but no C^2-C^6 cyclization product (detection limit 5%). The 2-aminoquinoline **11** is clearly derived from biradical **10** through hydrogen abstraction, which is indicative of a novel C^2-C^7 biradical cyclization in enyne-carbodiimides.

In conclusion, we have provided theoretical and experimental evidence for two novel biradical cyclizations triggered thermally from enyne-carbodiimides. The C^2-C^6 cyclization pathway via an azafulvene amine biradical is operative with aryl and trimethylsilyl groups at the alkyne terminus, and opens the way to a convenient synthesis of substituted 6*H*-indolo[2,3-*b*]quinolines with interesting pharmacological activity.[18] Conversely, the presence of a hydrogen atom at the alkyne terminus leads to the C^2-C^7 cyclization. The fact that a clean switch between C^2-C^6 and C^2-C^7 cyclizations can now be effected in enyne-allenes, enyne-ketenes, enyne-ketenimines, and enyne-carbodiimides points to a rather general, hitherto little known motif to control the regioselectivity of biradical cyclizations.

Received: March 23, 1998 [Z11625IE]
German version: *Angew. Chem.* **1998**, *110*, 2531 – 2533

Keywords: carbodiimides · cycloaromatizations · diradicals · enynes · quantum chemical calculations

[1] a) M. Schmittel, M. Strittmatter, S. Kiau, *Angew. Chem.* **1996**, *108*, 1952 – 1954; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1843 – 1845; b) B. Engels, C. Lennartz, M. Hanrath, M. Schmittel, M. Strittmatter, *Angew. Chem*. **1998**, *110*, 2067 – 2070; *Angew. Chem. Int. Ed.* **1998**, *37*, 1960 – 1963.

[2] a) A. G. Myers, E. Y. Kuo, N. S. Finney, *J. Am. Chem. Soc.* **1989**, *111*, 8057 – 8059; b) R. Nagata, H. Yamanaka, E. Okazaki, I. Saito, *Tetrahedron Lett.* **1989**, *30*, 4995 – 4998; reviews: c) K. K. Wang, *Chem. Rev.* **1996**, *96*, 207 – 222; d) J. W. Grissom, G. U. Gunawardena, D. Klingberg, D. Huang, *Tetrahedron* **1996**, *52*, 6453 – 6518.

[3] M. Schmittel, M. Strittmatter, K. Vollmann, S. Kiau, *Tetrahedron Lett.* **1996**, *37*, 999 – 1002.

[4] a) T. Gillmann, T. Hülsen, W. Massa, S. Wocadlo, *Synlett* **1995**, 1257 – 1259; b) J. G. Garcia, B. Ramos, L. M. Pratt, A. Rodríguez, *Tetrahedron Lett*. **1995**, *36*, 7391 – 7394.

[5] M. Schmittel, M. Strittmatter, S. Kiau, *Tetrahedron Lett.* **1995**, *36*, 4975 – 4978.

[6] a) M. Schmittel, S. Kiau, *Liebigs Ann.* **1997**, 733 – 736; b) M. Schmittel, M. Maywald, M. Strittmatter, *Synlett* **1997**, 165 – 166; c) M. Schmittel, J.-P. Steffen, I. Bohn, *Heterocycl. Commun*. **1997**, *3*, 443 – 447; d) M. Schmittel, J.-P. Steffen, D. Auer, M. Maywald, *Tetrahedron Lett*. **1997**, *38*, 6177 – 6180; e) Ó. de Frutos, A. M. Echavarren, *Tetrahedron Lett*. **1997**, *38*, 7941 – 7942.

[7] L. D. Foland, J. O. Karlsson, S. T. Perri, R. Schwabe, S. L. Xu, S. Patil, H. W. Moore, *J. Am. Chem. Soc.* **1989**, *111*, 975 – 989.

[8] M. Schmittel, J.-P. Steffen, M. Á. Wencesla Ángel, B. Engels, C. Lennartz, M. Hanrath, *Angew. Chem*. **1998**, *110*, 1633 – 1635; *Angew. Chem. Int. Ed.* **1998**, *37*, 1562 – 1564.

[9] A. Szabo, N. S. Ostlund, *Modern Quantum Chemistry*, Macmillan, New York, **1982**.

