SYNTHESIS OF NEW AB_2 MONOMERS FOR POLYMERIZATION TO HYPERBRANCHED POLYMERS BY 1,3-DIPOLAR CYCLOADDITION

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Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday in recognition of his outstanding contributions to the area of supramolecular chemistry.

A number of AB_2 monomers containing either one azide and two acetylene functions or vice versa have been prepared. Upon polymerization, these compounds were found to give rise to hyperbranched oligomers as detected by NMR spectroscopy. However, the formation of high-molecular-weight polymers could not be proven by GPC analysis. Crosslinking was found to be a major drawback of this approach to hyperbranched polymers. Two examples of the interesting situation in which the polymerization already starts during the introduction of the polymerizable group are described.
Keywords: Hyperbranched polymers; Dendrimers; Alkynes; Azides; 1,2,3-Triazoles; 1,3-Dipolar cycloadditions.

Hyperbranched polymers are of great interest as more readily available substitutes for dendrimers[1]. While the latter are very costly to prepare, the former can be obtained in a single polymerization step. Consequently, hyperbranched polymers are characterized by a broad molecular weight distribution and a degree of branching which is typically around 0.5 (instead of 1 in dendrimers). A large number of monomers have been polymerized to yield hyperbranched polymers[1]. In particular polycondensation of AB_n monomers has been very popular but also the use of the so-called inimers, molecules bearing a polymerizable and an initiating function at the same time, has been studied in detail[2]. Our group has been studying 1,3-dipolar cycloaddition reactions and has applied these reactions to the synthesis of molecules which are of particular interest in supramolecular chemistry[3]. In this paper, we present a preliminary study on the use of the 1,3-dipolar

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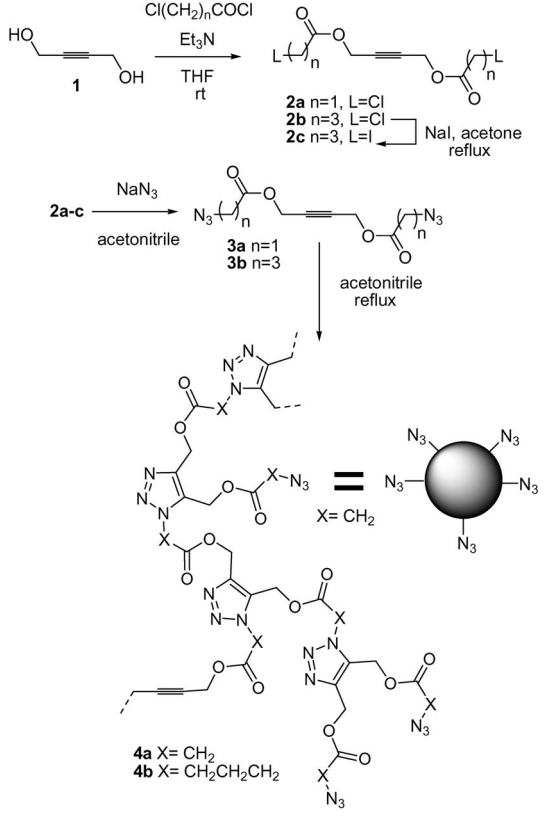
cycloaddition of acetylenes and azides to afford hyperbranched polytriazoles. Depending on the design of the used AB_2 monomers, having either one acetylene and two azide moieties or vice versa, hyperbranched polymers with azide or acetylene periphery could be obtained. The periphery of these species could readily be modified applying the very rich acetylene or azide chemistry. This is of high importance as the nature of the periphery dramatically influences physical properties such as solubility and glass transition temperature of hyperbranched polymers[1]. Furthermore, the hyperbranched polytriazoles could be of interest as cation-complexing agents.

