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GUANAMINE DENDRIMERIZATION

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ABSTRACT

A synthesis of dendrimers and hyperbranched polymers by using cycloaddition of cyanoguanidine to nitriles and cyanoethylation reaction is reported. Both reactions proceeded in the presence of a basic catalyst (alkaline hydroxides and Triton B, respectively).

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The guanamine dendrimerization process has been carried out up to 4th generations ended with cyano or amine groups. Intermediates and product substances, as well as by-products were identified by FT-IR, ^{1}H and ^{13}C NMR, MS, FIB-MS, and elemental analysis. Hyperbranched polymers were characterized by gel permeation choursomatography (GPC). Polyguanamine dendrimer (PGD) molecules exhibited expanded form in dimethylacetamide solution and low polydispersity (1.12-1.26). Observed contraction of the macromolecules was growing towards higher generations reaching an extreme at generation 4. The degree of branching of the products were within the range of 0.81-0.87 on the 0-1 scale.

Decyanoethylation, hydrolysis, and intramolecular cyclization, as side reactions, were observed on the cycloaddition steps of dendrimerization. Some main stream dendrimerization products, i.e., tetrakis [2-(2,4-diamino-1,3,5-triazin-4-yl)ethyl]2,4-diamino-6-phenyl-1,3,5-triazine and 2,2,6,6-tetrakis[2-(2,4-diamino-1,3,5-triazin-6-yl)ethyl]cyclohexanone as well as by-products, i.e., 2,6,6-tris[2-(2,4-diamino-1,3,5-triazin-6-yl)ethyl] cyclohexanone, 2,6,6-tris(2-cyanoethyl)cyclohexanone and a dilactam have been isolated as new compounds. Spectral data for $N^2N^2N^4N^4$-tetrakis(2-cyanoethyl)-6-phenyl-1,3,5-triazine, 2,2,-6,6-tetrakis(2-cyanoethyl)cyclohexanone, 1,1,1-tris(2-cyanoethyl)propanone-2 and 1,1,1-tris[2-(2,4-diamino-1,3,5-triazin-6-yl)ethyl]propanone-2 have been complemented.

INTRODUCTION

Process of the Guanamine Dendrimerization

Since the first reports on polymer dendrimers as shell molecules [1, 2, 3], the earliest of which was printed in this journal, various reactions have been used to develop syntheses of dendrimer (cascade branched, hyperbranched) macromolecules. Fundamental works on dendrimers were performed by groups of Tomalia [4], Newkome [5], Fréchet [6], Miller [7], Percec [8], Meijer [9], Moore [10], Seebach [11], followed by those of Shibaev [12], Majoral [13], Diederich [14], Frey [15], Schlueter [16], Zimmerman [17], and Crooks [18]. At the same time, investigations on hyperbranched polymers were carried out by groups of Kricheldorf (pioneering work) [19], Kim [20], Lescanec and Muthukumar [21], Gauthier and Möller [22], Fréchet and Hawker [23], and Hult [24]. Hyperbranched phenolic resins have also been prepared by our group [25].

For more knowledge about the area of dendrimers, one is referred to excellent reviews [26, 27, 28, 29].

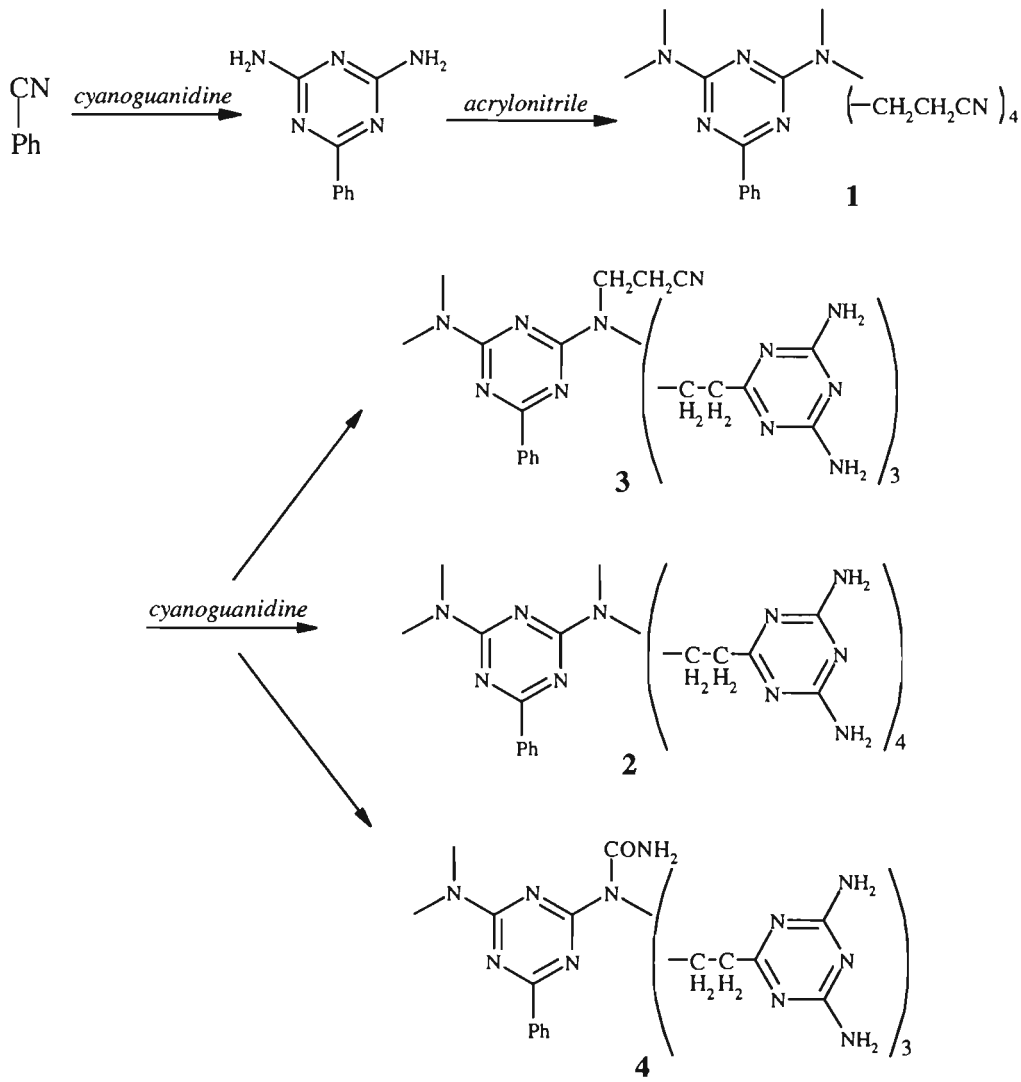
While the first works concerned so called divergent system of a growing dendrimer molecule and based on multiplying functions from one generation to next one, Fréchet [6] discovered an unusual (convergent) method of dendrimerization, in which a growing dendrimer molecule has paradoxically only one function independently on, which generation is concerned.

Both divergent and convergent methods are widely used now for synthesis of dendrimers. Many of them however, are complex systems. One of the simplest methods has been discovered by Vögtle [30] and considered theoretically as a way towards high molecular weight dendrimers [1], which was finally developed by Meijer [9]. This method is based on two reactions: cyanoethylation of amines and hydrogenation of nitriles obtained to recover amines. Using this procedure, one can obtain maximum two amine groups from one in a consecutive full generation of a growing dendrimer molecule. Such a fashion of functional groups multiplying (branch multiplicity 2) is the minimum, which allows a dendrimerization process to continue. On the other hand there is increasing interest in synthesis of dendrimers as shell molecules.

Such molecules are formed according to so called Malthusian packing paradox [1], from which it follows that the space available for a growing dendrimer molecule can not accommodate all structural units above a certain generation. In other words, a dendrimer molecule grows faster in its volume, than a volume of the space available does. This leads to crowding and can create a shell on peripheries of the molecule.

For this purpose, the higher the branch multiplicity, the greater effectiveness of completing the shell. With this in mind, we have been pursuing a set of two reactions, whose effectiveness is theoretically as high as 4 reactive sites from one. It is twice as many if compared with the system involving hydrogenation of nitriles. As early as in 1979, an attempt was made by us in consideration of cyanoethyl derivatives of cyanoguanidine as monomers to obtain polyguanamines [31]. N,N-Bis(2-cyanoethyl)-N-cyanoguanidine was thought to be a monomer of AB_2 type to produce guanamine dendrimers in one-pot procedure. However, we were not successful in that because the cyanoethyl derivatives underwent another cyclization to produce pyrimidinylidene compounds. The system currently investigated is illustrated in the Schemes 1, 2, 3, and 4.

