

# Condensation polymerization of AB<sub>2</sub> monomers – modeling and validation of model of polyreaction performed at the room temperature

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**Abstract:** Statistical and kinetic methods to model step polymerization of AB<sub>2</sub> type of monomers (A and B stand for functional groups) are briefly reviewed and the relationships linking conversion or reaction time with averages of polymerization degree are derived for systems fulfilling the Flory-Stockmayer assumptions, *i.e.*, for those with no reactivity changes of functional groups and absence of intramolecular linking. Results of kinetic studies are also presented for polymerization of 3,5-diaminobenzoic acid, aided with *N,N'*-diisopropylcarbodiimide, carried out at room temperature in NMR test tubes. For reaction carried out in dimethylsulphoxide, the relationship between conversion and time is well described by the simplest kinetic model. It was stated that in the case of reaction carried out in dimethylformamide the reactivity of the second amino group in the monomeric units seems to be ten times lower than that of the first one.

**Keywords:** hyperbranched polymer, statistical model, kinetic model, carbodiimide, apparent rate constant.

## Polimeryzacja kondensacyjna monomerów AB<sub>2</sub> – modelowanie i weryfikacja modeli polireakcji prowadzonej w temperaturze pokojowej

**Streszczenie:** Przedstawiono krótki przegląd statystycznych i kinetycznych metod modelowania stopniowej polimeryzacji monomerów typu AB<sub>2</sub> (A i B reprezentują grupy funkcyjne). Wyprowadzono relacje łączące stopień przereagowania ze średnimi stopniami polimeryzacji dla układów reagujących zgodnie z założeniami Flory'ego i Stockmayera, tj. bez zmian w reaktywnościach grup funkcyjnych oraz nieobecności wiązań wewnątrzcząsteczkowych. Przedstawiono wyniki badań kinetycznych przebiegu polimeryzacji kwasu 3,5-diaminobenzoesowego wspomaganego *N,N'*-diizopropylkarbodiimidem, którą prowadzono w temperaturze pokojowej w probówkach NMR. Kinetykę badanej reakcji, prowadzonej w dimetylosulfotlenku, dobrze opisuje najprostszy model kinetyczny polikondensacji. Stwierdzono, że w przypadku reakcji prowadzonej w dimetyloformamidzie, reaktywność drugiej grupy aminowej w jednostkach monomerycznych jest dziesięciokrotnie mniejsza, niż reaktywność pierwszej z tych grup.

**Słowa kluczowe:** polimer hiperrozgałęziony, model statystyczny, model kinetyczny, karbodiimid, pozorna stała szybkości.

Highly branched macromolecules have recently become important components of advanced materials. An interest in their synthesis and applications stems from various fields of modern technology. Two groups of these products were widely studied for the last two and a half decades. These were dendrimers and hyperbranched polymers. Dendrimers are prepared in rather tedious many-staged organic synthesis, whereas hyperbranched polymers can be prepared in a one pot synthesis. Hence, the dendrimers

consisting of macromolecules of rather regular and uniform structure are generally much more expensive than the hyperbranched polymers. The latter, on the other hand, consist of macromolecules of highly diversified both size and molecular structure. Despite of this disadvantage, Yates and Hayes [1] named at least 12 different applications of hyperbranched polymers in modern technology.

Although the pioneering theoretical works on hyperbranched polymers date back to Flory's fundamental paper [2, 3] published in 1952, the actual term of hyperbranched polymers was coined by Kim and Webster [4] nearly forty years later. Since then there was a multitude of publications on both dendrimers and hyperbranched polymers. A review by Brigitte Voit based on 15 years

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of research on hyperbranched polymers quotes over 250 publications [5].

In this paper we intend to review methods of modeling of formation of hyperbranched polymer limited to those prepared by polycondensation of  $AB_{f-1}$  (or  $ARB_{f-1}$  [2, 3]) type monomers where A and B stand for functional groups.

Flory [2, 3] derived the following expression for the number fraction of molecules of polymerization degree  $x$  as a function of conversion  $\alpha$  of groups B in a monomer  $AB_{f-1}$ :

$$n_x = \frac{(fx - x)!}{(fx - 2x + 1)! x!} \alpha^{x-1} (1 - \alpha)^{fx - 2x + 1} \quad (1)$$

The size distribution of molecules represented by this equation is very broad, in fact practically diverging as the conversion of B groups, approaches its highest attainable value of  $1/(f - 1)$ .

