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DIVERGENT SYNTHESIS OF POLYESTER TYPE DENDRIMERS CONTAINING AZOBENZENE IN THE CORE

AZOBENZOLA KODOLA POLIESTERA TIPA DENDRIMĒRU DIVERĢENTĀ SINTĒZE

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Key words: dendrimer, azobenzene, ester, divergent synthesis

1. Introduction

The azobenzene chromophore has wide variety of applications in nonlinear optical devices, all-optical switches and data storage due to its ability to undergo fast, efficient and fully reversible *cis-trans* photo isomerization not generating side-products even with innumerable isomerization cycles. To form practically useful materials different azobenzene type moieties have been incorporated into polymers [1] or more recently into dendrimers [2-6]. Azobenzene containing dendrimers appear to maintain the desirable photomotions and photo-switching properties, while allowing precise control of molecular architecture and thus material properties [1]. Dendrimers in contrast to polymers are monodisperse systems with regular, well defined and highly branched three-dimensional structure, which means, globular, void containing shape and unusual physical properties. Many kinds of dendrimers are known such as polyamidoamine (PAMAM), polyether, polyester type etc [7], among them, polyester type dendrimers attract considerable attention for well elaborated synthetic methods, high thermal stability [8-10], and reactivity of end carboxyl or hydroxyl groups [11].

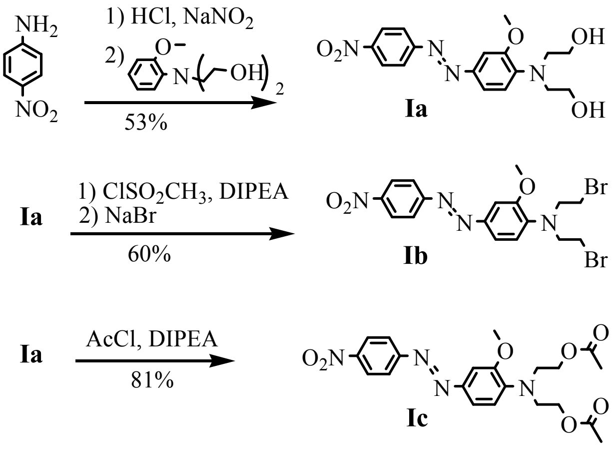
Dendrimers can offer the specific environment - give not only simple bulky substituent effects, but also voids in the dendrimer interior [12]. In order to study "dendrimer effect" on the nonlinear optical properties of photoresponsive azobenzene, substituted at the 4 and 4' positions with electron-donating and electron-withdrawing groups (a "push-pull" chromofore) we have synthesized polyester type dendrimer containing 4-[*N,N*-bis(2-hydroxyethyl)amino]-3-methoxy-4'-nitroazobenzene **(Ia)** in the core. We used 3,5-bis[2-(tetrahydro-2*H*-pyran-2-yloxy)ethoxy]benzoic acid (**IIa**) as a building block to assemble dendrimer from the core to the periphery. In this paper we report synthesis and describe spectral characterization of dendrimer three generations (**G1, G2, G3**).

2. Results and discussion

2.1. Synthesis of components of dendrimer

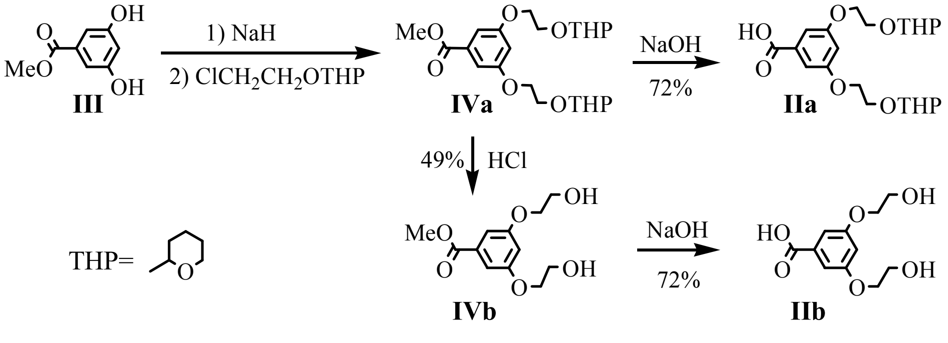
Azocompounds **Ia-Ic** were synthesized according to Scheme 1 using standard methods of organic synthesis.

Scheme 1



Methyl 3,5-dihydroxybenzoate **III** was alkylated (Scheme 2) with 2-(2-chloroethoxy)-tetrahydro-2*H*-pyran in DMF with NaH as base to give compound **IVa**, that without isolation was saponified yielding acid **IIa** or after removal of tetrahydro-2*H*-pyran-2-yl (THP) protecting groups was saponified giving acid **IIb**.

