A facile strategy to control polymer topology by variation of controlled radical polymerization mechanisms†

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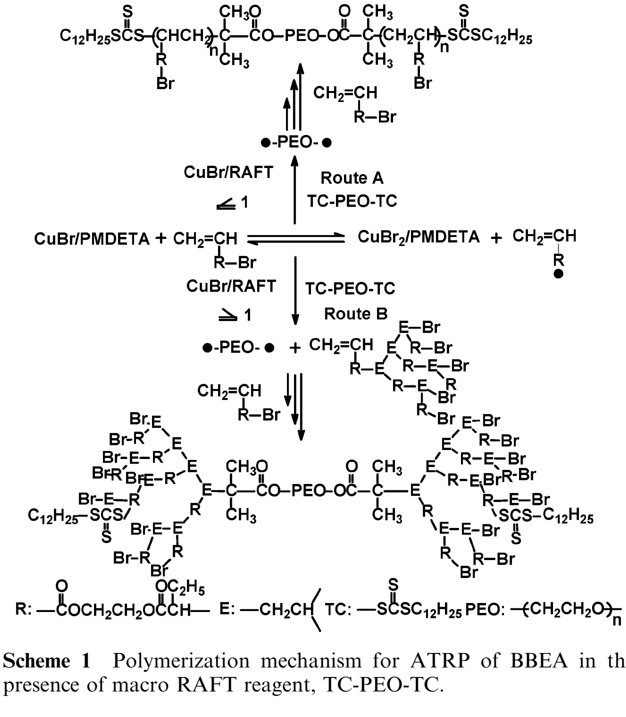
A facile strategy for control of the polymer topologies can be achieved simply by tuning the feed molar ratio of catalyst to transfer agent in the controlled radical polymerization.

The properties of polymers rely strongly on their chemical compositions and topologies, and finding facile and feasible synthetic methods for polymers with different topological structures remains a goal for polymer chemists.[1] Hyperbranched polymers have unique physical and chemical properties in comparison with their linear analogues due to their special shapes, highly branched structures and high density of functional groups at the periphery.[2] However, most hyperbranched polymers are prepared from specially designed monomers, and the synthesis of polymers with tunable topological structures from the same monomer simply by varying the polymerization conditions would be highly desirable.

It is well known that the polymerization conditions and feed molar ratios influence the topological structures of the resultant polymers. Guan *et al.* successfully controlled the branching topology of polyethylene or ethylene polar copolymers through control of the competition between isomerization (chain-walking) and monomer insertion processes.[3] Yan *et al.* studied the polymerization of 1-(2-aminoethyl)piperazine and divinyl sulfone using β-cyclodextrin as the host, and they found that the polymer architecture can be controlled by merely adjusting the amount of host molecules.[4] We found a facile strategy to tune the topology of the poly(amido ester)s formed from Michael-addition polymerization simply by varying the polymerization temperature.[5] The monomers used in the aforementioned synthetic strategies are limited, and the commercially available vinyl monomers, such as styrene and (meth)acrylates, are not suitable in these synthetic strategies.

Self-condensing vinyl polymerization (SCVP) is one important strategy in the synthesis of hyperbranched polymers.[6–9] Since Fréchet *et al.* proposed the concept of SCVP in 1995,[6] this strategy has developed greatly by taking advantage of advances in controlled polymerizations, including living ionic polymerization,[6] group transfer polymerization (GTP),[7] and controlled radical polymerizations.[8] However, no study on controlling the topological structures of the polymers formed from SCVP has been reported. In this article, we report a facile strategy to control the polymer topologies from linear triblock to hyperbranched–linear–hyperbranched copolymers (later called dumbbell polymers) simply by tuning the amount of catalyst. The principle of this strategy is that for atom transfer radical polymerization (ATRP) of inimer in the presence of a reversible addition–fragmentation transfer (RAFT) reagent (route A in Scheme 1), the radicals formed *via* ATRP react with the macro RAFT agent to produce radicals *via* a RAFT process, and following RAFT polymerization yields only linear polymers. Since CuBr cannot be regenerated *via* a reversible ATRP process due to competition from the RAFT process, ATRP stops for a molar ratio of CuBr/RAFT agent ≤1. When this ratio is greater than 1, excess CuBr can catalyze the initiating sites in the polymer to form chain radicals, and further ATRP produces hyperbranched polymers (route B in Scheme 1).