Since the year *ca.* 2000, there appeared a number of papers devoted to finding a quantitative relationship between the molecular weight of hyperbranched polymers prepared by various techniques and conversion of monomers or their functional groups. Different methods of modeling were used, usually adopted or devised to be consistent with the mechanism of polymer formation.

Here, we will concentrate on models of hyperbranched polymerization that proceed according to the classical self-polycondensation of an  $AB_2$  monomer. To our knowl-

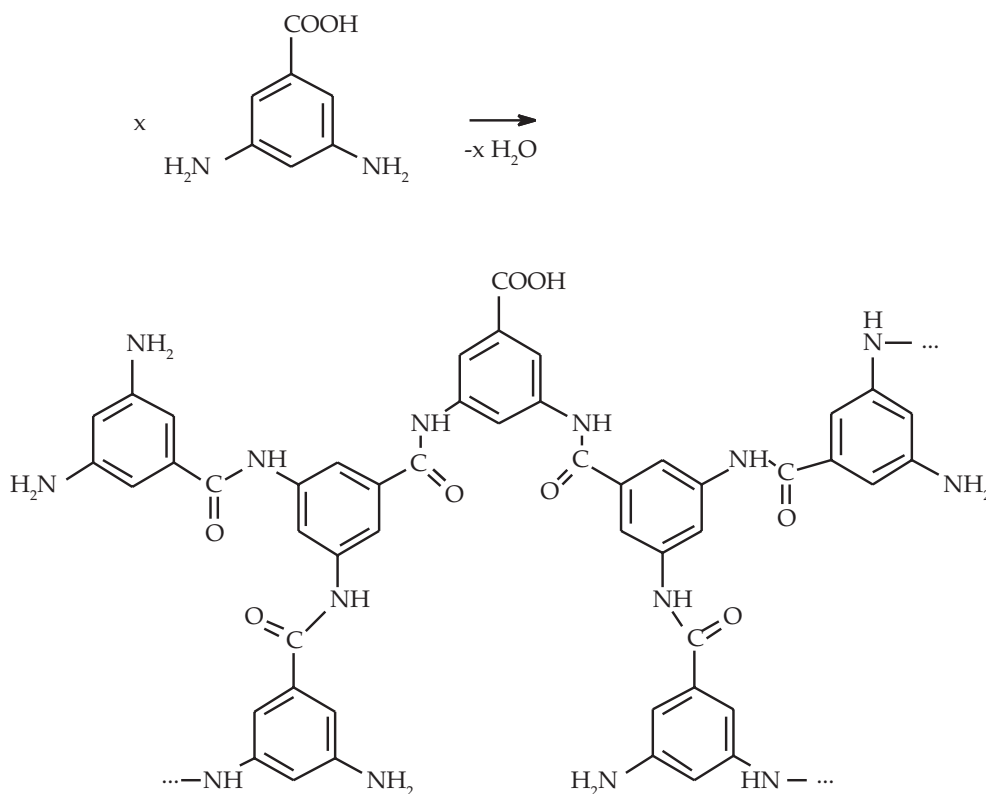
edge, one of the statistical models presented here, the one based on the cascade theory, has not been used for that purpose, before. Burchard [6] used the cascade theory to analyze polymers derived from similar monomers of  $ABB'$  type, but his aim was to study scattering behavior of branched natural polysaccharides.

In the second part of this report, we intend to show that the simple models of hyperbranched polycondensation are often sufficiently accurate to describe growth of polymer molecules, even in processes where links between units are formed in chemically complex reactions. To do this, we will present some results of kinetic studies on polymerization of 3,5-diaminobenzoic acid carried out at room temperature with  $N,N'$ -diisopropylcarbodiimide as a carboxyl group activator.

### SIMPLE CLASSICAL MODELS OF HYPERBRANCHED POLYCONDENSATION

We will consider a polymerization of an  $AB_2$  monomer, such as the process shown in Scheme A.

Two statistical models of the hyperbranched polymerization like that shown in Scheme A are to be presented. In statistical models, it is the conversion of functional groups which is the key independent parameter. By assuming certain probability distribution of finding a functional group to be reacted, the statistical models build up the entire molecular size distribution in the reacting system. In particular, moments of this distribution can quite easily be extracted.



Scheme A

In the simplest case one has to assume that the polymerization proceeds according to the Flory-Stockmayer [7] rules:

- all functional groups of the same kind have equal reactivity, independently of the size of macromolecule which they are attached to;
- only intermolecular links can be formed, *i.e.*, only acyclic macromolecules are formed.

