Preparation of Hyperbranched Polyacrylates by Atom Transfer Radical Polymerization. 2. Kinetics and Mechanism of Chain Growth for the Self-Condensing Vinyl Polymerization of 2-((2-Bromopropionyl)oxy)ethyl Acrylate

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ABSTRACT: The self-condensing vinyl polymerization (SCVP) of 2-((2-bromopropionyl)oxy)ethyl acrylate (BPEA) has resulted in the formation of hyperbranched polyacrylates. The polymerization mechanism used to polymerize the BPEA was atom transfer radical polymerization (ATRP), a "living"/controlled radical polymerization. This paper details the study of the kinetics of polymerization and the growth of the macromolecule during the polymerization. The results obtained in the polymerization were compared to the theoretical predictions for SCVP. It was determined that the polymerization deviated from the ideal case, as a consequence of the establishment of a dynamic equilibrium in ATRP resulting in the addition of more than one monomer unit in a single activation step.

Introduction

The development of polymers with well-controlled and/or novel architectures has been the subject of increasing interest among polymer scientists.[1,2] In particular, dendrimers are among the most well-defined synthetic polymer structures prepared today.[2] These perfect macromolecules have chains emanating from a central core with a branch point at each repeat unit. Each successive level, or generation, of monomer has precisely twice as many repeat units as the previous generation (when the repeat units branch in two directions), resulting in a highly symmetrical and monodisperse polymer. As each repeat unit is a branch point, a perfectly branched macromolecule is obtained with degree of branching (DB) = 1.[3] However, achieving the high levels of architectural and molecular weight control that these materials afford, and their resulting properties, requires that each successive generation of the dendrimer be prepared in single steps.[1,4] After each step, the polymer must be isolated and purified before the next generation can be added. Because of the added steps required to prepare dendrimers, the synthesis of these novel molecules are often long and tedious, thus generally precluding their commercial development.

The search for simpler methods to prepare dendrimer-like polymers, resulted in the design and synthesis of hyperbranched polymers.[5−12] These polymers are highly branched but are not as well defined as dendrimers, both in terms of molecular weight and degree of branching. Flory had proposed that highly branched structures could be prepared by the condensation of AB_2 monomers.[13] These AB_2 monomers were trifunctional with one A group and two B groups. The requirement to prepare these highly branched polymers was that A could react with B, but A (or B) could not react with itself. It was proposed that the final polymer would be highly branched with only one A group and $n + 1$ B groups, where $n =$ the degree of polymerization.

It was not until almost 40 years later that this concept was put to use by Webster and Kim.[5,6] They prepared AB_2-substituted phenyl rings to prepare "hyperbranched" polyphenylenes. This synthesis demonstrated that highly branched polymers could be prepared in a one-pot reaction. Since then, the preparation of hyperbranched polymers has been extended to other step-growth polymerization systems.[7−12]

Recently, Frechet *et al.*, have developed a polymerization method to prepare hyperbranched polymers from alkenes called self-condensing vinyl polymerization, SCVP.[14] This method uses vinyl monomers containing a functional group that can be activated to initiate the polymerization of the double bonds. Their original work used substituted styrenes in a cationic polymerization to prepare hyperbranched polystyrene. Later, the synthesis of hyperbranched polystyrene was extended to radical polymerizations by Hawker *et al.*[15] and by our group.[16] Hyperbranched polystyrene has also been prepared by the ruthenium catalyzed polymerization of 4-acetylstyrene.[17] SCVP has been extended to anionic systems using group transfer polymerization.[18]

The statistics of chain growth in SCVP have been recently studied.[19,20] It was shown that the evolution of molecular weights and the expected degrees of branching in SCVP are different from those predicted by Flory[13] for AB_2 polymerizations. The monomers were described as AB*, so as to allow for a better understanding of the structure of the monomers and macromolecules.

Previously, we had reported the synthesis of AB* acrylic monomers for use in SCVP to prepare hyperbranched polyacrylates.[21] These monomers contained a (meth)acrylic group (A) connected to a (2-bromopropionyl)oxy (or 2-isobutyryloxy) group (B*) by an ethylene linkage. We have studied the kinetics and the mechanism of chain formation in the polymerization of 2-((2-bromopropionyl)oxy)ethyl acrylate, BPEA, by atom transfer radical polymerization, ATRP, to prepare hyperbranched polyacrylates. This work is focused on the comparison of the experimental data obtained in the

