

Synthesis and Characterization of Polystyrene-*b*-Poly(ethylene oxide)-*b*-Polystyrene Triblock Copolymers by Atom-Transfer Radical Polymerization

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ABSTRACT: Well-defined polystyrene (PS)-*b*-poly(ethylene oxide) (PEO)-*b*-PS triblock copolymers were synthesized by atom-transfer radical polymerization (ATRP), using C—X-end-group PEO as macroinitiators. The triblock copolymers were characterized by infrared spectroscopy, nuclear magnetic resonance spectroscopy, and gel permeation chromatography. The experimental results showed that the polymerization was controlled/living. It was found that when the number-average molecular weight of the macroinitiators increased from 2000 to 10,000, the molecular weight distribution of the triblock copolymers decreased roughly from 1.49 to 1.07 and the rate of polymerization became much slower. The possible polymerization mechanism is discussed. According to the Cu content measured with atomic absorption spectrometry, the removal of catalysts, with CHCl₃ as the solvent and kaolin as the *in situ* absorption agent, was effective. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2882–2888, 2000

Key words: PS-*b*-PEO-*b*-PS triblock copolymer; atom-transfer radical polymerization; characterization; removal of catalysts

INTRODUCTION

The synthesis of block copolymers, with a controlled molecular weight, a narrow molecular weight distribution, and a better-designed macromolecular structure and composition, is one of the most meaningful and challenging works in the field of polymer chemistry. Well-defined block copolymers can show a series of excellent and special properties, and not only have they been used to research the solution theory,¹ but also have already been much advanced in industrial applications. In the previous decades, living ionic po-

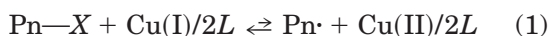
lymerization² and group-transfer polymerization³ have been primarily reported to synthesize well-defined polymers. The block copolymers of polystyrene (PS) and poly(ethylene oxide) (PEO) were synthesized before by anion living polymerization,^{4,5} but it is regretted that only well-defined PS-*b*-PEO diblock and PEO-*b*-PS-*b*-PEO triblock copolymers have been made, since the alkoxy anion is not active enough to initiate the polymerization of styrene.⁶ Although the synthesis of PS-*b*-PEO-*b*-PS triblock copolymers by coupling PS-*b*-PEO diblock copolymers has been reported, the resultant copolymers, to say the least, are not well defined, due to the unavoidable presence of diblock copolymers.⁷

In 1995, Jinshan and Matyjaszewski^{8,9} reported a new kind of living polymerization method—

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atom-transfer radical polymerization (ATRP), which has been considered as an important discovery of polymer synthesis¹⁰ and has received extensive attention.¹¹ In this polymerization process, a copper(I) complex, CuX/2L (X = Cl or Br and L = 2,2'-bipyridine [bpy] or a 4,4'-disubstitute-2,2'-bpy) activates reversibly the dormant polymer chains via a halogen atom-transfer reaction and it is this dynamic equilibrium which is responsible for the controlling behavior of the polymerization:



ATRP appears to hold the most promise for solving the problem of stringent reaction conditions, cost, monomer range, and ease of use. An even greater benefit from the use of ATRP is that polymers with complex topology and compositions can be made with a simple polymerization system, for example, many block copolymers have been synthesized, including PS-*b*-poly(methyl methacrylate),¹¹ PS-*b*-polyisobutylene-*b*-PS,¹² PS-*b*-polysulfone-*b*-PS,¹³ PS-*b*-polydimethylsiloxane-*b*-PS,¹⁴ PS-*b*-poly(propylene oxide)-*b*-PS,¹⁵ and PS-*b*-poly(vinyl acetate).¹⁶ In this article, we report the synthesis of well-defined PS-*b*-PEO-*b*-PS triblock copolymers by ATRP technology, using C—Cl-end-group PEO as a macroinitiator, which were made by the transformation of the end group of poly(ethylene glycol) (PEG) by chloroacetyl chloride.

EXPERIMENTAL

Materials

Styrene was stirred over CaH₂ overnight and vacuum-distilled before use. CuCl was purified according to the procedure of Keller and Wycoff.¹⁷ Toluene was refluxed over Na overnight and distilled before use. Absolute ethyl ether was dried over CaH₂ overnight. Unless specified, all other reagents were purchased from commercial sources and used without further purification.

