8790 *Macromolecules* **2010**, *43*, 8790–8798
DOI: 10.1021/ma101807y

Macromolecules
ARTICLE

Controlling Polymer Topology by Atom Transfer Radical Self-Condensing Vinyl Polymerization of *p*-(2-Bromoisobutyloylmethyl)styrene

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Received August 8, 2010; Revised Manuscript Received September 23, 2010

ABSTRACT: A new unsymmetrical AB* inimer, *p*-(2-bromoisobutyloylmethyl)styrene (BiBMS), was applied to the atom transfer radical polymerization (ATRP) to prepare a family of polymers with the topologies ranging from linear to branched. The catalyst system was Cu/$CuBr_2$ coupled with 2,2′-bipyridine (Bipy) or *N,N*-bis(2-pyridylmethyl)octylamine (BPMOA) as a ligand in toluene or anisole at different temperatures, which ensured a very low catalyst (CuBr) concentration throughout the polymerization by a slow reduction process. First, BiBMS was polymerized in anisole at 0 °C using Cu/$CuBr_2$/BPMOA as a catalyst system; at this temperature, the initiating activity of the formed A* was frozen and the polymerization was a step-growth polymerization, resulting in the formation of a linear polymer (LP1) whose main chain was linked by ester bonds. Second, BiBMS was polymerized in toluene at 20 °C using Cu/$CuBr_2$/Bipy as a catalyst system. Under this condition, initiation from the B* of BiBMS was slow, followed by a fast radical polymerization of the BiBMS vinyl bonds and a slow deactivation, thereby affording another linear polymer (LP2), the structure of which was the same as that obtained by common free radical polymerization of BiBMS except the end groups. The conversion of BiBMS was controlled to be moderate to suppress the possible initiation from the pendant B* along the polymer main chain. Third, BiBMS was polymerized in anisole at various temperatures using Cu/$CuBr_2$/Bipy as a catalyst system; three branched polymers (BP1, BP2, BP3) with different degree of branching (DB) were obtained, the DB of which could be easily adjusted by changing temperature (BP1, DB = 0.12 at 20 °C; BP2, DB = 0.26 at 40 °C; BP3, DB = 0.37 at 60 °C).

Introduction

Polymer scientists have long been interested in controlling macromolecular architecture and topology because the physical properties of polymers and their potential applications are inherently related to their architectures.[1] As a typical example, hyperbranched polymers (HBPs), compared to their linear analogues, show distinct properties, such as low viscosity, high solubility, and a high degree of functionality.[2−6] HBPs have been mainly synthesized by the polycondensation of AB_x type monomers. Self-condensing vinyl polymerization (SCVP) of AB* inimers has been another very useful method to prepare HBPs from vinyl monomers.[7] The AB* inimer combines the features of an initiator (B*) and a monomer (A), polymerization is initiated from B*, and the formed active species is then reacted with the vinyl group of another inimer to form a dimer having a vinyl group (A) and two latent active species (A* and B*). Both A* and B* groups can be converted to active species and continuously react with vinyl groups of other monomers, oligomers, or polymers, thereby generating branched polymers. Recent development of controlled radical polymerization (CRP)[8−10] and the combination of CRP with the SCVP of inimers have greatly expanded the applications of vinyl polymerization in synthesizing HBPs. Owing to the easy synthesis of inimers, clear demonstration of mechanism, and simple control of polymer structures, atom transfer radical polymerization (ATRP) of inimers (ATR-SCVP) has been widely studied, and a variety of branched polymers, such as polystyrenics and poly(meth)acrylates, have been synthesized.[11−14] Very recently, Pugh et al. reported for the first time the synthesis of new hyperbranched analogues of linear polyacrylates by the ATR-SCVP of a new inimer.[15] For an AB* inimer used for ATR-SCVP, A is a vinyl group and B* is an ATRP initiator, which can be activated to produce a radical under certain conditions. To suppress the side reactions of radicals, the catalyst concentration should be low, especially when the methacrylate-type AB* inimer is polymerized.[11e,13] In an ATR homopolymerization of a single inimer, control over the degree of branching (DB), one of the key structural parameters of HBPs, can be manipulated by the inherent reactivity of A* and B* and varying polymerization conditions. Both theoretical studies and experimental approaches have elucidated that in the ATR-SCVP of inimers, polymerization conditions, such as temperature, solvent, ligand, the ratio of CuBr to monomer, and adding Cu, etc., exhibit effects on the DB.[11−16] ATR copolymerization of an inimer with another vinyl monomer is the more convenient way to vary the DB and at the same time can endow functionalities on the hyperbranched polymers.[17−21]

Control over polymer topology from a single monomer by manipulating the catalyst and polymerization conditions has been challenging. The general idea is to control the relative polymerization, chain transfer, and termination rates. For example, Guan et al. developed a new kind of “chain walking” catalyst for the polymerization of ethylene or other olefinic monomers. Homopolymerization of ethylene under different ethylene pressures resulted in the formation of a series of polyethylenes ranging from linear to hyperbranched to dendritic.[22] By copolymerization of ethylene with other simple olefinic monomers at different monomer concentrations, they developed a one-pot synthetic

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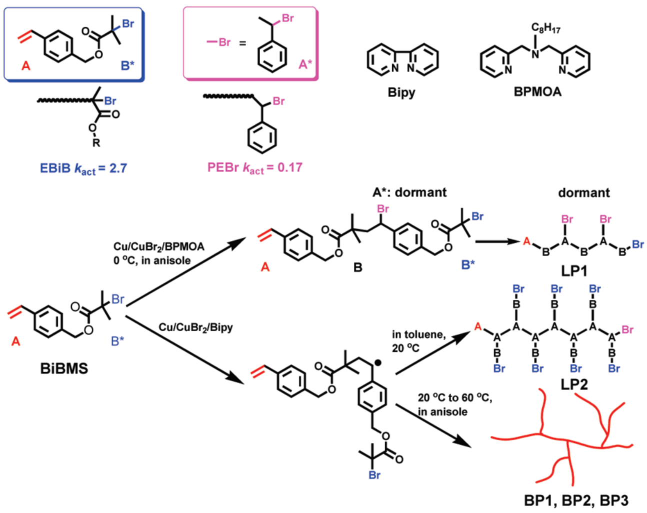
Scheme 1. Control of Polymer Topology in the ATR-SCVP of BiBMS



method of functional copolymers having controllable topologies; in addition, tandem chain walking copolymerization and ATRP of other vinyl monomers allowed them to produce dendritic nanoparticles with tunable size and reactive surface functionalities.[23,24] Hong et al. reported the thermo control over the topologies of polymers, from linear to hyperbranched structures, by the Michael addition polymerization of a diacrylate and *N*-methylethylenediamine. Owing to the relative high steric hindrance of the formed secondary amine on the polymer backbone, a linear copolymer was formed at a temperature lower than 40 °C. Elevating the polymerization temperature would activate the Michael addition reaction of the secondary amine with the double bond of acrylate, thus leading to the formation of hyperbranched polymers, the DB of which was increased with increasing temperature.[25] Quite recently, Ueda et al. reported a new approach to control the polymer topology by the self-polycondensation of an AB$_2$ monomer through varying the ratio of monomer to trifluoromethanesulfonic acid.[26] In the ATR-SCVP of inimers, Kamigaito et al. synthesized a series of linear polyesters by (co)polymerization of a special AB* monomer under ATRP conditions.[27] In this system, the formed A* was completely inactive; thereby the polymerization was essentially a step-growth polymerization based on atom transfer radical addition (ATRA).

