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Preparation of Branched Polystyrene Using Atom Transfer Radical Polymerization Techniques and Protection-Deprotection Chemistry

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Abstract: A new strategy using protection-deprotection chemistry was used to prepare branched polymers using the ATRP method only. Among the several monomers with different protecting groups, vinyl benzyl *t*-butyloxy carbonate (VBt-BOC) and 4-methyl styrene (4-MeSt) could be polymerized successfully to form backbones using the ATRP method in a controlled fashion. The protected groups in the backbones were converted to alkyl bromides and used as initiating sites for branch formation. The benzyl *t*-butyloxy carbonate groups in the backbones containing VBt-BOC units were first deprotected to benzyl alcohol by trifluoroacetic acid, then converted to benzyl bromide by reacting them with triphenylphosphine/carbon tetrabromide. The benzyl bromide groups in the backbones containing 4-MeSt units could be generated by bromination of the methyl groups using *N*-bromosuccinimide/benzoyl peroxide. The structures of the prepared polymers were well-controlled, as evidenced by the controlled molecular weight as well as the narrow and unimodal molecular weight distribution.

Keywords: atom transfer radical polymerization, protection-deprotection chemistry, branched polymer.

Introduction

Changing the architecture of a polymer can endow the polymers with unique physical properties.[1] In order to fashion polymers with different architectures to be realized, there must be simultaneous improvements in polymer synthetic methods. Living polymerizations have been used extensively to this end.[2] Living polymerization was first defined by Szwarc[3] as a chain growth process without chain breaking reactions (transfer and termination). Ionic polymerizations techniques have been excellent tools for researchers to achieve such goals. However, in terms of preparing branched structure, ionic pathways are not always applicable due to the highly reactive nature of initiating species.

Even though "living"/controlled free radical polymerizations are not perfect living systems, they are more than adequate to a sufficient level of control to afford the synthesis of various architectures.[4-6] This is due to the facts that irreversible termination reactions are minimized by maintaining a dynamic equilibrium between active radicals and a large concentration of the dormant species, and that the initiation step is fast and quantitative. As a result, there have been an enormous number of reports of using controlled radical polymerization methods to prepare polymers with specific architectures. Examples include block copolymers, branched and hyperbranched polymers, star polymers, and dendritic polymers.[4,5,7-10] We too, have been interested in the development of strategies to prepare polymers having various architectures using controlled radical polymerization techniques.

One way to prepare branched polymers using controlled free radical polymerization is using nitroxide-mediated polymerization (NMP) and ATRP sequentially.[11] In this scheme, monomers having initiating groups in ATRP are polymerized via NMP and branches are generated from the initiating groups in backbone via ATRP. However, the initiator containing monomers cannot be used directly in the preparation of backbone polymer by ATRP method because of their premature initiation during the polymerization to form a hyperbranched structure. To solve this problem, a protection-deprotection strategy was adapted in this work. The graft initiating sites were protected by suitable groups during the preparation of the parent backbone polymer. The latent initiating sites for the graft polymerization were then deprotected using simple chemical transformation (Scheme I).

There have been reports using this concept in preparing branched polymers. Patten *et al.* used acetoxymethyl or methoxymethyl functional groups as latent initiating sites for ATRP.[12] Boyce *et al.* polymerized 2-(trimethylsilyloxyl)-ethyl methacrylate using ATRP catalyst as a precursor polymer that was converted to poly(2-(2-bromopropionyloxy)ethyl methacrylate) multifunctional macroinitiator via transesteri-

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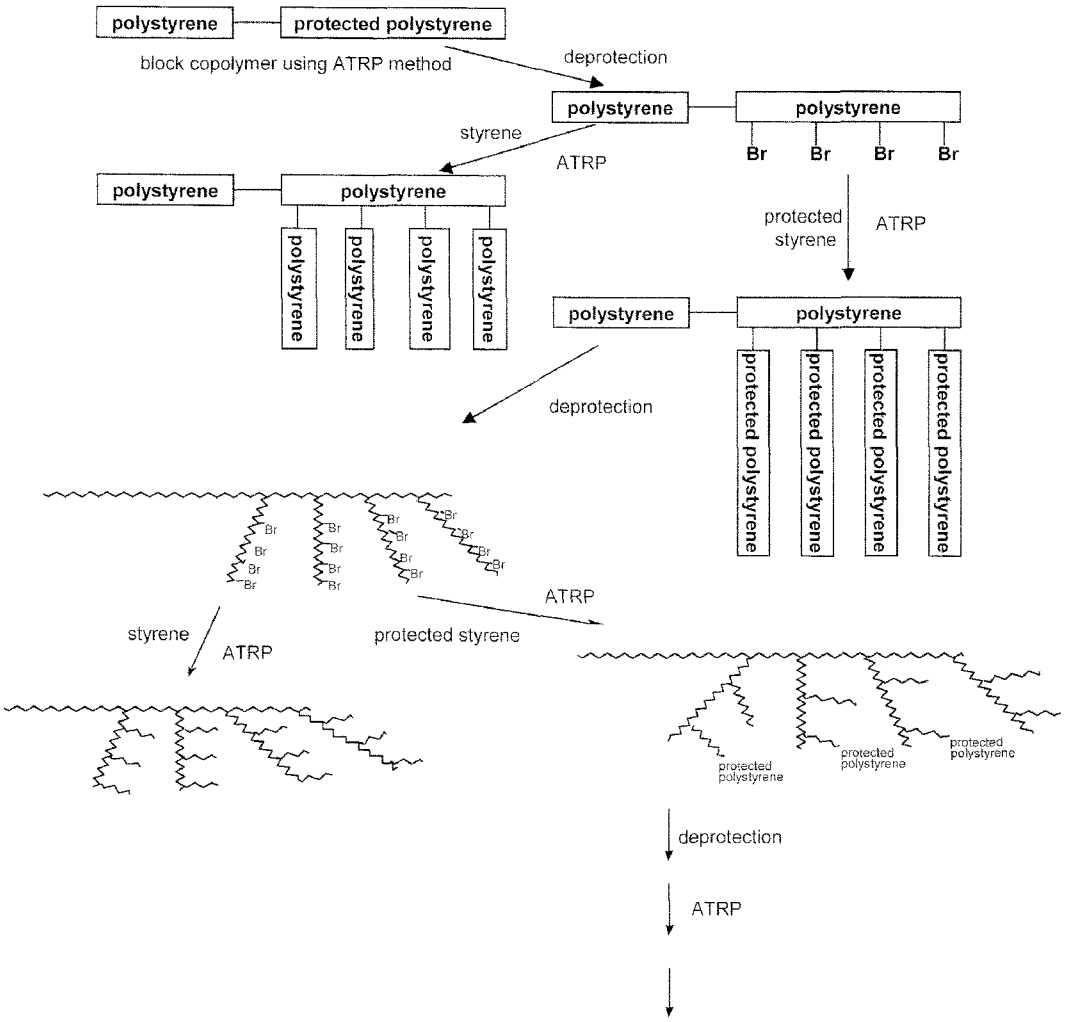


