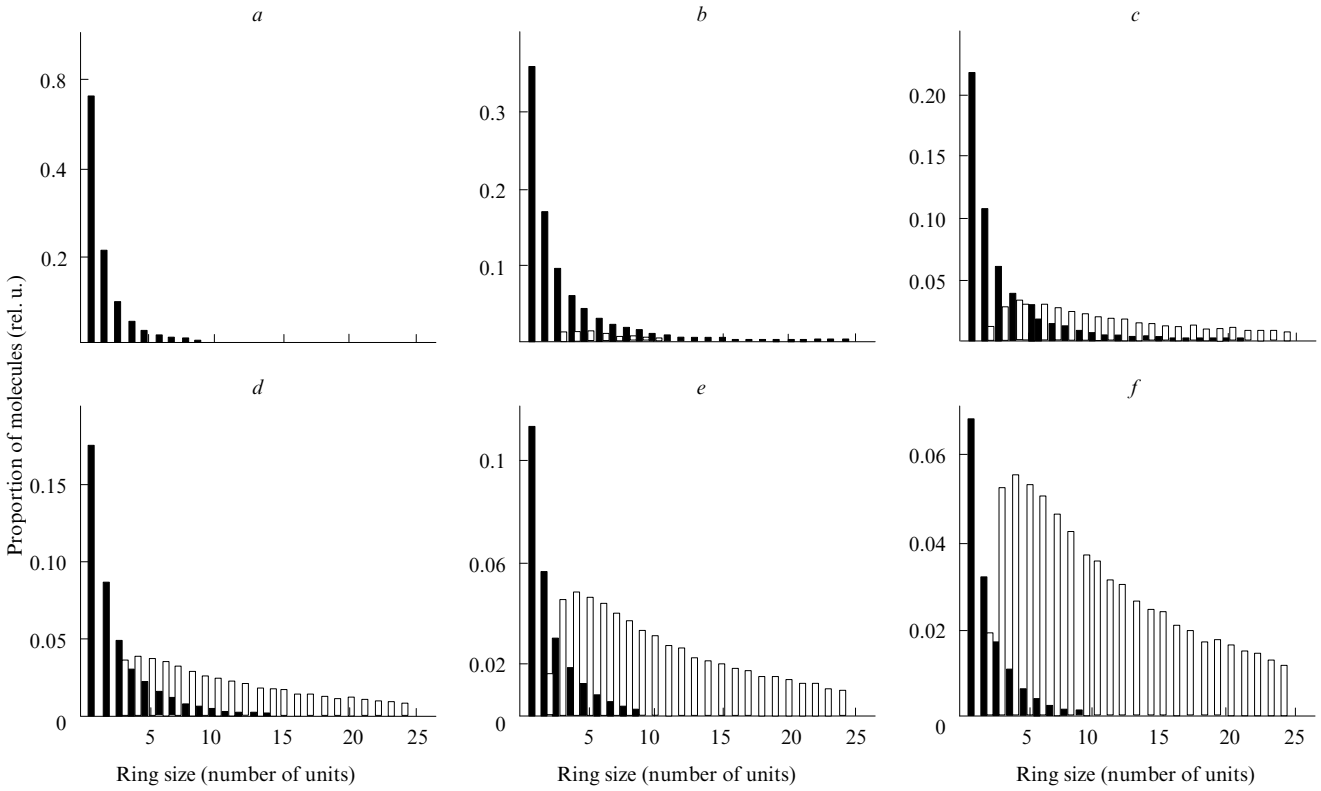


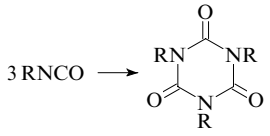
Figure 13. Proportion of cyclic (open rectangles) and acyclic (filled rectangles) molecules as function of ring size and conversion α_A.[50] α_A = 0.5 (*a*), 0.8 (*b*), 0.94 (*c*), 0.96 (*d*), 0.98 (*e*), 0.99 (*f*).

Table 2. Mole fraction of cyclic products as function of the degree of polymerisation (*P*) of BHMPA.[50]

P	α_A = 0.840		α_A = 0.947		α_A = 0.981	
	experiment	calculations	experiment	calculations	experiment	calculations
4	0.16	0.16	0.30	0.46	0.48	0.73
5	0.30	0.21	0.47	0.52	0.60	0.77
6	0.39	0.25	0.46	0.58	0.83	0.83
7	0.28	0.28	0.47	0.63	0.75	0.86
8	0.29	0.30	0.42	0.68	0.75	0.88
9	0.34	0.34	0.66	0.72	0.77	0.90
10	0.27	0.35	0.61	0.74	0.74	0.91
11	0.24	0.39	0.48	0.76	0.68	0.92
12	0.29	0.42	0.64	0.78	0.87	0.93
13	–	0.46	0.63	0.78	0.92	0.94

III. Polycyclotrimerisation

The polycyclotrimerisation reaction is characteristic of isocyanates,[56–58] cyanic acid derivatives[59,60] and alkynes.[61–65] Kinetically, this is a particular case of polycondensation, because propagation of the polymer chain is due to the interaction between three rather than two functional groups.



Irrespective of chemical features of the mechanism of the process, the reaction can be treated[21] as trimolecular in certain time dummy. Since the problem of correct form of kinetic equations for complex chemical reactions is of common importance, we will dwell on the problem taking into account the fact that usually the complexity is due to the presence of a system of donor-acceptor interactions.

Let the functional groups of oligomer X be bonded to some agent Z to form a complex characterised by the equilibrium constant K and let the complexed reactant species be involved in bonding. Thus, for dimerisation

$$X_1 + X_1 \longrightarrow X_2$$

one gets

$$\frac{dX_2}{d\tau} = k\left(\frac{KZ}{1+KZ}\right)^2 X_1^2,$$

where X_1 and X_2 are the monomer and dimer concentrations, respectively, τ is the running time, Z is the concentration of the agent Z, and k is the rate constant for the reaction. This seemingly complex equation is simplified by introducing the time dummy (θ)

$$\frac{dX_2}{d\theta} = kX_1^2,$$

where

$$\theta = \int_{\xi=0}^{t} \left(\frac{KZ}{1+KZ}\right)^2 d\xi.$$

Table 3. Cyclotrimerisation reactions of mono- and bifunctional oligomers.

Reaction equation	Rate constant	Process name
$R(1,1) + R(1,1) + R(1,1) \rightarrow R(3,0)$	k_{111}	cyclotrimerisation of three monofunctional oligomers
$R(1,1) + R(1,1) + R(1,2) \rightarrow R(3,1)$	k_{112}	cyclotrimerisation of two monofunctional oligomers and one bifunctional oligomer
$R(1,1) + R(1,1) + R(n,b) \rightarrow R(n',b')$, where $n' = n + 2, b' = b-1$	k_{113}	cyclotrimerisation of two monofunctional oligomers and one polyfunctional oligomer
$R(1,1) + R(1,2) + R(1,2) \rightarrow R(3,2)$	k_{122}	cyclotrimerisation of one monofunctional oligomer and two bifunctional oligomers
$R(1,1) + R(1,2) + R(n,b) \rightarrow R(n',b')$, where $n' = n + 2, b' = b$	k_{123}	cyclotrimerisation of one monofunctional, one bifunctional and one polyfunctional oligomer
$R(1,1) + R(n_1,b_1) + R(n_2,b_2) \rightarrow R(n',b')$, where $n' = n_1 + n_2 + 1, b' = b_1 + b_2 - 2$	k_{133}	cyclotrimerisationof of one monofunctional oligomer and two polyfunctional oligomers
$R(1,2) + R(1,2) + R(1,2) \rightarrow R(3,3)$	k_{222}	cyclotrimerisation of three bifunctional oligomers
$R(1,2) + R(1,2) + R(n,b) \rightarrow R(n',b')$, where $n' = n + 2, b' = b + 1$	k_{223}	cyclotrimerisation of two bifunctional oligomers and one polyfunctional oligomer
$R(1,2) + R(n_1,b_1) + R(n_2,b_2) \rightarrow R(n',b')$, where $n' = n_1 + n_2 + 1, b' = b_1 + b_2 - 1$	k_{233}	cyclotrimerisation of one bifunctional oligomer and two polyfunctional oligomers
$R(n_1,b_1) + R(n_2,b_2) + R(n_3,b_3) \rightarrow R(n',b')$, where $n' = n_1 + n_2 + n_3, b' = b_1 + b_2 + b_3 - 3$	k_{333}	cyclotrimerisation of three polyfunctional oligomers

Note. $R(n,b)$ are macromolecules, where n is the number of units in the macromolecule, b is the number of functional groups; R(1,1) and R(1,2) are the initial mono- and bifunctional oligomers; $n = 1, 3, 5, \ldots$, $b = 0, 1, 2, \ldots, (n + 3)/2$.

The general scheme of cyclotrimerisation of mono- and bifunctional oligomers with allowance for different reactivities of functional groups and for the substitution effect is summarised in Table 3.[66,67]

Assuming additivity of the free energy of activation, *i.e.*, assuming that the rate constant for the reaction A + B + C can be written as

$$k_{ABC} = k_A k_B k_C,$$

one gets:

$$\frac{dR(1,1)}{d\tau} = -k_1 R(1,1) F^2,$$

$$\frac{dR(1,2)}{d\tau} = -2k_2 R(1,2) F^2,$$

$$\frac{dR(n,b)}{d\tau} = -bk_3 R(n,b) F^2 + k_1^2 R(1,1)^2 k_3 R(n-2,b+1) +$$
$$+ k_1 R(1,1) k_3^2 \sum_{\substack{i=1 \\ j=1}}^{\substack{n-1 \\ b+1}} j(b-j+2) R(i,j) R(n-i,b-j+2) +$$
$$+ 4k_2^2 R(1,2) 2k_3 R(n-2,b-1) +$$
$$+ k_1 R(1,1) k_2 R(1,2) k_3 R(n-2,b) +$$
$$+ 2k_2 R(1,2) k_3^2 \sum_{\substack{i=1 \\ j=1}}^{\substack{n-1 \\ b}} j(b-j+2) R(i,j) R(n-i,b-j+2) +$$
$$+ \frac{1}{3} k_3^3 \sum_{\substack{i=1 \\ m=1}}^{n-2} \sum_{\substack{j=1 \\ l=1}}^{b-2} jl(b-j-l+1) R(i,j) R(m,l) \cdot$$
$$\cdot R(n-i-m, b-j-l+1),$$

where

$$F = k_1 A + k_2 B + k_3 C,$$

A, B and C are the concentrations of functional groups of mono-, bi- and polyfunctional oligomers, respectively.

