Preparation of hyperbranched polyacrylates by atom transfer radical polymerization, 4[a]

The use of zero-valent copper

Krzysztof Matyjaszewski, Jeffrey Pyun, Scott G. Gaynor*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA

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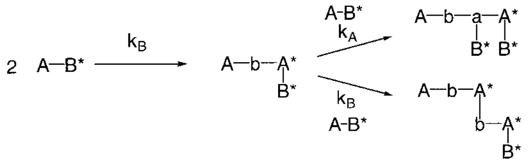
SUMMARY: The addition of zero-valent copper to the self-condensing vinyl polymerization (SCVP) of novel AB* (meth)acrylic monomers using atom transfer radical polymerization (ATRP) catalyst systems has allowed for their successful polymerization. Polymerization under homogeneous and heterogeneous catalyst conditions without additional Cu(0) were unsuccessful. The catalyst system that was designed comprised of Cu(I) bromide, 4,4′-bis(5-nonyl)-2,2′-bipyridine, and Cu(0) metal (powder or turning). From ^{1}H NMR spectroscopy, the degree of branching was estimated for the acrylic polymers, $DB = 0.48$. The degree of branching could not be determined for methacrylates by this method due to overlapping signals in the ^{1}H NMR spectra.

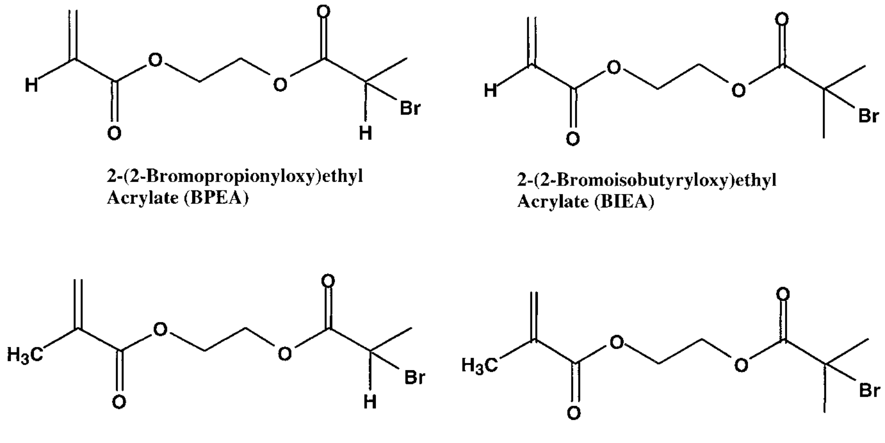
Introduction

The development of self-condensing vinyl polymerization (SCVP)[1)] has enabled the synthesis of hyperbranched polymers from vinyl monomers, Scheme 1; A = double bond, B* = functional group that can initiate polymerization. While the original system reported by Frechet *et al.* was cationic in nature[1)], SCVP has also been applied to group transfer polymerization[2)], ruthenium catalyzed polymerization[3)] and free-radical polymerizations mediated by a nitroxyl radical[4)] and atom transfer radical polymerization (ATRP)[5–9)]. In a previous report, 2-(2-bromopropionyloxy)ethyl acrylate (BPEA) as well as three other AB* (meth)acrylic monomers were proposed for the synthesis of hyperbranched polymers by ATRP, Fig. 1[6)].

Scheme 1:



Of these monomers, only BPEA was polymerized to successfully yield a hyperbranched polymer. Using heterogeneous catalyst system comprising of Cu(I) and 4,4′-di-*tert*-butyl)-2,2′-bipyridine at 50 °C was determined to be the optimal reaction conditions yielding hyperbranched BPEA[6–8)]. Polymerization of BPEA did not occur at 50 °C with a homogeneous Cu(I) bromide, 4,4′-bis(5-nonyl)-2-2′-bipyridine (dNbpy) catalyst. At 130 °C, however, polymerization with the homogeneous catalyst was obtained,



2-(2-Bromopropionyloxy)ethyl Acrylate (BPEA)

2-(2-Bromoisobutyryloxy)ethyl Acrylate (BIEA)

2-(2-Bromopropionyloxy)ethyl Methacrylate (BPEM)

