Synthesis of Polybenzamide-*b*-Polystyrene Block Copolymer via Combination of Chain-Growth Condensation Polymerization and Atom Transfer Radical Polymerization

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INTRODUCTION Rod-coil block copolymers have received enormous attentions due to their fascinating self-assembly behaviors in solution and solid state.[1] With the development of living polymerizations, such as living free-radical polymerization,[2] ring-opening (metathesis) polymerization[3], many types of well-defined diblock copolymer with coil chains can now be easily obtained through the use of dissimilar polymerization techniques via difunctional initiators[4] or chain-end transformations.[5] However, the preparation of well-defined rod segments is still a challenge due to the tedious nature of the synthetic steps[6] and the problem of low solubility.[7]

We have developed chain-growth condensation polymerization (CGCP) to provide rod-like polymers with controlled molecular weight, low polydispersity, and functionalities through manipulating the resonance effect (+*R* effect) and the inductive effect (+*I* effect) on aromatic monomers.[8] Different from conventional polycondensation, the monomers show high selectivity and react preferentially with the polymer end groups than the other monomers. The +*R* effect was efficiently mediated through deprotonation of the amino group of 4-aminobenzoic acid esters using a commercially available base (lithium hexamethyldisilazide [LiHMDS]) and well-defined polybenzamides (PBzAm) were obtained.[9] Explorations of *para*-type monomers with various leaving groups could diversify the access to well-defined poly(*para*-benzamide).

Essentially, well-defined condensation polymers yield telechelic structures, which can be used or modified for the production of block copolymers by polymer–polymer coupling or sequential polymerizations. By using this strategy, we have developed efficient approaches in the preparation of aromatic polyamide (i.e., PBzAm)[10–12] and aromatic polyether[13] block/star copolymers. In addition, polystyrene-*b*-polybenzamide (PSt-*b*-PBzAm) was successfully synthesized by the combined use of anionic polymerization[14] or reversible addition-fragmentation chain transfer (RAFT) polymerization.[15] In the case of first anionic polymerization of St followed by CGCP, PSt macroinitiators (MI) with high molecular weight hindered the sequential CGCP resulting in the occurrence of self-condensation. In the case of first CGCP followed by RAFT polymerization of St, the hindrance problem could be overcome with CGCP as the first polymerization sequence, but elaborate work was needed for the preparation of PBzAms as macromolecular chain transfer agents for RAFT polymerization.

The strategy of using CGCP first, followed by atom-transfer radical polymerization (ATRP) of St for the synthesis of well-defined polybenzamide-*b*-polystyrene block copolymers has not been reported yet. This "CGCP first" approach might overcome the above-mentioned hindrance problem resulting from the use of high-molecular-weight MI and also avoid the tedious synthesis of macromolecular chain transfer agent. An anticipated problem during ATRP is that the metal-catalyzed system might be interrupted by coordination of the amide structure with the catalyst leading to interference with the activation/deactivation equilibrium constant of the metal complex. Therefore, metal/ligand complexes with appropriate redox affinity are needed.

Herein, we first synthesized three monomers by one-step reaction from commercially available methyl 4-aminobenzoate, ethyl 4-aminobenzoate, and methyl 3-aminobenzoate, respectively. Two difunctional initiators for CGCP were examined and an efficient initiator was chosen (Scheme 1). In addition, poly(*meta*-benzamide) with the *N*-octyloxybenzyl (OOB) side group (PmOOBBzAm), which can be further deprotected to poly(*N*-H-*meta*-benzamide) (PmNHBzAm), was synthesized. For chain extension with styrene (St) via

Additional Supporting Information may be found in the online version of this article. Correspondence to: T. Yokozawa (E-mail: yokozt01@kanagawa-u.ac.jp)

