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Synthesis and characterisation of hydroxyl end-capped telechelic polymers with poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate) backbones via atom transfer radical polymerisation

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Abstract

Hydroxyl end-capped telechelic polymers with poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate) (PMMA-*b*-PBA) backbones have been prepared via atom transfer radical polymerisation (ATRP) together with a nucleophilic substitution reaction. A hydroxyl-functionalised PMMA macroinitiator (HO-PMMA-Br) was prepared via ATRP at the optimised reaction temperature (60 °C) using 2-hydroxyethyl 2-bromoisobutyrate as the initiator. The high functionality of the bromo end group in the macroinitiator was confirmed by both ^{1}H NMR technique and a chain-extension reaction. Electrospray ionisation mass spectrometer proved to be a valuable tool for characterising PMMAs with a bromo end group (PMMA-Br), which provided signals corresponding to the intact polymers although multiply charged polymer chains were observed. The well-defined block copolymers HO-PMMA-*b*-PBA-Br were obtained by the ATRP of *n*-butyl acrylate using HO-PMMA-Br as a macroinitiator in a one-pot reaction at 100 °C. The kinetics as well as the dependence of the $M_{\mathrm{n,SEC}}$ and PDIs of the obtained block copolymers on the conversions of *n*-butyl acrylate in the chain-extension reaction suggested negligible radical termination during the reaction, demonstrating that the well-defined HO-PMMA-*b*-PBA-Br with a high functionality of bromo end group were obtained. The nucleophilic substitution reaction of a monohydroxyl-functionalised block copolymer HO-PMMA-*b*-PBA-Br with 5-amino-1-pentanol in dimethyl sulfoxide at room temperature was verified with ^{1}H and ^{13}C NMR techniques, which resulted in a series of telechelic polymers HO-PMMA-*b*-PBA-OH with a functionality of hydroxyl groups up to 1.7 according to the gradient polymer elution chromatography.

Keywords: Atom transfer radical polymerisation; Telechelic polymers; Hydroxyl end-group

1. Introduction

Recently atom transfer radical polymerisation (ATRP) has gained rapidly increasing interest due to the relatively mild reaction conditions, availability of plenty of monomers, initiators, and catalysts, and in particular its versatility in the synthesis of polymers with predictable molecular weights, low polydispersities, specific functionalities and various architectures [1–3]. ATRP is based on a fast, dynamic equilibrium established between the dormant species (alkyl halides or arenesulfonyl halides) and active species (radicals) with transition metal complexes acting as reversible halogen atom transfer reagents, which keeps a very low radical concentration (approximately 10^{-8}–10^{-7} M) [4] in the reaction system and thus results in negligible radical termination and controlled polymerisation. The end groups of the polymers prepared via ATRP are defined by the utilised initiators. When an alkyl halide (or arenesulfonyl halide) is used as the initiator, the one end group of the obtained polymer chain is the alkyl (or arenesulfonyl) group of the initiator while the other end group is the halide. This characteristic makes ATRP very useful for preparing various end-functionalised polymers because the halogen end groups of the polymers prepared via ATRP can be transformed to other functional groups using standard organic procedures such as nucleophilic substitution, atom transfer radical addition (ATRA), and so on [3]. Polymers with various functional end groups such as

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hydroxyl [5–12], azide [13,14], amine [13,15,16], allyl [7,8], hydrogen [17], maleic anhydride [8,18], and oxazoline [19] have been obtained in this way. The utilisation of an initiator that contains a hydroxyl group [19–21] or some other functionality provides polymers with a functional end group, the other end group being a halide [3]. Further transformation of the halogen group to the same functional group as the other end group will result in telechelic polymers [5,6,9,11].

Synthesis of well-defined (meth)acrylate-based polymers and exploring their potential applications in coatings are of high interest nowadays [22]. For a better understanding of the structure–property relationships of the coatings, polymers with more specific architectures, defined molecular weights, and low polydispersities are required. From this point of view, the well-defined (meth)acrylate-based telechelic polymers containing hydroxyl or other UV–vis/heat-sensitive functional end groups with predetermined molecular weights, low polydispersities, and high functionalities are highly desirable. The availability of many different (meth)acrylate monomers allows systematic tuning of the properties of (meth)acrylate-based telechelic polymers. The uniform structures of the coatings prepared from these telechilic polymers are expected to impart coatings with improved mechanical properties. Well-defined (meth)acrylate-based telechelic polymers with hydroxyl end groups have been prepared by anionic polymerisation [23] and group transfer polymerisation [24], but these polymerisations are difficult to perform due to the stringent reaction conditions required. Recently ATRP has also been used to synthesize (meth)acrylate-based telechelic polymers with hydroxyl end groups and various polymer backbones. Shim et al. synthesized hydroxyl-functionalised telechelic poly(methyl acrylate)s (PMAs) via the ATRP of methyl acrylate (MA) using a difunctional initiator (Br-R-Br) or a hydroxyl-functionalised initiator (HO-R-Br) together with ATRA (with allyl acohol) or a coupling reaction, and the hydroxyl functionality (i.e., f_{OH}) of the resulting telechelic products was determined to be as high as 1.9 [5]. Keul et al. synthesized telechelic poly(methyl methacrylate)s (PMMAs) with hydroxyl end groups via the ATRP of methyl methacrylate (MMA) in butyl acetate in the presence of allyl alcohol using 4-hydroxybutyl chloro(phenyl)acetate as the initiator and f_{OH} was determined to be 1.8 [6]. Peters et al. also reported the synthesis of a hydroxyl end-capped telechelic PMMA via the ATRP of MMA using 2,2,2-trichloroethanol as the initiator together with the subsequent ATRA with 3-methyl-3-buten-1-ol, but f_{OH} of the telechelic product was very low (~1.2) [11]. Recently Snijder et al. prepared well-defined hydroxyl end-capped telechelic polymers with random copolymers of MMA and *n*-butyl acrylate (BA) as backbones (f_{OH} close to 2) via ATRP using 2,2,2-trichloroethanol as the initiator together with a subsequent addition-fragmentation transfer reaction with trimethyl(1-(4-(2-trimethylsiloxyethoxy))phenylethenyloxy)silane [9]. As far as we know, however, the hydroxyl end-capped telechelic polymers with poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate) (PMMA-*b*-PBA) backbones (i.e., HO-PMMA-*b*-PBA-OH) have not been synthesized up to now, which might provide coatings with some interesting morphologies and properties. Besides, although many methods are available for determining the end group functionality of hydroxyl-functionalised telechelic polymers, such as ^{1}H NMR [5,6,11], ultraviolet spectroscopy (UV) [9], specific OH titration [6,11], and liquid chromatography under critical concentrations (LC-CC) [11,25], the development of other new and effective techniques for this purpose is still of high importance. Herein, we describe the synthesis of HO-PMMA-*b*-PBA-OH via ATRP together with a subsequent nucleophilic substitution reaction and the application of gradient polymer elution chromatography (GPEC) [26] in the determination of f_{OH} of the obtained telechelic polymers. The synthetic procedure, the verification of the high functionality of the bromo end group in the intermediate products (i.e., HO-PMMA-Br and HO-PMMA-*b*-PBA-Br) prepared via ATRP under the optimised reaction conditions, the confirmation of the occurrence of nucleophilic substitution reaction between HO-PMMA-*b*-PBA-Br and 5-amino-1-pentanol with ^{1}H and ^{13}C NMR techniques, and the determination of the functionality of the obtained telechelic polymers with GPEC are presented in detail.