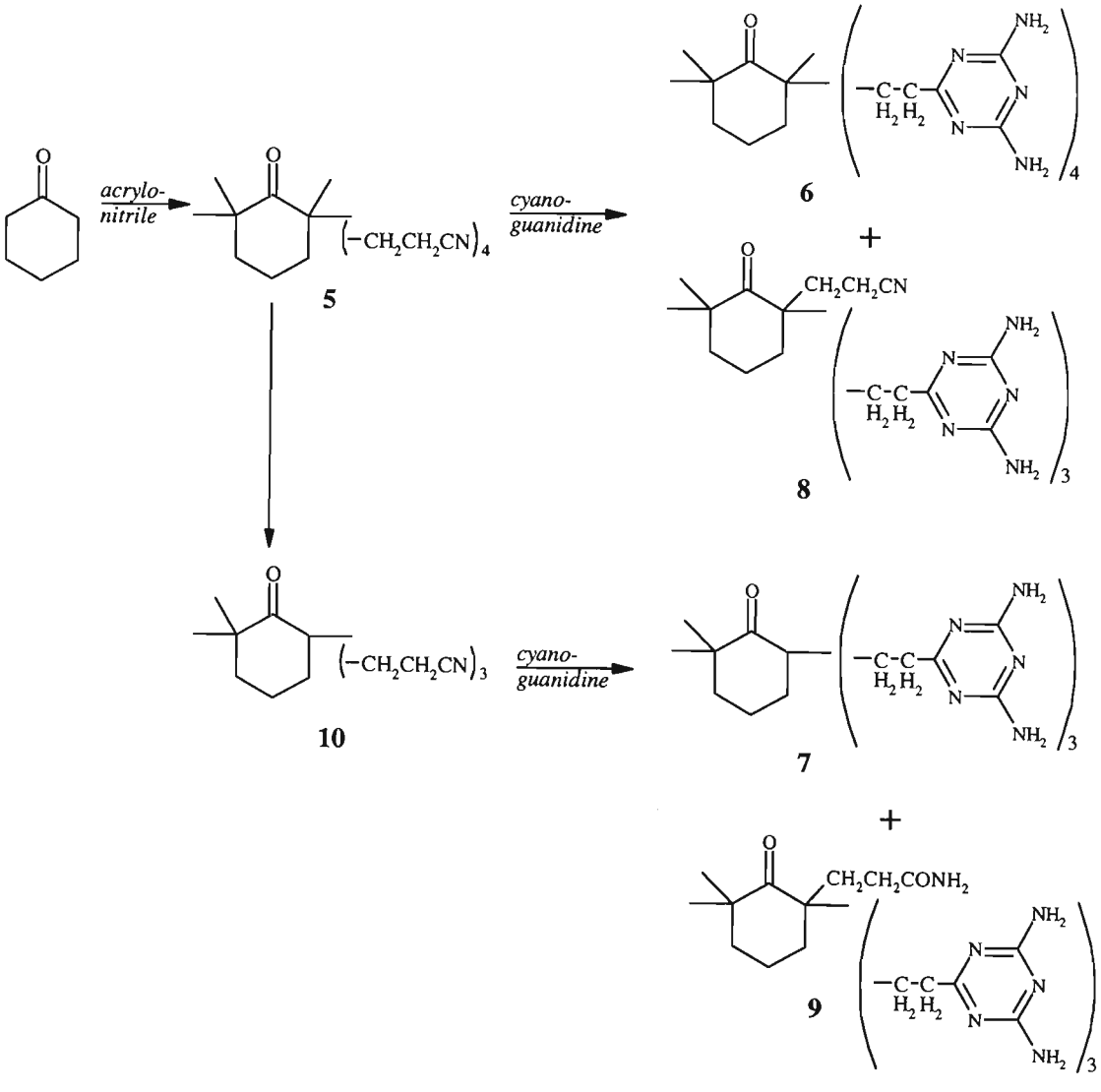
Another advantage of our route is that the cycloaddition reaction (nitriles + cyanoguanidine) contributes to an increase in mass of product substance 21 times as many as hydrogenation of nitriles does. On the contrary, hydrogenation



Scheme 1.

does not afford a significant increase in mass. The mass increase is very important from economical point of view when a dendrimer is considered the one to be applied.

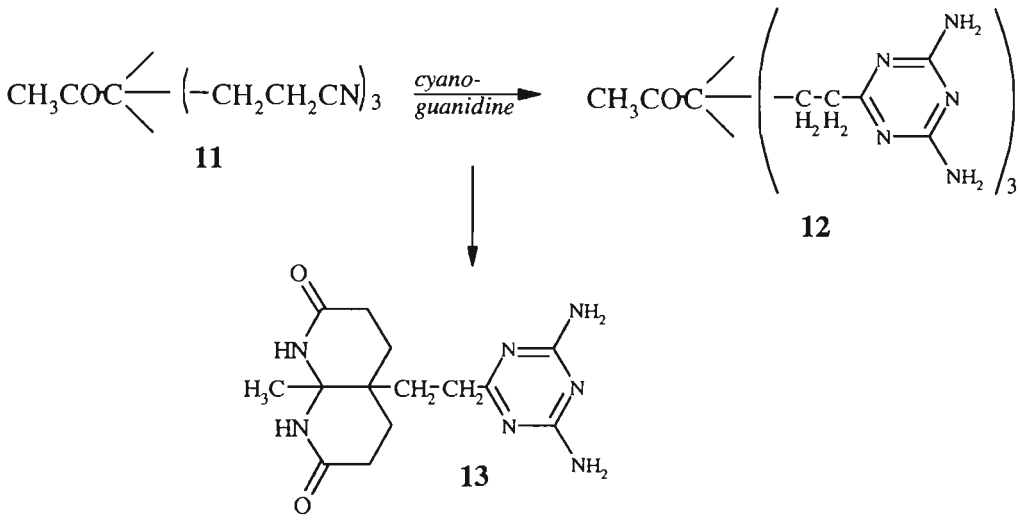
Both reactions involved in our system are well known. Cyanoethylation has already been used in the dendrimerization processes [9, 30], and cycloaddition of nitriles to cyanoguanidine is the main method to produce 2,4-diamine-1,3,5-triazines (guanamines).



Scheme 2.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded with Varian INOVA 500 NMR spectrometer (unless it is stated otherwise). Samples were dissolved in DMSO-d_6 or acetone-d_6 and TMS was used as an internal reference. Typical conditions



Scheme 3.

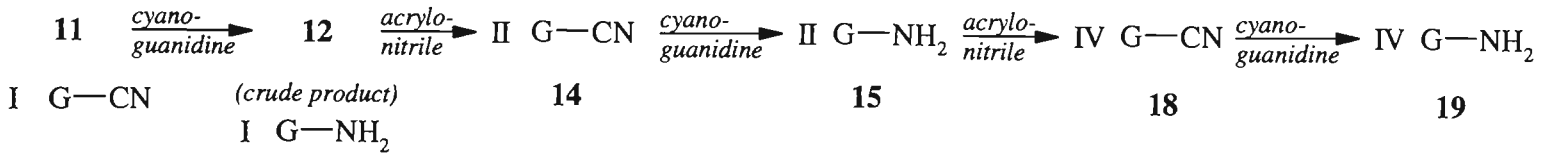
used to the ^{13}C spectra were as follows: 30° pulse, acquisition time 1.1 s, relaxation delay 2 s. For some compounds, the DEPT spectra were recorded routinely. ^{13}C NMR spectra for individual compounds are presented on Figures 1-4. All protons and carbon atoms were assigned according to Figure 5 with the exception of names. MS spectra were recorded on a Finnigan MAT-8200 mass spectrometer: high resolution, double focusing, EB apparatus equipped with direct inlet probe (DI), electron ionization (EI) and chemical ionization (CI) facilities and combined with data system INCOS 2200 d.

FIB MS spectra (corresponding fully to FAB) were measured on a Finnigan MAT 95 spectrometer with glycerine or m-nitrobenzyl alcohol as a matrice. Amine terminated substances were measured in the presence of HCl. Samples were ionized with Cs+ of 13 keV. Temperature of ion source: 40°C. At least 10 measurements were made to produce an average spectrum.

GPC system was furnished with Differtial Refractometer Detector HP1047A (Hewlett Packard). Column Set: PL gel MIXED B 10 μm, 600 mm (Polymer Laboratories Ltd.); PL Caliber GPC Software (Polymer Laboratories Ltd.);

Chomatographic parameters: dimethylacetamide/0.5% LiCl as solvent, 80°C, flow rate: 0.8 ml/min, conc.: 0.1%, injection volume: 70μ.

Commercial grade reagents and solvents were used.


11
cyano-guanidine
12
acrylo-nitrile
II G—CN
cyano-guanidine
II G—NH2
acrylo-nitrile
IV G—CN
cyano-guanidine
IV G—NH2
I G—CN
(crude product)
I G—NH2
14
15
18
19

Scheme 4.

$N^2N^2N^4N^4$-Tetrakis (2-cyanoethyl)-6-phenyl-1,3,5-triazine (1)

The tetra(cyanoethyl)benzoguanamine was obtained according to [32].

IR: 3053, 2948, 2246, 1590, 1546, 1526, 1426, 1379, 1330, 1243, 1183, 1023, 983, 943, 828, 708.

^{1}H NMR (DMSO-d_6/TMS): 8.32 (ar, 2H, m); 7.48(ar, 3H, m); 3.92 (at C_{12}, 8H, dt) ; 2.85 (at C_{13}, 8H, m).

^{1}H NMR (acetone-d_6/TMS): 8.47 (ar: o, 2H, m); 7.56 (ar: p, 1H, m); 7.50 (ar: m, 2H, m); 4.15 (at C_{12}, 8H, dt); 3.00 (at C_{13}, 8H, m).

^{13}C NMR (acetone-d_6/TMS): $C_{4'}$ = 132.64; $C_{2'}$, $C_{3'}$, $C_{5'}$, $C_{6'}$ = 129.32, 129.15; $C_{1'}$ = 137.68; C_6 = 171.35 ; C_2, C_4 = 166.16; C_{12} = 45.21, 44.99; C_{13} = 17.03, 16.95; C_{14} = 119.42, 119.30.

MS (Cl) : m/z = 399.4

$C_{21}H_{21}N_9$	Calcd.:	C 63.16	H 5.26	N 31.58
399	Found:	63.18	5.29	31.27

m.p.: 163°C.

$N^2N^2N^4N^4$–Tetrakis[2-(2,4-diamino-1,3,5-triazin-6-yl)ethyl]2,4-diamino-6-phenyl-1,3,5-triazine (2)

To a stirred mixture of **1** (1 g) with cyanoguanidine (1.2 g) in ethyl cellosolve 0.09 g of KOH in 0.22 ml of H_2O was added. The mixture was heated at 91-93°C for 3 hours. It was cooled to 60°C and filtered. A precipitate was washed with hot water and ethanol, and dried under vacuum at 70°C. 0.9 g of a white powder was obtained.

