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Comprehensive Study on Chain-End Transformation of Polymer-Iodides with Amines for Synthesizing Various Chain-End Functionalized Polymers

Chen Chen,^{1‡} Longqiang Xiao,^{1‡} Atsushi Goto^{1}*

¹Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences,
Nanyang Technological University, 21 Nanyang Link, 637371 Singapore

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chain-end transformation, primary amines.

ABSTRACT: Chain-end functionalized polymers (Polymer-NHR) were successfully synthesized through the reaction of a polymer-iodide (Polymer-I) with a primary amine (NH_2R), where the R moiety contains a functional group. This reaction was comprehensively studied for three different polymers, i.e., poly(butyl acrylate), polystyrene, and poly(methyl methacrylate), and six different functional amines with phenyl, alkyl, triethoxysilyl, SH, OH, and NH_2 functionalities, and the detailed reaction mechanisms were probed by using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). This chain-end transformation reaction is easy to perform, amenable to various polymers and functional amines, and also quantitative and selective in many cases. This synthetic technique may serve as a useful platform method for synthesizing various chain-end functionalized polymers.

INTRODUCTION

Chain-end functionalized polymers are employed in many applications.¹⁻³ They can be connected to other polymers and are widely used as building blocks for synthesizing block copolymers and topological polymers such as star, comb, and network polymers. They can be connected to small molecules and biomolecules and also on solid surfaces to generate polymer brushes on surfaces. Such connection can be via chemical and physical bonding. External stimuli such as heat, light, moisture, pH, catalysts, and enzymes can trigger the connection and also the disconnection of the polymers. Thus, chain-end functionalized polymers can create advanced stimuli-responsive materials, where structures can be controllably constructed and deconstructed by external stimuli.

Functional groups can be attached at the initiating and terminating (growing) polymer chain ends. Living radical polymerization (LRP) enables the rational design of polymers possessing well-defined initiating and growing chain ends. LRP utilizes the reversible activation of a dormant species (Polymer-X) to a propagating radical (Polymer[•]) (Scheme 1a).⁴⁻¹⁹ We may design functional initiating dormant species and/or conduct post chain-end transformation of the capping agents X to functional groups for obtaining various chain-end functionalized polymers.

Scheme 1. Reversible activation: (a) General scheme and (b) Organocatalyzed LRP.

(a) Reversible activation (general scheme)

(b) Organocatalyzed LRP

We developed organocatalyzed LRP using iodine as X and organic molecules as catalysts (Scheme 1b).²⁰⁻²⁸ This is the first LRP for the use of organic catalysts. Attractive features of this LRP include no use of special capping agents or expensive catalysts. This LRP is metal-free, easy to operate, and amenable to a wide range of monomers and polymer structures. The obtained polymer (polymer-iodide (Polymer-I)) has iodine at its growing chain end. In this work, we attempted to transform iodine to functional groups to synthesize chain-end functionalized polymers. Polymer-I was reacted with a primary amine (NH_2R) (through a substitution reaction) to generate polymer-NHR, where the R moiety can contain a functional group. We synthesized various chain-end functionalized polymers using various functional amines.

The reaction with NH_2R was utilized for the chain-end transformation of polymer-bromide (Polymer-Br)²⁹⁻³¹ prepared by atom transfer radical polymerization (ATRP).⁶⁻⁹ Chain-end functionalized polymers with an OH functionality were successfully obtained from Polymer-Br (polyacrylate and polystyrene) using $\text{NH}_2(\text{CH}_2)_4\text{OH}$.^{29,31} Polymer-I (studied in the present work) should be more reactive than Polymer-Br, because the carbon-iodine bond is weaker than the carbon-bromine bond, and hence faster reaction is expected. In the present work, we did not limit our study to the OH functionality for the two polymers. Instead, we comprehensively studied this reaction for three important polymers, poly(butyl acrylate) (PBA), polystyrene (PSt), and poly(methyl methacrylate) (PMMA), and six different functional amines, and synthesized a range of chain-end functionalized polymers. The mechanistic details were also probed. The combination of organocatalyzed LRP and this post chain-end transformation may serve as a useful technique for preparing chain-end functionalized polymers.

RESULTS AND DISCUSSION

Table 1. Preparation and Characterization of Polymer-I.

entry	Polymer-I	Polymerization Condition	Conv (%)	M_n	$M_{n,theo}$	PDI	Iodine chain-end fidelity (%)
1	PBA-I (polymer 1)	$[BA]_0/[CP-I]_0/[Bu_4NI]_0 = 8000/80/320$ (mM) at 110 °C for 6 h	36.7	5200	4900	1.36	
		after purification	–	5300	–	1.36	>95%
2	PSt-I (polymer 7)	$[St]_0/[CP-I]_0/[AIBN]_0/[Bu_4NI]_0 = 8000/160/60/40$ (mM) at 80 °C for 9 h	85.0	4200	4500	1.25	
		after purification	–	4500	–	1.21	90%
3	PMMA-I (polymer 9)	$[MMA]_0/[CP-I]_0/[Bu_4NI]_0 = 8000/80/80$ (mM) at 70 °C for 35 min	27.1	3000	2900	1.16	
		after purification	–	3100	–	1.15	98%

