Direct Growth of Hyperbranched Polymers on Both Ends of a Linear Polymer

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Hyperbranched polymers have treelike structures and high density of terminal functional groups on their surfaces; thus, they have unique physical and chemical properties such as low viscosity both in solution and in the molten state in comparison with their linear analogues.[1–3] One of the synthetic strategies for hyperbranched polymers is self-condensing vinyl polymerization (SCVP).[4–8] Since Fréchet et al. proposed the concept of SCVP in 1995,[4] this strategy has been greatly developed by taking advantage of advances in controlled polymerization techniques, including living ionic polymerization,[5] group transfer polymerization,[6] and controlled radical polymerizations.[7,8] Utilizing high solubility and low viscosity of the hyperbranched polymers, the SCVP method has been used to graft various hyperbranched polymers on the surface of solid materials including carbon nanotubes,[9–11] silicon wafer,[12] silica nanoparticles,[13–15] zinc oxide nanoparticles,[16] and cross-linked polystyrene beads.[17] Although hyperbranched polymerization has achieved great success in surface modification of these solid supports, one problem existed is low grafting efficiency due to SCVP of inimers occurred both on and off the supports, such as only about 10−20% of inimers converted were grafted on the supports,[13] which is not economic for practical applications. In synthesis of linear−hyperbranched block copolymers, Frey et al. pointed out that the use of monofunctional poly(ethylene oxide) (PEO) for direct grafting of glycidol is not feasible because of undesired and concurrent homopolymerization of glycidol and also broad molecular weight distribution of the block copolymer formed.[18] Thus, they proposed a synthetic strategy that a linear AB diblock copolymer with a polyfunctional B block as macroinitiator was used in the polymerization of AB_2-type monomer for greatly enhancing the chain growth on the macroinitiator, and slow addition of the monomer was adopted for control of the hyperbranched structure onto the macroinitiator segment.[18–20] With this synthetic strategy the linear−hyperbranched block copolymers with narrow molecular weight distribution were successfully prepared. However, this method cannot solve the problem existing in the hyperbranched polymerization of AB_2 monomer in the mere presence of one terminal functional group in a linear polymer; that is, it cannot control the hyperbranched chain growth on the end of a linear macroreagent. In addition, there was a small fraction of hyperbranched homopolymer in the products,[18–20] and atom transfer radical polymerization (ATRP) using a polyfunctional macroinitiator for synthesis of densely grafted polymers should be stopped at low conversion, such as 12% in order to avoid cross-linking reactions.[21] The same problem occurred when Frey synthetic strategy was used in preparation of the linear−hyperbranched diblock copolymers via the ATRP process.

Here, we report a facile method for synthesis of hyperbranched−linear−hyperbranched triblock copolymers via hyperbranched chain growth on both ends of a linear homopolymer, and slow monomer addition is not needed. The principle of this synthetic strategy is to interrupt propagation of the hyperbranched chain radicals formed off the linear polymer supports by transforming their active species onto the ends of a linear homopolymer 2 (Scheme 1); that is, the functional group of the linear polymer is activated through sacrificing the activity of hyperbranched propagation chains. Successively, the macroradicals 2′ formed propagate via their attacking low molecular weight hyperbranched chains 3 and inimer, and the newly formed hyperbranched−linear−hyperbranched triblock copolymers, which is called the dumbbell polymer later, have much more initiating sites than the hyperbranched polymer chains do (Scheme 1). Therefore, with the same reason for Frey synthetic strategy, hyperbranched chain growth on the dumbbell polymer chains will be predominant.

