

## Preparation of Hyperbranched Polyacrylates by Atom Transfer Radical Polymerization. 1. Acrylic AB\* Monomers in "Living" Radical Polymerizations

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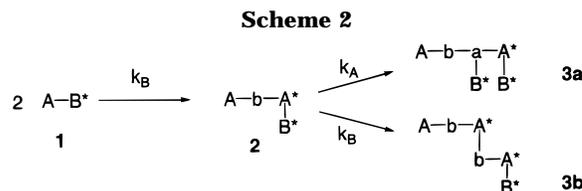
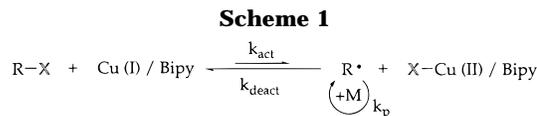
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In 1952, Flory<sup>1</sup> proposed that the polymerization of AB<sub>2</sub> monomers would lead to branched, but not cross-linked (network), structures. This proposal was first applied in the step-growth synthesis of polyphenylenes.<sup>2,3</sup> Subsequently, it was extended to other step-growth polymerizations such as aromatic<sup>4</sup> and aliphatic<sup>5</sup> esters,<sup>6</sup> siloxanes,<sup>7</sup> and amines.<sup>8</sup> Frechet *et al.*<sup>9</sup> later developed the concept of self-condensing vinyl polymerization, SCVP, to prepare hyperbranched polymers by carbocationic systems. Shortly afterward, SCVP was adapted to the radical polymerization of functionalized styrenes by Hawker *et al.*<sup>10</sup> and by our group.<sup>11</sup> Here we report the synthesis of hyperbranched polyacrylates by atom transfer radical polymerization, ATRP.

ATRP allows for the controlled polymerization of certain vinyl monomers, such as styrenes, acrylates, and methacrylates, by a radical mechanism. This is achieved by a reversible redox reaction between copper(I) salts and an alkyl halide (R–X), Scheme 1. Reaction of copper(I) with the alkyl halide results in the formation of a carbon centered radical and copper(II)–X, with the rate constant of activation,  $k_{act}$ . The radical can then initiate the polymerization of the monomer. However, the copper(II)–X readily reacts with the propagating radical to form copper(I) and a short oligomer with a halogen end group, with the rate constant of deactivation,  $k_{deact}$ . The process then repeats itself, with the polymer chain growing in short lengths and in a controlled manner. The final result is a polymer with  $DP = \Delta[M]/[I]_0$  and  $M_w/M_n < 1.4$ .

To describe the monomers for SCVP, the designation AB\* will be used instead of AB<sub>2</sub>.<sup>12,13</sup> AB\* allows for a better description of the final polymer structure due to the subtle differences in the polymer microstructure (cf. Figure 3), and the different statistics of chain growth and branching found in SCVP. The double bond is described by **A**, while **B\*** is a functional group which can be transformed to an active center and initiate the polymerization of the double bonds. The **B\*** group can be transformed to a cationic,<sup>9</sup> radical,<sup>10,11</sup> or anionic<sup>14</sup> active center. The activated **B\*** adds across the double bond **A**, to form the dimer. Scheme 2 shows the idealized case of one addition of monomer followed by deactivation to form the new group **A\***. The dimer, **2**, can now be reactivated at either **B\*** or **A\***. Addition of monomer at **A\*** results in **3a**, while addition at **B\*** yields **3b**. Further addition of monomer, or *n*-mer, to either **3a** or **3b**, can result in a polymer that is branched.

For AB\* monomers to be used in ATRP, they must contain a halogen atom capable of reacting with the copper(I). In a general description, the double bond (**A**) is separated from the **B\*** group by a spacer, **R**. Currently, the types of monomers that can be polymerized by ATRP, and consequently the type of **A** group, include styrenes, acrylates, and methacrylates. The **B\*** group

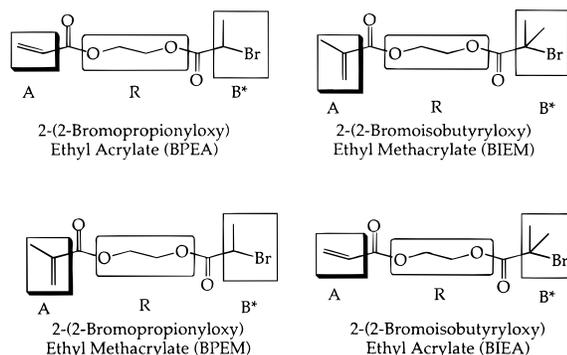


can be a (2-halopropionyl)oxy, (2-haloisobutyryl)oxy, 2-halopropionitrile, or benzyl halide.<sup>15</sup> The versatility of this approach is enhanced by the wide variety of **R** groups that can be inserted between the double bond, **A**, and the functional group, **B\***. By changing the various groups, **A**, **R** or **B\***, numerous monomers/materials can be developed.