2-(2-Bromoisobutyryloxy)ethyl Methacrylate (BIEM)

Fig. 1. AB* (meth)acrylic monomers used for SCVP by ATRP

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[a] Part 3: ref.[8)]

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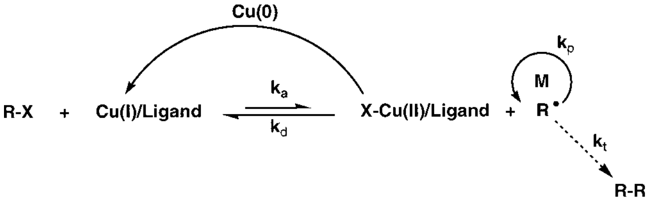
although side reactions were also observed[8]. The other acrylic AB* monomers could not be successfully polymerized despite variations in ligand structure and temperature. Neither heterogeneous nor homogeneous catalyst systems at various temperatures yielded polymer for BPEM, BIEA and BIEM. It was speculated that the tertiary radical sites generated from methacrylate moieties (**A**) and/or the 2-bromoisobutyryloxy moieties (**B***) coupled rapidly, forming an excessive amount of deactivating Cu(II) species and prevented polymerization.

Scheme 2:



Scheme 2 illustrates the general ATRP process[10–13]. **R-X** is an alkyl halide from an initiator, which is catalyzed by a Cu(I) bromide/bipyridine complex (Cu(I)/2ligand) to generate radicals, $\mathbf{R}^\bullet$, with a rate constant of activation, k_a. Cu(I) is converted to an X-Cu(II) complex by abstraction of the halogen (**X**) from the initiator. Radicals can then be deactivated by X-Cu(II), with a rate constant of deactivation, k_d. Because k_d is much greater than k_a, a low concentration of monomeric and polymeric radicals is maintained during the polymerization. This allows for a controlled polymerization to occur, with a rate constant of propagation, k_p. Termination, with rate constant of termination, k_t, can not be avoided, but can be effectively neglected due to a low pseudostationary concentration of radicals. Recently, the use of zero-valent metals for the ATRP of styrene and (meth)acrylates was reported[14]. When added to an ATRP reaction mixture, Cu(0) reduces the X-Cu(II) complexes to generate two equivalents of Cu(I). For polymerizations where excess deactivator (X-Cu(II)) is present, the addition of Cu(0) enhances the rate of the polymerization, while still maintaining control of the molecular weights and polydispersities during the polymerization.

For SCVP, the inherently high initiator (monomer/initiator) concentration favors a shift of the equilibrium towards the active radicals, initially forming a large concentration of radicals which terminate much more efficiently, leaving an excess of X-Cu(II). In the process, Cu(I) may be nearly consumed, or at least reduced to levels preventing the (re)activation monomeric and polymeric alkyl halides. Because the radical concentration is dependent on the ratio of Cu(I) to Cu(II), successful SCVP by ATRP requires that a sufficient concentration of Cu(I) be maintained throughout the polymerization. A heterogeneous catalyst system can be employed for this purpose in the SCVP of BPEA by ATRP[8], thus limiting the solubility of the Cu(II) species. However, in order to conduct the SCVP of BPEA, BPEM, BIEA and BPEM using a homogeneous ATRP catalyst, a better method to retain or rejuvenate Cu(I) throughout the reaction must be designed.

Herein, we report the use of zero-valent copper for SCVP by ATRP of the aforementioned AB* (meth)-acrylic monomers. With the addition of Cu(0), we have designed a system whereby a sufficient amount of Cu(I) is continuously generated by the redox reaction of Cu(0) with X-Cu(II) (cf. Scheme 2), allowing for polymerization with a homogeneous Cu(I) complex (Cu(I)/dNbpy).

Experimental part

Polymerization of AB monomers.* To a 5 ml round bottom flask with magnetic stir bar was added dNbpy[8], Cu(I)Br, copper(0) (Aldrich, copper for organic synthesis, used as received) and *p*-dimethoxybenzene (0.5 g) as an internal standard for GC. An excess of ligand (3 eq.) was used to solubilize additional Cu(I) generated from the redox reaction of Cu(0) and Cu(II). The flask was then fitted with a rubber septum and evacuated and back-filled with N_2 (3 times). Degassed monomer (27 mmol) was then added to the reaction vessel via syringe and allowed to stir at the appropriate temperature. Samples were periodically removed to monitor conversion (by ^{1}H NMR, GC) and evolution of molecular weights (SEC). Molecular weights were determined by use of a calibration curve prepared from linear polystyrene standards.

