Atom Transfer Radical Polymerization of Styrene and Acrylates: Effects of Catalyst, Ligand, Solvent, and Initiator

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Abstract

Well-defined polystyrenes were successfully prepared by the CuX/(dN)bpy or CuX/ PMDETA catalyzed atom transfer radical polymerization of styrene using 1-phenylethyl bromide (1-PEBr) or benzyl bromide (BnBr) as initiators. We found that the CuX/PMDETA catalyzed ATRP of styrene proceeded faster than CuX/(dN)bpy catalyzed counterpart in bulk, diphenyl ether (DPE) and anisole. Using CuX/(dN)bpy catalyst, well-defined polystyrenes were obtained with good chain-end functionalities and low polydispersity (M_w/M_n <1.5) compared to CuX/PMDETA catalyst. The CuBr/PMDETA catalyzed ATRP of *n*-butyl acrylate (*n*BA), *n*-butyl methacrylate (*n*BMA), and *tert*-butyl methacrylate (*t*BMA) were also proceeded in a controlled manner. The molecular structure and molecular weight of polymers were determined by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and size exclusion chromatography (SEC), respectively.

Keywords: Atom transfer radical polymerization; Well-defined polymer; Low polydispersity; Chain-end functionality.

1. Introduction

Free radical addition polymerization is one of the most used industrial polymerization techniques, widely used to produce a wide variety of polymeric materials such as plastics, rubbers, and fibers [1]. This method can be employed under simple conditions, and it has some advantages like insensitivity to impurities, moderate temperatures, and multiple polymerization processes. However, this method has poor control over the molecular weights and polydispersity of the resulting polymer. The preparation of well-defined polymers or copolymers with predetermined molecular weights and chain-end functionalities is complicated. To overcome these disadvantages, various

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controlled/''living'' radical polymerizations (CRPs) such as nitroxide-mediated radical polymerization (NMP) [2,3], atom transfer radical polymerization (ATRP) [4-9], reversible addition-fragmentation chain transfer (RAFT) polymerization [10-12], single electron transfer (SET) [13], and single-electron transfer-reversible addition-fragmentation chain transfer (SET-RAFT) polymerization [14-16] have been developed. Among these techniques, ATRP has become an important technique for preparing well-defined polymers because of its good control over the polymer chain length, chain-end functionalities, broad applicability to a wide range of monomers, and mild reaction conditions. It was developed independently by Matyjaszewski and Wang [4,5] and Sawamoto *et al*. [7] in 1995. There have been reported various well-defined homopolymers, block, and random copolymers synthesized by ATRP [4,5,17-41]. In ATRP, the ratio of monomer to the initiator in the polymer chain is used to determine the molecular weights of the resulting polymer. New advanced materials can be synthesized by varying the composition of the polymer chains and the topology of the polymer.

The controlled ATRP of styrene [5,19,42) and acrylates [4,5,43] have been reported using a copper-based catalytic system.

Qiu and Matyjaszewski reported the ATRP of substituted styrenes in diphenyl ether at 110 °C using the molar ratio of $[S]_o/[I]_o/[CuBr]_o/[bpy]_o = 100/1/1/3$. The number-average molecular weights of poly(styrenes) were in good agreement with the calculated one, and polydispersities were relatively low ($M_w/M_n < 1.5$) [44].

Davis and Matyjaszewski synthesized poly(*n*-butyl methacrylate) with controlled molecular weights and low polydispersities by the CuX/PMDETA catalyzed ATRP performed in anisole setting the molar ratio of $[nBMA]_o/[I]_o/[CuBr]_o/[PMDETA]_o$ to 100/1/1/1 [45].

Krishnan's group reported the CuX/PMDETA catalyzed ATRP of *t*-butyl methacrylate (*t*BMA) in bulk and diphenyl ether. They investigated the initiator, ligand, and solvent effects on the yield and the M_n of P*t*BMA [46].

In the present work, we have successfully synthesized well-defined linear polymers with chain-end functionalities by the atom transfer radical polymerization (ATRP) of various monomers such as styrene (S), *n*-butyl acrylate (*n*BA), *n*-butyl methacrylate (*n*BMA), and *tert*-butyl methacrylate (*t*BMA) using the molar ratio of [monomer]$_o$/[initiator]$_o$/[copper halide]$_o$/[ligand]$_o$ = 100/2/2/6. The effects of catalyst, ligand solvent, and initiator on the yields, the molecular weights (M_n), the polydispersity (M_w/M_n), and the chain-end functionalities were investigated in detail. These polymers were characterized by nuclear magnetic spectroscopy (^{1}H NMR) and size exclusion chromatography (SEC).

