Hyperbranched polyamides of 3,5-diaminobenzoic acid (*Rapid Communication*)

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Abstract: Low-temperature polycondensation of 3,5-diaminobenzoic acid (DABA) was carried out with the aid of *N*,*N*-diisopropylcarbodiimide (DIC) as carboxyl group activators. Reaction conditions were selected to obtain oligomeric hyperbranched polyamides. The polycondensation was found to proceed according to the simple model of hyperbranched polymerization with the apparent rate constant of reaction between carboxyl and amino groups equal to $8.58 \cdot 10^{-3}$ min^{-1}.

Keywords: low-temperature polycondensation, non-linear polyamides, hyperbranched oligomers.

Hiperrozgałęzione poliamidy kwasu 3,5-diaminobenzoesowego

Streszczenie: Przeprowadzono niskotemperaturową polikondensację kwasu 3,5-diaminobenzoesowego (DABA) z wykorzystaniem *N*,*N*-diizopropylokarbodiimidu (DIC) jako aktywatora grup karboksylowych. Dobrano warunki reakcji pozwalające na otrzymanie oligomerycznych hiperrozgałęzionych poliamidów. Stwierdzono, że polikondensacja przebiega zgodnie z prostym modelem polimeryzacji hiperrozgałęzionej z pozorną stałą szybkości reakcji grupy karboksylowej z grupą aminową równą $8{,}58 \cdot 10^{-3}$ min^{-1}.

Słowa kluczowe: niskotemperaturowa polikondensacja, poliamidy rozgałęzione, oligomery hiperrozgałęzione.

In recent years, hyperbranched polymers brought attention of a number of researchers because of their unique properties related to the specific molecular architecture. Among them are hyperbranched polyamides [1—3]. This group of polymers has excellent thermal and mechanical properties. Unlike their linear counterparts they are well soluble in aprotic organic solvents, such as dimethylformamide, dimethylacetamide, or *N*-methylpyrrolidone yielding solutions of relatively low viscosity [4—6]. On the other hand, the presence of rigid amide group and hydrogen bonding result in their high glass transition and melting temperature [5]. An important advantage of the hyperbranched polymers is the presence of a large number of reactive groups, both inside and at the peripheries of each molecule. The one-step method of synthesis makes the hyperbranched polymers much easier to synthesize as compared to dendrimers [2, 7].

Hyperbranched polymers have potentially many practical applications as precursors of magnetic nanocomposites [8], crosslinking agents, sensor elements, rheology modifiers [3], drug and gene carrying biodegradable materials [7, 9] and materials used in dentistry [1].

Hyperbranched polyamides can be prepared by polycondensation involving various monomers. One of them is 3,5-diaminobenzoic acid (DABA), an AB_2 monomer (A and B standing for functional groups capable of reacting with each other). As early as in 1991 this monomer was used by Fréchet in his famous synthesis of dendrimers [10]. By using the so called orthogonal linking, Ishida et al. and other researchers [4, 11, 12] prepared polyamide dendrimers in the reaction of DABA and 3,5-diaminobromobenzene catalyzed with palladium compounds. Some authors [11, 13, 14] polymerized DABA in 1-methyl-2-pyrrolidone with pyridine as the condensation agent facilitating formation of amide links. The same researchers carried out copolycondensation of DABA with monomers of AB type in the presence of pyridine and triphenoxyphosphine [15—17].

In this paper we present preliminary results on a low-temperature carbodiimide-aided method of preparing hyperbranched polymers from DABA. We have not found any literature data on this kind of hyperbranched polyamide synthesis.

EXPERIMENTAL PART

Materials

3,5-diaminobenzoic acid (DABA, 98 %, Aldrich), *N*,*N*-diisopropylcarbodiimide (DIC, >99 %, Merck),

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N,N-dicyclohexylcarbodiimide (DCC, >99 %, Fluka), *N,N*-dimethylformamide (DMF, p.a., Chempur), *N,N*-dimethylacetamide (DMA, p.a., Acros Organics), *N*-methylpyrrolidone (NMP, p.a., Sigma-Aldrich) and methanol (p.a., Chempur) were used as supplied without further purification. 4-(*N,N*-dimethylamino)pyridine-4-toluenesulphonate (DPTS) was prepared as described in [18].