Considering the different initiating abilities of ATRP initiators and the effects of factors, such as temperature, ligand, solvent, and the [Cu^{I}]/[Cu^{II}] ratio, etc., on the ATRP of vinyl monomers,[8,28,29] we are pursuing development of a new method to synthesize polymers with different topologies by the ATR-SCVP of a single AB* monomer. Therefore, in this report, we have designed a new AB * monomer, *p*-(2-bromoisobutyloylmethyl)styrene (BiBMS), and studied its homopolymerization under different ATRP conditions (Scheme 1). BiBMS is an unsymmetrical inimer containing a styrenic double bond (A) and a methacrylate-type ATRP initiator (B*). When the ATRP of BiBMS is conducted, B* will be activated to produce a methacrylate-type radical, and subsequently this radical will add one vinyl bond of another BiBMS molecule to produce a dimer with B* and a new initiator (A*); the structure of A* is similar to a styrene-type ATRP initiator. Because of the significant difference between the activation rate constants of A* and B*,[28] especially at low temperatures, the subsequent polymerization is very much dependent on the reaction conditions, i.e., temperature, ligand, and solvents. At a low temperature, and using Cu/CuBr$_2$ coupled with *N*,*N*-bis(2-pyridylmethyl)octylamine (BPMOA) to form an active catalyst system in anisole, the polymerization of BiBMS is slow, and the initiation from the formed A* is frozen; thus, the polymerization proceeds like a stepwise polyaddition to form a linear polyester. Next, using Cu/CuBr$_2$ coupled with 2,2′-bipyridine (Bipy) to form a less active catalyst system in toluene, the initially formed methacrylate radicals of BiBMS can continuously add a large amount of inimers before it is terminated by deactivation. The whole polymerization thus behaves like a common radical polymerization; longer reaction time allows the formation of more radicals from BiBMS, leading to an increase of inimer conversion with slight increase of polymer molecular weights. Finally, if we polymerize BiBMS by Cu/CuBr$_2$/Bipy in anisole instead of toluene as a solvent and at relatively high temperatures, the number of inimer added by initiation from B* is decreased, and the initially formed A* can partially be activated; therefore, the whole process is like a SCVP of normal inimers, affording branched polymers with different DB by changing the temperature.

Experimental Section

Materials. Copper (Cu, 200 mesh, 99.5%, Beijing Chemical Co.), copper(I) bromide (CuBr, 99.999%, Aldrich), copper(II) bromide (CuBr$_2$, 99%, Aldrich), sodium azide (99%, Alfa Aesar), tin(II) 2-ethylhexanoate (Sn(EH)$_2$, 97%, Alfa Aesar), 1-phenylethyl bromide (PEBr, 97%, Aldrich), ethyl 2-bromoisobutyrate (EBiB, 98%, Aldrich), 2,2′-bipyridine (Bipy, 99%, Alfa Aesar), 4,4-di-*tert*-butyl-2,2-dipyridine (dTbipy, 98%, Aldrich), 4-vinylbenzyl chloride (VBC, 90%, Acros), 2-bromoisobutyryl bromide (98%, Aldrich), 2-(chloromethyl)pyridine hydrochloride (98%, Acros), *n*-octylamine (99%, Aldrich), and triethylamine (99%, Shan Tou Xi Long Chemical Factory) were used as received. Styrene (St, 98%, Beijing Chemical Co.) was washed with 2 M NaOH, dried with CaCl$_2$, and distilled over CaH$_2$ under vacuum. Tetrahydrofuran (THF, 99.9%, Beijing Chemical Co.) was refluxed over CaH$_2$ and distilled. Other reagents were commercially obtained from Beijing Chemical Co. and used without further purification.

p-Hydroxymethylstyrene was synthesized in 90% yield from 4-vinylbenzyl chloride according to the literature method.[30] *N*,*N*-Bis(2-pyridylmethyl)octylamine (BPMOA) was obtained in 50% yield by the reaction of *n*-octylamine and 2-(chloromethyl)pyridine hydrochloride with the literature method.[31] *p*-(2-Bromoisobutyloylmethyl)styrene (BiBMS) was synthesized by the reaction of *p*-hydroxymethylstyrene with 2-bromoisobutyryl bromide in 90% yield. ^{1}H NMR (300 MHz, CDCl$_3$, TMS), δ (ppm): 1.95 ($(CH_3)_2C(Br)-$, 6H, s), 5.19 ($-COO-CH_2-$, 2H, s), 5.27, 5.76 ($CH_2=$, 2H, d), 6.71 ($=CH-$, 1H, q), 7.40 ($-C_6H_4-$, 4H, m).

Comparison of Initiating Activity of A* (PEBr) and B* (EBiB). PEBr and EBiB were used as initiators for the ATRP of St in THF at different temperatures. General procedure: In a polymerization tube containing Cu (10 mg, 0.16 mmol) and CuBr$_2$ (18 mg, 0.08 mmol), PEBr (0.45 g, 2.4 mmol) or EBiB (0.47 g, 2.4 mmol), St (0.25 g, 2.4 mmol), and THF (0.5 mL) were added. The mixture was degassed by two freeze−pump−thaw cycles, and BPMOA (75 mg, 0.24 mmol) was added when the mixture was frozen. One more freeze−pump−thaw cycle was conducted before the tube was sealed under vacuum. The tube was then put into an ice/water mixture at 0 °C (for PEBr) or an ethanol/water mixture cooled to −20 °C (for EBiB). After 24 h, the tube was broken; the solution was diluted with THF and filtered over neutral alumina. The obtained solution was condensed to about 2 mL, 0.1 mL of which was taken out and put into a NMR tube, after the residual THF was completely removed by purging with nitrogen; 0.5 mL of CDCl$_3$ was added before NMR spectrum was measured.