FIB MS: m/z (M+1) = 652.3; 670.4; 736.4.

0.5 g of the precipitate was treated with 5 ml of DMSO at room temperature for 4 hours, filtered, washed with 2.5 ml of DMSO two times, then a residue precipitate was dissolved in 5 ml of DMSO by heating and precipitated with 15 ml of water, was next washed with an excess of water and ethanol and dried under vacuum. A powder was obtained, which decomposed at around 300°C without melting.

IR: 3466, 3327, 3132, 2953, 1635, 1543, 1437, 1402,1369, 1327, 1000, 821,781

^{1}H NMR (DMSO-d_6/TMS): 8.37 (ar: o, 2H, br); 7.55 (ar: p+m, 3H, br); 6.62 (NH_2, 16H, br); 3.95 (at C_{10}, 8H, br); 2.77 (at C_{11}, 8H, br).

^{13}C NMR (DMSO-d_6/TMS): C_6 (in outer layer triazine rings) = 176.02, 175.80; C_6 (in benzoguanamine core) = 168.86; C_2 C_4(in outer layer) = 166.96, 166.90; C_2 C_4(in core) = 164.34; $C_{1'}$ = 137.23; $C_{4'}$ = 131.07; $C_{2'}$ $C_{3'}$ $C_{5'}$ $C_{6'}$ =

128.26, 127.87; C_{10} = 45.96, 45.77; C_{11} = 36.64, 36.48.
FIB MS : m/z (M+1)=736.5

$C_{29}H_{37}N_{25}$	Calcd.:	C 47.34	H 5.03	N 47.62
735	Found:	47.10	5.07	46.91

2,2,6,6-Tetrakis(2-cyanoethyl)cyclohexanone (5)

It was obtained according to [33].

^{1}H NMR (DMSO-d_6/TMS): 2.35 (at C_{13}, 8H, m); 1.89 (at C_{12}, 4H, m); 1.78 (at C_{12}, 4H, m); 1.69 (at $C_{3''}$ $C_{4''}$ $C_{5''}$, 6H, m).

^{13}C NMR(DMSO-d_6/TMS): $C_{1''}$ = 214.80; C_{14} = 120.51; $C_{2''}$ $C_{6''}$ = 49.47; $C_{3''}$ $C_{5''}$ = 31.38; C_{12} = 30.65; $C_{4''}$ = 15.52; C_{13} = 11.46.

MS (CI) : m/z (M+1) = 311.3

m.p. : 165°C

2,2,6,6-Tetrakis[2-(2,4-diamino-1,3,5-triazin-6-yl)ethyl]cyclohexanone (6)

0.5 g of NaOH dissolved in 1 ml of water was added to 13.3 ml of cellosolve, containing 4 g (0.013 mol) of **5** and 4.37 g (0.052 mol) of cyanoguanidine. The mixture was stirred for 8 hours at 95°C, and poured into an excess of water. A precipitate was filtered and dried. 3 g of a crude product was obtained, which was treated with 20 ml of boiling ethanol for 1 hour under reflux. Undissolved portion was filtered on heating and dried. 1.8 g of a powder was obtained. An analytical sample was obtained by crystallization of 0.2 g of the powder from 10 ml of DMSO + ethanol (1:1 vol.), next-from 1 ml of the solvent mixture two times. The sample was washed with an excess of ethanol and dried.

IR: 3340, 3192, 2935, 1668, 1656, 1550, 1480, 1450, 1000, 822.

^{1}H NMR (DMSO-d_6/TMS): 6.56 (NH_2,16H, br); 2.22 (at C_{11}, 8H, m); 1.88 (at C_{10}, 4H, m); 1.74 (at $C_{3''}$,$C_{4''}$,$C_{5''}$, 6H, m) and (at C_{10}, 4H, m).

^{13}C NMR(DMSO-d_6/TMS): $C_{1''}$ = 216.84; C_6 = 177.66; C_2 C_4 = 166.91; $C_{2''}$ $C_{6''}$ = 49.55; C_{10}, C_{11} = 34.71, 32.74; $C_{3''}$ $C_{5''}$ = 31.92; $C_{4''}$ = 16.32

FIB MS : m/z (M+1) = 647

2,6,6-Tris[2-(2,4-diamino-1,3,5-triazin-6-yl)ethyl]cyclohexanone (7)

0.72 g KOH dissolved in 1.75 g of water was added to 30 ml of DMSO, next 4 g of **5** and 4.32 g of cyanoguanidine was introduced in the solution. The mixture was stirred for 8 hours at 110°C. A product was precipitated with an excess of methanol poured into the reaction mixture. After filtration, the precipitate was washed with methanol and dried. The crude product 2.4 g had the

chemical composition: C 46.38, H 6.18, N 38.41. It was treated with 45 ml of DMF+H_2O (1.25:1 vol.) at boiling temperature for a short time. An undissolved portion was filtered and dissolved in 45 ml of boiling DMF + H_2O (1.25:1) (almost completely soluble now). After filtration on heating, the filtrate crystallized. The crystal precipitate was crystallized again for three times in the same way, using 20 ml of the solvent each time, was next washed with 120 ml of hot ethanol twice, and dried at 70°C under vacuum. A white powder was obtained which melted at 195°C, which crystallized soon from melt at around 213°C, and started to color at 270°C, getting very dark at around 300°C without melting.

IR: 3466, 3324, 3187, 2934, 2868, 1700, 1628, 1547, 1441, 1405, 1254, 1117, 995, 824, 598.

^{13}C NMR (DMSO-d_6/TMS): $C_{1''}$= 214.54; C_6 = 178.28, 177.75, 177.25; C_2 C_4 = 166.86, 166.79; $C_{6''}$ = 50.21; $C_{2''}$ = 45. 53;

C_{10} C_{11} $C_{3'}$ $C_{5'}$ = 37.07, 35.47, 33.60, 32.35, 32.11, 31.93, 31.74, 27.21; $C_{4'}$ = 20.38

FIB MS : m/z (M+1) = 510

$C_{21}H_{31}N_{15}O$	Calcd.:	C 49.51	H 6.09	N 41.26
509	Found:	49.45,	6.11	40.87

2,6,6-Tris(2-cyanoethyl)cyclohexanone (10)

7.4 g of **5** was heated at 180°C for 2 hours. After cooling, a brown mixture was extracted with 100 ml of methanol which turned brown. The methanol solution crystallized to afford a precipitate (unreacted **5**). After filtration, methanol was evaporated and a residue was crystallized from 10% (weight) water-ethanol (1:4 vol.) solution. A rectangular single crystal substance (2.6 g) was obtained.

IR: 2942, 2855, 2250, 1750, 1440, 1426, 1380, 1360, 1263, 1253, 1140, 1113, 1091, 1074, 1028, 973, 947, 925, 879, 829, 773, 737, 613.

^{13}C NMR (acetone-d_6/TMS): $C_{1''}$= 213.57; C_{14} = 120.96, 120.66, 120.15; $C_{6''}$ = 51.50; $C_{2''}$ = 46.25; C_{12} $C_{3'}$ $C_{5'}$ = 36.67, 34.24, 30.65, 30.37, 26.52; $C_{4''}$ = 21.00; C_{13} = 15.07, 12.20, 12.16.

MS (CI) : m/z (M+1) = 258

$C_{15}H_{19}N_3$)	Calcd.:	C 70.01	H 7.44	N 16.33
257	Found:	70.16	7.41	16.29

m.p. 82°C

1,1,1–Tris(2 -cyanoethyl)propanone-2(11)

It was obtained according to [33]

^{1}H NMR (DMSO-d_6/TMS): 2.34 (at C_{13}, 6H, m); 2.18 (CH_3, 3H, s); 1.90 (at C_{12}, 6H, m).

^{13}C NMR (DMSO-d_6/TMS): C_8 = 209.88; C_{14} = 120.26; C_9 = 52.28; C_{12} = 27.32; C_7 = 25.68; C_{13} = 11.39.

$C_{12}H_{15}N_3O$	Calcd.:	C 66.35	H 6.91	N 19.35
217	Found:	66.47	6.99	19.37

1,1,1-Tris[2-(2,4-amino-1,3,5-triazin-6-yl)ethyl]propanone-2 (12)

A solution of **11** (33 g , 0.15 mol) and cyanoguanidine (40 g, 0.47 mol) in 150 ml of DMSO was prepared by heating at 65C. Subsequently, 2.8 ml of 50% KOH in water was added to the solution. It was then stirred at 140°C for 3 hours. A white powder precipitated from the reaction mixture, which turned dark. The powder was filtered, washed with ethanol and water, and dried. 60 g of a crude product was obtained.

A 3.2 g sample of the crude was treated with a new 30 ml portion of DMSO for 48 hours at room temperature, filtered, washed with another 20 ml of DMSO and, subsequently with 120 ml of water. 2.2 g of a solid remained. A 1 g sample of the solid was treated with 30 ml of DMSO again at room temperature and with 10 ml of DMSO at 100°C. Next it was filtered while heating, washed with an excess of ethanol and dried. 0.33 g of a final product was obtained. No effective solvent was found for the substance. It was scarcely soluble in DMSO even at boiling point.

IR: 3485, 3442, 3423, 3376, 3312, 3126, 2978, 2868, 1694, 1646, 1543, 1446, 1401, 1280, 1238, 1173, 1131, 1019, 829, 819, 746, 594.

