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Backbone-Thermoresponsive Hyperbranched Polyethers

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Thermoresponsive dendritic polymers, which combine the advantages of dendritic polymers[1,2] and thermoresponsive polymers,[3] have attracted considerable attention. To date, two different strategies have been employed to prepare thermoresponsive dendritic polymers. One is the incorporation of temperature-responsive groups[4a] or polymers[4b−e] onto the surface of a dendrimer or hyperbranched polymer. The other is the grafting of hydrophobic and hydrophilic functionalities into a highly branched polymer,[5] and the temperature sensitivity is given to the dendritic polymer by the appropriate balance of hydrophilic and hydrophobic moieties. In both cases, the backbone of the dendritic polymer is not thermoresponsive, and the temperature sensitivity is imparted by modification moieties. To the best of our knowledge, the dendritic polymer with a temperature-responsive backbone has not yet been prepared. We noted that Fréchet and co-workers[6] had reported the synthesis of hyperbranched polymers via proton-transfer polymerization[7] of 1,2,7,8-diepoxyoctane and trimethylolethane (TME). The obtained hyperbranched polyethers were hydrophobic so that they were insoluble in water. It has been well realized that an appropriate combination of hydrophilic/hydrophobic balance in the polymer chains is required for the occurrence of phase transition. Therefore, it can be inferred that, if 1,2,7,8-diepoxyoctane is replaced by a more hydrophilic monomer, the hyperbranched polymer with a thermoresponsive backbone might be obtained. Fortunately, we succeeded in preparing such backbone-thermoresponsive hyperbranched polyethers by proton-transfer polymerization of 1,4-butanediol diglycidyl ether (BDE) and various triols.

The polymerization of BDE and triol was carried out in dimethyl sulfoxide (DMSO) at 40 °C through one-step polymerization. The reaction proceeded homogeneously, and no gel formation took place throughout the course of polymerization. Details of the polymerization are described in the Supporting Information. Scheme 1 gives the polymerization mechanism: The triol **1** first reacts with potassium hydride (KH) to originate the initiator **1***. In the subsequent propagation step, the alkoxide potassium **1*** reacts with the epoxide ring of BDE **2** and generates a secondary alkoxide **3**. Rapid proton transfer from secondary alkoxide to primary alkoxide would facilitate the formation of **4**. Finally, continuous propagation and proton transfer afford the hyperbranched polyether **5**. The experimental condition and the correspondent characterization data for the final products are listed in Table 1.

The hyperbranched architecture for the obtained polyethers was confirmed by nuclear magnetic resonance (NMR) analysis. Details of architecture elucidation and degree of branching (DB) determination can be found in the Supporting Information. The calculated DB values are summarized in Table 1. With increasing the mole ratio of BDE to TME, the DB value increases.

Scheme 1. Schematic Representation of Proton-Transfer Polymerization of 1,4-Butanediol Diglycidyl Ether and Triol

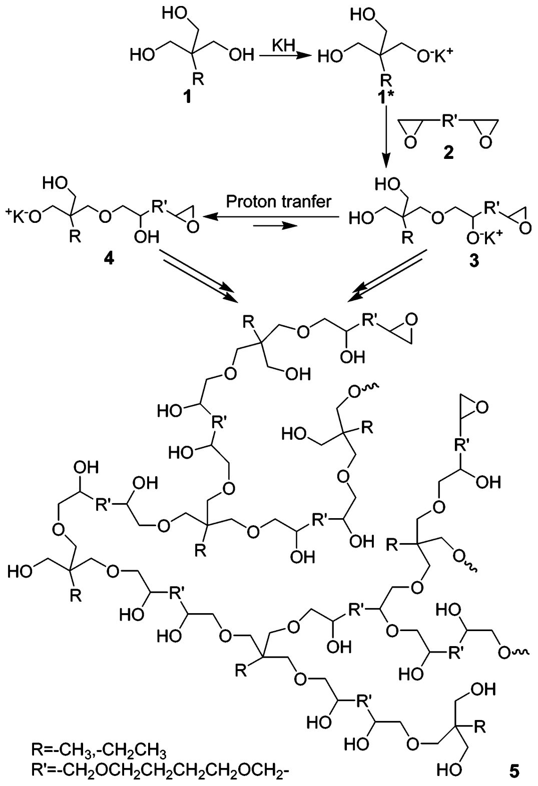

Table 1. Reaction Condition and Results of Proton-Transfer Polymerization of BDE and Various Triols[a]

No.	triol	yield (%)	M_n[i]	M_w/M_n[i]	DB	LCST[j] (°C)
1	TMP[b]	53	14900	3.63	0.50	19.0
2	TMP/TME[c]	72	10600	3.91	0.49	27.5
3	TMP/TME[d]	57	9300	3.23	0.47	35.7
4	TME[e]	68	11100	3.82	0.47	40.3
5	TME[f]	49	12700	3.60	0.53	36.3
6	TME[g]	48	12100	3.68	0.59	34.0
7	TME[h]	50	15900	3.19	0.63	28.1

[a] Reaction conditions: KH/triol = 1/4, temperature 40 °C, time 27 h. [b] BDE/TMP = 1/1 (mol:mol). [c] BDE/TMP/TME = 1/0.5/0.5. [d] BDE/TMP/TME = 1/0.1/0.9. [e] BDE/TME = 1/1 [f] BDE/TME = 1.2/1. [g] BDE/TME = 1.5/1. [h] BDE/TME = 2.0/1. [i] Molecular weights and polydispersity of the benzoyl chloride end-capped hyperbranched polymers, determined by GPC-MALLS. [j] Determined by UV−vis.