Using the generating function

$$\Phi(s,q) = \sum_{n,b} s^n q^b R(n,b),$$

the kinetics of the process can be described by the system of equations

$$\frac{dR(1,1)}{d\tau} = -k_1 R(1,1) F^2,$$

$$\frac{dR(1,2)}{d\tau} = -2k_2 R(1,2) F^2,$$

$$\frac{\partial \Phi(s,q)}{\partial \tau} = -k_3 q \frac{\partial \Phi(s,q)}{\partial q} F^2 +$$
$$+ \frac{1}{3} \left[sk_1 R(1,1) + 2sqk_2 R(1,2) + k_3 \frac{\partial \Phi(s,q)}{\partial q} \right]^3.$$

The generating function includes only reaction products and, therefore, $n = 3, 5, 7, \ldots$.

Obtaining[66,67] of systems of equations for the moment-generating function made it possible, first, to determine the range of conversions corresponding to the formation of HBPs (to the gel point) and, second, to obtain information on the topological structure of HBPs.

Figure 14 presents the results of calculations [66] of the (i) dependence of critical conversion α_c on the chemical composition of the reaction mixture and (ii) relative reactivity of functional groups ignoring the substitution effect ($k_1 \neq k_2$, $k_1 \neq k_3$, $k_2 = k_3$).

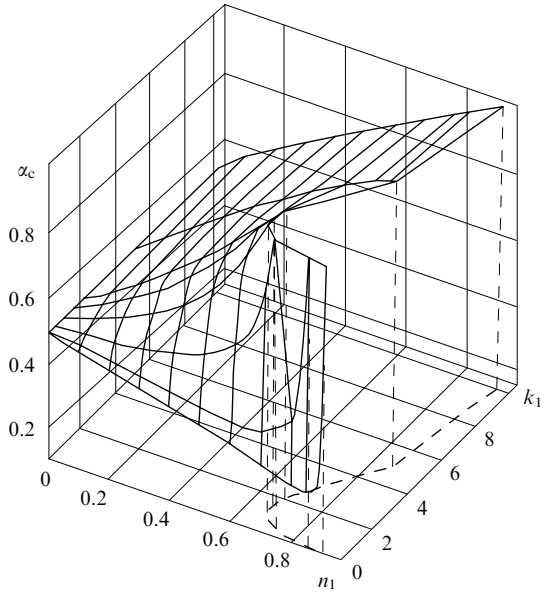


Figure 14. Parameter α_c plotted *vs.* n_1 and reactivity of monoisocyanate ($0.1 \leqslant k_1 \leqslant 10$).[66]
Both isocyanate groups of diisocyanate have identical reactivities: $k_2 = k_3 = 1$.

An exotic character of this dependence, namely, a decrease in critical conversion with an increase in the concentration of chain-terminating agent (monofunctional agent) provided its low reactivity is due to the fact that the network is mainly formed due to the bifunctional agent, but its content decreases and correspondingly α_c decreases.

Figure 15 presents the results of calculations [67] of the dependence of critical conversion α_c on the chemical composition of the reaction mixture and the magnitude of substitution effect [*i.e.*, on the relative reactivity of functional groups C (*i.e.*, on k_3) provided that $k_1 = k_2$]. It is noteworthy that in the case of positive substitution effect at relatively low content of the monofunctional component the critical conversion decreases, in the case of negative substitution effect the parameter α_c somewhat increases.

In Fig. 16 the parameter DB is plotted *vs.* kinetic characteristics of the process, that is, the reactant ratio and the substitution effect. It should be noted that the polycondensation of AB_2 and cyclotrimerisation are basically different from each other with respect to formation of the topological structure (*cf.* Fig. 16 and Figs 4, 10). In the former case, at negative substitution effect, the parameter DB decreases, whereas in the latter case it considerably increases, although only at high conversions. This is due to the fact that, owing to preferred consumption of terminal groups, mainly the reaction between *l*-units occurs at moderate conversion at the end of the process, which leads to accumulation of branching points.

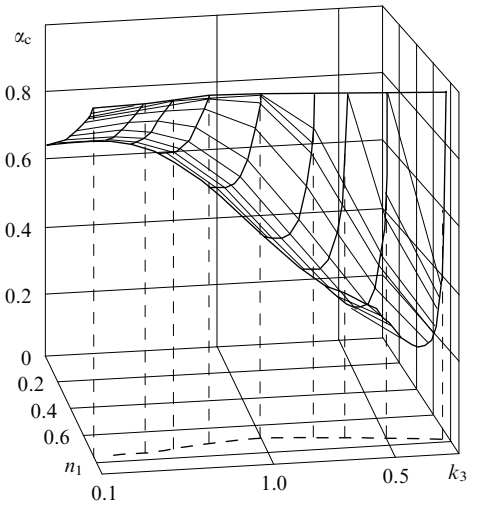


Figure 15. Parameter α_c plotted *vs.* n_1 and *vs.* change in reactivity of one functional group of bifunctional monomer ($0.1 \leqslant k_3 \leqslant 10$) after the first functional group has reacted.[67]
Assuming identical initial reactivities of all functional groups: $k_1 = k_2 = 1$.

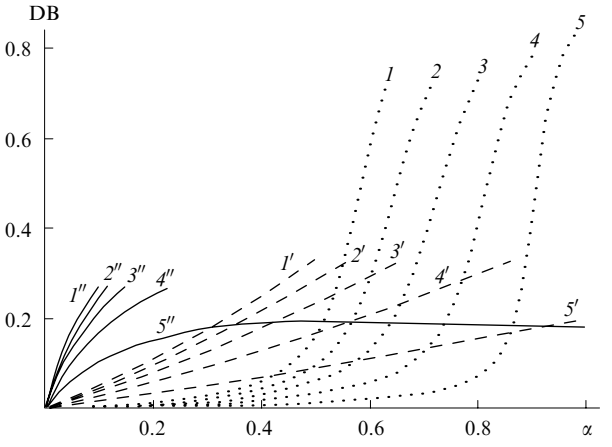


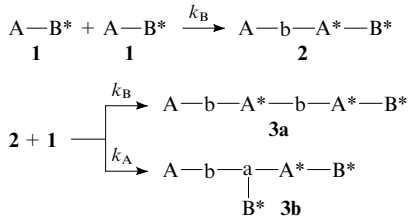
Figure 16. Parameter DB plotted *vs.* α, k_3 and n_1.[67]
$k_3 = 0.1$ (*1–5*), 1 (*1′–5′*), 10 (*1″–5″*); $n_1 = 0$ (*1*, *1′*, *1″*), 0.2 (*2*, *2′*, *2″*), 0.4 (*3*, *3′*, *3″*), 0.6 (*4*, *4′*, *4″*), 0.8 (*5*, *5′*, *5″*). The curves terminate at the critical point.

IV. Self-condensing vinyl polymerisation

The process called self-condensing vinyl polymerisation (SCVP) [68] is treated as a kind of polymerisation,[5] but kinetically this is a typical polycondensation reaction. Here, the role of 'building blocks' is played by the so-called inimers, that is, compounds simultaneously bearing a vinyl group, which can enter into polymerisation reactions, and an initiating group.[69–71]

Having denoted the inimer molecule as AB*, where A is the vinyl group and B* is the initiating group, and ignoring the chemical mechanism of initiation, the scheme of the process can be written as follows:[71–74]

Scheme 3



The asterisked species is the active centre, namely a cation,[68] a 2,2,6,6-tetramethylpiperidinyl oxide (TEMPO) stabilised radical,[69] or labile alkyl—halogen bonds,[70,71] which ensure the possibility for 'living' polymerisation to proceed by the atom transfer radical polymerisation (ATRP) mechanism[8,75] and a triethylsiloxy group,[76] which can reversibly be eliminated from the inimer under the action of nucleophilic agent (reversible addition fragmentation chain transfer or RAFT).

The chain propagation step begins with dimerisation. Then, branching (**3b**) becomes possible. Generally, the process is consistent with the polycondensation scheme of macromolecules,[77,78]

$$R_i + R_j \xrightarrow{k_A, k_B} R_{i+j},$$

where the subscripts i and j denote the number of units in the chain.

Kinetic analysis of SCVP has been reported.[72,73] From Scheme 3 it follows that, starting with the dimer, polymers obtained in this process and by polycondensation of AB_2 monomers are undoubtedly similar. First, each macromolecule contains one group A capable of entering into reactions with A* and B*, which are analogous to groups B in the AB_2-based HBPs. Second, in both cases the higher the degree of polymerisation of macromolecule the larger the proportion of these groups. An insignificant difference is that

$$A^* + B^* = P,$$

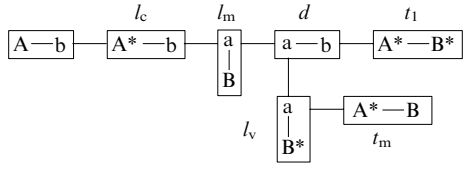
whereas

$$B = P + 1.$$

Here P is the degree of polymerisation. The structure of monomers also meets these conditions ($A^* = 0$, $B = 2$ at $P = 1$).

As in the case of polycondensation, macromolecules prepared by SCVP contain three types of structural units, namely, terminal (t_m and t_l), linear (l_c, l_m and l_v) and branching (d) ones (Scheme 4). Linear units can also be classified with respect to their origin[73] as a result of the reaction of the vinyl A group of monomer (subscript v) or polymer (subscript c).