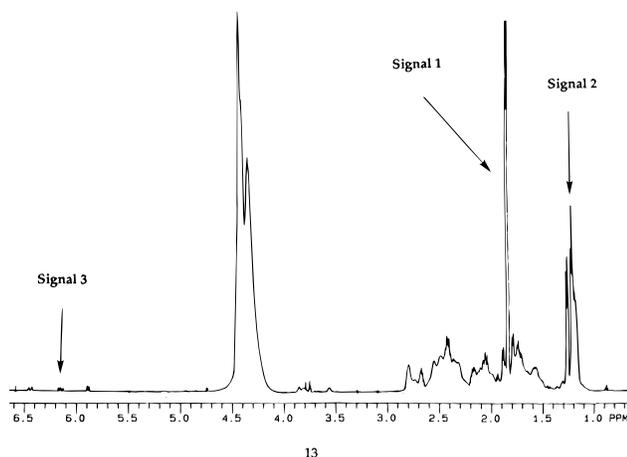
The polymers prepared with *p*-chloromethylstyrene<sup>11</sup> were high  $T_g$  materials due to the rigidity of the styrene units. To prepare materials with a lower  $T_g$ , acrylic AB\* monomers with more flexible structures were synthesized by reaction of 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate with an acid halide, such as 2-bromopropionyl bromide or 2-bromoisobutyryl bromide. Additionally, the polar (meth)acrylate structure provides polymers with new properties and with potential applications for new coatings materials. With these two monomers, and the acid halides, the four acrylic AB\* monomers shown in Figure 1 were synthesized.<sup>16</sup> This report is directed at the preparation of hyperbranched polymers using BPEA, as the asymmetric monomers (BPEM, BIEA) may lead to lower degrees of branching due to differences in the reactivity of the **A\*** and **B\*** groups.<sup>17,18</sup>

Hyperbranched polymers were synthesized by bulk homopolymerization of BPEA in the presence of 1 mol % copper(I) bromide and 0.1 mol % copper(II) bromide.<sup>19</sup> The copper(I) abstracts the bromine from the 2-bromopropionyloxy group (**B\***) to form the radical. This radical then initiates the polymerization of the acrylic bonds, and the propagating radical is then returned to the dormant state by reaction with the copper(II) bromide to form the new active center, **A\***. Subsequent activation of either **A\*** or **B\*** can then add monomer, or *n*-mer (the macromolecule is a macromonomer due to the double bond), to the macromolecule. One will note upon examination of the resulting microstructure that a hyperbranched, aliphatic polyester/polyacrylate is formed (cf. Figure 3).

Figure 2 is a 620 MHz <sup>1</sup>H NMR spectrum of the hyperbranched poly(2-((2-bromopropionyl)oxy)ethyl acrylate). The large doublet at 1.85 ppm, denoted signal 1, is assigned to the methyl group geminal to a bromine atom (see Figure 3), in agreement with the analogous assignment for the monomer BPEA. This signal is due to the presence of unreacted bromine groups (**B\***), i.e., homolytic cleavage of the carbon–bromine bond and subsequent addition of a double bond did *not* occur at these groups. A new group of signals from 1.3 to 1.1 ppm, denoted signal 2, are assigned to methyl groups which are pendent to the carbon–carbon polymer chain. These signals arise only when homolytic cleavage of the carbon–bromine bond and subsequent addition of a double bond occurs resulting in the formation of **b**. The group of signals from 6.5 to 5.8 ppm, denoted signal 3,



**Figure 1.** AB\* monomers synthesized for polymerization by ATRP to prepare hyperbranched acrylic polymers.



**Figure 2.** 620 MHz  $^1\text{H}$  NMR spectrum of poly(2-((2-bromopropionyloxy)ethyl acrylate).

are characteristic of the protons from the double bond, **A**. In addition, a broad set of signals in the range 1.5–2.9 ppm appears due to the polymer backbone (both  $\text{CH}_2$  and  $\text{CH}$  groups) as well as a strong signal from 4.1 to 4.5 ppm due to the ethylene glycol spacer group and the methine protons on both the **B\*** and the **A\*** groups.