General Procedure for the ATR-SCVP of BiBMS. The polymerization procedure was essentially the same as the above ATRA. Detailed conditions are compiled in Table 1. For kinetics studies, samples were taken periodically with a syringe to follow the kinetics of the polymerization. The conversions were determined by ^{1}H NMR spectroscopy with toluene or anisole as the internal reference. After 48 h, the solution was diluted with

Table 1. ATR-SCVP of BiBMS[a]

polymer	ligand	solvent	temp (°C)	conv[b] (%)	M_n[c]	M_n[d]	PDI[d]	DB[e]
LP1[f]	BPMOA	anisole	0	> 98 (70)	6200	5800	2.72	0
LP2[f]	Bipy	toluene	20	40 (32)	9900	7800	1.61	≈0
BP1[f]	Bipy	anisole	20	76 (65)	10900	6800	1.80	0.12
BP2[f]	Bipy	anisole	40	90 (78)	21600	8300	1.96	0.26
BP3[g]	Bipy	anisole	60	93 (75)	18900	5600	1.68	0.37

[a] $[Cu]_0/[CuBr_2]_0/[ligand]_0/[BiBMS]_0$ = 2/1/(3 for BPMOA, 6 for Bipy)/50, 48 h. [b] As determined by ^{1}H NMR (consumption of double bonds); data in the parentheses are the purified polymer yield determined gravimetrically. [c] As determined by ^{1}H NMR, assuming one end double bond per macromolecule. [d] As determined by GPC vs linear PSt standards. [e] DB was determined according to eq 2. [f] $[BiBMS]_0$ = 1.8 mol/L. [g] $[BiBMS]_0$ = 2.8 mol/L.

THF and filtered over neutral alumina. The obtained solution was concentrated to about 20 mL, and then it was precipitated into petroleum ether (~200 mL) to obtain a gel-like polymer, which was redissolved in THF (20 mL) and reprecipitated from cold petroleum ether (−30 °C, 150 mL) for two times to yield the polymer as a white solid. All the polymer samples were dried in vacuum at room temperature for 24 h.

Synthesis of Linear Polymer LP1. Conditions: Cu (10 mg, 0.16 mmol), $CuBr_2$ (18 mg, 0.08 mmol), BPMOA (75 mg, 0.24 mmol), BiBMS (1.14 g, 4.0 mmol), $[Cu]_0/[CuBr_2]_0/[BPMOA]_0/[BiBMS]_0=2/1/3/50$, $[BiBMS]_0=1.8$ mol/L in anisole, 0 °C, 48 h. Procedure for polymer purification was the same as described in the general procedure.

Synthesis of Linear Polymer LP2. Conditions: Cu (10 mg, 0.16 mmol), $CuBr_2$ (18 mg, 0.08 mmol), Bipy (73 mg, 0.48 mmol), BiBMS (1.14 g, 4.0 mmol), $[Cu]_0/[CuBr_2]_0/[Bipy]_0/[BiBMS]_0$ = 2/1/6/50, $[BiBMS]_0$ = 1.8 mol/L in toluene, 20 °C, 48 h. Procedure for polymer purification was the same as described in the general procedure.

Synthesis of Branched Polymer BP1, BP2, and BP3. Conditions: Cu (10 mg, 0.16 mmol), $CuBr_2$ (18 mg, 0.08 mmol), Bipy (73 mg, 0.48 mmol), BiBMS (1.14 g, 4.0 mmol), $[Cu]_0/[CuBr_2]_0/[Bipy]_0/[BiBMS]_0$ = 2/1/6/50, $[BiBMS]_0$ = 1.8 mol/L (2.8 mol/L for BP3) in anisole, 48 h. BP1 (20 °C), BP2 (40 °C), and BP3 (60 °C). Procedure for polymer purification was the same as described in the general procedure.

Transformation of Polymer LP1. Bromo groups on the polymer chains of LP1 were transformed to azido groups by substitution reactions with NaN_3. Typically, polymer LP1 (100 mg, 0.35 mmol of −Br) was dissolved in 10 mL of DMF in a 25 mL round-bottom flask. Then, sodium azide (33 mg, 0.5 mmol) was added, and the reaction mixture was stirred at room temperature for 24 h. The final mixture was put into water to yield a viscous solid. This solid was redissolved in THF (10 mL) and precipitated into cold petroleum ether (100 mL) to get a white solid, which was further dried at room temperature in vacuum for 24 h.

Typical Procedure for the Preparation of LP1-*g*-PS1 and LP1-*g*-PS2. LP1 was used as a macroinitiator to initiate the normal ATRP of St in anisole at 120 °C. Conditions: $[CuBr]_0/[Bipy]_0/[-Br \text{ of } LP1]_0/[St]_0$ = 1/2/1/200, $[St]_0$ = 3.8 mol/L. In a polymerization tube containing a stirring bar, a mixture of LP1 (29 mg, 0.10 mmol of −Br), Bipy (31 mg, 0.20 mmol), St (2.1 g, 20 mmol), and anisole (3.0 g) was degassed by three freeze−pump−thaw cycles. CuBr (14 mg, 0.10 mmol) was then added in the N_2 atmosphere when the mixture was frozen, and the polymerization tube was sealed under vacuum. The mixture was warmed to room temperature and stirred for 0.5 h. The tube was then put into a preheated oil bath at 120 °C. After 4 h (LP1-*g*-PS1) or 72 h (LP1-*g*-PS2), the tube was broken, and the mixture was diluted with THF and filtered over neutral alumina. The obtained solution was concentrated and precipitated into methanol for three times to yield polymer, which was dried in vacuum at room temperature for 24 h.

Typical Procedure for Hydrolysis of the Polymers. Polymer (30 mg) was added to a polymerization tube containing a stirring bar and a mixture of KOH (0.3 g), ethanol (2 mL), and THF (4 mL). The tube was degassed by one freeze−pump−thaw cycle and sealed under vacuum. The tube was heated under stirring at 60 °C for 72 h, and then 2 mL of 37% HCl was added. The formed KCl was removed by filtration, THF was removed by evaporation, and then the residue was characterized directly by GPC. Further separation of hydrolyzed products was performed with a preparative GPC.

Characterization. Molecular weights and polydispersity index (PDI = M_w/M_n) of polymers were measured with a gel permeation chromatography (GPC) equipped with a 2414 refractive index detector, a Waters 1525 binary HPLC pump, and three Waters Styragel HT columns (HT2, HT3, HT4). The columns were thermostated at 35 °C, and THF was used as an eluent at a flow rate of 1.0 mL/min. Calibration was made against standard monodisperse linear polystyrene (PSt); the obtained datum was processed on professional software. ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Bruker ARX-400 spectrometer or a Varian Gemini 300 spectrometer with tetramethylsilane (TMS) as the internal reference for chemical shifts. Preparative GPC was performed with a LC-9201 recycling preparative HPLC (Japan Analytical Industry) equipped with a JAIGEL-1H column (600 × 200 mm^2). Chloroform was used as the eluent at a flow rate of 3.5 mL/min.