In real polycondensation systems, especially in the processes involving monomers of functionality higher than two, the second assumptions cannot be fulfilled, but usually the extent of cyclization in polycondensation becomes significant at conversions close to the gel point or, in the case of aromatic  $AB_2$  monomers, at the conversion exceeding *ca.* 90 % [8].

A model based on the cascade theory makes use of the formalism introduced to polymer science by Gordon [9], back in 1962. In the theory applied to polycondensation of an  $AB_2$  monomer let us consider an equilibrium system at the conversion of A groups equal to  $p_A$ . Clearly, the conversion of B groups is  $p_B = p_A/2$  for stoichiometry reasons. In the theory, one selects at random one unit from the entire system and places it in the zeroth generation of the molecular family tree. Suppose the unit selected belongs to a pentamer as shown in Fig. 1. The unit in zeroth generation (the root or ancestor) is distinguished from the two types of units (offsprings) in the first and higher generations. The offsprings of type  $\alpha$  have one of its reacted B functional groups (thin line) directed towards the preceding generation. The offsprings of type  $\beta$  are linked to preceding generation through its reacted A group (thick line). The yet unreacted functional groups bear letters A or B.

With the assumption described above, one can write down the probability generating functions (PGF) for the

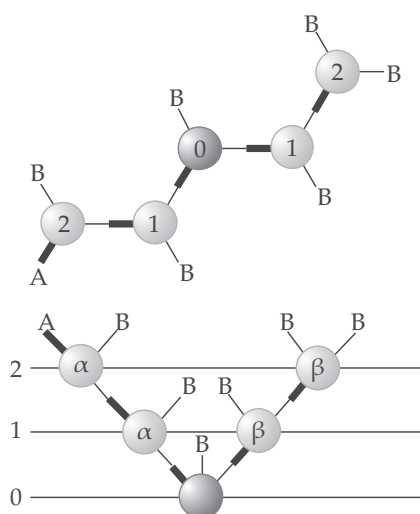


Fig. 1. A pentamer obtained in polycondensation of an  $AB_2$  monomer (top) where the unit labeled 0 happened to be selected as the root of molecular family tree (bottom)

number of offsprings for each type of unit. Thus, for the root one can define PGF in the form:

$$F_0(\mathbf{s}) = (1 - p_A + p_A s_\alpha)(1 - p_B + p_B s_\beta)^2 \quad (2)$$

where:  $s_\alpha, s_\beta$  – dummy variables of no physical meaning.

Parameters  $s_\alpha$  and  $s_\beta$  are conveniently considered as the algebraic vector  $\mathbf{s} = (s_\alpha, s_\beta)^T$ . Note that  $F_0$  is simply the product of PGF's for the functional groups (for example, the probability of finding group B reacted is  $p_B$  and the resulting link leads to a unit of type  $\beta$  in the next generation, hence  $p_B$  is multiplied by  $s_\beta$ ; the probability of finding the group unreacted is  $1 - p_B$  with  $s_\beta^0 = 1$  for no link obviously omitted).

As can be seen by inspection, for the units in generation 1 and higher one has:

$$F_{1\alpha}(\mathbf{s}) = (1 - p_A + p_A s_\alpha)(1 - p_B + p_B s_\beta) \quad (3)$$

for a unit of type  $\alpha$ , since it may have both types of offsprings, and:

$$F_{1\beta}(\mathbf{s}) = (1 - p_B + p_B s_\beta)^2 \quad (4)$$

for units of type  $\beta$ , which are parents of only  $\beta$  type of offsprings. It is convenient to use the vector form of PGF for the first and higher generations:

$$\mathbf{F}_1(\mathbf{s}) = \begin{bmatrix} F_{1\alpha}(\mathbf{s}) \\ F_{1\beta}(\mathbf{s}) \end{bmatrix} \quad (5)$$

Now, in the standard manner [7, 9], one can calculate the number and weight average polymerization degrees using the following formulas. The number average polymerization degree,  $\bar{P}_n$  is:

$$\bar{P}_n = \frac{1}{1 - \mathbf{j}^T \mathbf{F}'_0} \quad (6)$$

$$\mathbf{F}'_0 = \left( \begin{array}{c} \frac{\partial F_0}{\partial s_\alpha} \\ \frac{\partial F_0}{\partial s_\beta} \end{array} \right) \Bigg|_{\mathbf{s} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}} \quad (7)$$

where:  $\mathbf{j}^T = (1 \ 1)$ .