In this study, *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA), CuBr, and 2-((bromobutyryl)oxy)ethyl acrylate (BBEA) were used as ligand, catalyst, and inimer in ATRP, respectively. Selecting BBEA as inimer was due to easy purification of the hyperbranched polyBBEA (HPBBEA) from the polymer products because HPBBEA is soluble, but PEO is insoluble in cold diethyl ether. The *S*-1-dodecyl-*S*-(α,α′-dimethyl-α″-acetic acid)trithiocarbonates-terminated PEO (TC-PEO-TC) was selected as macro-transfer agent due to its high transfer constant (4×10^6 L/(mol s)).[22] For testing synthetic strategy we proposed that SCVP of BBEA with feed molar ratio of $[\text{BBEA}]_0/[\text{TC-PEO-TC}]_0/[\text{CuBr}]/[\text{PMDETA}] = 400/1/4/4$ was carried out at 80 °C for 48 h. After precipitation from petroleum ether and diethyl ether, the gel permeation chromatography (GPC) curves of the resulting polymers are shown in parts Ab and Ac of Figure 1, respectively. For comparison, the GPC curve of TC-PEO-TC is also shown in Figure 1Aa. We could observe a tail at high elution volume in Figure 1Ab; this tail might be ascribed to HPBBEA because it disappeared completely after precipitation from diethyl ether, and a unimodal GPC curve was observed in Figure 1Ac. For characterizing the structure of the polymer obtained, ^{1}H NMR spectra of TC-PEO-TC and the triblock polymer obtained from precipitation in diethyl ether were measured, and they are shown in Figure 1B. The characteristic signal of PEO at $\delta = 3.6$ ppm (a) and the characteristic signals of HPBBEA at $\delta = 4.0-4.6$ (f, j), 2.8−1.4 (d, e, g, h, k), and 0.8−1.1 ppm (i, l) appeared in Figure 1Bb, indicating the successful control growth of hyperbranched polymer chains on the terminal RAFT group and the formation of the dumbbell polymer. Meanwhile, the resulting triblock copolymer chains with many ATRP initiating sites, Br, and reversible addition−fragmentation chain transfer (RAFT) sites on their surfaces can continue to propagate.

The shapes of triblock copolymers formed like dumbbells because the two hyperbranched polyBBEA structures are connected by a linear PEO with number-average degree of polymerization (DP_n) = 454. The number-average DP_n (153) of every treelike structure can be calculated on the basis of the integration ratio of the signals at $\delta = 3.60$ (a) and 0.8−2.8, 4.0−4.6 ppm. Another important parameter of the hyper-

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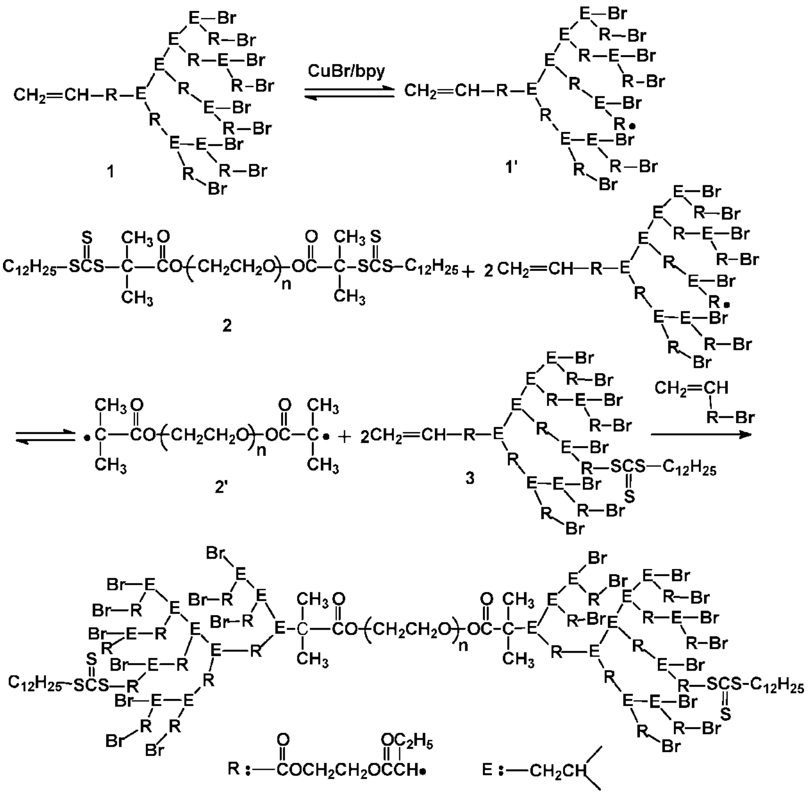
Scheme 1. Suppression of the Hyperbranched Chain Growth off the Support



branched structures is degree of branching (DB). For equal reactivity of active sites, DB ($\mathrm{DB_{NMR}}$) at full conversion can be calculated on the basis of ^{1}H NMR data according to eq 1, and $B^* + b = 1$.[23]

$$\mathrm{DB_{NMR}} = 2\left(\frac{b}{\gamma+1}\right)\left[1-\left(\frac{b}{\gamma+1}\right)\right] \qquad (1)$$