Results and Discussion

A good control of ATRP relies on the ratio of the activation rate constant to the deactivation rate constant ($K_{ATRP} = k_{act}/k_{deact}$) and the ratio of $[Cu^I]$ to $[Cu^{II}]$.[8] To keep a low radical concentration, it is essential to keep a low ratio of $[Cu^I]$ to $[Cu^{II}]$. In the ATR-SCVP of an AB* inimer, the initiator concentration is high; if the polymerization is carried out under conditions similar to a normal ATRP of a vinyl monomer, much higher radical concentration will be generated at the beginning of polymerization, which will increase the side reactions, such as bimolecular coupling and disproportionation. To lower the radical concentration, one can lower the ratio of $[Cu^I]$ to $[Cu^{II}]$ by adding $CuBr_2$ or using activators generated by electron transfer atom transfer radical polymerization (AGET ATRP). But for a homogeneous AGET-ATRP, lower radical concentration can only be realized at the very beginning; the rapid reduction of $CuBr_2$ by reducing agent will result in a rapid increase of Cu^I, which will in turn accelerate the polymerization.[32] Both the styrene-type and the acrylate-type ATRP initiators have small activation rate constants; ATR-SCVP of symmetrical inimers derived from these two monomers can reach a high conversion of inimers, yielding HBPs with controlled molecular weights and DB. But for the methacrylate-type inimers, the initiation is much faster; high radical concentration leads to both limited inimer conversion and molecular weights of polymers due to the accumulated Cu^{II}. Therefore, for the ATR-SCVP of BiBMS, we used zerovalent copper powder instead of soluble reducing agent to reduce the $CuBr_2$ in a heterogeneous condition. In addition, high concentration of $CuBr_2$ was used to lower the ratio of $[Cu^I]$ to $[Cu^{II}]$ and efficiently deactivate the polymerization.

Comparison of Initiating Activity of PEBr (A*) and EBiB (B*). BiBMS is an unsymmetrical inimer, ATRP of which will generate two families of initiators: one is similar to PEBr (A*), and the other is the same as EBiB (B*). Because of the

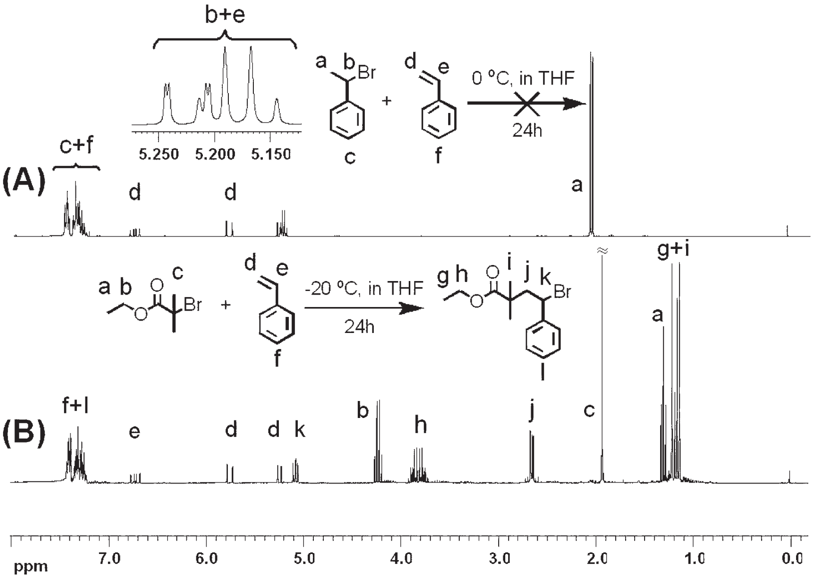


Figure 1. ^{1}H NMR spectrum of the reaction mixture of PEBr and St at 0 °C (A) and that of EBiB and St at −20 °C (B). Conditions: $[Cu]_0/[CuBr_2]_0/[BPMOA]_0/[PEBr]_0$ or $[EBiB]_0/[St]_0 = 2/1/3/30/30$, $[St]_0 = 2.0$ mol/L, in THF, 24 h.

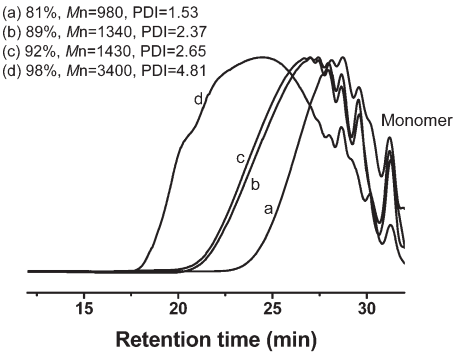


Figure 2. GPC traces of ATR-SCVP of BiBMS under different conditions: $[BiBMS]_0 = 1.8$ mol/L, in anisole at 0 °C for 48 h: (a) $[CuBr]_0/[BPMOA]_0/[BiBMS]_0 = 3/3/50$; (b) $[Cu]_0/[CuBr]_0/[BPMOA]_0/[BiBMS]_0 = 2/1/3/50$; (c) $[Sn(EH)_2]_0/[CuBr]_0/[BPMOA]_0/[BiBMS]_0 = 1/1/3/50$; (d) $[Cu]_0/[CuBr_2]_0/[BPMOA]_0/[BiBMS]_0 = 2/1/3/50$.

structural difference, these two species show quite different activation rate constants, with B* much higher than that of A* under similar conditions.[28] Therefore, it seems possible to freeze the initiation from A* while maintaining the initiation of B* by lowering temperature and/or selecting ligand or solvent. To testify this hypothesis, we first carried out the ATRA of PEBr and EBiB to St in THF under ATRP conditions with BPMOA as the ligand. The concentrations of both initiator and styrene were relatively high. During the polymerization, the color of the solution soon became dark green due to the formation of soluble complex of $CuBr_2$ with BPMOA, and this color remained throughout the polymerization. Figure 1A presents the ^{1}H NMR spectrum of the reaction mixture of PEBr and St at 0 °C; it can be seen that besides the signals of St and PEBr, no new signals appeared, indicating that no reaction occurred, and PEBr could not be activated to add even a St monomer. This can be understood considering the low temperature and high concentration of $CuBr_2$ complexed with BPMOA. Figure 1B shows the ^{1}H NMR spectrum of the reaction mixture of EBiB and St at −20 °C. We observed new signals besides those from EBiB and St, and these new signals are corresponding exactly to the monoadduct of an EBiB radical to one St; the conversion of St was 47% as determined by ^{1}H NMR. ^{13}C NMR spectra also supported the formation of monoadduct (Figure S1). These results confirm that EBiB can be activated even at −20 °C, and each of the formed methacrylate-type radical can add one St; but the subsequently formed styryl radical quickly deactivated to be dormant species, which could not be activated again to add more St. Therefore, we conclude that by using the heterogeneous catalyst system ($Cu/CuBr_2$ coupled with BPMOA) to generate CuBr in situ at low temperature, we can freeze the activation of PEBr, and the ATRP of St initiated by EBiB is converted to an ATRA. We obtained similar results by changing the solvent from THF to anisole.