Low-temperature polycondensation of DABA

To a 100 cm^3 three-necked flask equipped with magnetic stirrer, DABA monomer, a solvent (DMF, DMA, or NMP), and DPTS catalyst were introduced. The syntheses were carried out in argon atmosphere. After dissolution of crystalline components, one of carbodiimides: DIC or DCC was introduced. The reaction was carried out at the room temperature for 24 h with continuous stirring. The by-product: *N,N'*-diisopropylurea (DPU) or *N,N'*-dicyclohexylurea (DCU), depending on the carbodiimide used, precipitated in crystalline form. After a predetermined time, a sample of reaction mixture was dissolved in DMF and the amount of unreacted carboxyl groups was determined by titration with NaOH solution in order to determine conversion value. DPU or DCU was filtered out from the remaining portion of reaction mixture through a chromatographic filter with 0.45 μm mesh size. Then, the filtered solution was slowly poured into cooled down precipitating solvent while vigorously stirring. The resulting mixture was left for 24 h in a refrigerator at 0—5 °C. The polymer precipitate was then filtered out on Büchner funnel, washed with cold precipitating solvent and dried at 40 °C to constant weight.

Table 1. Reaction conditions and the amounts of reagents in low-temperature polycondensation of DABA

Amount, mol/mol AB$_2$			Yield, %	Conversion, %
DPTS catalyst	DIC	DMF		
0.1	1.5	10	89.6	97.0[a]
0.1	1.5	10	88.7	97.7
0.1	1.5	10	88.1	94.4[b]
0.1	—	10	90.3	88.2[c]
0.1	1.2	10	90.2	91.7
0.1	1.3	10	90.1	91.2
0.1	1.4	10	90.6	94.2
0.1	1.5	—	91.1	89.3[d]
0.1	1.5	—	91.1	78.8[e]
0.1	1.5	7	90.9	84.9
0.1	1.5	8	90.7	83.3
0.1	1.5	9	91.2	83.3
0.1	1.5	11	90.1	83.3
—	1.5	10	99.6	—[f]
0.15	1.5	10	86.8	75.9
0.08	1.5	10	91.6	77.1
0.06	1.5	10	93.8	79.2
0.04	1.5	10	95.8	80.4
0.02	1.5	10	97.6	51.6
0.01	1.5	10	98.8	24.2
—	1.5	10	99.6	—[g]

[a] Reaction time: 72 h, [b] reaction temperature: 0 °C, [c] 1.5 mole of DCC per mole AB$_2$ was used as carboxyl groups activator, [d] DMA solvent was used (10 cm^3/g AB$_2$), [e] NMP solvent was used (10 cm^3/g AB$_2$), [f] only 4-(*N,N*-dimethylamino)pyridine was used as catalyst, [g] no catalyst used.

A series of reactions was carried out changing reaction conditions to find out optimal ones. The reagent ratios and other parameters applied in the series of experiments are listed in Table 1. The yield is the amount of product isolated after the reaction.

Kinetics of 3,5-diaminobenzoic acid low-temperature polymerization

The reaction rate was determined by following the polycondensation reaction in NMR spectrometer. The reagents, i.e. DABA (47.4 mg) and DPTS (7.4 mg, 0.08 mole/mole DABA) were dissolved in 1 cm^3 of d$_6$-dimethylsulphoxide and placed in an NMR tube. After recording the first spectrum, DIC (55.1 mg, 1.4 mole/mole DABA) was added to the tube and spectra were recorded every 5 min for the first hour, every 10 min for next two hours and every 15 min up to the total time of 6 h.

