Hyperbranched Polyglycerols by Ring-Opening Multibranching Polymerization

A. Sunder, H. Frey*, R. Mülhaupt

Freiburger Materialforschungszentrum und
Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität
Stefan-Meier-Str. 21, D-79104 Freiburg, Germany

SUMMARY: Glycidol represents a latent cyclic AB_2-type monomer that can be polymerized in a ring-opening multibranching polymerization (ROMBP). Hyperbranched aliphatic polyethers with controlled molecular weights and narrow molecular weight distribution have been prepared via anionic polymerization of glycidol with rapid cation exchange equilibrium. The degree of branching and degree of polymerization were determined via ^{13}C NMR spectroscopy. MALDI-TOF, vapor pressure osmometry (VPO) and GPC were used for further characterization. Molecular weights of the polyols formed were in the range of 1,300 to 6,500, showing polydispersities below 1.5, i. e. exceptionally low for hyperbranched polymers. The polyglycerols were used for the preparation of a novel hyperbranched liquid crystalline (LC) topology.

Introduction

Hyperbranched polymers are characterized by a randomly branched structure, precisely one focal unit and at least two branching points. Such polymers are generally prepared by polymerization of AB_m-type of monomers[1]. Recently, this class of polymers has become of increasing interest as a potential alternative for the perfectly branched dendrimers that have to be constructed in a usually tedious, stepwise approach[2].

Two strategies for the preparation of hyperbranched polymers are currently employed, polycondensation of AB_m-monomers and the self-condensing vinyl polymerization (SCVP)[3].

The main drawback of hyperbranched polymers prepared via both pathways lies in the extremely broad molecular weight distributions and polydispersities in the range of $DP_n/2$. Recent theoretical work by Müller et al.[4] as well as simulation work by our group[5] has shown that copolymerization of a core molecule of the structure B_f (representing a polyfunctional initiator in the case of the SCVP, and a poly-B-functional molecule for the AB_m-type polycondensation-type reaction) can be used to lower the polydispersity considerably. Additional slow monomer addition was calculated to result in even lower polydispersities and should result in complete control of the number-average molecular weights by the

 CCC 1022-1360/00/$ 17.50+.50/0

monomer/initiator ratio, as in this case every macromolecule formed is expected to be attached to the core unit.

A third pathway to hyperbranched polymers, hitherto mentioned only in a few examples[6] is the ring-opening polymerization of cyclic latent AB_2-type of monomers. With respect to the ring-opening isomerization being the driving force of this type of reaction, in the further course of this article, this strategy is designated *"ring-opening multibranching polymerization"* (ROMBP). Fig. 1 demonstrates the analogy between AB_2 polycondensation and the ROMBP-approach.

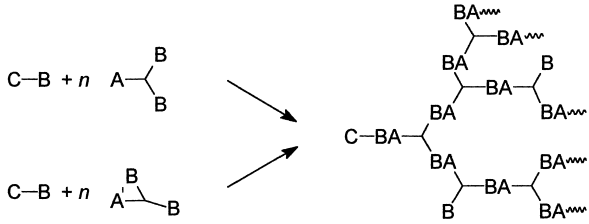


Fig. 1: Analogy between formation of hyperbranched polymers by polycondensation (step growth) and ROMBP copolymerization (chain growth) of an AB_2-type monomer with a monofunctional initiator C-B. (C: core unit/initiator, A, B: complementary reactive groups).

Glycidol, a commercially available and highly reactive hydroxy-epoxide represents a latent AB_2-monomer that can be polymerized to hyperbranched polyethers with numerous hydroxyl end groups. Vandenberg et al. characterized the branched structures formed to a certain extent[7]. Furthermore, glycidol has been polymerized cationically to branched polymers in elegant work by Penczek and Dworak[8,9]. However, controlled polymerization of glycidol to hyperbranched polymers with well-defined molecular weights has not been reported yet. In this paper we demonstrate that anionic polymerization with rapid cation exchange equilibrium, using slow monomer addition conditions can be employed to obtain hyperbranched polyols with polyether structure in a controlled manner.