Results and discussion

It has been reported that for ATRP, tertiary alkyl halides produce higher concentrations of radicals than secondary active sites (methyl methacrylate vs. methyl acrylate)[10]. Because each AB* monomer contained varying amounts of tertiary and secondary active sites, both B* and A*, the radical concentrations for each monomer would be different under identical reaction conditions. Indeed this was true, as some conditions generated insoluble polymer. To overcome these problems, we tried to slow the overall rate of polymerization, which is directly related to radical concentration. This was accomplished by lowering the initial catalyst concentration (down to 0.1 mol-% relative to monomer), dilution of the reaction, and variation of the form of copper metal. As the reduction of Cu(II) to Cu(I) by Cu(0) must occur at the surface of the copper metal, the use of metals with lower surface area would slow the reduction of Cu(II), allow for faster deactivation of the growing radicals and reduce the overall polymerization rate. The conditions used to polymerize the four monomers are summarized in Tab. 1.

The polymerization of BPEA with a 1% Cu(I)Br/dTbpy (dTbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) catalyst, was

Tab. 1. Reaction conditions and the results of the SCVP of AB* (meth)acrylic monomers[a]

Monomer	Catalyst	Time in h	Temp in °C	Bulk/Soln.	Conv.[a]	$\overline{M}_{\text{n}}$[b]	$\overline{M}_{\text{w}}/\overline{M}_{\text{n}}$[b]	$\overline{M}_{\text{n}}$[c]	$\overline{M}_{\text{w}}/\overline{M}_{\text{n}}$[c]
BPEA	1 mol-% Cu(I)Br/dTbpy	7.0	50	bulk	0.99	1820	6.4	—	—
BPEA	1 mol-% Cu(I)Br/dNbpy 1 mol-% Cu(0) powder	2.5	50	bulk	0.99	2950	4.7	5690	2.5
BIEA	1 mol-% Cu(I)Br/dNbpy 1 mol-% Cu(0) powder	0.5	24	bulk	0.99	2270	14.2	7830	3.5
BPEM	1 mol-% Cu(I)Br/dNbpy, 1 mol-% Cu(0) powder	26	24	benzene (20 vol.-% monomer)	0.95	1990	6.6	9600	1.6
BIEM	0.1 mol-% Cu(I)Br/dNbpy, Cu(0) turning	24	24	benzene (20 vol.-% monomer)	0.67	650	4.3	2650	1.4

[a] As determined by 300 MHz ^{1}H NMR (consumption of double bonds).

[b] Molecular weight values based on SEC in THF against linear polystyrene standards (prior to precipitation and including monomer).

[c] Molecular weights determined after precipitation of the polymer.

used as a standard system to compare the effect of Cu(0) on the polymerization of AB* (meth)acrylic monomers[7]. Polymerization of BPEA using the Cu(I)/dNbpy/Cu(0) (dNbpy = 4,4′-bis(5-nonyl)-2,2′-bipyridine) catalyst system reached high conversion (p = 0.99) in 2.5 h, as compared to the polymerization using the less soluble Cu(I)/dTbpy catalyst which required 7.0 h to reach comparable conversions. It should be noted that polymerization was not observed at 50 °C using Cu(I)Br/dNbpy[8] unless Cu(0) was added. Reactions with the Cu(I)/dNbpy/Cu(0) catalyst system were faster primarily because of the redox reaction of Cu(0) with Cu(II) to form Cu(I). Despite the differences in reaction time, comparable molecular weights and polydispersities were obtained for poly(BPEA) prepared using either the Cu(I)/dNbpy/Cu(0), or Cu(I)/dTbpy catalyst systems.

