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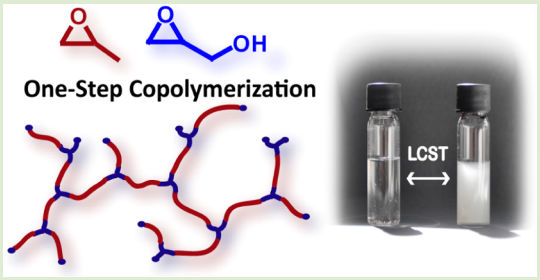
Hyperbranched Poly(propylene oxide): A Multifunctional Backbone-Thermoresponsive Polyether Polyol Copolymer

Martina Schömer, Jan Seiwert, and Holger Frey*

Institute of Organic Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, D-55099 Mainz, Germany

Supporting Information

ABSTRACT: Backbone-thermoresponsive hyperbranched poly(propylene oxide)-based polyether polyols have been synthesized by anionic ring-opening copolymerization of glycidol and propylene oxide. The number of functional hydroxyl end groups and the lower critical solution temperature (LCST) can be readily adjusted by varying the comonomer ratio. Molecular weights in the range of 1200−2000 g/mol were achieved. Hyperbranched polyether polyols with LCST values between 24 and 83 °C can be obtained in a convenient one-step reaction.

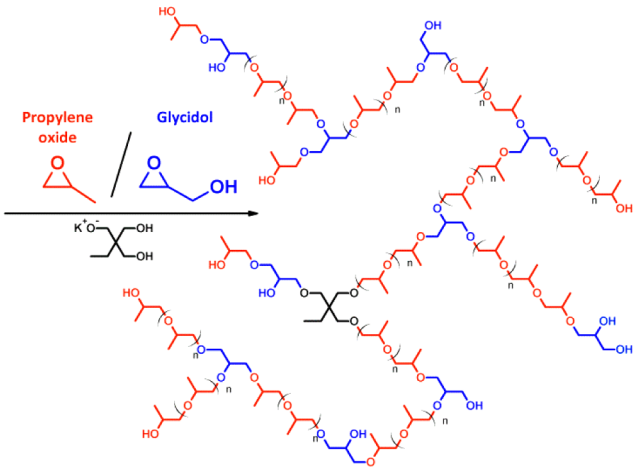


Hyperbranched polymers have attracted broad attention, due to their unique molecular structures and distinct chemical and physical properties, as well as their numerous potential applications.[1−9] Among them, thermoresponsive polymers, which combine the advantages of a multifunctional structure with "smart" behavior are of particular interest. To date, two different strategies have been employed to prepare thermoresponsive hyperbranched polymers. One is the modification with temperature-responsive functional groups or oligomer segments.[10−14] The other option is the combination of hydrophobic and hydrophilic functionalities into a highly branched polymer backbone. This type of backbone-thermoresponsive hyperbranched polymer has been hardly investigated. Recently, some examples, prepared through proton transfer polymerization of diglycidyl ethers[15−17] or cationic polymerization,[18] were reported. Furthermore, poly(ether-ester)s[19] and poly(ether-amine)s[17,20,21] are known.

Here we report the synthesis of a backbone-thermoresponsive hyperbranched polyether by anionic polymerization. Combining the two commercially available monomers propylene oxide and glycidol allows for the generation of copolymers with adjustable functionality and lower critical solution temperature (LCST) in one single step. Both monomers have been combined before to generate linear structures and block architectures,[22−27] but a random copolymerization, as it has recently been reported for the monomer combination ethylene oxide/glycidol[28] has not been successful to date.

We present a straightforward random copolymerization protocol for the preparation of multifunctional and thermoresponsive poly(propylene oxide) (PPO) copolymers in one single step. The degree of functionality and the LCST can be controlled by the comonomer ratio. The synthetic route to the multifunctional hyperbranched PPOs is given in Scheme 1. The polymerization of propylene oxide (PO) and glycidol was carried out in bulk at 120 °C. These conditions result in an anionic ring-opening multibranching copolymerization. An alkoxide initiator first reacts with one of the monomers and opens the epoxide ring. Rapid proton transfer from the secondary alkoxide to a primary alkoxide (either intra- or intermolecular) leads to branching during the reaction, generating hyperbranched poly(propylene oxide) copolymers with glycerol branching units. Protic termination is necessary to release the hydroxyl groups. The copolymerization can be carried out without any solvent and hyperbranched PPO copolymers in 80−90% yield are obtained.