Preparation and Characterization of Polymer-Iodides. Table 1 summarizes the synthetic conditions, number-average molecular weight M_n , and polydispersity index (PDI) (M_w/M_n , where M_w is the weight-average molecular weight) of the polymer-iodides, i.e., PBA-I, PSt-I, and PMMA-I used in the following chain-end transformation. These polymer-iodides were synthesized in the polymerizations of BA, St, and MMA using 2-iodo-2-methylpropionitrile (2-cyano-2-propyl iodide (CP-I (Figure 1))) as an initiating alkyl iodide and tetrabutylammonium iodide (Bu_4NI) as a catalyst.²⁸ For St, a small amount of azobis(isobutyronitrile) (AIBN) was added to increase the polymerization rate. The polymer chains generated from both AIBN and CP-I bear the 2-cyano-2-propyl (CP) group. The polymerizations were intentionally stopped at relatively small M_n values (= 3000-5200) to retain the high chain-end fidelity of iodine. The polymers were purified by reprecipitation and subsequently by preparative GPC to remove trace amounts of small molecules such as monomers, catalysts, and possible impurities. The obtained polymers possess the CP group at the initiating chain-end and iodine at the growing chain-end and are termed polymer **1** (PBA-I) (Scheme 2), polymer **7** (PSt-I) (Scheme 3), and polymer **9** (PMMA-I) (Scheme 4).

Figure 1. Structures of alkyl iodide initiator and catalyst used in this work.

Scheme 2. Possible Processes of Chain-End Transformation of PBA-I with NH₂R.

R	n	Theoretical mass		
		polymer 1	polymer 2	polymer 3
(CH ₂) ₂ Ph	21	2907.70	2900.88	2826.81
(CH ₂) ₂ SH			2856.82	2782.75
(CH ₂) ₃ Si(OEt) ₃			3000.94	2926.86
(CH ₂) ₄ CH ₃			2866.90	2792.82
(CH ₂) ₂ OH			2840.84	2766.77
(CH ₂) ₂ NH ₂			2839.86	2765.79
(CH ₂) ₄ OH			2868.88	2794.80
(CH ₂) ₄ NH ₂			2867.89	2793.82

For R = (CH₂)₂OH

For R = (CH₂)₂NH₂

R	n	Theoretical mass		
		polymer 4	polymer 5	polymer 6
(CH ₂) ₂ OH	21	2692.70	2753.75	—
(CH ₂) ₂ NH ₂		—	—	2691.71

Scheme 3. Possible Process of Chain-End Transformation of PSt-I with NH₂R.

R	n	Theoretical mass	
		polymer 7	polymer 8
(CH ₂) ₂ Ph	25	2819.51	2812.69
(CH ₂) ₂ SH			2768.63
(CH ₂) ₃ Si(OEt) ₃			2912.74
(CH ₂) ₄ CH ₃			2778.70
(CH ₂) ₂ OH			2752.65
(CH ₂) ₂ NH ₂			2751.67

Scheme 4. Possible Processes of Chain-End Transformation of PMMA-I with NH₂R.

R	n	Theoretical mass			
		polymer 9	polymer 10	polymer 11	polymer 12
(CH ₂) ₂ Ph	26	2819.31	2677.38	2798.47	2766.44
(CH ₂) ₂ SH				2754.41	2722.38
(CH ₂) ₃ Si(OEt) ₃				2898.52	2866.50
(CH ₂) ₄ CH ₃				2764.48	2732.46
(CH ₂) ₂ OH				2738.43	2706.41
(CH ₂) ₂ NH ₂				2737.45	2705.42

Figure 2. MALDI-TOF-MS spectra of (a and b) PBA-I, (c) PSt-I, and (d) PMMA-I.

Figure 2 shows the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra of these polymer-iodides. For the MALDI-TOF-MS sample preparation, we used *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (for PBA, PSt, and PMMA) or dithranol (for PSt) as a matrix and NaI (for PBA) or CF₃COONa (for PSt and PMMA) as an additive salt. The studied polymers can possess ¹²C and ¹³C atoms. For simplicity, the theoretical masses discussed below and the experimental masses given in the figures (MALDI-TOF-MS spectra) are those without ¹³C atom (i.e., with only ¹²C atoms); unless otherwise specified, those masses are compared.

For PBA, the theoretical mass (formula weight) of the monomer (BA) unit is 128.0838. The initiating chain end is the CP group whose mass is 68.05. The additive cation is Na⁺ whose mass is 22.99. Let *Y* be the mass of the terminal chain-end group and *n* be the degree of polymerization. Then, the theoretical mass of PBA will be:

$$68.05 + 128.0838 \times n + Y + 22.99 \quad (\text{for PBA}) \quad (1)$$

For polymer **1** (PBA-I), the terminal group is iodine whose mass is 126.90.

Figures 2a and 2b show the MALDI-TOF-MS spectrum of the obtained PBA-I. Figure 2b shows the isotope distribution in the mass region of 2906-2916. The experimental mass distribution well matched the theoretical one. The far left peak (experimental mass = 2907.64) corresponds to the polymer without ¹³C atom (with all carbon atoms being ¹²C) whose mass is provided in Figure 2a. The second peak from the left (experimental mass = 2908.65) corresponds to the polymer possessing one ¹³C atom, and the other peaks (experimental mass = 2909.65 and so on) correspond to those possessing two or more ¹³C atoms.

As shown in Figure 2a, the peaks appeared at 128.1 mass unit intervals corresponding to the monomer unit. The experimental mass (2907.64) well matched the theoretical mass (2907.70) with $n = 21$ for polymer **1** as calculated according to eq (1). We observed only a single series of repeated peaks (i.e., only one product) in Figure 2a, confirming the high chain-end fidelity of iodine for the obtained PBA-I (>95%).