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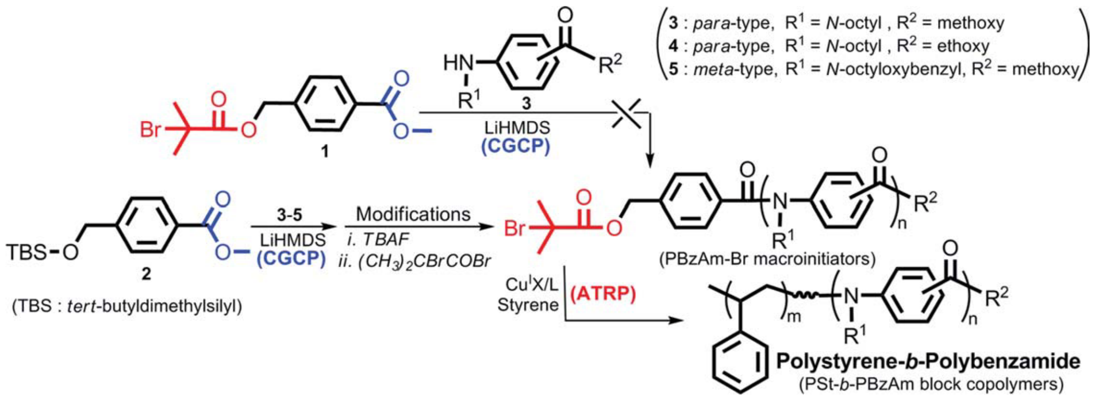

SCHEME 1 Synthetic routes to polystyrene-*b*-polybenzamide (PSt-*b*-PBzAm) block copolymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ATRP, PBzAm MIs with quantitative chain end modifications were obtained. Afterward, copper-catalyzed systems composed of different ligands were examined to understand the influence of amide structure on ATRP. Eventually, we developed an efficient synthetic approach using the combination of CGCP and ATRP for the synthesis of well-defined polybenzamide-*b*-polystyrene block copolymers with high molecular weights. Poly(*N*-H-*meta*-benzamide)-*b*-polystyrene (PmNHBzAm-*b*-PSt), which has strong intermolecular multiple hydrogen bonding between the amide bonds and π—π stacking of the aromatic rings, was synthesized through removal of the OOB group.

EXPERIMENTAL

General Methods

Conversion of the monomer was monitored by analytical gas chromatography on a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu Rtx-1 column (15 m) and an FID detector. Naphthalene and anisole were used as internal standards for CGCP and ATRP, respectively. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL ECA-600 instrument. The internal standards for ^{1}H NMR experiments in $CDCl_3$ and deuterated dimethylformamide (DMF-d_7) were tetramethylsilane (0.00 ppm) and the midpoint of DMF (2.74 ppm), respectively; for ^{13}C NMR experiments in $CDCl_3$ it was the midpoint of $CDCl_3$ (77.0 ppm), and for ^{13}C NMR experiments in DMSO-d_6 it was the midpoint of DMSO-d_6 (39.5 ppm). FT-IR spectra were recorded on a JASCO FT/IR-410. The M_n and M_w/M_n values of polymers were measured with a Shodex GPC-101 gel permeation chromatography (GPC) unit (eluent: tetrahydrofuran [THF]; calibration: polystyrene standards) equipped with two Shodex KF-804L columns, Shodex UV-41, and Shodex RI-71S.

Synthesis of Monomer 4

Ethyl 4-aminobenzoate (8.23 g, 50 mmol) and octanal (7.08 mL, 45 mmol) were mixed with THF (100 mL). Acetic acid (2.9 mL, 50 mmol) was gradually added and the mixture was stirred at room temperature for another 10 min. Then, sodium triacetoxyborohydride (16.30 g, 77 mmol) was added directly. The mixture was stirred at room temperature for 24 h, then saturated $NaHCO_3$ was added to make the solution slightly basic (pH = 8), and the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed and the residue was recrystallized from methanol to give the monomer **4** as colorless crystals with melting point: 80-82 °C (7.80 g, yield 62%).

^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.87-7.84 (m, 2H), 6.54-6.52 (m, 2H), 4.31 (q, $J = 7.2$ Hz, 2H), 4.05 (s, 1H), 3.15 (t, $J = 7.2$ Hz, 2H), 1.65-1.60 (q, $J = 7.6$ Hz, 2H), 1.42-1.26 (m, 13H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 166.88, 152.03, 131.46, 118.35, 111.24, 60.11, 43.38, 31.78, 29.33, 29.31, 29.21, 27.06, 22.63, 14.45, 14.08.