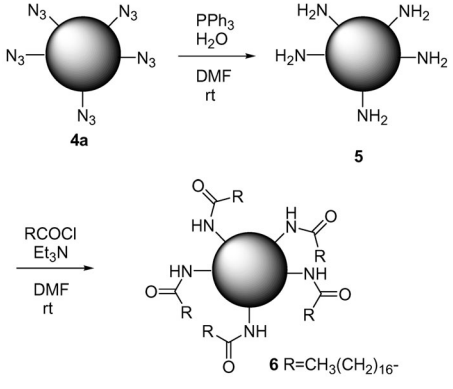
In order to keep the chemistry as simple as possible, readily available and cheap chemicals were used and high-yield reactions applied. In the first approach, but-2-yne-1,4-diol (**1**) was esterified with chloroacetyl chloride in the presence of triethylamine yielding bis(chloroacetate) **2a**, which could be converted to the diazide **3a** by substitution with sodium azide at room temperature in DMF (Scheme 1). First, the polymerization of **3a** was per-



SCHEME 1

formed in 1,2-dichloroethane resulting in a precipitation of oligomers **4a**. Hence, the solvent was changed to acetonitrile in which the hyperbranched molecules **4a** proved soluble, stressing their high polarity. To isolate the product, the solvent was simply evaporated under reduced pressure. The residue obtained was analyzed by ^{1}H NMR spectroscopy in DMSO-d_6. A set of singlets around 5.3 ppm is observed, which is characteristic of CH_2 groups in different microenvironments at N-1 of the triazole units. Singlets around 5.5 ppm can be attributed to the CH_2 groups at C-4 and C-5 of the triazole cores. These observations, together with the disappearance of the signals of CH_2 groups of the monomer (δ 4.85 and 3.94 ppm) clearly indicate that the polymerization has proceeded. However, molecular weights significantly higher than those of oligomers could not be detected by GPC or ES MS.

After a few days of storage, crosslinking of the solid oligomer occurred resulting in a formation of insoluble fraction. This crosslinking is likely to result from the decomposition of azide groups giving rise to highly reactive nitrenes. In order to avoid this side reaction, we converted the oligomer **4a** with peripheral azide functions into the corresponding amine **5** by treatment with triphenylphosphine in DMF with 5% of water (Scheme 2). The resulting polyamine was in situ acylated with stearoyl chloride and triethylamine. It was not possible to separate the obtained hyperbranched oligomer **6** from the stearic acid formed upon hydrolysis of the reaction mixture. However, the disappearance of the azide group absorption at 2112 cm^{-1} (asymmetric stretch) and the presence of the amide absorption at 1671 cm^{-1} in the IR spectrum clearly indicated that the acylation was successful. This was confirmed by the fact that **6** turned out to be well soluble in halogenated solvents such as dichloromethane and chloroform, in contrast to the initial azide.

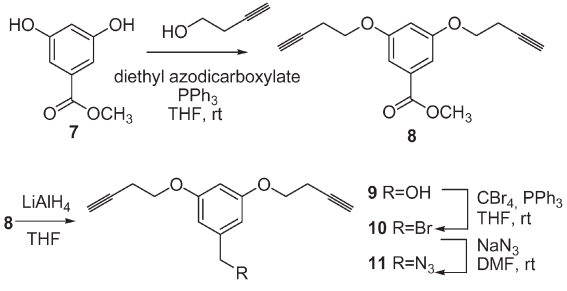


SCHEME 2

Analogously, bis(chlorobutanoate) **2b** was prepared (Scheme 1). As the primary 3-chloropropyl groups are far less reactive in the substitution reaction with azide, this reaction had to be performed at elevated temperature (in refluxing acetonitrile), obviously resulting in a formation of oligomers of type **4b**. This could be of great interest as such cases where the polymerization occurs concomitantly with the introduction of the polymerizable group have not been described before in the literature concerning hyperbranched polymers. In order to prepare diazide **3b** without an interference of the cycloaddition, we prepared the diiodide **2c** under Finkelstein conditions. However, substitution of diiodide **2c** with azide turned out to require elevated temperatures as well and, in consequence, also resulted in a concomitant polymerization.

The presence of a set of singlets at 5.4 ppm in the ^{1}H NMR spectrum, which can be attributed to CH_2 groups at N-1 of the triazole units, clearly shows that polymerization has occurred. Oligomers up to the hexamer could be detected by ES MS. Unfortunately, the GPC data showed only low-molecular-weight species, which is again contradictory to the NMR data.