Thus, since  $\mathbf{F}'_0 = \begin{pmatrix} p_A \\ 2p_B \end{pmatrix}$ , by substituting  $p \equiv p_A = 2p_B$ , we obtain

$$\bar{P}_n = \frac{1}{1 - p} \quad (8)$$

The weight average polymerization degree is again calculated in the cascade theory in the standard manner from the equation which for  $AB_2$  monomer has the form:

$$\bar{P}_w = 1 + (\mathbf{F}'_0)^T [\mathbf{I} - \mathbf{F}'_1]^{-1} \mathbf{j} \quad (9)$$

where:  $\mathbf{I}$  – a unit matrix  $\left( \mathbf{I} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \right)$ .

Standard calculations yield:

$$F_1 = \begin{bmatrix} p_A & p_B \\ 0 & 2p_B \end{bmatrix} \quad (10)$$

$$[I - F]^{-1} = \begin{bmatrix} 1 - p_A & -p_B \\ 0 & 1 - 2p_B \end{bmatrix}^{-1} = \frac{1}{(1 - p_A)(1 - 2p_B)} \begin{bmatrix} 1 - 2p_B & 0 \\ p_B & 1 - 2p_A \end{bmatrix} \quad (11)$$

hence:

$$\bar{P}_w = \frac{1 - p^2/2}{(1 - p)^2} \quad (12)$$

An alternative statistical approach provides the recursive method based on the elementary probability law and formalism developed by Macosko and Miller [10, 11]. This approach was used by Fredet and Tessier [10] to model, among other systems, also homopolymerization of an  $AB_f$  monomer. In this approach, the fundamental relation concerning the total probability is used:

$$E(Y) = E(Y|A)p_A + E(Y|\bar{A})p_{\bar{A}} \quad (13)$$

where:  $E(Y)$  – the expected (average) value of random variable  $Y$ ,  $Y|A$  – the conditional probability of occurring  $Y$  provided that  $A$  occurs with probability  $p_A$ ,  $\bar{A}$  – the event complementary to  $A$ , occurring with probability  $p_{\bar{A}}$ , usually equal to  $1 - p_A$ .

Calculation of the averages of polymerization degrees for polymerization of  $AB_2$  monomer is particularly easy. Without going into details, one may show that the weight average polymerization degree at certain conversion of groups  $A$  is [12]:

$$\bar{P}_w = 1 + E(N_A^{out}) + 2E(N_B^{out}) \quad (14)$$

where:  $E(N_A^{out})$ ,  $E(N_B^{out})$  – the expected numbers of units linked to a randomly selected unit from the entire system, looking out from the unit through reacted functional group  $A$  and  $B$ , respectively.

Help in evaluating these numbers can serve Fig. 2. The randomly selected units are labeled with numbers and directions 'in' and 'out' for the units through  $B$  group (unit 1) or through  $A$  group (unit 2).

The following procedure of evaluating  $E(N_A^{out})$  and  $E(N_B^{out})$  is used [10].  $N_A^{out}$  equals to  $N_B^{in}$ , if  $A$  group reacted (with probability  $p_A$ ), or is 0, if the group remained unreacted (probability  $1 - p_A$ ). On the other hand,  $N_B^{out}$  equals to  $N_A^{in}$ , if group  $B$  reacted with  $A$  (probability  $p_B$ ) or equals to 0, if  $B$  were not reacted (probability  $1 - p_B$ ). Looking at Fig. 2 one can see that, considering unit 1 through its reacted  $B$  group (thin line) one can write:

$$N_B^{in} = 1 + N_B^{out} + N_A^{out} \quad (15)$$

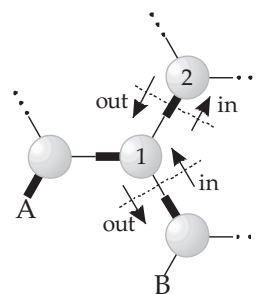


Fig. 2. Illustration of the recursive method of evaluating the averages of polymerization degrees in polycondensation of an  $AB_2$  monomer

while for unit 2 through reacted  $A$  group (thick line):

$$N_A^{in} = 1 + 2N_B^{out} \quad (16)$$

Now, the expressions describing the total probability yield the following set of equations:

$$E(N_A^{out}) = p_A E(N_B^{in}) + 0(1 - p_A) = p_A E(N_B^{in}) \quad (17)$$

$$E(N_B^{in}) = 1 + E(N_B^{out}) + E(N_A^{out}) \quad (18)$$

$$E(N_B^{out}) = p_B E(N_A^{in}) \quad (19)$$

$$E(N_A^{in}) = 1 + 2E(N_B^{out}) \quad (20)$$

Solution of the set yields:

$$E(N_B^{out}) = \frac{p_B}{1 - 2p_B} \quad (21)$$

$$E(N_A^{out}) = \frac{p_A(1 - p_B)}{(1 - p_A)(1 - 2p_B)} \quad (22)$$

The last two equations and substitution  $p = p_A = 2p_B$  finally give:

$$\bar{P}_w = \frac{1 - p^2/2}{(1 - p)^2} \quad (23)$$

It is also not difficult to show that:

$$\bar{P}_n = \frac{1}{1 - p_A} = \frac{1}{1 - p_B} = \frac{1}{1 - p} \quad (24)$$

Thus, for the simplest case, both statistical methods give identical expressions linking conversion of functional groups with averages of molecular size distribution in polycondensation of an  $AB_2$  monomer.

## KINETIC MODELS

In the kinetic models the independent variable is time, not conversion, like in the statistical ones. The simplest kinetic models, *i.e.*, the models with similar simplifying assumptions as those applied in the statistical analyses were presented in several versions [13–15]. They were ap-

plied to systems with the so called core monomer, usually of  $B_g$  type ( $g = 1, 2, \dots$ ) added to  $AB_f$  monomer in order to reduce dispersity of the polymer product [15–17]. Kinetic models were also studied in computer simulations [8, 18, 19] usually in attempts to interpret experimental data. The computer simulations allowed for relaxing the classical assumptions, including formation of cyclic structures, changes in reactivity of functional groups or even steric hindrances. A disadvantage of these approaches is that they either cannot be generalized [18] or applied to a particular system [19].

Our attempt to implement cyclization in the kinetic analysis [14] was rightly criticized as unphysical [20]. In fact, in all theoretical approaches beside the computer simulations, Flory's confession [2, 3]: "Intramolecular condensations are neglected out of despair at the difficulty of treating the problem otherwise" seems still valid.

While describing a kinetic model basing on the same classical assumptions as adopted in statistical approaches, we intend to demonstrate the equivalence of the two alternative methods of modeling of hyperbranched polycondensation.

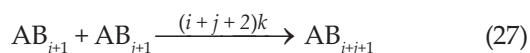
Consider a polymerization system involving an  $AB_2$  monomer at time  $t$ . Let the concentration of an  $i$ -mer at this time be  $[i]$ , conveniently expressed as the number of molecules of this size, independently of their structure, divided by the total number of monomeric units in the system. Note that this definition of the distribution of molecular sizes of species implies that the first moment of the distribution is necessarily equal to 1:

$$\sum_{i=1}^{\infty} i[i] = 1 \quad (25)$$

Zeroth moment is the reciprocal of the number average polymerization degree:

$$\sum_{i=1}^{\infty} [i] = \frac{1}{P_n} \quad (26)$$

Each acyclic hyperbranched macromolecule of size  $i$  has exactly one unreacted A group and  $i + 1$  unreacted B groups. Hence the reaction between  $i$ -mer and  $j$ -mer can be written as:



where:  $k$  – the rate constant of reaction between functional groups.

The rate at which an  $i$ -mer appears in and vanishes from the system is described by the Smoluchowski coagulation equation [21], which can be converted [13] into the partial (master) differential equation:

$$\frac{\partial G}{\partial \tau} = \left( \frac{\partial G}{\partial x} + G \right) (G - G_0) - (G_x + G_0) G \quad (28)$$

This equation describes the time dependence of the entire size distribution in the polymerizing system expressed by the function:

$$G(\tau, x) = \sum_{i=1}^{\infty} [i] e^{ix} \quad (29)$$

The time units have been scaled to  $\tau = kt$  and the other symbols stand for the zeroth and first moments of distribution, respectively.

$$G_0 = G_0(\tau, 0) = \sum_{i=1}^{\infty} [i] \quad (30)$$

$$G_x = G_x(\tau) = \left. \frac{\partial G}{\partial x} \right|_{x=0} = \sum_{i=1}^{\infty} i[i] \quad (31)$$

Parameter  $x$  is here a dummy variable of no physical meaning, while  $i$ , the polymerization degree, should not be confused with imaginary unit.

Solutions of differential equations extracted from the master equation by its successive differentiation with respect to  $x$ , followed by putting  $x = 0$  yield the following results [13]:

$$\overline{P}_n = 2e^\tau - 1 \quad (32)$$

$$\overline{P}_w = 2e^{2\tau} - 1 \quad (33)$$

$$p_A \equiv p = 2 \frac{e^\tau - 1}{2e^\tau - 1} \quad (34)$$

A reader may wish to verify that the relationships between the averages of polymerization degrees and conversion  $p$  are identical as those obtained using the statistical approaches.

