Phase Transition Dynamics and Mechanism for Backbone-Thermoresponsive Hyperbranched Polyethers

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1. Calculation of the degree of branching

Quantitative ¹³C NMR characterization was conducted to determine the hyperbranched structure of resultant polymers. According to the literature¹⁻⁴ and NMR results, the obtained hyperbranched polyethers consist of six kinds of repeating units, including the linear THF unit (L_T), 1,2-linked and 1,3-linked linear glycidol units (L_{G12} and L_{G13}), 1-linked and 2-linked terminal glycidol units (T_{G1} and T_{G2}), and dendritic glycidol unit (D_G), as shown in the quantitative ¹³C NMR spectrum (Figure S1).



Figure S1. Quantitative ¹³C NMR spectrum of HP-3

In particular, all the terminal groups were formed by hydrophilic glycidol units; however, no THF terminal unit was observed. The result could be further confirmed by the absence of the signal at δ 29.4 corresponding to HO-PTHF- units in the ¹³C NMR as shown in Figure S2. Similar result was reported in the copolymerization process of THF and ethylene oxide.⁵ It was because the rate constants of the reactions of tertiary oxonium ions with THF and HO- are close to each other,⁶ causing that the excess of THF over HO- groups is becoming insufficient to maintain effective incorporation of THF into a copolymer at the last stage of the polymerization.⁵



Figure S2. ¹³C NMR spectra of HP1 (a) and PTHF (b). PTHF was purchased from Sigma (TERATHANE[®] 1000), 25.9 (-OCH₂CH₂CH₂CH₂O-), 70.0 (O<u>C</u>H₂CH₂CH₂CH₂O-), 29.4 (-OCH₂CH₂CH₂CH₂OH), 61.7 (-OCH₂CH₂CH₂CH₂OH).

The DB of hyperbranched polyether was calculated using Frechet's equation (Eq. 1)⁷ and Frey's equation (Eq. 2)⁸ respectively. The ratio of glycidol units incorporated into the structure [G] was also determined by Eq. 3. All the results are listed in Table S1.

$$DB_{Frechet} = (D+T)/D + T + L$$

= $(D+T_{G1}+T_{G2})/(D+T_{G1}+T_{G2}+L_T+L_{G12}+L_{G13})$ (1)

$$DB_{Frev} = 2D/(2D+L) = 2D/(2D+L_T+L_{G12}+L_{G13})$$
(2)

$$[G] = \frac{D_G + L_{G12} + L_{G13} + T_{G1} + T_{G2}}{L_T + D_G + L_{G12} + L_{G13} + T_{G1} + T_{G2}}$$
(3)

Table S1. Distribution of structural units and DB of the hyperbranched polyethers ^a

Sample	L_T %	L_{G12} %	L_{G13} %	T_{G1} %	T_{G2} %	$D_G \%$	[G] %	DB _{Frey}	DB _{Frechet}
HP1	57.0	12.4	9.2	10.5	1.4	9.5	43.0	0.20	0.21
HP2	53.2	13.7	10.7	10.1	1.4	10.9	46.8	0.22	0.22
HP3	49.2	15.2	11.2	10.8	1.5	11.5	50.2	0.23	0.24

^a determined by quantitative ¹³C NMR measurement in DMSO-*d6*.

2. SEC-MALLS-VS measurement

To study the compact conformation of hyperbranched polyethers, their molecular weight and intrinsic viscosity values $[\eta]$ were measured by SEC-MALLS equipped with a viscosity detector, as shown in Figure S3. The intrinsic viscosity of polymers is related with their molecular weight by the Mark-Houwink-Sakurada equation, $[\eta] = KM^{\alpha}$. The exponent α often reflects the topology of a polymer in solution. In general, the α value varies between 0.2 and 0.5 for the various hyperbranched polymers and depends on the degree of branching. While, for a linear polymer in a good solvent with a random coil conformation, the α value is typically in the region of 0.6-0.8.⁹ The viscosity measurements of the hyperbranched polyethers are summarized in Table 1, and the Mark-Houwink-Sakurada plots are presented in Figure S3 (b). Our experimental α values of HP-1, HP-2 and HP-3 are all less than 0.5, demonstrating their hyperbranched architectures and compact shapes in solution. Meanwhile, with the increase of the ratio of glycidol unit in polymer structure, the DB value slightly increases while the α value is almost unchanged, suggesting a constant compact conformation of hyperbranched polyethers prepared by our synthetic route.