[10] To compute the biradical intermediates an individually selecting MR-CI approach was used: a) M. Hanrath, B. Engels, *Chem. Phys.* **1997**, *225*, 197 – 202. The reference space consisted of up to 15 configurations. This led to total MR-CI configuration spaces of more than 500×10^6 configuration state functions (CSFs), whereby the secular equations actually solved were in the order of 5×10^6—8×10^6 CSFs. The influence of the neglected CSFs was estimated by the Buenker – Peyerimhoff extrapolation: b) R. J. Buenker, S. D. Peyerimhoff, *Theor. Chim. Acta* **1975**, *39*, 217 – 228; c) R. J. Buenker, S. D. Peyerimhoff, W. Butscher, *Mol. Phys.* **1978**, *35*, 771 – 791; d) R. J. Buenker, R. A. Phillips, *J. Mol. Struct.* **1985**, *123*, 291 – 300, and references therein. The influence of higher excitations was estimated by the normalized form of the usual Davidson correction: e) J. E. Del Bene, E. A. Stahlberg, I. Shaviatt, *Int. J. Quantum Chem. Symp.* **1990**, *24*, 455 – 466. In these calculations (in the following abbreviated as MR-CI + Q) all 34 valence electrons were correlated. The calculations were performed with the DIESEL-MR-CI program package: f) B. Engels, M. Hanrath: DIESEL-MR-CI (*d*irect *i*nternal *e*xternal separated individually *sel*ecting MR-CI) program package, Universität Bonn, Germany, **1997**. To determine the TSs the energy for fixed C^2-C^7 and C^2-C^6 distances, which represent the reaction coordinates for the C^2-C^7 and C^2-C^6 cyclizations, respectively, was computed. In these calculations all other geometrical parameters were optimized. These calculations were performed with the Gaussian94 program package[10g] and the Turbo-Mol program:[10h, i] g) M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Pittsburgh, PA, **1995**; h) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165 – 169; i) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346 – 354.

[11] The MR-CI computations for **1f**, **3f** (R = Ph) were too demanding. Hence, we estimated ΔE^r for **2f** → **1f**, **3f** using an increment derived from the corresponding enyne-allene cyclization reaction energies.[1b]

[12] a) M. Schmittel, M. Keller, S. Kiau, M. Strittmatter, *Chem. Eur. J.* **1997**, *3*, 807 – 816; b) P. Chen, *Angew. Chem*. **1996**, *108*, 1584 – 1586; *Angew. Chem. Int. Ed. Engl*. **1996**, *35*, 1478 – 1480.

[13] S. Kubota, K. Horie, H. K. Misra, K. Toyooka, M. Uda, M. Shibuya, H. Terada, *Chem. Pharm. Bull.* **1985**, *33*, 662 – 666.

[14] J. B. Fell, G. M. Coppola, *Synth. Commun.* **1995**, *25*, 43 – 47.

[15] Two examples for the pericyclic reactivity of in situ generated enyne-carbodiimides (starting with the corresponding iminophosphoranes) are known: a) M. Alajarín, P. Molina, A. Vidal, *J. Nat. Prod.* **1997**, *60*, 747 – 748; b) P. Molina, M. Alajarín, A. Vidal, P. Sánchez-Andrada, *J. Org. Chem.* **1992**, *57*, 929 – 939.

[16] T. Saito, H. Ohmori, T. Ohkubo, S. Motoki, *J. Chem. Soc. Chem. Commun.* **1993**, 1802 – 1803.

[17] R. Brückner, R. Huisgen, J. Schmid, *Tetrahedron Lett*. **1990**, *31*, 7129 – 7132.

[18] W. Peczyńska-Czoch, F. Pognan, Ł. Kaszmarek, J. Boratyński, *J. Med. Chem.* **1994**, *37*, 3503 – 3510.