Scheme 4



However, there is a fundamental difference between these two processes. Polycondensation involves consumption of both reactive groups, A and B, whereas only group A is consumed in SCVP; here, the total content of active centres ($A^* + B^*$) remains unchanged. Nevertheless, the kinetic regularities for both processes (character of the increase in degree of polymerisation, polydispersity index, degree of branching) were shown[72,73] to be quite similar (Fig. 17 *a*). The difference between the kinetic constants k_A and k_B corresponds to the substitution effect in polycondensation. However, the dependences of the parameter DB on the ratio of kinetic constants for these processes are different. Indeed, for polycondensation the larger the ratio k_2/k_1 the larger the DB value, whereas for SCVP the dependence of DB on k_A/k_B passes through a maximum equal to 0.5 at $k_A/k_B = 2.6$ (Fig. 17 *b*). This is a distinctive feature of the last-mentioned process, namely, preferred reaction of the vinyl bond with both group A* and group B* promotes the formation of linear structure.

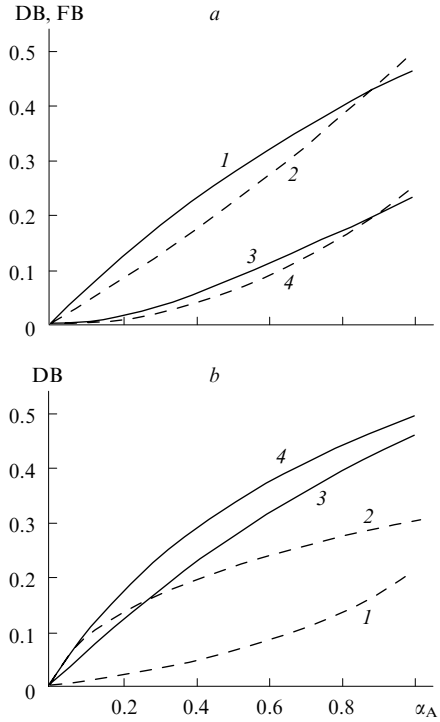


Figure 17. Parameters DB and FB plotted *vs.* conversion of groups A for AB* and AB_2 (*a*) and the parameter DB of AB* plotted *vs.* conversion of groups A and relative reactivity $\beta = k_A/k_B$ (*b*).[73] (*a*) DB for AB* (*1*), DB for AB_2 (*2*), FB for AB* (*3*) and FB for AB_2 (*4*); (*b*) $\beta = 0.1$ (*1*), 40 (*2*), 1 (*3*) and 2.6 (*4*).

Comparison of calculated dependences with experimental data on SCVP 2-(2-bromopropionyloxy)ethyl acrylate showed[74] that the kinetics of consumption of groups B* is best described at $k_A/k_B = 4.5$. At the same time it was found that the experimental finite values of both the molecular mass and the polydispersity index are much smaller than the calculated ones (Fig. 18); therefore, the possibility of cyclisation should be taken into account.

By analogy with polycondensation Müller and co-workers[79–81] proposed the use of multifunctional initiator and a procedure for gradual introduction of inimer into the system during the reaction[79–82] as efficient method of reduction of the polydispersity index γ.

At equal kinetic constants $k_A = k_B = k$, the general scheme is as follows:[79–82]

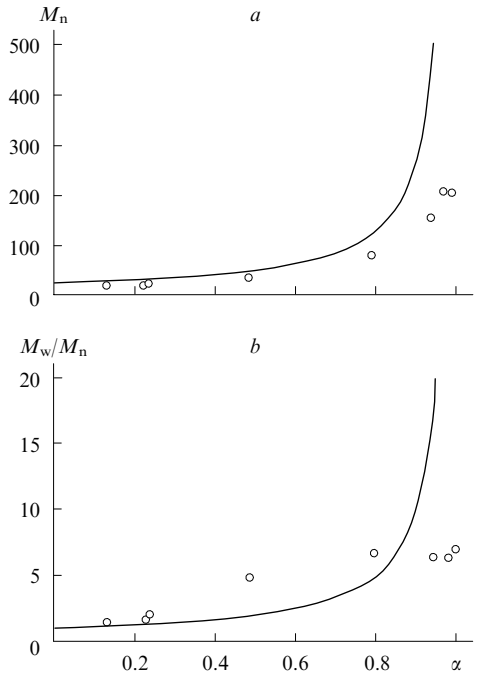


Figure 18. Number-average molecular mass (*a*) and polydispersity index (*b*) plotted *vs*. conversion for SCVP of 2-(2-bromopropionyloxy)ethyl acrylate.[74]
Points denote experimental data and solid lines denote the results of calculations.

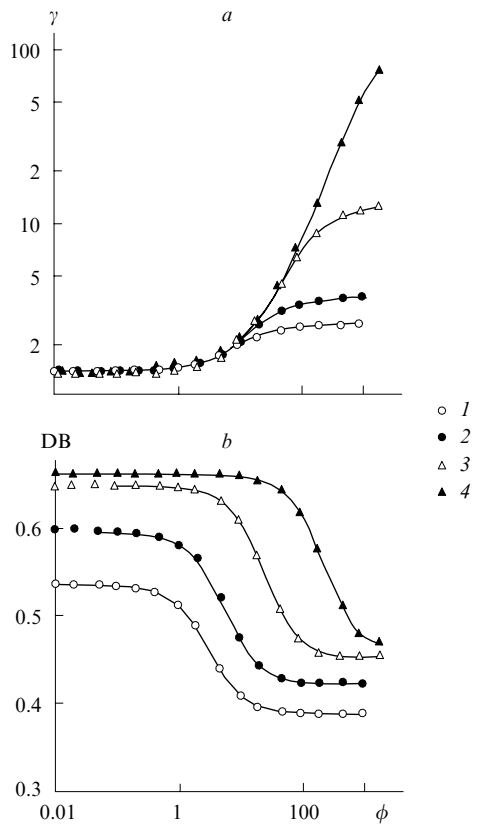


Figure 19. Polydispersity index (*a*) and degree of branching (*b*) of HBP plotted *vs*. concentration of core unit C_3 and AB* inimer feed rate.[82]
C_3 mole fraction: 0.1 (*1*), 0.05 (*2*), 0.01 (*3*) 0.001 (*4*); ϕ is the feed-rate-to-reaction-rate ratio.

$$\begin{aligned} &R_i + R_j \xrightarrow{(i+j)k} R_{i+j}, \\ &C_f + R_i \xrightarrow{fk} P_{i,f-1}, \\ &P_{i,g} + R_j \xrightarrow{(i+f-g)k} P_{i+j,g}, \\ &P_{i,g} + R_j \xrightarrow{gk} P_{i+j,g-1}. \end{aligned} \tag{9}$$

Here R_i is the macromolecule of size i containing the group A; $P_{i,g}$ is the molecule of size i containing no group A and having g active centres from initiator; the number of active centres in this macromolecule is $i + f$; and C_f is the f-functional initiator.

A solution to equations describing the system (9) gave the following results.[79,80] At $\alpha_A \to 1$, one gets

$$\overline{P}_n = f\varphi,$$

$$\overline{P}_w = f\varphi + (1+\varphi)^2,$$

where

$$\varphi = \frac{M_0}{fC_f}$$

is the ratio of the concentrations of active groups in inimer and initiator.

Thus, the limiting value of the polydispersity index is much lower[79] (in the absence of initiator $\gamma_{lim} \approx \overline{P}_n$):

$$\gamma_{lim} = 1 + \frac{(1+\varphi)^2}{f\varphi} \approx \overline{P}_n f^{-2}.$$

If $\varphi \gg 1$ (the most practically interesting case), the probability of chain transfer to initiator is low compared to that of interaction between the groups A and the initiating groups of polymer chains. This reduces the efficiency of the technique. By gradually dosing the inimer one can significantly increase the degree of utilisation of initiator. Indeed, in this case the ratio of initiating groups in the early stage of the process will change in favour of the initiator (this will increase the efficiency of initiator). Corresponding results are presented in Fig. 19.[82] As the inimer dosage rate decreases, the polydispersity index decreases considerably and the parameter DB increases.

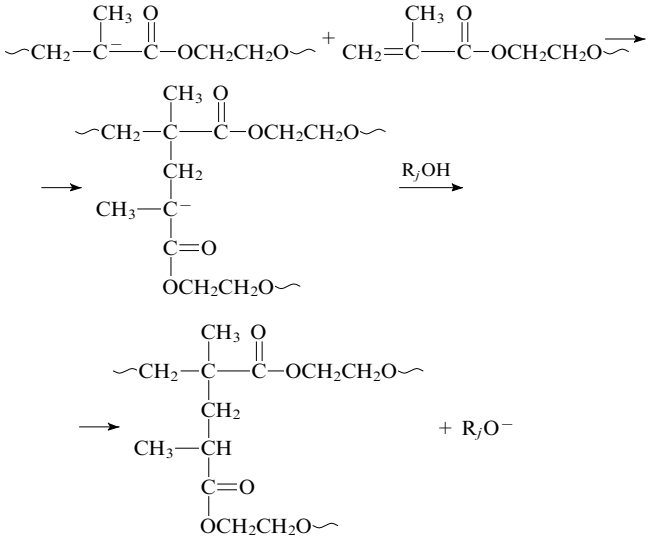
V. Proton-transfer anionic polymerisation

The so-called proton-transfer polymerisation obeys essentially the same pattern, which combines some features of 'living' polymerisation (constant concentration of active centres) and polycondensation (reaction of macromolecules with one another). The process was practically implemented[83,84] taking diglycidyl esters of 5-hydroxyisophthalic acid and 4,4-bis(hydroxyphenyl)pentanoic acid as examples. Copolymerisation of 2-(dimethylamino)ethyl methacrylate with methacrylic inimer occurs analogously.[85]

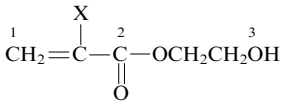
In particular examples B is the epoxy group and A is the phenol[83] or carboxyl[84] group, processes were activated with some nucleophilic agents, in particular, KOH[83] and teramethylammonium chloride.[84] Owing to higher acidity of the group A compared to the secondary hydroxyl group, which is formed in the epoxy ring opening, proton is rapidly transferred to the epoxy ring; this is accompanied by regeneration of the active centre A. As a result, the process mainly involves the formation of ab-bond; polymerisation

of epoxy groups and, correspondingly, a dramatic increase in the molecular mass manifest themselves only after consumption of groups A.[83]

Esters and amides of acrylic and methacrylic acids have been studied.[86] It was shown[86,87] that in the case of polymerisation of hydroxyalkyl (meth)acrylates under the action of potassium the carbanion initially formed upon adding a growing alkoxy anion to the double bond is able not only to add proton, but also interact with the double bond of the other molecule. This results in a carbochain fragment and regeneration of carbanion capable of abstracting a proton from any hydroxyl group. The results of a study[88] using NMR spectroscopy confirmed the mechanism of formation of carbochain fragments, which results in the formation of HBPs.