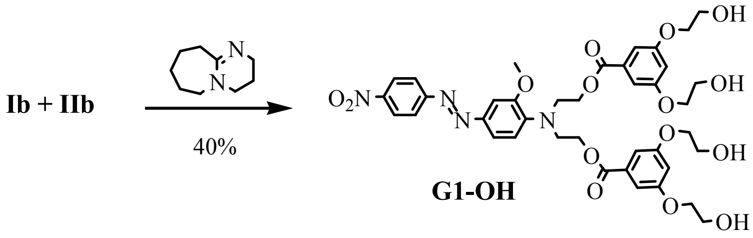
Scheme 2



*2.2. Synthesis of dendrimer generations **G1, G2** and **G3***

We used mild ester formation methods for dendrimer growth such as alkylation of acid with alkylbromide in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 3), that allow esterification of carboxylic acids having hydroxyl groups without protection of these groups [13] and *N,N'*-dicyclohexylcarbodiimide (DCC) method [14].

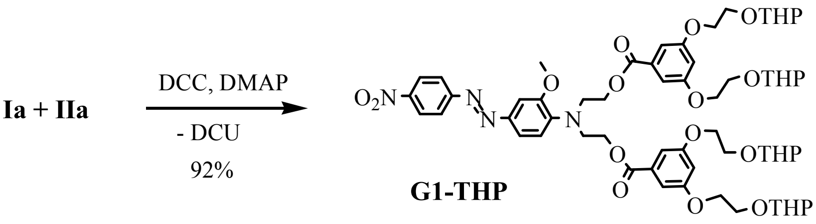
Scheme 3



Compound **Ib** did not react with acid **IIb** at room temperature and even after prolonged heating only moderate yield of dendrimer **G1-OH** was isolated.

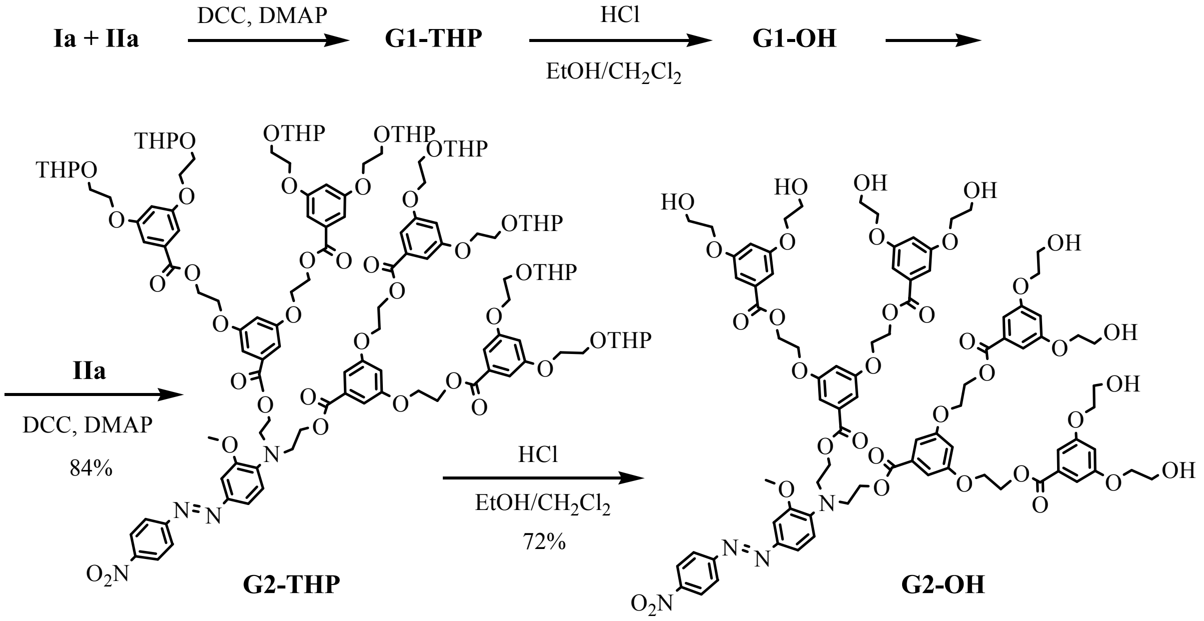
DCC method gave better results. Protected with THP groups first generation dendrimer **G1-THP** was formed from core azobenzene moiety **Ia** and branching unit **IIa** with DCC under catalysis of 4-(*N,N*-dimethyl)aminopyridine (DMAP) in 92% yield (Scheme 4). **G1-THP** was purified by chromatography.