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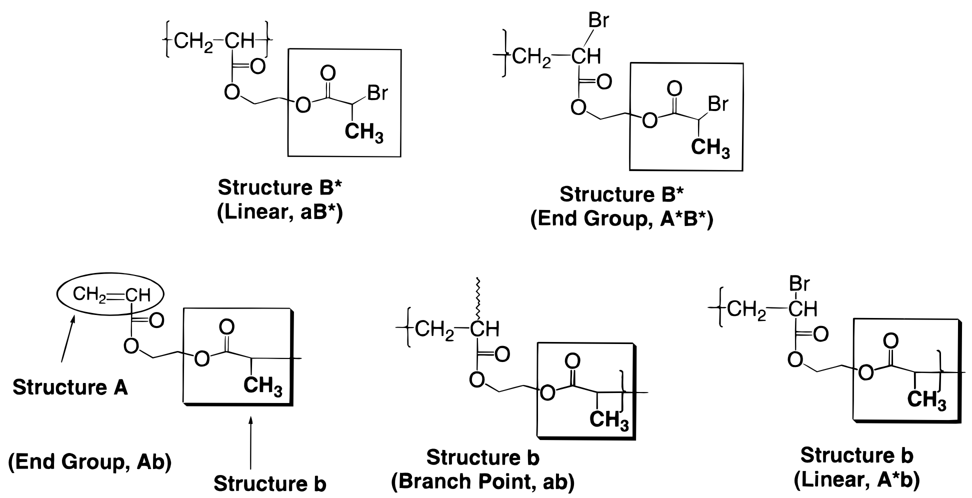
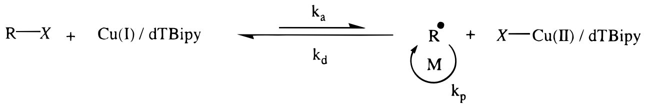


Figure 1. Microstructures obtained in the atom transfer radical polymerization of BPEA.

Scheme 1



ATRP of BPEA with the theoretical predictions for SCVP.[19,20]

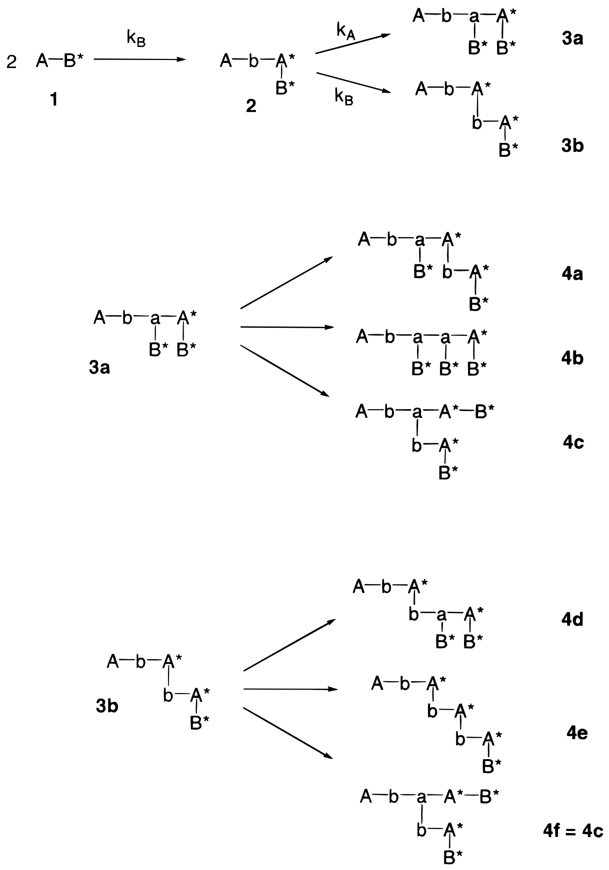
Atom transfer radical polymerization is a "living" radical polymerization system that has been demonstrated to successfully polymerize styrenes,[22-25] (meth)acrylates,[22,26-30] and acrylonitrile.[31,32] This system utilizes a reversible redox reaction between a metal salt, e.g., Cu(I), and a halogen containing initiator (R−X) to form a radical and the higher oxidation state metal halide, copper(II)−X, Scheme 1. This is a generalized scheme to impart the basic mechanism of the reaction. The actual structure of the copper complex may be more complex, the study of which is beyond the scope of this paper.

This radical then initiates the polymerization of vinyl monomers. The propagating radical reacts with the copper(II)−X to reform copper(I) and an oligomer with a halogen chain end. The oligomer is "reactivated" by reaction between the copper(I) and the halogen chain end. Repetition of this process results in the synthesis of well defined polymers with $DP_n = \Delta[M]/[I]_o$ and $1.01 < M_w/M_n < 1.5$.

When an AB* monomer is used in SCVP, the B* group is initially activated to begin the polymerization, Scheme 2. Upon activation of a B* group, the polymerization begins by propagation through the double bond of the monomer resulting in the formation of the dimer with the Ab, A*, b, and B* groups. The * indicates that at this structural group monomer can be added; it can be either an active center or in its dormant form. Ab indicates that the double bond is a part of the macromolecule. The lower case letter, b, describes how the site has been consumed and can no longer participate in the polymerization.

As can be seen, the dimer, **2**, now has two sites for possible chain growth besides the vinyl monomer. Addition of a third monomer unit at either site results in the formation of the trimer, **3a**−**b**, which can now grow in three directions. Two dimers can also react with each other to form a tetramer. A fourth monomer, **4a**−**f**, or *n*-mer can add by reaction at the lone double bond in each *n*-mer. The degree of branching is governed by the relative number of units added at either A* or B* sites. This number is closely related to the rate constants of reaction at either A* or B* (k_A vs k_B).[20] Should k_A or k_B dominate, a mostly linear chain would result. Figure 1 shows the various structures that can be obtained for the homopolymerization of BPEA by ATRP. As will be later demonstrated, the degree of branching is, however, affected not only by the ratio of k_A/k_B but also by the dynamics of the activation/deactivation process.

