Effect of Halogen Chain End Fidelity on the Synthesis of Poly(methyl methacrylate-*b*-styrene) by ATRP

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Abstract Poly(methyl methacrylate-*b*-styrene) (PMMA-*b*-PS) block copolymers are synthesized by two consecutive ATRPs and ~~fractionated into four fractions. The halogen chain end fidelity (CEF) in PMMA-*b*-PS is quantified based on the analysis of each fraction.~~ Compared to ethyl 2-phenyl-2-bromoacetate/CuBr/2,2′-bipyridine (EPBA/CuBr/bpy) and CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (CuBr/PMDETA) catalysts, PMMA-*b*-PS synthesized using *p*-toluenesulfonyl chloride/CuCl/bpy (TsCl/CuCl/bpy) and CuCl/PMDETA catalysts has a higher halogen CEF and a better control on molecular weight.

Keywords Atom transfer radical polymerization; Chain end fidelity; Block copolymer

INTRODUCTION

Atom transfer radical polymerization (ATRP) is a powerful technique to prepare well-defined polymers with complex architecture and functionality[1−4]. Compared to living anionic polymerization, the loss of chain end functionality is unavoidable in ATRP due to the nature of free radicals[5−8]. A number of ATRP techniques have been developed to suppress or minimize the chain termination[9−14]. Under certain circumstances, high dilution of the initiator is typically required to achieve negligible termination to synthesize high molecular weight polymers, but the molecular weight distribution is usually relatively broad. In addition to high initiator efficiency, high halogen chain end fidelity (CEF) which strongly depends on the polymerization conditions is critical to synthesize block copolymers.

Zhong *et al.* systematically studied the relationship between halogen CEF and the rate of polymerization, the degree of polymerization, the initial monomer concentration, the monomer structure and conversion by kinetic analysis and computation[13]. Low monomer conversion is beneficial for high CEF in any case. Longer polymerization time is good to preserve CEF for the same monomer. At a fixed polymerization rate, CEF can be improved by increasing the initial monomer concentration and lowering the degree of polymerization. Nystrom *et al.* synthesized the methacrylate (MA) oligomer at high monomer conversion, ~99%, by copper-mediated radical polymerization and the CEF was as high as ~95% by electrospray-ionization mass spectroscopy (ESI-MS) analysis[15]. They also demonstrated that CEF could be increased by addition of Cu(II). Wang *et al.* showed that the loss of CEF occurred when a highly active ligand, such as TPMA and Me_6TREN, was used in ATRP due to the Cu(I)-induced radical termination[16]. The loss of CEF can be significantly reduced by lowering the Cu/L concentration to $< 1\ mmol\cdot L^{-1}$. Oh *et al.* synthesized polystyrene (PS) at low styrene conversion (28%) and converted the halogen end group to a hydroxyl chain end which altered the polarity of living chains[17]. The polarity change allowed the separation of living and dead chains by HPLC. Dead chains of 16% were separated and their PDI was broader than that of the living chain since the dead chains were formed by both coupling and dispro-portionation reaction. Min *et al.* synthesized PMA-*b*-PS block copolymers by AGET-ATRP in miniemulsion. 2D HPLC-GPC chromatography analysis of the product showed that only ~1 wt% coupling product was identified in the final product and there was no detectable homopolymers[18].

Previous studies on halogen CEF focused on relatively low molecular weight homopolymers and block copolymers. In this work, high molecular weight PMMA-*b*-PS block copolymers were synthesized by two consecutive ATRPs. The as-synthesized PMMA-*b*-PS block copolymers were purified by cyclohexane extraction and THF/cyclohexane fractionation in 10 g scale due to the solubility dependence of different components, and each fraction was analyzed by

^{1}H-NMR spectroscopy (ICP-MS), GPC and inductively coupled plasma mass spectrometry. The chain end fidelity of two initiation systems was compared and discussed. After purification, symmetric PMMA-*b*-PS block copolymers were characterized by SAXS analysis and used forthin film study.

EXPERIMENTAL

General Considerations

Styrene (St, 99%), methyl methacrylate (MMA, 99%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), copper halides (99%), deuterated chloroform ($CDCl_3$) with 1% tetramethylsilane (TMS), ethyl 2-phenyl-2-bromoacetate (EPBA, 98%), *p*-toluenesulfonyl chloride (TsCl, 98%), and 2,2′-bipyridine (bpy, 98%) were purchased from Aldrich. Anisole, anhydrous methanol and tetrahydrofuran (THF) were obtained from Aladin. St and MMA were passed over an alumina column before use. PMDETA was distilled under vacuum and stored at 0 °C. Copper halides were stirred in glacial acetic acid for 2 h under N_2, washed consecutively with glacial acetic acid and anhydrous methanol, dried at 25 °C for 2 days, and stored in the glove box. The other chemicals were used without further purification.