In the cases of the two oligomers described above, isolation by precipitation proved to be very difficult as a sticky oil was obtained, presumably because the glass transition temperature of these "polymers" is far below room temperature. Therefore, we turned our attention to monomers containing benzene rings as we reasoned that the glass transition temperature could increase dramatically upon introduction of aromatic rings. Moreover, we designed a monomer containing one azide and two acetylene groups in order to prepare a polymer with acetylene end groups to avoid the aforementioned crosslinking reactions. Therefore, methyl 3,5-dihydroxybenzoate (**7**) was allowed to react with but-3-yn-1-ol under Mitsunobu conditions resulting in bisacetylene **8** (Scheme 3). After reduction with $LiAlH_4$, the resulting benzyl alcohol **9** was brominated using CBr_4 and triphenylphosphine. The obtained bromide **10** easily underwent conversion to azide

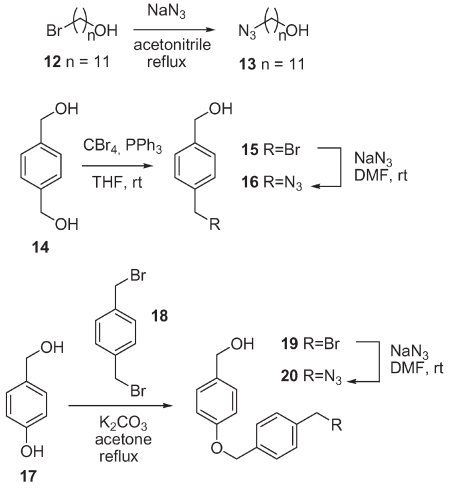


SCHEME 3

11 by treatment with NaN_3 in DMF at room temperature, allowing the preparation of this monomer without interference of cycloaddition reactions. Polymerization of monomer **11** was carried out in 1,2-dichloroethane under reflux. Again, ^1H NMR spectrum of the resulting product revealed the presence of CH_2 groups connected to N-1 nitrogens of triazole units (set of singlets at 5.4 ppm). Unfortunately, this could not be confirmed by GPC measurements.

Since we found that nonactived acetylenes are not reactive enough to yield high-molecular-weight hyperbranched polymers, we turned our attention to acetylenedicarboxylates, which are known to undergo cycloaddition with azides far more readily. As both azide anions and organic azides readily react with acetylenedicarboxylate, we reasoned that protection of the acetylene grouping is necessary. Conversion to dibromofumaric moiety was chosen as the protecting reaction as this moiety can readily be converted to the acetylenedicarboxylate by treatment with zinc in THF in the presence of a catalytic amount of iodine[4]. Since the substitution with azide anions on a substrate containing the dibromofumaric moiety was anticipated to be problematic, a number of azidoalcohols was prepared in order to couple them with dibromofumaric acid under Mitsunobu conditions.

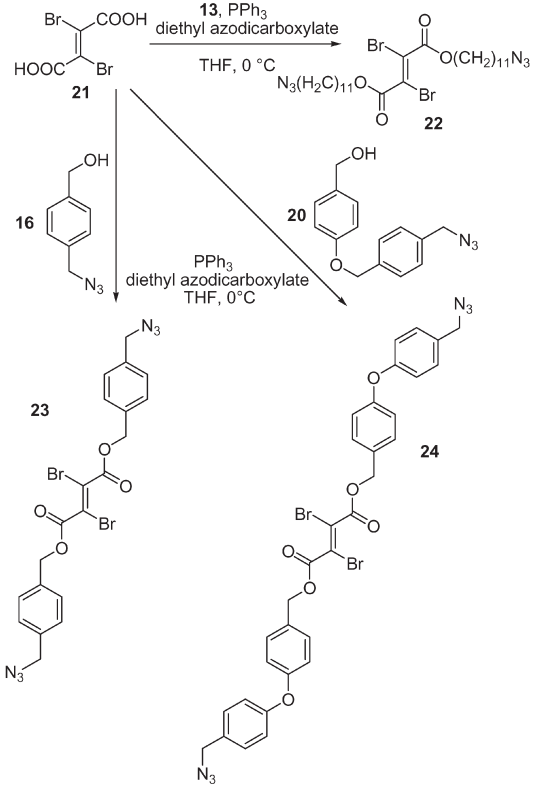
Three bromoalcohols were prepared. The first one had a long aliphatic spacer which was expected to facilitate polymerization due to lowering steric hindrances and to yield rather nonpolar polymers. Therefore, 11-azidoundecan-1-ol (**13**) was prepared by simple treatment of the corresponding commercial bromide **12** with sodium azide in refluxing acetonitrile (Scheme 4). 4-(Azidomethyl)benzyl alcohol (**16**) was obtained by