Three series of minor peaks were also observed at 2851.85, 2797.94, and 2794.01. These species seemed to be generated during the MALDI-TOF-MS analysis and were not originally present in the prepared polymer; the first one (experimental mass = 2851.85) seemed to be a species losing C_4H_9I (generating a lactone ring end group) during the MALDI-TOF-MS analysis (theoretical mass = 2851.81),³² and the second one (experimental mass = 2797.94) seemed to be a species associated with a water (H_2O) molecule (theoretical mass = 2797.62), and the third one (experimental mass = 2794.01) remains unclear. Because this polymerization is a radical polymerization, a radical-radical termination product CP-PBA-PBA-CP (theoretical mass = 2848.85) should be generated during the polymerization. However, the corresponding peak was not clearly detected, suggesting that the amount of the termination product is negligible in this case.

Similarly, the theoretical mass of PSt is:

$$68.05 + 104.0626 \times n + Y + 22.99 \quad (\text{for PSt}) \quad (2)$$

The theoretical mass for polymer **7** with $n = 25$ is 2819.51, but polymer **7** was not observed in the spectrum (Figure 2c). The carbon-iodine bond of polymer **7** is so weak that this bond could be cleaved during the MALDI-TOF-MS analysis. Therefore, we observed PSt-macromonomer

(theoretical mass = 2795.66 and experimental mass = 2795.46) with an unsaturated C=C bond generated through the elimination of HI from polymer **7**. This PSt-macromonomer seemed to be generated during the MALDI-TOF-MS analysis.³³⁻³⁸

Figure 3. ^1H NMR spectra (CDCl_3) of (a) PSt-I (polymer **7**) and (b) PMMA-I (polymer **9**).

Thus, it was difficult to characterize the obtained PSt-I by MALDI-TOF-MS. To check the iodine-chain-end fidelity, the polymer was analyzed by ^1H NMR (Figure 3a). The spectrum clearly shows signals for the methine proton at the iodine end (4.5-4.8 ppm: peak a') and the methyl protons at the CP chain end (0.8-1.2 ppm: peak d). This polymer could contain polymer **7** bearing one CP group and one iodine and also a radical-radical termination product bearing two

CP groups. Assuming that these two species are present, based on the peak area (peaks a' and d), we calculated the fraction of polymer **7** to be 90% (with $\pm 5\%$ experimental error), confirming the high iodine-chain-end fidelity (90%).

The radical-radical termination product CP-PSt-PSt-CP (theoretical mass = 2864.72 and experimental mass = 2864.48) was observed by MALDI-TOF-MS (Figure 2c), and the peak ratio of CP-PSt-PSt-CP and PSt-macromonomer (hence polymer **7**) was 30/70. This ratio is much larger than the actual ratio (10/90) determined by ^1H NMR (Figure 3a). This large discrepancy would be because the ionization of polymer **7** accompanies the reaction of polymer **7** to PSt-macromonomer and is less effective than the ionization of CP-PSt-PSt-CP which accompanies no reaction.

The theoretical mass of PMMA is:

$$68.05 + 100.0524 \times n + Y + 22.99 \quad (\text{for PMMA}) \quad (3)$$

We did not observe polymer **9** (theoretical mass = 2819.31 with $n = 26$) in the spectrum (Figure 2d). Instead, we observed two species generated from polymer **9**. One was polymer **10** (theoretical mass = 2677.38 and experimental mass = 2677.51) with a lactone ring structure generated through the elimination of CH_3I . The other was PMMA-macromonomer (theoretical mass = 2691.39 and experimental mass = 2691.57) with an unsaturated $\text{C}=\text{C}$ bond generated through the elimination of HI . These two species seemed to be generated from polymer **9** during the MALDI-TOF-MS analysis.^{38,39}

Therefore, we checked the iodine-chain-end fidelity of the obtained PMMA-I by ^1H NMR (Figure 3b). The methyl protons (a, a', and a'') at the side chain appeared at 3.55-3.77 ppm. The

main peak at 3.55-3.62 ppm and its shoulder peak at 3.62-3.65 ppm were assigned to the monomer units (a) in the middle of the chain. (The shoulder peak at 3.62-3.65 ppm may be due to a chain-end penultimate unit.) The down-field-shifted peak at 3.73-3.77 ppm was assigned to the ω -terminal chain-end unit (a') adjacent to iodine. Such a down-field shift for the ω -terminal chain-end unit was reported for PMMA-bromide.⁴⁰ From the peak area and the M_n (= 3100) determined by GPC (calibrated with standard PMMAs), the fraction of the iodine chain end was calculated to be 98% (with $\pm 5\%$ experimental error). This result means that the amount of a radical-radical termination product was small in this case. The peak at 3.65-3.68 ppm was due to the α -terminal chain-end unit (a'') adjacent to the CP group. This NMR analysis confirms the high iodine-chain-end fidelity of this polymer (98%).

Chain-End Transformation of PBA-I with $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$. We studied the chain-end transformation of PBA-I (polymer **1**) with $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$. We heated PBA-I (M_n = 5300 and PDI = 1.36) (1 eq) and excess $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ (20 eq) in a mixed solvent of diethylene glycol dimethyl ether (diglyme) (40 wt%) and 1-butanol (40 wt%) (with 20 wt% polymer) at 100 °C for 8 h (Table 2 (entry 1)). Diglyme is inexpensive and environmentally friendly and is therefore widely used as a solvent in industry. 1-Butanol is a polar solvent and accelerated the chain-end transformation reaction. After the reaction, the obtained polymer was purified by reprecipitation with methanol/water (50/50 wt%) and was further purified with preparative GPC to remove trace amounts of $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ and other low-molecular-weight species. Some oligomers might also be removed by this purification. Because the removed amount varied among runs, the molecular weight distribution (Figures 4 and 6-14) differed slightly among runs (even when the same polymer-iodide reactant was used).

