# New polynitrogen hyperbranched polymers

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A method for the preparation of new representatives of polynitrogen hyperbranched polymers of heterocyclic series was developed involving polymerization of monomeric 2,4-diazido-6-propynyloxy-1,3,5-triazine by 1,3-dipolar cycloaddition. Kinetics of polymerization of diazidoacetylene monomer was compared with the kinetic data of polymerization of its closest analog, 2-azido-4,6-bis(propynyloxy)-1,3,5-triazine monomer. Properties of hyperbranched poly(1,2,3-triazole-1,3,5-triazine)s with terminal azide groups and terminal triple bonds were compared, as well.

**Key words:** hyperbranched polymers, 1,3-dipolar cycloaddition, azides, alkynes, 1,2,3-triazoles, 1,3,5-triazines, kinetics, size exclusion chromatography, light scattering detector (SEC-MALLS).

Dendritic polymers (regular (dendrimers) and irregular (high- and hyperbranched polymers (HBP))) attract attention of researches due to the unique combination of physical and chemical properties, providing a wide field of their possible application in science, technique, and medicine, in developing new materials, nano- and supramolecular appliances.[1—5]

It is obvious that the choice of both the synthetic strategy and the starting reactants from enormous number of possible variations determines structural and physicochemical characteristics of three-dimensional polymers obtained. In this connection, researches actively develop new approaches to the synthesis and modification of such polymers, study their properties, and quest new directions of their efficient application.[6—8] One of the promising methods for the synthesis of dendritic polymers consists in the use of 1,3-dipolar cycloaddition reaction (1,3-DCA) of azides to alkynes, which belong to the "click chemistry" reactions. However, despite such advantages of this method as a possibility of regioselective catalysis, high yields and the reaction rate, it is relatively seldom used as a preparative method at the present time, rather for modification of branched polymers.[9—11] At the same time, HBP obtained by this reaction are of interest as objects for the studies due to the specificities of their composition and structure, in particular, the high content of 1,2,3-triazole rings.

Earlier, we have developed a method for the synthesis of crystalline azido-acetylene monomer of the type $AB_2$ stable at room temperature, *viz.*, 2-azido-4,6-bis(prop-2-yn-1-yloxy)-1,3,5-triazine (**1**). Hyperbranched poly(1,2,3-triazole-1,3,5-triazine)s with the terminal triple bonds (HBP-T) were obtained on their basis.[12,13]

The present work is devoted to the synthesis of new hyperbranched poly(1,2,3-triazole-1,3,5-triazine)s with the terminal azide groups (HBP-A) based on a crystalline azido-acetylene monomer of the type $A_2B$ of the triazine series, *i.e.*, 2,4-diazido-6-(prop-2-yn-1-yloxy)-1,3,5-triazine (**2**), as well as to the studies and comparison of properties of HBP-A and HBP-T.

Polymerization of monomer **2** was carried out in bulk (Scheme 1), since its polymerization in solutions of polar solvents, alike for monomer **1**, is accompanied by a number of side reactions (presumably, isomerization of the triazine ring to triazinone one, destruction, *etc.*[13]), which significantly affect properties and topology of macromolecules.

Method of isothermal microcalorimetry showed that kinetic parameters of the reaction used for the synthesis of HBP-A based on the monomer **2** and HBP-T based on the monomer **1** (see Ref. 14) are virtually the same, which can be judged from the values of efficient rate constants of the reaction ($k_{\text{eff}} \cdot 10^5$/L g-equiv.$^{-1}$ s$^{-1}$) calculated based on the linear sections of anamorphosis of polymerization kinetic curves in the second order coordinates with allowance for the nonequivalence of the concentrations of reacting groups and shown below.

| Monomer | 80 °C | 100 °C |
|---|---|---|
| **1** | 3.2 | 12.0 (see Ref. 14) |
| **2** | 4.0 | 11.0 |

In addition, in both cases polymerization carried out in the isothermal regime virtually stops at a certain conversion and the limited conversion, determined from the $^1$H NMR data, depends on the reaction temperature