2. Experimental

2.1. Materials

MMA (Aldrich, 99%) and BA (Aldrich, 99 + %) were washed twice with an aqueous solution of sodium hydroxide (5%) and twice with distilled water, dried with anhydrous magnesium sulfate overnight, and then distilled over calcium hydride under vacuum. The distillates were stored at -18 °C before use. Toluene (Biosolve Ltd., AR) was distilled over calcium hydride. CuBr (Aldrich, 98%) was purified according to a reported procedure [27] and stored in an argon atmosphere before use. *N*-(*n*-Hexyl)-2-pyridylmethanimine (NHPMI) was synthesized by condensation of pyridine-2-carboxaldehyde (Acros, 99%) and *n*-hexylamine (Acros, 99%) as described elsewhere [28]. 2-Hydroxyethyl 2-bromoisobutyrate (HEBIB) was provided by DSM Resins and used as received. Deuterated dimethyl sulfoxide (DMSO-d6, 99.9%, Cambridge Isotope Laboratories, Inc.) was dried with molecular sieves for two days before use. 5-Amino-1-pentanol (Aldrich, 95%), dimethyl sulfoxide (DMSO, Aldrich, 99.9% HPLC grade), and all the other chemicals were used as received.

2.2. Synthesis of HO-PMMA-Br

CuBr (0.6724 g, 4.69 mmol) was added to a mixture of MMA (14.0771 g, 140.60 mmol) and toluene (26.0176 g) in a three-neck round-bottom flask (100 ml). After the reaction mixture was bubbled with argon for 20 min in an ice bath, NHPMI (2.6452 g, 13.90 mmol) was added. The reaction mixture was bubbled again with argon for 20 min in an ice bath, and then the flask was immersed into a thermostated oil bath at 60 °C and stirred for 20 min. The initiator HEBIB (0.9855 g, 4.67 mmol) was added into the system in 2 min to start the reaction. Samples were taken from the reaction mixture at suitable time periods throughout the reaction, which were diluted with tetrahydrofuran (THF). Parts of them were used for gas chromatography (GC) measurements to determine monomer conversions, and the rest were passed through a column of neutral aluminium oxide prior to size exclusion chromatography (SEC) measurements. The reaction was stopped by cooling down the solution at a reaction time of 23 h. The obtained reaction mixture was passed through a column of neutral aluminium oxide and then precipitated in pentane to provide a white polymer ($M_{n,SEC} = 5570$ and PDI = 1.13, Table 1, entry 1) in 73% yield.

2.3. General procedure for the synthesis of HO-PMMA-b-PBA-Br

The ATRP of MMA using HEBIB as the initiator and CuBr/NHPMI as the catalyst was utilised to prepare HO-PMMA-Br according to the procedure described above. The polymerisation was sampled at a reaction time of 23 h (to determine monomer conversion and the molecular weight and polydispersity of the resulting polymer) and then 1 equiv. of BA relative to MMA was added. The reaction mixture was stirred at 60 °C for 4 h and then heated to 100 °C. A viscous solution was obtained when the reaction was stopped after 20 h, which was passed through a column of neutral aluminium oxide and then precipitated in pentane to provide a light brown polymer ($M_{n,SEC} = 9640$ and PDI = 1.22, Table 1, entry 4) in 66% yield.

2.4. Synthesis of HO-PMMA-b-PBA-OH

5-Amino-1-pentanol (2.5789 g, 25.00 mmol) was added into a solution of HO-PMMA-*b*-PBA-Br ($M_{n,SEC} = 9640$ and PDI = 1.22, Table 1, entry 4) (4.8001 g, 0.50 mmol) in DMSO (50 ml). The reaction system was stirred at 25 °C and sampled at suitable time periods throughout the reaction. The sampled solutions were extracted with water/chloroform mixture, and the chloroform phase was collected, dried with anhydrous magnesium sulfate, and evaporated to remove most of the solvent. The residual solutions were precipitated in pentane to provide the telechelic polymers.

2.5. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrometer with TMS as the internal reference. Monomer conversions were determined from the concentrations of residual monomers using a Hewlett-Packard 5890 GC, equipped with an AT-Wax capillary column (30 m × 0.53 mm × 10 μm) using toluene as the internal reference. Molecular weights and polydispersities of the polymers were measured with a Waters SEC equipped with a Waters model 510 pump and a model 410 differential refractometer (40 °C). THF was used as the eluent at a flow rate of 1.0 ml/min. A set of two linear columns (Mixed-C, Polymer Laboratories, 30 cm, 40 °C) was used. The calibration curve was prepared with polystyrene (PS) standards, and molecular weights were recalculated using the universal calibration principle and Mark–Houwink parameters (PS, $K = 1.14 \times 10^{-4}$ dL g^{-1} and $\alpha = 0.716$; PMMA, $K = 0.944 \times 10^{-4}$ dL g^{-1} and $\alpha = 0.719$). Note that the Mark-Houwink parameters of PMMA were used when the molecular weights of the block copolymers of MMA and BA were calculated using the universal calibration principle. Electrospray ionisation mass spectrometry (ESI-MS) experiment was carried out in a Q-TOF

Table 1
Synthesis of hydroxyl-functionalised macroinitiators HO-PMMA-Br and their block copolymers HO-PMMA-*b*-PBA-Br via ATRP

Entry	$M_{n,SEC}$ (PDI) (HO-PMMA-Br)[a]	BA/MMA (molar ratio)	$M_{n,SEC}$ (PDI) (t)[b] (HO-PMMA-*b*-PBA-Br)	$M_{n,SEC}$ (PDI)[c]	$M_{n,SEC}$ (PDI)[d]
1	5340 (1.18)	0		5570 (1.13)	5660 (1.11)
2	5090 (1.18)	0.5	5790 (1.41) (16 h)		
3[e]	5070 (1.17)	1	8530 (1.30) (20 h)		
4[f]	4830 (1.21)	1	7880 (1.32) (20 h)	9640 (1.22)	9700 (1.20)
5	4810 (1.23)	3	14,730 (1.18) (21 h)		
6	4810 (1.23)	3	21,350 (1.23) (44 h)		

[a] $[MMA]_0/[HEBIB]_0/[CuBr]_0/[NHPMI]_0 = 30:1:1:3$, MMA/toluene = 1/2 v/v, reaction temperature: 60 °C, reaction time: 23 h, the polymers were purified by passing through a column of neutral aluminium oxide.

[b] $M_{n,SEC}$ and PDI values of the block copolymers at a reaction time t (reaction temperature: 100 °C), the polymers were purified by passing through a column of neutral aluminium oxide.

[c] The polymers were purified by passing through a column of neutral aluminium oxide and then precipitated once in pentane.

[d] The polymers were further precipitated once in pentane to remove the trace amounts of toluene and monomer present and they were only used for NMR measurements.

[e] The reaction is the same as that shown in Fig. 4.

[f] A repeated reaction for entry 3.