Scheme 4



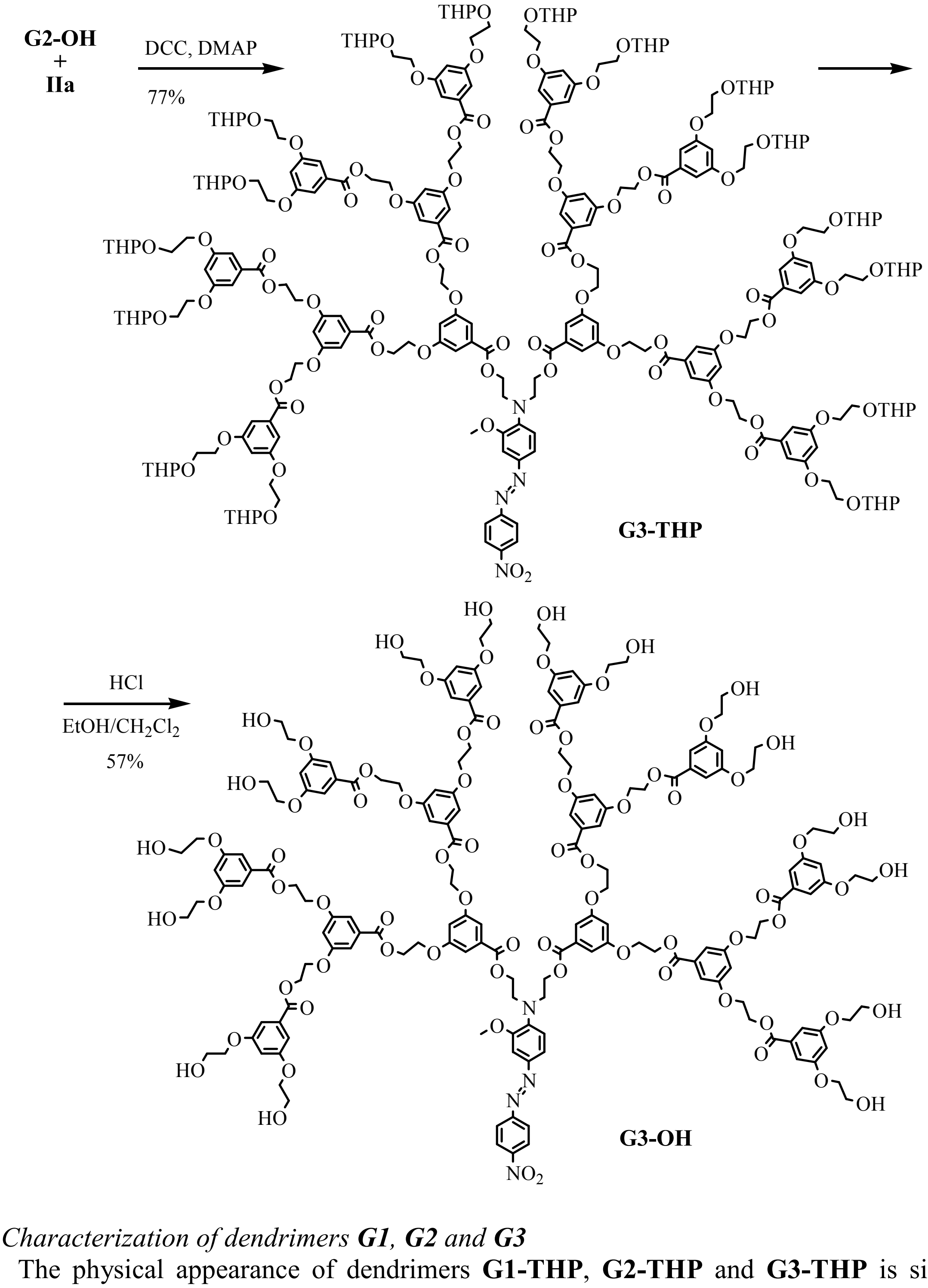
The optimum method for removal of THP protecting groups from **G1-THP** was studied. Standard conditions [15] for THP-deprotection with diluted acetic acid was not successful even at 45 °C for several days. Boiling with pyridinium *p*-toluenesulfonate (PPTS) in EtOH [15] gave similar results first, but eventually decomposition of the reaction mixture happened. Clean formation of **G1-OH** is afforded, when **G1-THP** was dissolved in mixture of EtOH and CH_2Cl_2 and conc. HCl was added. Yield of **G1-OH** was 75%.

Scheme 5



After optimisation of dendrimer growth and protection group removal steps, synthesis was carried out for second and third generations. Yields in both steps decrease with number of generation because of increasing possibility of incomplete reactions with the growth of number of terminal groups. The reaction of acid **IIa** with **G1-OH** and DCC gave **G2-THP** in 84% yield, and after subsequent removal of THP groups with HCl, **G2-OH** has been prepared in 72% yield (Scheme 5). **G3-OH** was synthesized by the same two step procedure – by reaction of **G2-OH** with acid **IIa** followed by THP removal with HCl (Scheme 6) only this time larger amount of colourless by-products were formed diminishing yields in steps to 77% in the first and 57% in the second. All three THP protected dendrimers need to be dried long in vacuum to get rid of all enclosed solvent.

Scheme 6



2.3. *Characterization of dendrimers **G1**, **G2** and **G3***

The physical appearance of dendrimers **G1-THP**, **G2-THP** and **G3-THP** is similar: they are red, amorphous and translucent substances. **G1-THP** and **G2-THP** are very viscous, they take flattened or drop like shape with time, but **G3-THP** is hard. In the same way properties of dendrimers **G1-OH**, **G2-OH** and **G3-OH** are similar: they all are red powders and far less soluble in any solvent than THP protected dendrimers. Table 1 lists the UV-Vis characteristics in acetone, melting points for powdery dendrimers and glass transition temperatures for amorphous dendrimers, which were gained from differential scanning calorimetry studies.