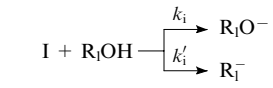
Under conditions of anionic polymerisation, hydroxyalkyl (meth)acrylates exhibit multiple reactivity towards the initiating and growing anions in three positions simultaneously:



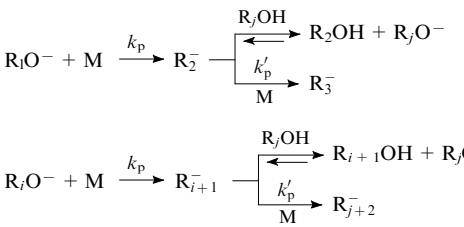
X = H, CH_3.

Such a multiple reactivity, which governs the polymerisation mechanism, can be represented by the following simplified kinetic scheme:[86,87]

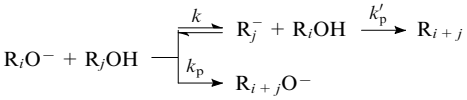
initiation



chain propagation



$j = 1, 2, 3, \ldots$; $i = 1, 2, 3, \ldots$;



proton transfer

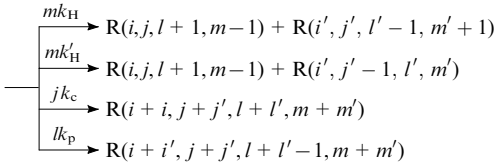
$$R_jO^- + R_iOH \rightleftharpoons R_iO^- + R_jOH;$$

chain transfer to polymer

$$R_jO^- + R_iOH \rightleftharpoons \text{adduct}^- \rightleftharpoons$$
$$\rightleftharpoons R_iOCH_2CH_2COOR_{i-n} + {}^-OCH_2CH_2OR_{n-1}OH.$$

Here R_j denotes the double-bond terminated j-mer and R_i^- is the carbanion formed upon addition of any anion to the double bond or in the reaction of acid-base equilibrium with the equilibrium constant K.

Anionic polymerisation of hydroxyalkyl (meth)acrylates was described[89] by the following main reactions:



(10)

Here $R(i,j,l,m)$ is the concentration of macromolecules containing i monomer units (degree of polymerisation), j enolate anions, l oxyanion centres and m OH groups and k_c is the rate constant for chain transfer to carbanion.

Analysis of scheme (10) revealed the following.

The kinetics of consumption of double bonds is highly sensitive to the rate of proton transfer to enolate anion (k'_H). This reaction completes the addition of macromonomer to the growing alkoxy anion and leads to its regeneration. The polymerisation rate increases with an increase in k'_H, but at a relative rate of proton transfer to the enolate anion of the order of $k'_H/k_p \geqslant 10^2$ the rate of consumption of the double bonds no longer depends on the further increase in the rate of proton transfer. In other words, if this correspondence does occur, the polymerisation rate is determined by the rate of alkoxy-anion addition to the double bond of the macromonomer. If the rate of proton transfer is lower than this critical value, *i.e.*, the enolate anion is sufficiently stable, polymerisation occurs on both types of active centres simultaneously. It is this situation that does occur in anionic polymerisation of hydroxyethyl methacrylate.

Enhanced competitiveness and concentration of the enolate anion compared to the alkoxy anion causes an increase in the polydispersity index of the polymer formed. The larger this difference the lower the conversion at which the ratio P_w/P_n begins to increase; this is in agreement with experimental observations. The dependence of the polydispersity index on conversion upon increase in the concentration of growing chains behaves analogously (Fig. 20).

Proton exchange causes that, similarly to the classical version of polycondensation, the number-average degree of polymerisation is one-to-one function of conversion, being independent of the kinetic parameters (concentration of active of centres and rate constants for elementary reactions; Fig. 21).

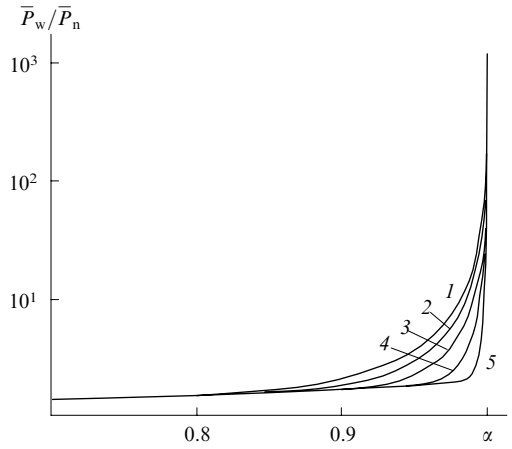


Figure 20. Effect of initiator concentration on MMD of polymer.[89] $k_p = 1$; $k_c/k_p = 1$; $k_H/k_p = k'_H/k_p = 10^3$; $[I]_0/[M]_0 = 0.2$ (*1*), 0.15 (*2*), 0.1 (*3*), 0.05 (*4*), 0.02 (*5*).

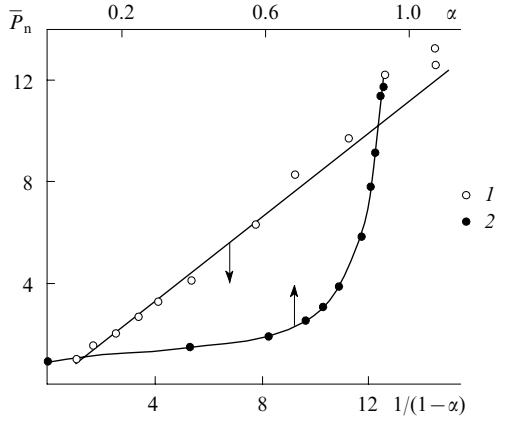
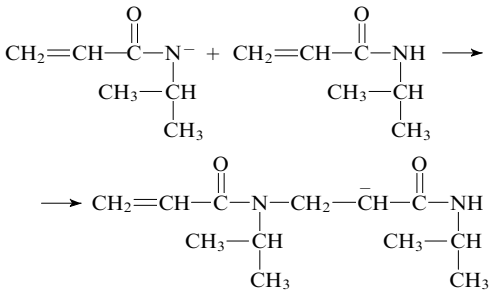
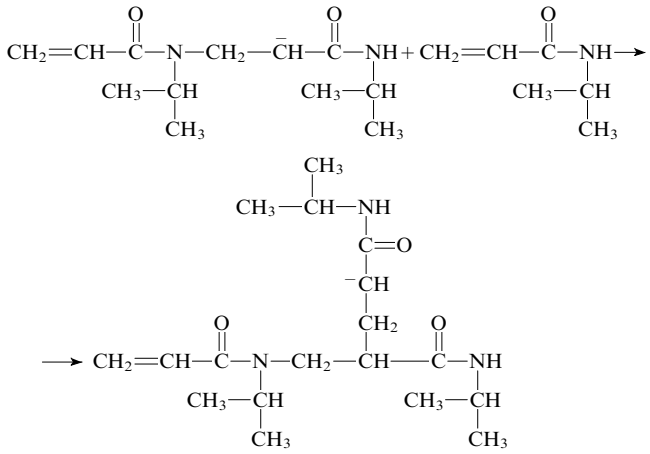


Figure 21. Kinetics of changes in $\overline{P}_n$ for bulk polymerisation of hydroxyethyl acrylate initiated by lithium *tert*-butoxide in the coordinates $P_n - 1/(1-\alpha)$ (*1*) and $P_n - \alpha$ (*2*).[89]
$[I]_0/[M]_0 = 0.0167$ at 23 °C.

Anionic polymerisation of *N*-methylol-(meth)-acrylamide results in HBPs containing heterochain and carbochain fragments with terminal C=C bonds and amido groups.[90]

Heterochain and carbochain fragments are formed in the reactions





Thus, proton-transfer anionic polymerisation of such monomers as esters and amides of acrylic and methacrylic acids is accompanied by branching of macromolecules and formation of HBPs due to the multiple nature of their reaction centres.

VI. Polymerisation of vinyl monomers

Polymerisation and/or copolymerisation of bifunctional (generally, polyfunctional) vinyl oligomers is straightforward method of synthesis of HBPs.[5–8] In this connection it is of particular importance to consider the problem of the gel point, because conventionally it corresponds to rather low conversions.[7,20,91]

Now we will consider the simplest example, namely, instantaneously initiated 'living' polymerisation of *f*-functional monomers ($f = 1, 2, ...$).[92] Here, the following conditions are met: the total concentration of monomers at $t = 0$ is

$$M = \sum_f M_f = M_0 ,$$

the concentration of reactive groups (double bonds) is

$$F = \sum_f f M_f = F_0,$$

the concentration of active centres is R, the number of chains is

$$N = M + R,$$

$M \gg R$.

One can show with ease that

$$M_f = M_{f,0} e^{-f k_p \tau},$$

($M_{f,0}$ is the initial concentration of the *f*-functional monomer).

$$F = F_0 e^{-k_p R \tau}.$$

The conversion of functional groups is given by

$$\alpha = \frac{F_0 - F}{F_0} = 1 - e^{-k_p R \tau}, \qquad (11)$$

$M_f = M_{f,0}(1-\alpha)^f$.

