Proton-Transfer Polymerization: A New Approach to Hyperbranched Polymers

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We report a new polymerization process termed "proton-transfer polymerization" (Scheme 1), and its use in producing a novel hydrolytically stable epoxy or hydroxyl functionalized hyperbranched[1−3] polymer. A key feature of this new polymerization is that each propagation step involves a proton transfer for the activation of the nucleophile used in epoxide opening. Several polymerizations involving "activated monomer"[4] and some related processes[5] have been described in the literature. Unlike these, our process involves the added complexity of an AB$_2$ system combining growth and branching with a rapid increase in the number of reactive chain-ends.

Conceptually, the polymerization of H-AB$_2$ monomer **1** is initiated by the addition of a catalytic amount of initiator such as hydroxide ion, that abstracts a proton affording the reactive nucleophile **2**. Coupling of **2** with another monomer unit affords dimer **3** in which latent reactivity is now carried by one of the original B groups. This process is akin to that found in numerous conventional addition and ring-opening polymerizations. In this case, however, the active dimer **3** does not propagate directly but instead undergoes a thermodynamically driven proton exchange with another monomer **1** to produce nucleophile **2** and neutral dimer **4**. Subsequent nucleophilic additions and proton transfers afford a polymeric product. Given the multiplicity of reactive B species in each growing molecule that contains a single H-A group, the polymerization proceeds with branching, affording the desired hyperbranched structure. This novel propagation mode is clearly distinct from that found in the preparation of other hyperbranched polymers involving acid- or base-catalyzed esterifications,[2,6] etherifications,[7] cationic or radical promoted vinyl condensation,[3,8] or metal-assisted ring couplings.[1,9]
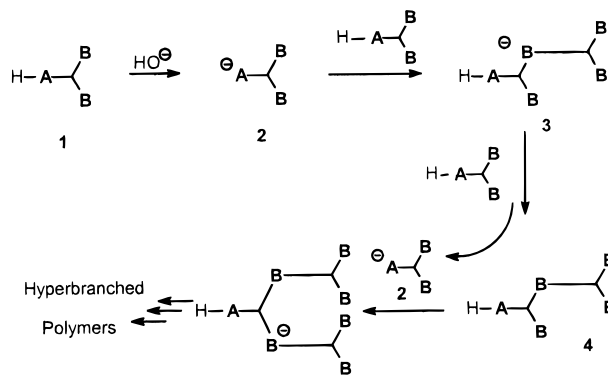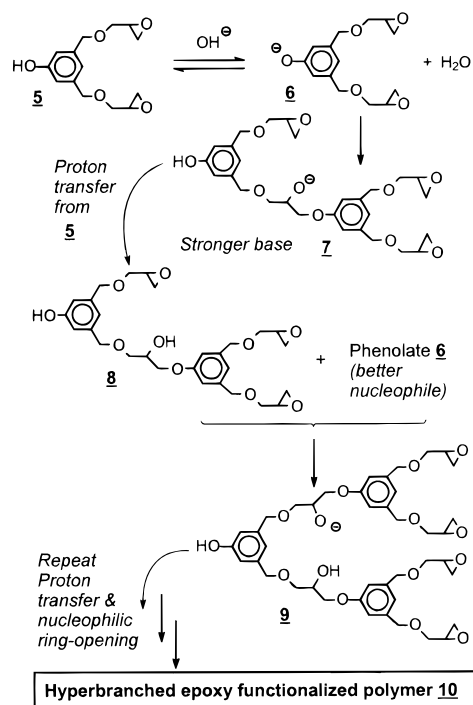
(1) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990,** *112,* 4592.
(2) (a) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991,** *113,* 4583. (b) Malmström, E.; Hult, A. *Macromolecules,* **1996,** *29,* 1222.
(3) Fréchet, J. M. J.; Hemmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* 1995, *269,* 1080.
(4) (a) Wichterle, O.; Sebenda, J.; Kralicek, J. *Czech. Chem. Commun.* **1964,** *29,* 610. (b) Acrylamide Bush, L. W.; Breslow, D. S. *Macromolecules* **1968,** *1,* 189. (c) Camino, G.; Guaita, M.; Trossarelli, L. *Makromol. Chem.* 1970, *136,* 155. (d) Sebenda, J. In *Polymerization of Heterocyclics*; Vogl, O., Furukawa, J., Eds.; Marcel Dekker: New York, 1973; p 153. (e) Otsu, T.; Yamada, B.; Itahashi, M.; Mori, T. *J. Polym. Sci., Polym. Chem. Ed.* **1976,** *14,* 1347. (f) Sekiguchi, H. In *Ring Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: New York, 1984; Vol. 2, p 809. (g) Gabbert, J. D.; Hedrick, R. M. *Polym. Process Eng.* **1986,** *4,* 359. (h) Udipi, K.; Dave, R. S.; Kruse, R. L.; Stebbins, L. R. *Polymer* **1997,** *38,* 927.
(5) (a) Imanishi, Y. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: New York, 1984; Vol. 2, p 523. (b) Kricheldorf, H. R. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: London, 1989; Vol. 3, Chapter 36. (c) Penczeck, S. Cationic Ring-opening Polymerization. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, T., Eds.; Pergamon Press: London, 1989; Vol. 3, Chapter 48. (d) Suzuki, M.; Sawada, S.; Yoshida, S.; Eberhardt, A.; Saegusa, T. *Macromolecules* **1993,** *26,* 4748. (e) Okada, M. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 4, p 2834.
(6) (a) Wooley, K. L.; Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *Polym. J.* 1994, *26,* 187. (b) Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1994,** *27,* 1611.
(7) (a) Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J.; Turner, S. R. *Macromolecules,* **1992,** *25,* 4583. (b) Chu, F.; Hawker, C. J. *Polym. Bull.* **1993,** *30,* 265. (c) Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *Macromol. Symp.* **1994,** *77,* 35. (d) Percec, V.; Chu, P.; Unger, G.; Zhou, J. *J. Am. Chem. Soc.* **1995,** *117,* 11441.