^{1}H NMR (DMSO-d_6/TMS): 6.62 (NH_2, 12H, br); 2.15 (at C_{11} + C_7, 9H, m); 1.90 (at C_{10}, 6H, m).

^{13}C NMR (DMSO-d_6/TMS): C_8 = 212.06; C_6 = 177.39; C_2 C_4 = 166.96; C_9 = 52.76; C_{10} C_{11} = 32.72, 31.09; C_7 = 25.61.

FIB MS : m/z (M+1) = 470

$C_{18}H_{27}N_{15}O$	Calcd.:	C 46.05	H 5.76	N 44.78
469	Found:	46.32	5.78	43.55

m.p. does not melt up to 300°C.

Dilactam (13)

A mixture of 10 g (0.046 mol) of **11**, 12 g (0.142 mol) of cyanoguanidine, 1.11 g of 50% KOH/H_2O, and 50 ml of ethylene glycol was stirred at 110°C for 5 hours. It was poured then into 300 ml of water. A precipitate was filtered off while the filtrate was evaporated to obtain a viscous slurry. The later was mixed with 250 ml of methanol at boiling temperature. After filtration, the methanol solution was allowed to stay for 1 week. Crystallization occurred to produce 1.8 g of a solid substance in the form of clusters of needles. It was crystallized again from methanol and water to produce a single crystal substance of rhomb shape.

IR: 3411, 3335, 3204, 2944, 1620, 1537, 1454, 1402, 1202, 1144, 1120, 1026, 992, 832, 759, 726, 607.

^{1}H NMR (DMSO-d_6/TMS): 7.4 (NH, 2H, s); 6.6 (NH_2, 4H, s); 1.5-2.4 (CH_2, 12H, m); 1.3 (CH_3, 3H, s).

^{13}C NMR (DMSO-d_6/TMS): C_6 = 177.73; $C_{1'''}$ $C_{6'''}$ = 168.96; C_2 C_4 = 166.97; $C_{10'''}$ = 72.09; $C_{9'''}$ = 34.53; C_{10} C_{11} = 32.24, 30.33; $C_{2'''}$ $C_{5'''}$ = 27.10; $C_{11'''}$ = 25.72; $C_{3'''}$ $C_{4'''}$ = 23.91.

FIB MS : m/z (M+1) = 320

$C_{14}H_{21}N_7O_2 \cdot H_2O$	Calcd.:	C 49.80	H 6.82	N 29.08
319 + 18	Found:	49.00	6.94	28.74

m.p. 296°C

Hyperbranched Guanamine Oligomers

According to Scheme 4, tris(2- cyanoethyl)aceton **11** was considered first generation cyano terminated hyperbranched oligomer (I G-CN), while the crude **12** – first generation amine terminated hyperbranched oligomer (I G-NH_2).

Cyano Terminated 2nd Generation Hyperbranched Guanamine Oligomer (II G-CN)

A 2 ml of 50% water solution of KOH, 27.72 g (0.33 mol) of cyanoguanidine, and 21.7 g (0.1 mol) of **11** were mixed with 100 ml of DMSO. The mixture was heated at 130°C, while stirring for 4 hours. It turned dark and a white powder precipitated. After cooling, the precipitate was washed with an excess of ethanol and dried at 70°C under vacuum. The yield of the crude **12** (I G-NH_2): 38 g (81%), containing 95.7% of amine protons in respect to pure **12**. Table 1 contains characteristics of I G-NH_2.

A mixture of DMSO (300 ml), Triton B (0.34 ml), crude **12** (10 g), and acrylonitrile (13.8 g) was stirred at 70°C. After 6 hours, unreacted **12** was fil-

tered off and the filtrate treated with 700 ml of H_2O. As a result, a kind of emulsion was obtained, which had to be treated with 6 g of NaCl to produce a sediment. This was dissolved in 30 ml of acetone and precipitated with 150 ml of water. The precipitate was centrifuged, washed with an excess of water and methanol, and dried at 70°C under vacuum. Yield: 5.1 g.

According to the IR, it was estimated as a fraction of cyanoethylated product of the highest substitution and considered cyano terminated hyperbranched guanamine oligomer of second generation (II G-CN). Table 1 contains characteristics of the oligomer.

Amine Terminated 2nd Generation Hyperbranched Guanamine Oligomer (II G-NH_2)

3 g of II G-CN was dissolved in 15 ml of DMSO at 40°C, and 2.7 g of cyanoguanidine; 1.86 g of KOH in 4.5 ml of H_2O were added to the solution. The final mixture was heated at 120°C for 7 hours. The product mixture was poured into 50 ml of ethanol to produce 4.66 g of a precipitate after treating it again with 50 ml of ethanol 2 times, filtering, and drying at 70°C under vacuum.

II G-NH_2 is a slightly yellow powder soluble in DMSO and water. Table 1 contains characteristics of II G-NH_2.

Cyano Terminated 3rd Generation Hyperbranched Guanamine Oligomer (III G-CN)

1.5 g of II G-NH_2 was dissolved in 36 ml of DMSO at 50°C. After cooling to 20°C, 0.06 ml of Triton B was added to the solution, and 3.6 g of acrylonitrile was introduced dropwise. The mixture was stirred first for 0.5 hours at room temperature and next for 6 hours at 70°C. It was poured into 120 ml of H_2O and an emulsion obtained was treated with 3 g of NaCl to isolate a precipitate. After centrifugation, the precipitate was dissolved in 15 ml of acetone and evolved again by adding 75 ml of water and 2 g of NaCl, then centrifuged and washed with an excess of water and dried at 100°C under vacuum. Yield: 2.98 g of yellowish substance. Characteristics of III G-CN are contained in Table 1.

Amine Terminated 3rd Generation Hyperbranched Guanamine Oligomer (III G-NH_2)

1.4 g of III G-CN and 1.2 g of cyanoguanidine were dissolved in 10 ml of DMSO at 60°C. After the solution has been cooled to 30°C, 1.75 ml of 30%

TABLE 1. Characteristics of Hyperbranched Oligomers

Substance	Mol weight VPO	Mol weight MW GPC polystyrene units	Poly dispersity	ν (cm-1) N – H		
				N-H	C≡N	triazine ring
I G-NH_2				3413 – 3207 1620		820
II G-CN	650	6257	1.120	3487-3195	2249	822
II G-NH_2				3332 – 3197 1626		821
III G-CN	1480	8244	1.264	3478-3197	2249	821
III G-NH_2				3333 – 3196 1631		822
IV G-CN	3180	7655		3478-3196	2249	821
IV G-NH_2				3330 – 3197 1626		822
V G-CN		Product of limited solubility		3474-3208	2247	825

TABLE 1. Continued

Substance	^{1}H NMR: δ (relative amounts of hydrogenes) Varian XL-400			^{13}C NMR : δ Varian XL – 400			
	N-H	N-CH	C-H	C_4	C_2 C_6	C_{14}	C_9
I G-NH_2	6.78 (23H)		1.5-2.4 (30H)	177.3	166.8		52.8
II G-CN	6.92 (1H) 6.56 (5H)	3.86 (31H)	2.85 (44H) 1.8-2.4 (47H)	177.4	166.6 164.1	119.2 120.3	53.0
II G-NH_2	6.68 (148H)	3.5	1.7-2.4 (116H)	177.5	166.8 165.5		52.8
III G-CN	6.92 (15H) 6.56 (19H)	3.86 (180H)	2.82 (207H) 1.7-2.4 (124H)	177.6	167.0 164.2	119.2	53.0
III G-NH_2	6.63	suitable resolution in this region was not gained		177.0	167.0 164.2	119.2 traces	53.0 traces
IV G-CN	6.9+6.58 (42H)	3.83 (147H)	2.81 (166H) 1.7-2.4 (109H)	175 (multiplet)	166.8 165.4	119.2 (multiplet)	
IV G-NH_2	6.66	suitable resolution was not gained in this region					
V G-CN							

KOH aq. was added. The mixture was heated at 130°C for 6 hours, while stirring. After cooling, 70 ml of ethanol was added and a sediment was centrifuged and washed with 140 ml of ethanol 2 times. Then it was dried at 70°C under vacuum. 1.99 g of III G-NH_2 (a yellow powder) was obtained. Characteristics of the compound are placed in Table 1.

Cyano Terminated 4th Generation Hyperbranched Guanamine Oligomer (IV G-CN)

1.8 g of III G-NH_2 was dissolved in 80 ml of DMSO at 70°C, and after cooling to 40°C, 0.42 ml of Triton B was added, and 4.32 g of acrylonitrile was poured into the mixture dropwise for 0.5 hours while stirring. Then stirring was continued for 11 hours at 70°C. A precipitate was obtained by adding 80 ml of water. The precipitate was dissolved in 15 ml of acetone and isolated again by adding a new portion of 80 ml of water and 2 g of NaCl, filtering, and washing with an excess of water. Drying at 100°C under vacuum yielded 3.14 g of IV G-CN (a yellow powder). Characteristics of the compound are placed in Table 1.

Amine Terminated 4th Generation Hyperbranched Guanamine Oligomer (IV G-NH_2)

To a solution of 1.5 g of IV G-CN in 17 ml of DMSO, prepared at 70°C, 1.27 g of cyanoguanidine, and 2.3 ml of 30% KOH aq. were added at 40°C. Then the mixture was stirred for 5 hours at 130°C. Next, it was cooled and treated with 50 ml of ethanol, which yielded a yellow precipitate. This was washed with two new 50 ml portions of ethanol. After drying at 70°C under vacuum, 1.75 g of IV G-NH_2 was obtained. Characteristics of the compound are in Table 1.