The concentration of polymer chains

$$N = R + M_0 - \sum_f M_{f,0}(1-\alpha)^f - F_0\alpha.$$

The condition $\overline{P}_n \to \infty$, or $N = 0$, defines the critical conversion according to Carothers.[93]

In the case of high functionality, the gel point corresponds to low conversions. Therefore, by expanding the expression under the sum in powers of α_c, one gets

$$R - \frac{1}{2}\alpha_c^2 \sum_f f(f-1)M_{f,0} \cong 0 \tag{12}$$

i.e.

$$\alpha_c^2 \cong \frac{2R}{\Phi_{22}(0)},$$

where $\Phi_{22}(0)$ is the second moment of the generating function with respect to functionality

$$\Phi_{22} = \sum_f f(f-1)M_f.$$

For a conventional system $M_1 + M_2$, one gets an exact expression:

$$R + M_0 - M_{1,0}(1-\alpha_c) - M_{2,0}(1-\alpha_c)^2 - F_0\alpha_c = \\ = R - M_{2,0}\alpha_c^2 = 0,$$

$$\alpha_c^2 = \frac{R}{M_{2,0}}. \tag{12a}$$

However, the α_c value is overestimated if condition (12) is met. The true critical conversion, as was shown by Flory[94] and Stockmayer,[95] depends on $\overline{P}_w$ rather than $\overline{P}_n$.

Kinetic analysis[91,96,97] showed that at high mass-average functionality the critical conversion α_c is calculated using the following relations.

'Living' polymerisation

instantaneous initiation

$$\alpha_c = \left(\frac{I}{\Phi_{22}(0)}\right)^{1/2}, \tag{13}$$

slow initiation

$$\alpha_c = \left(\frac{k_i I}{k_p \Phi_{22}^2(0)}\right)^{1/3}. \tag{14}$$

Radical polymerisation

chain termination through recombination

$$\alpha_c = 0.33\frac{k_t R}{k_p \Phi_{22}(0)}, \tag{15}$$

where k_t is the constant for bimolecular termination,

chain termination through recombination + chain transfer

$$\alpha_c = \frac{0.33k_t R + 0.5k_X X}{k_p \Phi_{22}(0)}, \tag{16}$$

chain termination through recombination + linear chain termination

$$\alpha_c = \frac{0.33k_t R + 0.5k_Y Y}{k_p \Phi_{22}(0)}. \tag{17}$$

Here I, X and Y are the initial concentrations of initiator, chain-transfer and linear chain termination agents; respectively; R is the stationary concentration of radicals; and k_i, k_p, k_x, k_y are the kinetic constants for chain initiation, propagation, transfer and termination.

Thus, high critical conversion can be attained by increasing the concentrations of initiator, chain-transfer agents and chain-termination agents. It is these techniques that were used for preparation of HBPs, namely, an increase in the concentration of initiator[98–104] and the use of chain-transfer reaction.[105–110]

In this case the quadratic dependence with respect to α_c [see Eqn (13)] is not a result of approximation; rather, it has a clear physical meaning.[111] The formation of a cross-link requires at least two consecutive processes with participation of functional groups. The first reaction involves the polyfunctional oligomer in the polymer chain and, therefore, leads to the appearance of a 'pendant' functional group (U). The second reaction with participation of U results in the formation of a cross-link (Z). For a bifunctional oligomer M_2 one has

$$\frac{d\alpha}{d\tau} = k_p(1-\alpha)R, \tag{18}$$

$$\frac{dM_2}{d\tau} = -2k_p M_2 R,$$

$$\frac{dU}{d\tau} = 2k_p M_2 R - k_p U R,$$

$$\frac{dZ}{d\tau} = k_p U R,$$

$$Z = M_{2,0}\alpha^2.$$

Taking into account the relationship for the critical conversion in instantaneously initiated 'living' polymerisation of the system $M_1 + M_2$ [see Eqn (13)], one gets:

$$I = 2Z_c.$$

In other words, the gel point is reached at one cross-linking unit per initial (non-cross-linked) chain. This result meets the criterion expressed by the Flory–Stockmayer relation

$$\alpha_c = (\rho\overline{P}_w - 1)^{-1},$$

where ρ is the proportion of the units being cross-linked, $\overline{P}_w$ is the mass-average degree of polymerisation of the chains being cross-linked with allowance for very close values of $\overline{P}_w$ and $\overline{P}_n$ in the case of 'living' (not 3D!) polymerisation. Clearly, this is a more severe condition compared to the expression $I = Z_c$ corresponding to the Carothers criterion (infinitely high number-average degree of polymerisation). Flory pointed[94] that the number-average degree of polymerisation is doubled at the gel point.

The kinetics of 'living' copolymerisation of 2-hydroxypropyl methacrylate (HPM) with a disulfide-based dimethacrylate (DSDMA), ethylene glycol dimethacrylate (EGDMA) and bisphenol A dimethacrylate (BADMA)

have been studied.[112–114] The consumption of the cross-linking co-monomer in the course of the reaction is described by relation (11), which indicates identical reactivities of all reactants. The number-average molecular mass linearly increases with conversion, which is typical of 'living' polymerisation. In addition, the kinetics of consumption of the double bonds obeys a first-order law for both homo- and copolymerisation, thus indicating constant concentrations of active centres.

The average number of cross-links per homopolymer macromolecule (see note above) was calculated using the following relation:

$$n_b = \frac{\bar{M}_{n,b}}{\bar{M}_{n,0}} - 1,$$

where $\bar{M}_{n,b}$ and $\bar{M}_{n,0}$ are the number-average molecular masses of the HPM copolymers and HPM homopolymer. The polydispersity index of the homopolymer was a bit higher than unity. Degradation of the copolymer through cleavage of disulfide bonds gave a nearly initial homopolymer, which substantiated the computational technique. By varying the ratio of comonomers it was established that gelation occurs when the following condition is met:

$$\frac{\bar{M}_{n,b} - \bar{M}_{n,0}}{\bar{M}_{n,b}} \to 1.$$

This condition was proved[112–114] by the results of corresponding measurements of the average molecular masses at limiting conversions, which usually were in the range from 95% to 99% (Table 4). Note that the condition can be met at different ratios of co-monomers. For instance, under identical synthesis conditions the mole fraction was 3.0% for DSDMA, 4.5% for EGDMA and 2.7% for BADMA (see Table 4, systems 2, 4 and 7). This effect was

Table 4. MMD parameters for copolymerisation of HPM.

No.	Co-monomer	Mole fraction (%)	$\bar{M}_n$	$\bar{M}_w$	$\frac{\bar{M}_{n,b} - \bar{M}_{n,0}}{\bar{M}_{n,b}}$	$\frac{\bar{M}_{w,b} - \bar{M}_{w,0}}{\bar{M}_{w,b}}$	Ref.
1	DSDMA	0	14 100	17 300	–	–	106
		0.4	19 100	27 100	0.26	0.36	
		1.0	22 600	46 400	0.38	0.63	
		1.6	30 400	91 400	0.54	0.81	
		1.9	67 300	540 000	0.79	0.97	
		2.1			gel		
2	DSDMA	0	7950	8600	–	–	108
		1.5	25 000	38 000	0.68	0.77	
		1.9	21 700	33 500	0.63	0.74	
		2.3	29 100	202 000	0.73	0.96	
		2.5	22 000	180 000	0.64	0.95	
		2.7	30 300	202 800	0.74	0.96	
		3.0			gel		
3	EGDMA	0	6000	6300	–	–	107
		1.4	29 000	106 000	0.79	0.94	
		1.6	66 000	190 000	0.91	0.97	
		1.8	192 000	645 000	0.97	0.99	
		2.0	243 000	365 000	0.98	0.98	
		2.2			gel		
4	EGDMA	0	7950	8600	–	–	108
		1.9	13 400	26 400	0.41	0.67	
		2.7	24 100	134 000	0.67	0.94	
		3.16	73 500	327 100	0.89	0.97	
		3.6	49 900	201 100	0.84	0.96	
		4.5			gel		
5	BADMA	0	4700	6000	–	–	107
		2.33	36 000	125 000	0.87	0.95	
		2.67	82 000	235 000	0.94	0.97	
		3.00			gel		
6	BADMA	0	6000	6300	–	–	107
		1.4	30 000	57 000	0.80	0.89	
		1.6	69 000	302 000	0.91	0.98	
		1.8	112 000	319 000	0.95	0.98	
		2.0	131 000	363 000	0.95	0.98	
		2.2			gel		
7	BADMA	0	7950	8600	–	–	108
		1.80	18 300	109 000	0.57	0.92	
		2.34	43 100	266 500	0.82	0.97	
		2.5	114 300	421 600	0.93	0.98	
		2.7			gel		

attributed to cyclisation assuming that its intensity depends on the flexibility of the cross-linking co-monomer chain.

Physically, the gelation condition proposed is similar to the Carothers criterion (unrestricted increase in the number-average molecular mass). However, from the data in Table 4 it follows that the reverse statement, namely, a trend towards an infinite mass-average molecular mass is more correct under the same conditions.

The kinetics of 'living' polymerisation methyl acrylate (MA) and its copolymerisation with ethylene glycol diacrylate (EGDA) were studied experimentally and theoretically.[115] Experimental and calculated data (numerical solution to the system of equations corresponding to the kinetic scheme of 'living' radical copolymerisation using the Predici program by Wulkow[116]) were found to be in reasonable agreement.

Figure 22 presents the kinetic curves for accumulation of cross-linking units (denoted as $2Z$) at different diacrylate content. According to the Flory–Stockmayer criterion, the gel point corresponds to a conversion at which one cross-linking unit per primary chain is formed (this is indicated by the dashed line in Fig. 22). Comparison of the calculated and experimental data on the dependence of critical conversion on the relative concentration of EGDA (Fig. 23) showed that theory somewhat underestimates the situation, which can probably be explained by the occurrence of cyclisation reaction.