Synthesis of Hyperbranched Aminopolysaccharides

Jun-ichi Kadokawa,* Mitsuru Sato, Masa Karasu, Hideyuki Tagaya, and Koji Chiba

Dendritic polymers such as dendrimers and hyperbranched polymers have a highly branched backbone and exhibit very different properties compared to their linear analogues. Dendrimers, which have a perfect branched and exact monodisperse structure, are prepared by either divergent or convergent methods.[1] However, their preparation normally

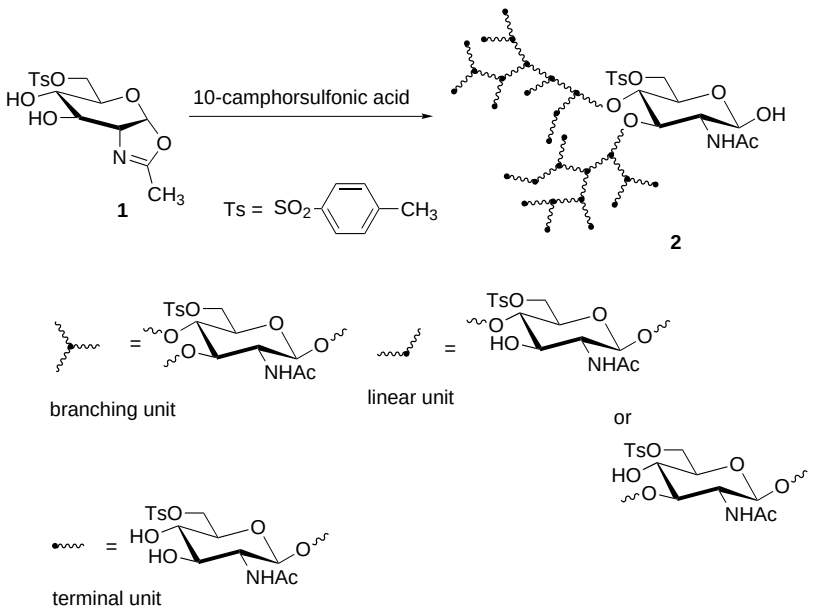
[*] Dr. J. Kadokawa, M. Sato, M. Karasu, Prof. Dr. H. Tagaya, Prof. Dr. K. Chiba
Department of Materials Science and Engineering
Faculty of Engineering, Yamagata University
Yonezawa, Yamagata 992-0038 (Japan)
Fax: (+81) 238-26-3413
E-mail: tj321@dip.yz.yamagata-u.ac.jp

  1433-7851/98/3717-2373 $ 17.50+.50/0

involves numerous protection, deprotection, and purification procedures.

Hyperbranched polymers can be prepared more easily than dendrimers by the polymerization of AB_x monomers, where x is generally 2 or 3. Although the concept of such materials was described by Flory in 1952,[2] synthesis and characterization of this class of polymers have been undertaken only in recent years.[3] Interest has since increased, and several new hyperbranched polymers have been described.[4] Recently, sugar-carrying multibranched glycopolymers and glycodendrimers with terminal sugar residues have been prepared.[5] However, synthesis of a hyperbranched polysaccharide has so far not been reported.

Various oligosaccharides with branched chain structures are found in glycoproteins at cell surfaces and in intercellular systems.[6] Examples include oligosaccharides isolated from calf thyroglobulin,[7] immunoglobulin glycopeptide,[8] and ovalbumin.[9] Chemical syntheses of these oligosaccharides have been achieved, which has allowed further study of their biological functions and unique structures.[10] Synthesis of a hyperbranched polysaccharide would also be very interesting, for such a polysaccharide can be expected to have unusual properties.



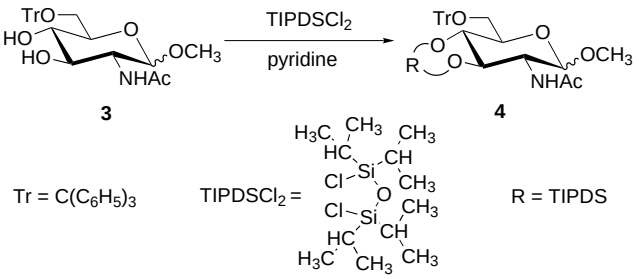
Scheme 1. Synthesis of hyperbranched aminopolysaccharide.