Table 2. Chain-End Transformation of PBA-I (polymer 1) with Amines (NH₂R)

entry	R	Equiv of NH ₂ R	T (°C)	Solvent	t (h)	Observed polymers (%) (percentages are rough estimate from MALDI-TOF-MS spectra with 10% estimate error)		
						Polymer 2	Polymer 3	Others
1	(CH ₂) ₂ Ph	20	100	D/B ^a	8	0	100	0
2	(CH ₂) ₂ Ph	20	100	D/B ^a	1	45	55	0
3	(CH ₂) ₂ Ph	2	100	D/B ^a	24	0	100	0
4	(CH ₂) ₃ Si(OEt) ₃	20	100	diglyme ^b	8	0	100	0
5	(CH ₂) ₃ Si(OEt) ₃	20	100	diglyme ^b	1	50	50	0
6	(CH ₂) ₃ Si(OEt) ₃	2	100	diglyme ^b	24	0	80	20 (unidentified)
7	(CH ₂) ₄ CH ₃	20	100	D/B ^a	8	0	100	0
8	(CH ₂) ₄ CH ₃	20	100	D/B ^a	1	50	50	0
9	(CH ₂) ₄ CH ₃	2	100	D/B ^a	24	0	100	0
10	(CH ₂) ₂ SH	20	100	D/B ^a	8	0	50	50 (PBA-H)
11	(CH ₂) ₂ SH	20	70	D/B ^a	8	0	80	20 (PBA-H)
12	(CH ₂) ₂ SH	20	25	D/B ^a	12	0	100	0
13	(CH ₂) ₂ OH	20	100	D/B ^a	8	0	0	100 (polymer 5)
14	(CH ₂) ₂ OH	20	100	D/B ^a	1	0	80	20 (polymer 5)
15	(CH ₂) ₂ OH	2	100	D/B ^a	24	0	100	0
16	(CH ₂) ₄ OH	20	100	D/B ^a	8	0	100	0
17	(CH ₂) ₂ NH ₂	20	100	D/B ^a	1	0	0	100 (polymer 6)
18	(CH ₂) ₂ NH ₂	20	100	D/B ^a	0.17	0	30	10 (polymer 1) 60 (polymer 6)
19	(CH ₂) ₂ NH ₂	2	100	D/B ^a	1	0	0	100 (polymer 6)
C1	Ph(CH ₂) ₂ SH	20	100	D/B ^a	8	0	0	100 (PBA-H)

^a polymer 1/diglyme/1-butanol = 20/40/40 wt%. ^b polymer 1/diglyme = 20/80 wt%.

Scheme 2 shows possible mechanisms and products in the chain-end transformation of PBA-I (polymer **1**). Process (a) is the substitution of iodine of polymer **1** with an amine to produce polymer **2**. Process (b) is the intramolecular amidation of polymer **2** to produce polymer **3**, giving a 5-membered ring at the chain end. Scheme 2 shows the theoretical masses of these polymers (including the mass of Na⁺ for the MALDI-TOF-MS analysis).

Figure 4a shows the MALDI-TOF-MS spectrum. The experimental mass (2826.70) matched the theoretical mass (2826.81) of polymer **3**. We observed only a single series of repeated peaks (i.e., only one product) and did not observe the reactant polymer **1** (theoretical mass = 2907.70). Thus, polymer **1** was successfully converted to polymer **3** in a quantitative manner.

Figure 4. MALDI-TOF-MS spectra of polymers obtained through reactions of PBA-I (polymer **1**) with NH₂(CH₂)₂Ph in Table 2 (entries 1-3). The reaction conditions are given in the figure.

We also confirmed the inclusion of the $\text{NCH}_2\text{CH}_2\text{Ph}$ moiety in the polymer by ^1H NMR. Figure 5 shows the ^1H NMR spectrum. The signal of C_6H_5 (7.2-7.4 ppm) was clearly observed, demonstrating the introduction of the $\text{NCH}_2\text{CH}_2\text{Ph}$ moiety. The chain-end functionality can be estimated from the relative peak areas of C_6H_5 and the monomer units (OCH_2). We calculated the number of monomer units ($= 40$) using the M_n determined by GPC and estimated the chain-end functionality to be 105% (with $\pm 5\%$ experimental error). Thus, the chain-end functionalized polymer was quantitatively obtained.

Figure 5. ^1H NMR spectrum (acetone- d_6) of polymer obtained with a reaction of PBA-I (polymer **1**) with $\text{NH}_2(\text{CH}_2)_2\text{Ph}$ in Table 2 (entry 1).

Figure 4b shows the MALDI-TOF-MS spectrum of the polymer obtained after a shorter reaction time 1 h instead of 8 h. We observed a mixture of two products, polymer **2** (experimental mass = 2900.94 and theoretical mass = 2900.88) and polymer **3**. The relative ratio of the peak intensities was approximately 45% for polymer **2** and 55% for polymer **3**. This ratio may not necessarily correspond to the actual product ratio, because the ionization of polymer during the MALDI analysis depends on the polymer structure. In the present case, because the polymer backbones are the same (CP-PBA) and the only difference is the growing chain end, the

observed ratio should be close to the actual product ratio. This result demonstrates that polymer **1** is initially transformed to polymer **2**, which then forms polymer **3**, as described in Scheme 2.