Scheme 2



Experimental Section

General Data. The monomer, 2-(2-bromopropionyloxy)ethyl acrylate, BPEA, was prepared according to the previously reported procedure.[21] 4,4′-Di-*tert*-butyl-2,2′-bipyridine (dTBipy) was prepared by coupling 4-*tert*-butylpyridine in the presence of 5% Pd-C (10 w/v %, Pd-C to pyridine) after heating

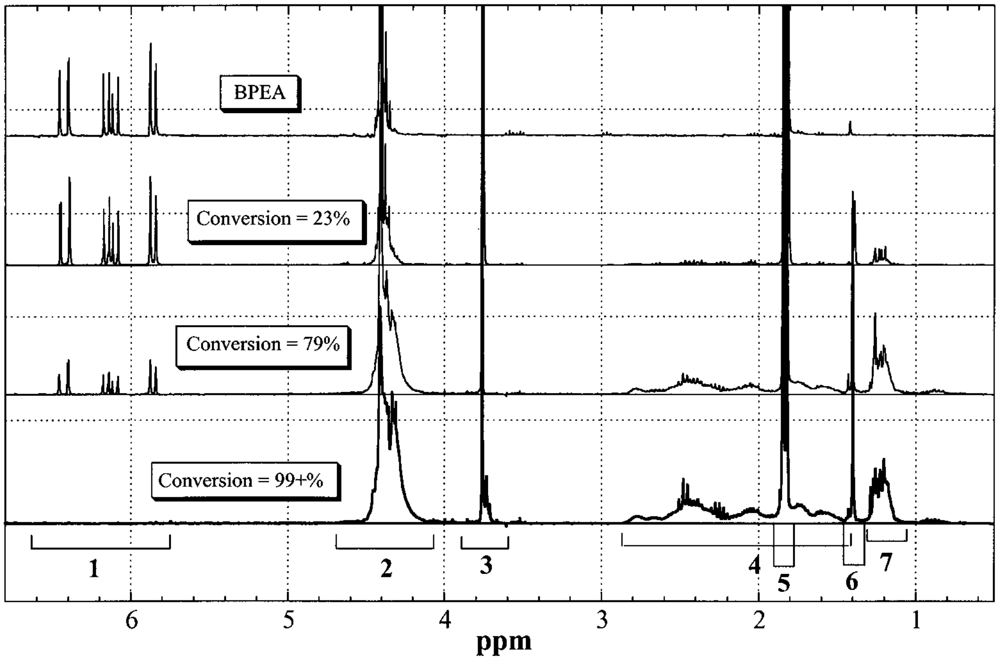
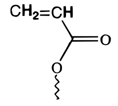
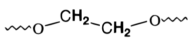
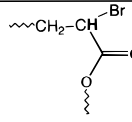
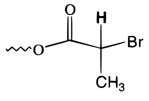
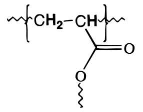
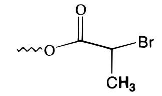
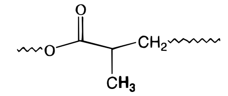


Figure 2. ^{1}H NMR spectra of BPEA and polymer samples at various conversions.

to 150 °C for 1 week.[24] Copper (I) bromide was purified by stirring in glacial acetic acid, washing with ethanol, and then drying under vacuum at 70 °C. NMR were obtained in CDCl$_3$ using a 300 MHz Brüker NMR with TecMAG processing software. Molecular weights were obtained by size exclusion chromatography (SEC) using a Waters 510 pump, a Waters WISP 712 autosampler, and a Waters 410 differential refractometer with 5μ Waters Styrogel columns (guard, 0.5HR, 4E HR, 5HR). The data were processed using Polymer Standards Service software against linear polystyrene standards. Gas chromatography (GC) was performed using a Shimadzu GC-14A with a Chromatopac 501. Conversion of monomer was measured by GC using *p*-dimethoxybenzene as an internal standard to determine the residual monomer content of the polymer samples taken during the polymerization. Conversion of the double bonds was monitored by ^{1}H NMR.

Polymerization. To a dry 10 mL round bottom flask with a magnetic stir bar were added dTBipy (223.5 mg, 0.83 mmol), *p*-dimethoxybenzene (500 mg), and Cu^{I}Br (40.4 mg, 0.28 mmol). The *p*-dimethoxybenzene was added as an internal standard for GC measurements. The flask was sealed with a rubber septum, and the contents of the flask were placed under vacuum and then back-filled with nitrogen (3×) to remove oxygen from the flask. Degassed BPEA (4.5 mL, 27.8 mmol) was added, and the reaction mixture was then stirred at 50 °C. Samples were taken periodically to monitor the conversion (^{1}H NMR = double bonds, GC = monomer) and the molecular weight growth with conversion (SEC).