We have recently reported that benzyl-protected sugar dihydrooxazole monomers with a free hydroxyl group at position 4 or 6 undergo acid-catalyzed polymerization to give aminopolysaccharides.[11] The polymerization proceeds by stereoregular glycosylation of an alcohol group with the dihydrooxazole ring[12] to give aminopolysaccharides with natural (dibenzylchitin) and nonnatural structures. This polymerization method is not limited to the synthesis of linear polysaccharides, but can be extended to the formation of a hyperbranched compound from an AB_2 saccharide monomer. Here we report the synthesis of such a hyperbranched aminopolysaccharide **2** by the acid-catalyzed polymerization of a sugar dihydrooxazole monomer, 2-methyl-(6-*O*-tosyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-4,5-dihydrooxazole (**1**; tosyl = 4-toluenesulfonyl) with two hydroxyl groups at positions 3 and 4 (Scheme 1), which can be considered as an AB_2 monomer.

The polymerization of **1** was carried out in 1,2-dichloroethane at reflux temperature out with 10-camphorsulfonic acid (CSA, 10 mol %)[13] as catalyst.[14] The polysaccharide was isolated as a diethyl ether insoluble fraction. It was soluble in highly polar organic solvents such as *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine, but insoluble in organic solvents of low polarity and water. The ^{1}H and ^{13}C NMR spectroscopic data of the product supported that each unit has the β-D-glucopyranan structure **2**.[15] As no peak attributable to C1 of an α-glycoside ($\delta = 90-95$) was observed in the ^{13}C NMR spectrum, only the β configuration was tenable within the sensitivity of the method.

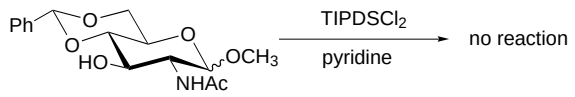
The number-average molecular weight (M_n) obtained by the reaction time of 3 h was calculated to be 6300 (degree of polymerization ca. 17.6) by gel permeation chromatography (GPC) with polystyrene as standard and DMF as eluent. On the other hand, the weight-average molecular weight (M_w) of the same product determined by the light-scattering method with RI detector and DMF as eluent was 4.5×10^5. Branched polymers are known to be of spherical conformation in solution.[16] Therefore, it may be considered that the actual M_n value of the present polysaccharide is larger than that estimated by GPC.

The degree of branching (DB) can be defined as the number of branched units relative to the number of total units. For polymers of high molecular weight, the number of branching points is nearly equal to the number of terminal units. To determine the DB value by the molar ratio of terminal units to total units, **2** was treated with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane ($TIPDSCl_2$), a reagent for the protection of two adjacent hydroxyl groups in a saccharide.[17] Each terminal unit in **2** has two hydroxyl groups, whereas only one hydroxyl group exists in each linear unit. To confirm the reactivity of $TIPDSCl_2$ toward the terminal and linear units, the reactions of methyl 2-acetamido-2-deoxy-6-*O*-trityl-D-glucopyranoside (**3**) and methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-D-glucopyranoside (**5**) with $TIPDSCl_2$ were carried out (Schemes 2 and 3); **3** and **5** are model compounds for the terminal and linear units, respectively.



Scheme 2. Model reaction of **3** with $TIPDSCl_2$.

  1433-7851/98/3717-2374 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **1998**, *37*, No. 17



5

Scheme 3. Model reaction of **5** with $TIPDSCl_2$.

The results of the model reactions indicated that the terminal units in **2** should be able to react quantitatively with $TIPDSCl_2$ to give disiloxane-bridged derivatives, whereas the linear and branched units should not react with $TIPDSCl_2$.[18] The reaction of **2** with $TIPDSCl_2$ was carried out in pyridine, and the product was isolated as a hexane-insoluble fraction.

The ^1H NMR spectrum ($CDCl_3$) of the reaction product shown in Figure 1 contains in comparison to **2** a new peak at around $\delta = 0.7 - 1.4$ for isopropyl groups. From the integrated ratio of this peak and the methyl peaks of the acetamido and