CGCP for the Synthesis of PBzAms from Initiator 2

A 10-mL flask equipped with a three-way stopcock was charged with 1.0 M LiHMDS/THF solution (0.5 mL, 0.5 mmol). A mixture of the monomer **4** (132 mg, 0.5 mmol) and the initiator **2** (14 mg, 0.05 mmol) in dry THF (1 mL) was added to the flask under nitrogen at −10 °C. To examine CGCP kinetics, aliquots were withdrawn at intervals during the polymerization to monitor the conversion of monomer by GC with naphthalene as an internal standard. After reaction had finished, the mixture was quenched with saturated NH_4Cl. The whole solution was extracted with CH_2Cl_2 and the organic layer was washed with water; then dried over $MgSO_4$. The crude oil was dissolved in CH_2Cl_2 and twice precipitated in methanol/water = 9/1 (v/v) to afford yellowish viscous poly(*para*-benzamide) with the *tert*-butyldimethylsilyl protecting end group (PpBzAm-OTBS) ($M_n = 3010$, $M_w/M_n = 1.07$, yield 72%).

Chain Extension with Styrene via ATRP to Synthesize Polybenzamide-*b*-Polystyrene Block Copolymers (PBzAm-*b*-PSt)

Preparations of *para*- and *meta*-type PBzAm MIs (i.e., PpBzAm-Br and PmOOBBzAm-Br) involve similar synthetic steps, as detailed in the Supporting Information. The resulting MIs were further used for St chain extension via ATRP. For example, St/MI/CuBr/tris(2-dimethylaminoethyl)amine (Me_6TREN) reagents were used in the ratio of 600/1/1/1/1 in 13% (v/v) anisole ($[St]_0 = 7.56M$). Styrene, Me_6TREN, PpBzAm-Br, and anisole were added to a Schlenk flask. The mixture was deoxygenated by three freeze-pump-thaw cycles

TABLE 1 Conditions of CGCP and Characterization of Polybenzamide

Entry	M	I	$[M]_0/[I]_0$	Time (h)	M_n[a]	M_w/M_n	Conv.[b] (%)	$k_{app}\times10^5$ (s^{-1})
1	**3**	**1**	10	19	–	–	21	–
2	**3**	**2**	10	12	3,000	1.07	99	–
3	**3**	**2**	40	19	7,600	1.09	92	5.34
4	**4**	**2**	10	24	3,010	1.07	85	–
5	**4**	**2**	40	26	5,900	1.09	75	1.69
6[c]	**5**	**2**	10	1	4,520	1.09	88	–

[a] M_n was determined by GPC (eluent: THF) using polystyrene calibration standards.

[b] Conversion of monomer was determined by GC with 10 mol.% naphthalene as an internal standard.

[c] Five-fold molar excess of LiCl to base was added.[12]

and the flask was backfilled with nitrogen. CuBr was then added to the frozen solution. The flask was closed, evacuated, and deoxygenated by additional two freeze-pump-thaw cycles. An initial sample was taken via a syringe and the flask was then immersed in an oil bath preheated at 70 °C to start the polymerization. Aliquots were withdrawn at intervals during the polymerization to monitor the conversion by GC, with anisole as an internal standard. The polymerization was stopped by placing the flask in an ice bath and exposing the contents to air. The resulting mixture was diluted with THF and passed through a neutral aluminum oxide column to remove the copper catalyst. The mixture was precipitated in methanol, filtered, and dried in a vacuum ($M_n = 23{,}400$, $M_w/M_n = 1.24$, conversion = 40%).

RESULTS AND DISCUSSION

Three monomers were first synthesized via one-step reaction from commercially available methyl-4-aminobenzoate, ethyl-4-aminobenzoate, and methyl-3-aminobenzoate. Based on the combination of CGCP and ATRP reported, two difunctional initiators **1** and **2** were synthesized. As outlined in Scheme 1, the major advantage of the initiator **1** having an ATRP initiating site is that the sequential polymerizations from CGCP to ATRP can proceed without the need for chain end modifications. In CGCP, addition of a base that abstracts a proton of the amino group of monomer generates the aminyl anion. This anionic group deactivates the electrophilic carbonyl site on the *para*-position through the resonance effect (+*R* effect), resulting in the suppression of self-condensation of the monomer, and allowing selective reaction with initiator and the propagating end. A possible problem arises from the halogen atom at the ATRP initiating site, which might react with the aminyl anion of monomer, leading to quenching of the anion, and side reactions. To examine this issue, CGCP of the monomer **3** from two initiators **1** and **2** was carried out. As shown in Table 1 (entry 1) and can be seen from the GPC profile (see Fig. S1 in the Supporting Information), low monomer conversion (21%) and tailing GPC traces were obtained using initiator **1**. On the contrary, CGCP from the initiator **2** with *tert*-butyldimethylsilyl (TBS) group (entry 2 in Table 1) proceeded with high monomer conversion (99%), giving a product with a narrow molecular weight distribution (M_w/M_n = 1.07). Hence, effective CGCP could not be achieved from initiator **1** with the ATRP initiating site.

