Control of the Molecular Weight of Hyperbranched Polyglycerols

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SUMMARY: Hyperbranched polyglycerols exceeding M_n > 15,000 g/mol (DP_n > 270) have been prepared, using a modified version of the synthetic protocol reported earlier. In the optimized process polydispersities recorded by SEC remained narrow, with M_w/M_n < 1.7 over a large molecular weight range. The drastic increase of viscositity in the course of the reaction, was found to be responsible for the increased fraction of cycles (MALDI-TOF MS) at high molecular weights.

Introduction

Recently, intense theoretical efforts[1)] have paved the way for the preparation of hyperbranched polymers with controlled molecular weights and well-defined degree of branching[2)]. It has been known for a long time that polycondensation of AB_m monomers leads to hyperbranched polymers possessing large polydispersity[3)] and does not permit control of molecular weights. An alternative strategy is based on the slow addition of suitable latent AB_m (mostly AB_2) monomers, which has recently been employed to control molecular weights and to lower the polydispersity of hyperbranched polymers. We reported on the controlled ring opening multibranching polymerization (ROMBP) of glycidol, representing a latent cyclic AB_2 monomer[4)]. The resulting polyether-polyols (Figure 1) possess polydispersities below 1.5. These flexible hyperbranched polyethers have proven useful polymeric precursors for the synthesis of amphiphilic molecular nanocapsules[5)] as well as for a new type of hyperbranched liquid crystalline polymers[6)]. However, to date, molecular weights of polyglycerol and respective copolymers have been limited to 6,000 g/mol (DP_n < 90), since the addition of larger amounts of monomer to the initiator-core had not been explored. In this report, we demonstrate that also higher molecular weight materials are accessible after modification of the synthetic procedure. In addition, a reactor with outlet valve permitted to take samples in

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the course of the polymerization under slow-monomer-addition conditions, allowing us to monitor polymer formation and potential side reactions in detail.

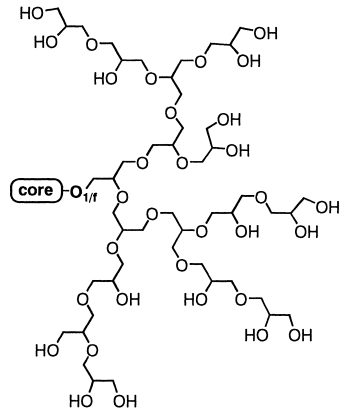

Fig. 1: Schematic structure of a hyperbranched polyglycerol consisting of dendritic, linear and terminal monomer units[9)]

Synthesis and Characterization

The basic synthetic protocol has been described previously[4)] and is based on the slow-monomer-addition principle: glycidol is added slowly and continuously to the partially deprotonated polyol initiator, using a dosing pump. A fast protonation/deprotonation equilibrium ensures activity of all potential propagation sites of the growing polyfunctional macromolecules. Usually, monomer addition is complete after a few hours. The slow-monomer-addition strategy results in a very low monomer concentration actually present in the reaction mixture. Thus, exclusive reaction of the monomer with the growing polyfunctional macromolecules occurs, resulting in controlled molecular weights.

We were able to scale-up the reaction using a 2l reactor which enables us to produce hyperbranched polyglycerols on a scale of 500 g within one day. Furthermore, an outlet valve permits to take samples in the course of the reaction. This is crucial to monitor the polymerization process in detail to optimize reaction parameters, such as stirring intensity, stirrer geometry and dilution.

Applying the same protocol as reported for the lower molecular weight samples (< 6,000 g/mol)[4)] resulted in considerably broader molecular weight distributions for higher

monomer/initiator ratios (M_W/M_n > 4; Figure 2, Table 1). In addition, SEC plots showed a bimodal molecular weight distribution with a shoulder in the lower molecular weight region (circled area in Figure 2).

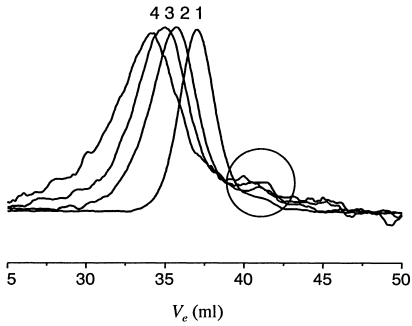

Fig. 2: SEC traces of hyperbranced polyglycerol samples taken from the same (non-optimized) reaction (measured in DMF, 45°C).