Table 1. Assignment of Structures to the Corresponding Regions of the ^{1}H NMR Spectra in Figure 2

Region	Structure
1	
2	  
3	Solvent: Dimethoxybenzene
4	
5	
6	Ligand: 4, 4'-di(**t-butyl**)-2, 2'-bipyridine
7	

Results and Discussion

The kinetics and molecular weight growth of the homopolymerization of 2-((2-bromopropionyl)oxy)ethyl acrylate (BPEA) was monitored by periodically removing samples from the reaction mixture followed by analysis using GC and ^{1}H NMR. Figure 2 shows the respective ^{1}H NMR spectra of the monomer and the polymerization samples at various conversions. The signals in region 1 correspond to the protons of the double bond. Region 2 is a compilation of the signals from the ethylene linkage and the proton geminal to bromine in either A* (polymer) or B* (monomer or polymer). Upon conversion of the double bonds to polymer backbone, the broad set of peaks in region 4 appear. The methyl protons geminal to bromine in BPEA (B*), region 5, are shifted upfield, region 7, as the bromine is removed and monomer added, forming b. The peaks in regions 3 and 6 are from the alkyl protons on *p*-dimethoxybenzene and dTBipy, respectively. The structures for the corresponding regions are summarized in Table 1 and Figure 1.

Conversion of the double bonds was monitored in the ^{1}H NMR spectra by comparison of the peak areas of regions 1 and 2. The area of region 2 should be constant throughout the polymerization as this region corresponds to the protons of the ethylene linkage and the protons which are geminal to bromine in either A* or B*. The number of ethylene linkages never changes during the polymerization and although B* is consumed during the polymerization, for every B* consumed one A* is formed and consequently, B* + A* = 1; the

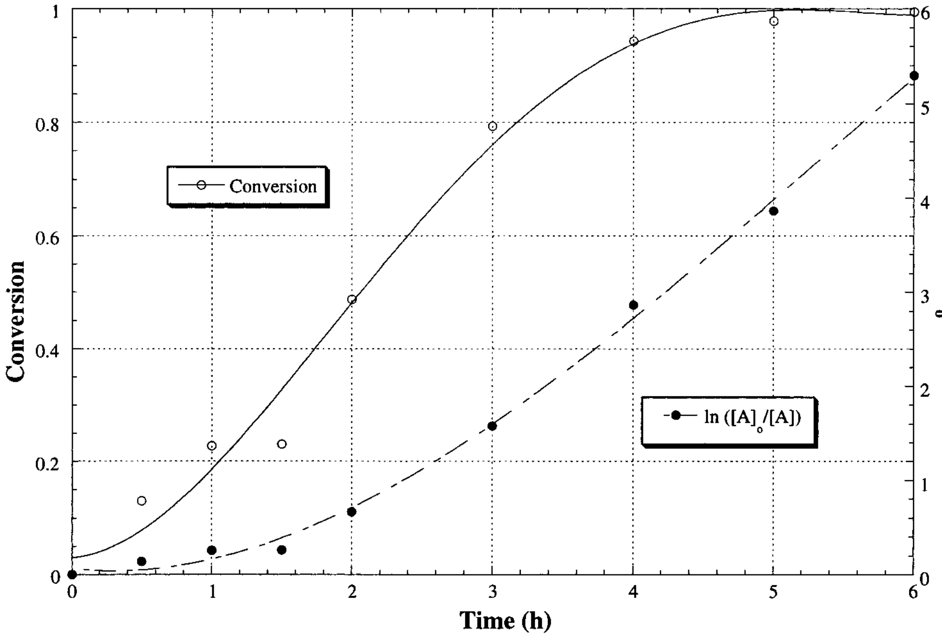


Figure 3. Conversion of double bonds in the AB* polymerization of BPEA by ATRP.

number of protons geminal to bromine remains constant.[33]

It was possible to determine the proportions of b and B* that were present in the macromolecules by further evaluation of the ^{1}H NMR spectra. The large doublet at 1.85 ppm is assigned to CH_3 of the 2-bromopropionyloxy group, B*, Table 1, region 5. Upon activation of the B* and subsequent addition of monomer, i.e., the formation of b, the CH_3 group is no longer geminal to the bromine and the signal attributed to it is shifted upfield to 1.1−1.3 ppm, region 7. The proportions of b and B* could then be calculated: b = (region 7)/(region 7 + region 5); B* = 1 − b.

Kinetics of the Polymerization

According to Scheme 1, the polymerization should follow the general rate expression in eq 1. Typically, ATRP is first order in monomer, initiator, and copper(I) concentration; it is negative first (or fractional) order in copper(II) concentration.[24] To obey the above rate law, the plot of ln([M]$_0$/[M]) vs time should yield a linear relationship, as observed in the ATRP of styrene, acrylates, and methacrylates.[22−24]

$$R = k_p[M][R^\bullet] = k_pK[M][R-X]\frac{[Cu(I)]}{[Cu(II)]} \qquad (1)$$

In an AB*, or AB_2, polymerization, the conversion of the double bonds (or functional groups in AB_2) is more significant in evaluating the kinetics than is the conversion of the monomer. In the following discussions, when conversion is used it will be understood that conversion of the double bonds is implied, unless stated otherwise. Also, [M] = [A] = concentration of all double bonds.