Cyano Terminated 5th Generation Hyperbranched Guanamine Oligomer (V G-CN)

0.85 g of IV G-NH_2 was mixed with 30 ml of DMSO at 110°C. After cooling to 40°C, 0.08 ml of Triton B was added and 2 g of acrylonitrile introduced dropwise into the mixture. Next, the reaction was carried out at 70°C for 5 hours. An insoluble part of the reaction mixture was centrifuged off and the centrifugate was treated with 150 ml of ethanol to obtain a coarse-grained yellowish precipitate. It was centrifuged and washed with 50 ml portions of ethanol two times. After drying at 100°C under vacuum, 0.45 g of V G-CN was obtained. Another portion of V G-CN was gained by thickening of the second centrifugate down to 5 ml and treating it with 20 ml of ethanol. Washing with another portion

of 50 ml of ethanol and drying the newly obtained precipitate yielded 0.87 g of V G-CN. Entire yield: 1.32 g. Characteristics of V G-CN are in Table 1.

RESULTS AND DISCUSSION

We report here the first results of investigations on synthesis of oligomeric dendrimers of the guanamine type and disclose some problems met during the process. The dendrimerization process has been mentioned earlier in [34] .

We have chosen compounds, having nitrile groups, as starting substances in the guanamine dendrimerization.

At the beginning, benzonitrile was used, for which a dendrimerization course of first generation was derived partially from literature data. During this stage benzonitrile was transformed into $N^2N^2N^4N^4$–tetrakis(2-cyanoethyl)-benzoguanamine thoursough cycloaddition to cyanoguanidine followed by cyanoethylation of benzoguanamine obtained [32] (Scheme 1).

Thus, the first generation dendrimer **1**, having four cyano groups, was obtained from a substance with one nitrile only.

The structure of **1**, known only from patent data [32], was confirmed by FTIR, NMR and MS measurements as well as chemical composition. The IR spectrum of **1** shows clearly the CN stretching vibration band at 2250 cm^{-1} and very characteristic triazine ring vibration at 821 cm^{-1} as well [35].

The ^{1}H NMR spectrum of **1** in aceton-d6 reveals a group of peaks at 8.47, 7.56, and 7.50 ppm due to aromatic protons of the phenyl substituent. This is consistent with an ^{1}H NMR spectrum of benzoguanamine [35]. In the spectrum two triplets are centered at 4.15 ppm due to eight protons of N-CH_2 and a multiplet appeared at 3.00 ppm due to another eight ones of CH_2-CN. A slight unequivalency of methylene groups is expressed by two signals close to each other in ^{13}C NMR spectrum (Figure 1) at 45.21 and 44.99 ppm as well as two signals at 17.03 and 16.95 ppm corresponding to N-CH_2 and CH_2CN, respectively. CN carbon signal is also splitted into ones at 119.42 and 119.30 ppm. All the split signals are of the same intensity within their pairs. Splitting of the signals will be discussed elsewhere.

The ^{13}C NMR spectrum shows correctly other carbon atoms in the compound: four aromatic carbons at 129.15, 129.32, 132.64, and 137.68 ppm, and carbons of the triazine ring: C_2C_4 at 166.16 ppm and C_6 at 171.35 ppm. A DEPT spectrum is consistent with the structure **1**. Our ^{13}C NMR measurements for ben-

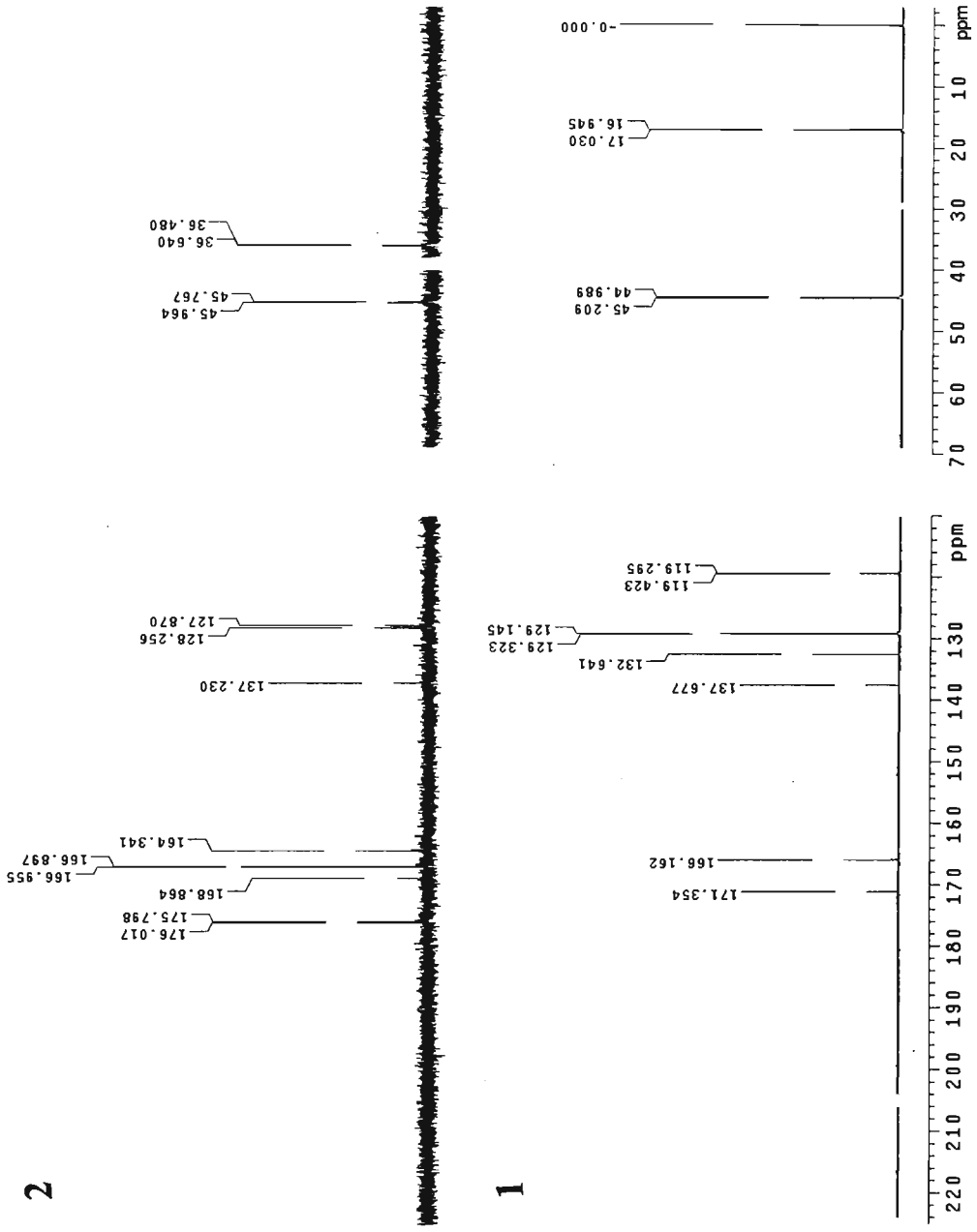


Figure 1. ^{13}C NMR spectra of **1** in acetone-d_6 and **2** in DMSO-d_6. For clarity the solvents peaks (acetone-d_6: 29.8 ppm and 206.0 ppm; DMSO-d_6: 39.5 ppm) and the 70-110 ppm interval (with no signals) have been removed.

zoguanamine are very close to respective carbon signals of tetra(cyano- ethyl) bezoguanamine.

We extended the dendrimerization route by cycloaddition of cyanoguanidine to **1** to produce a mixture of dendrimers of 1.5th generation having a sphere of guanamine moieties newly introduced. The mixture was collectively analyzed by ^{1}H NMR and FIB MS spectroscopy. According to the FIB MS spectrum of positive ions (M+1) peaks at masses: 652, 670, and 736 can be ascribed to compounds **3**, **4**, and **2,** respectively in Scheme 1. According to ^{1}H NMR spectrum of the mixture, the cycloaddition yield on this stage was 62.5 mol % in respect to -NH_2 groups created under applied conditions.

All the substances **2**, **3**, **4** can be considered 1.5th generation dendrimers with different algorithm of growth, though. These would also be collectively used to produce a mixture of dendrimers of higher generations. The main product $N^2N^2N^4N^4$-tetrakis[2-(2,4-diamino-1,3,5-triazin-6-yl)ethyl]2,4-diamino-6-phenyl-1,3,5-triazine **2** was isolated as an individual compound with 54 % yield. The main parts of the compound, which are guanamine moieties can be easily identified by carbon signals of C_2 C_4 and C_6 in its ^{13}C NMR spectrum (Figure 1). There are two kinds of the triazine moiety in the compound: one is the core unit afforded by starting substance **1** and the other one is an outer layer triazine ring as a result of cycloaddition reaction. The signals of C_2 C_4 (164.34 ppm) and C_6 (168.86 ppm) (in the core, **2**) are slightly shifted as compared with those of compound **1** (166.16 and 171.35 ppm, respectively). Outer layer guanamine moieties were unambiguously identified by signals at 166.96, 166.90 ppm (C_2 C_4), and 176.02, 175.80 ppm (C_6), which are characteristic for all the compounds examined within the series. Other NMR spectral data as well as IR, FIB MS, and elemental analysis are well consistent with the structure of **2**.

Another dendrimerization path was driven from carbonyl compounds, i.e. cyclohexanone and acetone. Cyclohexanone undergoes cyanoethylation easily to produce 2,2,6,6-tetrakis(2-cyanoethyl)cyclohexanone **5** [33] as it is shown in Scheme 2. The compound corresponds to spectral analysis (NMR, MS) made by us to complete literature data (Figure 2, Experimental).