In our previous study, we obtained well-defined PBzAms via CGCP of the methyl ester monomer **3**. The ethyl ester monomer **4**, which can be easily synthesized via one-step reaction from commercially available reagents, would also be a suitable monomer for preparing well-defined PBzAms. The influence of the alkoxy group of the ester moiety on the monomer reactivity can be rationalized on the basis of the CGCP kinetic study. CGCP of monomers **3** and **4** was carried out at −10 °C in THF, using **2** and LiHMDS as initiator and base, respectively, (M/I/LiHMDS = 40/1/40, $[M]_0$ = 0.3*M*). As shown in Figure 1(A), a linear first-order kinetic plot was

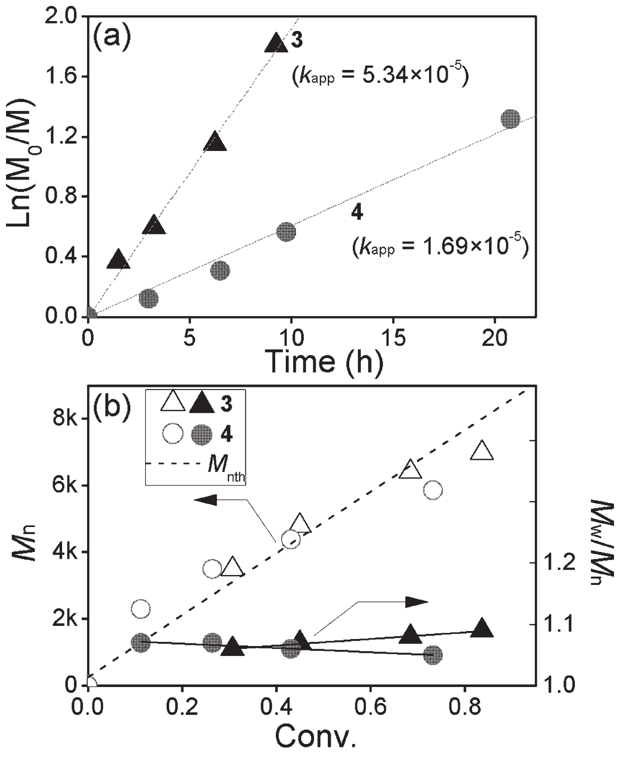

FIGURE 1 Chain-growth condensation polymerization (CGCP): (A) kinetic plots of ln(M_0/M) versus time, and (B) M_n and M_w/M_n versus conversion plots with monomers **3** and **4** (M/I/LiHMDS = 40/1/40 at −10 °C in THF with $[M]_0$ = 0.3 M).