SCHEME 4

monobromination of benzene-1,4-dimethanol **14** and subsequent substitution of the resulting bromide **15** by azide in DMF at room temperature. Finally, azidoalcohol **20** was prepared by alkylation of 4-hydroxybenzyl alcohol (**17**) with 1,4-bis(bromomethyl)benzene (**18**) followed by treatment of the resulting monobromide **19** with NaN_3 under similar conditions.

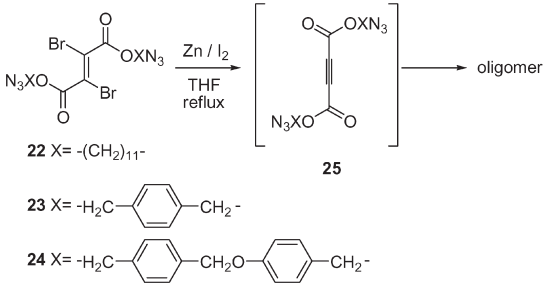
Dibromofumaric acid[5] (**21**) could readily be esterified with each of these azidoalcohols under Mitsunobu conditions resulting in the protected AB_2 monomers **22**–**24** (Scheme 5). To avoid formation of the iminophosphorane, triphenylphosphine was added to an ice-cool solution of the other reagents.



SCHEME 5

As the deprotection of the resulting protected monomers **22**–**24** was carried out in refluxing THF, it was impossible to isolate acetylenedicarboxylic esters **25** (active AB_2 monomers), because a polymerization already started during the deprotection step (Scheme 6). After 24 h reflux in the presence of zinc, the solid was filtered off and the residue was concentrated under re-

duced pressure. However, we found that the materials obtained underwent rapid crosslinking, so as only oligomers of **24** could be investigated by NMR spectroscopy. A broad singlet at 6.1 ppm, characteristic of the benzylic CH_2 group attached to N-1 of triazole units clearly indicated that polymerization occurred. Unfortunately, GPC measurements did not show any components with significantly high molecular weights. The disagreement observed in all cases between NMR and GPC data can be explained by the smaller hydrodynamic volume of hyperbranched as compared to linear polymers.



SCHEME 6

In conclusion, we found that it is possible to synthesize AB_2 monomers bearing one acetylene and two azide functionalities or vice versa which undergo oligomerization by 1,3-dipolar cycloaddition. This approach, however, suffers from several drawbacks such as crosslinking of obtained hyperbranched macromolecules and low molecular weight of a soluble polymer fraction. An interesting feature of this approach is the concomitant polymerization upon introduction of the polymerizable group. Recently, a copper(I)-catalyzed cycloadditon of azides and terminal acetylenes was described[6]. At present, the application of this procedure to the synthesis of hyperbranched polytriazoles is under investigation.

EXPERIMENTAL

But-2-yne-1,4-diyl Bis(chloroacetate) (**2a**)

Chloroacetyl chloride (25 g, 0.22 mol) was added dropwise during 15 min to a stirred solution of but-2-yne-1,4-diol (**1**; 8.6 g, 0.10 mol) and Et_3N (23 g, 0.22 mol) in dry THF (300 ml) at 0 °C under argon. The resulting suspension was stirred at room temperature for 30 min. The mixture was filtered and the precipitate was washed with diethyl ether (2 × 100 ml). Combined filtrates were washed with brine (2 × 100 ml) and 1 M hydrochloric acid (2 × 100 ml) saturated with NaCl. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuum. Bis(chloroacetate) **2a** was obtained as an oil in 82% yield. IR: 2951,

2552, 2112, 1753, 1426, 1380, 1340, 1178, 977. ^{1}H NMR (300 MHz, $CDCl_3$): 4.81 s, 4 H (CH_2O); 4.10 s, 4 H (CH_2Cl). ^{13}C NMR (75 MHz, $CDCl_3$): 167.1, 80.8, 53.6, 40.8.