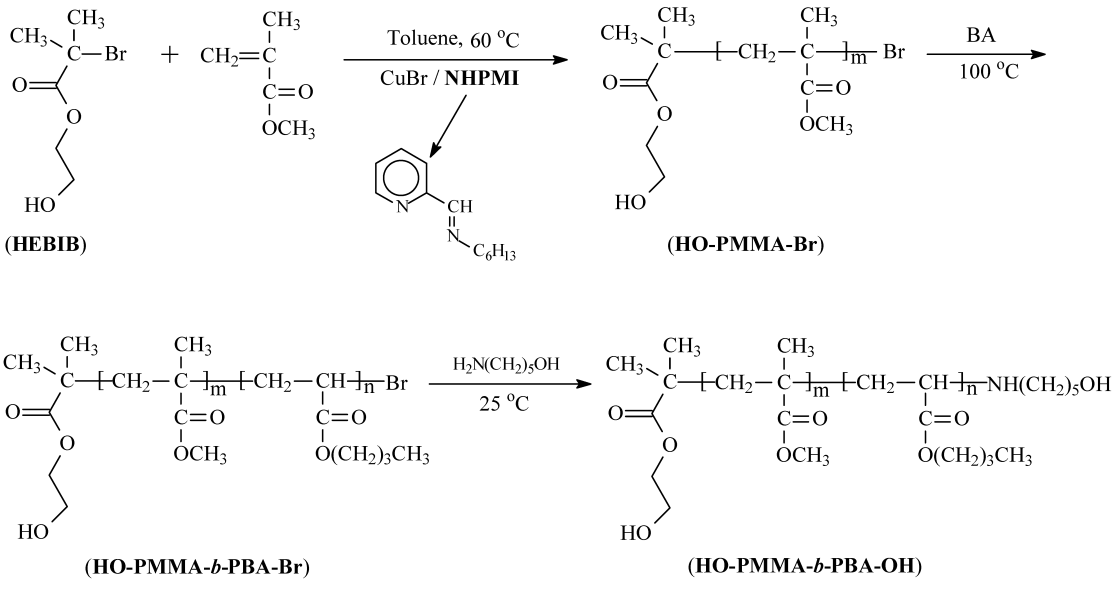
UltimaTM Global mass spectrometer (Micromass UK Ltd., Manchester, UK), which was calibrated with phosphoric acid in a mass range of 98–2058 Da. The polymer sample was dissolved in a 4:1 (v/v) mixture of dichloromethane and an ammonium acetate solution in methanol (0.5 mM) at a concentration of 0.5 mg/ml and then introduced into the electrospray interface at a flow rate of 5 μl/min. The sampling cone potential used was 31 V, and the capillary voltage was 3.0 kV. The electrospray source temperature was 80 °C and the desolvation temperature was 100 °C. The mass spectrum was scanned over a m/z range of 500–3000 in the positive ion mode. 147 scans were summed to produce the final spectrum. GPEC measurements were carried out at 35 °C on an Alliance Waters 2690 separation module with a Waters 2487 dual λ UV absorbance detector and a PL-EMD 960 evaporative light-scattering detector. A Jordi Gel DVB polyamine column ($250\ \mathrm{mm} \times 4.6\ \mathrm{mm}^2$, Alltech) was utilised in the study. Telechelic polymers were dissolved in dichloromethane at a concentration of about 10 mg/ml (10 ± 0.2 mg/ml). The eluent used in this work was a binary gradient starting from a 95:5 (v/v) mixture of heptane (nonsolvent for the polymers used in analysis) and THF (good solvent for the polymers used in analysis) to pure THF (50 min), which was described in detail elsewhere [9]. Experimental data were acquired by Millennium 32 (version 3.05) software. Evaporative light-scattering detection (ELSD) was calibrated with HO-PMMA-*b*-PBA-Br ($M_{\mathrm{n,SEC}} = 9640$ and PDI $= 1.22$, Table 1, entry 4) prepared via ATRP. The f_{OH} values of the telechelic polymers were calculated based on the assumption that the end-group modification of HO-PMMA-*b*-PBA-Br by nucleophilic substitution only led to HO-PMMA-*b*-PBA-OH and no side reactions took place.

3. Results and discussion

Scheme 1 shows the synthetic route of HO-PMMA-*b*-PBA-OH. The ATRP of MMA with HEBIB as the initiator and CuBr/NHPMI as the catalyst was utilised to prepare a hydroxyl-functionalised PMMA macroinitiator (HO-PMMA-Br), where the molar ratio of MMA to HEBIB to CuBr to NHPMI was 30:1:1:3 and the volume ratio of the solvent used (toluene) to MMA was 2. A homogeneous dark brown solution was obtained when the reaction mixture was heated to 60 °C. BA was added to the reaction mixture of the ATRP of MMA to prepare block copolymers HO-PMMA-*b*-PBA-Br in a one-pot reaction when MMA conversion was about 90%. The reaction mixture was firstly stirred at 60 °C for 4 h and then at 100 °C for a certain period (see Table 1). After purification by precipitating in pentane, the obtained HO-PMMA-*b*-PBA-Br was reacted with 5-amino-1-pentanol to provide telechelic polymers HO-PMMA-*b*-PBA-OH.

3.1. Synthesis of HO-PMMA-Br with a high functionality of bromo end group

ATRP has proven to be a valuable method for preparing block copolymers by the chain-extension of the macroinitiators containing halogen end groups with another monomer [29]. The successful synthesis of a well-defined block copolymer via ATRP requires a macroinitiator with a high chain end functionality and efficient cross-propagation from the macroinitiator to the second monomer. The efficient cross-propagation was observed for the ATRP of BA using PMMA-Br as the macroinitiator [30]. However,



Scheme 1.

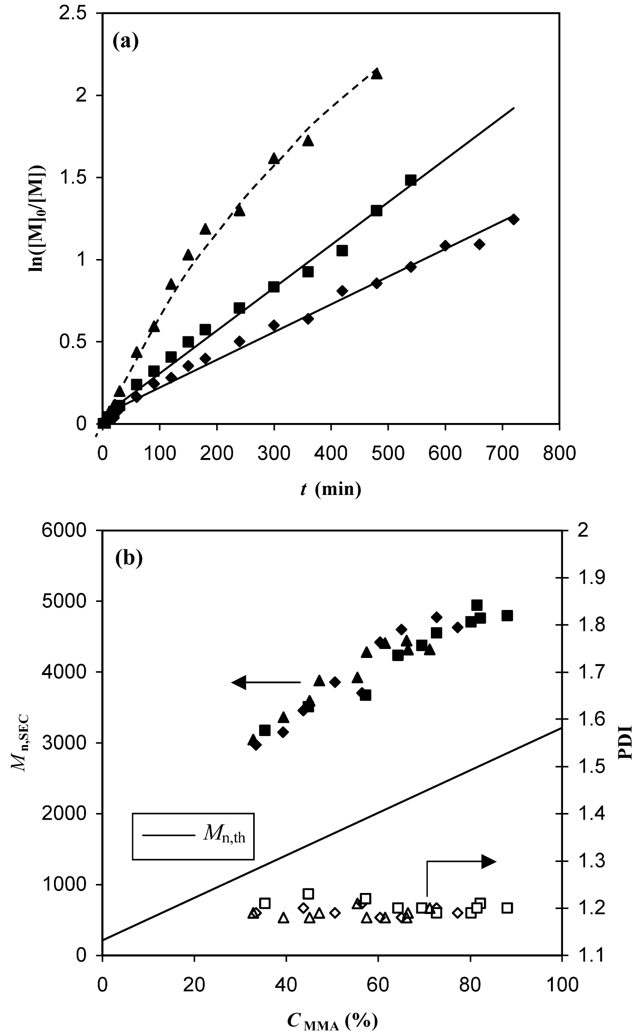


Fig. 1. (a) Kinetic plots of $\ln([M]_0/[M])$ versus reaction time t and (b) dependence of $M_{n,SEC}$ and PDIs of the polymers on monomer conversions for the ATRP of MMA in toluene at 60 (◆), 70 (■), and 90 °C (▲), respectively. $[MMA]_0/[HEBIB]_0/[CuBr]_0/[NHPMI]_0 = 30:1:1:3$, MMA/toluene = 1/2 v/v.

the preparation of PMMA-Br with a functionality close to 100% is difficult because the ATRP of MMA is usually so fast that radical termination takes place, in particular when the targeted molecular weights (i.e., the ratio of the initial concentrations of monomer to initiator) are low [31,32]. Recently we have shown that several methods can help minimize the radical termination in the ATRP of MMA, such as adding enough Cu(II) at the beginning of the reaction, reducing the initiator and/or catalyst concentrations, or lowering the reaction temperature [33,34]. Herein, the reaction temperature was optimised to synthesize the highly functionalised HO-PMMA-Br.

Fig. 1a shows that reaction temperature has a strong impact on the ATRP of MMA. The kinetic plot of $\ln([M]_0/[M])$ versus reaction time t was linear throughout the reaction when the polymerisation was carried out at a reaction temperature ≤ 70 °C, revealing that radical termination was negligible. However, a curved kinetic plot of $\ln([M]_0/[M])$ versus reaction time t was obtained when reaction temperature was increased to 90 °C, demonstrating that the polymerisation was better controlled at a lower reaction temperature. Therefore, a reaction temperature of 60 °C was chosen for the ATRP of MMA to prepare HO-PMMA-Br with a high functionality of bromo end group.