BIEA, in the presence of a 1% Cu(I)/dNbpy/Cu(0) catalyst system, polymerized rapidly at room temperature, reaching high conversion (p = 0.99) in 0.5 h. The dramatic difference in reaction time between the polymerization of BIEA and BPEA, both using a 1% Cu(I)/dNbpy/Cu(0) catalyst system, could be attributed to the enhanced reactivity of the bromoisobutyryloxy groups (tertiary halides) vs. bromopropionyloxy groups (secondary halides). In general, activation of the B* sites is faster for BIEA, i.e., more radicals are formed. While the $\overline{M}_{\text{n}}$ for poly(BPEA) and poly(BIEA) made using the Cu(0) systems are comparable, the polydispersity of poly(BIEA) was significantly larger ($\overline{M}_{\text{w}}/\overline{M}_{\text{n}}$ = 14.2) than that of poly(BPEA) made with the same catalyst system ($\overline{M}_{\text{w}}/\overline{M}_{\text{n}}$ = 4.7), Fig. 2. The conversion in the polymerization of both BPEA and BIEA, as determined by consumption of double bonds by ^{1}H NMR, was determined to be at least 99%. While small differences in conversion above 99% are beyond the sensitivity of the ^{1}H NMR integration, these differences may account for the disparity in the molecular weight distributions of poly(BPEA) and poly(BIEA) as both DP_{n} and $\text{DP}_{\text{w}}/\text{DP}_{\text{n}}$ are strongly dependent on conversion[15].

While the AB* methacrylate monomers, BPEM and BIEM, also polymerized in bulk with a 1% Cu(I)Br/dNbpy/Cu(0) powder catalyst system at 24 °C, their tendency to gel depended on the monomer and/or catalyst concentrations. Because of the faster rate of polymerization by ATRP of methacrylates versus those of acrylates, the polymerizations were carried out at 24 °C. In the polymerization of BPEM using a 1% Cu(I)Br/dNbpy/Cu(0) powder catalyst system, in solution (80% benzene), high conversion (p = 0.95; t = 26 h) was achieved. As expected, the low monomer (initiator) concentration required longer reaction times to reach comparable conversions than when polymerized in bulk. But, more importantly, the addition of solvent lowered the radical concentration during the polymerization, allowing for the synthesis of soluble poly(BPEM).

While a 1% Cu(I)Br/dNbpy/Cu(0) powder catalyst system yielded soluble poly(BPEM) in an 80 vol.-% benzene solution, the synthesis of soluble poly(BIEM) also required the use of a lower catalyst concentration (0.1% Cu(I)Br/dNbpy with a Cu(0) turning). For BIEM, the polymerization rate was attenuated by changing the surface area of Cu(0), i.e., powder to turning. By increasing the particle size and reducing the surface area of Cu(0), the regeneration of Cu(I) is presumed to occur at a slower rate, which lowered the radical concentration, reduced termination and allowed for the synthesis of soluble poly(BIEM).

In general, hyperbranched polymers prepared by the SCVP of AB* acrylic monomers have low molecular weights and high polydispersities. The reported molecular weights and polydispersities for these polymers are only apparent since linear polystyrene standards were used to calibrate the SEC. The high polydispersities observed for hyperbranched acrylic polymers are indicative of branch-

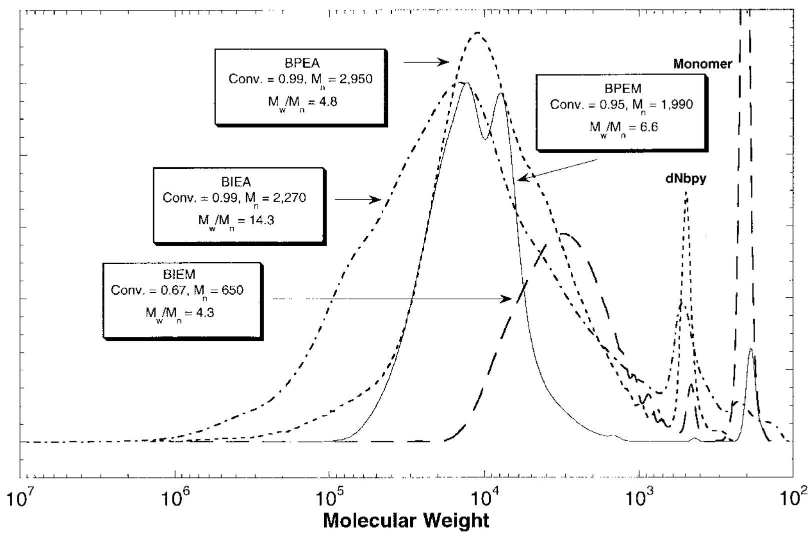


Fig. 2. SEC chromatograms of the polymerization of various (meth)acrylic AB* monomers