2. Experimental

2.1. *Materials and methods*

All the monomers (S, *n*BA, *n*BMA, and *t*BMA), catalysts (copper halide (CuX, X = Cl, Br)), and solvents (diphenyl ether, anisole) used in this study were purified according to a

standard procedure. The ATRP ligands (2,2'-bipyridine (bpy), 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA)) and initiators (1-penylethyl bromide (1-PEBr) and benzyl bromide (BnBr)) were used as received without further purification. The ^1H NMR of polymers were measured in CDCl$_3$ at 25 °C operating at 400 MHz using the JEOL JNM-ECS 400SS spectrometer, and the chemical shifts were expressed in δ ppm. The molecular weights and molecular weight distributions (M_w/M_n) of polymers were determined by size exclusion chromatography (SEC) with Tosoh instrument with HLC 8020 UV (254 nm) detection. DMF was used as a carrier solvent at a flow rate of 1.0 mL min^{-1} at 40 °C. Two polystyrene gel columns of bead size 10 μm (Shodex KF-806L, Showa Denko K. K.) were used.

2.2. *Synthesis of function linear polymers by ATRP*

Representative synthesis procedure for polystyrene, PS: CuCl (20.4 mg, 0.206 mmol), styrene (S) (1.05 g, 10.1 mmol), and diphenyl ether (DPE) (2.5 mL) were taken into a 6 mL of the vial, successively. The mixture was purged with argon for 5 min, and then bpy (93.9 mg, 0.601 mmol) was added. 1-PEBr (42.5 mg, 0.230 mmol) was added as an initiator into the mixture after an additional 5 min of argon bubbling. The molar ratio of $[S]_o/[1\text{-PEBr}]_o/[CuCl]_o/[bpy]_o$ was set to 100/2/2/6. The reaction was carried out in an oil bath at 110 °C for 24 h with stirring at 400 rpm. **PS** was precipitated by dropwise addition into 125 mL of methanol. The polymer mixture was again dissolved in 5 mL of THF and passed over an alumina column for removing copper metals. Finally, the resulting polymers were precipitated by dropwise addition into methanol, followed by filtration, and then dried in vacuo at 40 °C to afford a white powder. The molecular structure and molecular weights of **PS** were determined by ^1H NMR spectroscopy and SEC, respectively. **PS**: 59 % yield; $M_{n, th} = 3,260$, $M_{n, SEC} = 4,040$, $M_{n, NMR} = 3,930$, $M_w/M_n = 1.09$, $f_{SEC} = 98$ %, $f_{NMR} = 74$ %.
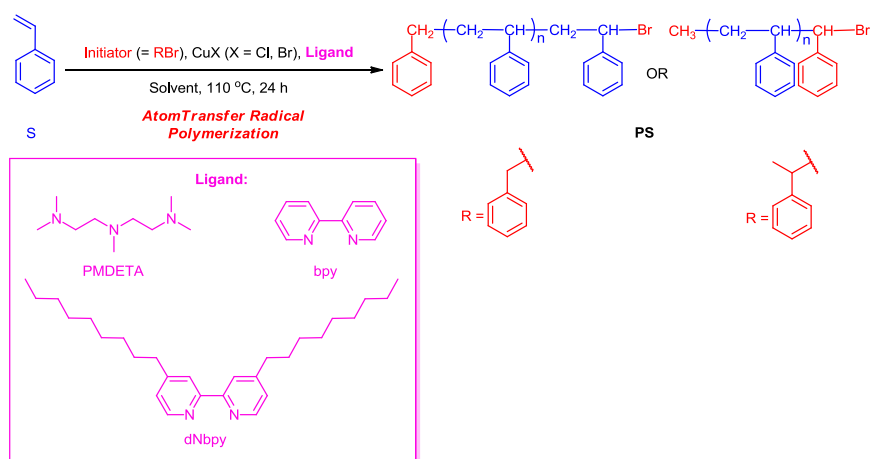
Scheme 1. Synthesis of **PS** by ATRP.