Scheme I. Preparation of branched and hyperbranched polymers using protection-deprotection chemistry.

fication with 2-bromopropionyl bromide.[13] In this work, we checked possibilities of various functional groups for this purpose in preparing branched polystyrene. The groups should not affect the activities of ATRP catalytic systems, and could be converted to alkyl bromides by simple and effective chemistry to be used as initiators in the branch formation.

Experimental

Characterization. IR spectra were determined with either a Perkin-Elmer 1600 series FT-IR or Jasco FT-IR-410 spectrometer as thin films coated on NaCl plates. ^{1}H and ^{13}C-NMR spectra were measured in $CDCl_3$ unless otherwise noted. Spectra were recorded on either a Varian 200, Bruker 200, 300, or GE 300 spectrometer. ^{1}H-NMR spectra were measured at 200 or 300 MHz. Proton decoupled ^{13}C-NMR spectra were recorded at 75 MHz. Gas chromatography (GC) was performed using either HP 5890 equipped with MS detector or HP 6890 equipped with FID detector. Non-polar HP-5 or medium polar HP-INNOWAX capillary column were used for the separation. Gel permeation chromatography/light scattering (GPC/LS) were performed using Hewlett-Packard (HP) 1050 series liquid chromatography pump equipped with a Wyatt Dawn DSP-F laser photometer, a Wyatt/Optilab interferometer and a Waters 746 data module integrator. Tetrahydrofuran (THF) was used as a mobile phase. Sample were prepared as 0.5-2% polymer (w/v) solution in THF and passed through 0.45 μm filters prior to injection. Residual metal complexes were removed by passing the polymer solution through active alumina column. Separation was effected by a multiple series of Polymer laboratory Mixed C columns.

Materials. Materials were obtained from commercial suppliers and used without further purification unless otherwise noted. Styrene, vinyl benzyl chloride, 4-methyl styrene (4-MeSt) and benzyl chloride were dried over CaH_2 overnight, and distilled twice under reduced pressure from CaH_2 prior to use. Benzoyl peroxide (BPO) was purified by dissolving in $CHCl_3$ at room temperature and adding an equal

amount of methanol. Imidazole was purified by sublimation two times before use. Bipyridine (bpy) was purchased from Aldrich, and purified by recrystallization from ethyl alcohol. 4,4′-di-5-nonyl-2,2′-bipyridine (dNbpy),[14] and 4,4′-diphenoxy-2,2′-bipyridine (pby)[15] were prepared following literature procedures. 4,4′-di-(*p*-ethylphenoxy)-2,2′-bipyridine (epy) and 4,4′-di-(*p*-methoxyphenoxy)-2,2′-bipyridine (mpy) were prepared by applying the same synthetic method for pby with slight modification. Ethylphenol and methoxyphenol, instead of using phenol, was used for synthesizing epy and mpy, respectively.

Preparation of Protected Monomers.

Vinyl Benzyl Acetate: To a 250 mL round-bottom flask containing 16 g (160 mmol) of potassium carbonate was added 50 mL of dimethyl sulfoxide and 22 g (140 mmol) of vinyl benzyl chloride. The yellowish heterogeneous mixture was stirred at 40 °C for 5 days, and then the reaction mixture was filtered and washed with 300 mL of water. The oily component was extracted with 20 mL of chloroform (three times), and the remaining water was removed drying over Na_2SO_4. The mixture was filtered and evaporated to remove most of chloroform. The remaining liquid was then distilled under vacuum to afford 22.4 g (90%) of vinyl benzyl acetate as a colorless liquid, bp 58 °C (60 mtorr), which was stored in the freezer until use. IR (neat): 3008 (m), 2955 (m), 1739 (s), 1378 (m), 1226 (s), 1028 (s), 991 (m), 912 (m) cm^{-1}. ^{1}H-NMR (300 MHz): δ (ppm) 7.22 (m, 4H), 6.67 (q, 1H), 5.62 (d, 1H), 5.13 (d, 1H), 4.95 (s, 2H), 1.97 (s, 3H). MS (EI): m/z 176 (M^+), 134, 115, 105, 91, 77.