Table 1

UV-Vis spectra and physical properties of synthesized dendrimers

Compound	$\lambda_{max,}$ nm	lgε	Melting point, °C	Glass transition, °C
G1-THP	468.96	4.324		15.6
G2-THP	470.73	4.354		23.7
G3-THP	472.04	4.351		27.0
G1-OH	465.50	n.d.*	148-149	
G2-OH	472.10	4.391	102-109	
G3-OH	472.26	n.d.*	99-100	

n.d. – not determined

All dendrimers **G1**, **G2** and **G3** have been characterized by IR (Table 2) and ^{1}H NMR (Table 3) spectroscopy. IR absorption about 3400 cm^{-1} was used to judge about completion of esterification reaction.

Table 2

IR spectra of synthesized dendrimers

Compound	Absorption maximum wave number (cm^{-1}) and interpretation [16]			
	-NO_2	Ester C=O	-OH	Other
G1-THP	1508	1721		1522, 1594, 2873, 2942, 3103
G2-THP	1508	1716		1521, 1592, 2873, 2941, 3077
G3-THP	1506	1716		1520, 1593, 2876, 2943, 3096
G1-OH	1508	1709	3369	1589, 2872, 2931, 3102
G2-OH	1508	1718	3400	1593, 2876, 2935, 3098
G3-OH	1508	1719	3378	1595, 2930

Structure of dendrimers **G1, G2** and **G3** was approved - integrated signals of aromatic protons of chromophore located at 8.37-8.16 ppm (H_a) and 7.97-7.83 ppm (H_b) were compared with integrated signals of dendrimer growth unit located at 6.80-6.61 ppm (H_g). Their ratio show the number of growth units per one chromophore unit. In addition for **G1-THP**, **G2-THP** and **G3-THP** there is a very characteristic triplet of the proton attached to THP group at 4.67 ppm for **G1-THP** and **G2-THP** or multiplet at 4.61 ppm for **G3-THP** integration of which shows number of THP protective groups per acid **IIa** unit.