PnBA: 53 % yield; $M_{n, th} = 3,580$, $M_{n, SEC} = 7,830$, $M_w/M_n = 1.47$.
PnBMA: 48 % yield; $M_{n, th} = 3,600$, $M_{n, SEC} = 5,450$, $M_w/M_n = 1.15$.
PtBMA: **PtBMA** was collected by the precipitation into 125 mL of a ratio of methanol and water (1/1). The polymer mixture was dissolved in 5 mL of THF and passed over the alumina column for removing copper metals. Finally, the resulting **PtBMA** was precipitated by dropwise addition in a 1/1 MeOH/H$_2$O mixed solvent, followed by filtration, and then dried in vacuo at 40 °C to provide a white powder. Yield: 39 %; $M_{n, th} = 2,960$, $M_{n, SEC} = 6,190$, $M_w/M_n = 1.24$.

3. Results and Discussion

3.1. *Synthesis of linear polystyrene (PS) by the atom transfer radical polymerization of styrene (S)*

PS was synthesized by the ATRP of S, as illustrated in Scheme 1. The effects of catalyst, ligand, solvent, and initiator on the yield, the polydispersity, and the chain-end functionalities were outlined in Table 1.

Table 1. Effects of catalyst, ligand, solvent, and initiator on ATRP of styrene.[a]

Entry	Solvent	Ligand	Catalyst	Yield (%)	$M_{n,th}$	$M_{n,SEC}$[b]	$M_{n,NMR}$[c]	M_w/M_n[b]	Degree of Functionality (%)	
									SEC	NMR
1	Bulk	PMDETA	CuBr	93	5,030	4,380	4,760	1.23	21	22
2	DPE	PMDETA	CuBr	81	4,400	4,470	4,240	1.27	40	38
3	DPE	PMDETA	CuCl	85	4,610	4,570	4,400	1.25	21	27
4	Anisole	PMDETA	CuBr	89	4,820	6,960	7,000	1.61	52	50
5	Bulk	bpy	CuBr	71	3,880	3,530	3,310	1.16	99	73
6	DPE	(dN)bpy	CuBr	54	3,000	3,070	2,980	1.06	99	75
7	DPE	bpy	CuCl	59	3,260	4,040	3,930	1.09	98	74
8[d]	DPE	bpy	CuBr	41	2,310	3,030	-	1.06	97	-
9[e]	DPE	bpy	CuBr	38	4,140	4,020	3,900	1.06	92	81

[a] Polymerizations were conducted out at 110 °C for 24 h. S/1-PEBr/CuX/PMDETA(bpy) = 100/2/2/6.
$M_{n, th} = [\{(MW)_S \times Conversion \times ([S]_o/[1\text{-}PEBr]_o)\} + (MW)_{1\text{-}PEBr}]$.
[b] Determined by SEC.
[c] Determined by ^{1}H NMR spectroscopy.
[d] BnBr was used as an initiator instead of 1-PEBr.
[e] S/1-PEBr/CuBr/bpy = 100/1/1/3 (molar ratio).

3.1.1. *Effect of catalyst in the polymerization of styrene*

The effect of copper halide (CuX, X= Cl, Br) and PMDETA/bpy ligand-based catalysts in the ATRP of styrene performed in bulk or DPE was investigated using 1-PEBr as an initiator. The yield was increased when polymerization with CuBr/PMDETA catalyst was conducted in bulk. On the other hand, the chain-end functionalities were lost compared to DPE, probably due to the chain termination (entry 2 vs 1). CuCl/PMDETA catalyst with 1-PEBr affects the yield of polymers compared to CuBr/PMDETA (entries 2 and 3), and the polydispersity index (M_w/M_n) was slightly low. The yield of polymers was also

enhanced when CuCl was used instead of CuBr with bpy (entries 6 and 7). CuCl with 1-PEBr showed high efficiency than CuBr with 1-PEBr in the ATRP of S. This mixed halogen system was assisted in decreasing the propagating rate since R−Cl has a stronger C−X bond than R−Br [47-50].

3.1.2. *Effect of ligand*

The complex formed from PMDETA with CuX showed higher reactivity than (dN)bpy in bulk and DPE due to its lower redox potential [51]. By contrast, when bpy or dNbpy was used as a ligand with CuX, higher chain-end functionalities were obtained, and the M_w/M_n values were relatively lower than in CuX/PMDETA catalyst (entry 1 vs. 5; entry 2 vs. 6; entry 3 vs. 7). The M_n of **PS** was in good agreement with that calculated when the CuX/PMDETA or CuX/(dN)bpy catalyzed ATRP was employed in bulk or DPE.