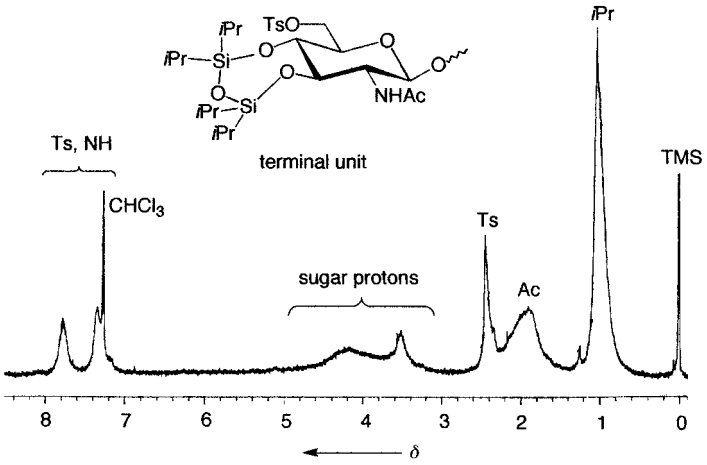


Figure 1. ^1H NMR spectrum ($CDCl_3$) of the reaction product of **2** with $TIPDSCl_2$.

tosyl groups, the content of the terminal units in the polymer could be calculated as 0.51. In the complete hyperbranched polymer, the content of the terminal units is nearly a half of the total units when the molecular weight of the polymer is high. Therefore, the DB of **2** synthesized here can be considered to be almost perfect.[19]

Table 1 summarizes the polymerization results under various reaction times. The DB of the polymers obtained with reaction times of 3–5 h was almost perfect, as, in each case, the ratio of the terminal units to the total units was about 0.5 (determined by ^1H NMR spectroscopic analysis after the reaction with $TIPDSCl_2$, entries 3 and 4). The ratio of the terminal units in the polymers obtained with reaction times of 1–2 h was 0.44–0.45, which indicates incomplete DB in these polymers (entries 1 and 2).

Polysaccharide **2** can be expected to have unusual properties because of the hyperbranched structure. The thermal properties of **2** were examined by thermogravimetric analysis (TGA). Decomposition of the tosyl group started at 166 °C and showed a 45% weight loss up to 337 °C. The residual material exhibited thermal resistance above 337 °C, but a second weight loss occurred at 510 °C. Decomposition was

Table 1. Polymerization of (**1**).[a]

Entry	t[a] [h]	Yield[b] [%]	$M_w\ 10^{-5}$[c]	M_n[d]	M_w/M_n[c]	y[e]
1	1	57.3	2.3	5500	1.44	0.45
2	2	48.5	2.9	4800	1.23	0.44
3	3	49.4	4.5	6300	1.31	0.51
4	5	57.5	7.6	6600	1.93	0.49

[a] Polymerization was carried out with **1** (0.20 mmol) and 10-camphorsulfonic acid (10 mol% relative to **1**) in 1,2-dichloroethane (2.0 mL) at reflux. [b] Fraction insoluble in diethyl ether. [c] Determined by the light-scattering method with DMF as eluent. [d] Determined by GPC with DMF containing lithium chloride (0.02 mol L^{-1}) as eluent and polystyrene standards. [e] Ratio y of terminal units to total number of units determined by ^1H NMR spectroscopy.

complete at 600 °C. The TGA trace of **2** indicated that the thermal stability of **2** was much higher than that of normal, linear polysaccharides. For example, chitin showed a significant weight loss at 275–428 °C.

Finally, detosylation of **2** was carried out under alkaline conditions (sodium hydroxide) in aqueous ethanol at reflux temperature to yield a free hyperbranched aminopolysaccharide. The product was isolated as a methanol-insoluble fraction, and is insoluble in common organic solvents and water, but soluble in formic acid. The IR spectrum of the product showed the disappearance of the absorptions at 1358 and 1176 cm^{-1} for the tosyl S=O group. These IR data strongly supported the conclusion that complete detosylation had taken place to give the free hyperbranched aminopolysaccharide. Partial deacetylation of the acetamido groups of **2** is possible, although the absorption at 1647 cm^{-1}, attributable to the C=O moiety of the acetamido group, was present in the IR spectrum of the product. More detailed studies on the optimum conditions for detosylation are in progress.

In conclusion, we have synthesized a hyperbranched aminopolysaccharide **2** by acid-catalyzed polymerization of the AB_2-type saccharide monomer **1**. This polymerization provides the first example of the synthesis of a hyperbranched polysaccharide.