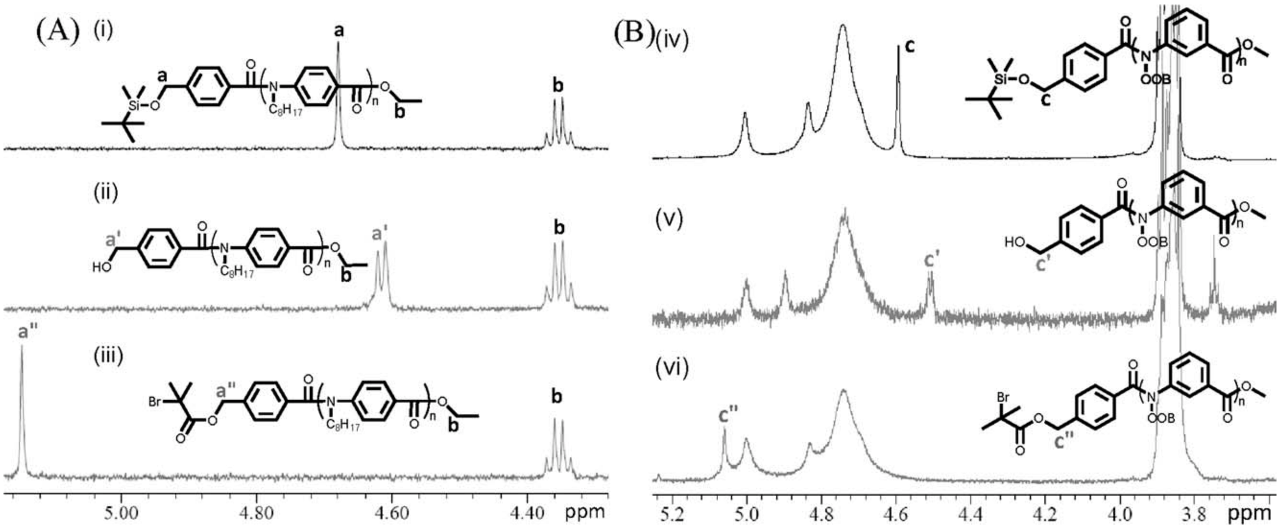

FIGURE 2 ^{1}H NMR (600 MHz, $CDCl_3$) spectra of chain end modifications of (A) PpBzAm: (i) TBS endprotected, (ii) deprotection of TBS, and (iii) acylation, and (B) PmOOBBzAm: (iv) TBS end-protected, (v) deprotection of TBS, and (vi) acylation.

obtained in each polymerization. The faster consumption of the methyl ester monomer **3** (triangles) indicated its higher reactivity, when compared with the ethyl ester monomer **4** (circles). The apparent rate constant of **3** ($k_{app} = 5.34 \times 10^{-5}$ s^{-1}) was about three times higher than that of **4** ($k_{app} = 1.69 \times 10^{-5}$ s^{-1}). Figure 1(B) shows a linear increase in molecular weight (M_w) with respect to conversion and a narrow molecular weight distribution ($M_w/M_n < 1.10$). From Figure 1, we can conclude that monomers **3** and **4** both undergo chain-growth polymerization and the monomer **4** has a slower CGCP rate than the monomer **3**, which is consistent with the ethoxy carbonyl group having lower electrophilicity than the methoxy carbonyl group. Well-defined *tert*-butyldimethylsilyl-protected poly(*para*-benzamide) (PpBzAm-OTBS) can be obtained from either monomer. The conditions and characteristics of the CGCP are summarized in Table 1.

For the next chain extension with styrene (St) via ATRP, chain-end modification to synthesize PBzAm-Br MI was carried out. As outlined in Scheme 1, the TBS group was removed with 1.0 M tetrabutylammonium fluoride/THF solution. The purified PBzAm-OH polymer was acylated with 2-bromoisobutyryl bromide to obtain PBzAm-Br MI. As revealed from the ^{1}H NMR spectra of Figure 2(A), quantitative conversion in chain-end modification was obtained, as can be distinguished from peaks **a** (4.67 ppm, singlet), **a′** (4.61 ppm, doublet, $J = 6.5$ Hz), and **a″** (5.14 ppm, singlet). A poly(*N*-octyl-*para*-benzamide) with the 2-bromoisobutyryl end group (PpBzAm-Br: $M_n = 3010$, $M_w/M_n = 1.07$) was obtained. Similarly, poly(*N*-octyloxylbenzyl-*meta*-benzamide) with the 2-bromoisobutyryl end group (PmOOBBzAm-Br: $M_n = 4520$, $M_w/M_n = 1.09$) was synthesized after CGCP of the monomer **5**; this can be quantitatively distinguished from peaks **c** (4.60 ppm, singlet), **c′** (4.50 ppm, doublet, $J = 5.5$ Hz) and **c″** (5.05 ppm, singlet) in Figure 2(B).