^{1}H-NMR spectra were recorded on a Bruker DMX-300 spectrometer. The gel permeation chromatography (GPC) measurements were performed on Waters 1515 with an isocratic HPLC pump using THF as eluent (35 °C and 1 $mL \cdot min^{-1}$). A Zeiss Merlin field-emission scanning electron microscope (SEM) was used to image all the samples after annealing. SAXS measurements were performed at the Beamline BL16B1 at the Shanghai Synchrotron Radiation Facility (SSRF), China, with a wavelength of 1.24 Å.

The amount of Cl/Br in samples was measured by using inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific X Series II, USA) or inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Scientific iCAP6300, USA). The average number of Cl or Br group per chain ($\overline{N_X}$) is calculated using the equation:

$$\overline{N_X} = \frac{m_X}{M_X} \times M_{n;\mathrm{polymer}} \times 10^{-6}$$

where X = Cl or Br, m_X is the halogen concentration in ppm, M_X is the atomic weight of Cl or Br, and $M_{n,\mathrm{polymer}}$ is the molecular weight of the polymer.

Synthesis of PMMA-1/PMMA-3

TsCl (190 mg, 1.0 mmol)/EBPA (195 mg, 1.0 mmol), CuCl (99 mg, 1.0 mmol)/CuBr (143 mg, 1.0 mmol), anisole (60 g, 0.54 mol) and MMA (55 g, 0.55 mol) were introduced to a flask equipped with a magnetic stirrer. The oxygen was removed by three freeze-pump-thaw cycles. Bpy (310 mg, 2.0 mmol) dissovled in MMA (5 g, 50 mmol) (oxygen was removed by three freeze-pump-thaw cycles) was added to the flask with a syringe. The sealed flask was immersed in an oil bath at 60 °C for a certain time. The polymerization mixture was cooled in an ice-water bath and dissoved in THF. The solution was then passed through an alumina column twice to remove the copper catalyst and then precipitated in methanol. After three disolution-precitation cycles, PMMA-1/PMMA-3 was dried under vacuum at 40 °C for 48 h.

Synthesis of PMMA-2/PMMA-4

TsCl (190 mg, 1.0 mmol)/EBPA (195 mg, 1.0 mmol), CuCl (99 mg, 1.0 mmol)/CuBr (143 mg, 1.0 mmol), and MMA (115 g, 1.15 mol) were introduced to a flask equipped with a magnetic stirrer. The oxygen was removed by three freeze-pump-thaw cycles. Bpy (310 mg, 2.0 mmol) dissovled in MMA (5 g, 50 mmol) (oxygen was removed by three freeze-pump-thaw cycles) was added to the flask with a syringe. The sealed flask was immersed in an oil bath at 60 °C for a certain time. The polymerization mixture was cooled in an ice-water bath and dissoved in THF. The solution was then passed through an alumina column twice to remove the copper catalyst and then precipitated in methanol. After three dissolution-precipitation cycles, PMMA-2/PMMA-4 was dried under vacuum at 40 °C for 48 h.

Synthesis of PMMA-*b*-PS Block Copolymers

PMMA-1/PMMA-3 (0.1 mmol) and CuCl (19.8 mg, 0.2 mmol)/CuBr (28.6 mg, 0.2 mmol) were added to a flask equipped with a magnetic stirrer. The flask was sealed with a rubber septum and underwent three vacuum-N_2 cycles to remove oxygen. After three freeze-pump-thaw cycles, PMDETA (69.2 mg, 0.4 mmol) in St (20 g, 0.2 mol) was added to the flask *via* syringe. The sealed flask was immersed in a oil bath at 100 °C for a certain time. The polymerization mixture was cooled in an ice-water bath and dissoved in THF. The solution was then passed through an alumina column twice to remove the copper catalyst and then precipitated in methanol. After three dissolution-precipitation cycles, PMMA-*b*-PS was dried under vacuum at 40 °C for 48 h.

Fractionation of As-synthesized PMMA-*b*-PS

The fractionation procedure was separated into three steps.

Step 1. The as-synthesized PMMA-*b*-PS was extracted under N_2 using cyclohexane in a Soxhlet extractor. Cyclohexane was changed until there was no detectable PS in cyclohexane. The solutions were combined and cyclohexane was evaporated to give PS (fraction 1).

Step 2. After extraction, the remaining solid was dissolved in THF to form a 5 wt% solution. Cyclohexane was added dropwisely into the solution at room temperature until the solution turned into slightly turbid. The solution was heated to clear and then cooled to room temperature until it separated into two layers, supernatant and precipitate. The precipitate was collected and dried in vacuum. The mixed solvents in the supernatant were evaporated and the resulting solid was purified using the same procedure until PS fraction was detected in the precipitate. The same procedure was repeated one more time. The precipitates containing only PMMA were combined. The supernatant was concentrated and then precipitated in methanol to give purified PMMA-*b*-PS (fraction 4).