According to the theory of SCVCP,[24] $\mathrm{DB_{theo}}$ at full conversion was represented as eq 2:

$$\mathrm{DB_{theo}} = \frac{2(1-e^{-(\gamma+1)})(\gamma+e^{-(\gamma+1)})}{(\gamma+1)^2} \qquad (2)$$

In the equations, γ is the molar ratio of monomer/inimer in feed, B^* is the fraction of initiating centers, and b is the fraction of branched units and linear units. In this study, $\gamma = 0$, so $\mathrm{DB_{theo}}$ was calculated to be 0.47. And $B^* + b = 1$, so on the basis of integral values of methyl protons signals (b) at 0.8−1.0 ($I_{0.8-1.0}$) and the proton signal of methyl groups (B^*) at 1.0−1.1 ($I_{1.0-1.1}$), b can be calculated according to equation $b = I_{0.8-1.0}/(I_{0.8-1.0} + I_{1.0-1.1})$. So the $\mathrm{DB_{NMR}}$ was determined as 0.37, and the $\mathrm{DB_{theo}}$ was 0.47.

In order to better understand the control growth of hyperbranched polymer on the desired group of PEO by SCVP process via ATRP in the presence of TC-PEO-TC, ^{1}H NMR and GPC methods were used to follow the polymerization with feed molar ratio of $[\mathrm{BBEA}]_0/[\mathrm{TC\text{-}PEO\text{-}TC}]_0/[\mathrm{CuBr}]/[\mathrm{PMDETA}] = 400/1/4/4$. The molecular weight progress of the triblock copolymers formed with conversion is shown in Figure 2a. The M_n(GPC)s are much lower than the corresponding M_n(th)s and M_n(NMR)s. The probable reason is that the hyperbranched−linear−hyperbranched triblock polymers have different hydrodynamic radius of the polystyrene standards. In addition, almost linear relationship of M_n with conversion was observed, and the M_n(NMR) is somewhat lower than M_n(th) because HPBBEA in the samples used for M_n(NMR) measurements was removed. On the basis of the difference between M_n(th) and M_n(NMR), the percentages of HPBBEA contaminant in the triblock copolymers formed at different time were estimated: 26% at 3 h, 36% at 6 h, 7% at 18 h, 4.6% at 24 h, 4.1% at 36 h, and 3.7% at 48 h, which is similar to the results calculated on the basis of weights of the triblock copolymers obtained before and after precipitation in diethyl ether. This indicates that only around 5% of HPBBEA in the products formed after 24 h polymerization was not attached to the PEO. Lower content (26%) of HPBBEA in the products obtained at 3 h polymerization than that (36%) formed at 6 h does not mean that higher portion of BBEA converted in the former was attached to PEO in comparison with the latter; this is due to very low conversion (9%) of BBEA in the former case, so macro-RAFT agent PEO had a big contribution to the total weight of the polymerization products. Actually, the HPBBEA formed on and off PEO was much less than the PEO added. In order to see directly the relationship of HPBBEA content in the triblock copolymers with conversion, the weight percentages of the PHBBEA attached to PEO at various conversions were calculated on the basis of weights of BBEA added and the triblock copolymers obtained after and before precipitation in diethyl ether, and the results are shown in Figure 2b. We can see that only 17% (9% conversion) and 28% (19%) of BBEA converted were attached to the PEO. This indicates that self-polymerization of BBEA was predominant due to high concentration of initial radicals formed via the ATRP process at initial polymerization. Complete interruption of the propagation of hyperbranched chain radicals by relatively low molar concentration of TC-PEO-TC at the initial stage of polymerization is difficult since reactions of the hyperbranched chain radicals with TC-PEO-TC and BBEA are competitive. So conversion of relatively high percentage BBEA to the hyperbranched chains at initial polymerization is understandable. Similar to the mechanism of RAFT polymerization

