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Proton Transfer Polymerization in the Preparation of Hyperbranched Polyesters with Epoxide Chain-Ends and Internal Hydroxyl Functionalities

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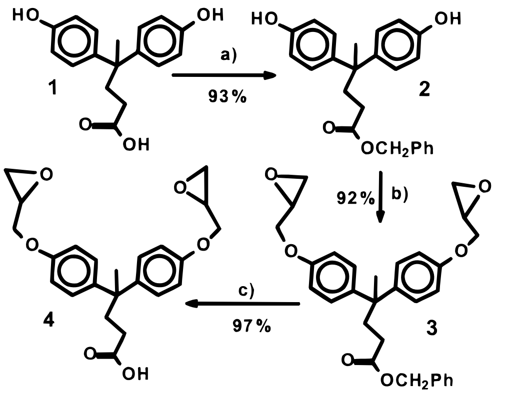
We have recently reported[1] the first purposeful preparation of hyperbranched polyethers from monomers containing hydroxyl and epoxide moieties by a process we termed “proton-transfer polymerization”. Related processes involving the ring-opening of epoxide groups by nucleophiles have since been described by Frey and co-workers, in their elegant work[2] on poly(glycidol), and by our laboratory[3,4] for $A_2 + B_3$ polymerization systems. It is clear that all of these previous polymerizations affording end-reactive hyperbranched polyethers involve a proton transfer as part of their growth mechanism.[1]

While all of these systems produce polymers with hydrolytically stable ether linkages, hyperbranched polyesters[5] are interesting for their potential be cleaved under relatively mild conditions. We now report a novel epoxy-terminated hyperbranched polyester prepared by proton-transfer polymerization of a AB_2 monomer.

Commercially available 4,4-bis(hydroxyphenyl)valeric acid **1**, is used for the preparation of monomer **4** (Scheme 1). Its carboxylic acid moiety of **1** is protected by reaction with 1 equiv of KOH in water to form the corresponding potassium carboxylate[6] followed by reaction with benzyl bromide to afford benzyl ester **2** in 93% yield. Subsequent reaction of ester **2** with epichlorohydrin in the presence of a base[7] afforded **3**, which was deprotected to the desired 4,4-bis(oxiranylmethoxyphenyl)valeric acid, **4**, by hydrogenolysis of the benzyl ester groups using palladium as the catalyst.

Scheme 1



a): i) KOH/H_2O, ii) $PhCH_2Br$;
b) epichlorohydrin,/K_2CO_3/Acetone; c) Pd/H_2/EtOAc.

As expected from its structure, monomer **4** should polymerize via a proton-transfer polymerization process[1] (Scheme 2). On the basis of our previous observation that epoxide ring opening was best controlled using a nucleophile, such as bromide ion, rather than a base, such as hydroxide ion, as the initiator, we first tested the polymerization initiated by tetrabutylammonium bromide. In the presence of bromide ion, an equilibrium between epoxide **4** and the ring-opened intermediate **5** is expected to be established. Rapid proton transfer from a carboxylic acid present in the reaction mixture (either another **4** or **5** itself) would occur producing a nucleophilic carboxylate-containing moiety **6** and a nonnucleophilic hydroxy-containing moiety **7**. Carboxylate **6** can then react with **4** or **7** to form a dimer **8**, in the propagation step. Scheme 2 outlines one of several possible growth pathways. The involvement of either **5** or carboxylate anion **6** is confirmed by control experiments in the absence of added nucleophilic initiator, for which no propagation was observed (Table 1, entry 1). Overall, polyester rather than polyether formation is expected to occur as a result of the very large difference in pK_a values between −COOH and −OH moieties as well as the higher nucleophilicity of carboxylate compared to that of hindered alkoxides. While the ring-opening of epoxide by alkoxide cannot be excluded, especially at high conversion, the process is unlikely as its occurrence would lead to cross-linking, which is not observed under our reaction conditions. An alternate mode of termination might involve a ring closing process in which the small amount of bromohydrin present in the growing macromolecules is converted again to epoxide moieties, as expected for such an equilibrium process.