But-2-yne-1,4-diyl Bis(4-chlorobutanoate) (**2b**)

4-Chlorobutanoyl chloride (31 g, 0.22 mol) was added dropwise during 15 min to a stirred solution of but-2-yne-1,4-diol (**1**; 8.6 g, 0.10 mol) and Et_3N (23 g, 0.22 mol) in dry THF (300 ml) at 0 °C under argon. The resulting suspension was stirred at room temperature for 30 min. The mixture was filtered and the precipitate was washed with diethyl ether (2 × 100 ml). Combined filtrates were washed with brine (2 × 100 ml) and 1 M hydrochloric acid (2 × 100 ml) saturated with NaCl. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuum. The bis(chlorobutanoate) **2b** was obtained as an oil in 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 4.74 s, 4 H (CH_2O); 3.60 t, 4 H, J = 6.6 (CH_2Cl); 2.55 t, 4 H, J = 6.9 (CH_2COO); 2.11 m, 4 H ($CH_2C\mathbf{H}_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): 172.3, 81.1, 52.6, 44.3, 31.3, 27.9.

But-2-yne-1,4-diyl Bis(4-iodobutanoate) (**2c**)

A solution of bis(chlorobutanoate) **2b** (10 g, 34 mmol) and sodium iodide (11.5 g, 77 mmol) in acetone (120 ml) was heated at reflux temperature under argon for 48 h. The reaction mixture was cooled to room temperature and evaporated in vacuum. Water (50 ml) was added and the mixture was extracted with diethyl ether (2 × 50 ml). Combined organic layers were dried over anhydrous magnesium sulfate and evaporated. The diiodide **2c** was obtained as an oil in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 4.73 s, 4 H (CH_2O); 3.25 t, 4 H, J = 7.0 (CH_2I); 2.51 t, 4 H, J = 7.0 (CH_2COO); 2.15 m, 4 H ($CH_2C\mathbf{H}_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): 171.9, 81.2, 52.6, 34.9, 28.7, 5.64.

But-2-yne-1,4-diyl Bis(azidoacetate) (**3a**)

A solution of bis(chloroacetate) **2a** (10 g, 42 mmol) and sodium azide (6.0 g, 92 mmol) in DMF (80 ml) was stirred at room temperature for 24 h under argon atmosphere. The mixture was poured into water (250 ml) and extracted with diethyl ether (3 × 100 ml). Combined ether layers were washed with water (3 × 100 ml), dried over anhydrous magnesium sulfate and evaporated in vacuum. After column chromatography over silica gel (CH_2Cl_2), diazide **3a** was obtained as an oil in 72% yield. IR: 2951, 2552, 2112, 1753, 1426, 1380, 1340, 1178, 977. ^{1}H NMR (300 MHz, $CDCl_3$): 4.85 s, 4 H (CH_2O); 3.94 s, 4 H (CH_2N_3). ^{13}C NMR (75 MHz, $CDCl_3$): 168.0, 81.1, 53.5, 50.5.

Methyl 3,5-Bis(but-3-yn-1-yloxy)benzoate (**8**)

To an ice-cool solution of methyl 3,5-dihydroxybenzoate (3.0 g, 18 mmol) and but-3-yn-1-ol (3.1 g, 45 mmol) in dry THF (100 ml) under argon atmosphere was added diethyl azodicarboxylate (7.8 g, 45 mmol) and triphenylphosphine (11.7 g, 45 mmol). After 15 min stirring at room temperature, water was added (100 ml) and the mixture was extracted with dichloromethane (3 × 50 ml). Combined organic layers were dried over anhydrous magnesium sulfate and evaporated in vacuum. The diacetylene **8** was obtained as a sticky oil in 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 7.20 d, 2 H, J(2,4) = 2.2 (H-2,6); 6.68 t, 1 H, J(2,4) = 2.2 (H-4); 4.11 t, 4 H, J = 6.9 (CH_2O); 3.90 s, 3 H (OCH_3); 2.69 dt, 4 H, J_1 = 6.9, J_2 = 2.7 (CH_2CH_2O);

2.05 s, 2 H, *J* = 2.7 (HCC). ^{13}C NMR (75 MHz, $CDCl_3$): 166.6, 159.4, 132.1, 108.1, 106.9, 80.2, 70.0, 66.2, 52.2, 19.4.