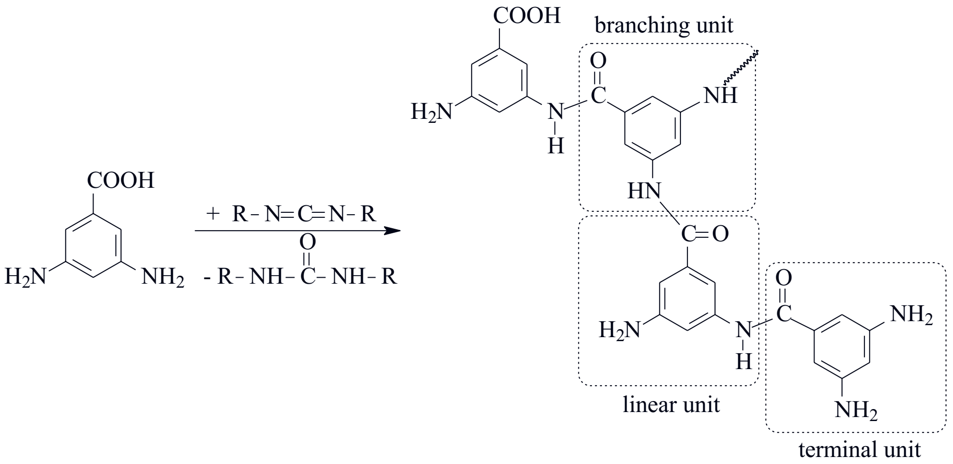
Methods of testing

The ^{1}H NMR spectra were recorded on an FT-NMR Bruker Avance 500 MHz machine at 25 °C using tetramethylsilane as internal standard. In the analysis a reference spectra of poly(3,5-diaminobenzoic acid) were used: (DMSO-d$_6$): δ = 10.37, 10.24, 10.15, 10.01, 9.92, 9.79 ppm (m, CON$\underline{\text{H}}$); δ = 8.40, 7.96 (dendritic units), 7.35, 7.27, 6.89, 6.80 (linear units), 6.35, 6.31, 6.00 ppm (terminal units), (m, aromatic); δ = 5.34 ppm (br, -NH$_2$).

MALDI-ToF Mass Spectroscopy measurements were made on a Bruker Autoflex Speed Spectrometer in linear mode with registration of positive ion. Ionization was achieved by SmartBeam II laser pulses of wavelength 352 nm. The pulse energy was from 70 to 100 μJ at frequency of 1000 Hz. Ion deflection below m/z = 450 was applied. The spectra were recorded for a total of 10 000 laser pulses with the random walk type of the plate movement. The data were processed using FlexAnalysis 3.3 software.

RESULTS AND DISCUSSION

In the preliminary experiments a series of syntheses was carried out aiming at selecting the most convenient reagent ratio and reaction parameters leading to hyperbranched polymers of possibly the highest molecular weight. The effect of reaction time and temperature as well as that of the type of precipitating solvent on the amount and quality of polymer was established. The type and amount of the carboxyl groups activator, namely DIC and DCC were also tested. Similarly, the role and amount of catalyst DPTS was verified. Three aprotic solvents: DMF, DMA and NMP were tested as the reaction environments. The reaction product was a light powder of pale-gray color.



Scheme A

The equation of carbodiimide enhanced polycondensation of DABA is presented on Scheme A.

The structure of hyperbranched polymers of DABA was confirmed by ^{1}H NMR. The following signals can be seen on spectra of the polymer: at 5.0—5.5 ppm from unreacted amino groups, broad triplets from aromatic protons coupled with amide ones at 6.0—8.5 ppm. The wealth of signals in this range confirms varying neighborhood of the protons. At 9.5—10.5 ppm there are signals from amide protons, slightly diffused due to varying surroundings. Weak signals can be seen in the spectra at 6.0 and 6.5 ppm confirming the presence of unreacted monomer.