According to the kinetic studies, with GPC monitoring of the growth process (Figure 1), chain growth only occurs slowly while monomers are consumed quite rapidly in the early stages. This implies that most of the monomers are rapidly transformed into low molecular weight oligomers. However, as the conversion approaches completion, the reaction reaches a “monomer-starved” state. Growth continues via the coupling of existing oligomers leading to a sharp change in the slope of the curve of GPC “molecular weight” vs time (Figure 1). Using Bu_4NBr as initiator, a polymer with M_w = 44 000 and PDI = 5.9 was produced within 27 h at 65 °C (Table 1, entry 2).

Because chloride ion is a weaker nucleophile than bromide, its use led to a slower polymerization, and formation of a lower MW polymer (M_w = 24 700) under the same conditions (Table 1, entry 2 vs 3d). Because of this relatively slow reaction, the polymerization can be quenched by precipitation into methanol−water at different polymerization times to afford polymers with a wide range of molecular weights (M_w = 3350 to 24 700) while the conversions remain essentially unchanged as the monomer disappears early in all cases (Table 1, entries 3a−d).

As expected, the polymerization is accelerated if the temperature is increased. Under otherwise identical condition with a reaction time of 18 h, a higher molecular weight polymer (M_w = 68 900) was obtained at 100 °C than at 60 °C (M_w = 3350) (Table 1, entry 4 vs 3a). While the use of polar solvents might be expected to facilitate the opening of epoxy ring, the polymerization was actually slower in DMF than in dioxane (Table 1, entry 5 vs 3d), and only a moderate molecular weight (M_w = 9110) was achieved using DMF as the solvent. This result is in agreement with our earlier observations

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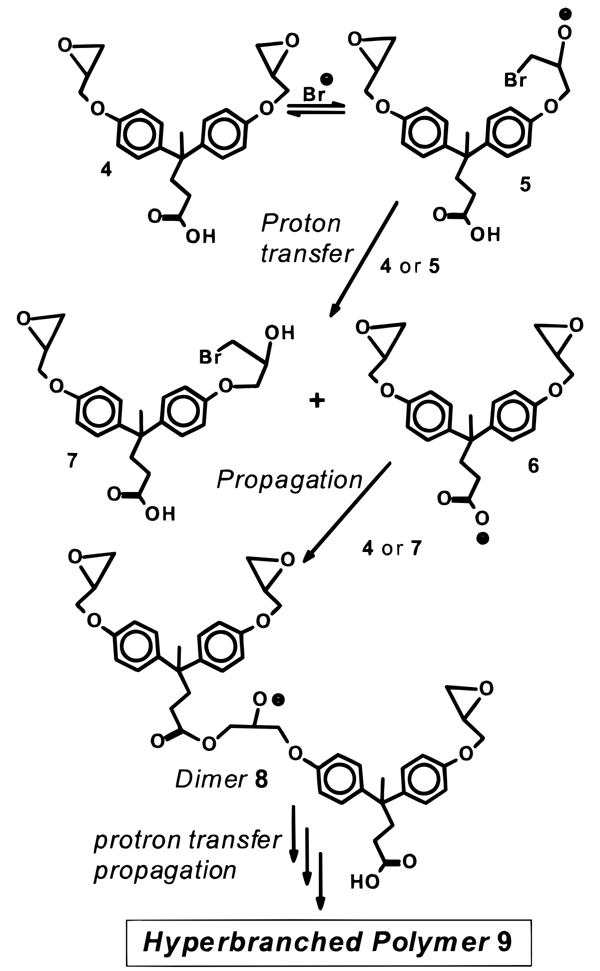
Scheme 2



and likely reflects the effect of hydrogen bonding:[1] a less polar solvent favors the H-bonding that assists the ring opening process and thus increases the polymerization rate. Another factor affecting the polymerization is the amount of initiator; the more initiator used, the faster the polymerization (Table 1, entry 6 vs 3a). Not unexpectedly, the weight-average molecular weight of polymer **9** (entry 4 in Table 1) measured by multiangle laser light scattering (204 000 with dn/dc = 0.16) is much higher than that measured by GPC using polystyrene standards (68 900). This difference reflects the highly branched nature and the globular shape of this hyperbranched polymer.