Vinyl Benzyl Alcohol (VBOH): To a 250 mL round bottom flask equipped with reflux condenser was added 22 g (120 mmol) of vinyl benzyl acetate, 12 g of sodium hydroxide in 12 mL of water, and 70 mL of ethyl alcohol. The reaction mixture was refluxed for 1.5 h, and diluted with 300 mL of water. The product mixture was extracted with 4 × 20 mL of chloroform, and then dried over Na_2SO_4. The solution was filtered and evaporated to remove most of chloroform. The distillation under reduced pressure afforded 14.5 g (87%) of VBOH as a colorless liquid, bp 58 °C (60 mtorr), which was stored in the freezer until next use. IR (neat): 3328 (br, s), 3006 (m), 2872 (m), 1629 (m), 1406 (s), 1211 (m), 1157 (m), 1013 (s), 990 (s), 908 (m) cm^{-1}. ^{1}H-NMR (300 MHz): δ (ppm) 7.37 (m, 4H), 6.72 (q, 1H), 5.78 (d, 1H), 5.27 (d, 1H), 4.67 (s, 2H), 1.81 (s, 1H). MS (EI): m/z 134 (M^+), 115, 105, 91, 77.

Vinyl Benzyl *t*-Butyldimethylsilyl Ether (VBOSi): To a 100 mL flask with magnetic stirring bar were added 6.7 g of vinyl benzyl alcohol (5×10^{-2} mol), 9.0 g of *t*-butyldimethylsilyl chloride (6×10^{-2} mol), 8.5 g of imidazole (1.25×10^{-1} mol), and 13 mL of dimethylformamide (DMF). After stirring for 24 h at 35 °C, water was added to the reaction mixture, and the organic layer was extracted with chloroform (4 times). The extracted chloroform solution was dried over Na_2SO_4. Filtration and evaporation under reduced pressure afforded VBOSi as a colorless liquid. ^{1}H-NMR (300 MHz): δ (ppm) 7.29 (m, 4H), 6.72 (m, 1H), 5.74 (m, 1H), 5.22 (m, 1H), 4.74 (s, 2H), 0.95 (s, 9H), 0.11 (s, 6H). MS (EI): m/z 248 (M^+), 191, 161, 117, 91, 75, 57.

Vinyl Benzyl *t*-Butyl Ether (VB*t*-Bu): A 100 mL flask was charged with 4.8 g of sodium *t*-butoxide (5×10^{-2} mol), 9.2 g of vinyl benzyl chloride (6×10^{-2} mol), and 30 mL of DMF. The reaction mixture was heated overnight and methylene chloride was added to give precipitate. After filtering, the solution was washed with water, and dried over Na_2SO_4. Methylene chloride was removed using a rotary evaporator, and distillation under reduced pressure afforded VB*t*-Bu as a colorless liquid (40 °C/60 mtorr). ^{1}H-NMR (300 MHz): δ (ppm) 7.22 (m, 4H), 6.61 (m, 1H), 5.65 (m, 1H), 5.13 (m, 1H), 4.37 (s, 2H), 1.22 (s, 9H). MS (EI): m/z 190 (M^+), 134, 117, 105, 91, 77, 57.

Vinyl Benzyl *t*-Butyloxy Carbonate (VB*t*-BOC): A solution of 2.3 g of VBOH (2.3×10^{-2} mol) in 5 mL of THF containing a catalytic amount of 18-crown-6 was treated with 3.0 g of powdered potassium carbonate and 4.4 g of di-*t*-butyl dicarbonate (2×10^{-2} mol). The mixture was stirred for 48 h at room temperature, and then 10 mL of water were added. The organic layer was extracted with 4 × 5 mL of chloroform, and dried over Na_2SO_4. After filtration, chloroform was removed by evaporation under reduced pressure. Distillation under reduced pressure afforded VB*t*-BOC as a colorless liquid (32 °C/75 mtorr). IR (neat): 2981 (m), 1740 (s), 1370 (s), 1277 (m), 1161 (s), 1119 (s), 1072 (s), 856 (m) cm^{-1}. ^{1}H-NMR (300 MHz): δ (ppm) 7.35 (m, 4H), 6.71 (m, 1H), 5.74 (d, 1H), 5.26 (d, 1H), 5.08 (s, 2H), 1.50 (s, 9H). MS (EI): m/z 234 (M^+), 178, 134, 117, 105, 91, 77, 57.

Deprotection Reactions.

Deprotection of *t*-Butyloxy Carbonate Group: 0.2 g of the copolymer of polystyrene-block-copoly(styrene/VB*t*-BOC) (styrene/VB*t*-BOC = 83/17; M_n = 17,850; PDI = 1.285) was dissolved in 5 mL of methylene chloride, and treated with 0.5 mL of trifluoroacetic acid. The mixture was stirred for 24 h, and the polymer was precipitated by pouring into petroleum ether. After filtration, the resulting polymer was dried overnight under reduced pressure (yield, 0.18 g). 0.17 g of the polymer was redissolved in 5 mL of THF, and treated with 79 mg of triphenylphosphine and 0.1 g of carbon tetrabromide. The mixture was stirred for 1.5 h at room temperature, and polymer was isolated by precipitating from methanol. Filtration and drying overnight under reduced pressure afforded 0.14 g of brominated polymer.

Bromination of Poly(4-Methyl Styrene): The polymer was allowed to react with NBS (NBS/methyl group molar ratio = 2 : 1) in anhydrous carbon tetrachloride solution in the dark, under a nitrogen atmosphere, in the presence of 2% by weight BPO, at the boiling point of the solvent for 2 h. The solutions were filtered to eliminate the insoluble succinimide produced and purified by passing through an Al_2O_3 column. The polymer was precipitated by methanol

and dried under vacuum.

Polymerizations.