Thus, the functionalized polymers, PBzAm-Br, were used for chain extension with St. It has been reported that amide structure can chelate metal ions[16] and chelation might affect the activation/deactivation equilibrium of metal-catalyzed systems. Therefore, kinetic studies were conducted to examine the efficiency of various ligands with copper(I) bromide using tris(2-dimethylaminoethyl)amine (Me_6TREN), tris[(2-pyridyl)methyl]amine (TPMA), *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine (PMDETA), and 2,2′-bipyridyl (Bpy). In the cases of PpBzAm-Br as an MI [solid symbols in Fig. 3(A)], four linear first-order kinetic plots for the St polymerization were obtained (entries 1-4 in Table 2: St/PpBzAm-Br/CuBr/L = 600/1/1/1; PpBzAm-Br: $M_n = 3010$, $M_w/M_n = 1.07$). As shown in Figure 3(B) (solid symbols), these four polymerizations proceeded with a linear increase in molecular weight with respect to conversion, and with low polydispersity ($M_w/M_n < 1.25$). When conversion was higher than 30%, however, molecular weight deviations were observed. This might be ascribed to the difference of hydrodynamic radius between the high-molecular-weight block copolymers and polystyrene standards. Monomodal GPC traces for the chain extensions are shown in Figure 3(C). Furthermore, a block copolymer with low polydispersity (entry 5 in Table 2: $M_n = 37{,}200$, $M_w/M_n = 1.25$) was synthesized from high-molecular-weight MI (PpBzAm-Br: $M_n = 7600$, $M_w/M_n = 1.09$; footnote in Table 2). These results suggest that well-defined poly(*N*-octyl-*para*-benzamide)-*b*-polystyrene block copolymers can be efficiently synthesized. Interestingly, TPMA ($k_{app} = 5.11 \times 10^{-6}$ s^{-1}) and Me_6TREN ($k_{app} = 5.74 \times 10^{-6}$ s^{-1}) as ligands show faster polymerization rates than those obtained with PMDETA ($k_{app} = 0.80 \times 10^{-6}$ s^{-1}) and Bpy ($k_{app} = 0.74 \times 10^{-6}$ s^{-1}) as ligands. This is due to the different redox potential of the copper complex.[17] Chain extension results are summarized in Table 2. Thus, the results of kinetic studies indicate that *N*-substituted PBzAms have an insignificant effect on the ATRP copper complex structures, although rather slow polymerization rates were obtained with less-active copper complexes. Further studies of chain extensions with various monomers and ATRP initiating sites are under way.