Experimental Section

Monomer **1**: A solution of *p*-toluenesulfonyl chloride (7.56 g, 40.0 mmol) in pyridine (24 mL) was added to a solution of *N*-acetyl-D-glucosamine (8.80 g, 40.0 mmol) in pyridine (60 mL) under argon, and the mixture was stirred overnight at 40 °C. After the reaction mixture had cooled to room temperature, acetic anhydride (40 mL) was added, and the solution was stirred for a further 4 h. The pyridine was evaporated under reduced pressure, and the concentrated solution was poured into a large amount of ice water. The precipitate was isolated by decantation, washed several times with water, and dissolved in chloroform. The solution was successively washed with 1M sulfuric acid, aqueous sodium hydrogen carbonate, and water. The chloroform layer was dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was dried under reduced pressure to give 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-tosyl-D-glucopyranose (7.73 g, 14.6 mmol, 36.5%). ^1H NMR ($CDCl_3$): $\delta = 1.98$, 2.03, 2.19 (s, 12H; $CH_3C{=}O$), 2.46 (s, 3H; $CH_3C_6H_4$), 4.03–4.39 (m, 4H; H2, H5, H6), 5.02–5.53 (m, 3H; H3, H4, NH), 5.64, 6.04 (d, $J = 2.07$, 8.92 Hz, 1H; H1 (β and α, respectively)), 7.36, 7.77 (d, $J = 8.11$ Hz, 4H; C_6H_4). The product (2.81 g, 5.63 mmol) was dissolved in 1,2-dichloroethane (20.0 mL) under argon and treated with trifluoromethanesulfonic acid (0.900 g, 6.00 mmol). The mixture was stirred overnight at 50 °C, cooled to room temperature, and treated dropwise with triethylamine (4.0 mL). After an additional 20 min the mixture was diluted with chloroform, washed with water, dried

  1433-7851/98/3717-2375 $ 17.50+.50/0

over anhydrous sodium sulfate, and evaporated. The syrupy residue was subjected to chromatography on silica gel with ethyl acetate/hexane/triethylamine (100/50/1, v/v/v) to give 2-methyl-(3,4-di-*O*-acetyl-6-*O*-tosyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-4,5-dihydrooxazole (0.895 g, 2.03 mmol, 39.5 %). ^{1}H NMR ($CDCl_3$): $\delta = 1.99$ (s, 3H; $CH_3C{=}N$), 2.03, 2.08 (s, 6H; $CH_3C{=}O$), 2.44 (s, 3H; $CH_3C_6H_4$), 3.60 – 4.12 (m, 4H; H2, H5, H6), 4.78 – 5.22 (m, 2H; H3, H4), 5.90 (d, $J = 7.30$ Hz, 1H; H1), 7.35, 7.78 (d, $J = 8.11$ Hz, 4H; C_6H_4). The product was dissolved in dry methanol (3.0 mL) under argon and treated with sodium methoxide (10.0 mg, 0.185 mmol) at room temperature. The reaction mixture was stirred at that temperature, and sodium methoxide (10.0 mg, 0.185 mmol) in dry methanol (3.0 mL) was added to the mixture every 1 h until complete consumption of the starting material was confirmed by thin layer chromatography (TLC). The reaction mixture was then poured into a large amount of ice water, and the aqueous phase was extracted three times with chloroform. The chloroform extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated at room temperature. The residue was dried under reduced pressure to give **1** (0.600 g, 1.68 mmol, 82.6 %). ^{1}H NMR ($CDCl_3$): $\delta = 1.99$ (s, 3H; $CH_3C{=}N$), 2.43 (s, 3H; $CH_3C_6H_4$), 3.62 – 3.90 (m, 5H; H3 – H6), 4.08 – 4.28 (m, 1H; H2), 5.89 (d, $J = 7.02$ Hz, 1H; H1), 7.34, 7.79 (d, $J = 8.11$ Hz, 4H; C_6H_4); ^{13}C NMR ($CDCl_3$): $\delta = 13.6$ ($CH_3C_6H_4$), 21.1 ($CH_3C{=}N$), 68.2 (C2), 69.0 (C6), 70.2, 70.6, 72.4 (C3, C4, C5), 99.7 (C1), 127.7, 130.3, 132.1, 145.1 (C_6H_4), 163.9 (N=C–O).