In Figure 3, the conversion of the double bonds is plotted vs time as both zero-order (conversion) and first-order (ln([A]$_0$/[A]) plots. The slope of the first-order plot appeared to increase with time. The increase in the rate of polymerization was ascribed to a reduction in the copper(II) concentration (vide infra).

The curvature of the first-order plot could also be explained by either an enhancement of the rate of activation of the A* (or B*) groups or the reactivity of the double bonds being lower in the low molecular weight species than in the higher molecular weight species. However, there is no reason as to why these groups (A*, B*, double bond) would become more, or less, reactive as the macromolecule grew. The polymerization does not produce groups that are any more active than those found in low DP_n molecules or even in the monomer.

The most likely possibility is that the copper(II) concentration was lowered during the polymerization. This would result in an increase in the overall rate of polymerization as it is inversely proportional to the copper(II) concentration. It has been demonstrated that the concentration of copper(II) in the polymerization solution has a profound influence on the behavior of the polymerization system.[34] It has also been shown that the maximum concentration of copper(II) complexed with dTBipy in pure monomer is relatively low (~0.4 mM),[34] and one would expect that it would be even less in the bulk polymer.

As the monomer was consumed and converted into polymer, the concentration of the copper(II) decreased from its original limits, due to its lowered solubility in the reaction medium. The excess copper(II) precipitated out of solution, effectively “leaving” the reaction. We were not able to directly measure the copper(II) concentration at this point, as the reaction medium was quite viscous under these conditions (bulk, 1 mol % Cu^IBr, 50 °C).

It should be noted that because the copper(II) is formed as a result of the redox reaction between copper(I) and B*, the maximum proportion of terminated chains could, in this case, be 1%. Since the polymerization continues to completion, it can be concluded that only a fraction of the copper(I) is converted to copper(II). As such, the proportion of irreversibly terminated chains is less than 1%. Consequently, higher amounts of copper(I) could lead to a higher percentage of terminated chains, possibly resulting in cross-linking.

Molecular Weight and Molecular Weight Distribution

Samples were taken from the reaction and used in SEC to obtain the apparent molecular weights of the

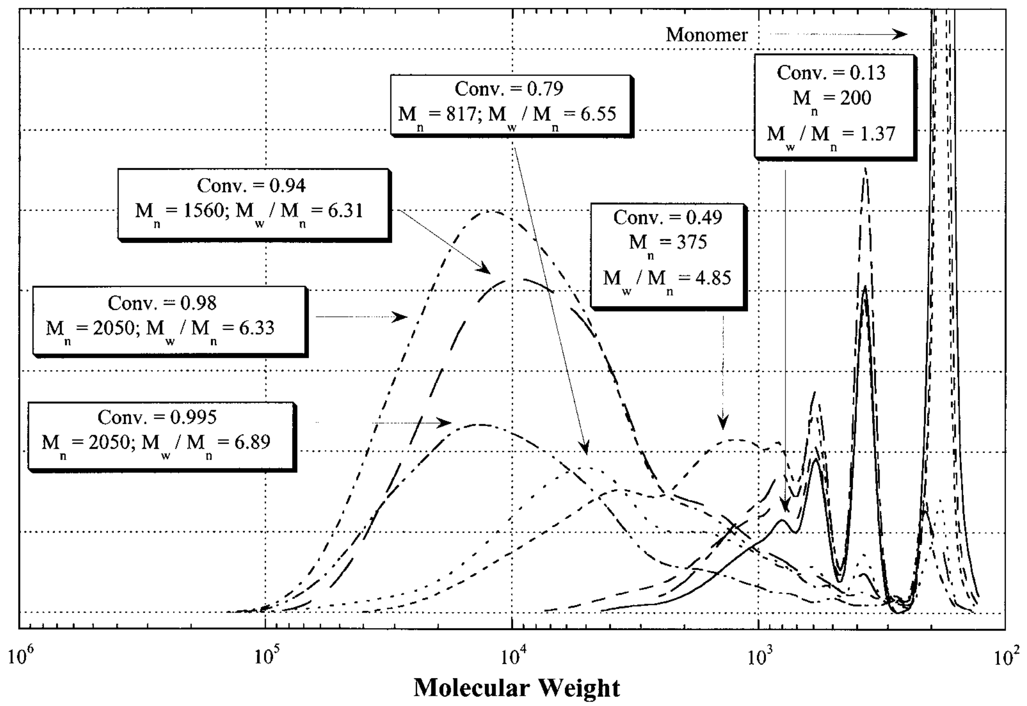


Figure 4. Overlay of SEC chromatograms of the ATRP of BPEA at various conversions.

Table 2. Comparison of Theoretical Molecular Weight Distributions in SCVP (Müller) and AB$_2$ Polymerizations (Flory) (x = Conversion)

	SCVP	AB$_2$
DP$_n$	$1/(1-x)$	$1/(1-x)$
DP$_w$	$1/(1-x)^2$	$1-(x^2/2)/(1-x)^2$
DP$_w$/DP$_n$	$1/(1-x)$	$1-(x^2/2)/(1-x)$

samples, Figure 4. The listed molecular weights were determined against linear polystyrene standards, and the real values are most likely higher as branched polymers have a smaller hydrodynamic volume than linear analogs of the same molecular weight. The presence of the lower molecular weight species in the polymer samples has prevented the accurate determination of the molecular weights by light scattering or by viscometry. Due to the very broad molecular weight distributions, MALDI-TOF has been ineffective at accurately determining the molecular weights.