Advantages of the kinetic approach over the statistical ones are the following. Calculations for systems with differences in reactivity of individual groups including the substitution effect [15, 17], are relatively simple and, more importantly, one may take into account variations in the composition of the reacting system. Such variations aim at reducing dispersity of the resulting condensation product and may involve carrying out the reaction starting with a core monomer, e.g.,  $B_2$  monomer, and adding the  $AB_2$  monomer in portions [22, 23] or continuously introducing it at different rates [24].

One version of kinetic models developed by us [14] takes into account the substitution effect for B groups, i.e., it considers a system where both B groups in a unit are equally reactive, but with the reactivity of the second group changing after the first one has reacted. The model produces a simple set of ordinary differential equations for partial moments of size distribution expressed this time by the function:

$$H(\tau, x, y) = \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} [i, j] x^i (\alpha y)^j \quad (35)$$

where:  $[i, j]$  – the concentration of molecules sharing  $i$  units with both B groups unreacted, and  $j$  units with one B group reacted, again expressed as the number of these molecules divided by the total of all units in the system,  $x, y$  – dummy variables,  $\alpha = k'/2k$  – the ratio of rate constants for reaction of the first B group ( $k$ ) and the second one ( $k'$ ).

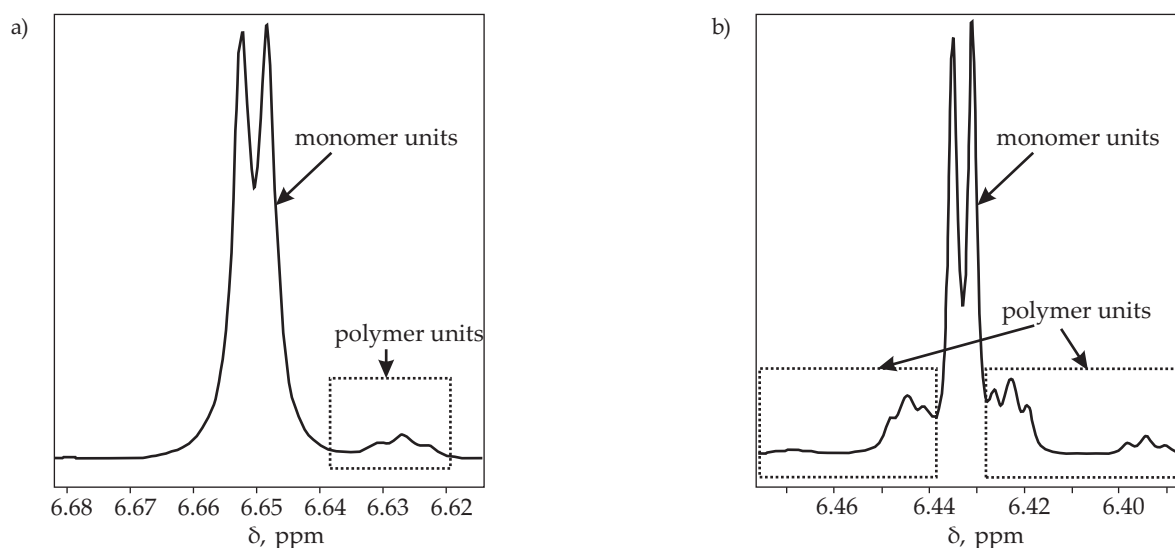


Fig. 3. Enlarged fragments of  $^1\text{H}$  NMR spectra of room temperature polycondensation reaction mixtures in (the peaks are ascribed to resonance signals from protons in position 2,6 in 3,5-diaminobenzoic acid units): a) DMF, b) DMSO

With no substitution effect,  $\alpha = 1/2$ .

The set of ordinary differential equations with respect to time, sufficient to follow the conversion of A groups has the form [14]:

$$\begin{cases} H_1 = -H_1(H_1 + H_x) \\ H_x = -H_1 H_x \\ H_y = \alpha H_1(H_x + H_y) \end{cases} \quad (36)$$

where:

$$H_1(\tau) = H(\tau, 1, 1/\alpha) \quad (37)$$

$$H_x(\tau) = \left. \frac{\partial H}{\partial x} \right|_{x=1, y=1/\alpha} \quad (38)$$

$$H_y(\tau) = \left. \frac{\partial H}{\partial y} \right|_{x=1, y=1/\alpha} \quad (39)$$

## EXPERIMENTAL KINETIC ANALYSIS

For a polycondensation carried out at room temperature, the kinetics is particularly easy to follow using NMR spectroscopy. Kinetic analyses of this kind were published for many systems, both for aliphatic [25–27] or aromatic [28] monomers.