The number-average molecular weights of the obtained polymers determined by SEC (i.e., $M_{n,SEC}$) increased linearly with monomer conversions for all the reactions at different temperatures, but they were much higher than the theoretical values calculated by $M_{n,th} = ([M]_0/[RX]_0)M_M C_M + M_{RX}$, where $[M]_0$ and $[RX]_0$ are the initial concentrations of monomer and initiator, respectively, M_M and M_{RX} are the molecular weights of monomer and initiator, respectively, and C_M is the monomer conversion (Fig. 1b). This may in part be attributed to the decrease in the alkyl halide concentrations in the ATRP systems following the radical termination at the beginning of the reactions due to the "persistent radical effect" [35]. Besides, the inaccuracies from the recalculation of the PS calibration curve to a PMMA calibration curve via the universal calibration principle may also be partially responsible for this discrepancy [9,33]. In all cases, the polydispersity indices (PDIs) of the polymers were almost the same and all close to 1.2 throughout the reactions, showing the typical characteristics of living polymerisations (Fig. 1b).

The ^{1}H NMR spectrum (in $CDCl_3$) of the macroinitiator HO-PMMA-Br ($M_{n,SEC} = 5660$ and PDI = 1.11, Table 1, entry 1) prepared via ATRP at 60 °C is shown in Fig. 2B. The multiple peaks around 4.18 ppm corresponded to methylene protons next to the ester oxygen in $COOCH_2CH_2OH$ and their integration was denoted as $A_{4.18}$. The peaks between 3.72 and 3.90 ppm could be ascribed to the protons of $COOCH_3$ in the MMA unit connected with the bromo end group and methylene protons next to the hydroxyl group in $COOCH_2CH_2OH$, and their total integration was denoted as $A_{(3.72-3.90)}$. The ratio of $A_{(3.72-3.90)}$ to $A_{4.18}$ was calculated to be 2.55, which agreed well with a theoretic value of 2.5. This demonstrated that the chain end functionality of the obtained polymer HO-PMMA-Br was close to unity. The large single peak around 3.60 ppm could be assigned to the protons of $COOCH_3$ in the MMA repeat unit in the polymer backbone (except those of $COOCH_3$ in the MMA unit connected with bromo end group) and the integration of this peak was denoted as $A_{3.60}$. A number-average molecular weight of 5300 determined by ^{1}H NMR (i.e., $M_{n,NMR}$) can thus be derived for the polymer by using Eq. (1).

$$M_{n,NMR} = \{[(A_{3.60} + A_{(3.72-3.90)} - A_{4.18})/3]/(A_{4.18}/2)\}M_{MMA} + M_{HEBIB} \qquad (1)$$

Where M_{MMA} and M_{HEBIB} are the molecular weights of MMA and HEBIB, respectively. In addition, the contents of HO-PMMA-Br with syndiotactic (i.e., rr) structures were calculated to be about 62% according to the ^{1}H NMR

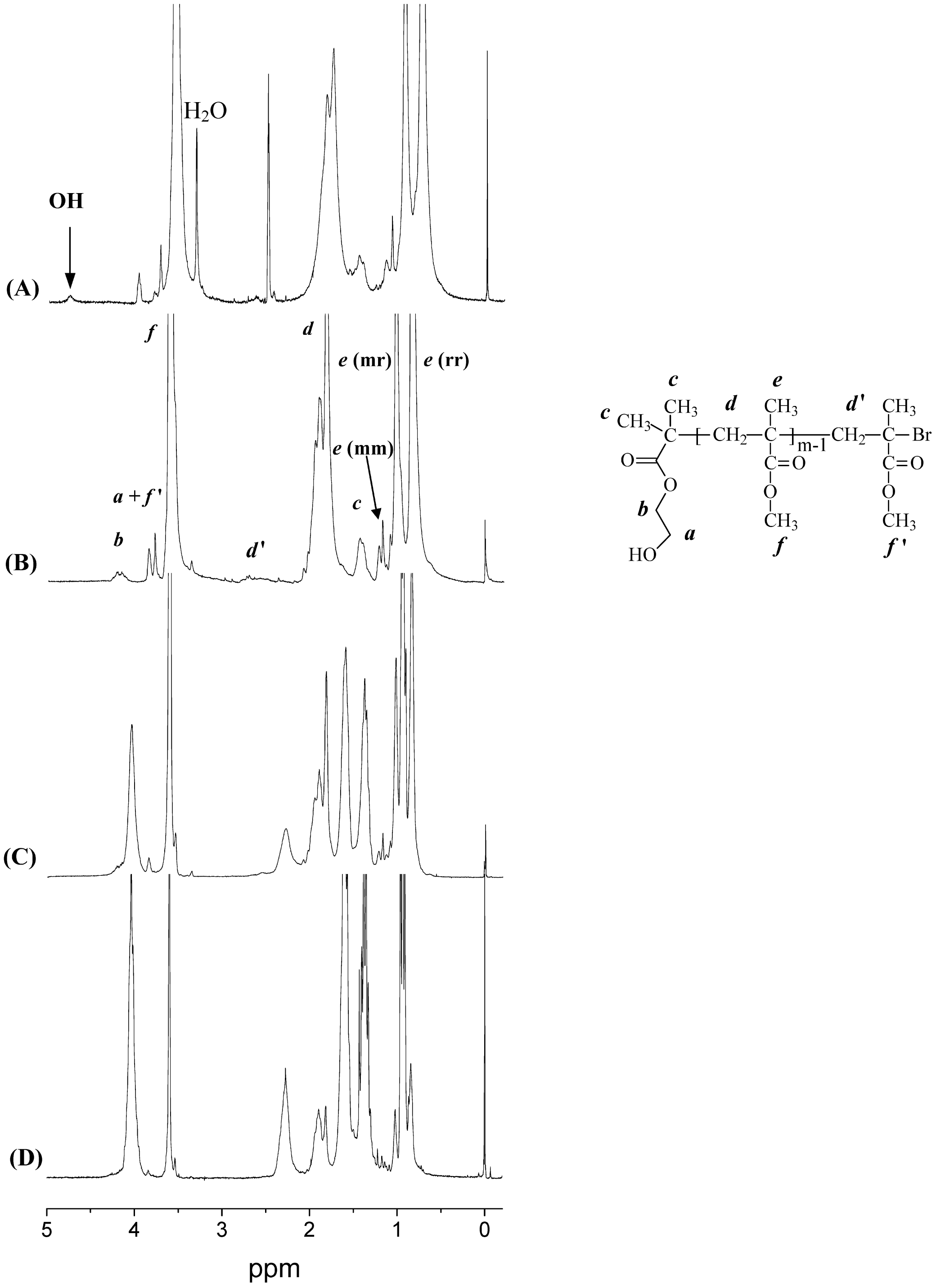


Fig. 2. ^{1}H NMR spectra of a macroinitiator (HO-PMMA-Br ($M_{n,SEC} = 5660$ and PDI = 1.11) in both DMSO-d6 (A) and $CDCl_3$ (B) and two monohydroxyl-functionalised block copolymers (HO-PMMA-*b*-PBA-Br: $M_{n,SEC} = 9700$ and PDI = 1.20, (C); $M_{n,SEC} = 21,350$ and PDI = 1.23, (D)) in $CDCl_3$.

spectrum [36,37], which fits the known tacticity of PMMAs prepared via the conventional radical polymerisation (58–64%) [37,38]. Fig. 2A shows the ^{1}H NMR spectrum of the same macroinitiator in dried DMSO-d6. The signal corresponding to the proton of hydroxyl end group in the polymer could be clearly observed as a single peak around 4.8 ppm in this case, which was not present in the ^{1}H NMR spectrum when $CDCl_3$ was used as the solvent. However, the peaks corresponding to the protons of $COOCH_3$ in the MMA unit connected with the bromo end group and methylene protons next to the hydroxyl group in $COOCH_2$-CH_2OH overlapped with that corresponding to the protons of $COOCH_3$ in the MMA repeat unit in the polymer backbone, which made it difficult to quantify the chain end functionality of HO-PMMA-Br.