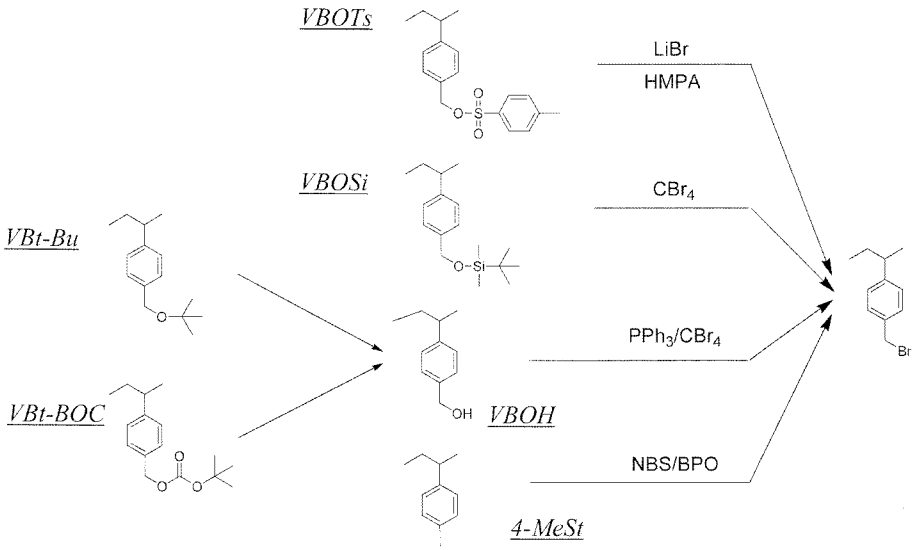
General Procedure: A suitable mixture of monomer, initiator, metal halide, ligand, solvent, and benzoyl peroxide/TEMPO was prepared in a 5 mL of drying tube in a drybox under an inert atmosphere. The tube was removed from the drybox. After degassing by three times by the freeze-thaw method, the tube was sealed under vacuum, and placed in an oil bath thermostated at the desired temperature. The polymerization was quenched by immerging in liquid N_2. The seal was broken, and THF was added to dissolve the solid product. The polymer was purified by precipitation in methanol and dried overnight under vacuum. The conversion was determined by gravimetry, and the resulting polymers were characterized by ^{1}H-NMR and GPC after removing the residual metal catalysis by passing the polymer solution through active alumina column.

Preparation of Linear-Branched Block Copolymer: From VB*t*-BOC; The initial polystyrene block segment was prepared from 0.31 g of styrene (3×10^{-3} mol), 8.7 mg of benzyl chloride (6.9×10^{-5} mol), 6.9 mg of copper(I) chloride (6.9×10^{-5} mol), and 56 mg of epy (1×10^{-4} mol). After 4 h reaction at 130 °C, polymerization was quenched by immerging in liquid N_2, and polystyrene was purified from metal catalysts by repeated dissolving in THF/precipitating from methanol. The small portion of this sample (0.12 g) was dissolved in 0.26 g of styrene and 0.18 g of VB*t*-BOC, and added to a 5 mL reaction tube containing 3.0 mg of copper(I) chloride and 24 mg of epy in a drybox. The polymerization was run following general procedure at 110 °C for 20 h, and the product copolymer of polystyrene-*b*-copoly(styrene/VB*t*-BOC) was isolated. After two steps of deprotection reactions described in the previous section, the polymer (0.016 g; [-Br] calculated as 1×10^{-5} mol) was dissolved in additional monomer (styrene or MMA; 2×10^{-3} mol) containing 1.0 mg of copper(I) chloride (1×10^{-5} mol) and 4.7 mg of bpy (3×10^{-5} mol) in a drybox. The polymerization was run following general procedure at 110 °C for 2.5 h (styrene) or 1 h (MMA), and the product copolymer of polystyrene-*b*-copoly(styrene/VB*t*-BOC) was isolated by precipitation from methanol, filtered, and dried under vacuum.

From 4-MeSt; The initial polystyrene block segment was prepared from 0.20 g of styrene (2×10^{-3} mol), 19 mg of 1-phenylethyl chloride (1×10^{-4} mol), 14 mg of copper(I) bromide (1×10^{-4} mol), and 82 mg of dNbpy (2×10^{-4} mol). After 5 h reaction at 110 °C, polymerization was quenched by immerging in liquid N_2, and polystyrene was purified from metal catalysts by repeated dissolving in THF / precipitating from methanol. The small portion of this sample (0.1 g) was dissolved in 0.13 g of styrene and 0.044 g of 4-MeSt, and added to a 5 mL reaction tube containing 3.9 mg of copper(I) bromide and 23 mg of epy in a drybox. The polymerization was run following general procedure at 110 °C for 20 h, and the product copolymer of polystyrene-*b*-copoly(styrene/4-MeSt) was isolated. After the deprotection reaction described in section 3.2, the polymer (0.01 g; [-Br] calculated as 1×10^{-5} mol) was dissolved in additional monomer (styrene or MMA; 2×10^{-3} mol) containing 1.0 mg of copper(I) chloride (1×10^{-5} mol) and 4.7 mg of bpy (3×10^{-5} mol) in a drybox. The polymerization was run following general procedure at 110 °C for 2 h (styrene) or 15 min (MMA), and the product copolymer of polystyrene-*b*-copoly(styrene/VB*t*-BOC) was isolated by precipitation from methanol, filtered, and dried under vacuum.

Results and Discussion

Styrenes with several functional groups were synthesized and tested as protected monomers. Scheme II shows the monomer structures for protected styrene and the deprotec-



Scheme II. Candidate structures for protected styrene.