Table 1. Characterization data of hyperbranched polyglycerols using bis(2,3-dihydroxypropyl)hexadecyl amine as initiator.

#	theor. M_n [a)]	M_W/M_n [b)]	exp. M_n [b)]
1	7,000	1.96	7,000
2	9,000	3.01	8,200
3	11,000	4.89	17,000
4	16,000	4.65	-

a) calculated from monomer/initiator ratio
b) measured by SEC in DMF using poly(propylene oxide) calibration

Both the bimodality of higher molecular weight samples as well as the general broadening of the main distribution mode are undesired effects, explained by limitations peculiar to the slow-addition procedure employed. Mixing of the reactants is a crucial issue for polymerizations carried out under slow-monomer-addition conditions. Under the reaction conditions reported previously, the viscosity increases drastically, reducing the accessibility of all propagation sites. A major prerequisite for a controlled multibranching polymerization is the reversible termination, i. e., due to intra- and intermolecular transfer all propagation site (i.e., hydroxyl groups) remain active. Thus, the broadening of the molecular weight distribution is explained by the increasingly impeded diffusion of the monomer to the active sites slowing down the reversible termination continuously. When this happens, self condensing steps that may eventually lead to intramolecular cyclization can become a side reaction competing with the initiated growth process. As a consequence, oligomers with polymerizable core unit are formed. Both reaction of these species with other polymer molecules as well as intramolecular cyclization are expected to lead to a broadening of the molecular weight distributions, similar to "classic" AB_2 polycondensations.

By modification of the process parameters, i.e. increasing stirring intensity and changing stirrer geometry we were able to achieve more efficient mixing. In addition to a reduction of

the monomer addition rate we introduced diethylene glycol dimethyl ether (diglyme) as an inert and emulsifying solvent (polyglycerols of higher molecular weight are not soluble in diglyme) in order to dilute the monomer and reduce viscosity of the polymerization mixture We were thus able to obtain hyperbranched polyglycerols with monomodal, narrowed molecular weight distributions as well as molecular weights closer to the theoretical values. For example, as demonstrated in Figure 3 and Table 2, M_W/M_n was lowered by a factor of 2 for M_n = 9,000.

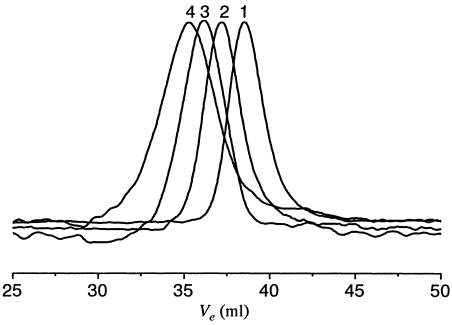

Fig. 3: SEC traces of various hyperbranched polyglycerol samples taken from the same reaction batch (optimized reaction parameters, measured in DMF at 45 °C)

Table 2. Characterization data of hyperbranched polyglycerols using bis(2,3-dihydroxypropyl)hexadecyl amine as initiator.

#	theor. M_n [a]	M_W/M_n [b]	exp. M_n [b]
1	2,400	1.62	2,700
2	5,300	1.80	6,000
3	9,000	1.65	12,000
4	17,000	2.99	20,000

a) calculated from monomer/initiator ratio
b) measured by SEC in DMF using poly(propylene oxide) calibration

In order to gain insight into potential side reactions, MALDI-TOF spectra have been recorded. It has to be noted that only a low molecular weight fraction of the whole molecular weight distribution can be detected by MALDI-TOF MS. However, since cycles are known to be present mainly in this fraction, as shown for hyperbranched polyesters[8], MALDI-TOF is a useful tool to determine whether cycles have been formed during the polymerization. Figure 4 a-c shows the MALDI-TOF spectra of the three samples taken from the same reaction after different portions of glycidol monomer had been added. Figure 4a gives the spectrum of a hyperbranched polyglycerol sample with M_n = 7,000 g/mol. Clearly, there is no subdistribution and the signals evidence 100% initiated (core-bearing) polymer molecules. When viscosity increases with molecular weight the formation of cycles is observed in the low molecular weight fraction, which is confirmed by a subdistribution in the MALDI-TOF spectrum (Figure 4 b). Calculations confirm that the newly appearing peaks belong to cyclic species bearing one potassium as counter ion (M = DP*74.1 + $M(K^+)$) (Table 3).