Synthesis of Macroinitiators

To a three-neck flask equipped with a reflux condenser and a magnetic stir bar, 100 mL purified toluene and 15 g PEG were added. After the complete dissolution of PEG, 15 mL toluene was distilled under reduced pressure for the removal of water in the system. An appropriate quantity of

chloroacetyl chloride dissolved in toluene was added slowly. The mixture was heated at 80°C to react for 10 h. After the reaction, the mixture was distilled under reduced pressure for the removal of most of the toluene, then poured into absolute ethyl ether to sedimentate for further purification. The products were vacuum-dried to a stable weight. The resultant macroinitiators appear to be a white powder. Their chemical structure were elucidated by IR (ν , cm⁻¹): 1740–1760(—CO—), 1100(—C—O—C—), and by ¹H-NMR (δ , ppm): 3.64(—CH₂—O—CH₂—).

General Procedures for Synthesis of PS-*b*-PEO-*b*-PS Triblock Copolymers by ATRP and Removal of Catalysts in Polymerization System

All polymerizations were carried out in a 250-mL three-neck flask equipped with a reflux condenser and a magnetic stir bar. The macroinitiator, CuCl, and bpy in a 1/1/3 mol ratio were added to the flask under an argon atmosphere and degassed three times with argon; then, styrene in an appropriate ratio was added by a syringe. Finally, the flask was immersed in an oil-bath thermostat at 140°C and reacted for 14 h. A positive argon pressure was maintained throughout the reaction. After the reaction ended, a suitable quantity of CHCl₃ and kaolin were added and refluxed in a water bath under a nitrogen atmosphere for 8 h for the removal of the catalysts. The mixture was flitted under the reduced pressure and extracted with distilled water three times, then distilled under reduced pressure to remove CHCl₃. The raw products were immersed in absolute ethyl ether for 8 h three times, then vacuum-dried to a stable weight. The purified products are a white powder.

Characterization of Block Copolymers

Infrared spectra were recorded on an IR 440 spectrometer using KBr tablets. The spectra were obtained over the frequency range 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. ¹H-NMR spectra operated at 200 MHz in the Fourier transform mode were obtained on a Varian XL-200 NMR instrument, using tetramethylsilane as the internal standard, and the CDCl₃ solvent provided the deuterium lock frequency at 25δC. The apparent M_n , apparent M_w , and molecular weight distribution of the triblock copolymers were determined by gel permeation chromatography using a PL-GPC 210 gel permeation chromatography instru-

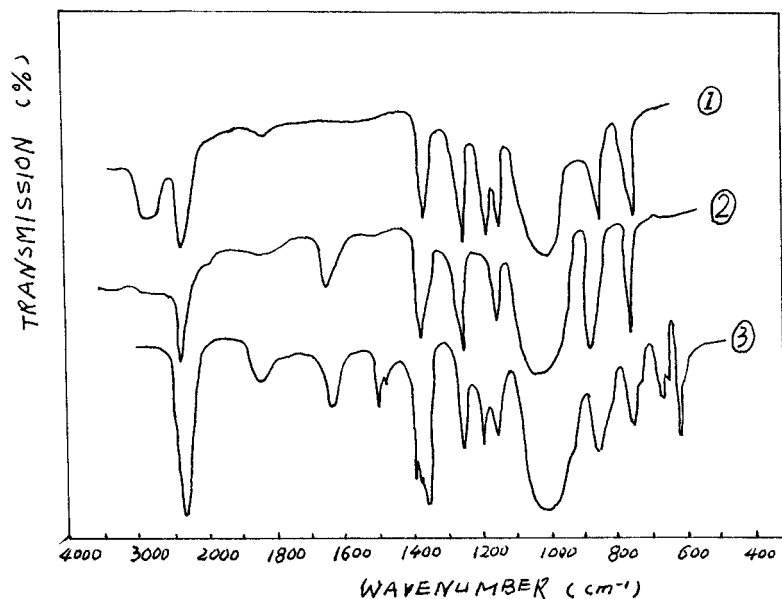


Figure 1 IR spectra of ①PEG, ②macroinitiators, and ③triblock copolymers.

ment of Polymer Laboratories Ltd., U.K., with one refractive index detector and two PL gel-mixed-B 10- μm columns (300×7.5 mm), operated with THF as the eluent at 35°C . The chromatograms were calibrated with PS standards. For the determination of the Cu content by AAS, the samples were first heated in a muffle furnace to carbonize at 650°C for 10 min, then solved in $\text{HNO}_3/\text{H}_2\text{O}$ (1:1 volume ratio) and diluted to a certain concentration. It was operated with a WFX-IF2 AAS, and the conditions of measurement were as follows: wavelength: 342.8 nm; slit: 0.2 nm; atomizer: burner; and HCL current: 1.8 mA.