We reduced the amount of $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ from 20 eq to 2 eq. The stoichiometric amount of amine in this chain-end transformation is 2 eq, because 1 eq of amine attaches to the polymer chain end and the other 1 eq of amine acts as a base to trap HI (hydroiodic acid) generated in this reaction. As Figure 4c shows, this stoichiometric amount (2 eq) of amine successfully provided polymer **3** virtually quantitatively, although the reaction took a relatively long time 24 h. Thus, 2 eq is sufficient to complete the reaction, when the reaction time is long enough. (HI can be trapped by the excess amine (primary amine) and also by polymer **3** (tertiary amine). The primary amine is more basic and would mainly trap HI. We did not observe the complex of HI and polymer **3** by MALDI-TOF-MS. The complex, if any present, would be unstable and release HI during the MALDI-TOF-MS analysis.) Table 2 (entries 1-3) summarizes these three results with $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$.

Figure 6. MALDI-TOF-MS spectra of polymers obtained through reactions of PBA-I (polymer **1**) with NH_2R in Table 2 (entries 4 and 7). The amines are given in the figure.

Chain-End Transformation to Alkyl and Si(OEt)₃ Groups. We used NH₂(CH₂)₄CH₃ and NH₂(CH₂)₃Si(OEt)₃ for the chain-end transformation of PBA-I (polymer **1**). Figure 6 shows the MALDI-TOF-MS spectra of the polymers obtained with 20 eq of amine at 100 °C for 8 h. In both cases, polymer **1** was virtually quantitatively converted to polymer **3** with CH₂(CH₂)₃CH₃ and CH₂(CH₂)₂Si(OEt)₃ groups at the chain end. Table 2 (entries 4-9) summarizes the results obtained at different reaction conditions.

Chain-End Transformation to SH Group. NH₂CH₂CH₂SH was used to obtain polymer **3** with a CH₂CH₂SH group. Figure 7a shows the MALDI-TOF-MS spectra of the polymer obtained with 20 eq of amine at 100 °C for 8 h. In the detailed mass distribution, we observed two products, i.e., polymer **3** (experimental mass = 2782.56 and theoretical mass = 2782.75) and PBA-H (experimental mass = 2781.60 and theoretical mass = 2781.81) with a hydrogen atom at the chain end (Figure 7d). The theoretical mass difference between the two products is 0.94 (2782.75 vs 2781.81 in Figure 7d). The observed peak intensity in Figure 7a suggests that the product yield was 50% for both polymer **3** and PBA-H.

The SH group in NH₂CH₂CH₂SH is an efficient radical chain transfer group. At the studied high reaction temperature of 100 °C, a small amount of PBA radical (PBA[•]) would be generated by the thermal dissociation of PBA-I (polymer **1**). PBA[•] can react with NH₂CH₂CH₂SH to generate PBA-H and the sulfur-centered radical NH₂CH₂CH₂S[•]. NH₂CH₂CH₂S[•] abstracts iodine from PBA-I to generate PBA[•]. This radical chain transfer cycle would lead to the observed large amount of PBA-H.

(a) 20 eq of $\text{NH}_2(\text{CH}_2)_2\text{SH}$ (100 °C, 8 h) (Table 2 (entry 10))

(b) 20 eq of $\text{NH}_2(\text{CH}_2)_2\text{SH}$ (70 °C, 8 h) (Table 2 (entry 11))

(c) 20 eq of $\text{NH}_2(\text{CH}_2)_2\text{SH}$ (25 °C, 12 h) (Table 2 (entry 12))

(d) Theoretical mass distribution

(e) 20 eq of $\text{Ph}(\text{CH}_2)_2\text{SH}$ (100 °C, 8 h) (Table 2 (entry C1))

Figure 7. MALDI-TOF-MS spectra of polymers obtained with reactions of PBA-I (polymer 1) with $\text{NH}_2(\text{CH}_2)_2\text{SH}$ and $\text{Ph}(\text{CH}_2)_2\text{SH}$ in Table 2 (entries 10-12 and C1). The reaction conditions are given in the figure.

To reduce the amount of PBA-H, we decreased the reaction temperature from 100 °C to 70 °C (Figure 7b) and 25 °C (Figure 7c). The radical generation (thermal dissociation of PBA-I) was suppressed at these lower temperatures. Thus, we successfully obtained polymer **3** with the SH functionality in a higher yield (80%) at 70 °C and a quantitative yield (100%) at 25°C. A slightly longer time 12 h was required to complete the reaction at 25 °C. An SH-functionalized polymer is difficult to obtain by using an SH containing initiator because the SH group is consumed via the chain transfer during the polymerization. It can only be obtained by post chain-end transformation, and in this regard, the obtained SH functionalized polymer is a unique polymer in the present work.

NH₂CH₂CH₂SH has NH₂ and SH groups. Both groups are nucleophiles and may undergo iodine substitution reactions. Experimentally, only polymer **3** (via the reaction with NH₂) was observed (Figures 7a, 7b, and 7c). Therefore, NH₂ is much more reactive than SH for the substitution reaction,³⁰ and SH remained as a functional group in the obtained polymer.

We in turn applied this radical chain transfer reaction to the chain-end transformation of polymer **1** to PBA-H using a thiol PhCH₂CH₂SH without the NH₂ group at a high temperature 100 °C for 8 h. In this case, only the chain transfer reaction occurred, and we quantitatively obtained PBA-H (Figure 7e). Thus, once the appropriate conditions were selected, the SH functionalized polymer (polymer **3**) (Figure 7c) and PBA-H (Figure 7e) were selectively obtained.

Chain-End Transformation to OH Group. Figure 8a shows the MALDI-TOF-MS spectrum of the polymer obtained with 20 eq of $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ at 100 °C for 8 h. The result did not match either polymer **2** or polymer **3**. Scheme 2 shows possible additional reactions of polymer **3** for $\text{R} = \text{CH}_2\text{CH}_2\text{OH}$. Similar reactions were experimentally demonstrated for low-mass alkyl bromides and polymer-bromides.²⁹ Process (c) is the intramolecular esterification of polymer **3** through the terminal OH group to produce polymer **4** with a 6-membered cyclic ester. Process (d) is the ring-opening amidation of polymer **4** through another amine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$) to produce polymer **5** with two OH groups. The result (experimental mass = 2753.76) matched polymer **5** (theoretical mass = 2753.75). We observed only a single product and hence could selectively attach two OH groups at the chain end.