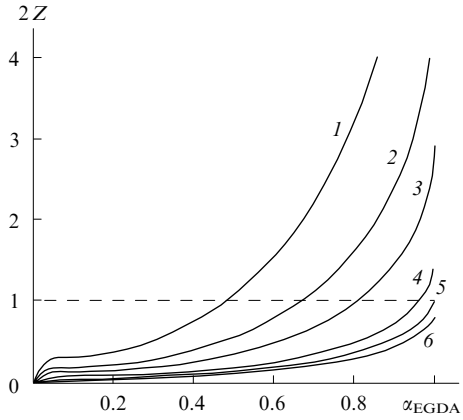


Figure 22. Kinetic curves of accumulation of cross-linking units with respect to the primary chain for copolymerisation of MA and EGDA.[115]
$[MA]_0$ = 5.98 mol litre^{-1}, $[EGDA]_0/[I]$ = 10 (*1*), 5 (*2*), 3 (*3*), 1.5 (*4*), 1.1 (*5*) and 0.9 (*6*).

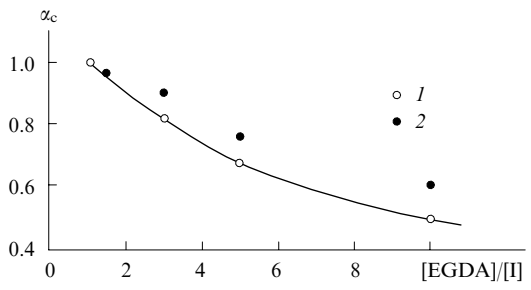


Figure 23. Critical conversion plotted *vs.* EGDA concentration.[115] Calculations (*1*) and experiment (*2*).

The concentration of cross-linking units in 'living' polymerisation[117] of EGDMA and BADMA monomers, measured by ^{1}H NMR spectroscopy, was found to be somewhat higher than that of initiator, which was explained by cyclisation. A marked contribution of cyclisation in anionic copolymerisation of EGDMA and 2-(dimethylamino)ethyl methacrylate was reported;[118] it was found that introduction of up to 25% EGDMA causes no gelation. Cyclisation from the very beginning of the process was reported in a study[119] on computer simulation of iniferter-initiated and controlled 3D 'living' copolymerisation.

Particular chemical mechanism of 'living' radical copolymerisation to some extent affects not only the rate, but also the character of branching. For instance, it was found[117] that the change in the Cu^+/Cu^{2+} ratio in ATRP of EGDMA and BADMA monomers causes not only the reaction rate, but also the critical conversion to change (Table 5).

Table 5. Effect of polymerisation conditions on the result of polymerisation.[117]

No.	M : I : Cu^+ : Cu^{2+}	Duration /h	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	HBP yield (%)
1	57 : 1 : 0.5 : 0	5	14 000	8.5	20.7
2	57 : 1 : 0.5 : 0.167	17	10 500	4.9	49.5
3	57 : 1 : 0.4 : 0	6	14 200	22.7	21.5
4	57 : 1 : 0.4 : 0.133	28	13 600	20.2	61.6
5	57 : 1 : 0.4 : 0.2	32	6700	3.2	27.1
6	57 : 1 : 0.25 : 0.25	36	3900	1.7	16.6
7	50 : 1 : 1 : 0	3	gel		
8	50 : 1 : 0.5 : 0	5	gel		
9	50 : 1 : 0.18 : 0.03	7	4400	3.1	38
10	100 : 1 : 0.3 : 0.1	15	4800	3.5	48
11	50 : 1 : 0.188 : 0.063	29	15 000	4.1	63

Note. M is divinylbenzene (DVB) in systems 1–6 and EGDMA in systems 7–11; I stands for initiator.

A feature of the ATRP mechanism is the equilibrium

$$R-Hal + Cu^+ \rightleftharpoons R^* + Hal-Cu^{2+}.$$

Here R is the polymer chain and Hal is the atom of a halogen (usually, bromine or chlorine). As the Cu^{2+} concentration increases, the equilibrium is shifted to the left and the polymerisation rate decreases (see Table 5, systems No. 2, 4, 5 and 9–11). At the same time, the critical conversion and, correspondingly, the yield of HBP increases.

It is believed[120,121] that RAFT 'living' polymerisation [more exactly, copolymerisation of methyl methacrylate with EGDMA using 2-(2-cyanopropyl)dithiobenzoate as the molecular fragment] results in HBPs characterised by much lower polydispersity index, which was higher than in ATRP. A similar conclusion was drawn in another study.[114]

From our consideration it follows that any modification of 'living' polymerisation (anionic, ATRP, RAFT, using stable radicals[122]) results in HBPs. As mentioned above, polymerisation by the mechanism involving chain termination requires shorter chains. To this end, high concentrations of initiators and/or chain transfer agents are used.

Polymerisation of divinyl adipate (DVA) with dimethyl 2,2′-azobis(isobutyrate) as initiator results in HBPs at com-

Table 6. Characteristics of DVA polymerisation.[104]

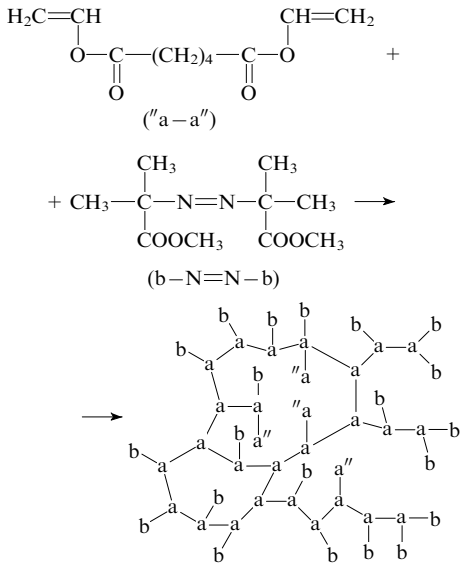
[DVA] /mol litre^{-1}	[I] /mol litre^{-1}	HBP yield (%)[a]	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.50	0.50	63	gel	
0.40	0.50	50	61 400	7.0
0.30	0.50	45	11 600	4.8
0.20	0.50	25	8400	1.3
0.30	0.40	52	11 900	5.2
0.30	0.30	59	13 800	6.4
0.30	0.20	68	17 100	9.2
0.30	0.10	79	18 500	12.7
0.30	0.05	87	16 800	13.0
0.30	0.01	93	gel	

[a] Polymerisation duration 4 h.

parable concentrations of the initiator and monomer (Table 6).[104]

The tentative structure of the polymer is shown in Scheme 5.

Scheme 5



In this case the degree of branching is reduced due to the high probability of reaction between pendant double bonds and the primary radical product of initiator dissociation.[123] As a result, the gel point is shifted towards higher conversions and the HBP is formed.

Critical point calculations for the system of mono- and polyfunctional oligomers ($M_1 + M_f$) in the presence of chain transfer to agent X give the following dependence (see Eqn. 16):[20, 96, 97, 124]

$$\alpha_c = \frac{a + kX}{k_p M_f f(f-1)},$$

$$a = 0.33\, k_t R,$$

$$k = 0.5\, k_X .$$

If at $X = 0$ the α_c value is a few fractions of a per cent (due to $a/k_p \sim 10^{-3}$ mol litre^{-1}), the concentration X of the order of a few per cent ensures a tenfold (and more) increase in the critical conversion[105–109] for, *e.g.*, such agents as mercaptans ($k_X/k_p \approx 1$).[125–128] The catalytic chain transfer reaction is even more efficient. In this case the term $k_c C(M_1 + fM_f)$ is in effect instead of kX, where k_c is the rate constant for catalytic chain transfer reaction and C is the catalyst concentration. Since k_c is 2000 litre mol s^{-1} (and more),[129] at $C \approx 10^{-3}$ mol litre^{-1} the critical concentration will increase by two orders of magnitude and more and can reach the limiting value, *i.e.*, no gel fraction will form at all.[106] The efficiency of this approach is substantiated by the data on the effect of the chemical composition of the system MMA : EGDMA : DDT = 100 : 15 : X containing dodecanethiol (DDT) as chain transfer agent on the yield of HBP (Table 7).[109]

Table 7. Effect of chemical composition of polymerisation system MMA : EGDMA : DDT = 100 : 15 : X on the yield of hyperbranched polymers.[104]

X	HBP yield (%)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
15	60	5280	2.94
14	62	6140	3.56
13	61	7845	5.68
12	71	7144	8.30
11	68	8137	10.74
10	84	5030	31.76
9	78	6830	30.21
8	72	6019	22.24
7	70	gel	

An efficient method of reduction of the molecular mass of growing polymer chains, which allowed HBPs to be prepared by simple radical polymerisation,[130] was proposed.[131] It was shown that at high temperatures (about 300 °C) polystyrene macromolecules undergo degradation by the β-scission mechanism. In the case of DVB this results in branching, the gel point being shifted towards high conversions; the formulation of the problem posed in Ref. 130 requires a large increase in dosage of the chain-branching monomer in the styrene + DVB mixture. Based on the preliminarily obtained value $\bar{P}_w$ for polystyrene and on the DVB concentration used in the experiments, the correctness of the Flory–Stockmayer relation was evaluated (Fig. 24).

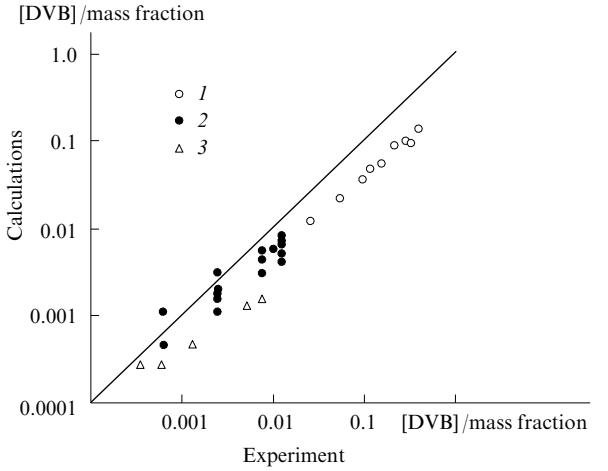


Figure 24. Theoretical amounts of DVB additives leading to gelation in the system styrene + DVB plotted *vs.* corresponding experimental amounts.
Straight line denotes the results of calculations using the Flory–Stockmayer theory; (*1–3*) are experimental data taken from Refs 130, 132 and 133, respectively.