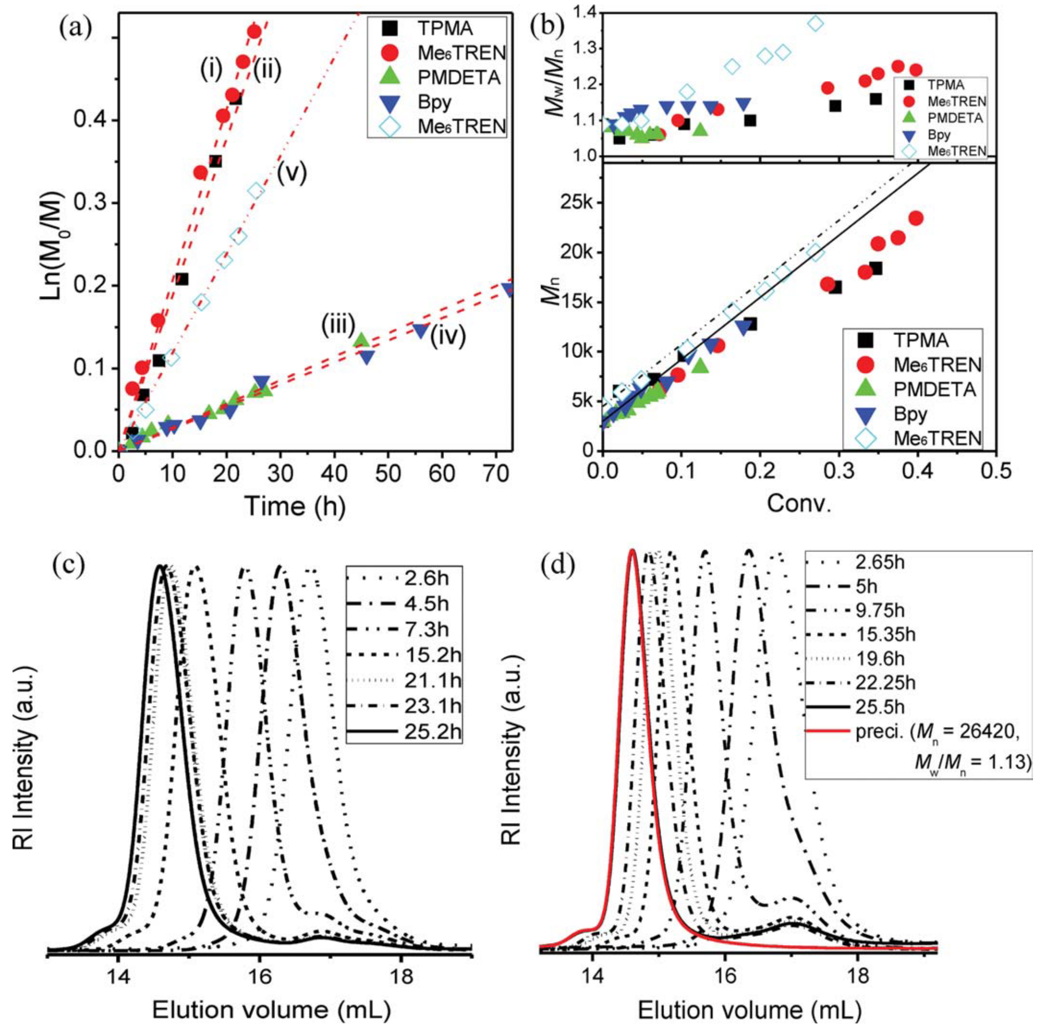

FIGURE 3 St chain extension: (a) kinetic plots of ln(M_0/M) versus time (solid symbols: PpBzAm-Br as an MI; hollow symbol: PmOOBBzAm-Br as an MI), (b) M_n and M_w/M_n versus conversion plots, (c) GPC traces of chain extension from PpBzAm-Br, and (d) GPC traces of chain extension from PmOOBBzAm-Br and precipitation (red line) of the resulting block copolymer (St/MI/CuBr/L = 600/1/1/1 at 70 °C in 13% (v/v) anisole).

TABLE 2 Reaction Conditions and Characterization of St Chain Extension Products Generated from Polybenzamide Macroinitiators via ATRP

Entry[a]	MI[b]	Ligands[a]	Time (h)	Conv.[c] (%)	M_n[d]	M_w/M_n	$k_{app}\times10^6$ (s^{-1})
1	PpBzAm-Br (M_n = 3,010)	TPMA	20	35	18,000	1.16	5.11
2		Me_6TREN	25	40	23,400	1.24	5.74
3		PMDETA	45	12	8,400	1.09	0.80
4		Bpy	72.5	18	12,580	1.15	0.74
5	PpBzAm-Br (M_n = 7,600)	Me_6TREN	8.25	25	37,200	1.25	–[e]
6	PmOOBBzAm-Br (M_n = 4,520)	Me_6TREN	24	27	20,000 (26,420)[f]	1.37 (1.13)[f]	3.30

[a] In 13% (v/v) anisole at 70 °C with St/MI/CuBr/L = 600/1/1/1, except for entries 4 (St/MI/CuBr/Bpy = 600/1/1/2) and 5 (St/MI/CuBr/Me_6TREN = 1000/1/1/1).

[b] PpBzAm-Br (M_n = 3,010, M_w/M_n = 1.07) for entries 1–4; PpBzAm-Br (M_n = 7,600, M_w/M_n = 1.09) for entry 5; and PmOOBBzAm-Br (M_n = 4,520, M_w/M_n = 1.09) for entry 6.

[c] Conversion of St was determined by GC with anisole as an internal standard.

[d] M_n was determined by GPC (eluent: THF) using polystyrene calibration standards.

[e] Not determined.

[f] After precipitation into 2-propanol/ethyl acetate = 50/6 (v/v).

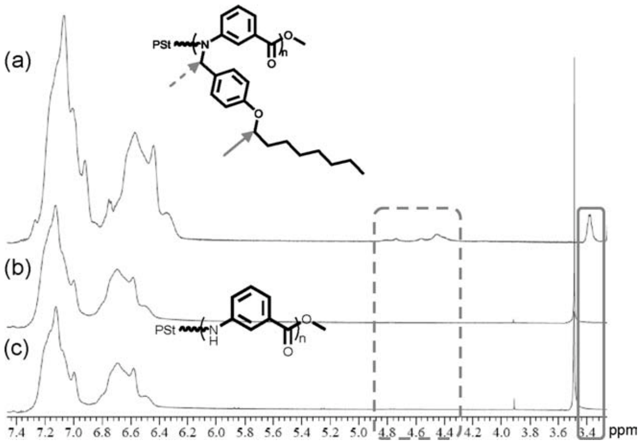

FIGURE 4 ^{1}H NMR (600 MHz, DMF-d$_7$) spectra before and after treatment of block copolymer with TFA: (a) PSt-b-PmOOBBzAm, treatment for (b) 1 day and (c) 4 days.