To attach only one OH group, we reduced the reaction time from 8 h to 1 h for avoiding the processes (c) and (d). We in fact obtained polymer **3** with one OH group in 80% yield but still observed polymer **5** with two OH groups in 20% yield (Figure 8b). We then reduced the amount of $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ from 20 eq to the stoichiometric amount (2 eq) to attach one OH group (Figure 8c). Because of the absence of additional $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ (which offered the second OH group), we successfully obtained polymer **3** with one OH group in virtually 100% yield. An alternative method for the selective attachment of one OH group was to use $\text{NH}_2(\text{CH}_2)_4\text{OH}$ with a longer alkyl chain. In this case, polymer **4** included an energetically unfavorable 8-membered cyclic ester and was hardly generated. This method (i.e., the use of $\text{NH}_2(\text{CH}_2)_4\text{OH}$ to attach one OH group) was previously reported for polymer-bromides.^{29,31} Figure 8d shows the M

ALDI-TOF-MS result. The spectrum matched polymer **3**, demonstrating the quantitative and selective attachment of one OH group. Thus, we can selectively attach one or two OH groups by selecting appropriate reaction conditions.

Figure 8. MALDI-TOF-MS spectra of polymers obtained with reactions of PBA-I (polymer 1) with $\text{NH}_2(\text{CH}_2)_2\text{OH}$ and $\text{NH}_2(\text{CH}_2)_4\text{OH}$ in Table 2 (entries 13-16). The amines and reaction conditions are given in the figure.

Chain-End Transformation to NH_2 Group. Figure 9a shows the MALDI-TOF-MS spectrum of the polymer obtained with 20 eq of $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ at 100 °C for 1 h. Similar to $\text{R} = \text{CH}_2\text{CH}_2\text{OH}$, the reaction did not stop at polymer 3. Scheme 2 shows a possible further reaction of polymer 3 for $\text{R} = \text{CH}_2\text{CH}_2\text{NH}_2$. Process (e) is the intramolecular amidation of

polymer **3** through the terminal NH_2 group to produce polymer **6** with a 6-membered cyclic amide. The spectrum (experimental mass = 2691.69) matched polymer **6** (theoretical mass = 2691.71). Because an amide is more stable than an ester, the subsequent ring-opening of polymer **6** by the attack of another amine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) did not occur. Polymer **6** does not possess an NH_2 functionality and may not be very useful.

Figure 9. MALDI-TOF-MS spectra of polymers obtained with reactions of PBA-I (polymer **1**) with $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ in Table 2 (entries 17-19). The amines and reaction conditions are given in the figure.

To attach an NH_2 group, we reduced the reaction time from 1 h to a very short time 10 min to avoid the process (e). We observed the desired polymer **3** with an NH_2 functionality in 30% yield

but still observed polymer **6** (60%) and polymer **1** (10%) (Figure 9b). Because we observed both reactant (polymer **1**) and further reacted (polymer **6**) polymers, it could be difficult to selectively stop the reaction at the intermediate polymer **3**. The reduced amount of $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ was not effective to provide polymer **3** (Figure 9c) (as expected). We used $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$ with a longer alkyl chain to avoid the generation of polymer **6** in the same manner as $\text{NH}_2(\text{CH}_2)_4\text{OH}$. However, we obtained only a mixture of polymer **6** and other unidentified side products and were unable to obtain polymer **3** (Supporting Information (Figure S1)).

Chain-End Transformation of PSt-I with Several Amines. We studied the chain-end transformation of PSt-I. We heated PSt-I ($M_n = 4500$ and $\text{PDI} = 1.21$) (polymer **7**) (1 eq) and $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ (5 eq) in *N,N*-dimethylformamide (DMF) (80/20 wt% DMF/polymer) at 100 °C for 8 h (Figure 10a). Scheme 3 shows the possible process and product of this chain-end transformation. Process (f) is the substitution of iodine with an amine to generate polymer **8**. Unlike PBA, PSt has no ester group, and hence polymer **8** undergoes no further reaction (no ring closure). Process (f) (substitution ($\text{S}_{\text{N}}2$) reaction) can compete with the elimination of HI from polymer **7** (elimination ($\text{E}2$) reaction) generating PSt-macromonomer.

In Figure 10a, we observed the desired polymer **8** in 85% fraction and the elimination product PSt-macromonomer in 15% fraction, in addition to the originally contained CP-PSt-PSt-CP impurity. Thus, high selectivity was achieved in DMF. The selectivity was slightly lower when a mixed solvent of diglyme and 1-butanol was used (70% for polymer **8** and 30% for PSt-macromonomer, as shown in Table 3 (entry 1)). Thus, DMF was used as the solvent for the PSt experiments. We decreased the reaction temperature from 100 °C to 25 °C, but the selectivity was unchanged (Table 3 (entries 2 vs 3)). As shown in Figures 10b, 10c, and 10d, we also

obtained polymer **8** with high selectivity (75-85%) for R = (CH₂)₄CH₃, (CH₂)₃Si(OEt)₃, and (CH₂)₂OH.

Figure 10. MALDI-TOF-MS spectra of polymers obtained with reactions of PSt-I (polymer **7**) with NH₂R in Table 3 (entries 2, 4, 5, and 7). The amines are given in the figure.