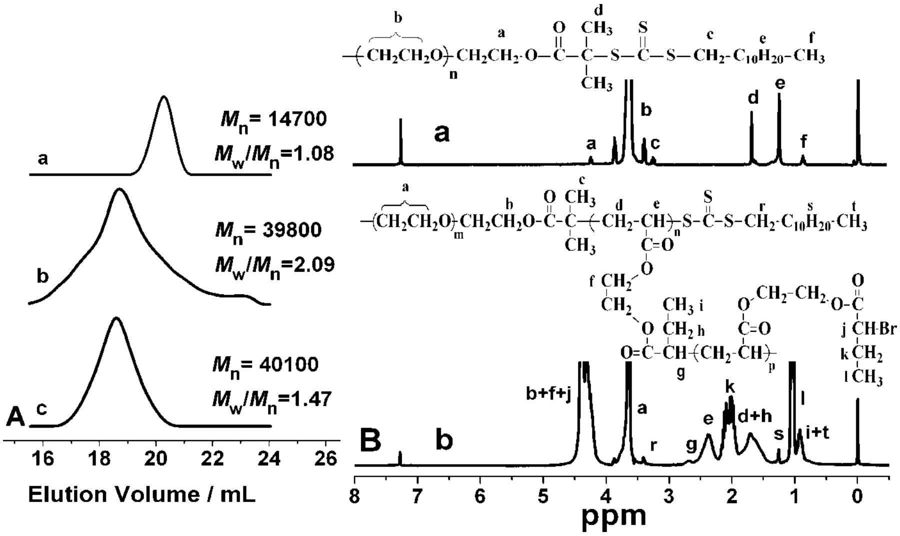


Figure 1. (A) Gel permeation chromatography curves of *S*-1-dodecyl-*S*-(α,α′-dimethyl-α″-acetic acid)trithiocarbonates-terminated poly(ethylene oxide) (TC-PEO-TC) (a), the polymers obtained from self-condensing vinyl polymerization (SCVP) of 2-((bromobutyryl)oxy)ethyl acrylate (BBEA) in the presence of TC-PEO-TC, and following precipitation from petroleum ether (b) or precipitation from diethyl ether (c). (B) ${}^1H$ NMR spectra of the TC-PEO-TC (a) and the polymers obtained from SCVP of BBEA using TC-PEO-TC as macro-reversible addition−fragmentation chain transfer agent and following precipitation from diethyl ether (b).