3.1.3. *Effect of solvent*

The yield of polymers in anisole, DMF (not reported due to low conversion), and DPE were comparable with CuBr/PMDETA catalyst system. In anisole, the M_n of **PS** with a high polydispersity ($M_w/M_n = 1.61$) was somewhat higher than that calculated due to the bimolecular termination at the early stage of the polymerization (entries 2 and 4).

3.1.4. *Effect of initiator*

When BnBr initiator was used instead of 1-PEBr in the ATRP of styrene, low reactivity was observed due to the formation of less active 1° radicals during polymerization. The yield of **PS** in polymerization using the molar ratio of 1-PEBr/CuBr/bpy (= 2/2/6) was higher than that using the ratio was 1/1/3 (entries 6 and 9).

From these results, the combination of bpy or dNbpy as a ligand and DPE as a solvent were the suitable ATRP conditions for the synthesis of well-defined **PS** with good chain-end functionalities.

The ^{1}H NMR spectra of **PS** are shown in Fig. 1. In all spectra, signals at 1.42, 1.85, and 6.20-7.23 ppm were observed for methylene (a), methine (b), and phenyl (c) protons, respectively. The signals that appeared at 1.10 and 4.20-4.62 ppm indicated the presence of methyl (–C<u>H</u>$_3$) and methine protons with bromine atom (−C<u>H</u>Br) at the chain end of **PS**. The signals for phenyl protons in the initiator moiety were overlapped with those of phenyl protons (c) in the styrene repeating units.
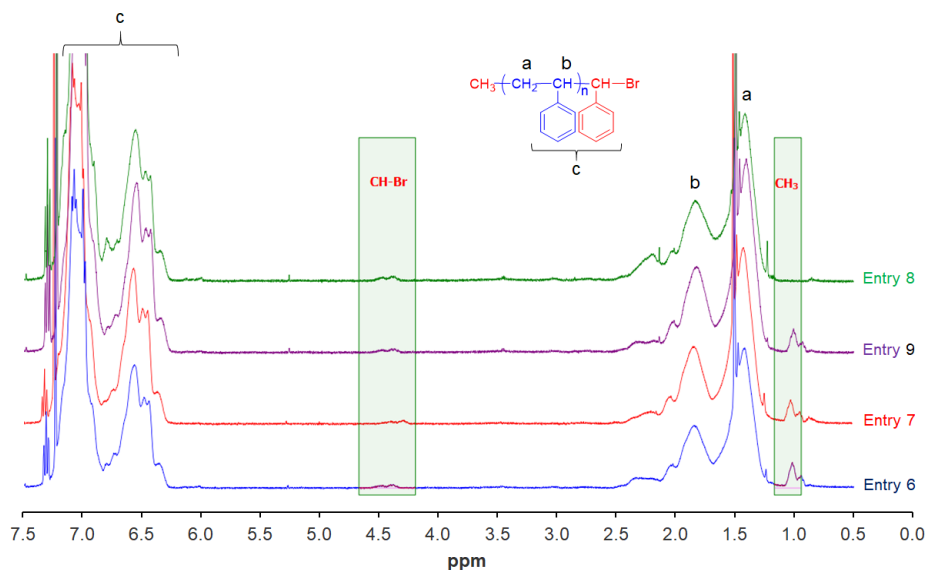
Fig. 1. ^{1}H NMR spectra of **PS** in CDCl$_3$.