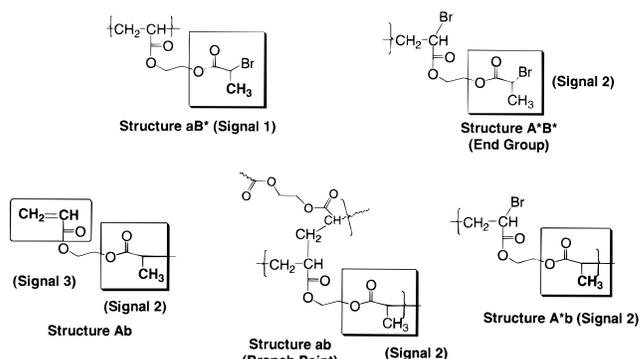
Assuming that there are no side reactions, such as termination by coupling or intramolecular cyclization, each hyperbranched polymer should have one double bond per macromolecule. The molecular weight can be calculated by comparison of intensities of the  $^1\text{H}$  NMR signals of the methyl group, (**b** or **B\***, on each repeat unit), and the double bond. Thus, the sum of the areas under the peaks of signals 1 and 2 (the  $\text{CH}_3$  groups—one per repeat unit) divided by the area under the peaks from the double bond (assuming one per macromolecule) gives the degree of polymerization, Table 1.

The molecular weight determined by NMR was higher than that determined by SEC. This observation may support the hyperbranched structure, as branched polymers are expected to have smaller hydrodynamic volumes than their linear analogues,<sup>20</sup> leading to longer

**Table 1. Results of the Homopolymerization of BPEA**

topology	time (h)	conv (%) <sup>a</sup>	$M_n^b$	$M_w/M_n^b$	$M_n^c$	DP <sup>c</sup>	<b>b/(b + B*)</b> <sup>d</sup>	$T_g$ (°C) <sup>e</sup>
hyperbranched <sup>f</sup>	3.5	89	4600	2.8	19 600	78	0.42	-11
	23.0	95	8300	2.0	25 400	101	0.44	-12
linear <sup>g</sup>			27800	2.3			0	-8

<sup>a</sup> As determined by 300 MHz  $^1\text{H}$  NMR (consumption of double bonds). <sup>b</sup> As determined by SEC vs narrow, linear poly(MMA) standards, after precipitation. <sup>c</sup> Degree of polymerization: as determined by 620 MHz  $^1\text{H}$  NMR, assuming one double bond per macromolecule, after precipitation. <sup>d</sup> **b/(b + B\*)** as determined by 620 MHz  $^1\text{H}$  NMR. <sup>e</sup>  $T_g$  measured on Rheometrics' DSC Plus with a heating rate of 20 °C  $\text{min}^{-1}$ . <sup>f</sup> Prepared by homopolymerization using ATRP. <sup>g</sup> Prepared by polymerization of BPEA with AIBN (0.1 mol %) in the presence of  $\text{CBr}_4$  (0.1 mol %) at 60 °C in benzene (50% v/v).



**Figure 3.** Polymer microstructures in the atom transfer radical polymerization of BPEA.

retention times in SEC and, consequently, apparently lower molecular weight values. However, intramolecular consumption of the double bonds could also partially contribute to the observed difference, as this would increase the  $M_n$  as calculated by  $^1\text{H}$  NMR. This intramolecular cyclization has been observed and will be discussed in a subsequent report.<sup>21</sup>

The integration of Signal 1 divided by the sum of the integration of signals 1 and 2 determines the proportion of remaining **B\***. If the polymer was linear, then either signal 1 or signal 2 would dominate. The dominance of one of the signals would be the result of the polymer having predominately one of the two structures (**aB\*** or **A\*b**) shown in Figure 3. If the structure of the macromolecule were perfectly dendritic, where only the branch point and end group structures were present, then the ratio of signal 1 to signal 2 would be 0.5 (**b = B\***). It is impossible to obtain a perfect dendrimer by SCVP without isolation and purification of the reaction intermediates. The growth of the hyperbranched macromolecule is governed by the relative rate of reaction at either **A\*** or **B\***. When considering the ideal statistics of chain growth for SCVP, assuming equal reactivity constants for **A\*** and **B\*** ( $k_A = k_B$ ), the proportion of **b** should equal 0.63 (**b/(b + B\*)**).<sup>17</sup> As can be seen in Table 1, the ratio of **b/(b + B\*)** is close, but not equal to that predicted for the statistical system with equal reactivities of **A\*** and **B\***. Since the chemical reactivity of **A\*** and **B\*** should be nearly equal, the difference may be due to slow deactivation of the propagating radicals (cf.  $k_{\text{deact}}$  in Scheme 1). However, the theoretical<sup>17,18</sup> behavior of the polymerization with  $k_A \neq k_B$  and a comparison of the observed behavior of the BPEA polymerization are beyond the scope of this report, and will be discussed in subsequent papers.