The molecular mass was varied from 625 to 4125. The experimental and calculated critical concentrations of DVB showed a nearly twofold difference, which was explained by cyclisation. It should be noted that nonefficient cyclisation in 3D polymerisation processes was established both experimentally [134–140] and by computer simulation.[119,141–151]

It was proposed [7,152] to synthesise HBPs using 3D radical polymerisation of vinyl monomers in the presence of oxygen, a strong inhibitor of chain radical processes [153] [rate constant k_y is $(2-3)\times10^9$ litre mol s^{-1}]. This ensures a decrease in the primary polymer chain length [see Eqn (17)]. The effect of polymerisation conditions (temperature, reactant concentrations) on the kinetic characteristics of the process and on the structural parameters of HBPs based on methacrylic and styrene-like monomers and synthesised using this technique was studied [152] theoretically.†

Reactions of peroxide radical formed in the inhibition step

$$R^{\bullet} + O_2 \xrightarrow{k_y} RO_2^{\bullet}$$

result in not only changes in the primary polymer chain length, but also in the formation of various oxygen-containing groups, in particular, hydroxyl, carboxyl, carbonyl and epoxy ones.

The effect of stationary concentration of dissolved oxygen on the parameter α_c for styrene-like monomers was studied and the results of corresponding calculations are presented in Fig. 25. Since these calculations were based on the Carothers criterion, the critical conversions thus obtained are overestimated. Nevertheless, one can assume that the regularities established are reasonable from the qualitative point of view. The authors of Ref. 152 reported the following.

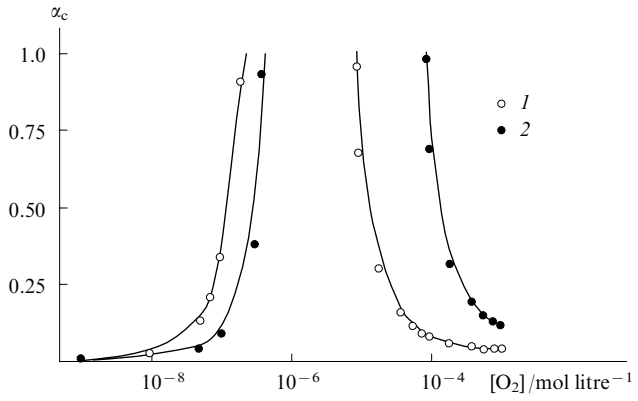


Figure 25. Critical conversion in oxidative polymerisation of styrene-like monomers plotted *vs.* stationary concentration of dissolved oxygen.[152]
$T = 58$ (*1*) and 95 °C (*2*). $[I]_0 = 0.01$ mol litre^{-1}, $k_i = 10^{-5}$ c^{-1}, $[M_2]_0 = 3$ mol litre^{-1}, $[M_1]_0 = 0$ mol litre^{-1}.

At low concentrations of dissolved oxygen (at most 1×10^{-9} mol litre^{-1}), gelation occurs at conversions $<1\%$. As should be expected, an increase in the oxygen concentration causes the parameter α_c to markedly increase and reach 100% at an oxygen concentration of 1×10^{-6} mol litre^{-1} (no gelation). However, the increase in the concentration of dissolved oxygen above 1×10^{-5} mol litre^{-1} leads to a decrease in α_c.

Such a nonmonotonic dependence of α_c on the concentration of O_2 is due to some reasons. First, the primary polymer chain length and, therefore, the α_c value are mainly determined by the rate of chain transfer to hydrocarbon RH using the radical $RO^{\bullet}$. Second, the presence of $O^{\bullet}$ in the system is mainly due to isomerisation of polystyrylperoxy radical. Third, the concentration of $RO^{\bullet}$ increases with an increase in the stationary concentration of dissolved oxygen; therefore, α_c increases at low oxygen concentrations. However, at some oxygen content the interaction of polystyrylperoxy radical with oxygen becomes competitive with the isomerisation reaction. As a result, an increase in the oxygen concentration causes the concentration of $RO^{\bullet}$ to decrease while the primary chain length to increase; this is accompanied by a decrease in α_c.

The effect of temperature (58 and 95 °C) on α_c also has some features. At low concentrations of dissolved oxygen (before transient region), α_c decreases as the temperature increases. The reverse is observed at oxygen concentrations higher than the transient region, namely, α_c increases as the temperature increases. In the former case, raising the temperature causes the rate constant k_p for chain transfer to the C-centred radicals to increase. As a result, the chain length increases and, therefore, α_c decreases. In the latter case, the determining role is played by the large number of peroxide groups present in the polymer chain (see below). These groups undergo more intense decomposition as the temperature increases and therefore the primary polymer chains become shorter and the parameter α_c increases.

Table 8 presents the structural parameters of HBPs prepared using oxidative polymerisation of styrene-like monomers at different stationary concentrations of oxygen and two temperatures. Polymers formed at oxygen concentrations before the transient region mainly represented carbochains with rare 'inclusions' (peroxide groups O—O) in the polymer chain. Polymers formed at higher oxygen concentrations have nearly one peroxide group per monomer unit. The closer the oxygen concentration to the transient region the higher the average density of branching (f_b). Outside the transient region, macromolecules formed have strongly different chemical compositions. At high oxygen concentrations, the polymer chain contains a large number of peroxide groups (p), whereas at low oxygen concentrations their proportion is low.

In all cases the proportion of 'pendant' epoxy groups (q) is small, being at most one group per macromolecule. Analysis of the data on the proportion of terminal functional groups points to the possibility of controlling the functionality of HBPs formed by varying the oxidaton regime. For instance, an increase in the oxygen concentration after the transient region leads to an increase in the proportion of hydroperoxide groups ROOH and to a decrease in the content of hydroxyl groups. The proportion of non-functionalised terminal groups remains almost unchanged, being at 95 °C only 10% lower than at 58 °C. The content of oxygen-containing functional groups formed in the decompositon of polyperoxides at higher temperature is $\sim15\%-20\%$ higher.

At oxygen concentrations lower than the transient region, the proportion of functional groups changes only

† The authors of Ref. 152 solved a system of several tens kinetic equations using the kinetic constants for polymerisation of styrene and (meth)acrylates available from the literature.

Table 8. Structural parameters of HBPs formed in oxidative polymerisation of styryl-like divinyl monomers at different oxygen concentrations.[152]

$[O_2]$ /mol litre^{-1}	T/°C	$\overline{P}_n$	f_b	Number of groups per macromolecule			Percentage of terminal functional groups (%)			
				p	z	q	ROOH	OH	O	C=O
1×10^{-3}	58	50.8	0.039	50.6	48.7	0.009	1.09	7.70	1.09	2.31
1×10^{-3}	95	17.3	0.116	16.4	14.7	0.067	18.02	13.65	18.02	0.54
4×10^{-4}	58	44.0	0.045	43.3	41.4	0.022	1.11	13.38	1.11	1.99
4×10^{-4}	95	12.2	0.164	10.9	9.2	0.154	16.61	21.94	16.61	0.46
1×10^{-4}	58	26.4	0.076	25.1	23.2	0.087	1.17	27.48	1.17	1.21
1×10^{-4}	95	4.9	0.408	3.3	1.2	0.601	20.14	29.16	20.14	0.47
4×10^{-5}	58	15.4	0.130	13.7	11.7	0.215	1.26	36.32	1.26	0.72
1×10^{-5}	58	5.9	0.339	3.9	1.4	0.809	6.04	42.19	1.26	0.36
3×10^{-7}	95	8.6	0.233	0.07	4.2	0.551	1.20	48.64	49.92	0.02
1×10^{-7}	58	9.4	0.213	0.19	4.9	0.132	0.90	48.90	50.13	0.06
1×10^{-9}	58	18.6	0.108	0.19	14.3	0.241	0.01	48.42	50.31	0.03
1×10^{-9}	95	51.8	0.039	0.07	47.9	0.078	2.63	47.06	50.29	0.03

Notes. $[I]_0 = 0.01$ mol litre^{-1} at $k_i = 1\times10^{-5}$ s^{-1}, $[M_2]_0 = 3$ mol litre^{-1}, z is the number of pendant double bonds.

slightly as the oxygen concentration changes and chain ends almost equiprobably bear non-functionalised and hydroxyl groups. The effect of temperature on these parameters is also very weak.

Similar results were obtained for methacrylates.

Thus, the authors of Ref. 152 laid the scientific foundations of the use of oxidative polymerisation for the synthesis of functionalised HBP.

Hyperbranched polymers with functional terminal groups were prepared by ionic polymerisation with ring opening in such monomers, as carbamates [154, 155] (leading to polyamines), glycidol [156–158] and hydroxycaprolactone,[159] hydroxyoxetane,[160–162] which results in the formation of hydroxy-terminated chain ends. From the standpoint of chemical mechanism these processes are in some sense analogous to proton-transfer polymerisation (see above, Section V); however, this is a typical chain polymerisation from the kinetic point of view. These monomers can be treated as inimers bearing a reactive group (*e.g.*, epoxy ring in glycidol) and a group capable of initiating ring opening (hydroxyl group). Polymers thus prepared are characterised by a low polydispersity index and a degree of branching (DB) $\geqslant 0.5$. Examples are provided by the corresponding data for HBPs based on 3-(hydroxymethyl)-3-ethyloxetane listed in Table 9.[162] In this case the negative substitution effect is pronounced: at low temperatures, chain propagation is mainly due to the involvement of terminal groups and therefore DB $\ll 0.5$. Raising the temperature causes equalisation of the reactivities of all types of functional groups and, finally, one gets DB $\to 0.5$.