Results and Discussion

Generally, the anionic polymerization of glycidol in the presence of alkoxides proceeds according to the mechanism shown in Fig. 2, which is analogous to the base-catalyzed polymerization of other epoxides. However, intra- as well as intermolecular transfer steps[14] subsequent to the ring-opening reaction can lead to the formation of a primary alkoxide as

active site, which further propagates, resulting in branched structures (Fig. 2). We used a partially deprotonated alcohol ≡COH as initiator / core unit. This enabled us to control the concentration of active sites (alkoxides) in the polymerization, leading to simultaneous growth of all chain ends and thus control of molecular weight and narrowing of the polydispersity. By reaction of the alcohol used as initiator with a suitable deprotonating agent (e.g. potassium methylate followed by removal of excess methanol) 10% of the hydroxyl group were converted into the alkoxide. In the subsequent propagation step the alkoxide initiator reacts with the epoxide ring on its unsubstituted end and thereby generates a secondary alkoxide. Rapid intra- as well as intermolecular proton exchange leads to simultaneous growth of all hydroxyl groups present in the system. When the polymerization proceeds, the initial concentration of 10% active species with respect to all hydroxyl groups decreases, since each incorporation of a glycidol monomer generates a new hydroxyl group that represents a dormant chain end. After terminating the polymerization by neutralization, the polyglycerols were in all cases obtained as transparent, viscous liquids.

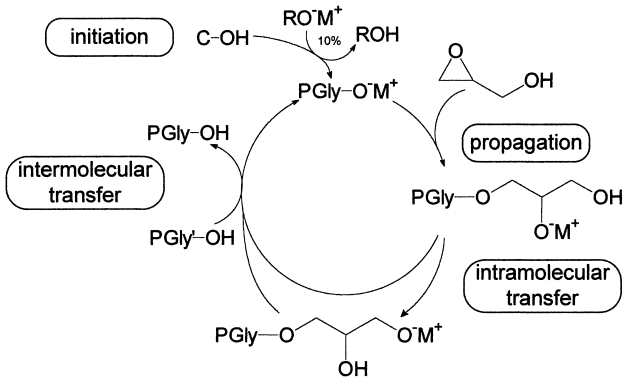


Fig. 2: Mechanism of the anionic polymerization of glycidol (**C**: core unit/initiator, RO^-M^+: deprotonating alkoxide, PGly: polyglycerol)

In addition to the control of the concentration of active chain ends, a challenge in controlling glycidol polymerization lies in the supression of cyclization, since this side reaction broadens polydispersity and lowers molecular weights achievable. Due to theoretical difficulties, in almost all theoretical approaches cyclization is not considered[10]. Clearly, cyclization is expected only if no initiator is used or if the concentration of monomer is somewhat higher

than that of the initiator, resulting in this case in deprotonation of glycidol and initiation by the deprotonated monomer.

Thus, in summary, the following reaction conditions were employed in order to control molecular weights, lower the polydispersity and suppress cyclization: a trifunctional initiator (trimethylolpropane) was partially deprotonated (10%) using potassium methylate and slow monomer addition conditions[5] were applied in the following polymerization.

A schematic structure of the hyperbranched polyglycerol macromolecules prepared via this approach is shown in Fig. 3. The initiator (a mono- or polyfunctional alcohol or a polyol) is incorporated as core unit (**C**). Since all hydroxyl groups remain potentially active in the course of the polymerization, the resulting structure is hyperbranched.