In this study, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), CuBr and 2-((bromobutyryl)oxy)ethyl acrylate (BBEA) were used in the polymerization. BBEA was chosen as inimer because of the easy separation of the hyperbranched poly-BBEA (HPBBEA) from the products because HPBBEA is soluble, but PEO is insoluble in cold diethyl ether. The *S*-1-dodecyl-*S*-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate-terminated poly(ethylene



Scheme 1 Polymerization mechanism for ATRP of BBEA in the presence of macro RAFT reagent, TC-PEO-TC.

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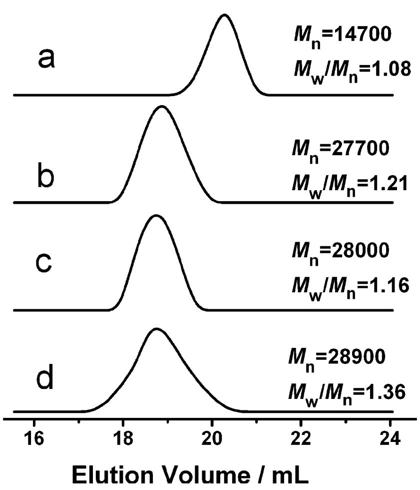

Fig. 1 GPC traces of TC-PEO-TC (a), the polymers obtained from polymerization of BBEA at 80 °C for 24 h in the presence of TC-PEO-TC with the feed molar ratios of $[BBEA]_0 : [TC\text{-}PEO\text{-}TC]_0 : [CuBr]_0$ = 400 : 1 : 1 (b); 400 : 1 : 2 (c); and 400 : 1 : 4 (d), respectively, and following precipitation from diethyl ether. Tetrahydrofuran was used as eluent in GPC measurements.

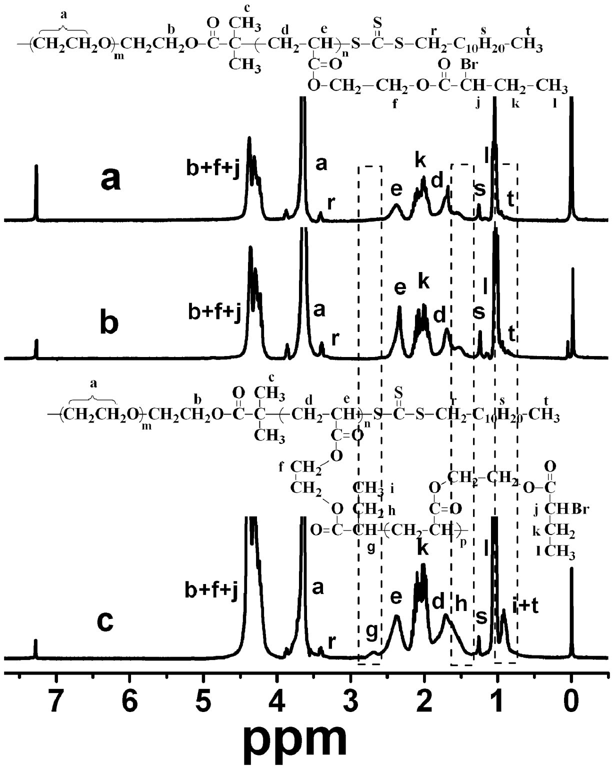

Fig. 2 ^{1}H NMR spectra of the polymers obtained from SCVP of BBEA at 80 °C for 24 h using TC-PEO-TC as macro RAFT agent with feed molar ratios of $[BBEA]_0 : [TC\text{-}PEO\text{-}TC]_0 : [CuBr]_0$ = 400 : 1 : 1 (a); 400 : 1 : 2 (b); 400 : 1 : 4 (c), respectively, following precipitation from diethyl ether.

oxide) (TC-PEO-TC, M_n of PEO: 20 000 g mol^{-1}) was selected as the macro transfer agent due to its high transfer constant of TC (4×10^6 L mol^{-1} s^{-1}).[10] The SCVP of BBEA in the presence of TC-PEO-TC, CuBr and PMDETA produced dumbbell polymers, which is the most facile synthetic strategy for this type of triblock copolymer.[11] For studying the influence of the feed molar ratio of macro RAFT agent to CuBr on the polymerization, SCVP of BBEA with a feed molar ratio of TC-PEO-TC/CuBr = 1/1, 1/2 and 1/4 ($[BBEA]_0 : [TC\text{-}PEO\text{-}TC]_0$ = 400 : 1) was carried out at 80 °C for 24 h. After precipitation of the polymers in diethyl ether, GPC traces of the resultant polymers are shown in Fig. 1, and all of them are unimodal and symmetrical.