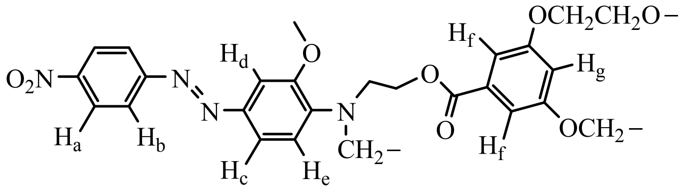


Table 3

^{1}H NMR spectral data of synthesized dendrimers

Compound	Chemical shifts of protons in $CDCl_3$, δ, ppm (multiplicity of resonance signal, number of protons, identification)	
	Signals for identification	Other signals
G1-THP	4.67 (t, J = 3.2 Hz, 4H, OCHO), 6.69 (t, J = 2.3 Hz, 2H, H_g), 7.97 (d, J = 9.0 Hz, 2H, H_b), 8.36 (d, J = 9.0 Hz, 2H, H_a)	1.44-1.90 (m, 24H, THP), 3.44-4.22 (m, 31H, OCH_2, NCH_2, OCH_3), 4.50 (t, J = 5.6 Hz, 4H, CH_2OCO), 7.11 (d, J = 2.3 Hz, 4H, H_f), 7.16 (d, J = 8.4 Hz, 1H, H_e), 7.44 (d, J = 2.1 Hz, 1H, H_d), 7.60 (dd, J = 8.4, 2.1 Hz, 1H, H_c)
G1-OH	6.61 (t, J = 2.4 Hz, 2H, H_g), 7.97 (d, J = 9.0 Hz, 2H, H_b), 8.37 (d, J = 9.0 Hz, 2H, H_a)	3.73 (s, 3H, OCH_3), 3.84 (m, 4H, NCH_2), 3.92 (m, 8H, $C\underline{H}_2OH$), 4.04 (m, 8H, CH_2OAr), 3.80-4.04 (m, 4H, OH), 4.52 (m, 4H, CH_2OCO), 7.06 (d, 4H, H_f), 7.13 (d, J = 8.5 Hz, 1H, H_e), 7.47 (d, J = 2.1 Hz, 1H, H_d), 7.62 (dd, J = 8.5, 2.1 Hz, 1H, H_c)
G2-THP	4.67 (t, J = 3.3 Hz, 8H, OCHO), 6.66-6.71 (m, 6H, H_g), 7.91 (d, J = 8.8 Hz, 2H, H_b), 8.28 (d, J = 8.8 Hz, 2H, H_a)	1.43-1.78 (m, 48H, THP), 3.47-4.22 (m, 63H, OCH_2, NCH_2, OCH_3), 4.50-4.57 (m, 12H, CH_2OCO), 7.09-7.19 (m, 13H, H_f, H_e), 7.44 (d, J = 2.1 Hz, 1H, H_d), 7.58 (dd, J = 8.5, 2.1 Hz, 1H, H_c)
G2-OH*	6.33-6.88 (m, 6H, H_g), 7.88 (d, J = 8.8 Hz, 2H, H_b), 8.25 (d, J = 8.8 Hz, 2H, H_a)	3.66 (m, 16H, $C\underline{H}_2OH$), 3.76 (s, 3H, OCH_3), 3.85 (m, 4H, NCH_2), 3.96 (m, 16H, CH_2OAr), 4.25 (m, 8H, OH), 4.41 (m, 4H, CH_2OCO), 4.48 (m, 8H, CH_2OAr), 4.84 (m, 8H, CH_2OCO), 6.92-6.99 (m, 12H, H_f), 7.20 (d, J = 8.4 Hz, 1H, H_e), 7.38 (d, J = 2.1 Hz, 1H, H_d), 7.53 (dd, J = 8.4, 2.1 Hz, 1H, H_c)
G3-THP	4.61 (m, 16H, OCHO), 6.58-6.75 (m, 14H, H_g), 7.83 (d, J = 8.9 Hz, 2H, H_b), 8.18 (d, J = 8.9 Hz, 2H, H_a)	1.40-1.75 (m, 96H, THP), 3.40-4.22 (m, 131H, OCH_2, NCH_2, OCH_3, CH_2OCO), 4.41-4.55 (m, 24H, CH_2OCO), 6.94-7.16 (m, 29H, H_f, H_e), 7.47 (d, J = 2.3 Hz, 1H, H_d), 7.58 (m, 1H, H_c)
G3-OH*	6.68-6.84 (m, 14H, H_g), 7.79 (d, J = 8.7 Hz, 2H, H_b), 8.16 (d, J = 8.7 Hz, 2H, H_a)	3.61 (m, 32H, $C\underline{H}_2OH$), 3.68 (s, 3H, OCH_3), 3.75 (m, 4H, NCH_2), 3.90 (m, 32H, CH_2OAr), 4.16-4.19 (m, 28H, CH_2OCO, CH_2OAr), 4.46 (m, 24H, CH_2OCO), 4.80 (m, 16H, OH), 6.99-7.10 (m, 28H, H_f), 7.12 (m, 1H, H_e), 7.29 (m, 1H, H_d), 7.43 (m, 1H, H_c)

* in DMSO-d_6

3. Conclusions

Polyester type dendrimers containing azobenzene are synthesized up to third generation. The best method to assemble dendrimer is repetition of two following steps: esterification of polyhydroxylcompound (**Ia, G1-OH**, **G2-OH** or **G3-OH**) with acid (**IIa**) ensured by *N,N'*-dicyclohexylcarbodiimide under catalysis of 4-(*N,N*-dimethyl)aminopyridine in absolute CH_2Cl_2, and removing of THP protecting group by hydrolysis with HCl in CH_2Cl_2/EtOH. Both steps give good yields decreasing with number of generation because of greater possibility of incomplete reactions with the growth of number of terminal groups. Structures of all dendrimers are approved by IR and ^{1}H NMR spectroscopy.

4. Experimental Section

Starting materials were purchased from Acros. Following substances were synthesized by literature methods: *N,N*-bis(2-hydroxyethyl)-2-metoxyaniline [17], methyl 3,5-bis(2-hydroxyethoxy)benzoate (**IVb**) [18], methyl 3,5-dihydroxybenzoate (**III**) [19]. CH_2Cl_2 was distilled from P_2O_5. Toluene was distilled from sodium. Purity of all compounds was checked by TLC method on Merck F_{254} silica plates. The spots were visualised when necessary in UV light and in iodine vapour. Chromatographic separations were carried out on silica gel (Merck). Melting points were taken on a Stuart SMP10 apparatus, DSC curves were taken on Mettler DSC-300 apparatus, samples were scanned at a heating rate 10 °C/min. IR spectra were recorded with Nicolet 5700 FT-IR spectrometer dispersing sample in hexachlorobutadiene and mineral oil, UV-Vis spectra were recorded with Perkin Elmer Lambda 35 spectrometer, and ^1H NMR spectra were obtained on a Varian Mercury BB 200 MHz spectroscope against TMS as internal reference.