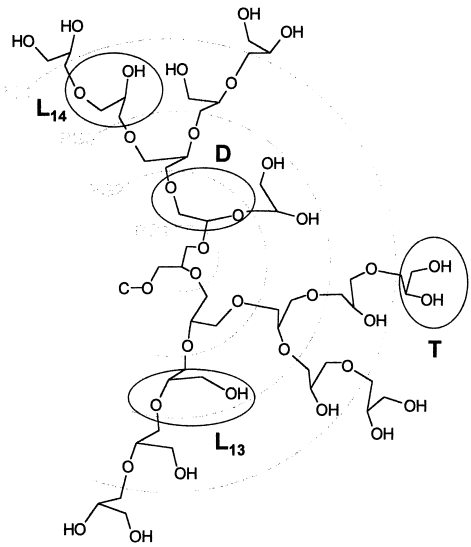


Fig. 3: Schematic architecture of a hyperbranched polyglycerol. Examples of terminal (T), dendritic (D), linear 1,3 (L_{13}) and linear 1,4-units (L_{14}) are circled, pseudo-generations (PG) are indicated by concentric lines, **C** indicates the core unit attached to the focal monomer unit.

In contrast to common hyperbranched polymers obtained from the polycondensation of symmetrical AB_2 monomers, due to the unsymmetric glycidol structure, four structural units have to be distinguished. If the secondary hydroxyl group has propagated, the polymer chain is attached to a glycerol-like unit and a linear 1,4-unit (L_{14}) is formed. If the primary hydroxyl group has undergone propagation, the corresponding linear 1,3-unit (L_{13}) is generated. If both hydroxyl groups have reacted with monomer, the result is a branched, i.e., dendritic unit (*D*).

If a monomer unit has been deactivated by proton exchange or by the final addition of acid a terminal unit (*T*) with two hydroxyl end groups is formed. All structural units are randomly incorporated into the structure.

The degree of branching of polyglycerol (i.e., the branching perfection of the structures) was determined from ^{13}C NMR. The spectrum of the branched polyglycerol possesses 7 well-resolved peak regions between 60 and 85 ppm. Fig. 4 shows this region with the assignments of all 12 carbons (i.e. 4 structural units with 3 carbons each). Having applied several NMR techniques (DEPT, COSY) in various solvents, the assignments are completing previous studies.[7-9].

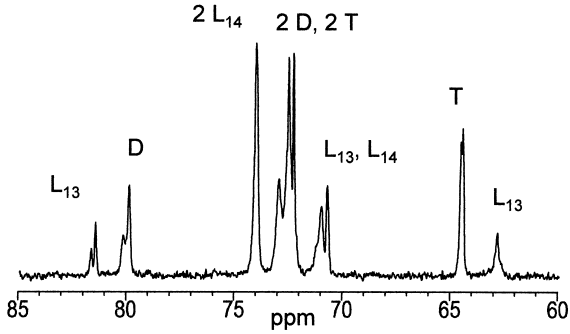


Fig. 4: ^{13}C NMR spectrum of polyglycerol with the assignment of all carbons belonging to the terminal (T), dendritic (D) and linear units (L_{13}, L_{14}).

The degree of branching (DB) measures the suitability of a hyperbranching reaction to create dendritic structures, in other words the perfection of a hyperbranched structure relative to the respective perfect dendrimer[11]. Thus, for linear structures the DB is 0, for homopolymerization of AB_2 monomers, the DB assumes the value 0.5 in a random polycondensation reaction with equal reactivity of the B-groups and for a perfect dendrimer the DB is 1. The degree of branching can be calculated on the basis of the intensity of NMR-signals from the fraction of structural units using a previously developed equation. (eq. 1)[12,13].

$$DB = \frac{2 \cdot D}{2D + L_{13} + L_{14}} \qquad (1)$$

In eq. 1, DB represents the degree of branching, D, L_{13}, L_{14} represent the fractions of dendritic, linear 1,3- and linear 1,4-units, respectively. The DB values (Table 1) for the polyglycerol samples range between 0.53 and 0.59, well above the value expected for a random AB_2-polycondensation (0.50), however below the theoretical value for an AB_2-

polymerization carried out in ideal slow addition mode, which would result in a DB of 0.66. This clearly illustrates that the polymerization of glycidol is comparable to common AB_2-polycondensation reactions with respect to the extent of branching units of the polymers formed.