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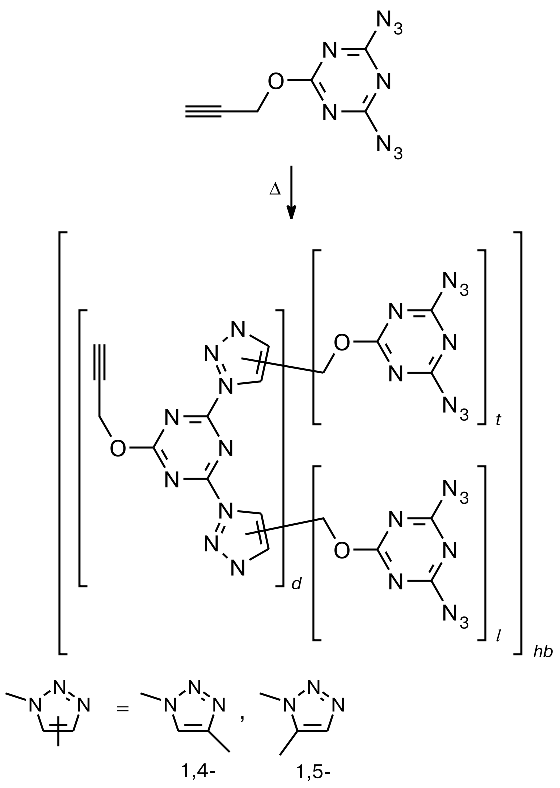
**Scheme 1**



(Table 1). Apparently, this is attributed to the diffusion hindrance emerged on the increase in viscosity of the system in the process of polymerization. A practically important conclusion followes from this: a change in the temperature regime of the bulk polymerization is an instrument for the preparation of polymers of a given degree of transformation and, consequently, with a given molecular weight (MW). A lower limited conversion for polymerization of compound **2** as compared to **1** at the same temperature can be explained by a greater conformational hindrance in HBP-A (higher density of the macromolecules formed), which decreases availability of reacting groups to each other.

The conclusion that the change in the temperature regime of the bulk polymerization is one of the most simple approaches to the synthesis of HBP with required MW was confirmed by the data of the size exclusion liquid chromatography in NMP (see Table 1).

As it was expected, the MW of polymerization products increases for both monomers on elevation of the reaction temperature, whereas an increase in the reaction time has little effect on the MW. It should be noted that a inverse dependence is observed for the polydispersity index (*D*) from the temperature of the synthesis (LS, an eluent LiCl/NMP), which can be explained by the decrease of the reactivity of the "focal" groups because of their shielding by the branched chains of the macromolecules. This leads to the fact that the terminal functional groups of relatively large macromolecules and the "focal" groups of relatively small macromolecules or molecules of monomer are involved into the 1,3-DCA reaction in the final steps of polymerization. The "focal" groups are the functional groups A for the monomer $AB_2$ (B for the monomer $A_2B$), which belong to the central/initial unit of the HBP chain, from which the growth of the HBP molecule starts, namely the azide groups for HBP-T and alkyne groups for HBP-A.

The high branching of the polymers obtained is confirmed by the fact that parameters of molecular-mass distribution (MMD) calculated using the polystyrene calibration is considerably lower than the "absolute" values of MW calculated from the data of the light scattering detector.

**Table 1.** Effects of polymerization conditions on the molecular-mass characteristics of HBP-T and HBP-A[a]

| HBP | Reaction conditions | | α (%) ($^1$H NMR) | Eluent NMP[b] | | Eluent LiCl/NMP | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $T$/°C | τ | | $M_w^{LS} \cdot 10^6$ | $D^{LS}$ | $M_w^{LS} \cdot 10^3$ | $D^{LS}$ | $M_w^{RI} \cdot 10^3$ | $D^{RI}$ |
| HBP-T | 25 | 20 days[c] | 73 | 600 | 1.8 | 8.5 | 3.4 | 2.5 | 1.31 |
| | 40 | 3 days | 80 | 19.2 | 1.6 | 11 | 3.9 | 2.5 | 1.55 |
| | 40 | 7 days | 81 | 13.2 | 2.6 | 11.5 | 2.9 | 2.6 | 1.41 |
| | 60 | 7 days | 89 | 3.3 | 2.9 | 12.6 | 2.7 | 2.8 | 1.51 |
| | 80 | 2 days | 95 | 2.7 | 2.8 | 15.2 | 2.8 | 3.1 | 1.47 |
| | 100 | 9 h | 97 | 1.7 | 1.7 | 16.9 | 2.2 | 3.4 | 1.43 |
| HBP-A | 25 | 4 months[c] | 80 | 1 | 2.0 | 43 | 18 | 1.7 | 1.34 |
| | 80 | 20 h | 92—93 | — | — | 73 | 9.3 | 1.9 | 1.34 |
| | 80 | 2 days | 92—93 | — | — | 78 | 12.4 | 2.0 | 1.37 |
| | 100 | 18 h | 97—98 | — | — | 125 | 9.5 | 2.4 | 1.32 |

[a] *D* is the dispersity index, LS is the calculation based on the light scattering detector data, RI is the calculation based on the polystyrene calibration (refractometric detector).