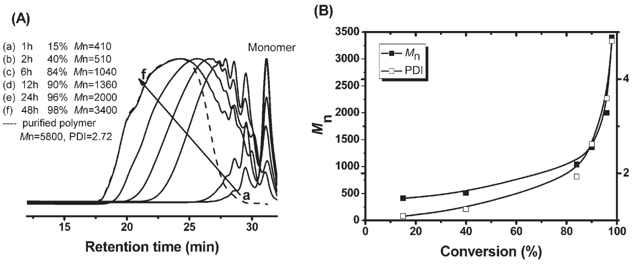


Figure 3. (A) GPC traces of polymer LP1 at various times. (B) Number-average molecular weight and PDI (M_w/M_n) versus BiBMS conversion. BiBMS conversion was determined by ^{1}H NMR (determined from the double bond of BiBMS); M_n and M_w/M_n (include monomer) were determined by GPC vs linear PSt standards. Conditions: $[Cu]_0/[CuBr_2]_0/[BPMOA]_0/[BiBMS]_0 = 2/1/3/50$, $[BiBMS]_0 = 1.8$ mol/L, in anisole at 0 °C.

Linear Polyester from BiBMS (LP1). We first studied the ATR-SCVP of BiBMS with different catalyst systems. The GPC traces of four experiments are presented in Figure 2. When CuBr/BPMOA was used, only oligomers were produced, and the conversion of BiBMS was 81%. Further addition of Cu or $Sn(EH)_2$ into this system could slightly increase both inimer conversion and M_n of the polymer. This result is understandable because both Cu and $Sn(EH)_2$ can reduce the formed $CuBr_2$ to CuBr, keeping a high concentration of radical; therefore, the polymerization is fast. However, high concentration of radicals may cause side reactions (coupling and disproportionation). When $Cu/CuBr_2$ was used, there was no CuBr in the beginning, and it could only be produced

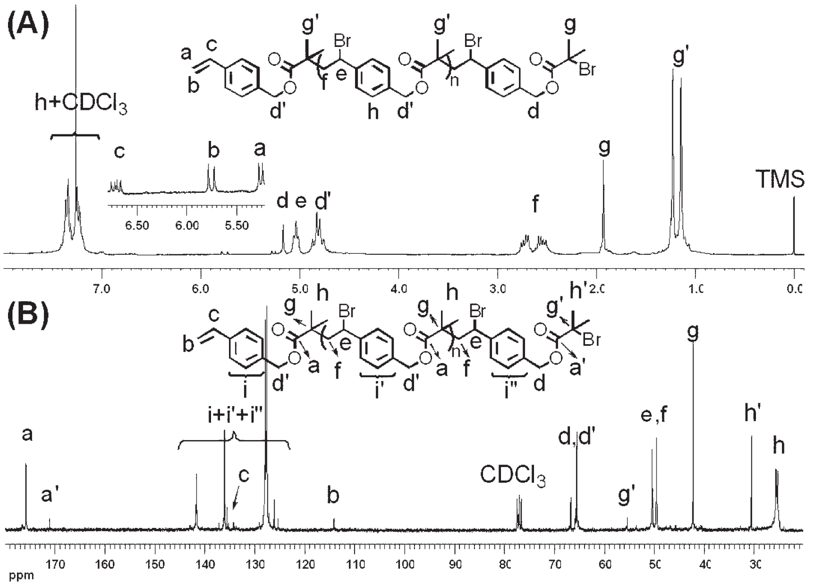


Figure 4. ^{1}H NMR (A) and ^{13}C NMR (B) spectra of polymer LP1 in $CDCl_3$.

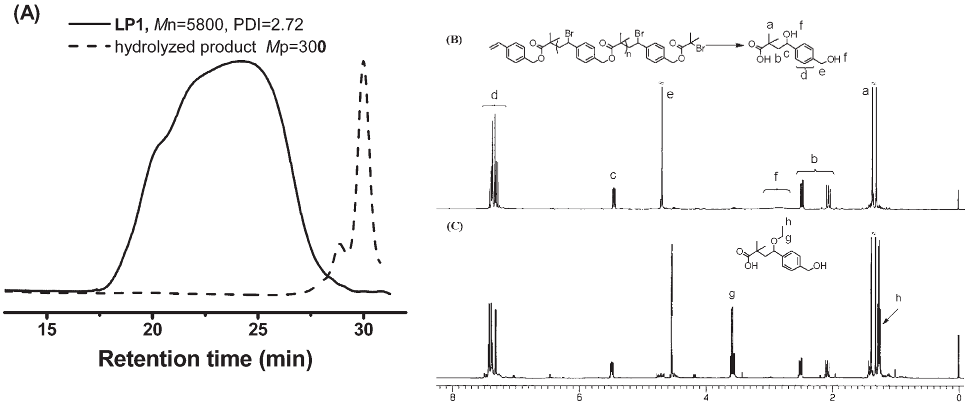


Figure 5. (A) GPC traces of polymer LP1 and its hydrolyzed products. Hydrolysis condition: LP1/KOH/ethanol/THF = 30 mg/300 mg/2 mL/4 mL, at 60 °C for 72 h. (B) ^{1}H NMR spectrum of the main component and (C) that of the minor component of the hydrolysis product of polymer LP1 in $CDCl_3$.

gradually by the heterogeneous reduction of $CuBr_2$ by Cu, so the radical concentration was low throughout the polymerization; thereby, both the BiBMS conversion and polymer molecular weight were increased.

On the basis of the above results, we studied the kinetics of the polymerization of BiBMS in anisole at 0 °C. Figure 3A presents the evolution of polymer molecular weights with time, and Figure 3B presents the change of polymer molecular weights with inimer conversion. After 2 h, the conversion of BiBMS reached 40%, but the molecular weights of the polymers were very low according to GPC results. Polymers with higher molecular weights and larger PDIs could only be obtained at a much longer polymerization time. These results indicate that the polymerization is via the step-growth polymerization mechanism; the kinetics behavior is the same as that reported by Kamigaito et al., which is an intermolecular transition-metal-catalyzed radical polyaddition.[27] After 48 h, the conversion of BiBMS reached 98%, and M_n of the purified polymer was 5800 with a PDI of 2.72.

To characterize the polymer structure, we measured the ^{1}H NMR and ^{13}C NMR spectra of the purified polymer as shown in Figure 4. Both spectra confirm that this polymer is a linear polyester with the structure shown in the figure. For example, resonances of the benzylic methylene protons in the polymer main chain appeared at 4.7−4.9 ppm (peak d′), while those of the benzylic methylene protons at the ω-end appeared at 5.1−5.2 ppm (peak d). The integration ratio of the α-end vinyl groups (peaks a−c in the inset of Figure 4A) to the ω-end benzylic methylene (peak d) and methyl groups (peak g) is 1/1/1/2/6. In addition, assuming no cyclization product, we could estimate the average degree of polymerization (DP) by comparing the integration ratio of peak f to that of b ((DP = f/2b + 1). The calculated value was 22, corresponding to a polymer with M_n of 6200. Therefore, this polymer should be linear polyester and designated as LP1.

