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Preparation of functional poly(acrylates and methacrylates) and block copolymers formation based on polystyrene macroinitiator by ATRP

Meizhen Yin[a,*], Wolf D. Habicher[a], Brigitte Voit[b]

[a]*Institute of Organic Chemistry, Dresden University of Technology, Mommsenstrasse 13, D-01062 Dresden, Germany*
[b]*Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany*

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Abstract

The polymerization by ATRP of hydroxy and amino functional acrylates and methacrylates with *tert*-butyldimethylsilyl (TBDMS) or *tert*-butyloxycarbonyl (BOC) protective groups has been studied for the first time achieving high control over molecular weight and polydispersity. Detailed investigation of the ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl acrylate (**M2b**) in bulk and 2-[(*tert*-butoxycarbonyl)amino]ethyl 2-methylacrylate (**M3a**) in diphenyl ether (DPE) showed that the type of ligand plays an important role on either the polymerization rate or the degree of control of the polymerization. Among the ligands used, *N,N,N*′,*N*″,*N*″-pentamethyl diethylenetriamine (PMDETA) was the most suitable ligand for ATRP of all functional acrylates and methacrylates. The kinetics of **M2b** and **M3a** polymerization using PMDETA as a ligand was reported and proved the living character of the polymerization. Well-defined block copolymers based on a halogen terminated polystyrene (**Pst**) macroinitiator and the functional acrylate and methacrylate monomers were successfully synthesized by ATRP, and subsequent deprotection of the protective groups from the acrylate or methacrylate segment afforded amphiphilic block copolymers with a specific solubility behavior.

Keywords: ATRP; Functional acrylate and methacrylate; Amphiphilic block copolymer

1. Introduction

Recently, there have been several reports on the synthesis of amphiphilic block copolymers and the study of their properties [1–4]. Amphiphilic block copolymers are important materials in the fields of natural science; such as colloid science and biochemistry, as well as in industrial fields [5]. Although anionic polymerization is an excellent method for the preparation of well-defined block copolymers, it is technically challenging and not compatible with electrophilic or acidic functional groups. Free-radical polymerization can be used more broadly with monomers containing polar functionalities; however, it was not amendable to the preparation of well-defined polymers, especially block copolymers, until the recent breakthroughs in living free-radical polymerization chemistries, including atom transfer radical polymerization (ATRP) [6,7], nitroxide-mediated radical polymerization (NMP) [8,9], and reversible addition fragmentation transfer polymerization (RAFT) [10,11].

ATRP has been successfully employed for the polymerization of a variety of acrylate and methacrylate monomers, such as methyl acrylate [12,13], *n*-butyl acrylate [14,15], methyl methacrylate [16], and the functional monomer 2-hydroxyethyl acrylate (HEA) [17,18], and its methacrylate analogue 2-hydroxyethyl methacrylate (HEMA) [19,20]. Due to poor solubility of the poly(HEA) and poly(HEMA) in non-polar solvents, the monomers are often polymerized in their protected forms, 2-trimethylsilyloxyethyl acrylate (HEA–TMS) [18] and 2-trimethylsilyloxyethyl methacrylate (HEMA–TMS) [19,21]. The resulting polymer is more compatible with organic media, especially when used for the synthesis of block copolymers. However, the protective group of 2-trimethylsilyl is not stable enough, e.g. in the wet atmosphere [22,23] and thus, unwanted deprotection with partial loss of control over the polymerization can occur. In this article, therefore, another more stable protective group of *tert*-butyldimethylsilyl

* Corresponding author. Tel./fax: +49 351 46334093.
E-mail address: yinmz@yahoo.com (M. Yin).

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(TBDMS) was used to protect the hydroxy functional group. Another hydrophilic monomer, the hydrochloride salt of 2-aminoethyl methacrylate (HCl-AEMA), was successfully polymerized by Armes et al. [24,25] in aqueous ATRP to high conversion (95%). However, it is hard to achieve well-defined block copolymer with this water-soluble monomer when based on a hydrophobic macroinitiator due to its incompatible with organic media. For that reason, we introduced the popular protective group of *tert*-butyloxycarbonyl (BOC) for the amine functional group in the presented work.