Scheme 1

Scheme 2

To achieve this type of growth without undesired propagation through the nucleophilic center of **2**, the activation of monomer **1** or of the H-A groups of growing species must be significantly faster than the nucleophilic propagation step. Our first implementation of this proton-transfer polymerization was achieved with the base-initiated polymerization of phenolic bisepoxide **5**. Monomer **5** (Scheme 2), obtained from the commercially available dimethyl 5-hydroxyisophthalate, possesses structural features that enable both a fast proton transfer for activation to the phenolate and a slow nucleophilic ring opening of the epoxide group[10] for growth. Chemo- and regioselective growth is preserved as a result of the significantly higher nucleophilicity of phenolate vs secondary alkoxide and the preference for ring opening at the less

(8) (a) Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995,** *117,* 10763. (b) Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998,** *36,* 955.
(9) (a) Fomina, J.; Fomine, S.; Salcedo, R.; Ogawa, T. *Polym. J.* **1996,** *28,* 1071. (b) Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1997,** *119,* 3391.
(10) (a) Boileau, S. Anionic Ring-Opening Polymerizations; Epoxides and Episulfide. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: London, 1989; Vol. 3, p 467. (b) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons Press: New York, 1993; p 538.
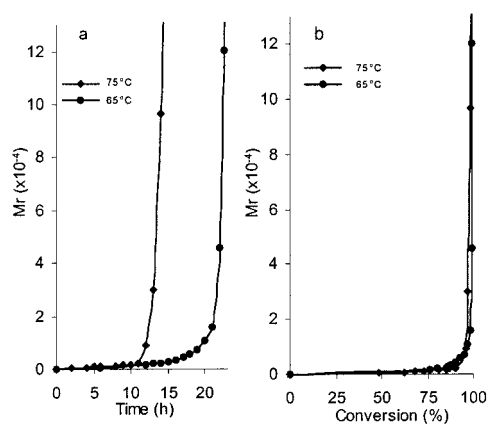
Figure 1. Kinetic profile of the base-catalyzed proton-transfer polymerization.

Table 1. Result of Polymerizations of **5**[a]

entry	temp. (°C)	time (h)	M_w[b] (MALLS)	M_w[c] (GPC)	M_n[b] (GPC)	PDI	yield (%)
1	70	13	8000	3200	2400	1.3	65
2	70	17	19000	12200	4900	2.5	96
3	70	18	59000	32700	5600	5.8	98
4	70	18.5	206,000	74,600	6200	12	94
5[d]	75	96	137000	57900	23800	2.4	75

[a] Conditions: 5% KOH was used, precipitation from methanol. [b] M_w was calculated from multi-angle laser light scattering in THF with dn/dc = 0.14. [c] M_w based on calibration with polystyrene standards. [d] Portionwise addition of monomer, material was precipitated from ether.

hindered site of the epoxide. The much lower pK_a (ca. 10)[11] of the phenolic group relative to that of the secondary alkoxide obtained by epoxide ring opening (pK_a ∼17)[12] enables the fast proton transfer from phenol **5** to the secondary alkoxide **7** or **9**. The fast kinetics of the proton-transfer step coupled with the slow kinetics of the epoxide ring-opening process and the high nucleophilicity of the phenoxide moieties all contribute to preserve the structural integrity of the product in terms of chemo- and regioselectivity. A key feature is that, despite the formation of secondary alcohol groups, polymerization proceeds through the unique phenolic moiety of each growing molecule, while the number of chain-end epoxide groups increases. The resulting hyperbranched epoxide materials are potentially useful in adhesives and coatings, while further modification of the versatile epoxy chain-ends can provide access to hydrolytically stable materials with a wide range of peripheral functionalities.