The number average degree of polymerization $\overline{DP}_n$ can also be calculated from the distribution of structural units, based on the prerequisite that only propagation onto the core unit has occurred (eq. 2), i.e. that each macromolecule formed contains one core molecule.

$$\overline{DP}_n = \frac{T + L_{13} + L_{14} + D}{T - D} \cdot f_C \qquad (2)$$

$\overline{DP}_n$ represents the number average degree of polymerization, T designates the terminal monomer units and f_c the core functionality (i.e. 3 for a trifunctional initiator like trimethylolpropane). The $\overline{DP}_n$ values calculated from the IG ^{13}C-NMR spectra are also listed in Table 1 and range between 15 and 83.

Table 1. Molecular weights and polydispersity of polyglycerols prepared by base-catalyzed ROMBP using trimethylolpropane as initiator.

Sample	^{13}C NMR			MALDI-TOF		VPO[a)]	GPC[b)]
	DB	DP_n	M_n	M_n	M_w/M_n	M_n	M_w/M_n
PG1	0.53	15	1,200	1,300	1.2	1,100	1.2
PG2	0.55	22	1,800	1,600	1.2	1,500	1.2
PG3	0.57	44	3,400	3,600	1.2	3,500	1.1
PG4	0.59	83	6,300	not detectable		6,500	1.5

[a)] in methanol
[b)] in DMF using poly(propylene glycol) standards

So far the only method that permits to investigate whether exclusively the initiator has been incorporated into the hyperbranched polyether polyol formed is MALDI-TOF mass spectrometry. Since the molecular weights of polyglycerols with incorporated cycles (due to autoinitiation as described above) differ significantly from polyglycerols with incorporated initiator, it is possible to estimate the extent of cyclization by the occurence of a distinct second molecular weight subdistribution (Fig. 5). For samples with molar masses below 4,000 it is even possible to obtain a GPC-like distributions of molar masses from which M_n and M_w

can be calculated (Tab. 1). As it is often the case, MALDI-TOF MS does not provide representative molecular weight distributions for samples with higher mass and/or higher polydispersity.

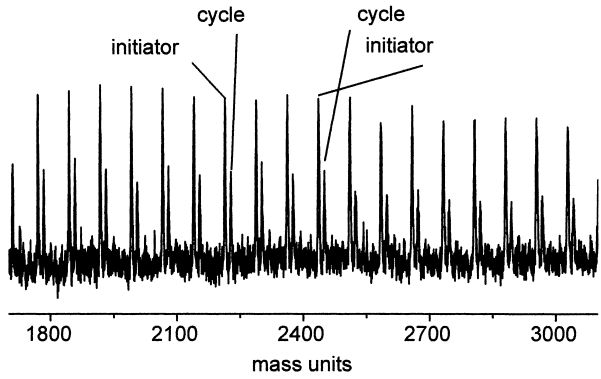


Fig. 5: Detail of a MALDI-TOF MS spectrum of a polyglycerol sample showing two molecular weight distributions caused by initiator incorporation and cyclization, respectively.

In addition to ^{13}C-NMR and MALDI-TOF, molecular weights of the polyglycerols have also been determined by vapor pressure osmometry (VPO) in methanol solution (Tab.1), showing good agreement with the previous results. In order to investigate aggregation effects, dilution viscosimetry experiments were performed in methanol over a wide concentration range, showing a linear relationship between viscosity and concentration. Thus, in the concentration range of the VPO experiments, molecular weights do not depend on concentration, i.e. aggregation does not seem very likely.

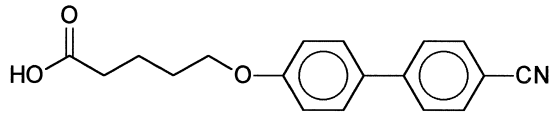
Since the hydrodynamic volume of hyperbranched polymers is both a function of the degree of polymerization and the degree of branching, GPC-calibration in order to achieve quantitative molecular weight measurements is difficult. Furthermore, hyperbranched polymers (particularly polyols) often exhibit aggregation or interaction with the GPC columns due to their large number of end groups, leading to erroneous molecular weight characterization[14]. Provided, no aggregation occurs, information on polydispersity can be obtained, when a suitable polymer standard is used for calibration. In contrast to the commonly used poly(styrene) standards, we employed linear poly(propylene oxide) for calibration of the GPC, since it possesses a structural backbone comparable to polyglycerol and is commercially available with low polydispersity (< 1.1) in the molar mass range between 1,000 to 12,000. Though number average molecular weights obtained were about five times higher than those

1) as well as the monomodal molecular weight distribution, formation of aggregates in DMF does not seem very likely. Furthermore, polydispersities measured by GPC agree well with the polydispersities calculated from the MALDI-TOF spectra.