Step 3. The precipitates in the last two cycles in Step 2 were combined and dissolved in THF to form 0.5 wt% solution. Cyclohexane was added dropwisely into the solution at room temperature until the solution turned into slightly turbid. The solution was heated to clear and then cooled to room temperature until it separated into two layers, supernatant and precipitate. The mixed solvents in the supernatant were evaporated and the resulting solid was purified using the same procedure until PS fraction was detected in the precipitate. The precipitates containing only PMMA were combined with PMMA from Step 2 to form fraction 2. The rest materials were PMMA-*b*-PS with low molecular weight PS blocks and labeled as fraction 3.

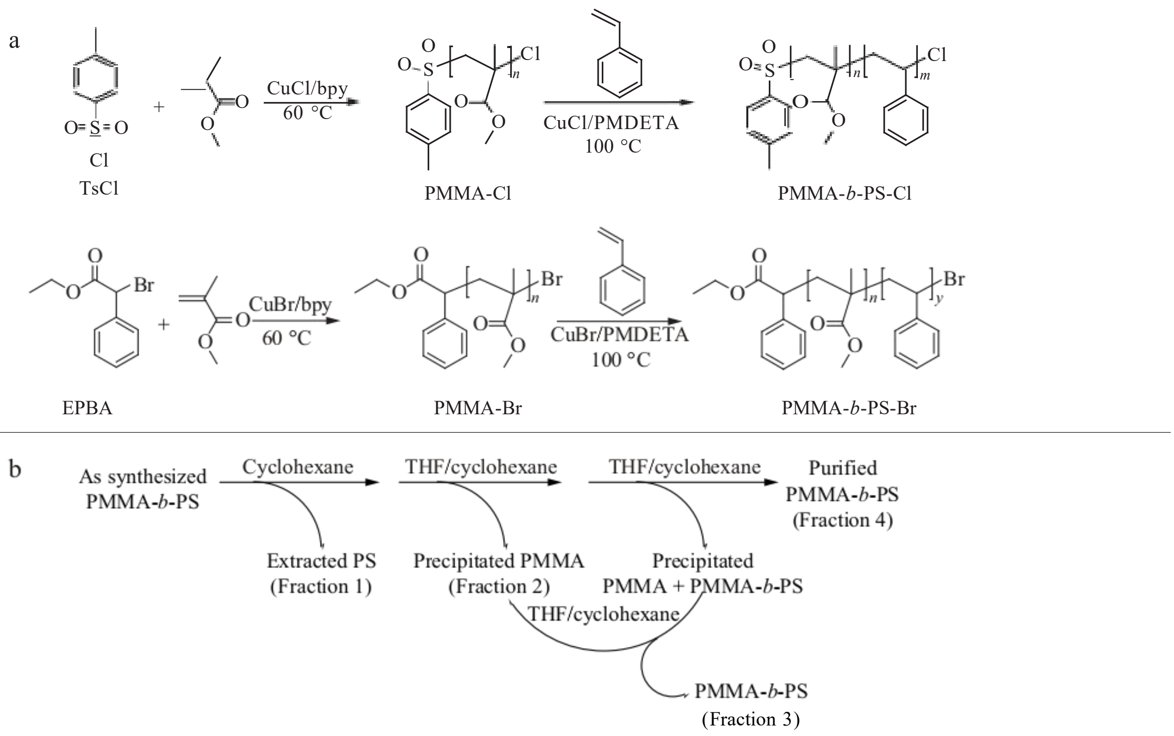
Self-assembly of Purified PMMA-*b*-PS

Hydroxyl-terminated random copolymer of styrene and methyl methacrylate (PS-*r*-PMMA-OH) with 55 mol% of St was synthesized by nitroxide mediated polymerization[19]. 0.5 wt% PS-*r*-PMMA-OH solution in toluene was spin-coated on the silicon substrate which was cleaned by O_2 plasma (100 w, 2 min) treatment to yield a film of ~20 nm thickness. The substrate was heated at 190 °C for 12 h to graft the copolymer brush onto the substrate and excess brush polymer was removed by sonication in warm toluene[20]. PMMA-*b*-PS solution (1 wt%) in THF was spin-coated on the PS-*r*-PMMA-OH modified substrate brush to form films with ~50 nm thickness. The PMMA-*b*-PS films were annealed at 250 °C for 10 min under nitrogen and then imaged by SEM with 1 kV acceleration voltage[21].