The theoretical evolution of molecular weight with conversion of the double bonds for SCVP[19,20] was compared with the conventional polymerization of AB$_2$ monomers[13] (x = conversion), Table 2. These equations include monomer in the calculation of DP$_n$, DP$_w$, and DP$_w$/DP$_n$. As can be seen, the weight average degree of polymerization (DP$_w$) for SCVP is expected to increase in a manner similar to, but not identical to, the AB$_2$ polymerization.

Although the SEC chromatograms do not yield quantitative information, it is helpful to analyze qualitatively the molecular weight growth. The presence of dimer, trimer, tetramer, etc. was observed in the earlier stages of the polymerization. Also, the polydispersities were observed to increase to large values ($M_w/M_n \sim 6$). At higher conversions, the intensity of the monomer peak decreased, and the monomer peak was replaced by that for a higher molecular weight polymer and a small peak with a slightly shorter retention time than the monomer. It was unclear what this small peak is, but it may be cyclized dimer.

Upon precipitation of the final polymer, the molecular weight increased to $M_n = 6570$ and the polydispersity decreased to $M_w/M_n = 3.3$. The result indicates that the higher molecular weight species were preferentially precipitated.

It should be possible to determine molecular weight by evaluation of the ^{1}H NMR. Comparison of the areas from the double bond vs a group present on each repeat unit would yield DP$_n$. However, the signals assignable to the double bond diminished at high monomer conversion (>95%), and vanished at very high conversion of monomer (>99%) (conversion of monomer was monitored by GC). After precipitation of the final polymer, the double bonds could not be detected in the ^{1}H NMR spectra. The apparent disappearance of the double bond may indicate a side reaction which consumed the double bond in the macromolecule, i.e., intramolecular reaction between a B* or A* group and the residual double bond.

To compare the observed molecular weights with those predicted by DP$_n$ = $1/(1 - x)$, the molecular weights obtained by SEC were plotted vs conversion, Figure 5. The molecular weights did increase with conversion in a pattern similar to that predicted by theory. However, the molecular weight increase appeared to reach a limit. The limiting of molecular weight indicates that there were side reactions hindering chain growth. This observation suggests the presence of an intramolecular reaction between A* or B* and the double bonds on the macromolecule.

For SCVP, the molecular weight distribution is expected to be equal to the number average degree of polymerization ($1/(1 - x)$). As a result, very broad molecular weight distributions were expected, and the observed polydispersities were indeed large, Figure 4, but did not increase to extremely high levels as predicted, Figure 6. This would also support the earlier observations that intramolecular cyclization is occurring, thus preventing the growth of the macromolecule to very high molecular weights/polydispersities.

Chain Branching

SCVP begins by activation of B* to initiate the polymerization of double bonds. After deactivation of

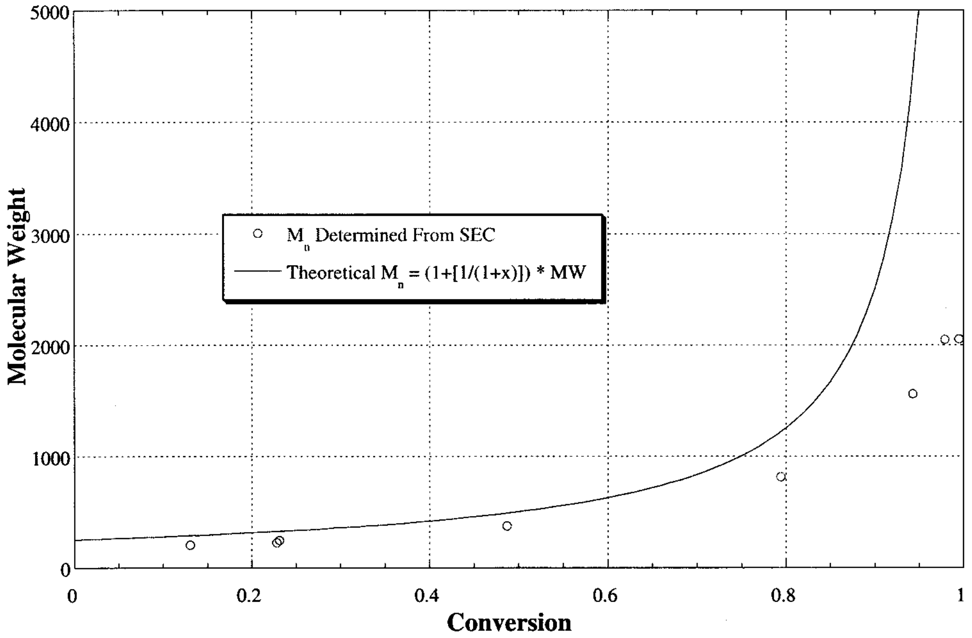


Figure 5. Comparison of observed vs predicted M_n for polymerization of BPEA by ATRP.