Fig. 2 shows the SEC traces of the 1-PEBr initiated ATRP of styrene. The molecular weight distributions (MWD) were narrowed in the SEC traces, i.e., the low polydispersity indexes (M_w/M_n). When the ATRP of styrene was carried out in anisole, the molecular weight distributions of **PS** were slightly broader (entry 4). These results indicated that well-defined **PS** with good chain-end functionalities were successfully synthesized by ATRP.
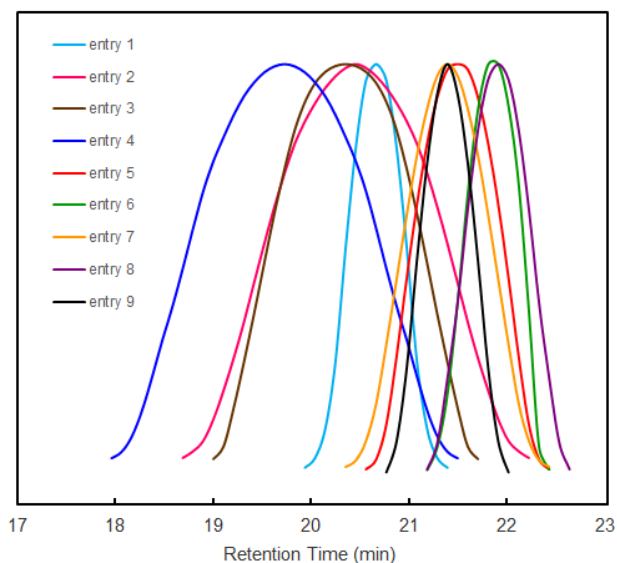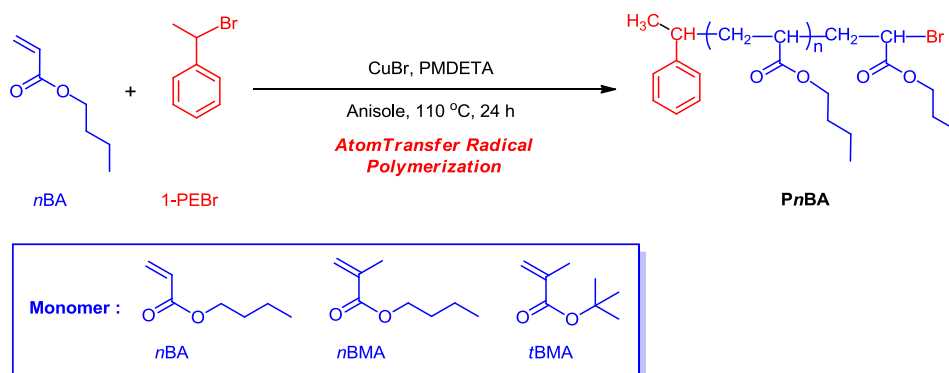

Fig. 2. SEC traces of **PS**.

Scheme 2. Synthesis of polyacrylates by ATRP.

Table 2. Characterization of polyacrylates synthesized by ATRP.[a]

Entry	Polymer	Monomer	Yield (%)	$M_{n,th}$	$M_{n,SEC}$ [b]	M_w/M_n [b]
1	P*n*BA	*n*BA	53	3,580	7,830	1.47
2	P*n*BMA	*n*BMA	48	3,600	5,450	1.15
3	P*t*BMA	*t*BMA	39	2,960	6,190	1.24

[a] Polymerizations were conducted out in anisole at 110 ^{o}C for 24 h. **M**/1-PEBr/CuBr/PMDETA = 100/2/2/6.
$M_{n, th} = [\{(MW)_{\mathbf{M}} \times Conversion \times ([\mathbf{M}]_o/[1\text{-}PEBr]_o)\} + (MW)_{1\text{-}PEBr}]$.
[b] Determined by SEC.

3.2. *Synthesis of polyacrylates by ATRP*

The polymerization system could be changed according to the monomer type of ATRP and SI-ATRP [52,53]. PMDETA as a ligand and anisole as a solvent was chosen for the ATRP of acrylate monomers (*n*BA, *n*BMA, and *t*BMA) (Scheme 2). The characterization data were summarized in Table 2.