4-[*N,N*-bis(2-hydroxyethyl)amino]-3-methoxy-4'-nitroazobenzene (Ia). 4-Nitroaniline (10.5 g, 0.076 mol) was dissolved in hot (80-90 °C) diluted HC1 (27 mL conc. HCl + 110 mL of water). The solution was poured onto 240 g of crushed ice. After additional cooling in an ice bath, a solution of $NaNO_2$ (5.30 g, 0.076 mol) in 65 mL of water was added at such a rate as to prevent temperature from rising above +5 °C. After the addition was complete, stirring was continued for 1 h at 0-5 °C then filtered. This p-nitrobenzenediazonium chloride solution was added dropwise at 0-5 °C to the solution of *N,N*-bis(2-hydroxyethyl)-2-metoxyaniline (16.03 g, 0.076 mol) in 26 mL of acetic acid, 13 mL of water and 13 g of sodium acetate trihydrate. If necessary a 10% solution of sodium acetate was added to hold pH 4-5. After 2 h the reaction mixture was refrigerated overnight. The mixture was filtered, washed with water till neutral pH and dried to afford 19.26 g of crude product, which was recrystallized from ethyl acetate. Yield 14.58 g (53%), m.p. 115-116 °C. ^1H NMR ($CDCl_3$) δ = 2.91 (bs, 2H, OH), 3.46 (m, 4H, NCH_2), 3.68 (m, 4H, CH_2O), 3.84 (s, 3H, OCH_3), 7.07 (d, J = 8.3 Hz, 1H, Ar), 7.48 (d, J = 2.1 Hz, 1H, Ar), 7.66 (dd, J = 8.3, 2.1 Hz, 1H, Ar), 7.88 (d, J = 8.6 Hz, 2H, Ar), 8.24 (d, J = 8.6 Hz, 2H, Ar).

4-[*N,N*-bis(2-bromoethyl)amino]-3-methoxy-4'-nitroazobenzene (Ib). Azocompound **Ia** (1.8 g, 5 mmol) was dissolved in dry CH_2Cl_2 (75 mL) and cooled in an ice bath. Diisopropylethylamine (DIPEA) (2.45 mL, 15 mmol) was added and during 1 h mesylchloride (0.85 mL, 11 mmol) was added dropwise while stirring. Reaction mixture was stirred another 2 h, and then washed with saturated soda solution and water. Solution was dried over Na_2SO_4, filtered, and evaporated. Resulting red oil was dissolved in DMF (12.5 mL) and powdery NaBr (5 g, 48 mmol) was added, mixture was heated at 80 °C over 1½ h while stirring, and then cooled to room temperature and water was added to form precipitate. Mixture was refrigerated overnight, then filtered and washed with water. Crude product was recrystallized from acetone to give yield 1.35 g (59%) of product, m.p. 146-149 °C. ^1H NMR ($CDCl_3$) δ = 3.46 (t, J = 7.3 Hz, 4H, CH_2Br), 3.75 (t, J = 7.3 Hz, 4H, NCH_2), 3.95 (s, 3H, OCH_3), 7.01 (d, J = 8.2 Hz, 1H, Ar), 7.49 (d, J = 2.0 Hz, 1H, Ar), 7.62 (dd, J = 8.2, 2.0 Hz, 1H, Ar), 7.97 (d, J = 8.6 Hz, 2H, Ar), 8.35 (d, J = 8.6 Hz, 2H, Ar).

4-[*N,N*-bis(2-acetoxyethyl)amino]-3-methoxy-4'-nitroazobenzene (Ic). Azocom-pound **Ia** (0.23 g, 0.62 mmol) was dissolved in 4 mL of absolute THF, acetylchloride (0.10 mL, 1.36 mmol) and DIPEA (0.33 mL, 1.86 mmol) were added and mixture was heated for 48 h. Reaction mixture was cooled and washed with saturated Na_2CO_3 and water, dried over

Na_2SO_4, evaporated and recrystallized from EtOH/hexanes to give yield 0.22 g (81%) of red powder, m.p. 88-89 °C. ^{1}H NMR ($CDCl_3$) δ = 1.95 (s, 6H, $COCH_3$), 3.59 (t, *J* = 6.0 Hz, 4H, NCH_2), 3.89 (s, 3H, OCH_3), 4.20 (t, *J* = 6.0 Hz, 4H, CH_2O), 7.00 (d, *J* = 8.5 Hz, 1H, Ar), 7.42 (d, *J* = 2.1 Hz, 1H, Ar), 7.57 (dd, *J* = 8.5, 2.1 Hz, 1H, Ar), 7.91(d, *J* = 9.0 Hz, 2H, Ar), 8.29 (d, *J* = 9.0 Hz, 2H, Ar).

2-(2-Chloroethoxy)-tetrahydro-*2H*-pyran. A modified procedure [20] was used. To a solution of 2-chloroethanol (27.1 mL, 0.4 mol) in dry CH_2Cl_2 (50 mL) catalyst pyridinium *p*-toluenesulfonate (1.58 g, 0.008 mol) was added. The mixture was cooled in an ice bath and a solution of 3,4-dihydro-2*H*-pyran (40 mL, 0.44 mol) in dry CH_2Cl_2 (35 mL) was added dropwise. Resulting solution was let for 2 days at room temperature. The reaction mixture was washed with cool saturated $NaHCO_3$ solution (3 x 40 mL) and cool brine (3 x 40 mL), dried over Na_2SO_4, filtered then evaporated and distilled at 85-86 °C/20 mmHg. Yield 56.65 g (86%).