Under applied conditions it reacted with cyanoguanidine to produce compounds **6-9**. **6** and **7** were isolated and examined as individual substances while only corresponding peaks in FIB MS spectrum were found, which could be ascribed to substances **8** and **9**. All the substances to the best of our knowledge were unknown earlier.

The structure of the basic product **6,** 2,2,6,6-tetrakis[2-(2,4-diamino-1,3,5-triazin-6-yl)ethyl]cyclohexanone, was established by routine examination

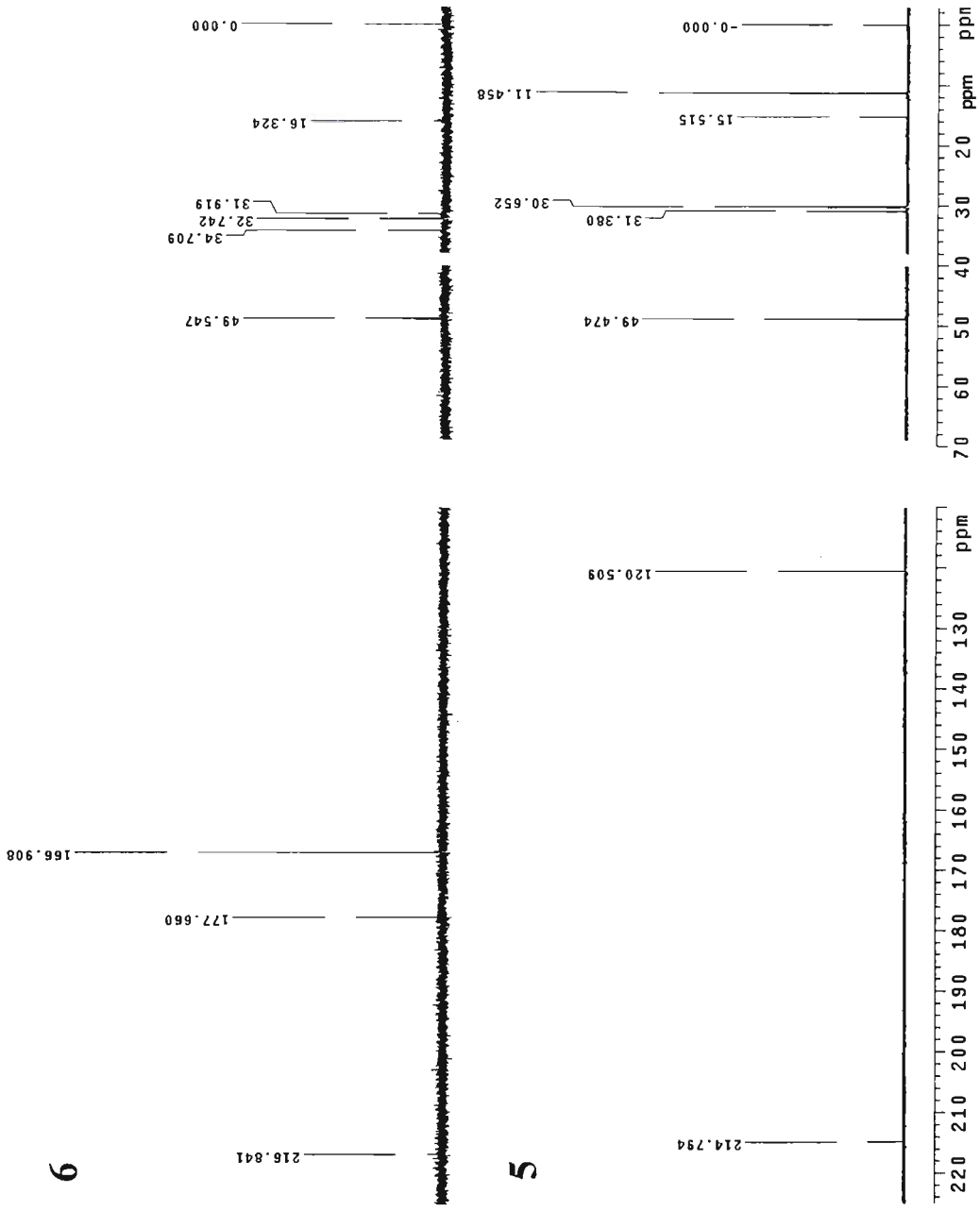


Figure 2. ^{13}C NMR spectra of **5** and **6** in DMSO-d_6. For clarity the solvent peak (39.5 ppm) and the 70-110 ppm interval (with no signals) have been removed.

(IR, NMR, FIB MS). In NMR spectra it is correctly represented by all the proton and carbon signals. The guanamine moieties in **6** are reflected by characteristic signals at 177.66 ppm (C_6) and 166.91 ppm (C_2 C_4) as well as 6.56 ppm NH_2) [35]. In the ^{13}C spectrum (Figure 2) substituted cyclohexanone is well represented by signals at 216.84 ppm (C=O) and 49.55 ppm (quaternal carbon atoms). The assignment of the carbon signals was secured by a DEPT spectrum. The compound **6** is also consistent with IR spectrum. Characteristic absorption bands are: 822 cm^{-1} (triazine ring vibration); 1656 cm^{-1} (NH_2 deformation vibration); and 3340, 3272 cm^{-1} (NH_2 stretching vibration) [35,36].

FIB MS shows molecular peak at 647 (M+I) in a positive ion spectrum.

It must be emphasized that the retro Michael reaction (decyano-ethylation) partially occurred under applied conditions of the cycloaddition reaction to produce 2,6,6-tris[2-(2,4-diamino-1,3,5-triazin–6-yl)ethyl]cyclohexa-none **7** . To confirm its structure, an independent synthesis of the compound from tris(2-cyanoethyl)cyclohexanone **10** was accomplished. The latter in turn was obtained by partial decyanoethylation of **5**, and routinely identified. The trisubstituted cyclohexanones have very characteristic ^{13}C NMR spectra that can be well distinguished from other compounds of the series: the compound **10** gave a split signal at around 120 ppm corresponding to thoursee non-equivalent cyanogroups (Figure 3). The similar splitting was observed at around 178 ppm for the same carbons, which were incorporated already now in the triazine rings **7** (Figure 3). This is in agreement with the mechanism of the guanamine cycloaddition reaction proposed [37]. Other carbon atoms correctly reflected symmetry of the compounds **7** and **10.** Especially, there are CH groups (45.53 ppm for **7** and 46.25 for **10)** along with quaternary carbons (50.21 ppm for **7** and 51.50 ppm for **10**). Structure of **7** and **10** were consistent with other experimental results (IR, MS, FIB MS, chemical composition).

The splitting is most probably connected with axial and equatorial locations of the substituents of cyclohexanone ring.

Another side reaction in the guanamine dendrimerization process was observed when acetone was used as a starting substance, according to the Scheme 3.

The compound **11** which can be considered the first generation dendrimer with cyano end groups has already been known from literature [33] though its structural data had to be complemented. It corresponded well to our measurements (NMR, MS, IR) anyway (Figure 4, Experimental). The compound **12**, known only from a patent [38] also was found to be in good agreement with our structural investigations (NMR, FIB MS, IR) (Figure 4, Experimental).

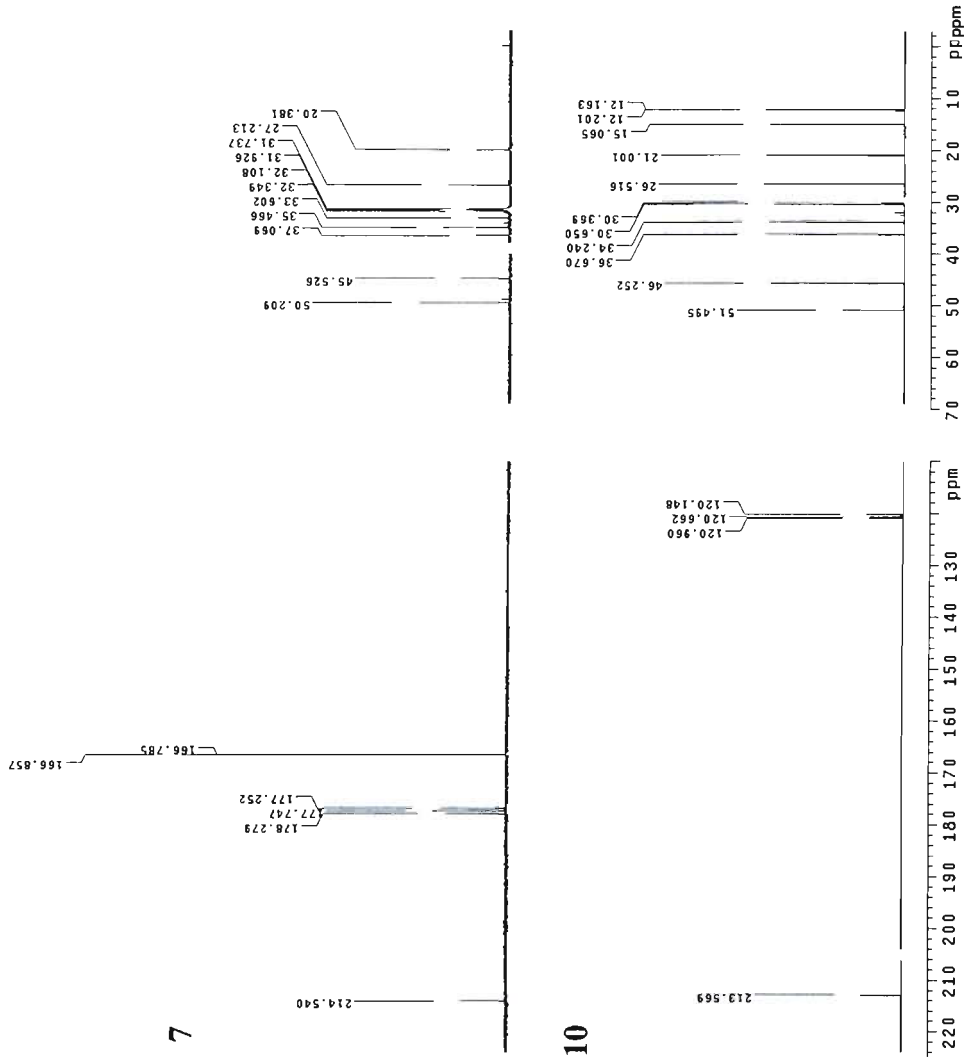


Figure 3. ^{13}C NMR spectra of **10** in acetone-d_6 and **7** in DMSO-d_6. For clarity the solvents peaks (acetone-d_6: 29.8 ppm and 206.0 ppm; DMSO-d_6: 39.5 ppm) and the 70-110 ppm interval (with no signals) have been removed.