For the catalyst system, CuBr/PMDETA catalyzed was more suitable than CuBr/bpy or CuBr/dNbpy in the ATRP [29,54] of (meth)acrylates. Low polydispersity indexes (M_w/M_n) in the ATRP of (meth)acrylate monomers were obtained when CuBr/PMDETA catalyst was used in anisole as a solvent instead of DPE. In **P*n*BA**, **P*n*BMA**, and **P*t*BMA**, the M_n of the polymer chains were slightly higher than that calculated due to the bimolecular termination at the early stage of the polymerization. The polydispersity indexes (M_w/M_n) were low.
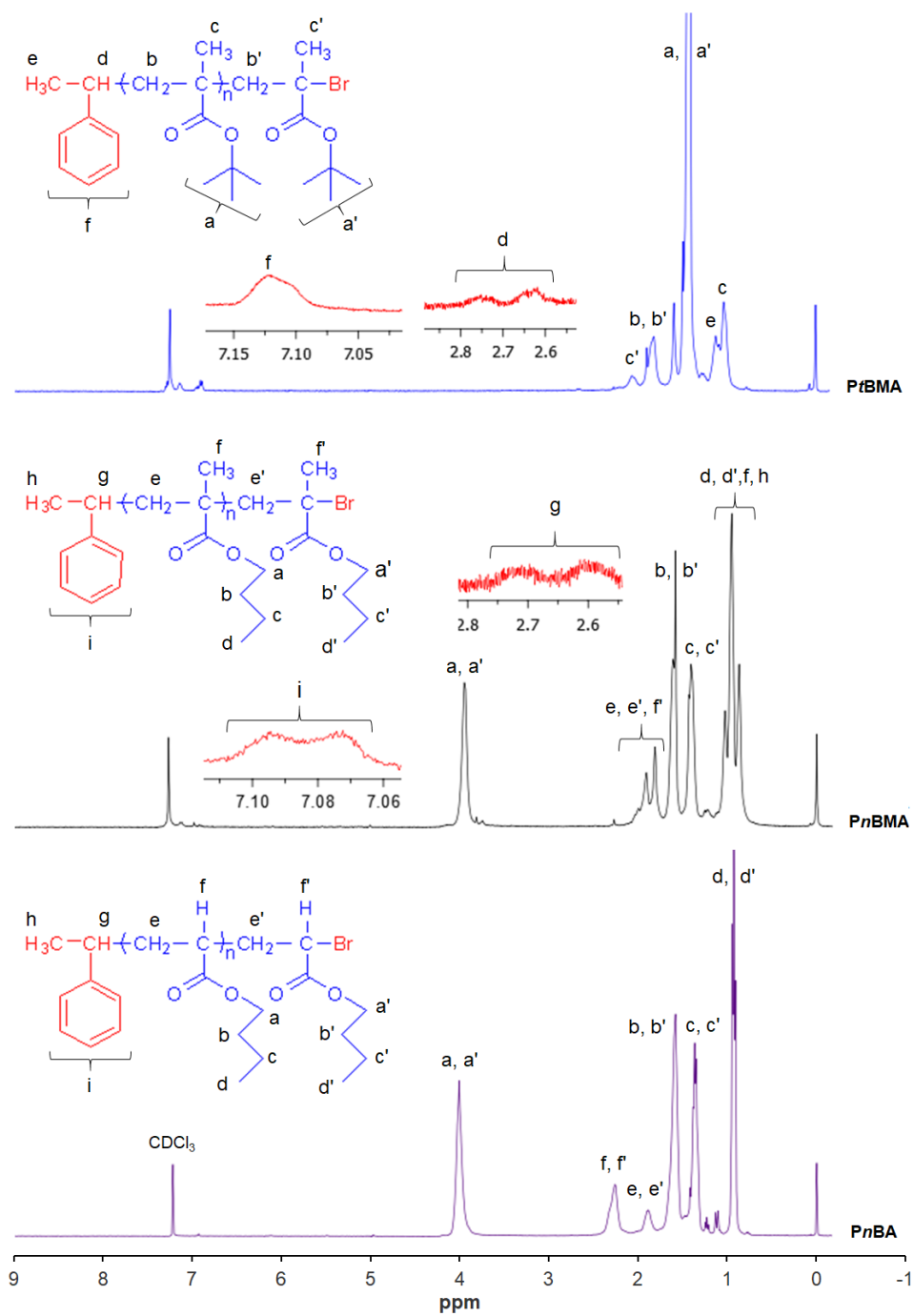
Fig. 3. ^{1}H NMR spectra of **PnBA, PnMBA,** and **PtBMA** in CDCl$_3$.