The data presented in Table 1 suggest that from the point of view of monomer conversion, the time and temperature seem not to have any significant effect on the reaction course. In ^{1}H NMR and mass spectra of polymers obtained at different conditions no significant differences were found. Hence, the suitable reaction conditions for sample preparation were the following: room temperature, DIC as the activator and DMF as the solvent. The time of reaction was found no longer than 12 h. An important matter was the proper choice of precipitating solvent. Water, acetone, methylene chloride, tetrahydrofuran, and methanol were tested. Acetone was eliminated right at the start as it partially dissolved the polymer. The samples precipitated with the remaining solvents were, after drying out, dissolved in d_6-DMSO and their ^{1}H NMR spectra were recorded. Basing on the spectra, tetrahydrofuran and methylene chloride were rejected as the polymer samples precipitated with these solvents contained, beside polymer and unreacted monomer, also other components of the reaction mixtures. Only the samples precipitated with water or methanol provided consistent spectra. Methanol was the final choice because of its volatility.

The solvents used in the synthesis step (DMF, DMA, NMP) were found to have practically no effect on the final monomer conversion. The dilution of the monomer-carbodiimide system had no significant effect, either. Hence, DMF was selected as the reaction medium and it was used in the amount of 9 cm^3 per 1 g of monomeric DABA.

While testing the two most popular carbodiimides, the use of DCC was found to provide slightly higher monomer conversion. Nevertheless, we have chosen liquid DIC, rather than solid DCC, as the one easier for handling. The amount used was 1.4 mole of DIC per mole of DABA.

The catalyst plays an important role in the low-temperature polycondensation of DABA. In previous experiments [19] we have found a complex of 4-(*N*,*N*-dimethyl)pyridine and 4-toluenesulphonic acid (DPTS) to be an effective catalyst for low-temperature polycondensation. In this work we also run the reaction without any catalyst or with 4-(*N*,*N*-dimethyl)pyridine alone. In all cases the conversion of carboxyl groups was high, but in the absence of DPTS the product could not be precipitated. It formed, after solvent evaporation, a resinous mass soluble in methanol. As regards to the amount of DPTS catalyst used, too small amount of catalyst led to side reactions in which carboxyl groups did react (high conversion), but a product of low molecular weight was predominantly formed. The conclusion was to use 0.08 mole of DPTS/mole DABA.

A sample MALDI-ToF spectrum of the product of low-temperature polycondensation of DABA is presented in Fig. 1. In the spectrum recorded in the range from 400 to 5000 *m*/*z*, one can see the presence of signals from homologous molecules built of five, six, etc., up to seventeen and more monomeric units. The molecular weights of species corresponding to the signals are multi-