Scheme 1. Synthesis Scheme for the Anionic Ring-Opening Multibranching Copolymerization of Propylene Oxide and Glycidol



Surprisingly, chain transfer to the monomer propylene oxide (which is a well-known side reaction for poly(propylene oxide)

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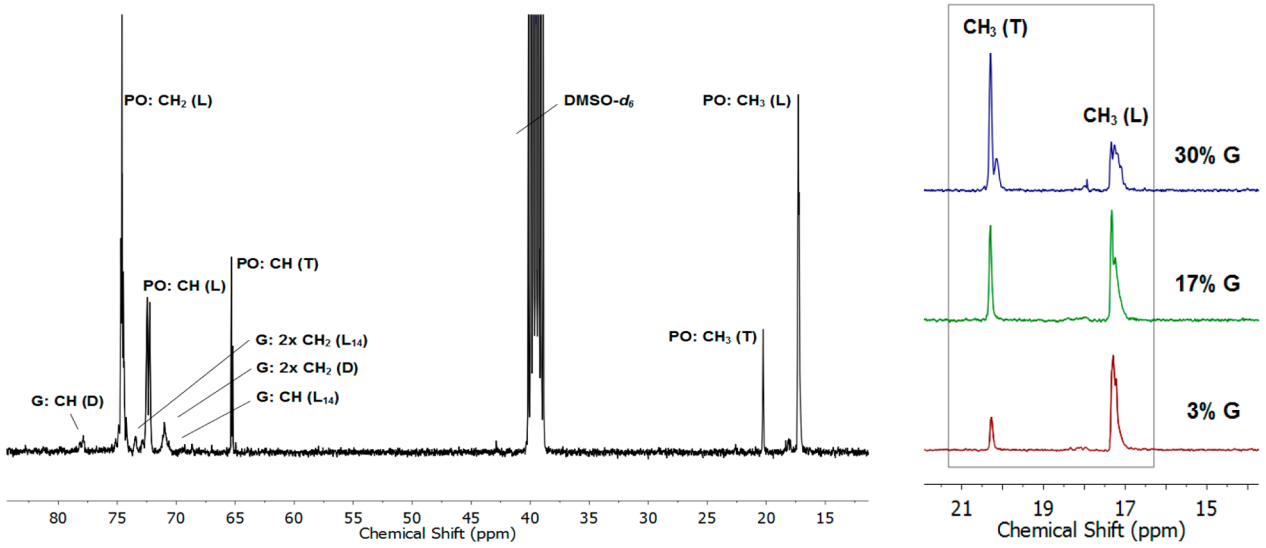

Figure 1. (a) ^{13}C NMR spectrum (100 MHz, inverse gated) of *hb*PPO-*co*-PG sample (3% glycidol) with signal assignment; (b) Comparison of the methyl region of ^{13}C IG NMR spectra (100 MHz) obtained from *hb*PPO-*co*-PG with different glycidol fractions.

Table 1. Characterization Data for *hb*PPO-*co*-PG Copolymers with Varying Monomer Compositions

sample	G^a (mol %)	G (mol %; th.)	DB^b (%)	$M_n{}^c$ (g mol^{-1})	PDI^c	T_g (°C)	LCST (°C)
*hb*PPO$_{0.97}$-*co*-PG$_{0.03}$	3	5	11	2000	1.48	−65	24
*hb*PPO$_{0.88}$-*co*-PG$_{0.12}$	12	10	18	1400	1.68	−62	33
*hb*PPO$_{0.83}$-*co*-PG$_{0.17}$	17	15	27	1350	1.65	−59	40
*hb*PPO$_{0.80}$-*co*-PG$_{0.20}$	20	20	37	1600	1.41	−54	43
*hb*PPO$_{0.70}$-*co*-PG$_{0.30}$	32	30	50	1700	1.69	−49	83
*hb*PPO$_{0.62}$-*co*-PG$_{0.38}$	38	40	53	1500	1.40	−48	
*hb*PPO$_{0.44}$-*co*-PG$_{0.56}$	56	50	59	1160	1.63	−35	

^{a}Determined from ^1H NMR. ^{b}Determined from inverse gated ^{13}C NMR. ^{c}Determined from SEC (solvent: DMF, PEO standard).

synthesis) is not observed. Therefore, potassium can be used as a counterion, and the use of the larger but more expensive cesium (that would lower the rearrangement tendency) can be avoided.