3,5-Bis(but-3-yn-1-yloxy)benzyl Alcohol (**9**)

A solution of ester **8** (2.0 g, 8.2 mmol) in dry THF (20 ml) was added to an ice-cool suspension of $LiAlH_4$ (0.31 g, 8.2 mmol) in dry THF (20 ml) under argon. After complete addition the reaction mixture was stirred at room temperature for 1 h. A solution of 1 M NaOH was added dropwise under ice cooling until a readily filterable precipitate was formed. The precipitate was filtered off and washed with THF (2 × 10 ml). Combined organic layers were dried over magnesium sulfate and evaporated in vacuum. The product **9** was obtained as a sticky oil in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 6.54 d, 2 H, *J*(2,4) = 2.6 (H-2,6); 6.41 t, 1 H, *J*(2,4) = 2.6 (H-4); 4.63 s, 2 H (CH_2OH); 4.08 t, 4 H, *J* = 6.9 (CH_2O); 2.67 dt, 4 H, J_1 = 6.9, J_2 = 2.6 (CH_2CH_2O); 2.05 s, 2 H, *J* = 2.6 (HCC); 1.72 s(br), 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 159.8, 143.5, 105.6, 100.9, 80.3, 69.9, 66.2, 65.2, 19.5.

1-(Bromomethyl)-3,5-bis(but-3-yn-1-yloxy)benzene (**10**)

Alcohol **9** (1.37 g, 5.6 mmol) and triphenylphosphine (2.2 g, 8.4 mmol) were added successively to an ice-cool solution of CBr_4 (2.8 g, 8.4 mmol) in dry THF (50 ml) under argon atmosphere. The mixture was stirred at 0 °C for 10 min, poured in water and extracted with CH_2Cl_2 (2 × 50 ml). Combined organic layers were dried over magnesium sulfate and evaporated in vacuum. The compound **10** was obtained as an oil after column chromatography over silica gel (CH_2Cl_2) in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 6.55 d, 2 H, *J*(2,4) = 2.2 (H-2,6); 6.41 t, 1 H, *J*(2,4) = 2.2 (H-4); 4.40 s, 2 H (CH_2Br); 4.07 t, 4 H, *J* = 7.0 (CH_2O); 2.67 dt, 4 H, J_1 = 7.0, J_2 = 2.9 (CH_2CH_2O); 2.05 s, 2 H, *J* = 2.9 (HCC). ^{13}C NMR (75 MHz, $CDCl_3$): 159.7, 139.8, 108.0, 101.7, 80.2, 70.0, 66.0, 33.4, 19.5.

1-(Azidomethyl)-3,5-bis(but-3-yn-1-yloxy)benzene (**11**)

A mixture of bromide **10** (1.68 g, 5.4 mmol) and NaN_3 (0.55 g, 8.4 mmol) in DMF (50 ml) was stirred at room temperature for 24 h under argon atmosphere. The mixture was poured into water (100 ml) and extracted with diethyl ether (3 × 50 ml). Combined organic layers were dried over magnesium sulfate and evaporated in vacuum. The azide **11** was obtained as a sticky oil in 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 6.48 d, 2 H, *J*(2,4) = 2.2 (H-2,6); 6.44 t, 1 H, *J*(2,4) = 2.2 (H-4); 4.26 s, 2 H (CH_2N_3); 4.00 t, 4 H, *J* = 7.0 (CH_2O); 2.67 dt, 4 H, J_1 = 7.0, J_2 = 2.6 (CH_2CH_2O); 2.05 s, 2 H, *J* = 2.6 (HCC). ^{13}C NMR (75 MHz, $CDCl_3$): 159.9, 137.7, 107.0, 101.4, 80.2, 70.0, 66.1, 54.7, 19.5.

Oligomerization of Monomers **3a** and **11**

A solution of an appropriate monomer **3a** (2 mmol) in acetonitrile or **11** (5 ml) in dichloroethane was refluxed for 4 days. The reaction mixture was evaporated in vacuum. The sticky residue readily underwent crosslinking upon standing.