To further confirm the linear polyester structure, we hydrolyzed polymer LP1 under alkaline conditions in ethanol/THF. The final product was first characterized by GPC as shown in Figure 5A. No high molecular weight polymers existed, but two components with lower molecular weights were clearly obtained. We further separated the mixture by preparative GPC and characterized the ^{1}H NMR spectrum of each component. The spectra are presented in parts B and C of Figure 5, respectively. Analysis of Figure 5B confirms that the main component is 4-hydroxy-4-(4-(hydroxymethyl)-phenyl)-2,2-dimethylbutanoic acid, corresponding to the complete hydrolysis product of both the polymer main chain and the benzylic bromides. Figure 5C is consistent with the

Table 2. Characterization of Graft Copolymers by ATRP of St Initiated by Polymer LP1 and the Hydrolysis Product PSt[a]

sample	time (h)	conv (%)[b]	M_n[c]	PDI[c]	M_n[d]	PDI[d]
LP1-*g*-PS1	4	9	13 800	1.62	2 170	1.13
LP1-*g*-PS2	72	49	107 000	1.33	12 600	1.15

[a] Polymerization conditions: $[CuBr]_0/[Bipy]_0/[-Br\text{ of }LP1]_0/[St]_0 = 1/2/1/200$ in anisole at 120 °C, $[St]_0 = 3.8$ mol/L. Hydrolysis conditions: polymer/KOH/ethanol/THF = 30 mg/300 mg/2 mL/4 mL, at 60 °C, 72 h. [b] As determined by ^{1}H NMR (determined from the double bond of St). [c] As determined by GPC vs linear PSt standards after purification. [d] Data of the purified hydrolysis products as determined by GPC vs linear PSt standards.

^{1}H NMR spectrum of 4-ethoxy-4-(4-(hydroxymethyl)phenyl)-2,2-dimethylbutanoic acid, which was formed by hydrolysis of the main chain ester bond and the substitution of the benzylic bromide with an ethoxy group. These results further confirmed that the structure of polymer LP1 was the proposed linear polyester structure.

The above results clearly show that using a high initial concentration of $CuBr_2$, and conducting the polymerization at low temperature (0 °C) in anisole, the initiating activity of the formed A* can be frozen; therefore, the ATRP process is an ATRA-based polyaddition reaction. The polymerization process (mechanism, polymerization rate, and linear polyester structure) is essentially the same as that reported by Kamigatito et al.[27] But one advantage of the present system is that the frozen A* is a benzylic bromide, which is very reactive toward substitution reactions, and can also act as an ATRP initiator at a higher temperature for further polymer modification. As one example of substitution reactions, we transformed the benzylic bromides of polymer LP1 to the azido groups under mild conditions. The ^{1}H NMR spectrum of the purified polymer is presented in Figure S2. The original signals of the methine groups connected to bromide at 5.1 ppm completely shifted to 4.5 ppm; at the same time, those of the methylene groups adjacent to this methine group shifted from 2.5 to 2.8 to 1.7−2.3 ppm, confirming the complete transformation. It can be anticipated that these azido groups on the polyester main chains can be further functionalized by the click chemistry as already reported for click modification of other polyesters.[33−36] For modification with polymerization reactions, we used polymer LP1 as the macroinitiator to initiate the ATRP of St at 120 °C to produce a graft copolymer by the "grafting from" approach. Polymerization results are summarized in Table 2. After 4 and 72 h, two graft copolymers (LP1-*g*-PS1 and LP1-*g*-PS2, Table 2) were obtained at 9% and 49% St conversion, respectively. The PDIs of these two graft copolymers were relatively large due to the high polydispersities of the parent polymer LP1. We also hydrolyzed the two polymers under basic conditions and obtained two linear PSt, whose PDIs were less than 1.2 as evidenced by their GPC traces (Figure S3), confirming the high initiating efficiency of the A* initiators (benzylic bromides) along the polymer LP1 chains toward the controlled ATRP of St at high temperature. It also offers the possibility for further functionalization of LP1 by ATRP of other functional vinyl monomers.

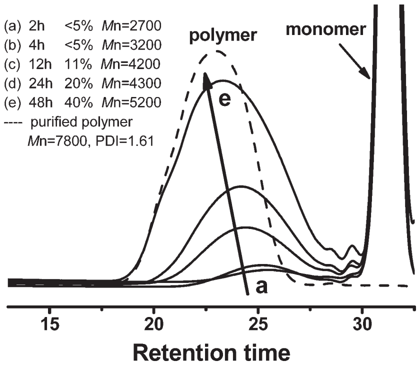


Figure 6. GPC traces of polymer LP2 at various times. Monomer conversion was determined by ^{1}H NMR. Polymerization conditions: $[Cu]_0/[CuBr_2]_0/[Bipy]_0/[BiBMS]_0 = 2/1/6/50$, $[BiBMS]_0 = 1.8$ mol/L, in toluene at 20 °C.

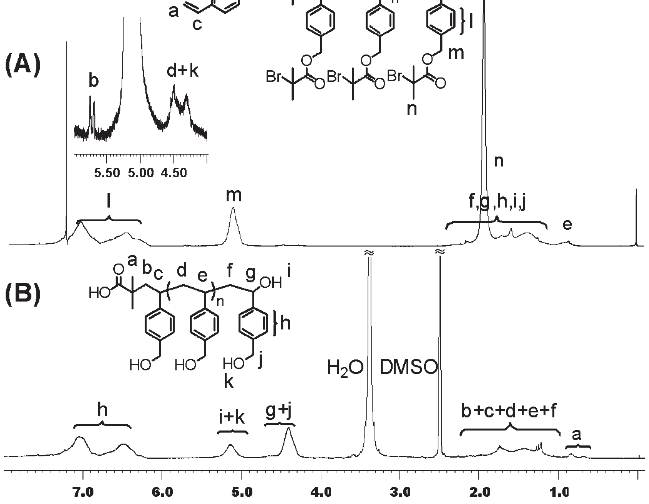


Figure 7. ^{1}H NMR spectra of polymer LP2 (A, in $CDCl_3$) and its hydrolyzed product (B, in d_6-DMSO).

Linear Polymer LP2. In ATRP of vinyl monomers, the concentration of soluble $CuBr_2$ and the ratio of $[Cu^{II}]$ to $[Cu^{I}]$ dictate the polymerization rate and the PDI of the polymer.[8] Adding a small amount of $CuBr_2$ to the polymerization system will slow the polymerization but improve the control over PDI. If the concentration of soluble $CuBr_2$/ligand complex in a polymerization system is too low, the ATRP will lose control and behave like a normal radical polymerization.[37] We carried out the ATRP of BiBMS in toluene at 20 °C catalyzed by $Cu/CuBr_2/Bipy$. CuBr/Bipy is less active than CuBr/BOMPA, and the solubility of $CuBr_2$/Bipy complex in toluene at 20 °C was very low.[38] The polymerization system maintained almost colorless though quite amount of $CuBr_2$ was used. Figure 6 presents the evolution of polymer molecular weights and inimer conversion with time. After 4 h, the inimer conversion was only about 5%, but M_n of the polymer was as high as 3200. With increasing polymerization time, the monomer conversion was increased, but M_n of the polymer was increased only slightly. After 48 h, the monomer conversion reached 40%, and a polymer (M_n = 7800, M_w/M_n = 1.61) was recovered after purification.