Fig. 3 shows the ^{1}H NMR spectra of **P*n*BA**, **P*n*BMA**, and **P*t*BMA**. In the NMR spectrum of **P*n*BA**, the signals at 2.28 and 1.88 ppm are the characteristic methine (f) and methylene (e) protons in the *n*BA repeating units. The signals observed at 4.04, 1.61, 1.36, and 0.94 ppm are corresponding to −OC$\underline{H}_2$ (a), −C$\underline{H}_2$ (b), −C$\underline{H}_2$ (c), and −C$\underline{H}_3$ (d) protons in the butyl group, respectively. In the NMR spectrum of **P*n*BMA**, the peaks due to methylene (e) and two different methyl (d, f) protons were observed at 1.81-1.91 and 0.87-1.03 ppm, respectively. The signals that appeared at 3.98, 1.61, and 1.43 ppm indicated OC$\underline{H}_2$, −C$\underline{H}_2$ (b), and −C$\underline{H}_2$ (c) protons of the butyl group, respectively. The characteristic signals for the phenyl (i) and methine (g) protons of the initiator were found at 7.06-7.12 and 2.50-2.80 ppm, respectively. The signals of the methyl (h) and −C(C$\underline{H}_3$)Br group (f´) protons at the chain ends were overlapped with the signals of the methyl (d, f) and methylene (e) protons in the repeating units. In the NMR spectrum of **P*t*BMA**, the signals for the methylene (b) and methyl (a, c) protons were appeared at 1.82, 1.44, 1.03 ppm, respectively. The presence of methyl (e), methine (d), and phenyl (f) protons in the initiator moiety and the −C(C$\underline{H}_3$)Br protons at the chain end were confirmed by the signals observed at 1.12, 2.50-2.80, and 7.05-7.15 ppm (in the magnified spectra) and 2.06 ppm, respectively. On the other hand, in the magnified spectra of **P*n*BA** (not shown in Fig. 3), the signal intensity (h, g, i) of the initiator moiety and methine protons with bromine atom (−C$\underline{H}$Br) at the chain end was lower compared to **P*n*BMA** and **P*t*BMA**.

The SEC traces of **P*n*BA**, **P*n*BMA**, and **P*t*BMA** are shown in Fig. 4. In SEC traces, the molecular weight distributions (MWD) of polymers were narrowed.
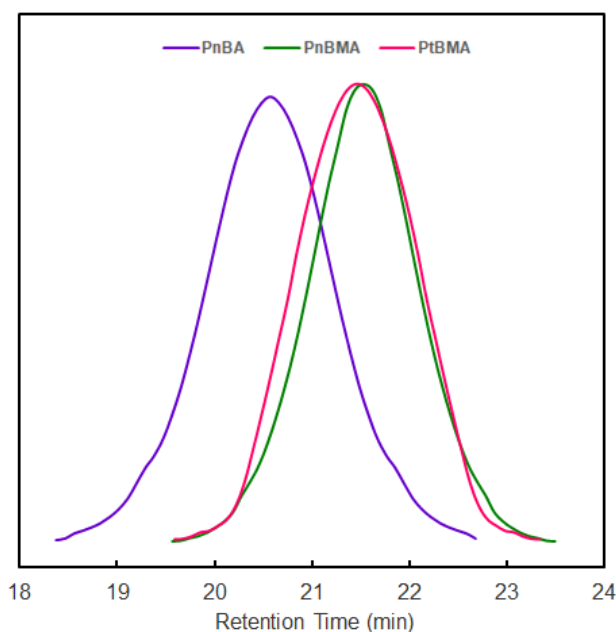

Fig. 4. SEC traces of **P*n*BA, P*n*BMA**, and **P*t*BMA**.

These results indicated that well-defined **P*n*BMA** and **P*t*BMA** with chain-end functionalities were successfully prepared by the CuBr/PMDETA catalyzed ATRP using 1-PEBr as an initiator in anisole.

4. Conclusion

Well-defined polymers were synthesized by the CuX/PMDETA(bpy) catalyzed atom transfer radical polymerization of vinyl monomers such as styrene, *n*-butyl acrylate (*n*BA), *n*-butyl methacrylate (*n*BMA), and *tert*-butyl methacrylate (*t*BMA) using 1-phenylethyl bromide as an initiator in bulk and solution. The effects of catalyst, ligand, solvent, and initiator on the yield, the molecular weights (M_n), the polydispersity (M_w/M_n), and the chain-end functionalities were investigated. We found that the CuX/PMDETA catalyzed ATRP of styrene proceeded faster in bulk, diphenyl ether, and anisole than the CuX/(dN)bpy catalyzed counterpart. Using CuX/(dN)bpy catalyst, **PS** were obtained with good chain-end functionalities and low polydispersity ($M_w/M_n < 1.5$) compared to CuX/PMDETA catalyst. The CuBr/PMDETA catalyzed ATRP of *n*-butyl acrylate (*n*BA), *n*-butyl methacrylate (*n*BMA), and *tert*-butyl methacrylate (*t*BMA) were also proceeded in anisole in a controlled manner. The molecular structure of polymers with chain-end functionalities and the M_n of polymers with molecular weight distributions (M_w/M_n) were determined by nuclear magnetic resonance (^{1}H NMR) spectroscopy and size exclusion chromatography (SEC), respectively.

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