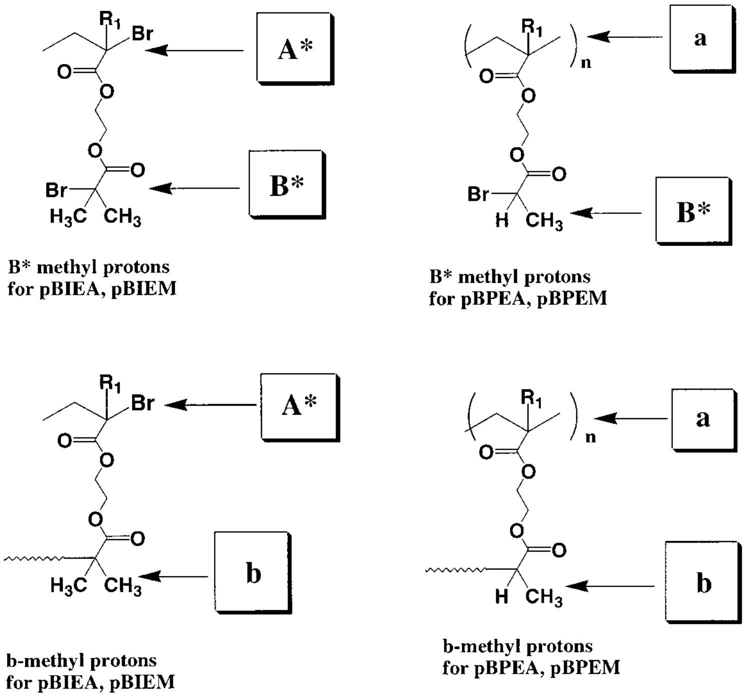


Fig. 3. Microstructures of linear vs. branched acrylic polymers. R_1 = H for poly(BPEA) and poly(BIEA), and R_1 = CH_3 for poly(BPEM) and poly(BIEM)

ing in the polymer architecture, as it is the result of the mixed step-growth/chain growth nature of SCVP. Additionally, to conform to theoretical predictions of molecular weight growth15), the molecular weights were calculated by including monomer; unfortunately some residual ligand remained that could not be removed.

The SEC chromatograms of the polymers obtained from the different monomers are shown in Fig. 2. As can be seen, the polymers have quite broad molecular weight distributions. However, only poly(BPEA), poly(BIEA) and poly(BIEM) appear to be hyperbranched due to the presence of both low and high molecular weight species in the SEC chromatogram. For poly(BPEM), the absence of oligomeric species and the relatively narrow distribution of the high polymer (polymer only: $\overline{M}_n = 9600$, $\overline{M}_w/\overline{M}_n = 1.6$) implied that the architecture of the polymer