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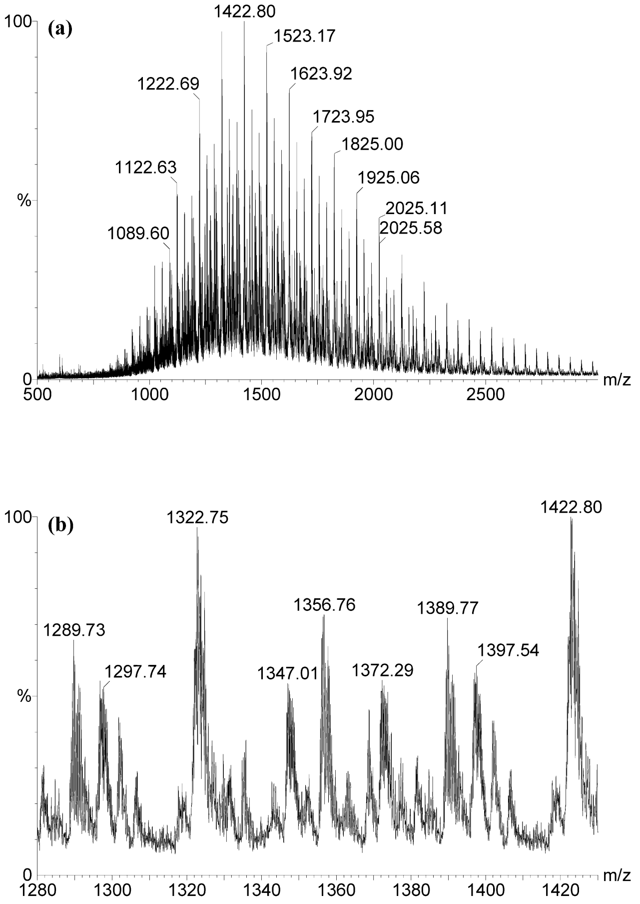

Fig. 3. (a) Full ESI-MS spectrum of HO-PMMA-Br ($M_{n,SEC} = 5570$, PDI = 1.13) and (b) a partially zoomed spectrum for a m/z range from 1280 to 1430.

Table 2
Assignments of the peaks in the ESI-MS spectrum

Entry	x	y	m/z (calcd)	m/z (in spectrum)
1	37	3	1323.17	1322.75
2	38	3	1356.54	1356.76
3	39	3	1389.92	1389.77
4	40	3	1423.29	1422.80
5	50	4	1322.27	1322.75
6	51	4	1347.30	1347.01
7	52	4	1372.33	1372.29
8	53	4	1397.36	1397.54
9	54	4	1422.39	1422.80

ESI-MS: $m/z = [131.15((CH_3)_2C(COOCH_2CH_2OH)-) + x \times 100.12$ (PMMA backbone) $+ 79.90(-Br) + y \times 18.04(NH_4)]^{y+}/y$, where x refers to the degree of polymerisation, and y the number of charges (NH_4^+) on polymer chains.

flight mass spectrometry (MALDI-TOF MS) and ESI-MS measurements are valuable tools for determining the end-groups of synthetic polymers [39,40]. However, the fragmentation of C–X (X = Cl, Br) bond in PMMA-X was usually observed during the MALDI-TOF MS measurements [41,42], which made it difficult to analyse the functionality of the halogen end group in PMMA-X with this technique. We also conducted the MALDI-TOF MS measurements for HO-PMMA-Br, but no signals corresponding to the intact polymers were observed. Since ESI proved to be a much softer ionisation method than MALDI [43,44], we measured the ESI-MS spectrum of HO-PMMA-Br ($M_{n,SEC} = 5570$ and PDI = 1.13, Table 1, entry 1) with a hope that ESI-MS might overcome the fragmentation problem and provide additional information for the polymer end groups. Addition of salt (ammonium acetate) into the polymer solution was found to be helpful in improving the ratio of polymer signals to noises in the ESI-MS measurement. Ionisation in Fig. 3 was by NH_4^+ addition to the polymer chains. Similar to the previously reported ESI-MS results for PMMA [45], multiply charged polymer signals were also observed in our case. Two main series of peaks were observed at 33-u intervals (e.g., $m/z = 1322.75$, 1356.76, 1389.77, and 1422.80) and 25-u intervals (e.g., $m/z = 1322.75$, 1347.01, 1372.29, 1397.54, and 1422.80), which corresponded to the intact polymer chains (HO-PMMA-Br) with three and four charges (NH_4^+), respectively (Table 2). Note that the signals of the polymer chains carrying three charges ($3NH_4^+$) overlapped with those of the polymer chains carrying four charges ($4NH_4^+$) at 100-u intervals (e.g., $m/z = 1322.75$, 1422.80, etc.). Although some small peaks in the spectrum could not yet be assigned at the moment, the above results already suggested that ESI-MS might be a more suitable tool for characterising PMMA-Br than MALDI-TOF MS. A detailed comparison between MALDI-TOF MS and ESI-MS measurements of PMMA-X is under way and will be included in a forthcoming paper.

3.2. Synthesis of well-defined HO-PMMA-b-PBA-Br

In order to prepare well-defined monohydroxyl-functionalised block copolymers of MMA and BA (HO-PMMA-*b*-PBA-Br) using HO-PMMA-Br as the macroinitiator, the ATRP of BA using ethyl 2-bromoisobutyrate (EBIB) as the initiator and CuBr/NHPMI as the catalyst was systematically studied to obtain the optimal reaction conditions [46]. EBIB was chosen as the initiator due to its structure analogy with the macroinitiator HO-PMMA-Br. The results showed that the ATRP of BA carried out in toluene at 100 °C provided the best results in terms of polymerisation rate and molecular weight control, which was, therefore, utilised in the present study.

The monohydroxyl-functionalised block copolymers HO-PMMA-*b*-PBA-Br were prepared by the sequential addition of BA into the ATRP of MMA when MMA was almost consumed (i.e., a one-pot reaction [47]). A reaction temperature of 60 °C was chosen for the ATRP of MMA in the first step and 100 °C for the ATRP of BA in the second step. A macroinitiator HO-PMMA-Br with a $M_{n,SEC}$ of 5070 and a PDI of 1.17 (Table 1, entry 3) was prepared via the ATRP of MMA in 23 h ($C_{MMA} = 87\%$). One equivalent of

