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Design and Synthesis**

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SIX ISOMERS OF DENDRIMER-LIKE STAR POLYMERS: DESIGN AND SYNTHESIS

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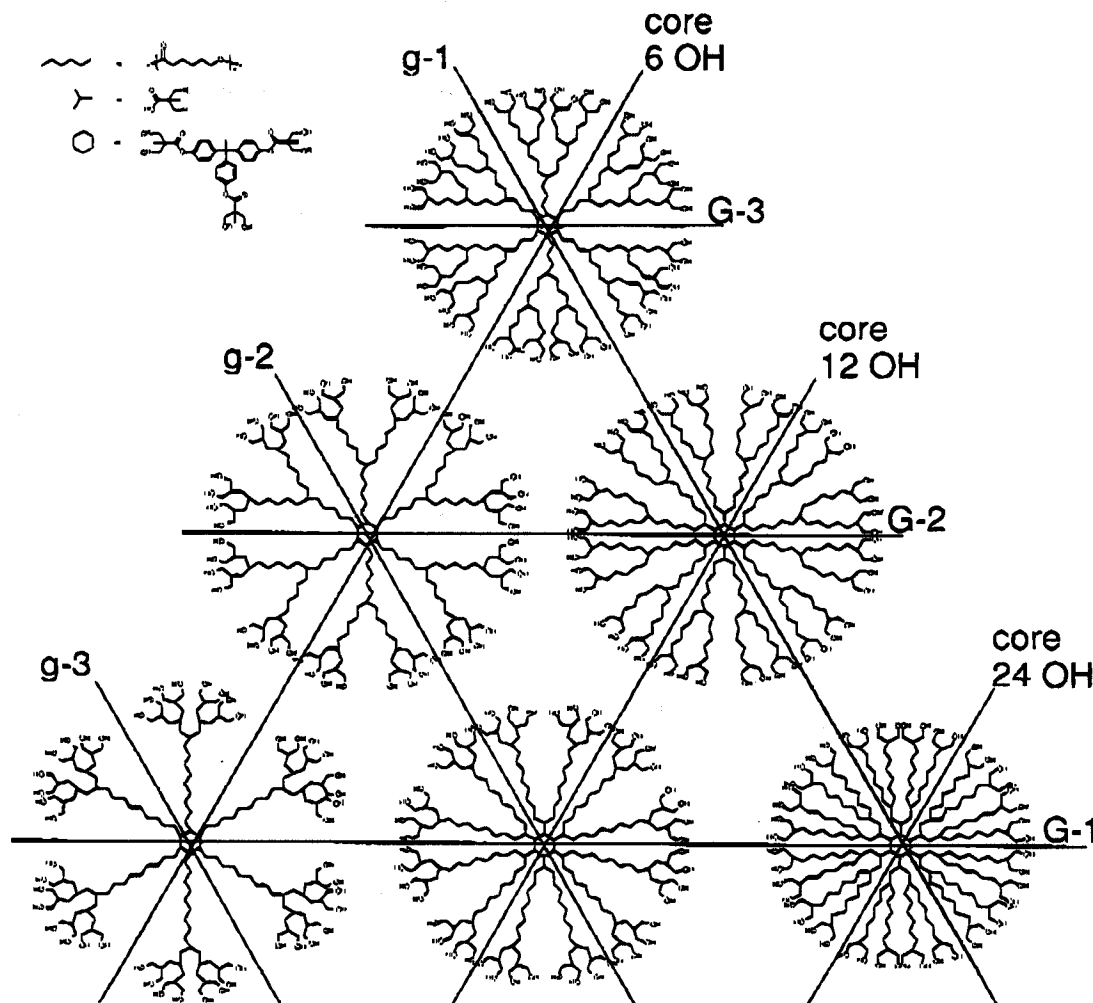
Introduction

The control of polymer properties through the synthesis of complex macromolecular architectures is central to many areas of research and advanced technological applications. Properties of novel materials are altered mainly through modification of their *constitution*. Examples of constitutional changes include the use of different monomers, variable molecular weights, block structures, grafted branching and so on.¹ Living polymerization techniques has facilitated the preparation of these structures. The use of new multifunctional initiators has enhanced the availability of for example star polymers, which are believed to have smaller hydrodynamic volume and lower melt viscosity than their linear counterparts.² Dendrimers³ and hyperbranched polymers⁴ are other classes of macromolecules which have received a lot of attention due to their unique architectures.

Constitutional isomers are molecular compounds that differ in the nature of the functional group, e.g., $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3 , or in the position of an atom or a group, e.g., 1-propanol and 2-propanol, or in the nature of the skeletal structure, e.g., *n*-butane and *i*-butane.⁵ Since the chemical structure of constitutional isomers can be very different, the affect on the chemical, physical and biological properties can also be considerable. Examples of polymeric constitutional isomers are poly(ethylene oxide) and poly(vinyl alcohol), as well as low density polyethylene (LDPE) and high density polyethylene (HDPE) which differ only in the nature of the skeletal structure. It is well known that LDPE and HDPE have completely different mechanical properties due to their different crystallization extents. However, it is difficult to use these materials to understand the influence of molecular structure on the properties in solution or in the melted matter since both polymers are highly polydisperse.