Table I. ATRP of Various Protected Styrenes

Run	Monomer	Catalysts	Condition	T (°C)	Time (h)	Conversion (%)	M_n[b]	PDI
1	VBOSi	CuCl/pby	solution[a]	110	1	47	66,700	2.32
2	VBOH	CuCl/pby	bulk	130	8	gelled		
3	VB*t*-Bu	CuCl/pby	solution[a]	130	4 days	low	low	2.9
4	VB*t*-BOC	CuCl/pby	solution[a]	130	6		10,500	1.85
5	VB*t*-BOC	CuCl/pby	solution[a]	110	3 days	80	8,900	1.33
6	VB*t*-BOC	BPO/ TEMPO	bulk	130	23	55	11,400	1.14
7	Styrene	CuCl/mpy	B*zt*-BOC	130	30	low	8,600	1.15
8	VB*t*-BOC	CuCl/pby	Copolymerization w/ styrene (1/1)	110	10	95	11,300	1.36

[a]in diphenylether (50%, v/v).
[b]The theoretical values of M_n can be calculated by $(MW_{monomer} \times 100 \times \frac{\text{conversion}}{100})$.

tion chemistry that we used. Several factors were considered in making these selections including ease of synthesis of protected monomer, simple and clean deprotection reactions, and inertness of the protecting group under ATRP conditions.

Among the candidates tested, vinyl benzyl tosylate and VBOSi did not work due to the difficulties in monomer synthesis and immature deprotection during polymerization (Table I, Run 1), respectively. Also an attempt using VBOH was failed because the benzyl alcohol group affected ATRP to form gelled products (Table I, Run 2). Polymerization of vinyl benzyl *t*-butyl ether using ATRP catalyst system was unsuccessful to give polymers with uncontrolled structures (Table I, Run 3).

Vinyl Benzyl *t*-Butyloxy Carbonate (VB*t*-BOC). *t*-Butyloxy carbonate (*t*-BOC) group is one of the most widely used protecting groups of amino functionalities, and is widely used in peptide synthesis.[16] However, there have been only a few reports on the *t*-butyloxy carbonylation of hydroxyls and thiols,[17] and most of the examples are characterized by generally low yields and/or the use of extremely toxic or unstable reagents. Rather recently, Houlihan, *et al.* used di-*t*-butyl dicarbonate as a *t*-butyloxy carbonylation reagent in the reaction of phenols, alcohols, enols, and thiols under phase transfer condition, and acquired *t*-BOC protected products in high yields.[18]

Following Houlihan's method, we protected the benzyl alcohol moieties of VBOH with *t*-BOC groups using di-*t*-butyl dicarbonate as a *t*-butyloxy carbonylation reagent. The reaction was slow but complete after 2 days with the use of a catalytic amount of 18-crwon-6 and an equilivalent amount of powdered anhydrous potassium carbonate. The infrared spectrum of the resulting carbonate showed a strong carbonyl band near 1740 cm^{-1}, and integration of NMR spectrum matched well with the expected resonances of VB*t*-BOC. The GC spectrum showed almost pure VB*t*-BOC with trace amounts of the initial VBOH, and the mass spectrum included a characteristic pattern for the loss of *t*-BOC ($m/e = 100$) and a peak at $m/e = 57$.

We polymerized VB*t*-BOC under variety conditions to test the reactivity of the monomer. In the first set of experiments, pby ligand was used along with copper halide to catalyze the polymerization (Table I, Run 4 and 5). The reaction was performed under solution polymerization conditions using diphenylether as a solvent to minimize the crosslinking reaction in case of any premature deprotection of *t*-BOC groups. The polymerization at 130 °C using CuCl was fast, and the molecular weight of the polymer was fairly well controlled. However, GPC chromatogram showed that molecular weight distribution of the resulting polymer was not unimodal but a mixture of two peaks (Figure 1(a)). The lower molecular weight peak had a narrow distribution, but was contaminated with a higher molecular weight shoulder, probably from the termination by a coupling reaction of two growing polymer radicals, that had exactly twice the molecular weight as the first. The polymer prepared at 110 °C using CuBr also had similar properties. The reaction was very slow and took 3 days to reach 80% conversion, but the molecular weight matched with the theoretical value calculated from the monomer/initiator ratio and conversion. However, the molecular weight distribution curve was again composed of a lower molecular weight peak having narrow distribution and a higher molecular weight shoulder of twice molecular weight (Figure 1(b)).

In Run 6, we polymerized VB*t*-BOC by an alternative controlled radical polymerization technique, the nitroxide-mediated SFRP method. Poly(VB*t*-BOC) prepared using BPO/TEMPO had a low PDI value of 1.14, even under the more extreme conditions of higher temperature (130 °C) and in the absence of solvent. Moreover, the portion of the higher molecular weight shoulder in the GPC chromatogram was smaller than that of polymers prepared by the ATRP method (Figure 1(c)). In the polymerizations of protected monomers by the ATRP technique, one of the persist-

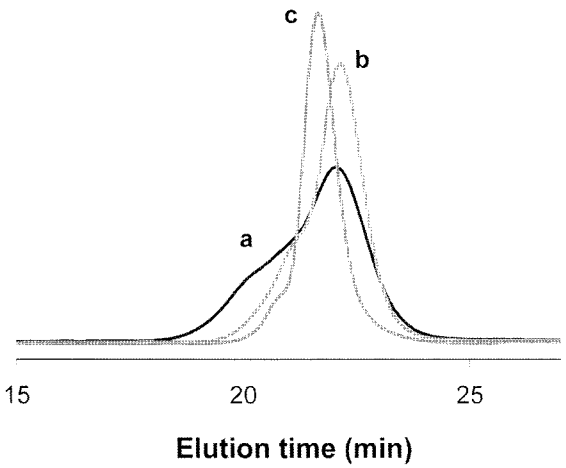


Figure 1. GPC chromatogram of poly(VB*t*-BOC) prepared using CuCl/pby as a catalyst at 130 °C, (a) Run 1, (b) Run 2, (c) Run 5 in Table I.