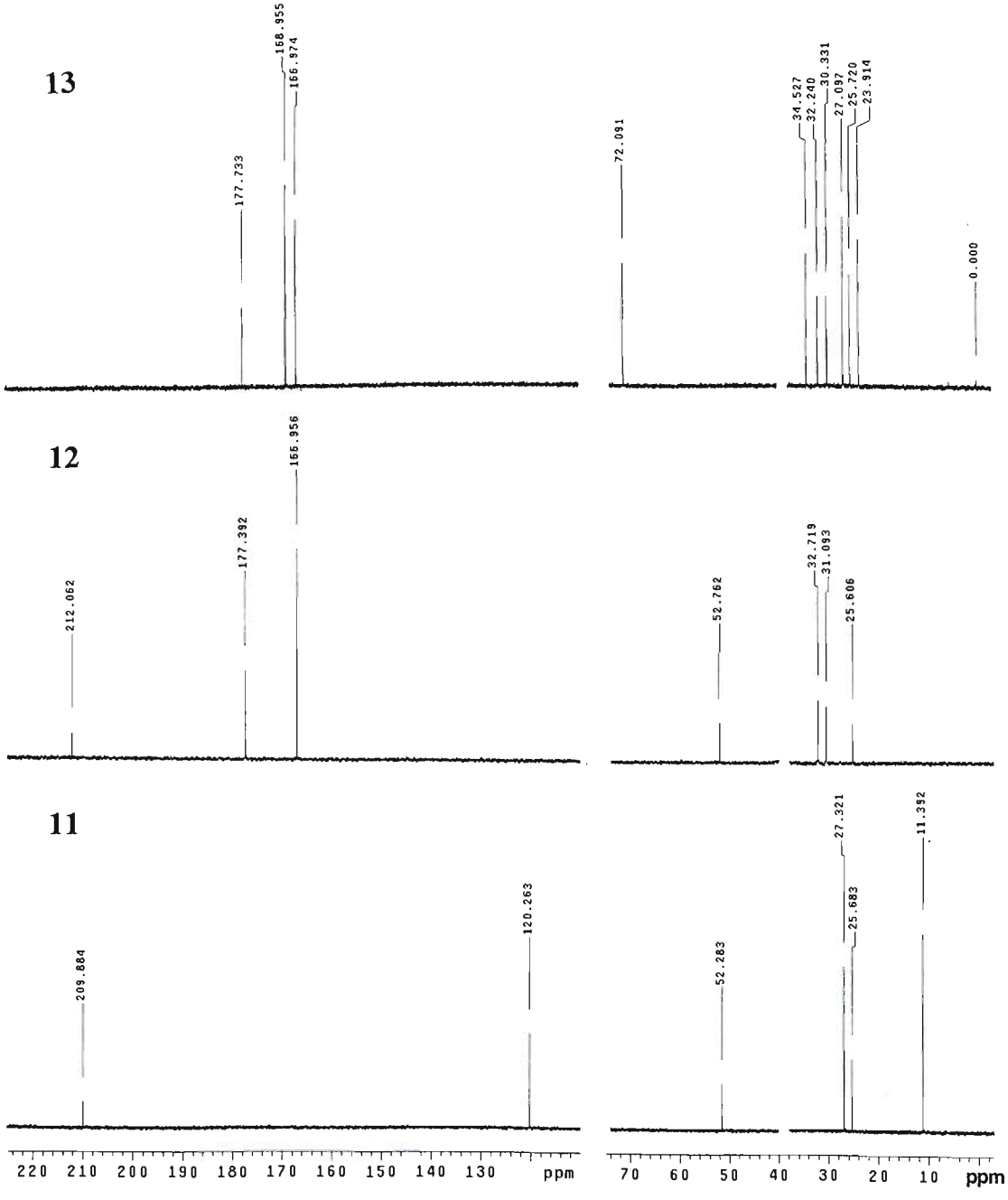


Figure 4. ^{13}C NMR spectra of **11, 12 and 13** in DMSO-d_6. For clarity the solvent peak (39.5 ppm) and the 75-110 ppm interval (with no signals) have been removed.

As a by-product a dilactam **13** was isolated, which indicated that hydrolysis as well as cyclization of amide groups must be taken into account in the guanamine dendrimer synthesis.

The compound **13** was identified by routine investigations (NMR, FIB MS, IR, chemical composition) (Figure 4, Experimental), and comparison with dilactams having other substituents which have already been known [39].

At this point, as a general conclusion, it can be stated that branch multiplicity can gain **4** only at the first steps of the guanamine dendrimerization process, i.e., when the main product dendrimers can be separated from defected ones (by-products). Of course, the defects are obviously chemically linked with dendrimer molecules of higher generations. Nevertheless, these can be characterized by spectral data collected for the isolated compounds.

We have described the dendrimerization process towards higher generations (up to 4th generation) for acetone as a core substance. It must be mentioned, that Scheme 4 could only be completed using a crude compound **12**, as it was better soluble, than pure **12**. The last one is scarcely soluble even in boiling DMSO.

The regular structural units of a growing dendrimer molecule are presented in Figure 5, where a is the core unit, b are repeat units, c and d are end groups. The dendrimerization process can be most easily characterized by NMR spectroscopy. The relation of peak intensity of carbon 14 at around 120 ppm to that of carbon 9 at around 53 ppm is growing rapidly towards higher generations and reflects the dendrimerization progress clearly. In the ^{13}C NMR spectra, starting from II G-CN, each generation is correctly represented by thoursee signals in the region of guanamine moieties. These are at around 177 and 167, as well as 164 ppm. The first two must be ascribed unambiguously to carbons C_6 and C_2 C_4, (respectively) in unsubstituted triazine rings (mostly outer layer rings in G-NH_2s and some unreacted inner rings in G-CNs). The third one can be ascribed to C_2 C_4 in the rings substituted in the course of dendrimerization process. The value of the chemical shift is exactly the same as in the case of cyanoethylated bezoguanamine **1**. Some unreacted CN groups (120.26 ppm) of the first generation (I G-CN) can be observed along with those of next generation (119.04, 119.19 ppm) in the ^{13}C NMR spectrum of II G-CN.

The dendrimer products of each generation can be characterized quantitatively by ^{1}H NMR analysis. Thus CH_3 protons appear at around 2.2 ppm (according to compound **11**), protons of carbon 10 connected with the core unit appear at close to 1.9 ppm (according to **12**). The same protons at carbon 10 connected with nitrogen in a repeat unit appear at around 3.9 ppm (according to **2**).

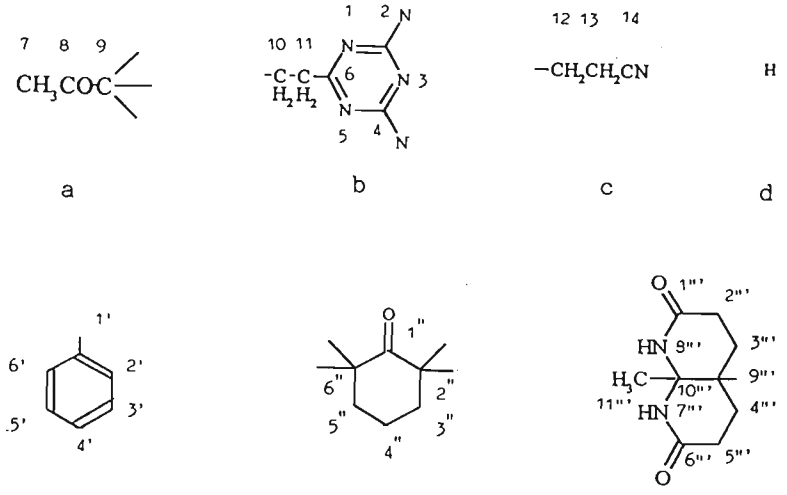


Figure 5. Structural units of quanamine dendrimer molecules.

Analogously protons of methylene groups 11 are found at around 2.2 and 2.7 ppm, depending on whether the ethylene radical is connected with the core unit (according to **6** and **12**) or with a nitrogen (according to **2**), respectively. Methylene groups 12 give proton signals at around 1.9 ppm, when connected with the core unit (according to **11**), and at around 3.9 ppm, while connected with nitrogen of a repeat unit (according to **1**). Proton signals of methylene 13 appear at around 2.3 ppm and 3.0 ppm, when cyanoethyl groups are connected with the core or repeat units respectively (according to **11** and **1**). Protons of $-NH_2$ end groups resonate at around 6.6 ppm (according to all the examined compounds having triazine rings and to literature data for benzoguanamine [35]).