Table 3. Chain-End Transformation of PSt-I (polymer 7) with Amines (NH₂R)

entry	R	Equiv of NH ₂ R	T (°C)	Solvent	t (h)	Observed polymers (%) (percentages are rough estimate from MALDI-TOF-MS spectra with 10% estimate error)		
						Polymer 8	PSt- macromonomer	Others
1	(CH ₂) ₂ Ph	5	100	D/B ^a	8	70	30	0
2	(CH ₂) ₂ Ph	5	100	DMF ^b	8	85	15	0
3	(CH ₂) ₂ Ph	5	25	DMF ^b	12	85	15	0
4	(CH ₂) ₄ CH ₃	5	100	DMF ^b	8	75	25	0
5	(CH ₂) ₃ Si(OEt) ₃	5	100	DMF ^b	8	85	15	0
6	(CH ₂) ₂ SH	5	100	DMF ^b	8	0	0	100 (unidentified)
7	(CH ₂) ₂ OH	5	100	DMF ^b	8	85	15	0
8	(CH ₂) ₂ NH ₂	5	100	DMF ^b	8	0	0	100 (unidentified)

^a polymer **7**/diglyme/1-butanol = 20/40/40 wt%. ^b polymer **7**/DMF = 20/80 wt%.

We observed unexpected and unidentified products for R = (CH₂)₂SH and (CH₂)₂NH₂ (Supporting Information (Figure S2)). Only a single species was observed in both cases, but they match neither the reactant polymer **7**, the desired product polymer **8**, nor the PSt-macromonomer and PSt-H (with a hydrogen atom at the chain end) byproducts, and remain unidentified. Table 3 summarizes the PSt results.

Chain-End Transformation of PMMA-I with Several Amines. We examined PMMA-I. We heated PMMA-I (*M_n* = 3100 and PDI = 1.15) (polymer **9**) (1 eq) and NH₂CH₂CH₂Ph (5 eq) in acetonitrile at 80 °C for 3 h (Figure 11a), producing polymer **10** with a lactone chain end almost quantitatively through the elimination of CH₃I (experimental mass = 2677.25 and theoretical mass = 2677.38) (Process (g) in Scheme 4). (The analysis of pure polymer **9** (PMMA-I) led to polymer **10** (50%) and PMMA-macromonomer (50%) as observed species (Figure 2d). Figure

11a shows only polymer **10** (100%); thus, polymer **9** was absent, and the entire observed polymer **10** was generated in the reaction with the amine.)

In the literature, polymer **10** was obtained from PMMA-Br in the presence of a metal base CH_3COOK ,⁴¹ as we also confirmed in Figure 11b using PMMA-I. This result indicates that the elimination of CH_3I (Process (g)) is a base-catalyzed reaction. This result motivated us to explore the use of an organic base, i.e., tributylamine, for this reaction instead of the metal base, and we quantitatively obtained polymer **10** (Figure 11c). Thus, the observed generation of polymer **10** with $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ (Figure 11a) must be attributed to the role of $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ as a base. These results are the first metal-free syntheses of PMMA with a lactone chain end. Table 4 summarizes the results with using polymer **9**.

(a) 5 eq of $\text{NH}_2(\text{CH}_2)_2\text{Ph}$ with polymer **9** (80 °C, 3 h) (Table 4 (entry 1))

(b) 5 eq of CH_3COOK with polymer **9** (80 °C, 3 h) (Table 4 (entry 2))

(c) 5 eq of $\text{N}((\text{CH}_2)_3\text{CH}_3)_3$ with polymer **9** (80 °C, 8 h) (Table 4 (entry 3))

Figure 11. MALDI-TOF-MS spectra of polymers obtained with reactions of PMMA-I (polymer **9**) with bases in Table 4 (entries 1-3). The bases are given in the figure.

Table 4. Chain-End Transformation of PMMA-I (polymer 9) with Amines (NH₂R)

entry	R	Equiv of NH ₂ R	T (°C)	Solvent	t (h)	Observed polymers (%) (percentages are rough estimate from MALDI-TOF-MS spectra with 10% estimate error)		
						Polymer 10	Polymer 12	Others
1	(CH ₂) ₂ Ph	5	80	AN ^a	3	100	0	0
2	CH ₃ COOK ^b	5	80	AN ^a	3	100	0	0
3	TBA ^b	5	80	AN ^a	8	100	0	0
4	(CH ₂) ₂ Ph	20	120	EB ^c	24	10	25	65 (polymer 11)
5	(CH ₂) ₄ CH ₃	20	120	EB ^c	24	25	25	50 (unidentified)
6	(CH ₂) ₃ Si(OEt) ₃	20	120	EB ^c	24	55	25	20 (unidentified)
7	(CH ₂) ₂ SH	20	120	EB ^c	24	10	0	90 (PMMA-H)
8	(CH ₂) ₂ OH	20	120	EB ^c	24	70	30	0
9	(CH ₂) ₂ NH ₂	20	120	EB ^c	24	0	0	100 (unidentified)

^a polymer **9**/acetonitrile = 20/80 wt%. ^b CH₃COOK (entry 2) and tributylamine (TBA) (entry 3) were used instead of primary amine (NH₂R). ^c polymer **9**/ethyl benzene = 20/80 wt%.