Interestingly, the high viscosity in the final stages of the reaction even leads to a reversal of the intensities of cyclic and initiated species (Figure 4 c). Once more, it should be emphasized that the main distribution mode containing the desired high molecular weight material can not be observed in this MALDI-TOF spectrum. The fraction of cycles revealed by MALDI-TOF is small when compared to the whole batch and could not be observed in SEC.

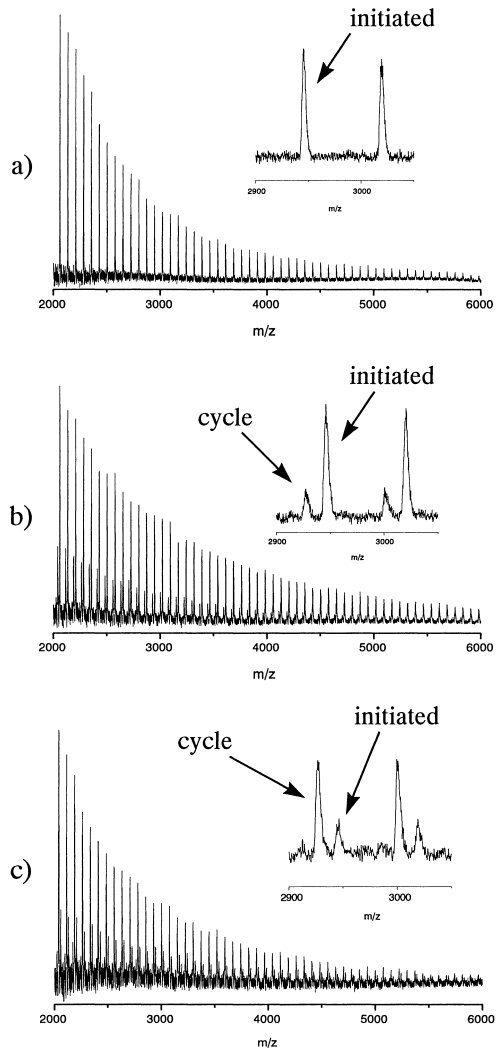

Fig. 4 a-c: MALDI-TOF MS spectra of three polyglycerol samples with increasing molecular weight taken from the same reaction batch, starting with a) M_n = 7000 (molar ratio glycidol : TMP = 95:1). Inserts display enlarged spectrum from m/z = 2,900 to 3,050 g/mol.

Table 3. MALDI-TOF m/z of cycles and initiated species (initiator: bis(2,3-dihydroxypropyl)hexadecyl amine)

	[cyclic species·K^+] m/z		[acyclic species·K^+] m/z	
DP_n	calcd.	found	calcd.	found
34			2947.4	2945.5
35			3021.5	3020.5
39	2928.2	2928.0		
40	3002.3	3001.7		

Materials properties change distinctively when comparing lower and higher molecular weight samples of hyperbranched polyglycerols. Whereas samples with molecular weight of a few thousand g/mol were obtained as honey-like, sticky oils, polyglycerols with M_n exceeding 10,000 g/mol are almost non-sticky, highly viscous materials that do not flow. Detailed rheological and mechanical characterization is in progress.

Absolute molecular weight determination of hyperbranched polyglycerols with M_n > 10,000 g/mol represents a challenge, since the commonly employed characterization methods reach their limits. NMR only gives reliable results for polyglycerols with molecular weight < 10,000 g/mol. The accuracy of the previously employed vapor pressure osmometry also decreases with molecular weight, especially for the highly polar polyglycerols. Nevertheless, with respect to experimental error, measurements with fully acetylated (hydrophobized) samples confirm the high molecular weights expected from the monomer/initiator ratio and SEC results.

Conclusions

We have been able to enhance molecular weight of hyperbranched polyglycerols up to 20,000 g/mol (DP_n = 270). Undesired cyclization leading to a broadening of the polydispersity and loss of control could be suppressed over a large molecular weight range by optimization of the polymerization process. The obtained samples, with up to 270 hydroxyl end groups, can be used as reactants for a wide range of possible applications. Currently, a detailed investigation of structure-property correlations of these high molecular weight hyperbranched polyglycerols and their intriguing rheological properties is in progress.

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