For characterization of the structures, their ^{1}H NMR spectra were measured, and are shown in Fig. 2. The characteristic signal of PEO at δ = 3.6 ppm (a) and the signals of HPBBEA at δ = 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 Fig. 2c, indicating the successful growth of hyperbranched polymer on the terminal RAFT group of PEO, forming a triblock copolymer, HPBBEA-PEO-HPBBEA. The reason for this can be briefly described as follows. RAFT reaction of TC-PEO-TC with hyperbranched chain radicals activated the PEO chains through sacrificial activity of the hyperbranched propagation chains formed off the PEO; the PEO chain radicals, propagated *via* their addition reaction with hyperbranched chains, and inimer formed triblock copolymers.[11] In comparison of Fig. 2c with Fig. 2a and b, we can see no proton signals at δ = 2.7, 1.5 and 0.9 ppm in Fig. 2a and b, but these signals are clearly seen in Fig. 2c. Considering the hyperbranched polymerization *via* chain radicals formed from terminal Br in BBEA units and following an ATRP process, the signals of methine, methylene and methyl protons in BBEA units at δ = 4.12, 2.0 and 1.05 ppm will change to the new chemical shifts at δ = 2.7 (g), 1.5 (h) and 0.9 (i) in the hyperbranched polymers formed, respectively. If only vinyl polymerization is taking place, linear block copolymers are produced, and the signals at δ = 2.7, 1.5 and 0.9 ppm will not appear. Thus we deduced that dumbbell polymers were formed for the polymerization with a feed molar ratio of TC-PEO-TC : CuBr = 1 : 4 (sample 1), and linear triblock copolymers were produced for the polymerization with a molar ratio of TC-PEO-TC : CuBr = 1 : 1 and 1 : 2 (sample 2).

To further verify this presumption, samples 1 and 2 were hydrolyzed. The GPC results in Fig. 3A demonstrate big differences between the two hydrolyzed products, which reflects their structural difference. For the products from hydrolysis of sample 2 prepared by polymerization with a molar ratio of TC-PEO-TC : CuBr = 1 : 2, we can see two GPC traces, one with M_n = 26 500 g mol^{-1}, other with M_n = 3300 g mol^{-1} (Fig. 3Aa); however, the GPC trace of the hydrolysis products from sample 1 shows only one peak with M_n = 24 700 g mol^{-1} (Fig. 3Ab). The peaks at M_n = 26 500 and 24 700 g mol^{-1} in Fig. 3A are ascribed to the PEO block. We consider the hydrolysis reactions of the two samples, all branch points and terminal units are connected *via* ester linkages, so the HPBBEA at both ends of the PEO chains was hydrolyzed to form PEO and oligoBBEA with DP = 1, 2, 3 *etc*. Based on the $M_{n,NMR}$ of the hyperbranched polymer, we can estimate the highest molecular weight of hydrolyzed products, poly(acrylic acid) (PAA) is around 600 g mol^{-1}. Thus only one PEO peak was observed in the GPC trace of Fig. 3Ab due to too low DPs of the hydrolyzed products of HPBBEA. But hydrolysis of the linear triblock copolymers produced PEO and PAA with M_n = 3300 g mol^{-1} because the AA units in PAA are connected *via* covalent linkages. Thus we