RESULTS AND DISCUSSION

Confirmation of Macromolecular Structure of Macroinitiators and PS-*b*-PEO-*b*-PS Triblock Copolymers

The IR spectra of PEG, the macroinitiator, and the triblock copolymer are shown in Figure 1. The strong absorption at $3300\text{--}3400\text{ cm}^{-1}$, which is the characteristic of the OH end group of PEG, disappeared completely in the IR spectrum of the macroinitiator and the absorption at $1740\text{--}1760\text{ cm}^{-1}$ was for the --CO-- group. This indicated the complete transformation of the end group of PEG. As to the triblock copolymer, there were absorption peaks for the phenyl ring at

1400 , 1500 , and 1599 cm^{-1} . The peaks at 710 and 770 cm^{-1} resulted from a single-substituted phenyl ring; at the same time, the wide and strong absorption peak at 1100 cm^{-1} still remained for --C--O--C-- . Figure 2 represents the $^1\text{H-NMR}$ spectra of the macroinitiator and triblock copolymers. A single peak at 3.64δ existed both in the macroinitiator and the triblock copolymer for the

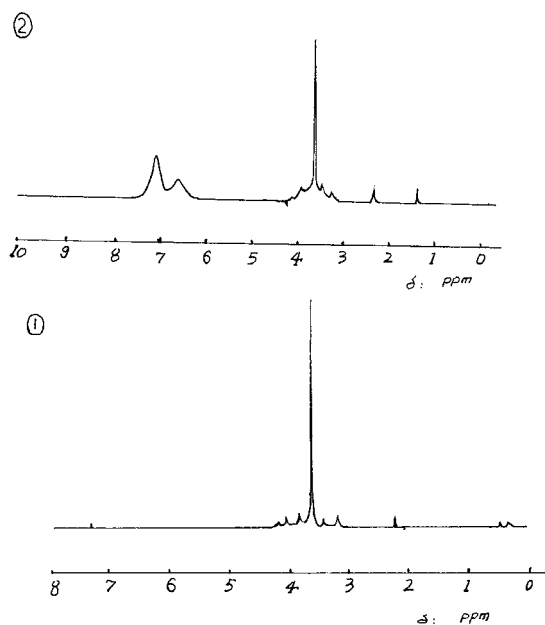


Figure 2 NMR spectra of ①macroinitiators and ②triblock copolymers (200 MHz).

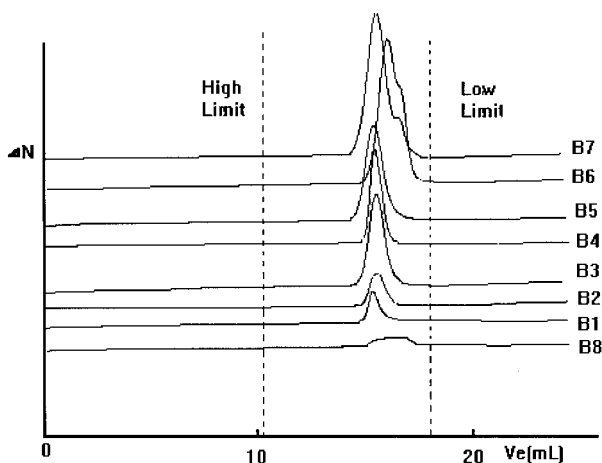


Figure 3 GPC curves of block copolymers.

methylene group of PEO, but for the triblock copolymers, two peaks at 6.64 δ and 7.05 δ appeared for the phenyl ring protons. Both the IR spectra and the $^1\text{H-NMR}$ spectra confirmed the coexistence of the PS chain and the PEO chain in the macromolecular structure.