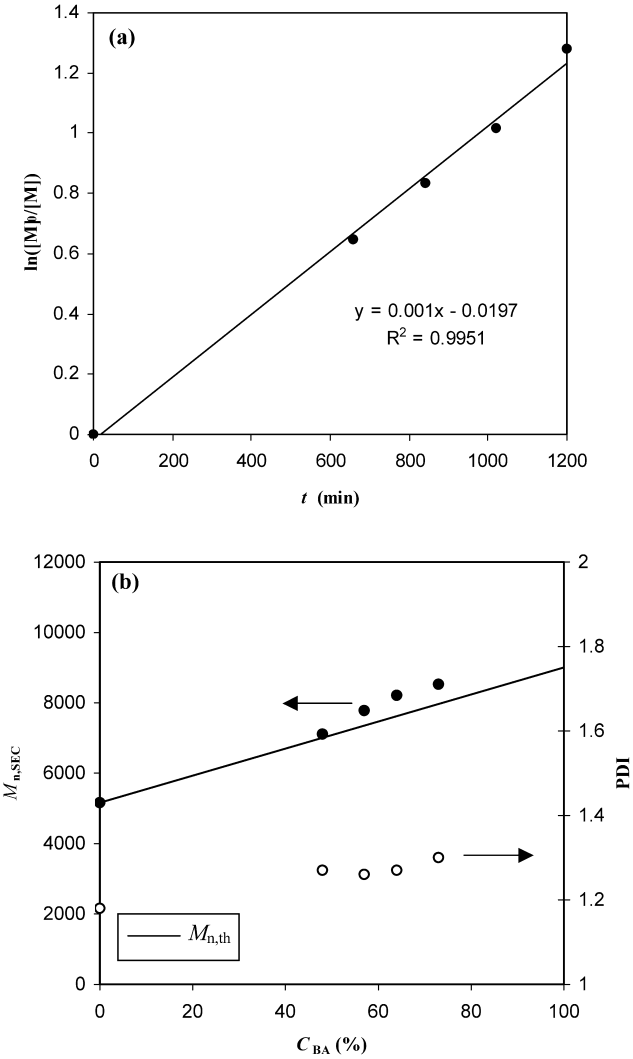

Fig. 4. (a) Kinetic plot of ln([M]$_0$/[M]) versus reaction time t and (b) dependence of $M_{n,SEC}$ and PDIs of the polymers on monomer conversions for the ATRP of BA in toluene at 100 °C using HO-PMMA-Br ($M_{n,SEC} = 5070$ and PDI = 1.17) as the macroinitiator ([BA]$_0$ = [MMA]$_0$).

BA with respect to MMA was then added into the system to start the second-step reaction (i.e., chain-extension reaction). The kinetic plot of ln([M]$_0$/[M]) versus reaction time t for the ATRP of BA using HO-PMMA-Br as the macroinitiator was linear throughout the reaction, revealing the absence of significant radical termination (Fig. 4a). The $M_{n,SEC}$ of the obtained polymers increased linearly with monomer conversions and were quite close to the $M_{n,th}$ values, and the PDI values of the block copolymers were around 1.3 throughout the reaction (Fig. 4b). The relatively larger PDIs of the obtained block polymers in comparison with the macroinitiator might be due to the relatively slow initiation during the reaction and the large propagation rate constant of BA [46]. All these results indicated that the chain-extension reaction was well controlled and HO-PMMA-*b*-PBA-Br with a high functionality of bromo end group was obtained. A series of similar block copolymers with different length of PBA blocks were also prepared in the same way by just changing the molar ratio of BA to MMA in the second-step reaction (Table 1).

The ^{1}H NMR spectra of a chain-extended polymer with a $M_{n,SEC} = 9700$ and a PDI = 1.20 (Table 1, entry 4) and another one with a $M_{n,SEC} = 21,350$ and a PDI = 1.23 (Table 1, entry 6) are displayed in Fig. 2C and D, respectively. $CDCl_3$ was used as the solvent in both cases. Peaks corresponding to the protons in the BA unit around 4.0, 2.3, 1.6, 1.4, and 0.9 ppm are clear evidences for the presence of PBA blocks in the obtained polymers [48]. The intensity ratio of the PBA block signals to the PMMA block signals increased with the increase of the molecular weights of PBA blocks in the chain-extended polymers. In addition, the peaks around 3.8 and 2.7 ppm in Fig. 2B, which corresponded to the protons of $COOCH_3$ and CH_2 in the MMA unit connected with the bromo end group in the macroinitiator, respectively, disappeared in the ^{1}H NMR spectra of the chain-extended polymers (Fig. 2C and D), demonstrating the success of the chain-extension. By comparing the integrations of the methylene protons next to the ester oxygen of $COOCH_2CH_2CH_2CH_3$ in the BA unit (4.0 ppm) and of the methyl protons of $COOCH_3$ in the MMA unit (3.6 ppm) on the basis of $M_{n,SEC}$ of the PMMA blocks (Fig. 2C and D), a number-average molecular weight of 4030 and 22,080 was obtained for the PBA block in the chain-extended polymer with a $M_{n,SEC} = 9700$ and a PDI = 1.20 and that with a $M_{n,SEC} = 21,350$ and a PDI = 1.23, respectively. It should be noted that the signal corresponding to the proton of hydroxyl end group in the chain-extended polymer with a $M_{n,SEC} = 9700$ and a PDI = 1.20 was also observed around 4.8 ppm as a single peak in its ^{1}H NMR spectrum with dried DMSO-d6 as the solvent (not shown). However, the solubility of the chain-extended polymer with a $M_{n,SEC} = 21,350$ and a PDI = 1.23 in dried DMSO-d6 was so low that it was only possible to obtain a ^{1}H NMR spectrum with very poor quality for this polymer in this solvent and no signal corresponding to the proton of hydroxyl end group in this polymer was visible.

Fig. 5 shows the SEC traces of a macroinitiator HO-PMMA-Br (line a) and two block copolymers HO-PMMA-*b*-PBA-Br (line b and c) obtained by the chain-extension of the macroinitiator with BA (the molar ratio of BA to MMA is 3) in different reaction time. The macroinitiator HO-PMMA-Br prepared via the ATRP of MMA in 23 h ($C_{MMA} = 84\%$) has a $M_{n,SEC}$ of 4810 and a PDI of 1.23 (Table 1, entry 5 and 6). BA was then added into the system to start the second-step reaction. A polymer with a $M_{n,SEC} = 14,730$ and a PDI = 1.18 (Table 1, entry 5) and another one with a $M_{n,SEC} = 21,350$ and a PDI = 1.23 (Table 1, entry 6) were obtained after 21 and 44 h at 100 °C, respectively. The large shifts of the molecular weights and the unimodal shapes of the SEC traces of the chain-extended polymers further confirmed that block copolymers HO-PMMA-*b*-PBA-Br were obtained. The absence of significant shoulders on the low molecular weight sides of the SEC traces of the

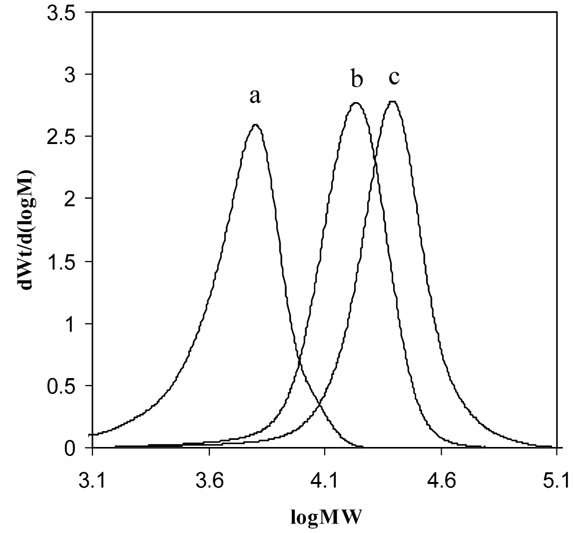

Fig. 5. SEC traces of a macroinitiator HO-PMMA-Br ($M_{n,SEC} = 4810$ and PDI = 1.23, line (a)) and its block copolymers (HO-PMMA-*b*-PBA-Br: $M_{n,SEC} = 14,730$ and PDI = 1.18, line (b); $M_{n,SEC} = 21,350$ and PDI = 1.23, line (c)) prepared via the ATRP of BA using HO-PMMA-Br as the macroinitiator.

block copolymers and their narrow molecular weight distributions (MWDs) again indicated that the chain end functionality of the macroinitiator HO-PMMA-Br was high.