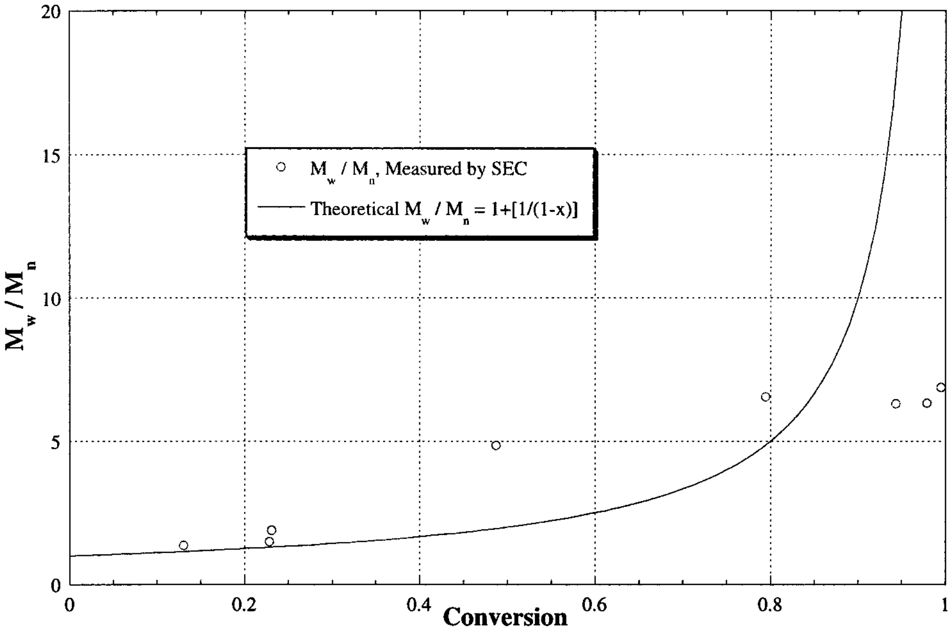


Figure 6. Plot of observed and theoretical polydispersities vs conversion of double bonds.

the active center, a new, latent, active center is formed, A*, **2** (Scheme 2). At this point either A* or B* can be activated to reinitiate the polymerization. Depending on where the next activation/addition occurs, either A* or B* will be consumed to form *only* a new A*. This is an important consideration when attempting to determine the degree of branching. A simple ratio of b/B* (b = A*) will not directly give an accurate description of the branching in the macromolecule. It will now be demonstrated how the ratio of b/B* can be used to determine the overall degree of branching.

Comparison of the areas of regions 5 and 7 in the ^{1}H NMR spectra, Figure 2, gives the respective proportions of B* and b, at various conversions, Figure 7. The solid lines in Figure 7 are theoretically predicted for B* and b based on $B^* = e^{-x} = 1 - b$ (where x = conversion), and when $r = k_A/k_B = 1$.[20] The deviation of B* and b from the expected behavior indicated that r did not equal 1.

The best fit of the experimentally obtained points was obtained when $r = 4.5$, Figure 7. The relatively good fit suggests that r remained constant throughout the polymerization, $r \sim 4.5$. This r value corresponds to an average degree of branching of DB $\sim$ 0.49.[20] The actual degree of branching is difficult to obtain explicitly, as there is no method to differentiate between the four microstructures to calculate the degree of branching at full conversion, DB = 2(A*B*) = 2(ab).[20]

$$r = \frac{k_A}{k_B} = \frac{(x + B^* - 1)}{(-\ln(B^*) + B^* - 1)} \tag{2}$$

The value of $r = 4.5$ indicated that addition of monomer occurred at A* at a rate approximately four and a half times faster than at B*. This would imply that the apparent rate of propagation was faster at A* than at B*. However, there should be no significant difference in the reactivities and stabilities of (2-