The single peak of the GPC curves of the products shown in Figures 3 indicated that the products could not be the blend of PS homopolymers and PEO homopolymers; if so, the GPC curves should appear as two peaks, one for the PS homopolymers and the other for the PEO homopolymers. In the experiment, we also found that the products formed micelles in water or in CH_3NO_2 , which were good solvents for PEO and poor solvents for PS. The micellization in a selective solvent also revealed that the products were not the mixture of the PS homopolymers and the PEO

homopolymers, but were triblock copolymers of PS/PEO, because neither the PS homopolymers nor the PEO homopolymers could form micelles in water or in CH_3NO_2 . When the PS chain and the PEO chain coexisted in a macromolecular chain, they could produce micelles with PS as the core and PEO as the shell. In relating the proofs from the IR spectra, $^1\text{H-NMR}$ spectra, GPC curves, and micellization in a selective solvent to the mechanism of ATRP elucidated that the synthesized products were PS-*b*-PEO-*b*-PS triblock copolymers.

Molecular Weight, Molecular Weight Distribution, and Composition of the Triblock Copolymers

By ATRP technology, a series of PS-*b*-PEO-*b*-PS triblock copolymers with different molecular weight and composition were synthesized, in which the molecular weight of PEO for B1, B2, and B3 are 10,000; for B4, B5, and B6, 6000; and for B7 and B8, 2000. Table I reveals the molecular characteristics of block copolymers by GPC and $^1\text{H-NMR}$ measurements. Figure 3 represents the GPC chromatograms of triblock copolymers. Figure 4 shows the GPC chromatograms of three kinds of macroinitiators whose molecular weight distribution by GPC for $M_n = 2000$ is 1.17; for $M_n = 6000$, 1.12; and for $M_n = 10,000$, 1.10.

The data from Table I indicated that all triblock copolymers had a narrow molecular weight distribution and a similar theoretical molecular weight (M_n^{the}) and experimental molecular weight (M_n^{exp}), which suggested that the polymerization was controlled/living. But it was interest-

Table I Molecular Characteristics of Triblock Copolymers by GPC and $^1\text{H-NMR}$ Measurement

Samples	M_n^{the} ($\times 10^{-4}$) ^a	M_n^{exp} ($\times 10^{-4}$) ^{b,c}	Theoretical PEO Content (wt %)	Experimental PEO Content (wt %) ^b	M_n^{app} ($\times 10^{-4}$) ^{a,c}	M_w^{app} ($\times 10^{-4}$) ^{a,c}	M_w/M_n ^b
B1	2.00	1.30	50	77	—	—	1.61
B2	1.66	1.10	60	91	1.53	1.64	1.07
B3	1.33	1.07	75	93	1.42	1.54	1.08
B4	2.00	1.43	30	42	1.19	1.67	1.29
B5	1.20	1.00	50	60	1.12	1.43	1.22
B6	0.80	0.68	75	88	0.54	0.76	1.38
B7	1.20	1.10	17	18	0.94	1.41	1.48
B8	0.6	0.58	33	34	0.52	0.75	1.47

^a M_n^{the} , M_n^{exp} , M_n^{app} , M_w^{app} denote theoretical number-average molecular weight, experimental number-average molecular weight, apparent number-average molecular weight, and apparent weight-average molecular weight, respectively.

^bData from $^1\text{H-NMR}$.

^cData from GPC.

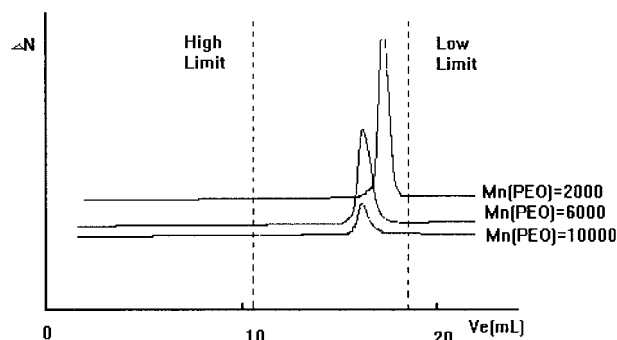


Figure 4 GPC curves of macroinitiator.

ing that, with increasing molecular weight of the macroinitiators, the difference between M_n^{the} and M_n^{exp} increased; inversely, the molecular weight distribution decreased. Figure 5 shows the influence of the molecular weight of the macroinitiators on the difference between the theoretical content of PEO and the experimental content of PEO ($^1\text{H-NMR}$ measurement). Figure 6 shows the influence of the molecular weight of the macroinitiator on the molecular weight distribution. When the the molecular weight of the macroinitiator increased from 2000 to 6000 to 10,000, the difference between theoretical and experimental content of PEO increased roughly from 1 to 10 to 20%, but the molecular weight distribution decreased from 1.49 to 1.07. It probably meant that the higher molecular weight macroinitiator, in the same condition of polymerization, produced a low radical concentration in the polymerization system. This low radical concentration slowed the