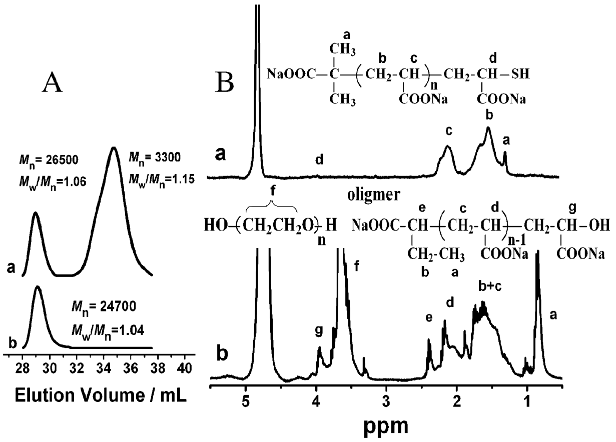

Fig. 3 A: GPC traces of the products obtained from hydrolysis of the samples formed from SCVP of BBEA with feed molar ratios of $[\text{TC-PEO-TC}]_0 : [\text{CuBr}]_0 = 1 : 2$ (a) and 1 : 4 (b), respectively. A buffer solution (pH 7.0) of 0.2 M Na_2HPO_4–NaH_2PO_4 was used as eluent. B: ^{1}H NMR spectra (in D_2O) of the products obtained from hydrolysis of the samples formed from SCVP of BBEA with feed molar ratios of $[\text{TC-PEO-TC}]_0 : [\text{CuBr}]_0 = 1 : 2$ (precipitation from methanol) (a) and 1 : 4 (no precipitation was made) (b), respectively. Hydrolysis was carried out in 0.6 wt% NaOH solution in water–THF (2 : 5, v/v) at 55 °C for 24 h.

can see two peaks in Fig. 3Aa. Their molecular weight difference can be observed on precipitation in methanol. When the hydrolyzed products from samples 1 and 2 were precipitated from methanol, for sample 2, a polymer was obtained, and no precipitation occurred for sample 1 due to too low molecular weights of the hydrolyzed products. Fig. 3B shows ^{1}H NMR spectra of the hydrolyzed products from sample 2 after precipitation in methanol and from sample 1 without purification. During the precipitation in methanol, PEO was not precipitated and there is no characteristic signal from PEO in Fig. 3Ba. But we can see the characteristic signals of the methine and methylene protons in PAA at around $\delta = 1.93$–2.3 ppm (c) and 1.30–1.83 (b), and the signal at $\delta = 1.27$ (a) is ascribed to the methyl protons in the terminal isobutyrate group, which indicates the PAA chains are connected to the PEO chain *via* butyrate ester groups. Thus the linear triblock copolymers PBBEA-*b*-PEO-*b*-PBBEA were obtained from the polymerization of BBEA with a feed molar ratio of TC-PEO-TC : CuBr = 1 : 1 and 1 : 2. For the polymer prepared by polymerization with a feed molar ratio of TC-PEO-TC : CuBr = 1 : 4, its ^{1}H NMR spectrum in Fig. 3Bb shows the characteristic PEO signal at $\delta = 3.63$ ppm, and the strong signal of the methyl protons in the BBEA units at $\delta = 0.9$ ppm (a) originates from the hyperbranched structure, which was formed from SCVP of BBEA. The DP of oligo(acrylic acid) was 3.3, estimated based on the integration ratio of signals c and b to a, which is consistent with the GPC result. So the GPC and ^{1}H NMR results of the polymers before and after hydrolysis of sample 1 demonstrate the formation of dumbbell polymers. From the above discussion, the structure of the polymer produced can be tuned from linear to dumbbell by varying the feed molar ratio of TC-PEO-TC : CuBr. A possible reason for this is as follows. When the molar ratio of TC to CuBr is equal to or less than 1, the initial radicals formed *via* reaction of BBEA with CuBr are converted to chain radicals *via* RAFT, resulting in a low concentration of CuBr. The chain radicals propagate *via* RAFT, and due to the higher concentration of TC than of $CuBr_2$, these radicals will not be converted to Br-terminated dormant chains *via* their reaction with $CuBr_2$, leading to a large decrease in the CuBr concentration. So RAFT polymerization of BBEA becomes predominant in the two competitive ATRP and RAFT polymerizations, and thus the linear triblock copolymer PBBEA-*b*-PEO-*b*-PBBEA is formed. When the feed molar ratio of TC : CuBr is equal to or larger than 2, SCVP of BBEA produces hyperbranched polymer chains due to the excess of CuBr used, and subsequently they attach to the PEO chains *via* a RAFT process as discussed above, and the dumbbell polymers are formed.

In summary, control of the topological structure of the polymers has been achieved simply by tuning the feed molar ratio of CuBr to macro RAFT agent in SCVP of the inimer. When the feed molar ratio of CuBr to RAFT sites is less than 1, with the aid of CuBr–PMDETA a little of the inimer acts as initiator in the RAFT polymerization of inimer, and linear triblock copolymers with one bromine in each inimer unit are produced. When this ratio is larger than 1, the initiating sites in the PEO chains initiates SCVP of the inimer to form dumbbell polymers. Thus, the topologies of the triblock copolymer can be tuned from linear to dumbbell polymers just by variation of the feed molar ratio of RAFT sites to CuBr.

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