Synthetic polymers obtained from functional acrylates and methacrylates have found wide use in industry, agriculture, and medicine owing to their remarkable properties such as water solubility and potential biocompatibility [26]. In connection with our investigation on the CRP of various modified acrylates and methacrylates with protected functional group, it was of interest to find optimized conditions in organic media for the synthesis of well-defined corresponding homopolymers and the formation of block copolymers having in addition a polystyrene block with a low polydispersity. The well-defined amphiphilic materials, obtained by the removal of the protective groups in the block copolymer synthesized by ATRP, are expected to show interesting physical properties, including special phase behavior in thin films, which will be addressed in future investigations.

2. Experimental

2.1. Materials

4,4′-di-*tert*-Butyl-2,2′-bipyridine (DTB-bpy, 98%, Aldrich), tris-(2-aminoethyl-amine) (96%, Aldrich), formic acid (85%, Fluka) and formaldehyde (30%, Merck), *N,N,N′,N″N″*-pentamethyl diethylenetriamine (PMDETA, 99%, Acrōs), methyl 2-bromopropionate (MBrP) (98%, Aldrich), ethyl 2-bromopropionate (EBrP, 98%, Aldrich), *tert*-butyldimethylchlorosilane (97%, Merck) were used as received, without further purification. Styrene (99%, Aldrich), 2-hydroxyethyl methacrylate (**M1a**, 97%, Aldrich) and 2-hydroxyethyl acrylate (**M1b**, 96%, Aldrich) were distilled under reduced pressure. Copper bromide (I) (98%, Aldrich) was purified by stirring over glacial acetic acid, followed by filtration and washing the remaining solid three times with methanol and twice with diethyl ether until there was no color of copper (II) and drying under vacuum for 1 day. Tris[2-(dimethylamino)-ethyl]amine (Me_6TREN) was synthesized according to procedures described in the literature [27].

2.2. Monomers

The structures of functional monomers used for investigation are given in Fig. 1.

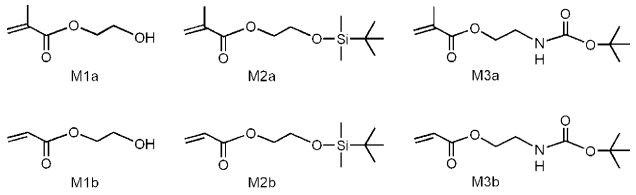

Fig. 1. Structures of functional monomers.

M1a and **M1b** are commercial available. The monomer 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl 2-methylacrylate (**M2a**) was synthesized according to the procedure by Mori et al. [28]. However, a ratio of 1:1 of *tert*-butyldimethylsilyl chloride and **M1a** was used instead of an excess of **M1a**. 2-[(*tert*-Butoxycarbonyl)amino]ethyl 2-methylacrylate (**M3a**) and 2-[(*tert*-butoxycarbonyl)amino]ethyl acrylate (**M3b**) were synthesized according to the literature [29].

2.2.1. 2-{[tert-Butyl(dimethyl)silyl]oxy}ethyl acrylate (M2b)