We have made several kinetic experiments involving 4-bis(4-hydroxyphenyl)pentanoic acid and 3,5-diaminobenzoic acid. Furthermore, the systems with core monomers and gradual introduction of  $\text{AB}_2$  monomers to the NMR tube where a core monomer had been already present were also studied. Details of the last experiments will be presented in a subsequent paper. Here, we report on the kinetic analysis of 3,5-diaminobenzoic acid homopolycondensation in different solvents. In the experiments, all carried out at 25 °C, calculated amounts of solvent ( $d_6$ -DMSO,  $d_7$ -DMF, 0.75 cm<sup>3</sup>),  $N,N$ -dimethylaminopyridinium 4-toluene sulfonate catalyst (7.5 mg), and

the monomer (48 mg) were placed in an NMR tube to record the first spectrum. Then,  $N,N'$ -diisopropylcarbodiimide (57 mg) was added using a microsyringe and spectra were recorded at predetermined time intervals. The whole experiment took *ca.* 6 h. The signals from protons 2,6 in the aromatic ring of monomer units were used as diagnostic ones [29]. In DMF, it was a doublet at 6.66 ppm (at 6.43 ppm in DMSO) which broadened as the reaction proceeded. The actual conversion was calculated from reduction of signal intensity from diagnostic protons in unreacted monomer. It was calculated after deconvoluting the broadened signals. The doublets recorded in DMF and DMSO are shown in Fig. 3.

The rate curve recorded in DMSO was sufficiently well described by eq. (36) derived from the simplest kinetic model [13] with  $\tau$  substituted back by  $kt$ , where  $t$  was the real time of reaction. The result is shown in Fig. 4. For monomer concentration of 0.416 mol/dm<sup>3</sup> the apparent rate constant calculated directly using eq. (36) was  $k = (4.30 \pm 0.07) \cdot 10^{-3}$  1/min.

In DMF, however, similar experiment revealed a considerable substitution effect exerted by the reacted amino group. For a very similar monomer concentration of 0.428 mol/dm<sup>3</sup>, the apparent rate constant calculated directly using eq. (36) was  $k = (9.7 \pm 0.33) \cdot 10^{-3}$  1/min. The best rate curve, however, calculated for different  $\alpha$  values from the set of differential equations (36) was that for  $k = (1.06 \pm 0.03) \cdot 10^{-2}$  1/min with  $\alpha = 0.05$ . The last value suggests that the second amino group reacts with carboxyl group at the rate ten times lower than the first one. Certainly, one has to bear in mind the approximations involved in this kinetic analysis. Only the effect of substitution of amino groups is taken into account, but not that of carboxyl groups. Furthermore, possible cyclization and other side reactions are disregarded. We believe, though, that the cyclization has a minor effect on the reaction and, as shown by recent Monte-Carlo studies [8],

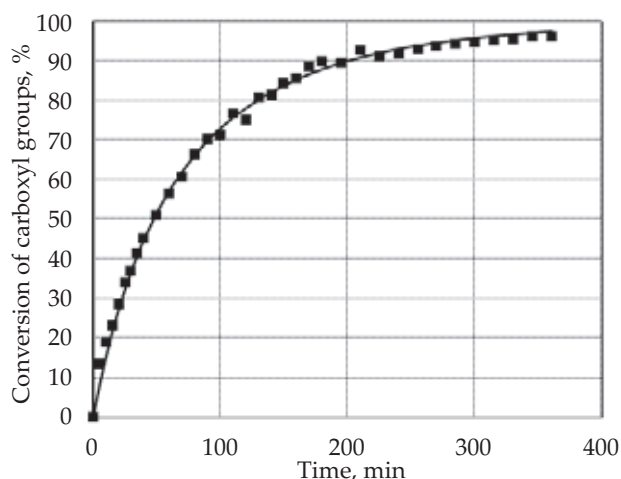


Fig. 4. The rate curve calculated from NMR test for homopolycondensation of 3,5-diaminobenzoic acid in  $d_6$ -DMSO (points) and calculated using eq. (34) (line)