To conclude, the synthesis of new, AB\*, acrylic monomers has been accomplished by a simple procedure. One of the AB\* monomers, 2-((2-bromopropionyloxy)ethyl acrylate) was polymerized in bulk, using a copper(I)/copper(II) catalyst system. The resulting polymer was demonstrated to be a branched polyester through analy-

sis of the  $^1\text{H}$  NMR spectrum. The polymer was a viscous solid with a subambient  $T_g$  ( $-11\text{ }^\circ\text{C}$ ).

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- (12) Previously, we had employed the terms  $\text{AB}_2$  and  $\text{ABC}^*$  to describe the monomers used to prepare hyperbranched polymers by SCVP. To remain consistent with other authors and to be able to describe the microstructures adequately, we are now adopting the term  $\text{AB}^*$ . The  $*$  indicates that this functional group can be activated to initiate the polymerization of the monomer. Lower case letters indicate that the functional group has been consumed and can no longer participate in the polymerization.
- (13)  $\mathbf{A}$  = double bond;  $\mathbf{B}^*$  = unreacted functional group;  $\mathbf{A}^*$  = functional group formed after addition to double bond followed by deactivation;  $\mathbf{a}$ ,  $\mathbf{b}$  = consumed double bond and functional group, respectively.
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- (15) Matyjaszewski, K.; Wang, J.-S. *Macromolecules* **1995**, *28*, 7901.
- (16) **Synthesis of Vinyl  $\text{AB}^*$  Monomers: BPEA:** Under argon, a solution of 2-bromopropionyl bromide (36.45 mL, 348 mmol) in 50 mL of  $\text{CH}_2\text{Cl}_2$ , was added dropwise to a stirring solution of 2-hydroxyethyl acrylate (40.0 mL, 348 mmol) and pyridine (31.0 mL, 383 mmol) in 250 mL of  $\text{CH}_2\text{Cl}_2$ . The reaction was cooled in an ice bath. During the addition, a white precipitate formed (pyridine-HBr). After complete addition of the acid bromide, 1 h, the reaction was stirred at room temperature for 3 h. The precipitate was then filtered and the  $\text{CH}_2\text{Cl}_2$  evaporated. Additional precipitate and a yellow oil were obtained. The precipitate was filtered and washed with  $\text{CH}_2\text{Cl}_2$ . The oil and  $\text{CH}_2\text{Cl}_2$  wash were combined and washed with water (50 mL,  $3\times$ ) and then dried over  $\text{MgSO}_4$  and treated with decolorizing carbon. The  $\text{CH}_2\text{Cl}_2$  was evaporated to give a yellow oil. Distillation of the oil ( $80\text{ }^\circ\text{C}/0.02\text{ mmHg}$ ) gave a colorless liquid, yield 39.5g (45%). 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ : 6.43 (d, 1H); 6.14 (dd, 1H); 5.89 (d, 1H); 4.39 (m, 5H); 1.82 (d, 3H). **BIEA:** yield 66%; bp  $88\text{ }^\circ\text{C}/0.02\text{ mmHg}$ . 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ : 6.43 (d, 1H); 6.14 (dd, 1H); 5.89 (d, 1H); 4.43 (s, 4H); 1.94 (s, 6H). **BIEM:** yield 77%; bp  $84\text{ }^\circ\text{C}/0.02\text{ mmHg}$ . 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ : 6.14 (s, 1H); 5.60 (s, 1H); 4.39 (m, 5H); 1.94 (s, 3H); 1.93 (s, 6H). **BPEM:** yield 85%; bp  $88\text{ }^\circ\text{C}/0.02\text{ mmHg}$ ; 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ : 6.14 (s, 1H); 5.60 (s, 1H); 4.43 (m, 5H); 1.94 (s, 3H); 1.83 (d, 3H).
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- (19) **Homopolymerization of BPEA by ATRP:** To a 10 mL round bottom flask were added copper(I) bromide (43.6 mg, 0.3 mmol), copper(II) bromide (6.7 mg, 0.03 mmol), 4,4'-di-*t*-butyl-2, 2'-dipyridine (272.4 mg, 0.99 mmol), and a magnetic stir bar. The flask was sealed with a rubber septum. The contents of the flask were then placed under vacuum and backfilled with argon ( $3\times$ ). Distilled and degassed BPEA (5.0 mL, 30.9 mmol) was then added via syringe. The flask was heated in an oil bath at  $100\text{ }^\circ\text{C}$ , and stirred for 3.5 h. During the 3.5 h, the reaction had turned green in color. Conversion was determined by  $^1\text{H}$  NMR (89%). The reaction mixture was dissolved in THF and precipitated into methanol/brine ( $3\times$ ). The polymer was obtained as a viscous solid and was dried under vacuum at room temperature for 2 days. SEC was performed on precipitated samples.
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