RESULTS AND DISCUSSION

Synthesis of PMMA and PMMA-*b*-PS

In order to compare the effect of the halogen chain end on the synthesis of PMMA-*b*-PS, EPBA and TsCl were chosen as the initiators to synthesize bromide/chloride terminated PMMA-Br and PMMA-Cl macroinitiators because they showed similar initiation rates under the same polymerization conditions and the resulting PMMAs had similar molecular weights and narrow PDIs (Scheme 1a)[22, 23]. The polymerization was performed both in bulk and in anisole solution and the target number-average molecular weight (M_n) was ~ 50 kg/mol. The polymerization time and the conversion of MMA monomers were very close when the target M_n of PMMA was the same for the EPBA/CuBr/bpy and TsCl/CuCl/bpy initiation systems in bulk (Table 1). However, when the polymerization was performed in anisole solutions, a shorter polymerization time was needed to achieve the same molecular weight for the EPBA/CuBr/bpy system. Compared to the TsCl/CuCl/bpy system, the monomer conversion was also lower for the EPBA/CuBr/bpy system, but it was proportional to the polymerization time. A lower monomer conversion required for the same molecular weight using the



Scheme 1 (a) Synthesis of PMMA macroinitiators and PMMA-*b*-PS by ATRP; (b) The purification process of as-synthesized PMMA-*b*-PS

Table 1 Characterization of PMMA macroinitiators initiated by TsCl or EBPA

Sample	Initiator	Catalyst	Solvent	Time (h)	Conv. (%)	M_n ^{c} (kg/mol)	M_w/M_n ^{c}
PMMA-1 ^{a}	TsCl	CuCl/bpy	Anisole	16	64.2	49	1.08
PMMA-2 ^{b}	TsCl	CuCl/bpy	–	3	31.9	50	1.26
PMMA-3 ^{a}	EBPA	CuBr/bpy	Anisole	9	48.2	50	1.10
PMMA-4 ^{b}	EBPA	CuBr/bpy	–	3	31.6	47	1.16

^{a} [Initiator]/[CuX]/[bpy]/[MMA]/[anisole] = 1/1/2/600/600; ^{b} [Initiator]/[CuX]/[bpy]/[MMA] = 1/1/2/1200; $_c$ Measured by GPC using THF as eluent based on PMMA standards. All reactions were carried out at 60 °C.

EPBA/CuBr/bpy system might becaused by a higher coupling rate. These two sets of data showed that the polymerization of MMA using the EPBA/CuBr/bpy and TsCl/CuCl/bpy initiation systems had similar polymerization rates.

The polydispersity indexes (PDIs) of PMMAs synthesized in bulk were 1.16 and 1.26 for the EPBA/CuBr/bpy and TsCl/CuCl/bpy initiation systems, respectively (Fig. S1 in electronic supplementary information, ESI). When anisole (50 wt%) was used as solvent, the PDIs were significantly reduced to 1.08 and 1.10, respectively. In this case, the total amount of anisole and MMA was the same as the amount of MMA in bulk polymerization, *i.e.*, $[\mathrm{MMA}]_{0,\mathrm{anisole}} = 1/2[\mathrm{MMA}]_{0,\mathrm{bulk}}$, and the viscosity was very close. Previous study showed that high dilution of initiator was typically required to achieve negligible termination to synthesize high molecular weight PMMA[13]. As the result, the use of anisole might suppress the chain transfer to MMA monomers. PMMA-Cl (PMMA-1) and PMMA-Br (PMMA-3) were then used to initiate the polymerization of styrene to synthesize PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br block copolymers using CuCl/PMDETA and CuBr/PMDETA catalysts, respectively[24−26]. Styrene is a good solvent for PMMA, and the polymerization was performed in bulk. Aliquots of polymerization mixtures were sampled out at different time intervals and the polymers were characterized by GPC (Fig. 1).

The GPC curves gradually shifted to high molecular weight end for both PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br block copolymers, but the GPC curves had both high and low molecular weight shoulders for PMMA-*b*-PS-Br block copolymers (Fig. 1b). Peak deconvolution showed that peak position of low molecular weight shoulders did not change. The above observations might suggest that more chain termination occurred in the synthesis of PMMA-3 than PMMA-1 and the non-functional PMMAs corresponding to low molecular weight shoulders did not initiate the polymerization of styrene. When the M_n was the same for both PMMA-*b*-PS block copolymers, lower conversion of styrene and shorter polymerization time were required for PMMA-*b*-PS-Br (Table2). The high molecular weight shoulders also moved with the increase of polymerization time, indicating that chain coupling happened in the synthesis of PMMA-*b*-PS-Br.