3,5-Bis(2-(tetrahydro-2*H*-pyran-2-yloxy)ethoxy)benzoic acid (IIa). A modified procedure [18] was used. NaH (6.12 g, 0.153 mol, 60% in mineral oil) was added to a solution of compound **III** (12.00 g, 0.071 mol) in 90 mL of DMF, and the mixture was heated at 110 °C for 2 h, cooled to 50 °C, and 2-(2-chloroethoxy)-tetrahydro-2*H*-pyran (24.19 mL, 0.162 mol) was added while stirring. After 5 days at 50 °C the mixture was cooled to room temperature, centrifuged and filtered through Celite, and concentrated in vacuum. The resulting yellow oil was dissolved in minimal amount of EtOH and solution of NaOH (8.40 g, 0.21 mol) in EtOH was added. Resulting solution was let for 4 days at room temperature. Ethanol was evaporated and resulting oil was dissolved in water, then washed with MTBE and cooled in ice bath. Cool 5-8% HCl solution was added dropwise while vigorously stirring and cooling, at pH = 7 oily precipitate was formed, which was extracted with MTBE, dried over Na_2SO_4, evaporated to afford light pink oil, which crystallized. Yield 21.10 g (72%), m.p. 59-60 °C. ^{1}H NMR ($CDCl_3$) δ = 1.48 - 1.92 (m, 12H, THP), 3.50 - 4.23 (m, 12H, CH_2O), 4.72 (t, *J* = 2.9 Hz, 2H, OCHO), 6.78 (t, *J* = 2.4 Hz, 1H, Ar), 7.28 (d, *J* = 2.4 Hz, 2H, Ar). Anal. calc. (%) for $C_{21}H_{30}O_8$: C 61.45; H 7.37. Found (%): C 59.19; H 5.92.

3,5-Bis(2-hydroxyethoxy)benzoic acid (IIb). Compound **IVb** (1.00 g, 3.9 mmol) was suspended in minimal amount of EtOH and water-solution of NaOH (0.23 g, 5.8 mmol) was added. After two days at room temperature solvent was evaporated, residue greenish-brown oil was dissolved in water and treated with HCl solution (16-18%) until acidic pH. Crystallization occurs and mixture was put in refrigerator overnight, then filtered and washed with cold water. Crude product was recrystallized from ethyl acetate to afford sand-colour crystals. Yield 0.68 g (72%), m.p. 136-139 °C. Anal. calc. (%) for $C_{11}H_{14}O_6$: C 54.54; H 5.83. Found (%): C 54.36; H 5.86.

Synthesis of first generation dendrimer (**G1-OH).** Azocompound **Ib** (0.63 g, 1.3 mmol) was dissolved in abs. toluene (12 mL) at heating, then cooled and a suspension of acid **IIb** (0.68 g, 2.8 mmol) and of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.42 mL, 2.8 mmol) in abs. toluene (10 mL) was added. Reaction mixture was heated at 80 °C for 4 days. Red precipitate formed, which was separated and washed with water and EtOAc, then recrystallized twice from EtOH to give yield 0.18 g (40%) of product in red crystals, m.p. 148-9 °C.

First generation dendrimer with THP protective groups (G1-THP) and general procedure for ester formation. To a solution of azocompound **Ia** (0.97 g, 2.7 mmol) and of acid **IIa** (2.48 g, 6.0 mmol) in dry CH_2Cl_2 (16 mL) was added catalyst 4-(*N,N*-dimethyl)aminopyridine (0.06 g, 0.5 mmol) while stirring in ice bath, a solution of *N,N'*-dicyclohexylcarbodiimide (DCC) (1.24 g, 6.0 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise over ½ hour. Reaction mixture was stirred for 2 days at room temperature, then monitored by TLC (eluent ethyl acetate) product **G1-THP** $R_f = 0.7$, reagent **Ia** $R_f = 0.13$. In case of uncompleted reaction mixture may be stirred for another day or more of reagent **IIa** and of DCC added to it. When reaction is complete flask was put in freezer for all *N,N'*-dicyclohexylurea to crystallize, then filtered and evaporated. The crude product was purified by silica gel chromatography, eluted with EtOAc/CH_2Cl_2 (2/1), substance was loaded onto column in CH_2Cl_2 solution. Yield 2.84 g (92%) of red **G1-THP**. Anal. calc. (%) for $C_{59}H_{76}N_4O_{19}$: C 61.88; H 6.69; N 4.89. Found (%): C 61.73; H 6.66; N 4.56.

Second generation dendrimer (G2-THP). The crude product was purified by chromatography on silica gel by gradient elution starting with pure CH_2Cl_2 and finishing with EtOAc/CH_2Cl_2 (4/1). Yield 84%. Anal. calc. (%) for $C_{123}H_{156}N_4O_{43}$: C 62.11; H 6.61; N 2.36. Found (%): C 62.17; H 6.77; N 2.62.