[b] *N*-Methylpyrrolidone.

[c] After melting the corresponding monomer.

At the same time, the data given in Table 1 indicate a strong interaction of HBP molecules in dilute solution of NMP, with the HBP-A macromolecules being less prone to association in solutions than those of HBP-T. It should be noted that in the case of HBP-T, the sizes of the associates formed are inversely proportional to MW of the polymer, however, even for the polymer with the highest MW, formation of complexes composed on average of 100 macromolecules is possible.

Analysis of the $^1$H NMR spectra also indicates considerable intermolecular interaction in the polymerization step in the melt. It was shown that HBP-T and HBP-A contain both the 1,4- and 1,5-disubstituted 1,2,3-triazole rings in the ratios ~40 : 60 and 30 : 70, respectively. However, an inverse ratio is characteristic of the products of the 1,3-DCA reaction of azides with alkynes, since formation of 1,5-disubstituted triazoles is sterically more hindered. In this connection, it can be suggested that the molecules of the starting monomer are preliminary oriented as a result of the donor-acceptor interactions of the triazine rings.

In conclusion, the 1,3-DCA reaction of diazidoacetylene monomer was used for obtaining and characterizing new hyperbranched polymers, completely soluble in aprotic polar solvents and containing conjugated heteroaromatic triazine and triazole rings in their structure, as well as terminal azide groups. We also studied kinetics of polymerization and dependence of MW of the polymers form the synthetic conditions.

## Experimental

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III Biospin spectrometer (500.13 and 125.76 MHz, respectively) in DMSO-d$_6$ relatively to the internal standard, $Me_4Si$ ($\delta$ 0.00). Chemical shifts were measured with the accuracy of 0.01, spin-spin coupling constant, with the accuracy of 0.1 Hz. IR spectra were obtained on a Specord M-82 and $\alpha$-Bruker spectrometers (KBr pellets).

To determine the actual MW of HBP, we used size exclusion chromatography (SEC-MALLS) on an Waters GPCV 2000 chromatograph (a PLgel MixedC column, 7.6×300 mm) equipped with a Dawn Heleos II multi angle light scattering detector (658 nm) and refractometric detector. Buffer solutions were used as eluents (in particular, 1% solution of LiCl in NMP). The elution temperature was 70 °C. The presence of LiCl in the eluent was necessary to prevent reaction of macromolecules with the sorbent and to destroy emerging intermolecular associates upon the action of electrostatic repulsion forces appearing on the formation of complexes $[\text{HBP-T}\cdot\text{Li}_n(\text{NMP})_m]^{n+}\text{Cl}_n^-$, in contrast to the case of pure NMP as an eluent. The absolute parameters of MMD were calculated based on the data from the light scattering detector, for comparison, the MMD were evaluated using calibration on the polystyrene standards. Applicability of the method was confirmed by comparison of experimental molecular-mass characteristics of the HBP obtained under different conditions of their synthesis and chromatography (see Table 1).

Elemental analysis was performed in the Laboratory of Physicsochemical Studies in the Community Analytical Center of the Institute of Problems of Chemical Physics RAS.

Kinetics of the 1,3-DCA reaction in the bulk was studied in a MK 17-27 isothermic microcalorimeter of the Tian—Calvet type equipped with the system of automatic recording thermal flow.

**2-Azido-4,6-bis(prop-2-yn-1-yloxy)-1,3,5-triazine (1)** was synthesized by the procedure given in the literature.[13] $^1$H NMR, $\delta$: 3.66 (d, 2 H, CH, $J$ = 2.4 Hz); 5.07 (d, 4 H, $CH_2O$, $J$ = 2.6 Hz). $^{13}$C NMR, $\delta$: 55.97 ($OCH_2$); 77.67 ($CH_2\underline{C}CH$); 78.72 ($C\underline{C}H$); 171.59 (N(N)CO); 171.84 ($N_3C$). IR, $\nu$/cm$^{-1}$: 3296 (≡CH); 2143, 1199 ($N_3$); 1555 (triazine); 1327, 1125 ($COCH_2$). Found (%): C, 47.3; H, 3.1; N, 36.2. $C_9H_6N_6O_2$. Calculated (%): C, 47.0; H, 2.6; N, 36.5.