The purified polymer was then characterized by NMR, and the spectrum is presented in Figure 7A. We could clearly see the resonances from both the α-end vinyl groups (peak b in the inset) and those from the *ω*-end benzylic methine groups (peak k in the inset); in addition, the resonances of the benzyl methylene protons ($-CH_2-O$) appeared only at 5.0−5.2 ppm (peak m), thereby implying that the polymerization of BiBMS was initiated by the B* group, and termination was through the deactivation of $CuBr_2$ as in a normal ATRP. The integration ratio of these two end protons was calculated based on (d + k)/b; the value was 3.1, very close to

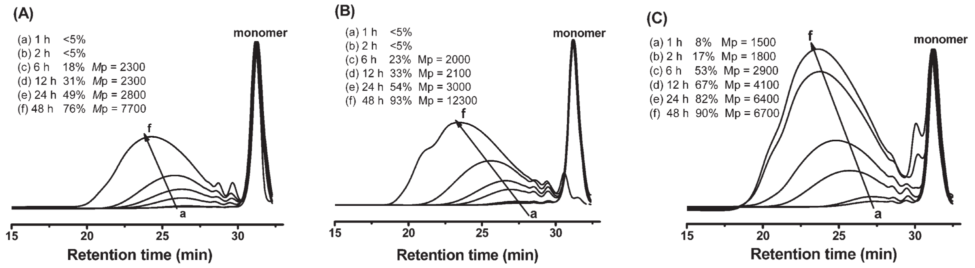


Figure 8. GPC traces of polymer BP1 (A), BP2 (B), and BP3 (C) at various times. Polymerization conditions: $[\mathrm{Cu}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{Bipy}]_0/[\mathrm{BiBMS}]_0 = 2/1/6/50$, in anisole; BP1 (20 °C), BP2 (40 °C), $[\mathrm{BiBMS}]_0 = 1.8$ mol/L; BP3 (60 °C), $[\mathrm{BiBMS}]_0 = 2.8$ mol/L. Peak molecular weight (M_p) is determined by GPC vs linear PSt standards.

the theory value (3) of a completely linear polymer structure as proposed in the figure. The DP of the polymer can be calculated by comparison of the integration corresponding to peak m to that of peak b [DP = (m/2b) + 1]; the calculated value was 35, corresponding to a polymer with M_n of 9900. In addition, controlled experiment by polymerization of BiBMS with AIBN gave essentially the same polymer except the end groups as revealed by NMR spectrum (data not shown). Thus, the polymer was considered to be a linear polymer. We also hydrolyzed the polymer by using the similar conditions as those for LP1, and the hydrolyzed product could not be dissolved in THF; therefore, we did not characterize the M_n of the polymer, and instead we characterized this polymer by NMR in DMSO-d_6 (Figure 7B). The structure is consistent with poly(4-vinylbenzyl alcohol). The DP of this polymer could also be calculated by comparing the integration corresponding to the phenyl ring (peak h) of the pendant groups to that of the end methyl groups (peak a) (DP = 6h/4a); the value was 37, which was very close to that of the parent polymer. These results confirmed that the formed polymer was the proposed linear structure (LP2).

In toluene, the in situ formed CuBr by slow reduction of $\mathrm{CuBr_2}$ with Cu can activate the initiator B* of BiBMS to produce a methacrylate type radical, which can continuously add several double bonds of BiBMS to form a polymer even at the beginning of polymerization. Because of the very low solubility of the deactivator $\mathrm{CuBr_2}$/Bipy in toluene, the ATRP equilibrium cannot be effectively established; the polymerization loses control and can only be stopped by the traces of soluble $\mathrm{CuBr_2}$/Bipy. With the proceeding of the polymerization, more B* of BiBMS as initiators are activated, thereby increasing the monomer conversion with time, but the whole process does not change, so M_n of polymers do not increase very much with time. From the probability point of view, at a very long time, the B* moieties located at the side chain of polymer LP2 could also be activated, yielding graft or branched polymers. Here, we stopped the polymerization at about 40% monomer conversion to ensure the obtained polymer with a predominantly linear structure. When another ligand dTbipy was used, completely different results were obtained (Figure S4). The CuBr/dTbipy complex has similar activity to that of CuBr/Bipy but shows higher solubility in toluene. The polymerization is very similar to that for the synthesis of LP1, but in a much slow manner.

Branched Polymers of BiBMS with Different DB, BP1, BP2, and BP3. From the above results, we know that in the system used to prepare LP2 if the solubility of the $\mathrm{CuBr_2}$/Bipy complex can be increased by increasing polymerization temperature and using a polar solvent instead of toluene, the initial radicals produced from B* would add less monomers before they are deactivated. With increasing monomer conversion, the B* moieties along the polymer side chains and the formed A* moieties will have more chances to be activated, thus resulting in the formation of branched chains along the polymer.

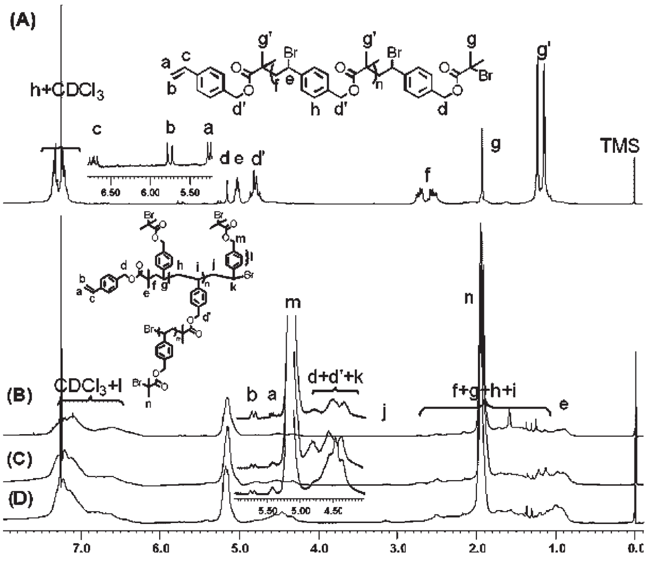
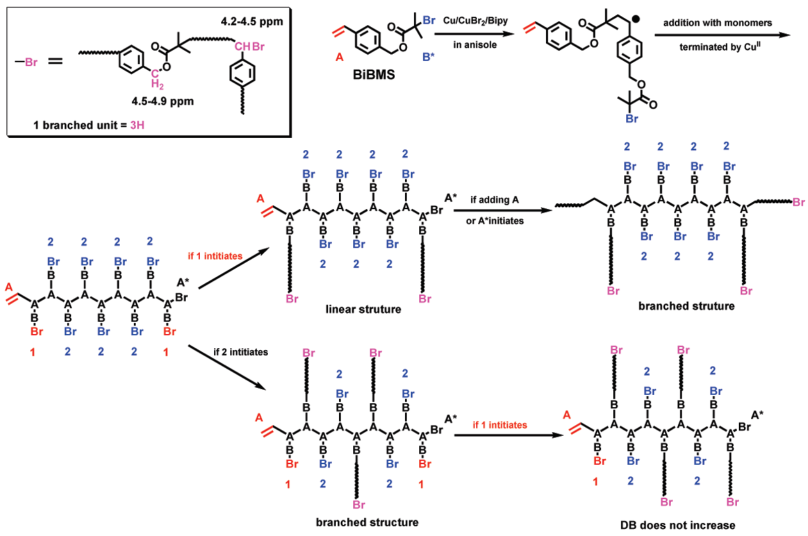


Figure 9. ^{1}H NMR spectra of polymer LP1 (A), BP1 (B), BP2 (C), and BP3 (D) in $\mathrm{CDCl_3}$.