Figure S3. (a) SEC profiles of the hyperbranched polyethers; (b) Mark-Houwink-Sakurada plot of hyperbranched polyethers.

3. DSC study

The DSC measurement showed that all the three hyperbranched polyethers were uncrystalline because no crystallization peak or melting peak was observed. The T_{gs} of HP1, HP2 and HP3 were -63.2, -64.7 and -66.3 °C respectively, indicating a slow increasing tendency with decreasing the content of glycidol in monomer feed.



Figure S4. DSC curves (2nd heating run with heating rate: 10 °C /min) of HP1, HP2 and HP3.

4. LCST Measurement

The transmittance of the linear PNIPAM aqueous solution decreased sharply between 38.4 and 41 °C, showing a typical LCST transition (Figure S5). Thus the LCST value of PNIPAM was about 38.4 °C. In addition, the LCST value was much higher than that of a general value of 32 °C. This finding may be attributed to the molecular weight effect of the narrowly distributed PNIPAM on its LCST.¹⁰ Similarly, the LCST values of HP2 and HP3 were 34.4 and 40.2 °C respectively (Figure S6 and S7).



Figure S5. Turbidity measurements of the linear PNIPAM aqueous solution (1 mg/mL). Heating rate = 1 °C /min



Figure S6. Turbidity measurements of the HP2 aqueous solution (1 wt%) increased step by step. Inset (a): Transmittance plots as temperature increased form 34.2 °C to 34.4 °C. Inset (b): Transmittance plots as temperature increased form 34.4 °C to 34.6 °C.



Figure S7. Turbidity measurements of the HP3 aqueous solution (1 wt%) increased step by step. Inset (a): Transmittance plots as temperature increased form 40.0 °C to 40.2 °C. Inset (b): Transmittance plots as temperature increased form 40.2 °C to 40.4 °C.

5. Dynamics parameters of phase transition



Figure S8. Phase transition time constant (τ) and final transmittance as a function of temperature for HP1 (A), HP2 (B) and HP3 (C) aqueous solution (1 wt%)

References

 Satoh, T.; Tamaki, M.; Taguchi, T.; Misaka, H.; Hoai, N. T.; Sakai, R.; Kakuchi, T. Synthesis of novel hyperbranched polymer through cationic ring-opening multibranching polymerization of 2-hydroxymethyloxetane. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 2353-2365.

- (2) Wilms, D.; Schömer, M.; Wurm, F.; Hermanns, M. I.; Kirkpatrick, C. J.; Frey, H. Hyperbranched PEG by Random Copolymerization of Ethylene Oxide and Glycidol. Macromol. Rapid Comm. 2010, 31, 1811-1815.
- (3) Tokar, R.; Kubisa, P.; Penczek, S.; Dworak, A. Cationic polymerization of glycidol: coexistence of the activated monomer and active chain end mechanism. Macromolecules 1994, 27, 320-322.
- (4) Dworak, A.; Walach, W.; Trzebicka, B. Cationic polymerization of glycidol. Polymer structure and polymerization mechanism. Macromol. Chem. Phys. 1995, 196, 1963-1970.
- (5) Bednarek, M.; Kubisa, P. Cationic copolymerization of tetrahydrofuran with ethylene oxide in the presence of diols: Composition, microstructure, and properties of copolymers. J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 3455-3463.
- (6) Tokar, R.; Kubisa, P.; Penczek, S.; Dworak, A. Cationic polymerization of glycidol: coexistence of the activated monomer and active chain end mechanism. Macromolecules 1994, 27, 320-322.
- (7) Hawker, C. J.; Lee, R.; Frechet, J. M. J. One-step synthesis of hyperbranched dendritic polyesters. J. Am. Chem. Soc. 1991, 113, 4583-4588.
- (8) Frey, H.; Hölter, D. Degree of branching in hyperbranched polymers. 3 Copolymerization of ABm-monomers with AB and AB_n -monomers. Acta Polymerica 1999, 50, 67-76.
- (9) Kong, J.; Schmalz, T.; Motz, G.; Müller, A. H. E. Novel Hyperbranched Ferrocene-Containing Poly(boro)carbosilanes Synthesized via a Convenient "A2 + B3" Approach. Macromolecules 2011, 44, 1280-1291.
- (10) Xia, Y.; Yin, X.; Burke, N. A. D.; Stöver, H. D. H. Thermal Response of Narrow-Disperse Poly(N-isopropylacrylamide) Prepared by Atom Transfer Radical Polymerization. Macromolecules 2005, 38, 5937-5943.