We have also tested the use of bases such as hydroxide as initiators. Given the fast kinetics of deprotonation, the base reacts with the carboxylic acid group of monomer **4** instead of opening the epoxy ring. The resulting carboxylate then opens an epoxy ring, initiating growth with the formation of a dimeric species, while simultaneously generating an alkoxide for subsequent growth via proton-transfer polymerization. While the polymerization was not successful using solid KOH alone, a high MW polymer (Table 1, entry 7b) was produced when 18-crown-6 was added to enhance the solubility of KOH in the reaction medium. With $(CH_3)_4NOH$, the polymerization proceeded with a kinetic profile similar to that for halide initiation (Figure 1) and high MW polymers were successfully obtained (Table 1, entry 8). Further experiments involving sodium *tert*-butoxide also led to successful polymerization with high MW achieved at a relatively high temperature (Table 1, entry 9 vs 10).

Table 1. GPC Results of Hyperbranched Polymers 9 under Different Polymerization Conditions[a]

entry no.	solvent	initiator[b] (type/mol %)	temp (°C)	time (h)	M_w[c] (Da)	PDI[c]	yield (%)
1	dioxane	none	65	40			0
2	dioxane	TBAB/2.4	65	27	44000	5.9	92
3a	dioxane	TBAC/2.4	65	18	3350	2.1	75
3b				21	7510	2.0	80
3c				24	14100	2.4	88
3d				27	24700	3.0	90
4	dioxane	TBAC/2.4	100	18	68900	4.2	93
5	DMF	TBAC/2.4	65	27	9110	2.5	81
6	dioxane	TBAC/7.2	65	18	29800	4.3	90
7a	dioxane	KOH/2.4[d]	65	27	7800	2.4[e]	
7b				46	54300	3.8	91
8a	dioxane	TMAH/2.4	65	27	3,600	1.9[e]	
8b				33	8,300	2.6[e]	
8c				39	59,000	3.9	89
9	dioxane	Na(*t*-BuO)/2.4	65	27	13,000	1.7[e]	
10	dioxane	Na(*t*-BuO)/2.4	100	27	26,900	3.1	89

[a] Monomer concentrations for all reactions are 1.26 M. Key: TBAC, tetrabutylammonium chloride; TBAB, tetrabutylammonium bromide; TMAH, tetramethylammonium hydroxide. [b] The mol % is relative to that of monomer **4**. [c] GPC results for precipitated polymers. [d] Ca. 4 equiv of 18-crown-16 with respect to KOH were used. [e] GPC measurements on aliquots without precipitation.

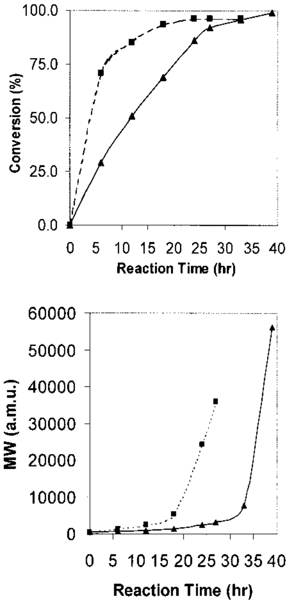


Figure 1. Polymerization kinetics for monomer **4** from GPC monitoring: (▲) dioxane, 65 °C, Me_4NOH; (■) dioxane, 65 °C, Bu_4NBr.

We have reported earlier that a seeded slow addition polymerization process can help control growth affording a lower polydispersity[1] product. However, this approach proved to be totally ineffective with this system, probably due to the inherently slower kinetics of the ring opening by carboxylate.

As implied in Scheme 2, the hyperbranched polyesters bear a multiplicity of epoxy groups at the chain-ends. These functional groups should prove useful in applications involving coatings or adhesives as the polymers can function as multifunctional cross-linkers. In addition, the epoxy groups may be transformed into a variety of other functionalities by simple post-modification reactions.

In conclusion, a large disparity of the pK_a values of the carboxylic acid and the secondary alcohol as well as the different nucleophilicities of their corresponding anions enabled the facile synthesis of a new class of hyperbranched polyester featuring multiple epoxy functionalities at its chain-ends as well as hydroxyl groups throughout its inner building blocks.

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Supporting Information Available: Text giving experimental information for the synthesis of monomer **4** and its polymerization and a figure showing GPC monitoring of a polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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