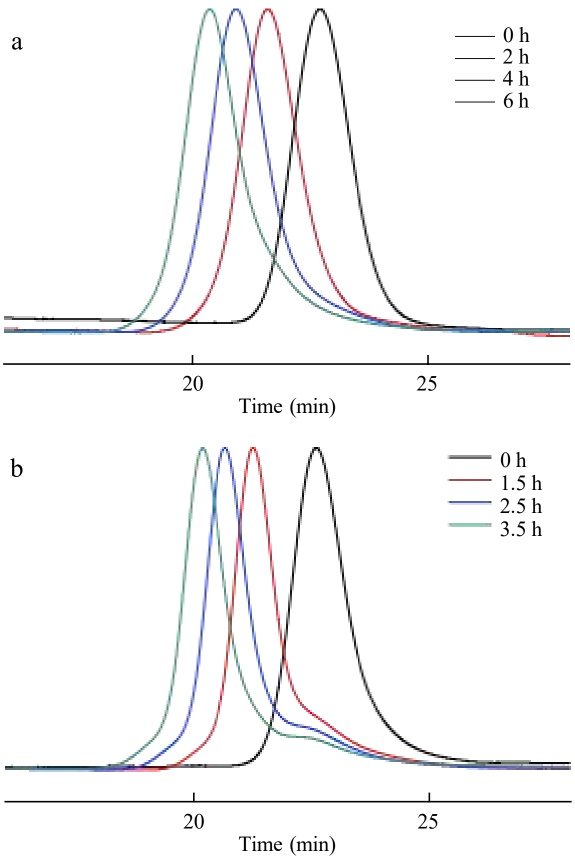


Fig. 1 Time evolution of GPC curves of PMMA-*b*-PS synthesized at 100 °C using (a) PMMA-1 and (b) PMMA-3 as macroinitiators in bulk

Fractionation and Characterization of As-synthesized PMMA-*b*-PS

PMMA-*b*-PS-Cl (AS-3) and PMMA-*b*-PS-Br (AS-6) block copolymers were fractionated to four fractions to quantify the CEF. The fractionation process contained both cyclohexane extraction and THF/cyclohexane precipitation procedures (Fig. 1b)[27]. Since the extraction and precipitation steps were performed at relatively low temperature without use of reactive solvents, the loss of CEF was negligible during fractionation. PS homopolymers were separated by cyclohexane extraction in a Soxhlet extractor since PMMA and PMMA-containing block copolymers were insoluble in cyclohexane. When the extraction solvent did not contain detectable amount of polymers by ^{1}H-NMR analysis (Fig. S2, in ESI), cyclohexane was evaporated. The resulting polymer was dissolved in THF and then precipitated in methanol. ^{1}H-NMR analysis of the precipitate showed that extracted fraction only contained PS (fraction 1).

Table 2 Characterization of as-synthesized PMMA-*b*-PS initiated by PMMA-1 and PMMA-3 at different time

Sample	Initiator	Time (h)	PS block		As-synthesized PMMA-*b*-PS	
			Weight percent [c] (wt%)	St conv. [d] (%)	M_n [e] (kg/mol)	M_w/M_n
AS-1 [a]	PMMA-1	2	–	–	71	1.15
AS-2 [a]	PMMA-1	4	–	–	93	1.19
AS-3 [a]	PMMA-1	6	65.6	47.6	120	1.21
AS-4 [b]	PMMA-3	1.5	–	–	73	1.20
AS-5 [b]	PMMA-3	2.5	–	–	95	1.24
AS-6 [b]	PMMA-3	3.5	50.6	25.6	118	1.28

[a] [PMMA-1]/[CuCl]/[PMDETA]/[St] = 1/1/2/200; [b] [PMMA-3]/[CuBr]/[PMDETA]/[St] = 1/1/2/200; [c] Mass fractions were caculated by ^{1}H-NMR analysis; [d] Conv. = $(m_{\mathrm{AS\text{-}x}} - m_{\mathrm{PMMA}})/m_{\mathrm{AS\text{-}x}} \times 100\%$; [e] Measured by GPC using THF as eluent based on PS standards. All reactions were carried out at 100 °C.

The insoluble portion after cyclohexane extraction was fractionated using THF/cyclohexane. The solid was dissolved in THF to form a 1 wt% solution, and cyclohexane was then added dropwisely under mixing until the solution turned turbid. The solution was then heated until the turbidity disappeared and cooled to room temperature. The resulting precipitate and supernatant were separated. The solvents in supernatant were evaporated and the resulting solid was ready for fractionation using the same precipitation procedure. The precipitates were analyzed by ^{1}H-NMR spectroscopy. When the PS component was detected in the precipitate, the precipitation fractionation step was repeated for one more time. The remaining supernatant was concentrated and precipitated into methanol to give PMMA-*b*-PS (fraction 4). The last two precipitates from the THF/cyclohexane fractionation were combined, dissolved in THF to form a 0.5 wt% solution, and then fractionated again using the same procedure. All PMMA precipitates from both fractionation steps were combined (fraction 2). The solvent in the refractionation supernatant was evaporated to give fraction 3. Fraction 3 contained both PS and PMMA contents. There were no detectable PS or PMMA homopolymers in fraction 3 by further cyclohexane extraction or THF/cyclohexane fractionation, indicating that fraction 3 was PMMA-*b*-PS block copolymer.