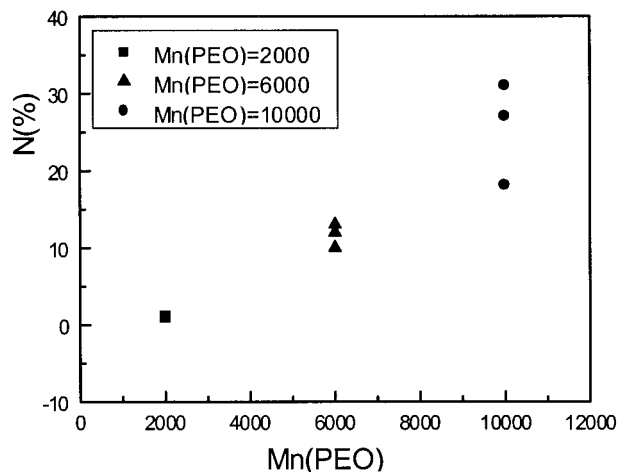


Figure 5 Influence of molecular weight of macroinitiator (M_n) on the difference of theoretical and experimental PEO content (N %).

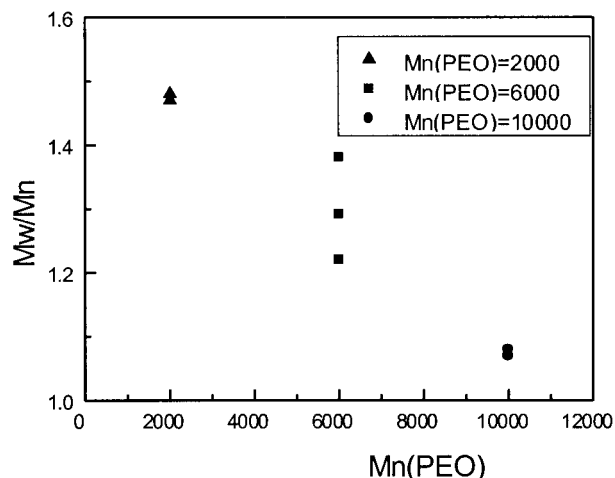
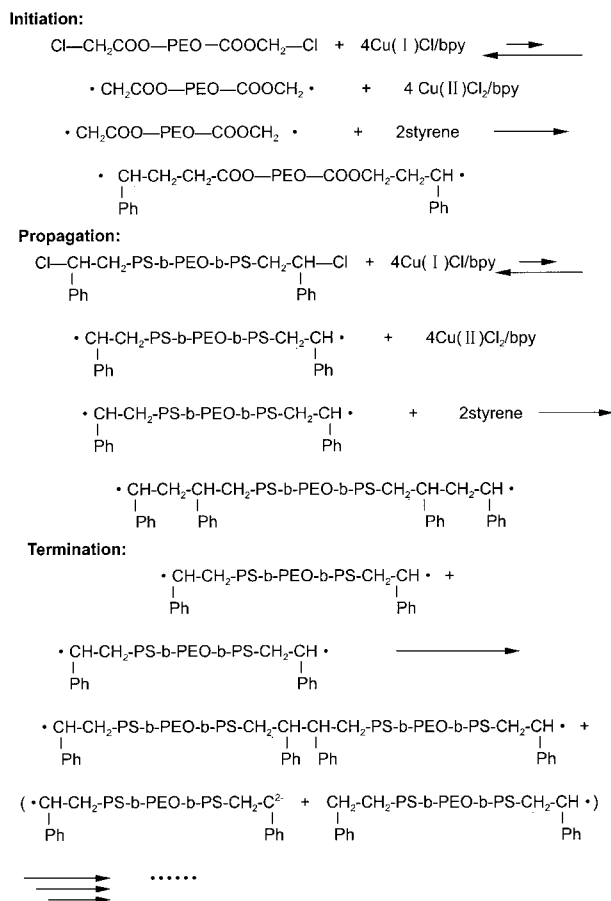


Figure 6 Influence of molecular weight of macroinitiator on the molecular weight distribution (M_w/M_n) of block copolymers.

rate of polymerization and decreased the conversion of the styrene monomers and, therefore, made the polymerization more controlled/living; in other words, the molecular weight distribution became much narrower. But, we did not discover that there existed a dependence of the controlled/living degree of polymerization upon the total molecular weight of the triblock copolymers.

