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An $A_2 + B_3$ Approach to Hyperbranched Aliphatic Polyethers Containing Chain End Epoxy Substituents

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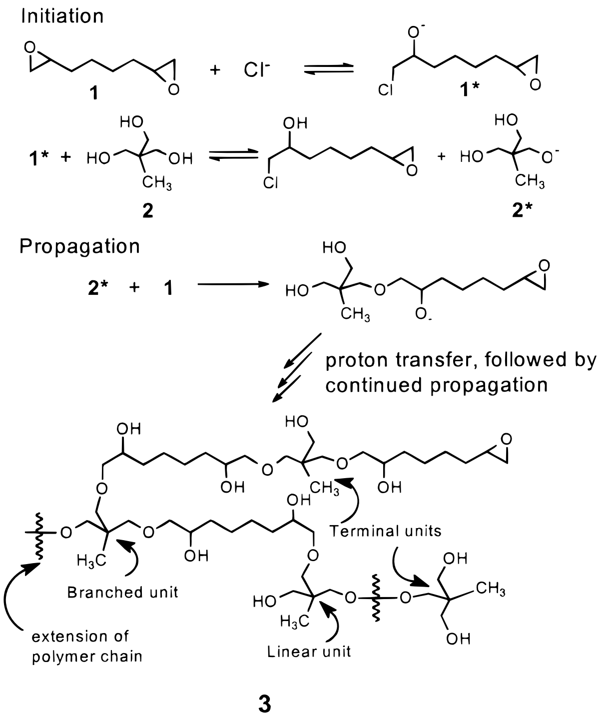
Over 50 years ago, Flory, Stockmayer, and others reported both statistical and experimental studies on polymerization systems that give polymers containing substantial chain branching.[1] Such work led to the theory of gelation,[1a] which explains in mathematical fashion the formation of cross-linked infinite networks obtained from various combinations of multifunctional monomers. One approach to such branched polymers utilizes two monomers in an $A_2 + B_3$ fashion, where the A and B monomers contain two and three reactive functionalities, respectively. The polycondensation of glycerol with phthalic anhydride is an early experimental example of the $A_2 + B_3$ approach.[1b,c] Salient features of an ideal $A_2 + B_3$ polymerization, as described by Flory, include the following assumptions: (1) the absence of intramolecular cyclization as a competing and chain terminating process during propagation, (2) equal reactivity of all A groups, as well as all B groups, in both the monomers and the growing polymers, and (3) the exclusive reactivity of A groups with B groups.

Today, many polymers that possess extensive chain branching are termed hyperbranched polymers.[2] These polymers mimic but do not duplicate the perfect branching found in dendrimers.[3] A practical advantage of hyperbranched polymers is their ease of preparation, typically a one-step polymerization from AB_n monomers (n usually ≥ 2), rather than the more tedious stepwise approach required in dendrimer synthesis. However, access to such AB_n monomers involves synthetic effort, which is potentially problematic, especially on a large scale. Thus, the key practical advantage of the $A_2 + B_3$ approach is that it precludes the need for an AB_n monomer synthesis due to the wider commercial availability of bi- and trifunctional monomers over AB_n monomers. This allows for faster and less costly preparation of the desired branched polymers.

In this communication we report our initial studies on an $A_2 + B_3$ polymerization approach to give branched polyethers,[4,5] employing 1,2,7,8-diepoxyoctane (**1**) as the A_2 monomer and 1,1,1-tris(hydroxymethyl)ethane (**2**) as the B_3 monomer. Tetra-*n*-butylammonium chloride (5 mol % based on **1**) was used as the nucleophilic catalyst. Initiation should occur by nucleophilic attack of chloride ion on an epoxide of **1** at the less-hindered, terminal carbon to give a secondary alkoxide. It can then be expected that equilibrium between primary and secondary alkoxides will be established through rapid proton exchange. Scheme 1 shows this proton-transfer polymerization process[6] where propagation proceeds by nucleophilic attack of primary alkoxides on epoxide rings to give the aliphatic polyether epoxy **3**. This type of propagation may compete favorably with nucleophilic attack by secondary alkoxides, in part due to steric considerations and in part due to the slightly greater acidity of a primary over a secondary alcohol. However, since these differences are small, propagation from secondary alkoxides is expected to occur as well, especially at the later stages of the reaction.

Scheme 1



We are very interested in the preparation of these branched aliphatic polyether epoxies for a variety of applications, including their potential use as low viscosity epoxies for adhesives and coatings. Thus, to provide a polymer with epoxy chain ends, an excess of diepoxide **1** over triol **2** was employed in the reaction mixture, in an $xA_2 + B_3$ manner, where $1.5 < x \leq 3$.

It was found that the rates of these polymerizations when carried out as solutions in THF were too slow to be practical. However, bulk polymerization at temperatures above 100 °C provided reasonable propagation rates. Optimum polymerization conditions involved simply heating **1**, **2**, and chloride catalyst in closed flasks at oil bath temperatures of about 120 °C.[7] Rigorous exclusion of air or moisture was not required for successful propagation.