The fidelity of halogen chain ends can be estimated by characterization of the fractions. The weight percentages of fractions 1−3 were ~1.8 wt%−1.9 wt% for AS-3, while the weight percentages of fractions 1−3 were 2.2 wt%, 7.0 wt% and 16.7 wt%, respectively, for AS-6 under the same fractionation conditions (3Table). The M_n and PDIs of fraction 1 from AS-3 (and AS-6) were 55 kg/mol (and 47 kg/mol) and 1.28 (1.38) (3Table). Such narrow PDI suggested that PS was not from thermal polymerization of St monomers. ICP-MS analysis showed that there was 0.7 Cl per chain and 0.6 Br per chain, respectively, indicating that chain transfer to St monomers happened to form PS homopolymers (Table 3). But chain transfer to St monomer was not significant since the weight percentage of fraction 1 was ~2% in both block copolymers.

Compared to AS-3, AS-6 had more isolated PMMA (0.71 g, fraction 2) and PMMA-*b*-PS with low M_n PS blocks (1.69 g, fraction 3), indicating that AS-6 has a higher level of chain termination than AS-3 (Table 3). The percentages of dead chains in PMMA macroinitiators were calculated to be 5.0 wt% and 14.2 wt% for PMMA-Cl and PMMA-Br, respectively. ICP-MS analysis showed that there was no detectable amount of halogen infractions 2 for both systems, while the starting PMMA-1 and PMMA-3 macroinitiators had 0.95 Cl/chain and 0.88 Br/chain, respectively. GPC analysis of fraction 2 showed that M_n of PMMA isolated from AS-3 was the same as that of the starting macroinitiator PMMA-1, while M_n of PMMA isolated from AS-6 was higher than that of the starting macroinitiator PMMA-3 (Fig. 2). The peak position for PMMA isolated from AS-6 shifted to the high molecular weight end and the GPC curve had an obviously high molecular weight shoulder. This difference might suggest that the chain termination mechanism might be mainly chain transfer and chain coupling for the synthesis PMMA-1 and PMMA-3, respectively. GPC analysis also showed that fraction 3 from AS-3 had a higher M_n than PMMA-1, while fraction 3 from AS-6 had similar M_n to PMMA-3. This observation also proved that chain coupling might be the main mechanism for chain termination in the synthesis of AS-6 and the low molecular weight fraction was the living chains containing Br functionality. Thus the peak position of fraction 3 was coincident with that of PMMA-3.

The weight ratios of PS components were 10.7% and 8.9% in fraction 3 separated from AS-3 and AS-6, respectively, which proved the high reproducibility of the fractionation process (Table 3 and Fig. S2 in ESI). In comparison, the PS components in fraction 4 from AS-3 and AS-6 were 67.2% and 63.3%, respectively. The halogen contents were measured to be ~0.9 Cl/chain and ~0.8 Br/chain infraction 4 from AS-3 and AS-6, respectively, by ICP-MS. The detection of ~0.1 Br/chain infraction 3 from AS-6 by ICP-MS also suggested that Br might chain transfer to the PMMA block. After the removal of PS (fraction 1) and PMMA (fraction 2) homopolymers and low molecular weight PMMA-*b*-PS (fraction 3), the purified PMMA-*b*-PS (fraction 4) had a much narrower molecular weight distribution than those of the corresponding as-synthesized PMMA-*b*-PS (Tables 2 and 3). Further attempts to fractionate fraction 4 using THF/cyclohexane resulted in the precipitates that contained a higher ratio of PS component

Table 3 Purification results of AS-3 and AS-6 by cyclohexane and mixtures of THF and cyclohexane

	Entry	Mass (g/wt%)	PS [e] (wt%)	PMMA[e] (wt%)	M_n [f] (kg/mol)	M_w/M_n [f]	N_X [g] (X = Cl/Br)
AS-3	Fraction 1 [a]	0.28/1.9	100	0	55	1.28	0.7
	Fraction 2 [b]	0.25/1.8	0	100	50	1.18	ND
	Fraction 3 [c]	0.26/1.8	10.7	89.3	85	1.10	ND
	Fraction 4 [d]	13.73/94.5	67.2	32.8	126	1.14	0.9
AS-6	Fraction 1 [a]	0.22/2.2	100	0	47	1.38	0.6
	Fraction 2 [b]	0.71/7.0	0	100	63	1.15	ND
	Fraction 3 [c]	1.69/16.7	8.9	91.1	45	1.16	0.1
	Fraction 4 [d]	7.50/74.0	63.3	36.7	138	1.18	0.8

[a] Extracted from AS-3/6 using cyclohexane, the starting masses for AS-3 and AS-6 were 14.53 and 10.14 g, respectively; [b] Combined precipitates from multiple treatments using THF/cyclohexane; [c] Combined precipitates from multiple treatments by THF and cyclohexane mixture followed by the removal of PMMA homopolymer using THF and cyclohexane mixture; [d] Purified PS-*b*-PMMA ; [e] PS and PMMA components were calculated by 1H-NMR analysis; [f] Measured by GPC using THF as eluent based on PS (fractions 1, 3, 4) and PMMA (fraction 2) standard; [g] Measured by ICP. The Cu content of all samples are below 7 ppm,ND is undetected.