ent concerns is the reaction between the metal complex and the protecting groups. Most protecting groups and the deprotected counterparts by the premature cleavage under the polymerization condition are all polar groups. Therefore, there is always the possibility of a reaction between these polar groups and the metal complexes, leading to catalyst deactivation, and ultimately loss of control in the polymerization. Another attempt to elucidate the cause of the reduced control in the polymerization of VB*t*-BOC was performed (Run 7). Styrene was polymerized in the presence of benzyl *t*-butyloxy carbonate (Bz*t*-BOC) that possesses the same functional group as VB*t*-BOC. A CuCl/mpy complex was used as a catalyst for the polymerization, and the reaction was run at 130 °C. The polymerization rate was very slow, even taking the dilution factor caused by Bz*t*-BOC into consideration, but the prepared polymer had the same narrow molecular weight distribution as that of polystyrene prepared without Bz*t*-BOC. The GPC chromatogram of the resulting polystyrene shows no high molecular weight shoulder (Figure 2). If in the polymerization using Bz*t*-BOC, premature deprotection occurred followed by coupling reactions, it would produce only the dimeric compound, and not produce the twice molecular weight polymers by the interchain combination reaction as in the polymerization of VB*t*-BOC. However, it appears that the metal complexes can be poisoned by reaction with the functional groups, which reduce the rate of polymerization.

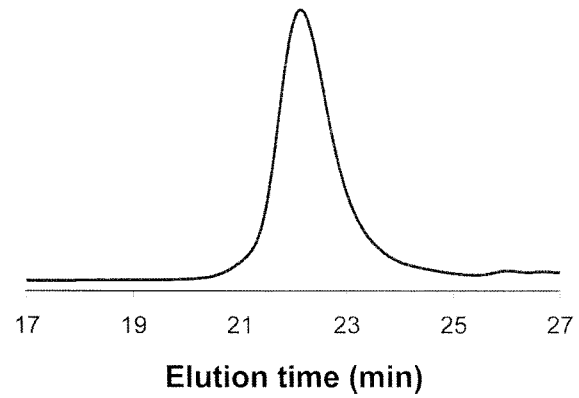


Figure 2. GPC chromatogram of polystyrene prepared in the presence of Bz*t*-BOC (Run 7).

In the preparation of branched polymers, copolymer of VB*t*-BOC and styrene was used as a backbone structure to control the branching density. If the branching density of the backbone was too high, the high density of active radicals could cause undesirable intra- and/or inter-chain coupling reactions. Run 8 shows the results of the copolymerization of VB*t*-BOC and styrene. A 50/50 mixture of VB*t*-BOC and styrene was polymerized with CuCl/pby in bulk at 110 °C. The polymerization was completed (conversion > 95%) after 10 h, and the resulting copolymer had a controlled molecular weight (M_n = 11,300) and relatively narrow polydispersity (PDI = 1.36). The higher molecular weight shoulder was still present, but not as significant as for the homopolymerization of VB*t*-BOC.

We prepared a block copolymer that was composed of two block segments: a linear polystyrene block and random copolymer of styrene and VB*t*-BOC. The block copolymer structure was used as a backbone to add one more complexity in the final structure. The initial polystyrene block segment was prepared using CuCl/epy as a catalyst. Upon workup after 4 h reaction at 130 °C, a good yield (> 90%) of polymer was obtained. Figure 3(a) shows the GPC chromatogram of the product polystyrene. The molecular weight of polystyrene is close to the expected value, and the molecular weight distribution was narrow (M_n = 2,000; PDI = 1.14). The isolated polystyrene segment was dissolved in an

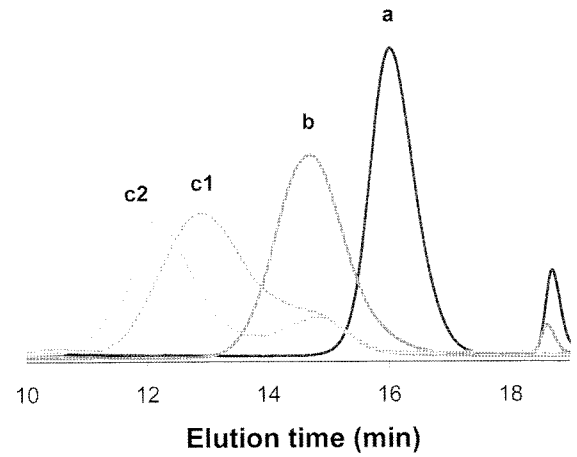


Figure 3. GPC chromatograms of linear-branched block copolymer, (a) initial polystyrene, (b) copoly[styrene-*b*-(styrene/VB*t*-BOC)] backbone, (c1) linear-branched block copolymer having polystyrene branches, (c2) linear-branched block copolymer having PMMA branches.

additional monomer mixture of styrene and VB*t*-BOC (75/25), and using the CuCl/epy catalyst, the second segment of the block copolymer was prepared by ATRP at 110 °C. Again high yields were attained and the product block copolymer had a molecular weight close to the theoretical value, and a relatively narrow molecular weight distribution (M_n = 22,000; PDI = 1.29; Figure 3(b)). Deprotection of *t*-BOC groups, to generate the benzyl bromide groups that are used as initiating sites for the graft polymerization, was performed in two steps. The *t*-BOC group was first cleaved by the reaction with trifluoroacetic acid at room temperature for 24 h. The resulting benzyl alcohol moieties were then transformed into the corresponding benzyl bromides by the reaction with triphenylphosphine and carbon tetrabromide in THF at room temperature for 1.5 h. Figure 4 is the ^{1}H-NMR spectra of parent protected polymer (a) and deprotected polymer (b). The peak at 1.5 ppm corresponding to the *t*-butyl proton from VB*t*-BOC disappeared, and the peak at 4.9 ppm corresponding to the benzylic proton from VB*t*-BOC is shifted upfield to 4.5 ppm corresponding to the benzylic proton from VBOH. The ^{1}H-NMR spectra of the final polymer (c) shows that new peak at 5.2 ppm corresponding to the benzylic proton from benzyl bromide moieties appears, and from the integration of these peaks, it was determined that there were on average 10.3 benzyl bromide groups per polymer chain.