DSC measurements show that all polyglycerols are flexible polymers, manifested by T_gs around -20°C, which renders these polymers interesting multifunctional platforms for further functionalization.

Liquid crystalline properties

Hyperbranched polymers are generally unable to crystallize due to the highly branched topology. However, incorporation of mesogenic units in an otherwise flexible hyperbranched macromolecule has been demonstrated to induce liquid crystalline order by Percec et al.[15,16] as well as Ringsdorf and coworkers[17]. In these works, each building unit of the hyperbranched structure contains calamitic mesogens. Furthermore, flexible dendrimers with mesogenic end groups have been found to form liquid crystalline (mainly smectic) phases[18,19]. In contrast to these approaches, LC hyperbranched polymers based on a flexible scaffold with mesogenic end groups have not been reported to date. Due to the narrow polydispersity and high flexibility, polyglycerol represents an ideal platform for the synthesis of this novel type of liquid crystalline polymer topology that can be considered to be formally analogous to side chain LC-polymers. Thus, 5-((4′-cyano(1,1′-biphenyl)-4-yl)oxy)valeric acid **1** was used for esterification of the end groups of polyglycerol sample PG3. Conversion of approximately 70% of the hydroxyl end groups was achieved.



1

The resulting polymers showed an apparent molecular weight M_n of 13,000 and a narrow polydispersity of 1.13 (GPC, PS-standard), confirming the narrow polydispersity of the hyperbranched polyglycerols. DSC and polarizing optical microscopy (Figs. 6 and 7) as well as WAXS evidence the formation of broad nematic mesophases. A systematic investigation of the influence of molecular weight and spacer length on liquid crystalline properties is in progress.

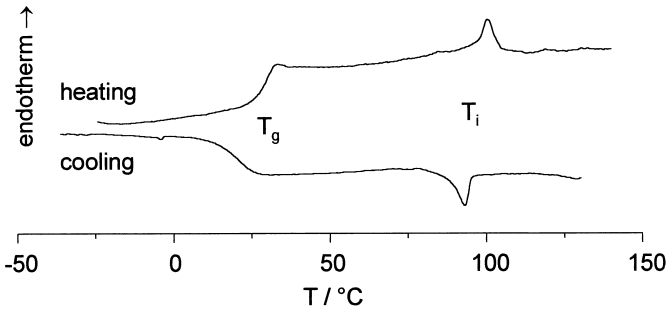


Fig. 6: DSC: T_g 22°C, transition into isotropic phase $T_{n\rightarrow i}$: 97°C; $\Delta H_{n\rightarrow i}$: 2.2 J/g (heating / cooling rate 10 K/min)