3.3. Synthesis of HO-PMMA-b-PBA-OH

With the well-defined HO-PMMA-*b*-PBA-Br in hand, we were ready to prepare the desired telechelic polymer HO-PMMA-*b*-PBA-OH. The halogen end groups of the polymers prepared via ATRP can be transformed to hydroxyl groups by nucleophilic substitution, ATRA, addition–fragmentation transfer reaction, or by reacting with stable radicals bearing hydroxyl groups [3,12]. In the current study, we chose the nucleophilic substitution by reacting the monohydroxyl-functionalised block copolymer HO-PMMA-*b*-PBA-Br ($M_{n,SEC} = 9640$ and PDI = 1.22, Table 1, entry 4) with 5-amino-1-pentanol according to the literature [10,14].

The ^{1}H and ^{13}C NMR techniques were utilised to follow the nucleophilic substitution reaction of the block copolymer HO-PMMA-*b*-PBA-Br with 5-amino-1-pentanol (Figs. 6 and 7). A peak around 3.0 ppm was observed in the ^{1}H NMR spectra of the polymers obtained from the nucleophilic substitution reaction in different reaction time (Fig. 6B and C), which was not present in the ^{1}H NMR spectrum of HO-PMMA-*b*-PBA-Br (Fig. 6A). This peak could be ascribed to the methine proton in the BA unit next to the BA unit connected with the ω-end group (i.e., $NH(CH_2)_5OH$) of the telechelic polymers. The above result clearly demonstrates that the nucleophilic substitution reaction really took place and telechelic polymers were obtained. Due to the significant overlap of the other peaks in the ^{1}H NMR spectra, no quantitative results about the f_{OH} of telechelic polymers could be derived. Fig. 7 shows the ^{13}C NMR spectra of HO-PMMA-*b*-PBA-Br and the telechelic polymers HO-PMMA-*b*-PBA-OH obtained from the nucleophilic substitution reaction at a reaction time of 4 and 8 h, respectively. The peaks in the spectra were assigned according to the literatures [49,50] as well as the ^{13}C NMR spectra of some model compounds such as HO-PMMA-Br, HEBIB, methyl 2-bromopropionate, and 5-amino-1-pentanol (Fig. 7A–C). The signal of the methine carbon of the BA unit connected with the bromo end group in HO-PMMA-*b*-PBA-Br should appear around 40 ppm, but overlapped with those of the methylene carbon next to the methine group of the BA repeat unit in the polymer backbone (Fig. 7A). Fortunately, the signal corresponding to the methylene carbon next to the ester oxygen of $COOCH_2CH_2CH_2CH_3$ in the BA unit connected with the bromo end group was observed as a single peak at 65.9 ppm (Fig. 7A), and was thus utilised to follow the nucleophilic substitution reaction. This peak was still visible at a reaction time of 4 h (Fig. 7B), but disappeared at a reaction time of

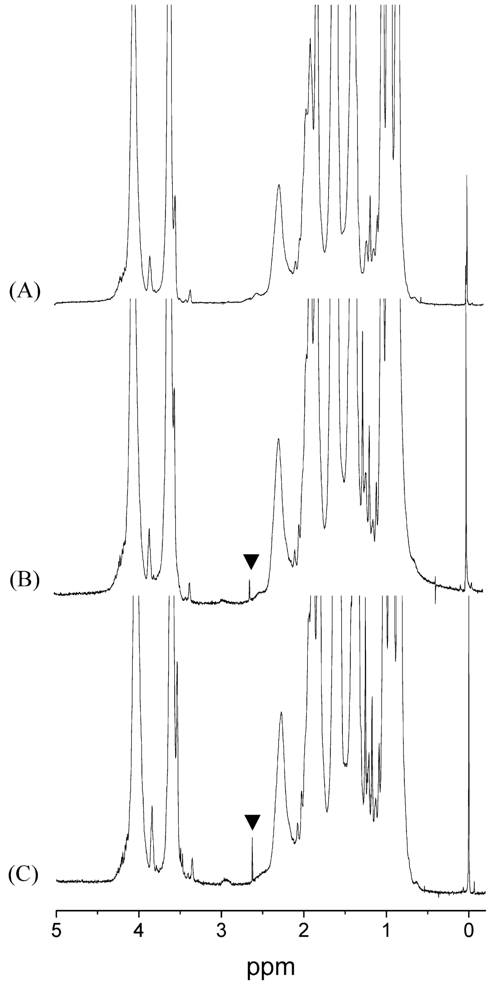

Fig. 6. ^{1}H NMR spectra (in $CDCl_3$) of HO-PMMA-*b*-PBA-Br ($M_{n,SEC} = 9700$ and PDI = 1.20) (A) and the telechelic polymers HO-PMMA-*b*-PBA-OH obtained from the nucleophilic substitution at a reaction time of 0.5 (B) and 8 h (C), respectively. The peak indicated by ▼ was due to the residual DMSO in polymers.

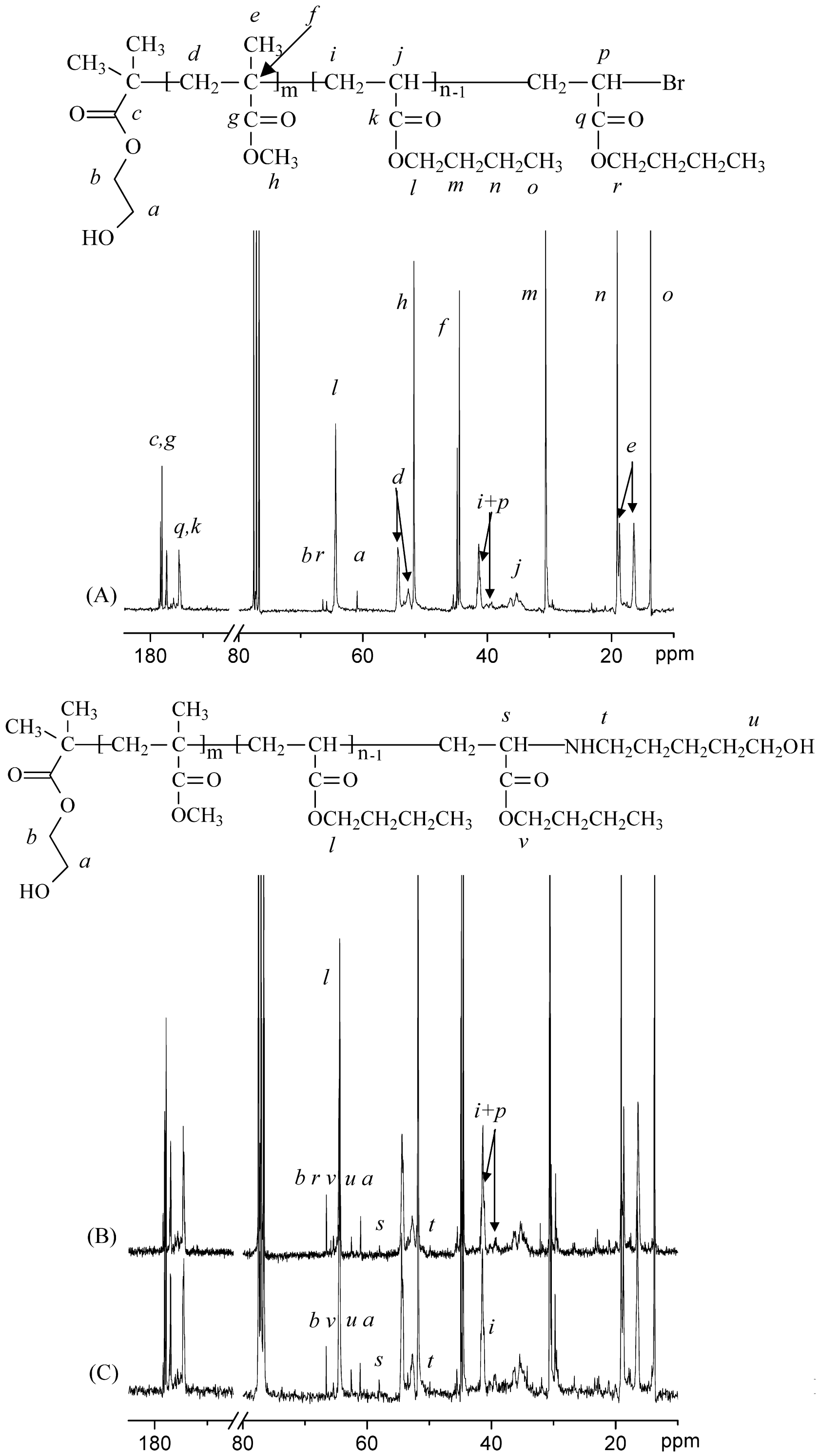

Fig. 7. ^{13}C NMR spectra (in $CDCl_3$) of HO-PMMA-*b*-PBA-Br ($M_{n,SEC}$ = 9700 and PDI = 1.20) (A) and the telechelic polymers HO-PMMA-*b*-PBA-OH obtained from the nucleophilic substitution at a reaction time of 4 (B) and 8 h (C), respectively.