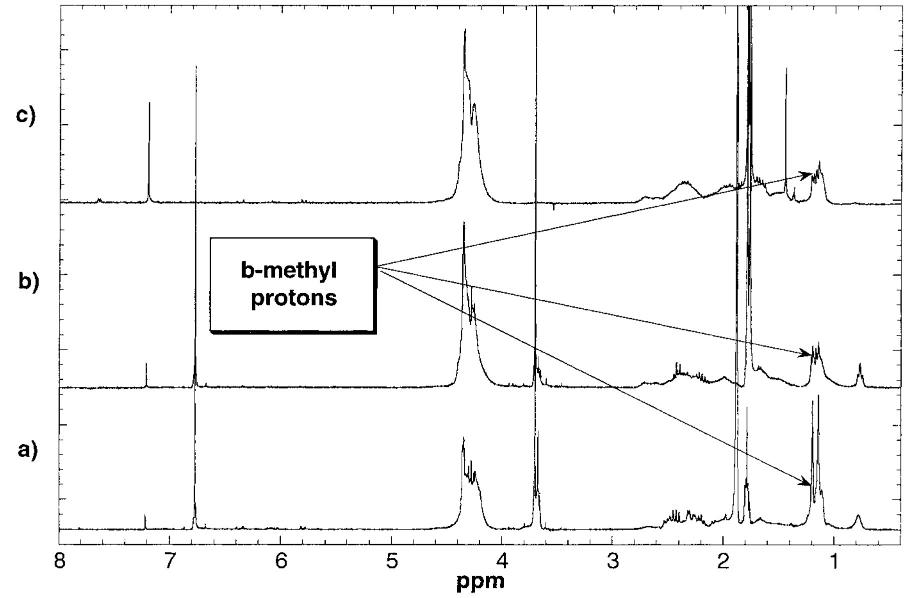


Fig. 4. ^{1}H NMR spectra of: a) poly(BIEA) prepared using 1 mol-% Cu(0) powder, 1 mol-% Cu(I)Br/dNbpy at 24 °C, DB = 0.48, conv. = 0.99; b) poly(BPEA) prepared using 1 mol-% Cu(0) powder, 1 mol-% Cu(I)/Br/dNbpy at 50 °C, DB = 0.48, conv. = 0.99; c) poly(BPEA) prepared using 1 mol-% Cu(I)Br/dTbpy at 50 °C, DB = 0.46, conv. = 0.99

was mainly linear. This result was not unexpected as the secondary **B*** groups, 2-bromopropionyloxy, are known to be inefficient initiators for methacrylate polymerization[16)]. The formation of linear polymer is the result of the apparent rate of activation of the secondary halogen of the initiator (**B*** group), being slower than that of the tertiary halogen at the end of the polymer chain; in linear polymerizations of MMA, slow initiation was observed. Based on this evidence, it can be concluded that in the SCVP of BPEM, the pendent **B*** groups were inefficient in initiating polymerization, and formed only a small number of branch points along the methacrylic backbone.

Determination of the degree of branching (*DB*) for the hyperbranched polyacrylates was performed by ^{1}H NMR. In a method described previously[7)], the relative proportion of **B*** and **b** groups in poly(BPEA) was determined by ^{1}H NMR and by using the statistical predictions derived by Müller[15,17)], an estimation of *DB* was determined (*DB* = 0.48). This approach was feasible because of the differences in the chemical shift between the methyl protons in the **B*** (1.8 ppm) and **b** (1.2 ppm) groups. Fig. 3 illustrates the structural differences of methyl protons from **B*** and **b** groups in the four AB* monomers.

These statistical models were based on ideal SCVP systems where side reactions, such as intramolecular cyclization, are avoided. Because the statistical models are based on ideal SCVP reactions, calculations of *DB* from this method can only be taken as approximations of the actual values of *DB*.

Fig. 4 shows the ^{1}H NMR spectra of hyperbranched polymers, poly(BIEA) and poly(BPEA), obtained with a 1% Cu(I)Br/dNbpy/Cu(0) catalyst system and poly(-BPEA) synthesized using the Cu(I)Br/dTbpy catalyst. In the case of poly(BPEM) and poly(BIEM), the proportion of **B*** and **b** could not be determined by this method because of overlapping signals of methyl protons in the polymer backbone (**R$_1$**) with the methyl protons from the **B*** and **b** groups.

As seen in Fig. 4, the methyl protons assignable to the **B*** groups for the polyacrylates were observed at δ = 1.9 ppm and 1.8 ppm for poly(BIEA) and poly(BPEA), respectively[b]. The methyl groups from the **b**-groups were observed at δ = 1.2 ppm for both poly(BIEA) and poly(-BPEA). For both poly(BIEA) (Fig. 4a) and poly(BPEA) (Fig. 4b), polymerized using the Cu(0) system, a *DB* = 0.48 was calculated[c]. Degree of branching was compar-

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[b] In the ^{1}H NMR spectra, the remaining signals were given the following peak assignments: a small triplet at δ = 0.9 ppm from the methyl protons of the dNbpy ligand, a sharp singlet at δ = 1.5 ppm from the *tert*-butyl protons of the dTbpy ligand, ill-resolved peaks from δ = 1.2 ppm to 2.8 ppm were assigned to the protons in the polymer backbone, a broad multiplet at δ = 4.3 ppm from protons of the ethylene oxide linkage and the proton geminal to Br in BPEA, two sharp singlets at δ = 3.7 ppm and δ = 6.8 ppm from the internal standard (1,4-dimethoxybenzene) and a sharp singlet at δ = 7.24 ppm from $CHCl_3$ impurities in $CDCl_3$.