Due to the problem with polydispersity little is so far known about the influence of branching on the properties of macromolecules. The reason primarily stems from the limited polymerization methods available for the preparation of well-defined, narrowly dispersed and branched macromolecules. As a means of addressing this problem, Hawker et al⁶ synthesized exact linear analogs of different generations benzyl ether dendrimers in a stepwise approach. They found that the molecular architecture had a tremendous influence on the hydrodynamic volume on polymers with a molecular weight up to 6 700.

A new class of materials is dendrimer-like star polymers (DSP).⁶ These polymers are interesting since controlled branching can be introduced in materials with molecular weights up to 150 000. In addition, they enable variation in the degree of polymerization as well as the preparation of block structures. Dendrimer-like star polymers have so far been based on ring-opening polymerization (ROP) of lactones and lactides and comprise derivatives of 2,2'-bis(hydroxymethyl)propionic acid (bis-MPA) as branching



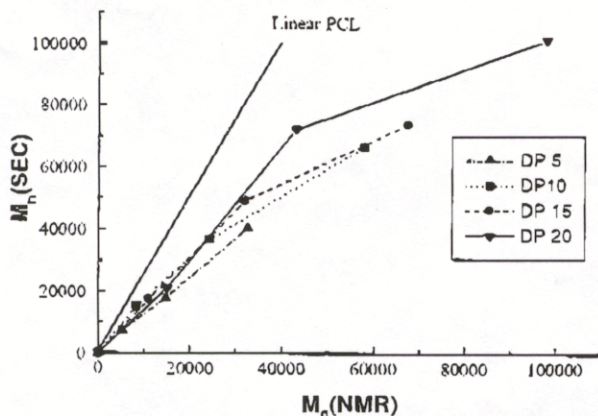


Figure 1. The hydrodynamic volume plotted as a function of the molecular weight determined by $^1\text{H-NMR}$ for dendrimer-like star polymers with different DPs.

units. Similar dendritic structures have also been prepared from poly(ethylene oxide) and via atom transfer radical polymerization (ATRP).⁷ Through the preparation of DSP based on ϵ -caprolactone, of the first, second and third generation with varying degree of polymerization (DP= 5, 10, 15, 20) it was possible to learn some differences between traditional dendrimers and star polymers, Figure 1.⁸ It was shown that, if the DP is 10 or higher, three generations of polymer are required to obtain a material with lower hydrodynamic volume than the traditional star polymers. For low DP's a more spherical structure seems to form even at the lower generations. In addition, it was found that the polymers seem to have a hydrodynamic volume which is either star-like or of dendritic origin. Through the introduction of lactide monomers it has been possible to alternate the molecular structure of the different generations, which has enabled the preparation of both amorphous and semi-crystalline materials.⁹ Moreover it has been possible to prepare optical active materials through the use of L- or D- lactide. By using optical active lactide as the monomer in one, two or all generations of the polymer it was shown that the optical activity is equal in all layers.¹⁰ This in turn allowed the structural composition to be verified. In another attempt to produce block copolymers, amorphous dendrons of bis-MPA were used as the second layer.¹¹

By altering the molecular structure of the core, the monomers, the branch units and the degree of polymerization the versatility of the dendrimer-like star polymers has been shown. In addition, it has been shown by $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectroscopy, SEC and optical activity measurements that the molecular structure correspond very well with the ideal structures. With this in mind, six isomers of the dendrimer-like star polymers were designed and synthesized, Scheme 1. All six polymers have a total DP of 600, comprise 45 units of bis-MPA and have 48 functional groups on the surface. By keeping the DP/arm constant within the same polymer it has been possible to prepare polymers according to Scheme 1. The six polymers in Scheme 1 are organized in a triangular form where the three bases correspond to the total number of generations (G-1, G-2 and G-3), the size of the surface dendrons (g-1, g-2 and g-3) and the size of the core molecules (6 OH, 12 OH and 24 OH).