We carried out the ATR-SCVP of BiBMS with $\mathrm{Cu/CuBr_2}$/Bipy as the catalyst in anisole at three temperatures: 20, 40, and 60 °C. The evolutions of polymer molecular weights with time are illustrated in Figure 8. After 2 h, the BiBMS conversion was very low (less than 5%) for the polymerizations carried out at 20 and 40 °C, but at 60 °C, the conversion of BiBMS reached 17%. Both the molecular weights of polymers and the conversions of BiBMS were increased with increasing polymerization time, and after 24 h, the BiBMS conversion at 60 °C reached 82%, and the peak molecular weights of the polymer was 6400. After 48 h, the conversions of BiBMS reached 76% (20 °C), 93% (40 °C), and 90% (60 °C), and the peak molecular weights of the three polymers were 7700, 12 300, 6700, respectively.

The structures of the purified polymers were characterized by ^{1}H NMR (Figure 9). Compared with the ^{1}H NMR spectrum of polymer LP1 (Figure 9A), it is clear that the integration ratio of resonances at 4.7−4.9 ppm ($-\mathrm{C}H_2-\mathrm{O}-$ in polymer side chains) to those at 5.0−5.2 ppm ($-\mathrm{C}H_2-\mathrm{O}-$ in polymer main chains) increased from polymer BP1 to BP2 to BP3. As discussed previously, in the ^{1}H NMR spectrum of linear polymer LP1, the phenyl proton resonances appeared at 7.1−7.5 ppm, while in linear polymer LP2, half of them moved upfield to 6.2−6.8 ppm. However, in the ^{1}H NMR spectra of polymers BP1, BP2, and BP3, these protons appeared at chemical shifts in-between. In the ^{13}C NMR spectra of BP1, BP2, and BP3 shown in Figure S5, we can also see the

Scheme 2. The Model for Calculating the Degree of Branching (DB)



difference of carbonyl groups. The signals of carbonyl groups were observed at 176 and 171 ppm, corresponding to those that existed in side chains (peak a) and main chains (peak a′), respectively; the resonances appeared at 67 and 65 ppm were those of $-CH_2O-$ in the side chains (peak d) and in main chain (peak d′), respectively. Therefore, the above results qualitatively implied the existence of branched chains in these three polymers.

We further hydrolyzed the three polymers, and the GPC traces of the hydrolyzed products are shown in Figure S6. Molecular weights of the hydrolyzed products decreased from BP1 (1900) to BP2 (1300) and to BP3 (1050), implying that the structure of the parent polymers become more branched from BP1 to BP2 to BP3 because each branching will produce an ester linkage, which is hydrolytically degradable. This can explained as follows: With increasing temperature, the concentration of soluble $CuBr_2$/Bipy complex increased in anisole; therefore, the number of added monomers decreased before branching occurred. In the meantime, the initiating ability from the formed A* increased, resulting in an increase of branching points.

We tried to estimate the DB of the branched polymers according to eqs 1 and 2 (Scheme 2).[16b] At the temperatures studied, initiation from A* is possible, but much slower than that from B*. Therefore, the following assumptions are made: first, no termination by coupling or intramolecular cyclization; second, once the B* at position 2 is activated, a branching point was formed; third, activation from A* at higher temperatures will increase branching. In the ^{1}H NMR shown in Figure 9, each branching will change the side-chain benzylic groups ($-CH_2-O-$, peak m, 5.1−5.2 ppm) to the main-chain type (peak d′, 4.7−4.9 ppm) and at the same time generate a new unit [$-CH_2-CH(C_6H_4)-Br$, peak k]. The calculated DBs of three polymers were 0.12 (BP1), 0.26 (BP2), and 0.37 (BP3) (Table 1). The trend is as expected; with increasing temperature, more benzylic bromides (A*) will be activated, thus increasing the branching points. In the ATR-SCVP of an AB* inimer, the DB of the resulting polymer is mainly determined by the relative reactivity of A*/B*,[16b] and the more active initiators exist as branched units while the low active initiators exist as chain ends. Here, due to the deactivation of existing high concentration of $CuBr_2$, structure control is just reverse; though B* is more active, it exists in the polymer chain end. We thus confirmed that control of DB of polymers by the ATR-SCVP of BiBMS can be easily realized by simply varying the polymerization temperature.

$$\mathrm{DB} = \frac{(\text{number of branched units}) + (\text{number of terminal units}) - 1}{(\text{total number of units}) - 1} = \frac{2(\text{number of branched units})}{(\text{total number of units}) - 1} \qquad (1)$$

$$\mathrm{DB} = \frac{2(\text{number of branched units})}{(\text{total number of units}) - 1} = \frac{2[(d + d' + k)/3b - 1]}{m/2b + (d + d' + k)/3b - 1} \qquad (2)$$

Conclusions

We demonstrate that a series of polymers varying in topologies have been synthesized by varying the ATR-SCVP conditions of the unsymmetrical AB* inimer BiBMS. In general, a slow AGET ATRP was used to lower the radical concentration and to get a high degree of monomer conversion. Through manipulating three polymerization parameters—temperature, ligand, and solvents—we can regulate the initiating abilities of different initiators, activity of the catalyst system, and the solubility of deactivators in polymerization solution. Two different linear polymers were synthesized. In the synthesis of a linear polyester LP1, the initiation from the formed A* was frozen by lowering temperature and using high concentration of deactivators. While for the synthesis of linear polymer LP2, by using low active catalyst and toluene to minimize the solubility of the deactivators, only initiation from the B* of inimer BiBMS was possible. Finally, through adjusting both the solubility of the deactivator in solution and the initiation of formed A* with temperature and solvent, we can obtain a series of branched polymers with different degree of branching. The feature that linear polymer LP1 is a polyester with many reactive benzylic bromides on the backbone is noteworthy, not only for the synthetic method but also it has the potential to be modified through organic and polymerization reactions to impart additional functionalities on the polymers.

Acknowledgment. The authors thank the National Natural Science Foundation of China (No. 20534010, 21074002) and Ministry of Education of China for financial support.

Supporting Information Available: Supporting ^{1}H NMR and ^{13}C NMR spectra and GPC traces of the polymerization and the hydrolyzed products. This material is available free of charge via the Internet http://pubs.acs.org.

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