Mechanism

A proposed mechanism for ATRP using PEO as the macroinitiator is shown in Scheme 1, (Scheme 1) which contained equations for the atom-transfer equilibrium, the propagation step, and the radical termination. The exclusive role for Cu(I) in this polymerization was to abstract chloride atoms from the inactive chains. The carbonyl group is an inductive stabilizing substituent for the chloride atom, which could lead to block copolymers with a narrow molecular weight distribution. A Cu(I) chloride–bpy complex reversibly abstracted chloride atoms from the dormant chain ends, which generated a small concentration of the block copolymer-based radicals and the corresponding Cu(II) chloride complex. These macroinitiator radicals could then add styrene monomers until they abstracted a chloride atom from the Cu(II) complex, thus completing the dormant-to-active chain-end catalytic cycle. In ATRP, the activation–deactivation cycle could minimize termination by creating a steady, low concentration of short-lived, active radical chain ends.



Scheme 1

Removal of Catalysts in Polymerization System

ATRP has been proved to be a “living” polymerization technology and would be very useful for macromolecule design, but very little literature has reported the removal of catalysts, which is one of the critical problems to be resolved for commercial polymers in this polymerization system. Wan et al.¹⁸ reported the removal of catalysts in the polymerization of styrene by ATRP using bpy and CuCl as catalyst systems. When using toluene, xylene, or THF as the solvent and an acid clay as the *in situ* absorption agent, their results showed that the content of Cu is low (in

parts per million), according to the data from AAS. Especially, they found toluene to be the best solvent. In the case of the synthesis of a block copolymer by ATRP, the success of the catalyst removal also depends heavily upon the choice of the solvent. Generally speaking, the different types of blocks within the copolymers are usually thermodynamically incompatible; these block copolymers will, consequently, tend to self-assemble in a selective solvent (i.e., a good solvent for one block but a precipitant for the other) and will reversibly associate to form different mesophasic structures.¹ The mesophasic structure would damage the successful absorption of the catalysts. Therefore, if using a nonselective solvent (e.g., CHCl₃ is a good solvent for two blocks of PS-*b*-PEO-*b*-PS triblock copolymers), it should decrease the damaging of the absorption of catalysts.

In the system of the PS-*b*-PEO-*b*-PS triblock copolymer catalyzed by bpy and CuCl, we used CHCl₃ as the solvent and kaolin as the *in situ* absorption agent. Table II shows the experimental data obtained by the AAS measurement; the results indicated that the content of Cu in the purified products was low (in parts per million). Therefore, the method of catalyst removal, which we described above, was effective. The Cu content of B4, B5, and B6 was much higher than that of the others (Table II), the reason being that these samples were carried out by *in situ* absorption of kaolin. For samples B4, B5, and B6, the polymerization mixture was first dissolved in the mixed solvent of benzene and THF (1:1 volume ratio), then poured into *n*-hexane.

CONCLUSIONS

Using the C—Cl-end-group PEO as macroinitiators and CuCl and bpy as catalysts, PS-*b*-PEO-*b*-PS triblock copolymers were synthesized by ATRP; the polymerization was controlled/living. The resultant PS-*b*-PEO-*b*-PS triblock copolymers were well defined, and the molecular weight

Table II Cu Content of Triblock Copolymers by AAS

Content	Samples							
	B1	B2	B3	B4	B5	B6	B7	B8
Cu content ($\times 10^6$)	1.84	12.67	1.86	655.41	618.41	96.40	0.85	3.85

distribution (M_w/M_n) was very narrow. Increasing the molecular weight of the macroinitiators caused the rate of polymerization to be much lower and the molecular weight distribution to be narrow. In our studied radical living polymerization system, a Cu(I) chloride–bpy complex reversibly abstracted chloride atoms from the dormant chain ends, which generated a small concentration of block copolymer-based radicals and the corresponding Cu(II) chloride complex. Accordingly, the polymerization appeared to be controlled/living. The removal of catalysts using CHCl_3 as the solvent and kaolin as the *in situ* adsorption agent was effective.

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