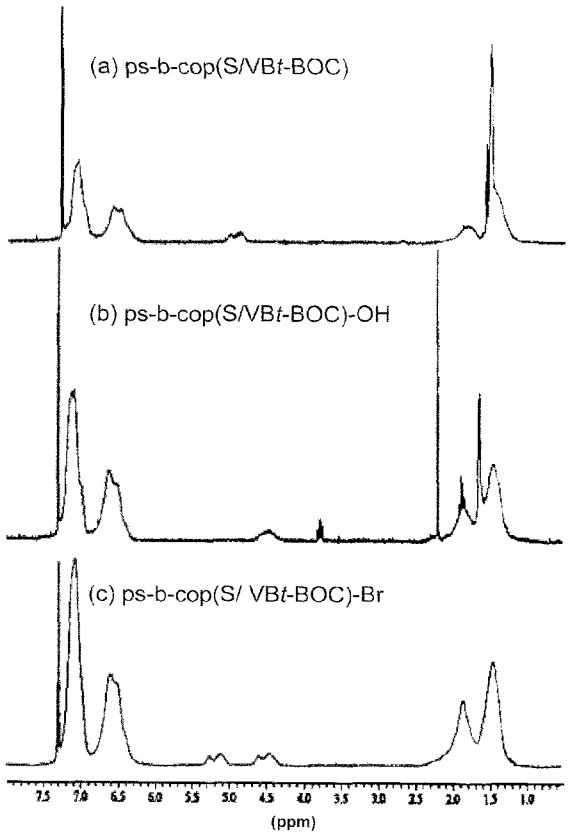


Figure 4. ^{1}H-NMR spectra of ps-*b*-cop(S/VB*t*-BOC) showing deprotection reactions of *t*-BOC group.

From this deprotected block copolymer, both polystyrene and PMMA branches were successfully grown using ATRP method. The graft polymerizations were performed using CuCl/bpy at 110 °C, and the reactions were stopped at low conversion to minimize side reactions. Figure 3(c) shows the GPC chromatogram of the grafted polymers. The molecular weight of grafted polymers increased to higher values for most part, but there is a residual peak for the backbone polymer. This seems to indicate that the deprotection reactions are not homogeneous and there are chains within the sample that have few, if any, benzyl bromide groups. The GPC chromatograms also show that there is a high molecular weight shoulder present, which is presumably the result of the inter-chain coupling reactions. These are especially pronounced for PMMA branched polymers where the amount of grafting was higher.

4-Methylstyrene (4-MeSt). In addition to the VBOH based protected monomers, an alternative, and potentially simplified, protection method was investigated. There have been several reports of halogenation of poly(4-MeSt) to introduce chloromethyl- or bromomethyl groups on to the rings.[19-21] Bromination reactions are, compared to chlorination reactions, highly selective toward formation of the monobromination of the methyl groups. Chung, *et al.* reported the radical bromination of α-olefin/4-MeSt copolymers.[22] Bromination by the reaction of copoly(α-olefin/4-MeSt) using *N*-bromosuccinimide (NBS) and benzoyl peroxide (BPO) in anhydrous carbon tetrachloride was highly specific and yielded a product with almost exclusive substitution on the *para*-methyl group to yield the benzylic bromide functionality.

This selectivity of the bromination reaction motivated us to use 4-MeSt as a protected monomer for the preparation of branched polymers. The same synthetic strategy used to prepare the linear-branched block copolymer was applied here. A block copolymers with polystyrene segments and random copoly(styrene/4-MeSt) segments were prepared by the ATRP technique. The methyl group along the second block segment of copoly(styrene/4-MeSt) were then brominated, and the resulting benzyl bromide functionalities were used as initiating sites for the graft polymerization via ATRP to give linear-branched block copolymer. In the first step, polystyrene was prepared by ATRP technique using the CuBr/dNbpy catalyst system. The resulting polystyrene was isolated and characterized by GPC chromatographic analysis and found to have a controlled structure (M_n = 2,900; PDI = 1.08; Figure 5(a)). This polymer was then reinitiated with an additional monomer feed of styrene/4-MeSt (mol ratio = 75/25) and the CuBr/epy catalyst system at 110 °C to form the second segment of the block copolymer (M_n = 5,100; PDI = 1.10; Figure 5(b)). The second block segment was composed of 75/25 ratio of styrene and 4-MeSt to control the density of branches in order to minimize the inter-chain coupling reaction during the grafting step. The methyl

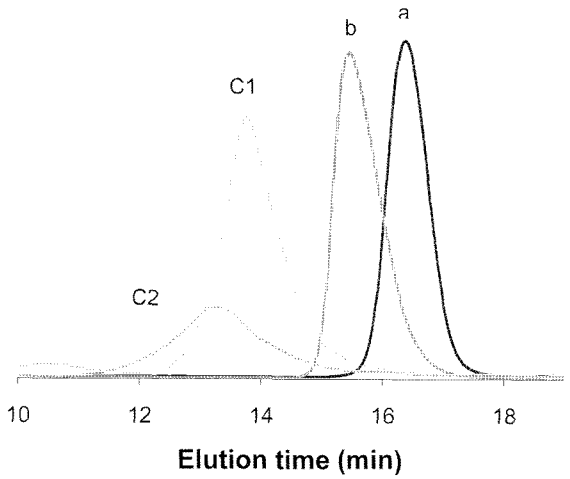


Figure 5. GPC chromatograms of linear-branched block copolymer, (a) initial polystyrene, (b) copoly[styrene-*b*-(styrene/4-MeSt)] backbone, (c1) linear-branched block copolymer having polystyrene branches, (c2) linear-branched block copolymer having PMMA branches.