Third generation dendrimer (G3-THP). Acid **IIa** and DCC were taken 1.5 equivalents to **G2-OH** dendrimer. The crude product was not fully evaporated from CH_2Cl_2, then mixed with MTBE and stirred briefly; the red dendrimer precipitates from the solution that contains colourless by-products and excess of reagent **IIa**. This procedure may be repeated. Following purification carried out by silica gel chromatography by gradient elution with EtOAc/CH_2Cl_2 (2/1 increasing to 5/1), yield 77%. Anal. calc. (%) for $C_{251}H_{316}N_4O_{91}$: C 62.22; H 6.57; N 1.16. Found (%): C 61.99; H 6.80; N 1.03.

First generation dendrimer with free OH groups (G1-OH) and general procedure for the removal of THP protective group. Dendrimer **G1-THP** (1.67 g, 1.5 mmol) was dissolved in mixture of CH_2Cl_2 and of EtOH (1:3), 6 mL of conc. HCl (0.5 mL conc. HCl for 0.5 mmol of THP group) was added, after 6 h neutralized with solution of sat. $NaHCO_3$. Resulting 2 layers were separated; organic part was washed with solution of sat. $NaHCO_3$ and distilled water, then dried over Na_2SO_4, evaporated and recrystallized from EtOH. Purity was controlled by TLC (eluent ethyl acetate/acetone 7/3), product $R_f = 0.13$. Yield of dendrimer **G1-OH** was 0.77 g (75%), m.p. 148-149 °C. Anal. calc. (%) for $C_{39}H_{44}N_4O_{15}$: C 57.92; H 5.48; N 6.93. Found (%): C 57.09; H 5.53; N 6.74.

Second generation dendrimer (G2-OH). Yield 72%, m.p. 102-109 °C. Anal. calc. (%) for $C_{83}H_{92}N_4O_{35}$: C 58.45; H 5.44; N 3.28. Found (%): C 56.93; H 5.56; N 3.10.

Third generation dendrimer (G3-OH). Hydrolysis reaction was taking 2 days, precipitate forms during neutralization, which were filtered, giving yield 57%, m.p. 99-100 °C. Anal. calc. (%) for $C_{171}H_{188}N_4O_{75}$: C 58.69; H 5.42; N 1.60. Found (%): C 56.23; H 5.47; N 1.43.

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Laipniece L., Kreicberga J., Kampars V. Azobenzola kodola poliestera tipa dendrimēru diverģentā sintēze. *Poliestera tipa dendrimēri sintezēti līdz trešajai ģenerācijai, par kodola molekulu izmantojot 4-N,N-bis(2-hidroksietil)amino-3-metoksi-4'-nitroazobenzolu un zarojumu veidojot no 3,5-bis(2-(tetrahidro-2H-piran-2-iloksi)etoksi)benzoskābes. Dendrimēra augšanas solis tika veikts ar dicikloheksilkarbodiimīdu absolūta* CH_2Cl_2 *šķīdumā, kā katalizatoru izmantojot 4-N,N-dimetilaminopiridīnu. Aizsarggrupu noņemšana veikta* $EtOH/CH_2Cl_2$ *šķīdumā ar HCl. Abi soļi dod labus iznākumus, kuri samazinās, pieaugot dendrimēra ģenerācijai, jo ir lielāka nepilnīgu reakciju iespējamība, palielinoties reaģētspējīgo grupu skaitam.*

Laipniece L., Kreicberga J., Kampars V. Divergent synthesis of polyester type dendrimers containing azobenzene in the core. *Polyester type dendrimers have been synthesized up to third generation using 4-[N,N-bis(2-hydroxyethyl)amino]-3-methoxy-4'-nitroazobenzene as core molecule and 3,5-bis[2-(tetrahydro-2H-pyran-2-yloxy)ethoxy]benzoic acid as branching unit. Growth of dendrimer was ensured by dicyclohexylcarbodiimide under catalysis of 4-N,N-dimethylaminopyridine in dry* CH_2Cl_2*, followed by deprotection of THP groups in* $EtOH/CH_2Cl_2$ *solution with HCl. Both steps give good yields decreasing with number of generation because of greater possibility of incomplete reactions with the growth of number of terminal groups.*

Лайпниеце Л., Крейцберга Я., Кампарс В. Расходящийся синтез полиэфирного типа дендримеров с азобензольным центром. *Синтез полиэфирного типа дендримеров до третьего поколения был осуществлён, используя в качестве центральной молеклы 4-N,N-бис(2-гидроксиэтил)амино-3-метокси-4'-нитроазобензол и 3,5-бис(2-(тетрагидро-2H-пиран-2-илокси)этокси)бензойную кислоту как увеличиваемый блок. Рост дендримера протекает с дициклогексилкарбодиимидом в растворе абсолютного* CH_2Cl_2 *в присудствие катализатора 4-N,N-диметиламинопиридина. Снятие защитных групп проводят в растворе* $EtOH/CH_2Cl_2$ *с помощью HCl. Оба этапа дают хорошие выхода, которые снижаются с увеличением поколения дендримера, поскольку увеличивается возможность протекания реакций не до конца с увеличением числа реакционноспособных групп.*