Polymerization of **1** (Table 1, entry 3): monomer **1** (0.0715 g, 0.20 mmol) and 10-camphorsulfonic acid (0.00465 g, 0.020 mmol) were dissolved in 1,2-dichloroethane (1.0 mL) under argon at room temperature, and the reaction mixture was heated under reflux for 3 h. The reaction mixture was cooled to room temperature and neutralized with pyridine. The solution was poured into a large volume of diethyl ether, and the precipitate was collected by filtration and washed with water. The material was dried under reduced pressure, dissolved in methanol, and the solution was poured into a large amount of diethyl ether. The precipitated product was isolated by filtration and dried under reduced pressure to give **2** (0.0353 g, 49.4 %).

Reaction of **2** with $TIPDSCl_2$: polymer **2** (0.100 g, 0.280 mmol) was dissolved in pyridine (2.2 mL) under argon, and $TIPDSCl_2$ (0.0397 g, 0.126 mmol) was added at room temperature. After the reaction mixture was stirred overnight, methanol was added. The solution was poured into a large amount of water, and the aqueous phase was extracted with 2-butanone. The extract was dried over anhydrous sodium sulfate, filtered, evaporated and dried in vacuo. Hexane was added to the residue, and the insoluble product was isolated by filtration and dried in vacuo (0.125 g).

Detosylation of **2**: Sodium hydroxide (0.300 g) and **2** (0.103 g) were dissolved in 50 % aqueous ethanol (10.0 mL). The solution was heated under reflux for 5 h, cooled, neutralized with acetic acid, and concentrated under the reduced pressure. Methanol was added to the residue and the insoluble material was isolated by filtration and dried in vacuo to give the detosylated product (0.0426 g).

Received: January 9, 1998
Revised version: May 18, 1998 [Z11348IE]
German version: *Angew. Chem.* **1998**, *110*, 2540 – 2543