The most essential is the relation between proton signals of amine and methylene groups. It shows the effectiveness of cyanoethylation and cycloaddition reactions corresponding to the degree of branching and reflecting presence of defect propagation chains [40]. IR provides additional information about structural units of guanamine dendrimers. Absorption bands at 2250 cm^{-1} (-CN), 1645-1616 cm^{-1}(-NH_2) and 832-821 cm^{-1} (triazine ring) [35, 36] are well distinguished and important.

The absorption at 2250 cm^{-1} corresponds to cyanoethyl groups. Its intensity grows in expense of one of 1645-1616 cm^{-1} band when amine ended gener-

ations are cyanoethylated. In turn intensity of the 1645-1616 cm^{-1} band grows in expence of 2250 cm^{-1} during the cycloaddition reaction. In the case of acetone core we obtained hyperbranched products up to 4th cyano and amino generations (**11–19**, Scheme 4). A cyano ended 5th generation hyperbranched product was also obtained, however it was of limited solubility. The term ihyperbranched products" was used for higher generations of the guanamine dendrimers as we examined them globally, like typical resins, without isolation of individual substances.

Nevertheless, the gel permeation choursomatography (GPC) measurements show the products to be fairly uniform substances (Figure 6, Table 1) of narrow molecular weight distribution (1.120-1.264) characteristic for dendrimers.

The choursomatography was performed for cyano ended products only because of lack of a suitable eluent for amine ended ones.

Geometrical progression in mol. weight growth from one cyano generation to the next one (Table 1) indicates the dendrimerization process to occur with chain multiplicity of 2 only.

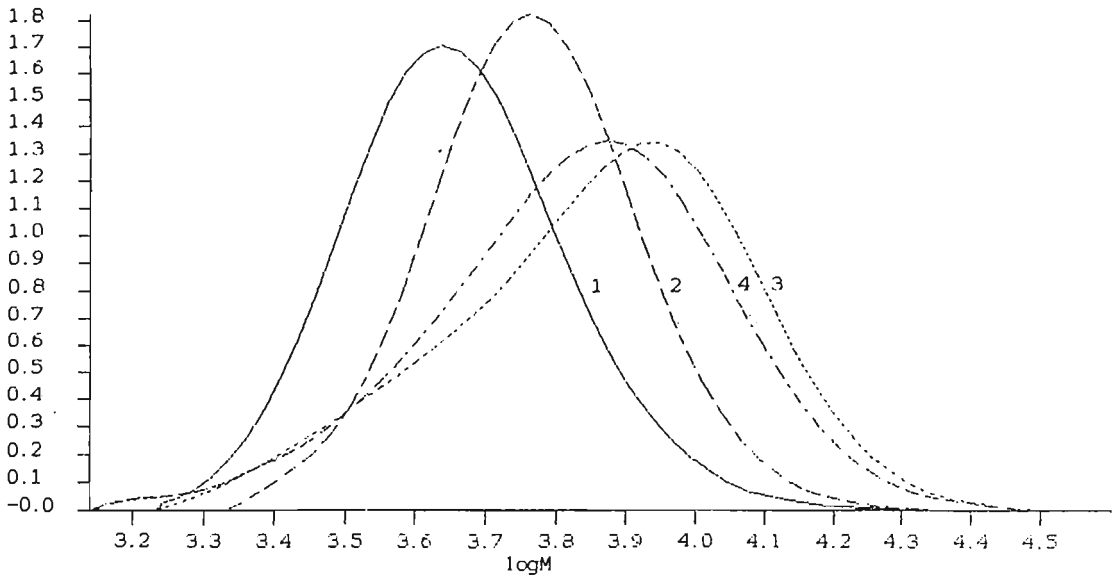
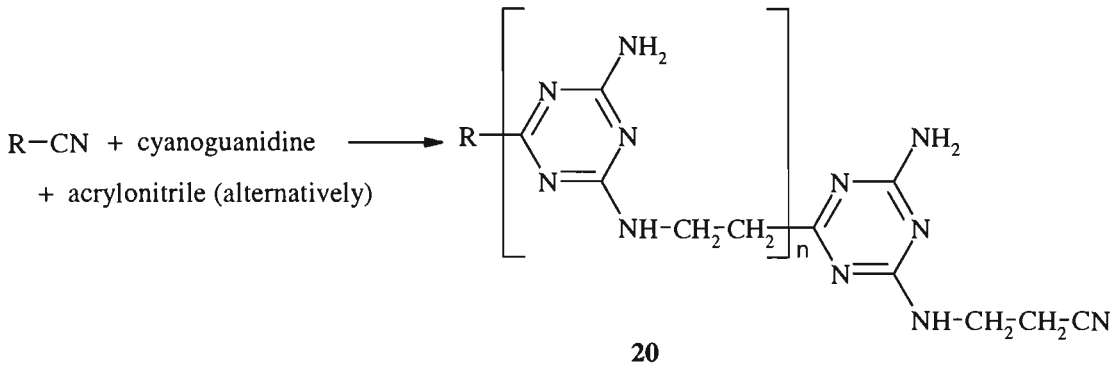


Figure 6. Overlaid differential molecular weight graphs of I G-CN (1), II G-CN (2), III G-CN (3), and IV G-CN (4).

It means, we should admit, that under applied conditions the mol. weight growth was approximately twice less than that expected theoretically due probably to the by-reactions. Crowding could be another reason, which prevented some functional groups from reacting. Thus some unreacted $-NH_2$ and probably partially reacted –NH were observed in ^1H NMR (6.56 and 6.92 ppm) and IR (3190 - 3490 cm^{-1}) spectra of cyanoethylated products. The signal at 6.92 ppm changed from around 6.60 (for unsubstituted $-NH_2$) towards lower field which seems to be consistent with values published for monocyanoethylated amine groups of some guanamines (7.43-7.72 ppm) [41]. Further investigations on conditions of the applied reactions, will show, whether it is possible to increase the rate of the mol. weight growth in the guanamine dendrimerization process.

Dendrimer behavior of the obtained cyano ended products was strikingly expressed by the relationship between the polystyrene equivalents (GPC) and their mol. weight measurements. The GPC results showed expanded structure of guanamine dendrimers in diethylacetamide solutions when compared with polystyrene standards. The dendrimer molecules of mol. weight e.g., of 650 and 1480 take hydrodynamic volumes corresponding to PS standards molecules of mol. weight 6257 and 8244, respectively (Table 1). It is compatible with the assumption, that dendrimer molecules can grow in an expanded form in a suitable solvent [1, 42]. This is particularly valuable while using the dendrimer to form a host-guest system [1]. This was practically proved already by works of Tomalia, Fréchet and Mejier [42, 43, 44, 45]. Another feature of the guanamine dendrimer molecules is that they grow in their molecular weight faster than in their hydrodynamic volume (according to polystyrene units). They reach a stage on which reversibly the hydrodynamic volume (in dimethylacetamide solution) is even slightly greater for a generation (III G-CN, mol.w. 1480) than for the next one (IV G-CN, mol.w.3180). Mol. weights of their PS standards are 8244 and 7655, respectively (Figure 6, Table 1). All the dendrimerization process has been successfully repeated to confirm the characteristic hydrodynamic volume - mol. weight relation. The extreme shoursinkage of the guanamine dendrimer molecules in the solution occurred approximately at the same point of the mol. weight of around 3000 (Table 1). A shoursinkage of dendrimers in solution were observed earlier by Tomalia [4].

The degree of branching of guanamine dendrimerization products can be characterized by a value X which derives from comparison of the dendrimer structure and linear one (compound **1** and Scheme 5). An equation can be derived for an X_1 value



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Scheme 5.

$$X_1 = \frac{NH_2 + NH}{NCH_2} \quad \text{or} \quad X = 1 - \frac{2}{3} \cdot \frac{NH_2 + NH}{NCH_2}$$

which equals the sum of amine protons, related to the amount of hydrogens of methylene groups connected with nitrogens. X = 0 corresponds to the linear polyguanamine, while X=1 (fully substituted amine groups) for the ideal polyguanamine dendrimers (PGD) with cyano end groups. The higher the X value the higher the degree of branching within the range between 0 and 1. The value X can be calculated directly from ^{1}H NMR measurements. Thus, ascribing ^{1}H NMR signals at around 3.9 ppm to all the protons of N-CH_2 of 2nd, 3rd , and 4th cyano ended generations, and signals at around 6.58, and 6.92 ppm to NH_2 and NH protons of triazine amine groups, one can state that the degree of branching of the 2nd, 3rd, and 4th generations remains approximately at the similar level though that of the 4th generations is correctly slightly less probably of the crowding discussed above . The X values are: 0.87, 0.87, and 0.81, respectively.

CONCLUSION

In summary, we have developed a new simple method for synthesis of dendrimers and hyperbranched polymers by using for the first time cyanoethylation reaction and cycloaddition of cyanoguanidine to nitriles. As a result polyguanamine dendrimers and guanamine hyperbranched polymers (we pro-

pose a common abbreviation PGD for both) have been obtained. They are correctly characterized by low polydispersity and exhibit an expansion state in dimethylacetamide. The expansion is lowering towards higher generations with the extreme of generation 4.

The basic advantages of the method is high branch multiplicity (4) at least in the early steps of the dendrimerization process, and the same kind of the catalyst (bases) used in both reactions. So it is possible to synthesize guanamine dendrimers "step by step" without changing the catalyst system, which can facilitate "one-pot" synthesis of the dendrimers. Dimethylsulfoxide was the solvent used everytime in the dendrimerization process. This is a ground for technical dendrimers and hyperbranched polymers to be sythesized without isolating intermediates. The method does not need any protection/deprotection procedure. The research has afforded new model substances **2**, **6**, **8**, **10**, **13**, and complete spectral data for **1**, **5**, **11**, and **12**. The compounds enable identification of polymer guanamine dendrimerization products.

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