To attach NH₂CH₂CH₂Ph to the polymer chain end, we increased the amount of NH₂CH₂CH₂Ph from 5 eq to 20 eq and the reaction temperature from 80 °C to 120 °C and also used purified polymer **10** as the reactant polymer. Because of the elevated temperature, we switched the solvent from acetonitrile to ethyl benzene, which has a higher boiling point. Scheme 4 shows possible processes and products. Process (h) is the ring-opening of the lactone of polymer **10** with an amine to generate polymer **11** with an amide. Process (i) is the intramolecular imidation of polymer **11** to generate polymer **12** with a ring imide bearing the R group. These chain-end functionalized polymers (polymers **11** and **12**) possess a tertiary OH group in addition to the attached R group. We observed the reactant polymer **10** (55%) and product polymer **12** (45%) after 6 h (Figure 12a). When the reaction time was extended to 24 h

(Figure 12b), we observed much less reactant polymer **10** (10%), intermediate polymer **11** (20%), and much more final product polymer **12** (70%), where polymer **11** was observed as a hydrolyzed polymer **11'**. Thus, we obtained the desired chain-end functionalized polymers

Then, instead of polymer **10**, we used polymer **9** (PMMA-I) as the reactant polymer. The reaction with polymer **9** was slightly slower than that with polymer **10**; we observed a small amount of polymer **10** (10%), more intermediate polymer **11** (65%), and less final product polymer **12** (25%) (Figure 12c). Nevertheless, we still obtained the desired chain-end functionalized polymers (polymers **11** and **12**) in a high yield (totally 90%).

Figure 12. MALDI-TOF-MS spectra of polymers obtained with reactions of PMMA-I (polymer **9**) and polymer **10** with $\text{NH}_2(\text{CH}_2)_2\text{Ph}$ in Table 4 (entry 4) and Table 5 (entries 1 and 2). The polymers and reaction conditions are given in the figure.

Figure 13. MALDI-TOF-MS spectra of polymers obtained with reactions of polymer **10** with NH_2R in Table 5 (entries 3, 4, and 6). The amines are given in the figure.

We studied other amines using polymer **10**. The product polymer **12** was obtained in 100% yield for $\text{R} = (\text{CH}_2)_4\text{CH}_3$ and $(\text{CH}_2)_2\text{OH}$ and in 60% yield for $\text{R} = (\text{CH}_2)_3\text{Si}(\text{OEt})_3$ (Figure 13). Polymer **12** with $\text{R} = (\text{CH}_2)_2\text{OH}$ is unique, possessing two OH groups of different types, i.e., a tertiary and a primary OH group at the chain end. No reaction occurred for $\text{R} = (\text{CH}_2)_2\text{SH}$, and only unidentified byproducts were generated for $\text{R} = (\text{CH}_2)_2\text{NH}_2$ (Supporting Information (Figure S3)). Table 5 summarizes the results with using polymer **10**.

Instead of polymer **10**, we used polymer **9** (PMMA-I) for these five amines. The reaction was quite slow, generating product polymer **12** in only 25-30% yield, for $\text{R} = (\text{CH}_2)_4\text{CH}_3$, $(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, and $(\text{CH}_2)_2\text{OH}$ (Figures 14a, 14b, and 14d). We obtained PMMA-H with a hydrogen atom by using $\text{NH}_2(\text{CH}_2)_2\text{SH}$ (Figure 14c); in this process, the SH group acted as a

chain transfer agent, and the (slow) thermal dissociation of polymer **9** (PMMA-I) triggered the reaction. Only unidentified byproducts were generated for $R = (CH_2)_2NH_2$ (Supporting Information (Figure S4)). Table 4 (entries 5-9) summarizes these results with polymer **9**. Although the results with polymer **9** were not very satisfactory, the chain-end transformation of PMMA with amines using polymer **10** should be fairly useful (as discussed above).

Figure 14. MALDI-TOF-MS spectra of polymers obtained with reactions of PMMA-I (polymer **9**) with NH_2R in Table 4 (entries 5-8). The amines are given in the figure.

Table 5. Chain-End Transformation of PMMA with a lactone ring chain end (polymer 10) with Amines (NH₂R)

entry	R	Equiv of NH ₂ R	T (°C)	Solvent	t (h)	Observed polymers (%) (percentages are rough estimate from MALDI-TOF-MS spectra with 10% estimate error)		
						Polymer 10	Polymer 12	Others
1	(CH ₂) ₂ Ph	20	120	EB ^a	6	55	45	0
2	(CH ₂) ₂ Ph	20	120	EB ^a	24	10	70	20 (polymer 11)
3	(CH ₂) ₄ CH ₃	20	120	EB ^a	24	0	100	0
4	(CH ₂) ₃ Si(OEt) ₃	20	120	EB ^a	24	40	60	0
5	(CH ₂) ₂ SH	20	120	EB ^a	48	100	0	0
6	(CH ₂) ₂ OH	20	120	EB ^a	24	0	100	0
7	(CH ₂) ₂ NH ₂	20	120	EB ^a	48	0	0	100 (unidentified)

^a polymer **10**/ethyl benzene = 20/80 wt%.

CONCLUSIONS

Chain-end functionalized polymers were successfully prepared through reactions of polymer-iodides and functional amines. Phenyl, alkyl, Si(OEt)₃, SH, and OH functionalities were attached at the chain end, and the reaction mechanisms were elucidated in detail. In addition, through radical chain transfer and CH₃I elimination reactions, hydrogen and lactone chain ends were also obtained. The reactant polymer-iodides can be synthesized by organocatalyzed LRP. The studied chain-end transformation reactions are metal-free, easy to perform, and versatile in wide ranges of polymers and functional groups. The combined use of organocatalyzed LRP and this post chain-end transformation may be useful for synthesizing various chain-end functionalized polymers.

ASSOCIATED CONTENT

Supporting Information

Experimental Section and MALDI-TOF-MS spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: agoto@ntu.edu.sg

Author Contributions

‡These authors (CC and LX) contributed equally.

Notes

The authors declare no competing financial interest.

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