Moreover, synthesis of poly(*N*-OOB-*meta*-benzamide)-*b*-polystyrene block copolymer was carried out. Compared with the same catalytic system with a different MI [entries 2 and 6 in Table 2: solid circles and hollow diamonds in Figs. 3(a, b)], chain extension with St showed a slower polymerization rate ($k_{app} = 3.3 \times 10^{-6}$ s^{-1}), which might be attributed to the higher M_w and bulkier nature of the PmOOBBzAm-Br MI. The GPC traces show some tailing toward low M_w [Fig. 3(d)], which would be due to self-condensation polymer without the initiator unit, resulting from the high reactivity of the *meta*-type monomer during the first step of CGCP.[11,12] For removal of the MI, the block copolymer was purified by precipitation into 2-propanol/ethyl acetate = 50/6 (v/v). A well-defined poly(*N*-OOB-*meta*-benzamide)-*b*-polystyrene block copolymer was obtained [Fig. 3(d) red line: M_n = 26,420, M_w/M_n = 1.13].

Selective removal of the OOB group was further carried out to synthesize poly(*N*-H-*meta*-benzamide)-based block copolymers with strong hydrogen bonding and good solubility in highly polar solvents. To examine the removal of the OOB group and the stability of the ester linkage between the PSt and PmOOBBzAm segments, reactions were carried out with trifluoroacetic acid (TFA) for 1 and 4 days, respectively. Figure 4 shows the ^{1}H NMR (600 MHz, DMF-d_7) spectra before and after treatment with TFA. Disappearance of the OOB group, whose signals were located at δ (ppm) = 4.25-4.85 and 3.35-3.45, was observed. Furthermore, FT-IR spectra demonstrated that the ether linkage had disappeared, whereas the ester and amide linkages remained (see the Supporting Information Fig. S2). These results indicate that selective deprotection and good stability of the ester linkage were both attained. Hence, poly(*N*-H-*meta*-benzamide)-*b*-polystyrene (PmNHBzAm-*b*-PSt) with controlled molecular weight and low polydispersity had been synthesized. This polymer exhibits strong intermolecular multiple hydrogen bonding between the amide bonds and π—π stacking of aromatic rings.

CONCLUSIONS

Two difunctional initiators (**1** and **2**) and three monomers (**3**, **4**, and **5**) were synthesized. An initiator **2** with a TBS-protecting group was chosen to avoid the problem of quenching between the aminyl anion of monomer and the halogen atom of initiator **1** during CGCP. The kinetics of CGCP was investigated for the *para*-type monomers **3** and **4** with different ester moieties. Polycondensation of each monomer proceeded in a CGCP fashion, and the apparent rate constants (k_{app}) showed a three-fold difference between the methyl ester **3** (5.34×10^{-5} s^{-1}) and ethyl ester **4** (1.69×10^{-5} s^{-1}). Then, quantitative chain end modifications were conducted for syntheses of *para*- and *meta*-PBzAm MIs. Various ligands, such as tris(2-dimethylaminoethyl)amine (Me$_6$TREN), TPMA, PMDETA, and Bpy with copper(I) bromide (CuBr), were used for ATRP. In chain extensions with St, a linear increase in molecular weight with respect to conversion, low polydispersity, and monomodal GPC traces was obtained. The kinetic studies indicated that N-substituted PBzAms are not detrimental to the ATRP copper complexes, although rather slow polymerization rates were obtained with less-active copper complexes (herein, CuBr/PMDETA and CuBr/Bpy). Thus, we were able to develop an efficient approach, by the combination of CGCP and ATRP, to the synthesis of well-defined PBzAm-*b*-polystyrene block copolymers with high molecular weight and low polydispersity (M_n = 37,200, M_w/M_n = 1.25). Selective removal of the OOB group was further carried out with TFA to obtain poly(*N*-H-*meta*-benzamide)-*b*-PSt block copolymers. Selective deprotection and good stability of the ester linkage between the polyamide and polystyrene segments were attained. Exploration of the self-assembly behavior of the PmNHBzAm-*b*-PSt block copolymers in solution and in the solid state is under way.

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