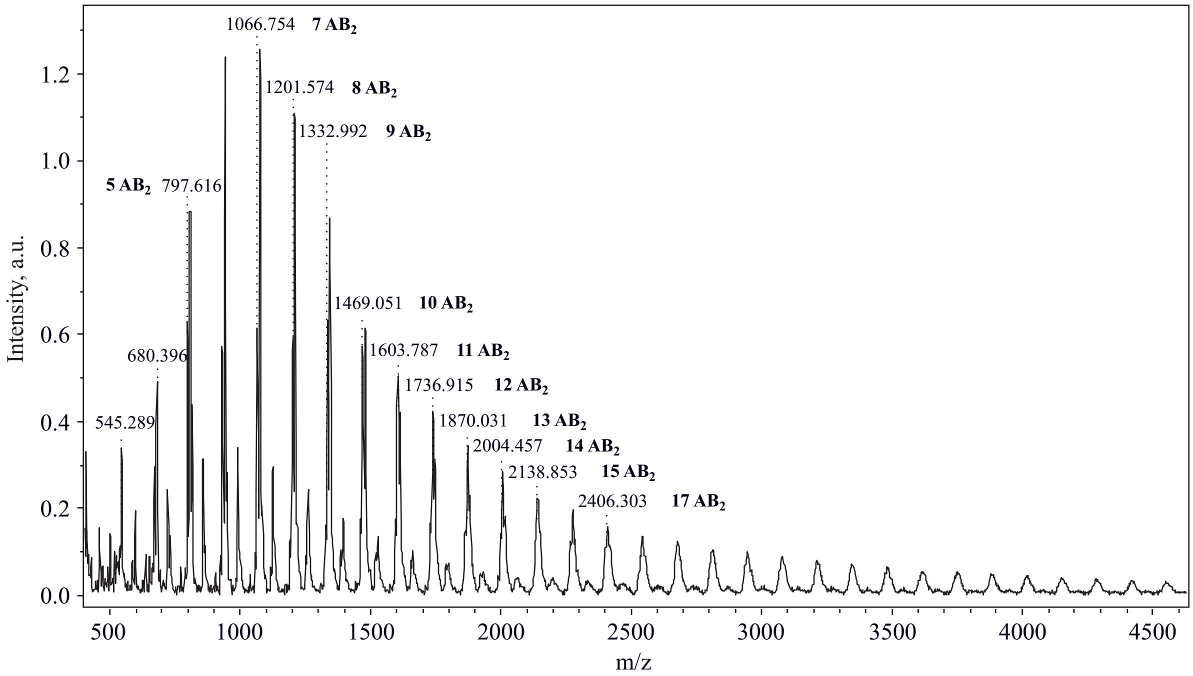


Fig. 1. MALDI-ToF spectrum of hyperbranched polyamide prepared from DABA

plicities of that of the monomeric units enlarged by the molecular weight of silver. Hence, the MALDI-ToF analysis confirms the oligomeric character of the resulting polyamides.

The time dependence of conversion was measured using ^{1}H NMR spectroscopy. The fragments of spectra at different time of polycondensation that illustrate the change in the neighborhood of aromatic protons in positions 2,6 and 4 are presented in Fig. 2. The conversion was determined by measuring the area under the doublet at 6.42—6.46 ppm from protons 2 and 6 and that of the triplet from proton 4 at 6.01—6.04 ppm in the aromatic ring of DABA moiety. The respective signals in the spectra of polymers were broadened as compared to that of starting monomer. By numerical deconvolution one could distinguish the monomer doublet or triplet, respectively, from that in polymer. The calculations were made using the NMR machine software.

The results of kinetic measurements are presented in Fig. 3. As one can see, the accuracy of deconvolution of signals from proton at position 4 seems worse than that of 2 and 6 protons. Hence, the kinetic analysis was made using the area under the doublet from protons 2 and 6 in aromatic rings built into the polymer structure.

A simple model of homopolymerization of an AB$_2$ monomer predicts the relationship between conversion of minority groups A and reaction time in the form [20]:

$$p = \frac{2e^{kt} - 2}{2e^{kt} - 1} \qquad (1)$$

where: k — the apparent rate constant of the reaction between functional groups.

The value of $k = 8.58 \cdot 10^{-3}$ min^{-1} was evaluated by applying regression analysis to points in Fig. 3, correspond-