Keywords: carbohydrates · dendrimers · glycosylations

[1] a) D. A. Tomalia, A. M. Naylor, W. A. Goddard III, *Angew. Chem.* **1990**, *102*, 119; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138; b) P. R. Dvornic, D. A. Tomalia, *Macromol. Symp.* **1994**, *88*, 123.
[2] P. J. Flory, *J. Am. Chem. Soc.* **1952**, *74*, 2718.
[3] a) Y. H. Kim, O. W. Webster, *J. Am. Chem. Soc.* **1990**, *112*, 4592; b) Y. H. Kim, O. W. Webster, *Macromolecules* **1992**, *25*, 5561.
[4] a) B. I. Voit, S. R. Turner, *Angew. Makromol. Chem.* **1994**, *223*, 13; b) J. M. J. Fréchet, C. J. Hawker, *React. Funct. Polym.* **1995**, *26*, 127; c) B. I. Voit, *Acta Polymer.* **1995**, *46*, 87; d) A. R. Brenner, B. I. Voit, D. J. Massa, S. R. Turner, *Macromol. Symp.* **1996**, *102*, 47.
[5] For example, a) R. Roy, D. Zanini, S. J. Meunier, A. Romanowska, *J. Chem. Soc. Chem. Commun.* **1993**, 1869; b) K. Aoi, K. Itoh, M. Okada, *Macromolecules* **1995**, *28*, 5391; c) P. R. Ashton, S. E. Boyd, C. L. Brown, N. Jayaramen, S. A. Nepogodiev, J. F. Stoddart, *Chem. Eur. J.* **1996**, *2*, 1115; d) D. Zanini, R. Roy, *J. Org. Chem.* **1996**, *61*, 7348; e) D. Zanini, R. Roy, *J. Am. Chem. Soc.* **1997**, *119*, 2088.
[6] R. Kornfeld, S. Kornfeld, *Annu. Rev. Biochem.* **1976**, *45*, 217.
[7] S. Ito, D. Yamashita, R. G. Spiro, A. Kobata, *J. Biochem. (Tokyo)* **1977**, *81*, 1621.
[8] a) J. Baenziger, S. Kornfeld, S. Kochwa, *J. Biol. Chem.* **1974**, *249*, 1897; b) J. Baenziger, S. Kornfeld, *J. Biol. Chem.* **1974**, *249*, 7260.
[9] a) T. Tai, K. Yamashita, S. Ito, A. Kobata, *J. Biol. Chem.* **1977**, *252*, 6687; b) K. Yamashita, Y. Tachibana, A. Kobata, *J. Biol. Chem.* **1978**, *253*, 3862.
[10] T. Ogawa, K. Katano, K. Sasajima, M. Matsui, *Tetrahedron* **1981**, *37*, 2779.
[11] a) J. Kadokawa, Y. Watanabe, M. Karasu, H. Tagaya, K. Chiba, *Macromol. Rapid Commun.* **1996**, *17*, 367; b) J. Kadokawa, S. Kasai, Y. Watanabe, M. Karasu, H. Tagaya, K. Chiba, *Macromolecules* **1997**, *30*, 8212.
[12] S. E. Zurabyan, T. P. Volosyuk, A. J. Khorlin, *Carbohydr. Res.* **1969**, *9*, 215.
[13] S. Nishimura, K. Matsuoka, K. Kurita, *Macromolecules* **1990**, *23*, 4182. It has been reported that 10-camphorsulfonic acid is a more effective catalyst than, for example, *p*-toluenesulfonic acid and trifluoromethanesulfonic acid in glycosylations with a dihydrooxazole glycosyl donor.
[14] Nucleophilic attack of a nitrogen atom in the dihydrooxazole group of **1** onto *p*-toluenesulfonate group at position 6 could take place during the polymerization. However, an acetyl-protected derivative of **1** was stable when heated under reflux in 1,2-dichloroethane, which indicates no reaction had occurred between the dihydrooxazole and *p*-toluenesulfonate groups.
[15] ^{1}H NMR (270 MHz, [D$_6$]DMSO/D$_2$O, 20 °C): $\delta = 1.62 – 2.18$ (br, 3H; $CH_3C{=}O$), 2.40 (s, 3H; $CH_3C_6H_4$), 3.09 – 5.00 (br, 7H; sugar protons), 7.46, 7.76 (2s, 4H, C_6H_4); ^{13}C NMR (67.8 MHz, [D$_6$]DMSO, 80 °C): $\delta =$ 19.2 – 26.2 (CH_3), 46.9 – 57.9 (C2), 68.0 – 71.7 (C3 – C6), 99.5 (C1), 125.4 – 146.4 (C_6H_4), 168.4 – 171.4 (C=O).
[16] a) S. Bywater, *Adv. Polym. Sci.* **1979**, *30*, 89; b) P. Rempp, E. Franta, J. E. Herz, *Adv. Polym. Sci.* **1988**, *86*, 145.
[17] a) C. H. M. Verdegaal, P. L. Jansse, J. F. M. de Rooij, J. H. van Boom, *Tetrahedron Lett.* **1980**, *21*, 1571; b) W. T. Markiewicz, B. Nowakowska, K. Adrych, *Tetrahedron Lett.* **1988**, *29*, 1561; c) M. D. Hagen, C. S-. Happ, E. Happ, S. Chládek, *J. Org. Chem.* **1988**, *53*, 5040.
[18] In the reaction of **3** with $TIPDSCl_2$, complete consumption of **3** and the formation of a single product were detected by TLC analysis. The product **4** was isolated in 60.0 % yield by chromatography on silica gel, and the structure was determined by ^{1}H NMR spectroscopy. In contrast, no reaction of **5** with $TIPDSCl_2$ was observed by TLC, and 75.6 % of **5** was recovered from the reaction mixture as a hexane-insoluble fraction.
[19] This method for the determination of the DB value may contain some inconsistencies owing to errors in the calculation of the integrated ratio in the ^{1}H NMR spectrum. Furthermore, in the reaction of **2** with $TIPDSCl_2$ some formation of the nonbridged units by the reaction of the linear units with $TIPDSCl_2$ is possible. It has been reported, however, that $TIPDSCl_2$ reacts almost exclusively with two adjacent hydroxyl groups, and that the reaction favors the formation cyclic disiloxane-bridged structures rather than nonbridged structures.[17]

  1433-7851/98/3717-2376 $ 17.50+.50/0