11-Azidoundecan-1-ol (**13**)

A mixture of 11-bromoundecan-1-ol (**12**; 2.0 g, 8.0 mmol), NaN_3 (0.80 g, 12 mmol) and KI (0.50 g, 3.0 mmol) in acetonitrile was heated at reflux temperature for 48 h under argon. Af-

ter cooling to room temperature, the solvent was evaporated in vacuum, water was added (50 ml) and the mixture was extracted with dichloromethane (3 × 50 ml). Combined organic layers were dried over magnesium sulfate and the solvent was evaporated in vacuum. The title compound was obtained as an oil in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 3.63 t, 2 H, *J* = 6.6 (C**H**$_2$OH); 3.26 t, 2 H, *J* = 6.9 (CH_2N_3); 1.57–1.62 m, 5 H (OH, C**H**$_2$CH$_2$OH, C**H**$_2$CH$_2$N$_3$); 1.27–1.31 m, 14 H (internal CH_2 groups). ^{13}C NMR (75 MHz, $CDCl_3$): 63.5, 52.0, 33.3, 30.0, 29.9, 29.6, 29.3, 27.2, 26.2.

[4-(Bromomethyl)phenyl]methanol (**15**)

To a solution of benzene-1,4-dimethanol (**14**; 3.0 g, 22 mmol) in dry THF (100 ml) were added successively CBr_4 (7.4 g, 22 mmol) and PPh_3 (5.9 g, 22 mmol) at 0 °C under argon. After stirring for 10 min, water was added (100 ml) and the resulting mixture was extracted with dichloromethane (3 × 50 ml). Combined organic layers were dried over magnesium sulfate and evaporated in vacuum. The desired compound **15** was obtained as an oil after column chromatography on silica gel (CH_2Cl_2) in 39% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 7.37 m, 4 H (phenyl); 4.70 d, 2 H (C**H**$_2$OH); 4.50 s, 2 H (CH_2Br); 1.65 s(br), 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 141.2, 137.2, 129.3, 127.3, 64.9, 33.3.

[4-(Azidomethyl)phenyl]methanol (**16**)

A mixture of bromide **15** (0.7 g, 3.5 mmol), NaN_3 (0.3 g, 4.5 mmol) and KI (0.10 g, 0.60 mmol) in DMF (50 ml) was stirred under argon for 2 days. The resulting suspension was poured into water (100 ml) and extracted with diethyl ether (3 × 50 ml). Combined organic layers were dried over magnesium sulfate and evaporated in vacuum. The azidoalcohol **16** was obtained as an oil in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 7.30 m, 4 H (phenyl); 4.63 d, 2 H (C**H**$_2$OH); 4.30 s, 2 H (CH_2N_3); 2.51 s(br), 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 141.5, 135.1, 128.9, 127.9, 65.4, 55.0.

4-{[4-(Bromomethyl)benzyl]oxy}benzyl Alcohol (**19**)

A suspension of 4-hydroxybenzyl alcohol **17** (5.0 g, 40 mmol), 1,4-bis(bromomethyl)benzene (**18**; 21 g, 81 mmol) and K_2CO_3 (6.8 g, 48 mmol) in acetone (100 ml) was refluxed under argon overnight. After cooling to room temperature, the solvent was evaporated in vacuum, water (100 ml) was added and the mixture was extracted with dichloromethane (3 × 50 ml). Combined organic layers were dried over magnesium sulfate and the solvent was evaporated in vacuum. The alcohol **19** was obtained as an amorphous solid after column chromatography over silica gel (CH_2Cl_2/EtOAc, 95:5) in 67% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 7.40 m, 4 H (bromomethylphenyl); 7.28 d, 2 H, *J* = 8.4 (C**H**CCH$_2$OH); 6.95 d, 2 H, *J* = 8.4 (CHCO); 5.06 s, 2 H (CH_2OPh); 4.61 d, 2 H (C**H**$_2$OH); 4.50 s, 2 H (CH_2Br); 1.61 s(br), 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 158.2, 137.6, 137.5, 133.5, 129.3, 128.6, 127.7, 114.9, 69.5, 65.0, 33.1.