**2,4-Diazido-6-(prop-2-yn-1-yloxy)-1,3,5-triazine (2).** In the first step, 2,4-dichloro-6-(prop-2-yn-1-yloxy)-1,3,5-triazine was synthesized by the known procedure.[15] In the second step, $NaN_3$ (2 g, 30.7 mmol) and water (5 mL) were added to a solution of 2,4-dichloro-6-(prop-2-yn-1-yloxy)-1,3,5-triazine (1.84 g, 9 mmol) in acetone (5 mL) with stirring and cooling, followed by the self-heating of the reaction mixture. After cooling, the mixture was stirred at ~20 °C for 14 h. After the reaction reached completion (TLC data), toluene (10 mL) was added to the reaction mixture, which was twice washed with water, concentrated *in vacuo* at the temperature ≤50 °C to obtain crude compound **2** (1.9 g, 97%) as a dense yellow oil. The product was subjected to chromatography on a column with $SiO_2$ eluting with dichloromethane and recrystallized from isopropanol; white crystalline powder, m.p. 57—58 °C (*cf.* Ref. 16: an oil). The yield was 1.45 g (74%). $^1$H NMR, $\delta$: 3.69 (d, H, CH, $J$ = 2.0 Hz); 5.08 (d, 2 H, $CH_2O$, $J$ = 2.1 Hz). $^{13}$C NMR, $\delta$: 56.11 ($OCH_2$); 77.49 ($CH_2\underline{C}CH$); 78.86 ($C\underline{C}H$); 171.08 (N(N)CO); 171.49 ($N_3C$). IR, $\nu$/cm$^{-1}$: 3298 (≡CH); 2140, 1205 ($N_3$); 1580, 1550 (triazine); 1352, 1177 ($COCH_2$). Found (%): C, 33.4; H, 1.9; N, 57.2. $C_6H_3N_9O$. Calculated (%): C, 33.1; H, 1.4; N, 57.9.

**Synthesis of HBP-T and HBP-A.** Polymerization was carried out in a thin film at the temperatures above the melting points of monomers (monomer **1**, at 40—100 °C, monomer **2**, at 80—100 °C) or at temperature below the melting points, preliminary melting the monomer. Solid glassy polymers HBP-T and HBP-A of light yellow color were thus obtained, whose yields without additional purification were close to the theoretical. HBP-T is completely soluble only in strongly polar aprotic solvents such as DMF, DMAA, and DMSO, HBP-A is soluble in these solvents on heating. The yields were quantitative.

Sample of HBP-T. $^1$H NMR, $\delta$: 3.52—3.78 (m, 1 H, CH at the triple bond); 5.03—5.32 (m, 2 H, $CH_2$ at the triple bond); 5.58—5.80 (m, 0.9 H, $CH_2$ at 1,4-triazole); 5.98—6.23 (m, 1.1 H, $CH_2$ at 1,5-triazole); 7.93—8.18 (m, 0.55 H, CH at 1,5-triazole); 9.00—9.27 (m, 0.45 H, CH at 1,4-triazole). $^{13}$C NMR, $\delta$: 56.64 ($OCH_2$ at the triple bond); 61.28 ($OCH_2$ at triazole); 77.31 ($CH_2\underline{C}CH$); 78.99 ($C\underline{C}H$); 125.00 ($CH_2\underline{C}$ in 1,4-triazole); 134.71 ($CH_2C\underline{C}$ in 1,5-triazole); 135.20 ($CH_2\underline{C}$ in 1,5-triazole); 142.09 ($CH_2C\underline{C}$ in 1,4-triazole); 162.47 (NCN(N) at 1,4-triazole); 163.28 (NCN(N) at 1,5-triazole); 171.72—172.25 (OCN(N)). IR, $\nu$/cm$^{-1}$: 3296 (≡CH); 3150 (C—H, of triazole); 1600, 1510 (triazole); 1555 (triazine); 1327, 1125 ($COCH_2$). Found (%): C, 47.3; H, 3.1; N 36.2. $C_9H_6N_6O_2$. Calculated (%): C, 47.0; H, 2.6; N, 36.5.

Sample of HBP-A. $^1$H NMR, $\delta$: 5.58—5.80 (m, 0.6 H, $CH_2$ at 1,4-triazole); 5.98—6.23 (m, 1.4 H, $CH_2$ at 1,5-triazole);

7.93—8.18 (m, 0.7 H, CH at 1,5-triazole); 9.00—9.27 (m, 0.3 H, CH at 1,4-triazole). IR, ν/cm$^{-1}$: 3150 (C—H, of triazole); 2140, 1205 ($N_3$); 1600, 1555, 1510 (triazole, triazine); 1350, 1180 ($COCH_2$). Found (%): C, 33.4; H, 1.9; N, 57.2. $C_6H_3N_9O$. Calculated (%): C, 33.3; H, 1.4; N, 57.9.

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