Polymer growth was monitored by conventional gel permeation chromatography (GPC) performed on THF solutions of the polymer against linear polystyrene standards. The kinetic plot in Figure 1 resembles that of a step-growth polyaddition, where molecular weight growth is slow early in the reaction time frame, then much faster in the later stages. If the polymerization is allowed to continue through the “fast growth” portion of the curve in Figure 1, the material solidifies and cannot be dissolved, indicating that cross-linking (i.e., gelation) has occurred. However, gelation can easily be avoided by removing the reaction vessel from the heating bath prior to the gel point. It should be noted that control experiments using **1** and Bu_4NCl in the absence of **2** resulted in the formation of only trace

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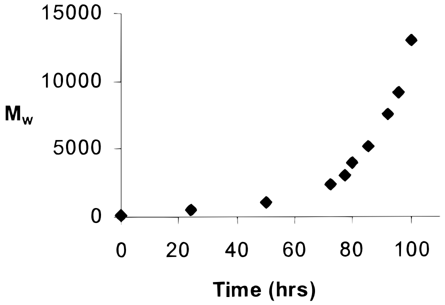

Figure 1. Growth of molecular weight (M_w) as a function of time (hours) for the reaction of diepoxide **1** with triol **2** ($3A_2 + B_3$).

amounts of oligomers. Furthermore, heating mixtures of **1** and **2** in the absence of chloride ion did not result in significant propagation.

The $xA_2 + B_3$ polymerizations were generally run until polymers with GPC weight-average molecular weights (M_w) of 5−15 000 amu were obtained. In the late stages of polymerization, viscous polymers were observed that were stirred with difficulty and flowed more slowly upon cooling to room temperature. Dissolution of the polymer product into minimal THF and subsequent precipitation into water effectively removed the catalyst (as well as low molecular weight polymer). The isolated polymer products were viscous, nearly colorless transparent liquids that showed good stability, as they readily redissolved after standing on the bench for months. Importantly, the reaction scale could be increased from our early milligram scale experiments to later runs employing 50 g of diepoxide.

It was found that increasing the starting relative ratio of diepoxide **1** to triol **2** increased the epoxy content of the isolated polymer product (as shown by ^{1}H NMR spectroscopy). The polydispersity (PD, defined as M_w/M_n) of the material increased with increasing molecular weight (e.g., ~1.5−1.8 at M_w ~1000 and ~5.0 at M_w ~7000). Such broad polydispersities are expected for polymers grown by this method. Precipitation resulted in a decrease in both M_w and PD, in accord with the removal of low molecular weight material. The purified polymers had polydispersity values of 3−4, depending on their molecular weights. Initial light-scattering studies, using multiangle laser light scattering (MALLS) in GPC mode, gave M_w values that are indeed much higher than those obtained by conventional GPC. This is in accord with the branched nature of polymer **3**.

The ^{1}H NMR spectra of the polymer products revealed the expected aliphatic and epoxy resonances. Interestingly, ^{1}H NMR spectroscopy could be used to interpret the substitution pattern of the polymer. The chemical shifts of the methyl resonances that result from the incorporated B_3 units were found to depend on the extent of triol substitution. Such chemical shift differences are known for di- and trisubstituted monomeric glycidyl ethers prepared from triol **2** and epichlorohydrin;[8] these are useful small molecule models for spectroscopic comparisons. In the polymer products of Scheme 1, branch units are possible only through trisubstituted B_3 units, while terminal and linear units are the result of mono- and disubstituted B_3 monomers. In the ^{1}H NMR (400 MHz in $CDCl_3$) spectrum of polymer **3**, the resonances at δ 0.82, 0.89, and 0.94 ppm are assigned to the methyl groups of the mono-, di-, and trisubstituted triol units, respectively. In contrast, the methyl group of monomer **2** is observed at δ 0.76 ppm in $CDCl_3$. This downfield trend in chemical shift with increasing triol substitution is in accord with the trend observed in the model compounds. The relative integration of these resonances provides an estimate of the extent of branching in polymer **3**. Indeed, we observe that at higher values of "*x*", the polymer product contained a higher percentage of trisubstituted B_3 units, as well as higher epoxy content. This should reflect both a higher percentage of trisubstituted internal branch units (i.e., dendritic units), as well as higher chain end substitution (i.e., "capping") to give terminal epoxides. The highest percentage of trisubstituted B_3 units was obtained for polymerizations carried out with $3A_2 + B_3$ stoichiometry. These polymerizations afforded a product that contained about 30−35% trisubstituted, 60−65% disubstituted, and only a very small percentage of monosubstituted B_3 units (as measured by integration of the ^{1}H NMR resonances).

In summary, we have prepared novel, highly branched aliphatic polyethers containing epoxy chain ends. The hyperbranched nature of the polymers is revealed through their ^{1}H NMR spectra. Even more extensive branching might be prohibited in this $A_2 + B_3$ system due to the congested nature of the B_3 monomer.

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(7) A typical polymerization was performed as follows: 1,2,7,8-Diepoxyoctane (2.27 g, 16.0 mmol), 1,1,1-tris(hydroxymethyl)ethane (768 mg, 6.40 mmol), and Bu_4NCl hydrate (222 mg, ca. 0.800 mmol) were combined in a screw cap vial. The mixture was stirred and heated at 120 °C for 96 h. The polymer was allowed to cool to room temperature and then dissolved in THF (10 mL) and precipitated into water (500 mL) to give after drying 1.7 g of **3** (55%). FTIR (KBR), ν: 3381 (br, OH), 2934, 2859, 2409, 2290, 1460, 1365, 1106, 1053, 846 cm^{-1}. GPC data: $M_n = 3000$; $M_w = 11\,300$; $M_p = 10\,600$; PD = 3.8. ^1H NMR, δ: 3.58−3.28 (br, CH and CH_2, polymer backbone), 2.92 (CH, epoxide), 2.75 (CH_2, epoxide), 2.47 (CH_2, epoxide), 1.64−1.22 (br, CH_2, polymer backbone), 0.92 (CH_3, trisubstituted units), 0.88 (CH_3, disubstituted units), 0.82 (CH_3, monosubstituted units).

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