4-{[4-(Azidomethyl)benzyl]oxy}benzyl Alcohol (**20**)

A mixture of bromide **19** (3.0 g, 10 mmol), NaN_3 (0.78 g, 12 mmol) and KI (0.50 g, 3.0 mmol) in DMF (80 ml) was stirred under argon atmosphere for 2 days. The resulting suspension was poured into water (100 ml) and extracted with diethyl ether (3 × 50 ml). Combined or-

ganic layers were dried over magnesium sulfate and evaporated in vacuum. The azidoalcohol **20** was obtained as an amorphous solid in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 7.47 d, 2 H, *J* = 8.0 (C**H**CCH$_2$N$_3$); 7.30–7.35 m, 4 H (C**H**CCH$_2$OH and C**H**CCH$_2$OC); 6.97 d, 2 H, *J* = 8.4 (CHCO); 5.09 s, 2 H (CH$_2$OPh); 4.63 d, 2 H (C**H**$_2$OH); 4.36 s, 2 H (CH$_2$N$_3$); 1.57 s(br), 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 158.8, 137.6, 134.0, 129.1, 128.9, 128.3, 115.4, 70.1, 65.5, 55.0.

Esterification of Dibromofumaric Acid with Azidoalcohols **13**, **16** and **20**

To an ice-cool solution of dibromofumaric acid (1.0 g, 3.7 mmol) and an appropriate azidoalcohol (8.8 mmol) in dry THF (20 ml) under argon atmosphere were added successively diethyl azodicarboxylate (1.54 g, 8.8 mmol) and PPh_3 (2.31 g, 8.8 mmol). After stirring at 0 °C for 15 min, water (20 ml) was added and the mixture was extracted with dichloromethane (3 × 25 ml). Combined organic layers were dried over magnesium sulfate and the solvent was evaporated in vacuum. The desired dibromofumarates were purified by column chromatography over silica gel (CH_2Cl_2/petroleum ether, 50:50–80:20).

Bis(11-azidoundecyl) dibromofumarate (**22**). Yield: 66%. ^{1}H NMR (300 MHz, $CDCl_3$): 4.30 t, 4 H, *J* = 7.0 (CH$_2$O); 3.26 t, 4 H, *J* = 7.0 (CH$_2$N$_3$); 1.73 m, 4 H (C**H**$_2$CH$_2$O); 1.60 m, 4 H (CH$_2$CH$_2$N$_3$); 1.27–1.31 m, 28 H (other CH$_2$ groups). ^{13}C NMR (75 MHz, $CDCl_3$): 162.1, 112.5, 67.1, 51.9, 29.8, 29.6, 29.5, 29.3, 28.7, 27.1, 26.2.

Bis[4-(azidomethyl)benzyl] dibromofumarate (**23**). Yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$): 7.38–7.40 m, 8 H (phenyl); 5.31 s, 4 H (CH$_2$O); 4.35 s, 4 H (CH$_2$N$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): 162.4, 136.5, 134.9, 133.3, 129.5, 129.0, 68.7, 54.9.

Bis(4-{[4(-azidomethyl)benzyl]oxy}benzyl) dibromofumarate (**24**). Yield: 66%. ^{1}H NMR (300 MHz, $CDCl_3$): 7.44 d, 4 H, *J* = 8.1 (**CH**CCH$_2$O); 7.31–7.35 m, 8 H (C$_6$**H**$_5$CH$_2$N$_3$); 6.96 d, 4 H, *J* = 8.1 (CHCO); 5.23 s, 4 H (CH$_2$OCO); 5.07 s, 4 H (CH$_2$OPh); 4.34 s, 4 H (CH$_2$N$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): 162.5, 159.5, 137.4, 135.7, 131.0, 128.9, 128.3, 127.3, 115.4, 113.2, 70.1, 69.0, 54.9.

Deprotection and Oligomerization of Dibromofumarates **22–24**

A suspension of zinc powder (0.81 g, 13 mmol) in dry THF (30 ml) was refluxed under argon atmosphere for 15 min. After cooling to room temperature, a solution of an appropriate fumarate (1.3 mmol) in dry THF (20 ml) was added and the reflux was continued under argon for 24 h. The suspension was allowed to cool to room temperature, the precipitate was filtered off with celite and washed with THF (2 × 10 ml) and acetone (2 × 10 ml). The filtrate was dried over magnesium sulfate and the solvent was evaporated in vacuum yielding a sticky mixture of oligomers, which readily crosslinked to give an insoluble material.

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