The end group functionality of the resulting copolymer depends on the number of incorporated glycerol branching units (because each glycerol unit adds exactly one additional hydroxyl group) and can thus be directly adjusted by the comonomer ratio. Incorporated glycidol monomer may result in branching points (if both functional groups propagate) as well as linear or terminal units.

The hyperbranched structure of the obtained copolymers was confirmed by detailed NMR analysis. The assignment given in Figure 1 is based on literature data as well as two-dimensional NMR spectroscopy that permits to correlate ^{13}C and ^1H NMR shifts (cf. Supporting Information, Figure S2). The occurrence of the methine carbon signal for the dendritic glycerol unit (78.0 ppm) is an unambiguous proof for the branched polymer structure together with the characteristic peak pattern of the PO methyl group (cf. Figure 1b). The glycidol content was varied from 3 to 56%. With increasing glycidol fraction the degree of branching (DB) value increases, starting with only slightly branched polymers with 3% glycerol units up to hyperbranched polymers with higher glycerol contents. The DB was calculated using the equation introduced by Hölter and Frey for random copolymerization of AB/AB$_2$ systems:[29]

$$D_{AB/AB_2} = \frac{2D}{2D + L_{CO}}$$

Details for the DB determination can be found in the Supporting Information. The calculated DB values are summarized in Table 1.

Introducing more glycerol units goes along with a rising number of end groups as each glycerol units adds exactly one additional hydroxyl end group. The methyl group of the propylene oxide unit shifts from 17.3 to 20.3 ppm when it is incorporated as a terminal unit, compared to the linear incorporation. In Figure 1b, a considerable shift of the intensities of the two resonances can be seen, which reflects the increase in terminal propylene oxide units, depending on the degree of branching.

In contrast to previous reports on PPO star copolymers with hyperbranched polyglycerol as a core,[24] random hyperbranched PPO copolymers are formed, as it is evident from NMR spectra and the dependence of the end group structure on the comonomer composition. For the random copolymers, the PO/G ratio can be adjusted and the so far necessary multistep synthesis can be reduced to one single polymerization step.

The thermal behavior of the hyperbranched polyethers has also been investigated. Differential scanning calorimetry (DSC) has been used to quantifiy the thermal properties of the materials. With increasing glycerol content, the glass transition (T_g) increases from the T_g of the linear homopolymer PPO (−73 °C)[23] to the T_g of the hyperbranched homopolymer polyglycerol (−25 °C).[30] We ascribe this to the additional

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interaction of the increasing number of hydroxyl groups via hydrogen-bonding in the multifunctional copolymers. In contrast to hyperbranched poly(ethylene oxide),[28] a completely amorphous and, thus, highly flexible hyperbranched polyether polyol is obtained.

Size exclusion chromatography (SEC) yields molecular weight distributions with M_w/M_n between 1.4 and 1.7 (Table 1, Figure S4). MALDI ToF mass spectrometry shows molecular weights in the same range and supports incorporation of both comonomers (cf. Figure S5, Supporting Information). Molecular weights are generally in the range of 1000−2000 g mol^{-1}, that is, in the same range as for numerous other hyperbranched materials.[6] It appears that the amount of initiator used does not permit to control molecular weights, in contrast to the hyperbranched polyglycerol homopolymer. Further work on this issue is under way. However, it is remarkable that hyperbranched PPO copolymers of moderate polydispersity index and adjustable functionality can be obtained, despite deviating from a slow addition protocol, as is typically employed to control the anionic hyperbranching homopolymerization of glycidol.[3,30]