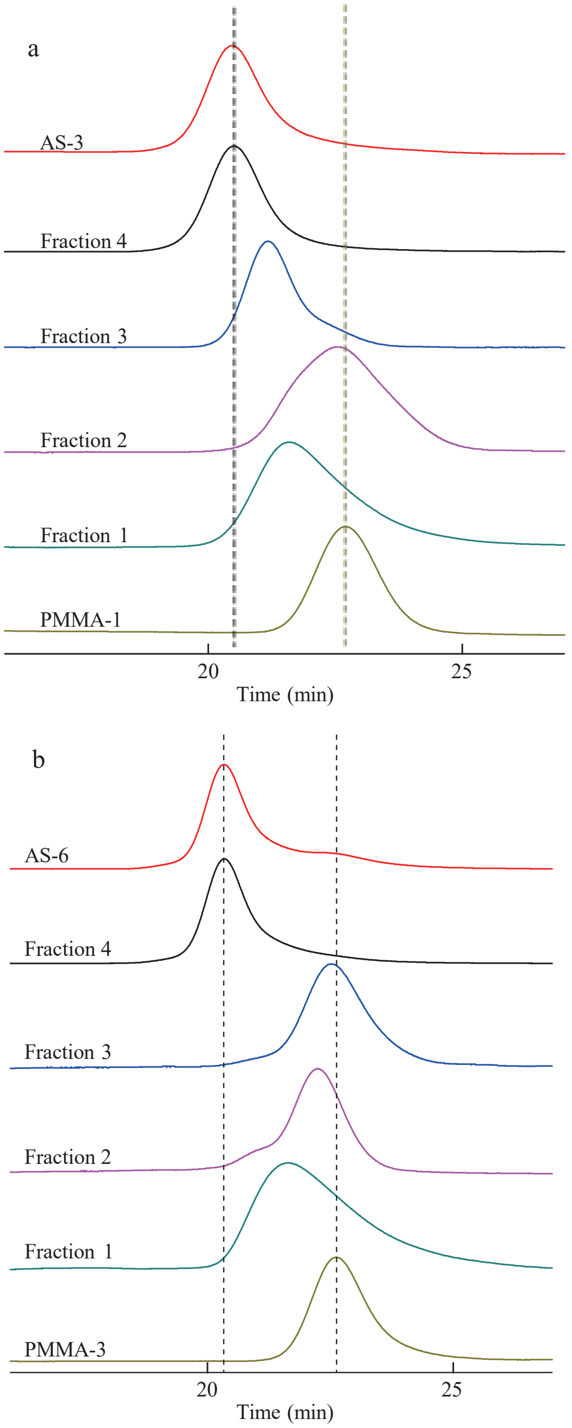


Fig. 2 GPC curves of (a) PMMA-1 macroinitiator, as-synthesized AS-3 and the corresponding fractions 1−4 from AS-3, (b) PMMA-3 macroinitiator, as-synthesized AS-6 and the corresponding fractions 1–4 from AS-6

along with the same successive precipitation step. Under the same fractionation conditions, more precipitates were obtained in fraction 4 of AS-6 than in fraction 4 of AS-3. These observations revealed that chain termination happened during the entire polymerization process, which resulted in the formation of PMMA-*b*-PS block copolymers with a range of molecular weights of the PS block, and the CuBr/PMDETA catalyst led to more chain termination than the CuCl/PMDETA catalyst did.

Self-assembly of PMMA-*b*-PS on Neutral Brush

CEF has a huge effect on the synthesis of PMMA-*b*-PS block copolymers. Although the macroinitiators had the same molecular weights and as-synthesized PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br block copolymers had the same volume fractions, defect-free directed self-assembly of as-synthesized PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br block copolymers was obtained on chemical patterns with different pattern periods. This result demonstrated that as-synthesized PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br block copolymers had different domain sizes (L_o). Analysis of the fractionation results confirmed that as-synthesized PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br contained different amounts of homopolymers and low molecular block copolymers, which contributed to such difference.