Table 1. Design and Structure of the Six Isomeric Polymers

Polymer	Mn target	DP/arm	Core	Surface Dendrons
G-1, 6OH, 100	79 500	100	6 OH	g-3
G-1, 12OH, 50	79 500	50	12 OH	g-2
G-1, 24OH, 25	79 500	25	24 OH	g-1
G-2, 6OH, 33.3	79 500	33.3	6 OH	g-2
G-2, 12OH, 16.7	79 500	16.7	12 OH	g-1
G-3, 6OH, 14.3	79 500	14.3	6 OH	g-1

Table 2. Molecular Weights and Thermal Transitions of the Prepared Polymers

Polymer ^a	Mn target	Mn (SEC)	Mw/Mn (SEC)	Tm ^b (°C)	ΔH ^b (J/g)
G-1, 6OH, 100	79 500	-	1.09	-	-
G-1, 12OH, 50	79 500	65 500	1.04	53.9	59.0
G-1, 24OH, 25	79 500	76 400	1.08	54.1	58.1
G-2, 6OH, 33.3	79 500	81 600	1.15	53.6	54.2
G-2, 12OH, 16.7	79 500	65 500	1.12	50.7	54.4
G-3, 6OH, 14.3	79 500	87 200	1.19	44.7	57.7

^a All the data are from polymers with protected hydroxyl groups. Tert-butyl dimethylsilyl (TBDMS) are used as protecting group.

^b DSC transitions observed on second heating.

Polymer (G1, 6OH, 100) was initiated from a core with six hydroxyl groups (6OH) and has a DP of 100/arm. Each arm is then end functionalized with bis-MPA dendrons of the third generation (g-3). Polymer (G2, 6OH, 33.3) was initiated from the same core (6OH) which generate six arms. Another twelve arms is then present in the second generation (G-2). The target DP for the arms in each generation was 33.3. The outer twelve arms were then finally functionalized with dendrons of the second generation. The other four polymers were named in an analogous fashion, Table 1. The polymers were all prepared by methods published elsewhere.^{26,11b} The DPs for each generation were measured by $^1\text{H-NMR}$ spectroscopy and correspond well to the target values. The theoretical data and results from SEC of all polymers are listed in Table 2. All polymers are monodisperse and have polydispersities below 1.25.

In conclusion, six isomers of dendrimer-like starpolymers with equal molecular weight have been designed and prepared. The six isomers comprise the same overall DP of 600, 45 units of bis-MPA and have 48 functional groups on the surface. The physical characterization of these six isomers gives a unique opportunity to investigate the effect of chemical structure on molecules with a molecular weight above 75 000.

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References

- (1) Nasipuri, D. (1991) in *Stereochemistry of Organic Compounds*, John Wiley & Sons, New Delhi.
- (2) (a) Rempp, P.; Franta, E. *Adv. Polym. Sci.* **1984**, *58*, 1. (b) Simms, J. A.; Spinelli, H. J. *Coat. Technol.* **1987**, *59*, 126. (c) Johansson, M.; Trollsås, M.; Hult, A. *J. Polym. Sci.: Part A: Polym. Chem.* **1992**, *30*, 2203. (d) Roovers, J.; Zhou, L. L.; Toporowski, P. M.; Van der Zwan, M.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 4324. (e) Vasilenko, N. G.; Rebrov, E. A.; Muzafarov, A. M.; Ehwain, B.; Striegel, B.; Möller, M. *Macromol. Chem. Phys.* **1995**, *199*, 881. (f) Trollsås, M.; Hedrick, J. L.; Mecerreyes, D.; Dubois, P.; Jerome, R.; Iltre, H.; Hult, A. *Macromolecules* **1997**, *30*, 8508. (g) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762. (h) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **1998**, *31*, 7218.
- (3) (a) Tomalia, D. A.; Naylor, A. M.; Goodard III, W. A. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138. (b) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (c) Iltre, H.; Hult, A. *J. Am. Chem. Soc.* **1996**, *118*, 6388.
- (4) (a) Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561. (b) Johansson, M.; Malmström, E.; Hult, A. *J. Polym. Sci.: Part A: Polym. Chem.* **1992**, *31*, 619.
- (5) Hawker, C. J.; Malmström, E. E.; Frank, C. W.; Kampf, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 9903.
- (6) Trollsås, M.; Hedrick, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 4644.
- (7) (a) Six, J.-L.; Gnanou, Y. *Macromol. Symp.* **1995**, *95*, 137. (b) Hedrick, J. L.; Trollsås, M.; Hawker, C. J.; Arthoff, B.; Claesson, H.; Heiss, A.; Miller, R. D.; Mecerreyes, Jerome, R.; Dubois, P. *Macromolecules* **1999**, *121*, xxx.
- (8) Pople, J. A.; Gast, A. P.; Trollsås, M.; Claesson, H.; Hedrick, J. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*(1), xxx.
- (9) Arthoff, B.; Trollsås, M.; Claesson, H.; Hedrick, J. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*(2), 76.
- (10) Trollsås, M.; Arthoff, B.; Claesson, H.; Hedrick, J. L. *submitted*.
- (11) (a) Claesson, H.; Trollsås, M.; Arthoff, B.; Hedrick, J. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*(2), 511. (b) Trollsås, M.; Claesson, H.; Arthoff, B.; Hedrick, J. L. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, xxx.