Our initial polymerization experiments using base catalysis showed that the reaction proceeds in a reasonable rate at temperatures above 60 °C. The choice of solvent was critical, and THF was found to be superior to DMF, diglyme, ethanol, and 2-propanol. The slower rates observed in polar or protic solvents such as DMF and alcohols—normally good solvents for the ring opening of epoxides—was surprising. This suggests that the internal hydroxy-assisted ring opening via hydrogen bonding may play an important role in the polymerization. The influence of the counterion in the hydroxide-catalyzed polymerization was unimportant with the exception that Li$^+$ was sluggish. With all other counterions including sodium, potassium, cesium, and tetramethylammonium, the reaction reached 100% conversion[13] in 15 h at 75 °C.

Polymerization kinetics were studied for potassium *tert*-butoxide catalysis in THF at 65 °C and 75 °C (Figure 1). A temperature-dependent reaction rate was observed (Figure 1a), while the plot of relative GPC molecular weight M_r vs conversion (Figure 1b) showed the temperature-independent growth profile of the polymerization. This exponential growth of molecular weight at near complete monomer conversion parallels previous observations for other hyperbranched systems.[3,8,14] However, the propagation mechanism of this hyperbranched polymerization is more complicated than that of a classical polycondensation because of the large disparity between the number of focal phenolic groups and the number of peripheral epoxide groups. This significantly increases the chance of intramolecular cycliza-

tion, normally a chain-terminating process in classical polycondensation. Such cyclization side reactions contribute to slower growth since scarce phenolic moieties are consumed, but cyclized molecules can continue to grow through reaction of their peripheral epoxy moieties. Another important factor that affects growth is the unequal reactivity of the focal groups of species of different sizes as a result of their different steric environments. All of these factors contribute to the high polydispersity that is characteristic of hyperbranched polymerizations.[1–3,15]

At high conversion, the molecular weight of the hyperbranched epoxy polymer increases rapidly through the coupling of large oligomeric or polymeric chains. As the concentration of the phenolic moieties becomes very low, the reaction becomes sluggish, and side reactions involving epoxide ring opening by secondary alkoxide may occur leading to cross-linking. Given the slow kinetics of the ring opening polymerization process, cross-linking is avoided by simply lowering the reaction temperature and precipitating the polymer in a protic medium. Alternatively, to avoid "monomer-starved" conditions—or rather conditions under which the concentration of phenolic moieties falls rapidly below a threshold—the monomer may be added portionwise or through continuous slow addition. As shown[16] in Table 1 this approach leads to excellent and reproducible results with the formation of soluble hyperbranched epoxy polymers within a broad range of molecular weights. As expected, molecular weight and polydispersity increase with time (entries 1–4). The lower yield in entry 1 is attributed to the removal of small molecules during precipitation. As expected the weight average molecular weight values (M_w) obtained from multi-angle light scattering are larger than those measured by size-exclusive column chromatography, a common finding for such globular hyperbranched polymers.

As an added precaution to prevent the possibility of cross-linking in the very late stages of the polymerization process, we are exploring alternative approaches involving the use of non-nucleophilic proton shuttles such as 2,6-di-*tert*-butyl-4-methylphenol (BHT), with acidities intermediate between those of the phenolic moieties involved in polymer growth and the secondary alcohol moieties produced by epoxide ring opening. In addition, preliminary experiments with the use of chloride ion instead of base as the initiator have led to a highly controlled polymerization in which cross-linking is avoided since the chlorohydrin species that are formed are in equilibrium with epoxide and free chloride under the conditions of the reaction.

(11) *The chemistry of the hydroxyl group*; Patai, S., Ed.; Interscience, London, New York, 1971; part 1, 374.
(12) Reeve, W.; Erikson, C. M.; Aluotto, P. F. *Can. J. Chem.* **1979**, *57*, 2747.
(13) Conversion based on the ratio of SEC peak area of polymer against peak area of monomer.
(14) Bolton, D. H.; Wooley, K. L. *Macromolecules* **1997**, *30*, 1890.

(15) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.
(16) Typical polymerization procedure: a 7-mL screw-cap vial with a stir bar was charged with **5** (532 mg, 2 mmol), KOH (6.5 mg, 5 mol %), and THF (1.56 mL, 1 M). The system was degassed by sonication, capped under N$_2$, and placed in a bath at the desired temperature. The crude material was precipitated into methanol (80 mL), and the polymer was dried under vacuum at 35 °C for 2 days. The colorless material is very soluble in THF, CHCl$_3$, and CH$_2$Cl$_2$.