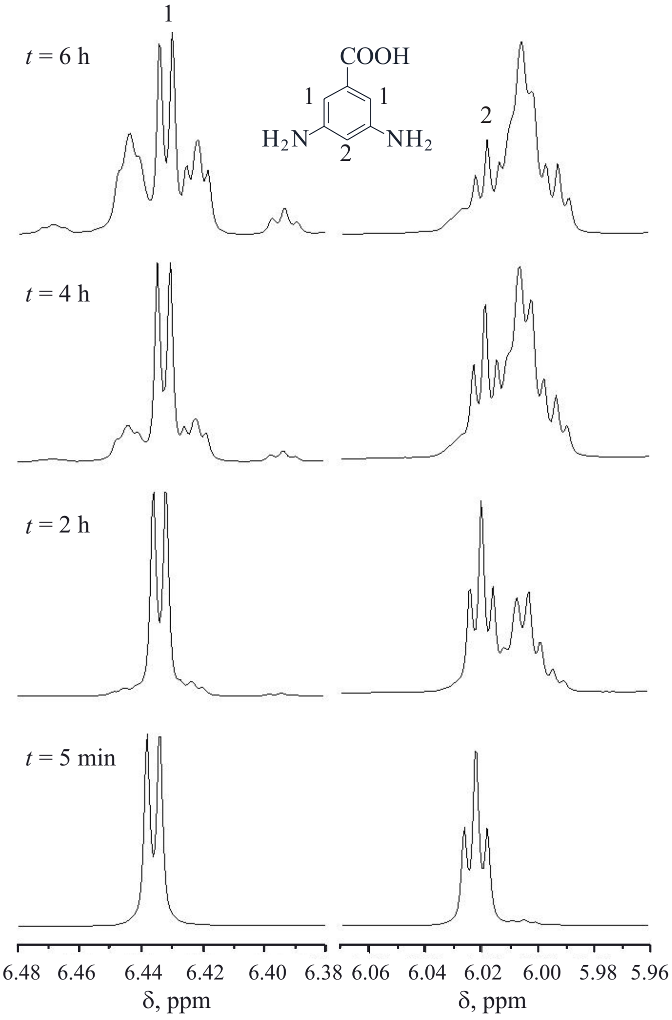


Fig. 2. The changes in fragments of ^{1}H NMR spectrum during conversion of DABA (the signals from the aromatic protons are shown)

ing to the change of the area under the signals from protons at position 2 and 6 in the constitutional units of the hyperbranched polymer. The model [20] uses concentrations of reacting groups in the form of weight-molar fractions, i.e., as the numbers of moles of a functional group divided by the total number of moles of the monomer.

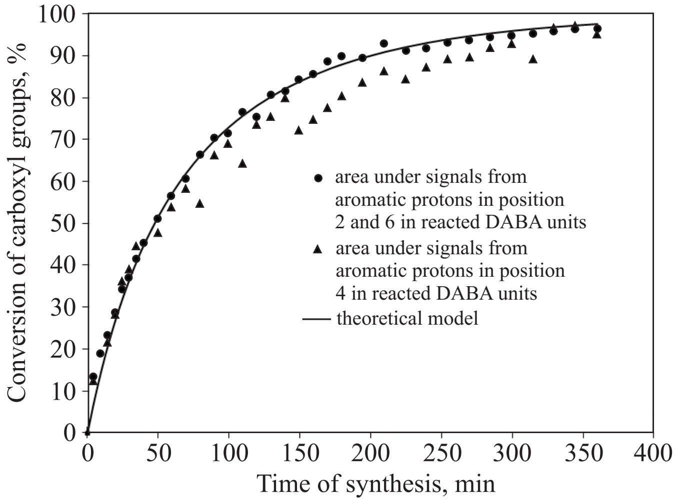


Fig. 3. Time dependence of carboxyl group conversion in DABA during low-temperature polycondensation

One should bear in mind that the low-temperature polycondensation with the aid of carbodiimides proceeds according to a more complex mechanism than just by reaction of carboxyl and amino groups. Nevertheless, when no substitution effect influences the reactivity of amino and/or carboxyl groups, formation of individual links follows the statistics common to all kinds of the step polymerization processes.

CONCLUSIONS

In a low-temperature polycondensation carried out in the presence of carbodiimides one can prepare oligomeric hyperbranched polymers of DABA. Convenient conditions at which the polycondensation takes place are: room temperature, 1.4-fold molar excess of DIC, 0.08 mole of DPTS per mole of monomer, DMF as the solvent, methanol as precipitant, and the time not exceeding 12 h. MALDI-ToF spectra confirm formation of polymeric structures. According to the simple kinetic model of AB_2 hyperbranched polymerization, the apparent rate constant of reaction between carboxyl and amino groups is $8.58 \cdot 10^{-3}$ min^{-1}.

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