The same polymerization and fractionation procedures were used to prepare symmetric lamellar-forming PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br. Although PMMA-Cl and PMMA-Br macroinitiators had similar M_n of ~50 kg/mol, L_os of purified lamellar-forming PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br were 50.5 and 40.2 nm (Figs. 3a and 3b), respectively, as characterized by small angle X-ray scattering (SAXS) (Fig. 3c). The disappearance of the secondary peak in SAXS profiles confirmed that purified PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br were highly symmetric. This difference in the molecular weight of the living initiators resulted in different L_os in final symmetric block copolymers. Such big difference in L_o of PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br

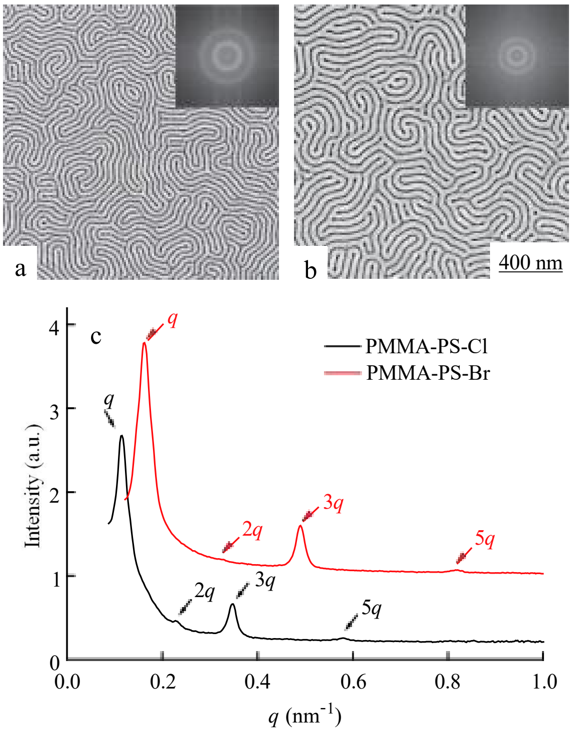


Fig. 3 (a, b) SEM images and 2D-FFTs (inset) of PMMA-*b*-PS-Br (a) and PMMA-*b*-PS-Cl (b) films assembled on PMMA-*r*-PS neutral brush at 250 °C for 10 min; (c) SAXS profiles of PMMA-*b*-PS-Br (L_o = 40.2 nm) and PMMA-*b*-PS-Cl (L_o = 50.5 nm)

also proved that the molecular weight of PMMA-Br macroinitiators with living Br chain ends was much smaller than that of PMMA-Cl macroinitiators with living Cl chain ends, while the dead PMMA in PMMA-Br macroinitiators had higher molecular weight than the dead PMMA in PMMA-Cl macroinitiators.

Compared to other CEF analysis techniques, *e.g.* ^{1}H-NMR spectroscopy[11], mass spectroscopy (MS)[8, 15], and 2D HPLC-GPC chromatography[18], our purification approach can not only provide information on the CEF, but also purify block copolymers in 10 g scale for further self-assembly study. Purified PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br were deposited on the silicon substrates modified with PMMA-*r*-PS random copolymer neutral brushes with 55 mol% of St fraction to yield films of ~50 nm thickness that were annealed at 250 °C for 10 min[19, 21, 28]. After self-assembly, SEM analysis showed that perpendicularly orientated fingerprint-like lamellar structures were obtained on neutral brushes in both films[29, 30]. The period of the fingerprints in the SEM image, as calculated by fast Fourier transform analysis, agreed well with the L_0 of the corresponding PMMA-*b*-PS block copolymer.

CONCLUSIONS

In summary, fractionation is an efficient and reliable approach to characterizing the CEF or the degree of chain termination in block copolymers prepared by ATRP and, more broadly, other polymerization techniques. PS and PMMA homopolymers and low molecular weight PMMA-*b*-PS fractions were separated by cyclohexane extraction and THF/cyclohexane fractionation and quantified. The amounts of dead chains in PMMA-Cl and PMMA-Br macroinitiators were 5.0 wt% and 14.2 wt%, respectively, indicating that the TsCl/CuCl/bpy initiation system had a better preservation of the halogen CEF than the EPBA/CuBr/bpy initiation system. The extent of chain transfer to St monomers was similar for both CuBr/PMDETA and CuCl/PMDETA catalysts, but chain termination was also more significant in PMMA-*b*-PS-Br catalyzed by CuBr/PMDETA than in PMMA-*b*-PS-Cl catalyzed by CuCl/PMDETA since the fraction of low molecular weight PMMA-*b*-PS was 16.7 wt% versus 1.8 wt% in the final products. When the same molecular weight PMMA-Cl and PMMA-Br macroinitiators were used, the L_0 of purified lamellae-forming PMMA-*b*-PS-Cl and PMMA-*b*-PS-Br diblock copolymers were significantly different due to the loss of CEF to different extents. As a result, a higher halogen CEF in the synthesis of PMMA-*b*-PS block copolymers, as well as a better control of target molecular weight, was achieved by the combination of TsCl/CuCl/bpy and CuCl/PMDETA than the combination of EPBA/CuBr/bpy and CuBr/PMDETA under the same polymerization conditions.

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