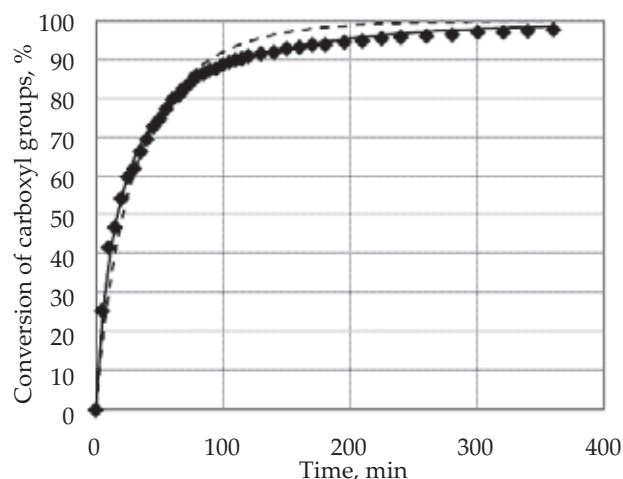


Fig. 5. The rate curve calculated from NMR test for homopolycondensation of 3,5-diaminobenzoic acid in  $d_7$ -DMF (points), calculated using eq. (34) (dashed line) and calculated from eq. (36) (solid line)

the cyclization reaction in homopolycondensation of the all aromatic monomer becomes appreciable at the conversion well above 90 %. The consistence of the models with the experiment for the reaction in DMF is well illustrated in Fig. 5, where the best lines calculated disregarding the substitution effect and that corresponding to  $\alpha = 0.05$  are plotted along with experimental results.

As one can see in Fig. 6, the rate of condensation reaction or, strictly speaking, the apparent rate constant is linearly dependent on the concentration of monomer and starts very close to origin. This means that the room temperature polycondensation is here the first order reaction with respect to monomer concentration. On the other hand, despite of rather complex mechanism of polycondensation carried out in the presence of carbodiimide [30–32], from the point of view of connectivity process, the formation of polymer well conforms to very much straightforward second order reaction between functional groups.

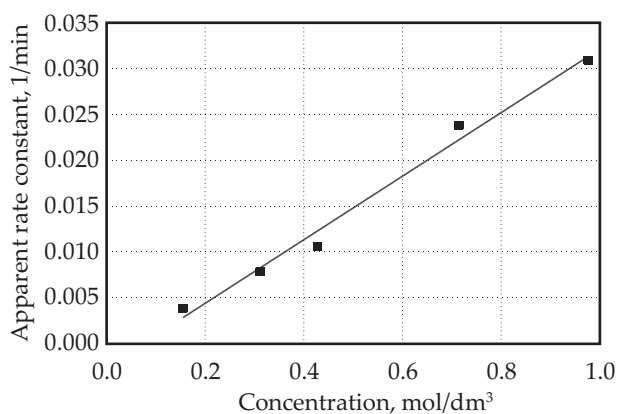


Fig. 6. The dependence of the apparent rate constant for homopolycondensation of 3,5-diaminobenzoic acid on its concentration in DMF (the substitution effect parameter  $\alpha = 0.05$ )

It is interesting that, unlike in DMF, no substitution effect was observed for the system in DMSO, although the proximity of amino groups in the monomer might suggest such an effect to be inevitable. The reason might be either some superposition of side effects or different solvating power of the two solvents. The latter manifests itself by different splitting of  $^1\text{H}$  NMR signals from protons 2,6 of monomeric units in different solvents (Fig. 3).

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**BAZĘ APARATURY DO OKREŚLANIA CHARAKTERYSTYKI I PRZETWÓRSTWA POLIMERÓW**

będącej w posiadaniu uczelni, instytutów PAN i instytutów badawczych.

Baza jest wyposażona w funkcje umożliwiające wyszukiwanie wg zadanych parametrów: nazwy, typu lub modelu aparatu, roku produkcji, producenta, charakterystyki parametrów technicznych, zastosowania do badań, lokalizacji, słów kluczowych, sposobu wykonywania badań, numerów norm, wg których prowadzi się badania, oraz adresu i kontaktu z osobą odpowiedzialną za dany aparat. Baza jest ciągle uaktualniana.

Dostęp do danych i wyszukiwanie informacji w bazie jest bezpłatne.

Instytucje i firmy zainteresowane zamieszczeniem w bazie informacji o posiadanej aparaturze prosimy o przesłanie danych na adres [polimery@ichp.pl](mailto:polimery@ichp.pl)

[aparaturapolimery.ichp.pl](http://aparaturapolimery.ichp.pl)