In contrast to the PPO homopolymer, the hyperbranched polyethers are highly soluble in water under ambient conditions. This is attributed to the introduction of additional hydroxyl end groups as a consequence of the incorporation of glycidol as a comonomer. Interestingly, the hyperbranched PPO-based polyethers show temperature-sensitive solubility in aqueous solution with a lower critical solution temperature (LCST). The thermoresponsive behavior can be explained by the interplay of the hydrophilic groups (especially the hydroxyl end groups) and the hydrophobic methyl groups of the rather apolar PPO segments. At temperatures above the cloud point of the solutions, the hydrophobic domains cause a phase separation from water due to aggregation. This forces the polymer chain to undergo a coil-to-globule transition and consequently results in the observed macroscopic precipitation. For linear aliphatic polyether copolymers, a similar temperature-dependent solubility behavior in aqueous solution has been reported recently.[22,31] Cloud points of aqueous copolymer solutions have been investigated by turbidimetry measurement, using a temperature-controlled UV−vis spectrometer. Figure 2 shows the temperature dependence of the light transmission of aqueous polymer solutions and the dependence of the LCST on the glycerol content. As can be seen from Figure 2a, the LCST behavior can be controlled by variation of the comonomer content. With increasing fraction of the more hydrophilic glycerol units, the LCST of the hyperbranched PPO copolymers increases. At this point, we assume that the unusual curve shape of the copolymers with intermediate glycidol content has to be ascribed to the hyperbranched nature of the copolymers, as they differ from analogous linear copolymers.[22] Figure 2b shows the effect of the glycidol content on the LCST. The LCST value increases almost linearly with increasing content of the hydrophilic glycerol comonomer.

This is consistent with previous reports on linear random polyethers based on ethylene oxide and PO or other glycidyl ethers.[31,32] Our study demonstrates that this behavior is also found for hyperbranched polyethers. The interception with the *y*-axis (19.7 °C) corresponds to the LCST of a polymer with 0% of comonomer incorporated (PPO homopolymer) and is in good agreement with previous experimental results for the PPO homopolymer.[33]

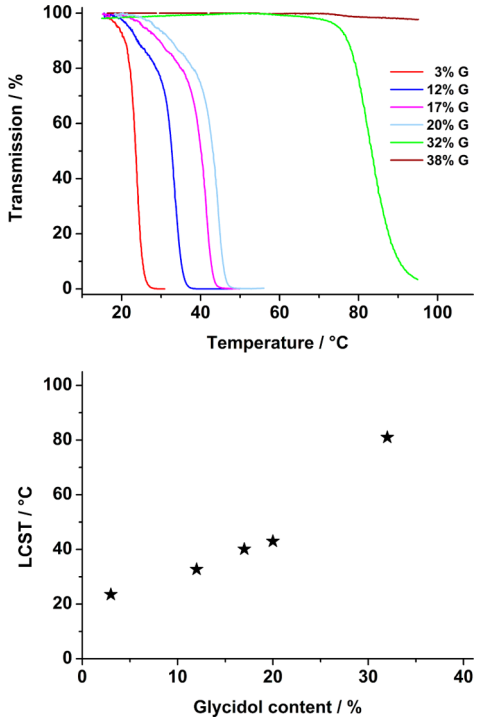

Figure 2. (a) Intensity of transmitted laser light vs temperature for *hb*PPO-*co*-PG copolymers of various compositions at a concentration of 5 mg mL^{-1} in aqueous solution. (b) Effect of glycidol content on LCST.

In summary, we have introduced a new type of backbone-thermoresponsive hyperbranched polyether prepared by solvent-free anionic copolymerization of propylene oxide and glycidol in one single step. The copolymer composition and the LCST values can be readily adjusted by varying the comonomer ratio. In all cases monomodal, moderate molecular weight distributions with PDIs generally below 1.7 were obtained. The hyperbranched polyethers with thermoresponsive backbone possess an adjustable number of hydroxyl end groups that can be used for further functionalization or cross-linking. Their possible use as building blocks for stimuli-responsive hydrogels or nanoparticles in the biomedical field or as flexible polyol component for polyurethanes renders them interesting for further exploration.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hfrey@uni-mainz.de.

Notes

The authors declare no competing financial interest.

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