groups of 4-MeSt moieties were brominated using NBS/BPO to afford the benzyl bromide functionalities. The reaction was monitored using ^{1}H-NMR analysis. The methyl proton resonance at 2.3 ppm decreased, and a new peak appeared at 4.4 ppm, which corresponds to the chemical shift of the methylene protons in benzyl bromide group. Additionally, the ^{13}C-NMR spectrum showed a new signal at 34 ppm, which is also diagnostic for the methylene carbon in benzyl bromide group. Molecular weight measurements showed that the number-average molecular weight and molecular weight distribution of the new copolymer were the same within experimental error as those of the starting copolymer. These data support the conclusion that, within detectable limits, the methyl groups of the starting backbone copolymer had been converted to bromomethyl groups without undergoing either chain cleavage or crosslinking reactions. From the ratio of the area of the peak for bromomethyl proton to the peaks for aromatic and aliphatic protons, we calculate that on average 5.7 benzyl bromide groups are present in a polymer chain.

The benzyl bromide groups were then used as branch-initiating sites for ATRP grafting. Two different branches were prepared using CuBr/bpy as a catalyst at 110 °C. In both cases, the grafting reactions were quenched at low conversion to avoid any undesired side reactions including interchain coupling reactions. The graft polymerization of styrene reached 20% of conversion after 2 h. Figure 5(c1) shows GPC chromatogram of the product polymer. The molecular weight of the backbone block copolymer was clearly extended to higher molecular weight after the grafting process (M_n = 44,900). However, it is higher than the theoretical value ($M_{n,theory}$ = 29,300) that is calculated as follows;

$$M_{n,theory} = M_{n,backbone} + n_{branch} \times \frac{[M]_0}{[I]_0} \times MW_{monomer} \times \text{conversion} \quad (1)$$

where, $M_{n,backbone}$ is the number average molecular weight of backbone polymer, n_{branch} is the number of initiating sites (benzyl bromide groups) in a backbone polymer chain, $[M]_0$ is the initial concentration of the grafting monomer, $[I]_0$ is the initial concentration of initiating sites, and $MW_{monomer}$ is the molecular weight of the grafting monomer.

The molecular weight distribution of the product polymer was unimodal, but significantly broadened during the grafting process (PDI = 1.66). The higher molecular weight and broad molecular weight distribution indicate that a wide range of branch lengths or numbers of grafts per backbone must exist in the grafted polymer. One possible explanation was that the bromination reaction of the methyl groups by NBS/BPO was not perfectly selective to form benzyl bromide groups. Although this type of bromination reaction is highly specific to give the benzyl bromide functionality, with an excess amount of NBS relative to the 4-MeSt moieties, bromination on other sites including the backbone methyne proton can take place. These unexpected brominated groups could also be active as initiating sites for the grafting process, but with different initiation reaction rates. As a result, the molecular weight distribution of the grafted polymer would be broadened.

Grafted polymers with PMMA branches were also prepared under the same reaction conditions. This reaction was very fast, and after 15 min, the reaction mixture was completely solidified. Upon workup the conversion of the grafting monomer was calculated to be 38%. Figure 5(c2) is the GPC chromatogram of the product polymer. The characteristics of the product polymer were similar to those with polystyrene branches. The molecular weight of the grafted polymer was extended from the starting backbone copolymer without any trace of residual backbone polymer. However, number average molecular weight of the polymer as higher than the theoretical value, and molecular weight distribution was broad (M_n = 68,700; PDI = 1.62).

Conclusions

To prepare branched polymers using the ATRP method only, a new strategy using protection-deprotection chemistry was employed. Alkyl halide groups that can be used as initiating sites in ATRP process were protected by suitable groups, and monomers containing these protected groups were polymerized by ATRP to form backbone polymer. The deprotection chemistry was then employed to regenerate initiating sites for the branch formation. Among the various

protected monomers tested, we could prepare branched polystyrene having controlled structure using VB*t*-BOC and 4-MeSt. We demonstrated the preparation of block copolymer of linear and branched polystyrene using this strategy, and the molecular weight distributions of the resulting polymers were narrow and unimodal.

This protection-deprotection strategy is very useful because it allows an ever-greater range of complex structural variations in the polymers prepared. Firstly, two or more different protected groups can be incorporated into the polymer backbones. These different protecting groups could be transformed into initiating sites under different deprotection reaction conditions. This makes it possible to attach various different kinds of branches to the same backbone, or in some cases, to prepare highly functional polymers by selective deprotection-grafting steps. An example of this would be the preparation of dendrigraft polymers. If just simple monomers such as styrene and MMA are used in the grafting steps, branched polymers can be prepared. Instead, however, if another protected monomer is copolymerized with the simple monomer and the same deprotection-grafting steps are applied, a second generation of branches (branches on branches) can be introduced in the polymer structure. In analogy with the divergent growth approach to dendritic macromolecules, this stepwise deprotection-grafting strategy can be continued to give larger and larger "comb-burst" macromolecules. The mild reaction conditions would permit a wide variety of monomer units and functional groups to be introduced at various stages of the synthesis, or at various 'levels' throughout the structure. Ideally, the deprotection-grafting step can be repeated to form very complex structures. However, because there always is the possibility of coupling reactions between active radicals, the reaction has a limitation and caution should be exercised in order to avoid uncontrolled crosslinking reactions.

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