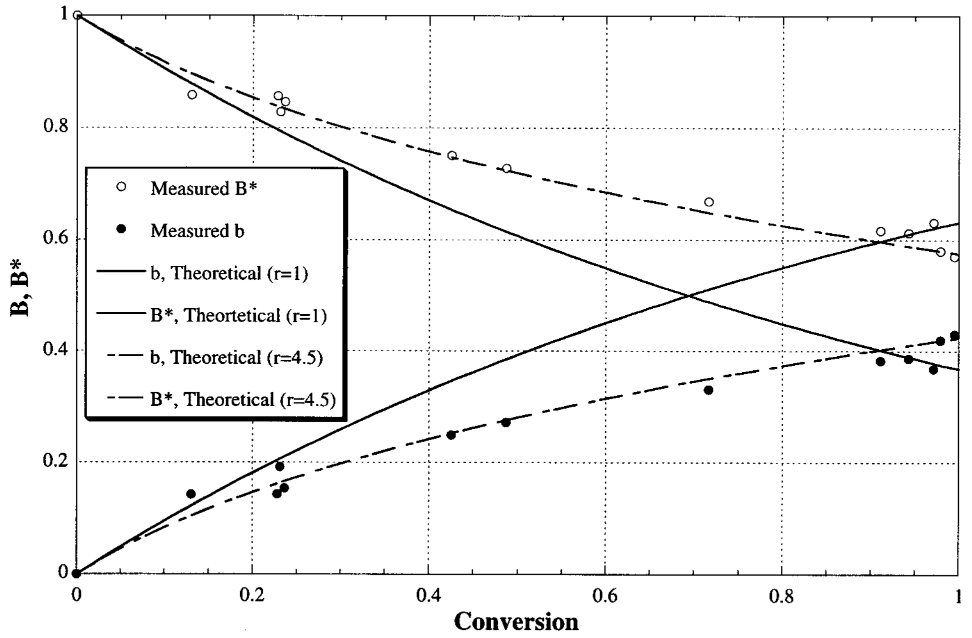
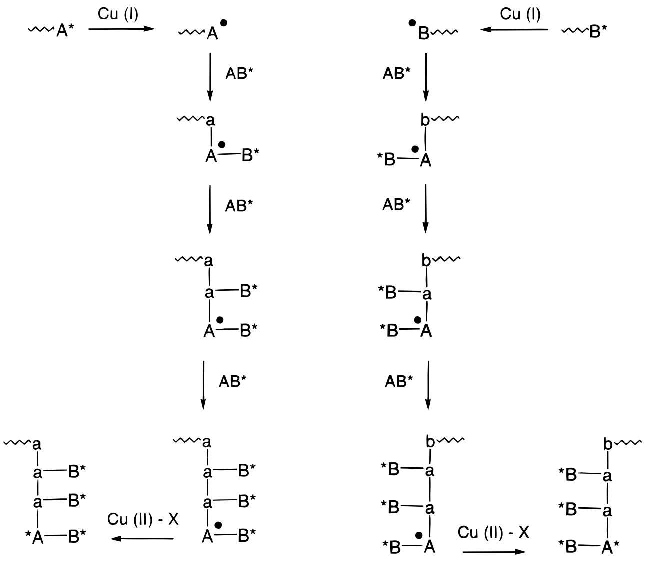


Figure 7. *b* and B^* vs conversion. Theoretical lines (solid) are derived from Müller *et al.*[19] $B^* = e^{-x} = 1 - b$, x = conversion, and $r = k_A/k_B = 1$ is assumed. Dashed lines are calculated for *b* and B^* for $r = 4.5$.

Scheme 3



bromopropionyl)oxy (B*) and (2-bromoalkyl)oxy (A*, to the first approximation). However, since activation of B* and addition of monomer always yields a new A*, and as the polymerization mechanism is based on a dynamic equilibrium between active and dormant species, another conclusion is more plausible.

Although the deactivation process of the radical reacting with copper(II)−Br is fast, $k_d \sim 10^7-10^8$, more than one monomer unit can add to the active center before being deactivated, due to the high k_p value of acrylates, Scheme 3. In this case, it appears that an average of five units was added before deactivation occurred. Of course, during this “uncontrolled” process only aB* units are formed regardless of starting from A* or B*. If three monomer units are added during one activation step and the reactivities of A* and B* are identical, three new B* groups are formed from A*, whereas, two new B* groups and one A* group are formed from B*, Scheme 3. Thus, the average k_A/k_B = 4.5, may indicate that approximately five monomer units add during one activation step in the BPEA polymerization. The effect of varing the reaction conditions and/or catalyst structure on the degree of branching will be discussed in the following paper.[34]

The number of units added during one activation step is defined by the ratio of rates of propagation to deactivation (k_p[M]/k_d[Cu(II)]) which roughly corresponds to the apparent ratio of reactivities of A* and B* sites ($r = k_A/k_B$). The apparently constant value of *r* during the polymerization suggests that the ratio of [M]/[Cu(II)] also remains constant. Thus, the decrease of the monomer concentration must be accompanied by a corresponding reduction in the concentration of Cu(II), which is consistent with the observed kinetic behavior discussed above in Figure 3.

Conclusions

The synthesis of a hyperbranched polymer containing both polyester and polyacrylate segments, by polymerization of 2-((2-bromopropionyl)oxy)ethyl acrylate (BPEA) by atom transfer radical polymerization (ATRP) has been studied. The curvature in the first-order plot of conversion was believed to occur as a result of the changing copper(II) concentration during the polymerization.

The growth of the macromolecules initially behaved in a manner similar to that predicted by theory, $DP_n = DP_w/DP_n = 1/(1 - x)$. Intramolecular cyclization was cited as a possible reason for a leveling in molecular weight at high conversion, >95%. The presence of intramolecular cyclization should not be unexpected in these types of polymerizations. There is no reason to expect the active centers on the polymer chain can not react with the double bond on the same molecule. At higher conversions, when monomer concentration is very low, the relative rate of intramolecular cyclization may even increase in these flexible polymer structures. By making the polymer chains stiffer, one may be able to decrease the contribution of intramolecular cyclization.

From calculations of the relative concentrations of b and B*, the apparent ratio of the rate constants k_A to k_B, was determined to be $r = 4.5$. This ratio reflects the average number of monomer units added to an active center before deactivation, rather than the true ratio of the rate constants. The value of $r = 4.5$ corresponded to the degree of branching, DB = 0.49.

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