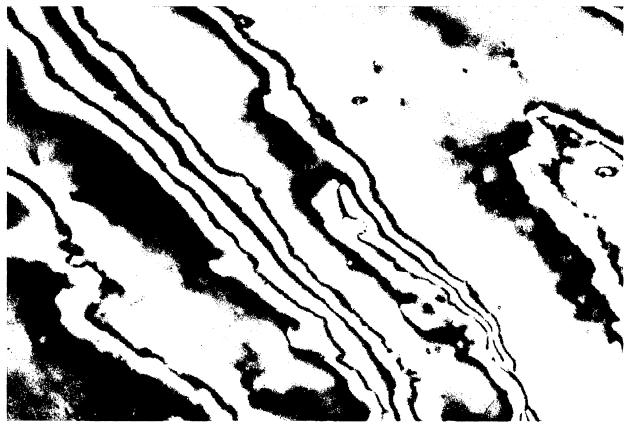


Fig. 7: Polarizing microscopic image, showing threaded textures

Conclusions

Hyperbranched aliphatic polyethers with hydroxyl end groups, possessing a $\overline{DP}_n$ in the range 15 to 83 can be prepared in a controlled manner by base-catalyzed ring-opening multi-branching polymerization of glycidol, making use of a fast proton exchange equilibrium. Polydispersities below 1.5 were achieved by slow addition of the monomer, which led to complete incorporation of the employed initiator into the hyperbranched macromolecules. $\overline{DP}_n$ could be controlled reasonably well by the ratio of initiator and monomer. A detailed ^{13}C NMR spectroscopic study permitted to determine $\overline{DP}_n$ and the degree of branching (DB), which was found to be enhanced in comparison to the value of 0.50 expected for a random

polymerization reaction, but still lower than the value expected under ideal core dilution / slow addition conditions (0.66). As evidenced by MALDI-TOF mass spectrometry, careful control of polymerization conditions allows to suppress autoinitiation, i.e. cyclization reactions.

In summary, the use of of a chain growth mechanism instead of commonly applied step growth reactions promises an excellent control of both molecular weight and architecture of (hyper)branched polymer structures. These polymers are interesting competitors for structurally perfect, yet tediously prepared dendrimers.

A novel type of hyperbranched liquid crystalline polymer based on a non-mesogenic scaffold and mesogenic end groups has been prepared.

References

1. P. J. Flory, *J. Am. Chem. Soc.* **74**, 2718 (1952)
2. O. A. Matthias, A. N. Shipway, J. F. Fraser-Stoddart, *Prog. Polym. Sci.* **23**, 1 (1998)
3. J. M. J. Fréchet, M. Henmi, I. Gitsov, S. Aoshima, M. R. Leduc, R. B. Grubbs, *Science* **269**, 1080 (1995)
4. W. Radke, G. Litvinenko, A. H. E. Müller, *Macromolecules* **31**, 239 (1998)
5. R. Hanselmann, D. Hölter, H. Frey, *Macromolecules* **31**, 3790 (1998)
6. M. Suzuki, A. Ii, T. Saegusa, *Macromolecules* **25**, 7071 (1992)
7. E. J. Vandenberg, *J. Polym. Sci., Polym. Chem. Ed.* **23(4)**, 915, (1985)
8. R. Tokar, P. Kubisa, S. Penczek, A. Dworak, *Macromolecules* **27**, 320 (1994)
9. A. Dworak, W. Walach, B. Trzebicka, *Macromol. Chem. Phys.* **196**, 1963 (1995)
10. C. Cameron, A. H. Fawcett, C. R. Hetherington, R. A. W. Mee, F. V. McBride, *J. Chem. Phys.* **108**, 8235 (1998)
11. C. J. Hawker, R. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.* **113**, 4583 (1991)
12. D. Hölter, A. Burgath, H. Frey, *Acta Polymer.* **48**, 30 (1997)
13. D. Hölter, A. Burgath, H. Frey, *Acta Polymer.* **48**, 298 (1997)
14. A. Möck, A. Burgath, R. Hanselmann, H. Frey, manuscript in preparation
15. V. Percec, M. Kawasumi, *Macromolecules* **25**, 3843 (1992)
16. V. Percec, M. Peihwei, M. Kawasumi, *Macromolecules* **27**, 4441 (1994)
17. S. Bauer, H. Fischer, H. Ringsdorf, *Angew. Chem. Int. Ed. Engl.* **32**, 1589 (1993)
18. K. Lorenz, D. Hölter, B. Stühn, R. Mülhaupt, H. Frey, *Adv. Mater.* **8**, 414 (1996)
19. S. A. Ponomarenko, E. A. Rebrov, A. Y. Bobrovsky, N. I. Boiko, A. M. Muzafarov, V. P. Shibaev, *Liq. Cryst.* **21**, 1 (1996)

20. Financial support by BAYER AG. Support in polymer characterization by Sonderforschungsbereich SFB 428 of the Deutsche Forschungsgemeinschaft.