[c] A perfectly linear polymer is defined as having a degree of branching, DB = 0. A perfectly branched polymer, i. e., a dendrimer, DB = 1. According to theoretical calculations, the maximum DB for an AB* monomer is 0.5.

able for poly(BPEA) (Fig. 4c) synthesized from the Cu(I)/dTbpy system (*DB* = 0.46).

Conclusion

We have demonstrated the utility of zero valent copper in ATRP catalyst systems to polymerize AB* (meth)acrylic monomers. The use of zero valent copper metals has allowed for the polymerization of three monomers which, previously, were not able to be polymerized. The success of the polymerizations was attributed to the reduction of excess deactivator, Cu(II), by reduction with Cu(0). Two of the polymers, poly(BIEA) and poly(BPEA), were determined to be hyperbranched by ^{1}H NMR (*DB* = 0.48). It was not possible to determine degree of branching in poly(BPEM) and poly(BIEM), due to the complexity of the ^{1}H NMR spectra. However, SEC indicated that poly(BPEM) may be primarily linear. Finally, it should be noted that the use of Cu(0) enhances, and is possibly required for, polymerizations where the $[\text{R-X}] \gg [\text{Cu(I)}]$, and not just specifically for the preparation of hyperbranched polymers by SCVP.

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1) J. M. J. Frechet, Henmi, I. Gitsov, S. Aoshima, M. Leduc, R. B. Grubbs, *Science* **269**, 1080 (1995)
2) P. F. W. Simon, W. Radke and A. H. E. Müller, Polym. Prepr. *(Am. Chem. Soc., Div. Polym. Chem.)* **38(1)**, 498 (1997)
3) P. Lu, J. Paulasaari, W. P. Weber, *Macromolecules* **29**, 8583 (1996)
4) C. J. Hawker, J. M. J. Frechet, R. B. Grubbs, J. Dao, J. *Am. Chem. Soc.* **117**, 10763 (1995)
5) S. G. Gaynor, S. Z. Edelmann, K. Matyjaszewski, *Macromolecules* **29**, 1079 (1996)
6) S. G. Gaynor, A. Kulfan, M. Podwika, K. Matyjaszewski, *Macromolecules* **30**, 5192 (1997)
7) S. G. Gaynor, K. Matyjaszewski, A. H. E. Müller, *Macromolecules* **30**, 7034 (1997)
8) S. G. Gaynor, K. Matyjaszewski, *Macromolecules* **30**, 7042 (1997)
9) M. W. Weimer, J. M. J. Frechet, I. Gitsov, *J. Polym. Sci., Polym. Chem.* **36,** 955 (1998)
10) K. Matyjaszewski, J.-S. Wang, *Macromolecules* **28**, 7901 (1995)
11) K. Matyjaszewski, T. Patten, J. Xia, T. Abernathy, *Science* **272**, 866 (1996)
12) K. Matyjaszewski, ACS *Symposium Series* **685**, 258 (1998)
13) S. G. Gaynor, K. Matyjaszewski, ACS *Symposium Series* **685**, 396 (1998)
14) K. Matyjaszewski, S. Coca, S. G. Gaynor, M. Wei and B. E. Woodworth, *Macromolecules* **30**, 7348 (1997)
15) A. H. E. Müller, D. Yan, M. Wulkow, *Macromolecules* **30**, 7015 (1997)
16) K. Matyjaszewski, J.-L. Wang, D. A. Shipp, *Macromolecules* **31**, 1537 (1998)
17) D. Yan, A. H. E. Müller, K. Matyjaszewski, *Macromolecules* **30**, 7024 (1997)