The hyperbranched polyethers obtained from BDE and various triols are highly soluble in water under low-temperature conditions. Interestingly, the transparent aqueous solutions of hyperbranched polyethers become opaque at a specific temperature as the temperature is increased and become transparent again when the temperature decreases. Moreover, the reversible phase transition

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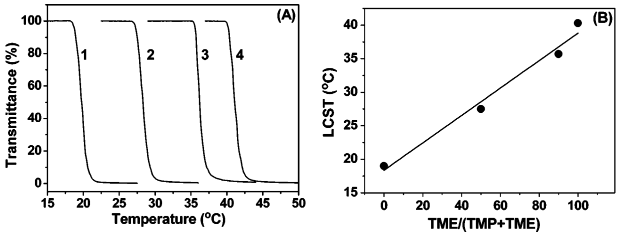

Figure 1. (A) Temperature dependence of light transmittance for aqueous solutions of samples 1−4. (B) Effect of TME/(TMP+TME) on LCST.

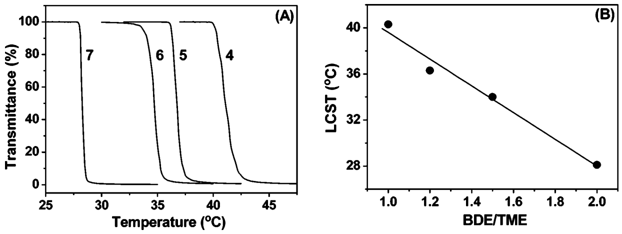

Figure 2. (A) Temperature dependence of light transmittance for aqueous solutions of samples 4−7. (B) Effect of mole ratio of BDE to TME on LCST.

occurs repeatedly. This phenomenon indicates that the obtained hyperbranched polyethers are temperature sensitive. The thermoresponsive behavior can be attributed to the combination of the hydrophilic groups (such as −OH and −O−) and hydrophobic groups (such as $-CH_3$, $-CH_2CH_3$, and $-C_4H_8-$) in the polymer backbone. At the temperature above the LCST, the interaction of the hydrophobic groups drives the polymeric chains to aggregate and then separate from water.[8]

The phase transition temperatures were determined in water by turbidimetry measurement on a temperature-controlled UV−vis spectrometer. Figure 1A and Figure 2A demonstrate the temperature dependence of the light transmittance of 1.0 wt % aqueous solution of samples 1−7 at 500 nm. The lower critical solution temperatures (LCSTs) were defined as the temperature corresponding to 90% transmittance of aqueous solution during the heating process. As can be seen, the transmittance decreases drastically in response to a minute change of the temperature around the LCST, indicating the highly sensitive phase separation.

A series of hyperbranched polyethers were prepared from BDE and various triols, such as trimethylolpropane (TMP) and trimethylolethane (TME). By increasing the hydrophilicity of triol, the LCST value of correspondent hyperbranched polyethers increases. Table 1 shows that the products prepared from TMP or TME show LCST values of 19.0 and 40.3 °C, respectively. By changing the ratio of TMP to TME, the LCST can be adjusted. Figure 1B displays the effect of the composition ratio on the phase transition behavior. It can be found that the LCST value increases almost linearly with increasing the content of TME in the range from 19.0 to 40.3 °C. Besides changing the ratio of different triols, the LCST can also be controlled by the initial mole ratio of diepoxide **2** to triol **1**. Figure 2B gives the effect of mole ratio of BDE to TME on LCST. The LCST decreases linearly with increasing the mole ratio of BDE to TME. These data suggest that LCST values can be easily adjusted at any desired temperature between 19.0 and 40.3 °C by controlling the hydrophilic−hydrophobic balance of BDE and various triols.

In conclusion, a new type of materials, the backbone-thermoresponsive hyperbranched polyether, has been successfully synthesized by proton-transfer polymerization of 1,4-butanediol diglycidyl ether (BDE) and various triols. Importantly, the LCST values can be readily adjusted from 19.0 to 40.3 °C by changing either the ratio of different triols or the ratio of BDE to TME. The hyperbranched polyether with a thermoresponsive backbone has a large number of hydroxyl and epoxide groups at the chain ends; therefore it is a potential intelligent matrix for further modification. For example, functional molecules, such as drug and probe, can be easily introduced, allowing favorable applications. Further studies on the backbone-thermoresponsive hyperbranched polymers and their functionalization are underway in our laboratory.

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

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