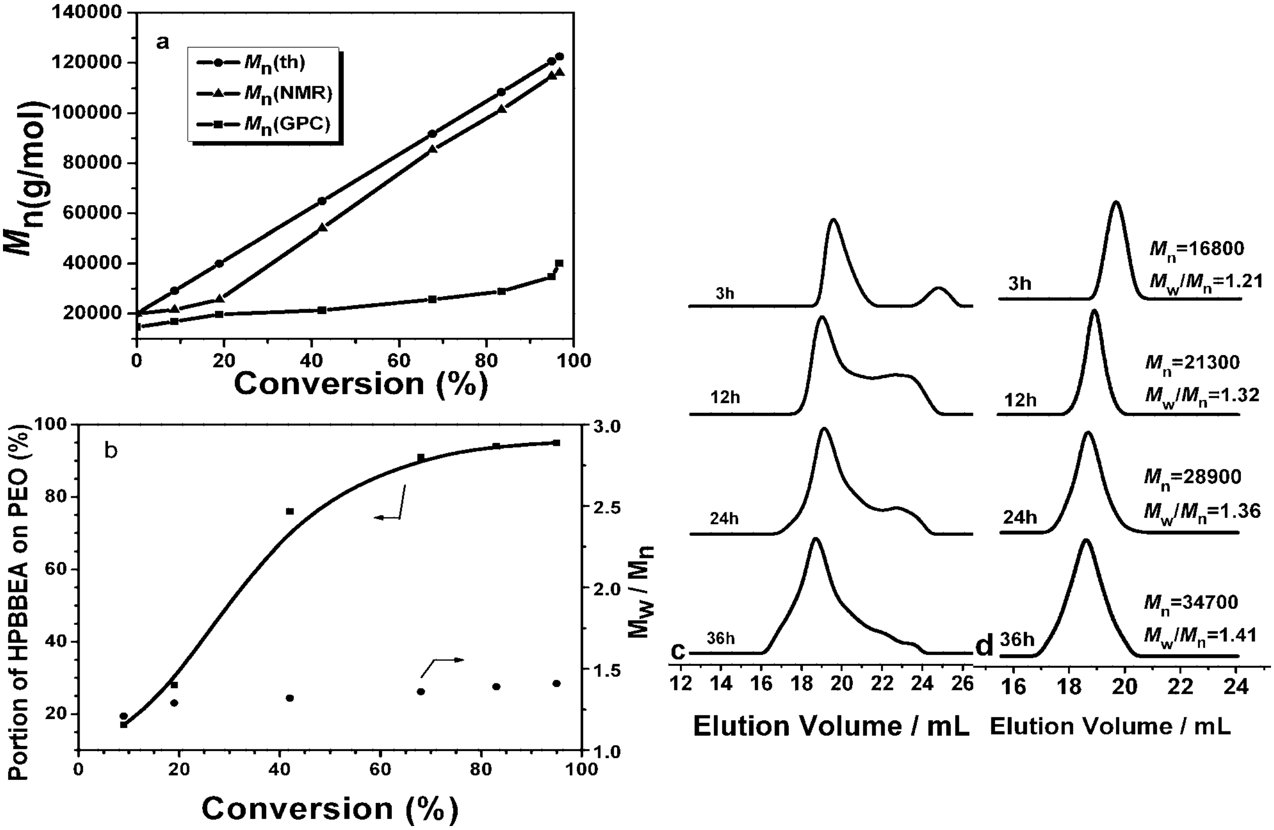


Figure 2. (a) Relationship of number-average molecular weight (M_n) with conversion of self-condensing vinyl polymerization (SCVP) of 2-((bromobutyryl)oxy)ethyl acrylate (BBEA) in the presence of *S*-1-dodecyl-*S*-(α,α′-dimethyl-α″-acetic acid)trithiocarbonates-terminated poly(ethylene oxide) (TC-PEO-TC). (b) Relationship of portion of hyperbranched BBEA formed on the PEO and M_w/M_n with conversion; the conversion was calculated on the basis of weights of the samples obtained from precipitation in petroleum ether; for M_n(NMR) and M_n(gel permeation chromatography (GPC)) measurements, the samples were obtained from precipitation in diethyl ether. (c) GPC traces of the polymers obtained from SCVP of BBEA using TC-PEO-TC as macro-reversible addition fragmentation chain transfer agent, at different polymerization times: 3, 12, 24, and 36 h, respectively, following precipitation from petroleum ether or (d) precipitation from diethyl ether. Polymerization conditions: feed molar ratio of $[BBEA]_0/[TC\text{-}PEO\text{-}TC]_0/[CuBr]/[N,N,N',N',N''\text{-pentamethyldiethylenetriamine}] = 400/1/4/4$; 80 °C.

containing monomer, initiator, and RAFT agent, more and more TC-PEO-TC molecules were activated via the RAFT process with progress of the polymerization until all macro-RAFT agent participated in the polymerization. We can see a big content decrease of HPBBEA in the products formed after 6 h polymerization (Figure 2b). At this stage of polymerization, triblock copolymers with many Br groups had great possibility to produce chain radicals via the ATRP process. In addition, the HPBBEA chain radicals formed would be interrupted via the RAFT process, so the propagation of triblock polymer chain radicals through their addition to HPBBEA and BBEA should be predominant in the polymerization (Scheme 1). This polymerization process can be verified by GPC results shown in Figure 2c also. Figure 2c is the GPC traces of the polymers obtained from precipitation in petroleum ether, and for the products obtained at 3 h, we can observe two peaks in the GPC curve, one at less elution volume is triblock copolymer and other at large elution volume is HPBBEA, which resulted from the polymerization on and off the PEO, respectively. When the polymers were precipitated from diethyl ether, their unimodal GPC traces in Figure 2d appeared at triblock copolymer position, indicating complete removal of HPBBEA. With progress of polymerization the GPC curves at low molecular weight position decreased greatly (Figure 2c). In comparison with broad molecular weight distribution of the hyperbranched polymers formed by SCVP of inimer, the triblock copolymers had low molecular weight distribution (M_w/M_n < 1.5 in Figure 2b). In the SCVP of inimer, the hyperbranched polymer chains with more initiating sites have a greater possibility to propagate in comparison with these hyperbranched chains with less initiating sites, so broad molecular weight distribution products formed. However, in this polymerization system we studied, every triblock polymer chain has the same possibility to propagate via the RAFT process in the whole polymerization process, so their addition to the hyperbranched chains with various molecular weights did not affect the molecular weight distribution of the final triblock copolymers.

In summary, control of hyperbranched chain growth on both ends of PEO has been achieved in the ATRP of inimer using the macro-RAFT agent. With this simple and feasible synthetic strategy, the hyperbranched−linear−hyperbranched triblock copolymers have been prepared successively. The principle of this synthetic strategy is interrupting propagation of the hyperbranched chain radicals by transforming the active species of their chains onto the terminal functional group of linear PEO; thus, propagation of hyperbranched chains is restricted, and the propagation at the end of PEO increases relatively. This provides a convenient method for grafting hyperbranched polymers on the polymer chains or solid material surface.

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Supporting Information Available: Text giving general experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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