8 h (Fig. 7C). In the meantime, some new peaks corresponding to the carbons of $CH(COOCH_2CH_2CH_2CH_3)$-$NH(CH_2)_5OH$ (i.e., the ω-end group) in HO-PMMA-*b*-PBA-OH appeared between 48 and 68 ppm in the ^{13}C NMR spectra of the telechelic polymers (Fig. 7B and C), further verifying the occurrence of the nucleophilic substitution reaction.

GPEC was then introduced to determine the hydroxyl functionality of the obtained telechelic polymers. In GPEC, separation of polymers is based on their interaction differences with the utilised column as well as precipitation and redissolution mechanisms as the eluent composition changes gradually in time. Therefore, it is possible to separate polymers according to molar mass, chemical composition, and chain or chain-end functionality with GPEC. Recently, polymers with only one hydroxyl end group difference (i.e., PBA and PBA-OH) have been successfully separated with this technique [12,51]. In our study, GPEC was used to monitor the end-group modification process of HO-PMMA-*b*-PBA-Br (Fig. 8). The GPEC peak of HO-PMMA-*b*-PBA-Br had a retention time of around 30 min and decreased with reaction time. In the meantime, the GPEC peak of the resulting telechelic polymer HO-PMMA-*b*-PBA-OH appeared around a retention time of about 43 min and increased with time (Fig. 8a). These two series of peaks were well separated. It should be noted that the ELSD response of a polymer is not linearly dependent on its concentration but is scaled with a power law [51,52], which depends on many operating parameters (mobile phase composition, gas pressure, and temperature) as well as on the nature of the polymer (e.g., end-groups) [25]. Calibration curves should thus be established and used carefully. Based on the calibration curve obtained from HO-PMMA-*b*-PBA-Br ($M_{n,SEC} = 9640$ and PDI = 1.22, Table 1, entry 4) and an assumption that f_{OH} of HO-PMMA-*b*-PBA-Br was 1, the f_{OH} values of the obtained telechelic polymers at different reaction time were calculated and the results are shown in Fig. 8b. It can be seen that the nucleophilic substitution reaction proceeded quite fast at the beginning of the reaction and a f_{OH} value of about 1.6 was obtained for the telechelic polymer in 2 h, but further prolonging the reaction time to 8 h only led to a slight increase of f_{OH}. The cause of this phenomenon is not very clear yet, and further investigation is going on. The highest f_{OH} of the obtained telechelic polymers was determined to be 1.7 (Fig. 8b). Further optimisation of the reaction conditions is ongoing in order to prepare telechelic polymers with a higher f_{OH}. In addition, two small peaks (retention time between 35 and 40 min) were present in the GPEC spectra of both HO-PMMA-*b*-PBA-Br and HO-PMMA-*b*-PBA-OH, which need further investigation.

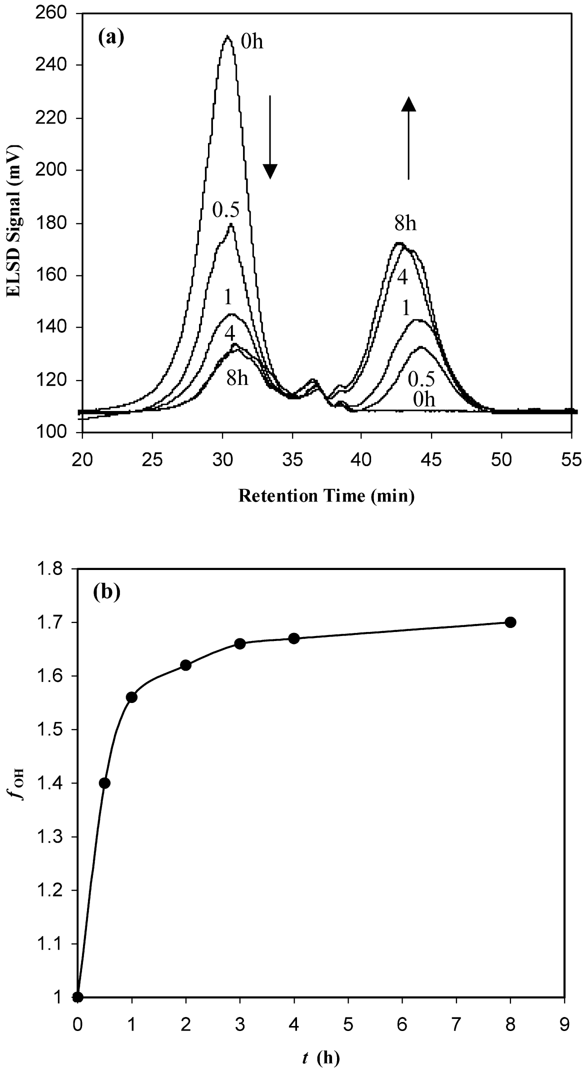

Fig. 8. (a) GPEC chromatograms for the end-group modification of HO-PMMA-*b*-PBA-Br with 5-amino-1-pentanol in DMSO at 25 °C at a reaction time *t* of 0, 0.5, 1, 4, and 8 h, respectively. (b) Dependence of f_{OH} of the telechelic polymers on reaction time *t* during the end-group modification of HO-PMMA-*b*-PBA-Br with 5-amino-1-pentanol in DMSO at 25 °C.

4. Conclusions

This paper describes the synthesis and characterisation of hydroxyl end-capped telechelic polymers with PMMA-*b*-PBA backbones via ATRP together with a nucleophilic substitution reaction. Firstly, a hydroxyl-functionalised PMMA macroinitiator (HO-PMMA-Br) was prepared via the ATRP of MMA using HEBIB as the initiator and CuBr/NHPMI as the catalyst under the optimised reaction temperature (60 °C), and the high functionality of the bromo end group was confirmed by both ^{1}H NMR technique and the chain-extension reaction with BA. ESI-MS proved to be a valuable tool for characterising PMMA-Br, and polymers remained intact (at least in most cases) during the measurements although multiply charged polymer chains were observed. The obtained HO-PMMA-Br was then utilised as a macroinitiator to polymerise BA at 100 °C in a one-pot reaction to provide the well-defined block copolymer HO-PMMA-*b*-PBA-Br. The kinetics as well as the dependence of the $M_{n,SEC}$ and PDIs of the obtained block copolymers on the conversions of BA in the chain-extension reaction suggested negligible radical termination during the reaction, demonstrating that the well-defined HO-PMMA-*b*-PBA-Br with a high functionality of bromo end group were obtained. Secondly, the bromo end group of HO-PMMA-*b*-PBA-Br was transformed to hydroxyl group by a nucleophilic substitution reaction with 5-amino-1-pentanol, resulting in a series of telechelic polymers (i.e., HO-PMMA-*b*-PBA-OH). The occurrence of the nucleophilic substitution reaction was verified with the ^1H and ^{13}C NMR techniques, and the hydroxyl functionality of the obtained telechelic polymers was determined to be as high as 1.7 according to the GPEC measurements.

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