Table 9. Effect of 3-(hydroxymethyl)-3-ethyloxetane polymerisation conditions on the structure of HBP.[162]

T/°C	Yield (%)	$10^{-3}M_n$	$\overline{P}_w/\overline{P}_n$	DB
−50	84	5.425	1.33	0.09
−40	83	4.987	1.57	0.11
−30	89	4.890	1.54	0.15
−20	85	5.243	1.38	0.22
−10	86	5.412	1.46	0.31
0	90	4.731	1.61	0.36
10	87	5.266	1.45	0.39
20	90	5.374	1.42	0.41
30	91	5.078	1.60	0.42

VII. Approaches to characterisation of the topological structure of hyperbranched polymers

The topological structure of HBPs is usually characterised using only three parameters, namely, the number-average molecular mass, polydispersity index (or mass-average molecular mass) and the average degree of branching (Frey parameter). All these parameters can be measured experimentally and calculated from the kinetic data. Theoretical evaluation of the distribution function over the type of structural units (cross-link points, linear, terminal) seems to be possible for polycondensation (as was demonstrated above) [24] and cyclotrimerisation. Corresponding calculations for 3D polymerisation [130, 163] are possible with allowance for certain admissions.[164]

The so-called method of numerical fractionation [163] consists in separate analysis of the kinetics of formation of macromolecules characterised by different degree of branching — zero, first, second, *etc.* generation. The zero generation is represented by linear macroradicals and macromolecules. The first generation is formed in the reaction of linear macroradicals with the formation of branchings, the second generation is a result of the interaction between two first-generation representatives, *etc.* The systems of equations for each generation were convoluted along the length of macromolecules and solved by the method of moments.

$$\frac{d\beta_{i,0}}{d\tau} = k_z\rho_{i,0} + k_{tc}\rho_{i,0}\sum_{j<i}\rho_{j,0} + \frac{k_{tc}}{2}\rho_{i-1,0}^2 - k_{fp}Y_0\beta_{i,1},$$

$$\frac{d\beta_{i,1}}{d\tau} = k_z\rho_{i,1} + k_{tc}\rho_{i,0}\sum_{j<i}\rho_{j,1} + k_{tc}\rho_{i,1}\sum_{j<i}\rho_{j,0} + k_{tc}\rho_{i-1,0}\rho_{i-1,1} - k_{fp}Y_0\beta_{i,2},$$

$$\frac{d\beta_{i,2}}{d\tau} = k_z\rho_{i,2} + k_{tc}\rho_{i,2}\sum_{j<i}\rho_{j,0} + 2k_{tc}\rho_{i,1}\sum_{j<i}\rho_{j,1} + k_{tc}\rho_{i,0}\sum_{j<i}\rho_{j,2} + k_{tc}\rho_{i-1,1}^2 + k_{tc}\rho_{i-1,0}\rho_{i-1,2} - k_{fp}Y_0\beta_{i,3}.$$

Here $\beta_{i,j}$ and $\rho_{i,j}$ are the jth moments of the ith generation of chains and macroradicals, k_z is the effective constant, which includes the chain transfer and chain termination through disproportionation, k_{tc} and k_{fp} are the kinetic constants for chain termination through recombination and chain propagation with the pendant group and Y_0 is the stationary concentration of radicals.

The problem is that the chain of differential equations for the moments is not closed, *i.e.*, the zero moment $\beta_{i,0}$ depends on the first moment $\beta_{i,1}$, the first moment depends on the second moment $\beta_{i,2}$, the second moment depends on the third moment $\beta_{i,3}$, *etc*. The chain was truncated using the following approximation [164] for each generation

$$\beta_{i,3} = 2\frac{\beta_{i,2}^2}{\beta_{i,1}} - \frac{\beta_{i,1}\beta_{i,2}}{\beta_{i,0}}.$$

This technique was used [130, 163] for estimation of the molecular mass and branching distribution functions and the possibility of formation of a bimodal MMD near the gel point was shown. It is assumed [163] that the method of numerical fractionation can be used for both the 3D polymerisation and chain transfer through polymer.

Thus, there are some approaches to the description of the topological structure of HBPs and its relation to the kinetics of formation. The situation with experimental evaluation is much worse. Branching is known to result in compactisation of macromolecules:[18] in particular, this manifests itself in a decrease in the exponent a in the expression relating the hydrodynamic radius of macromolecular globule (R_g) to its molecular mass,

$$R_g = KM_w^a,$$

K is a coefficient. However, the data suitable for assessment of the effect of the character of the branching distribution on the degree of branching are simply lacking.[54] In addition, an important role is played by the MMD.

We believe that relaxation methods are promising for analysis of the topological structure with allowance for distribution functions.[18] But their use requires preliminary theoretical and experimental research. Here, a healthy sign is that the relaxation properties of HBPs are governed by intramolecular rearrangements rather than intermolecular interaction (*e.g.*, entanglements), being immediately related to (not only) the topological structure (because the intrinsic viscosity also plays a significant role). An example of successful use of relaxation methods (although in studies of topologically simpler systems — dendrimers) is provided by the research done by Gotlib *et al.*[165–167]

Studies of HBPs using relaxation methods are in the early stage of development. An algorithm of calculations of relaxation time spectra of branched oligomers with different architectures has been formulated.[168] Relaxation spectra are calculated using a Dubovitskiy (Institute of Problems of Chemical Physics, Russian Academy of Science) general mathematical model for motion of chain molecules in the form of a linear system of differential equations on the connectivity graph. Müller [169] generalised the polymer chain model by Kargin–Slonimskii–Rouse and proposed a general approach to the description of the relaxation behaviour of macromolecules with arbibrary topology. The character [46, 170, 171] of the frequency dependence of the dynamic modulus for polymers based on AB_2 monomers is interpreted based on the fact that they are the closest to critical clusters in fractal characteristics. But in contrast to critical clusters for HBPs the loss tangent

$$\tan\delta = \frac{G''}{G'}$$

depends on the frequency of external action of the polymer.[172, 173] Strictly speaking, the real and imaginary components of the relaxation modulus ($G' = G''$) are equal only in the gel point,[174, 175] and the notion 'critical cluster' is applicable only in the gel point.

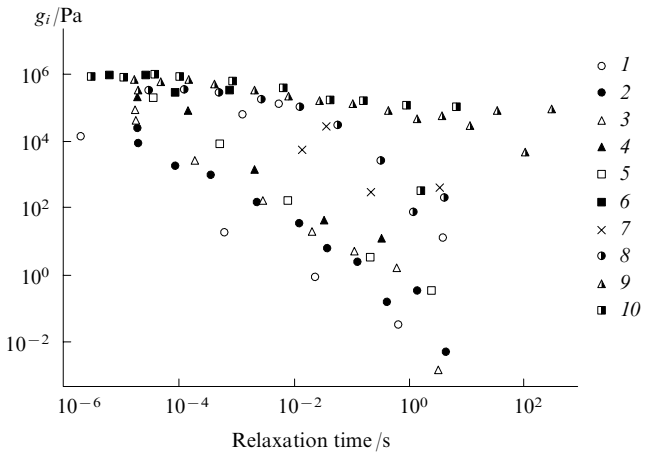


Figure 26. Relaxation spectra of hyperbranched polyglycerols.[157] Figures (*1–10*) denote the sample numbers in Table 10; g_i are coefficients in the spectral decomposition of shear modulus.

Figure 26 presents the data [157] illustrating the relation between the relaxation spectrum and structure (Table 10) of hyperbranched polyglycerols (HPG) synthesised by polymerisation of glycidol. The spectrum was calculated using a known procedure.[176] As can be seen (Table 10), the parameter a poorly correlates with the more complex polymer structure (*cf.* the calculated and experimental molecular masses). Its value, close to 1/3, only point to high compactness of the coil. In contrast to this the relaxation spectrum characterises all structural features of HBPs. As shown in Fig. 26, for most samples (not all!) the dependence of the statistical weight on the relaxation times obeys an exponential pattern. Undoubtedly, the molecular mass influences

Table 10. Polyglycerol properties at limiting conversion.[157]

HPG sample No.	Solvent	$\bar{M}_n$		$\bar{M}_w/\bar{M}_n$	a
		calculations	experiment		
1	no solvent	3000	3400	1.2	0.43
2	the same	20 000	25 000	1.6	0.35
3	"	40 000	42 500	1.8	0.34
4	diglyme	20 000	106 000	2.0	0.27
5	"	40 000	106 000	2.9	0.35
6	"	40 000	266 000	2.9	0.37
7	"	60 000	871 000	1.7	0.39
8	dioxane	20 000	359 000	1.4	0.31
9	"	40 000	540 000	1.1	0.34
10	"	60 000	670 000	1.1	0.31

the character of the spectrum, but the topological structure also contributes, namely, it is assumed [177] that the exponent is related to the fractal dimension of the macromolecule.

VIII. Conclusion

Analysis of the kinetics of formation of hyperbranched polymers allows their topological structure to be assessed; however, a number of issues are still to be clarified.

First, it is unclear how to characterise, both theoretically and experimentally, the branching distribution function and, correspondingly, what is the role of this distribution function in the determination of the desired properties (targets). A number of methods for reduction of the polydispersity index (with respect to molecular mass) have been developed, but there are no direct proofs of the fact that the parameters of the branching distribution vary to the same extent.

Second, analytical and numerical methods for solving kinetic equations ignore cyclisation. The occurrence of this reaction is established by computer simulation methods, and it was shown that the larger the HBP molecules (systems of the greatest practical interest) the more probable the cyclisation. However, it is a very complicated task to relate the results of computer simulation to particular kinetic coniditions; as a consequence, evaluation of the degree of cyclisation in actual HBPs is difficult.

Finally, it is important to relate the topological structure of HBPs to the spatial structure of macromolecule, which undoubtedly plays an important role in determining the relaxation properties.

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