Into a three-neck-flask equipped with an argon bleed, a stirrer, a thermometer and a condenser, 2-hydroxyethyl acrylate (**M1b**, 5.8 g, 0.05 mol) in THF (200 ml) was placed, and two equivalents of imidazole (6.8 g, 0.10 mol) were added. After cooling to 0 °C *tert*-butyldimethylchlorosilane (7.53 g, 0.05 mol) in CH_2Cl_2 (150 ml) was added slowly under stirring. After 12 h the white salt precipitate was filtered, the solvent was evaporated under reduced pressure, and the residue was further purified by flash chromatography (ethylacetate/pentane 1:3 (v/v), $R_f = 0.76$) to give the product **M2b** with a yield of 92.9% (10.7 g). IR (neat), $\tilde{\nu}$ (cm^{-1}): 2953.8, 2930.9, 2857.9 (m, $(CH)_3$), 1727.0 (s, C=O), 1636.5 (s, C=C), 1254.4 and 831.8 (s, $Si(CH_3)_3$). ^{1}H NMR ($CDCl_3$): δ (ppm) = 6.34 (dd, $^3J_{(H,\ H)} = 17.28$ Hz (*trans*), $^2J_{(H,\ H)} = 1.43$ Hz, 1H, C*H*H=), 6.06 (dd, $^3J_{(H,\ H)} =$ 17.28 Hz (*trans*), $^3J_{(H,\ H)} = 10.39$ Hz (*cis*), 1H, =C*H*), 5.76 (dd, $^2J_{(H,\ H)} = 1.43$ Hz, $^3J_{(H,\ H)} = 10.39$ Hz (*cis*), 1H, C*H*H=), 4.16 (t, $^3J_{(H,H)} = 5.00$ Hz, 2H, $COOCH_2$), 3.78 (t, $^3J_{(H,H)} = 5.00$ Hz, 2H, CH_2OSi), 0.82 (s, 9H, $C(CH_3)_3$), 0.00 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 166.1 (C=O), 130.9 (CH_2=), 129.4 (=CH), 65.7 ($COOCH_2$), 61.2 (CH_2OSi), 25.8 ($C(CH_3)_3$), 18.3 ($C(CH_3)_3$), −5.4 ($Si(CH_3)_2$). Calcd. for $C_{11}H_{22}O_3Si$ (230.38 g/mol): C, 57.35%; H, 9.63%. Found: C, 57.98%; H, 10.23%. GC–MS (70 ev), *m/z* (%): 173 (29.8%), 129 (100%), 75 (21.8%), 73 (15.1%), 55 (71.6%).

2.3. Measurements

^{1}H NMR spectra were recorded in solution with a Bruker AC-300P (300 MHz) spectrometer, with the TMS proton signal as an internal standard. The number-average (M_n) and weight-average (M_w) molecular weight and the molecular weight distribution (polydispersity, M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC)

under the following conditions: WATERS 600E instrument equipped with UV and RI detectors, using chloroform containing 0.1 vol % TEA as solvent (flow rate: 1.0 ml/min). The samples were measured at 30 °C with a concentration of 2 mg/ml, and calibration was done using poly(methyl methacrylate) (PMMA).

2.4. General procedure of radical polymerization by ATRP

The initiator or macroinitiator was placed in a Schlenk flask and dissolved in DPE (0.5 g/ml (monomer/solvent)), subsequently the monomer and the ligand were added, and the mixture was degassed by three freeze-pump-thaw cycles. Under stirring at 25 °C for 20 min, CuBr was added and the flask was placed in a thermostated bath at a given temperature to start the reaction. After a defined reaction time, cooling with liquid nitrogen and opening the flask stopped the polymerization. The reaction mixture was diluted and eluted through a column filled with neutral alumina or silica gel to remove the copper complex. The monomer conversion was determined by ^{1}H NMR spectroscopy. The solvent was removed under vacuum at room temperature and the polymer solution was repeatedly precipitated into methanol or diethyl ether. Finally the homopolymers or block-copolymers were dried in vacuo to a constant weight.

2.5. Deprotection procedure

The removal of TBDMS group in block copolymer was done in 0.01 N HCl at 50 °C, after 5 h the product was purified by precipitation in diethyl ether.

Deprotection of the Boc group in block copolymer was accomplished by treatment with 1:1 (v/v) solution of CF_3COOH/CH_2Cl_2 at room temperature for 2 h to give the ammonium salts with trifluoroacetic acid in quantitative yield, which can be transformed into amphiphilic block copolymer after treating with anion exchange resin. The purification of the deprotected polymers was accomplished by precipitation in cold diethyl ether.

3. Results and discussion

Although the polymerization of the *tert*-butyldimethylsilyl protected hydroxyethyl methacrylate **M2a** by anionic technique was reported extensively [28,30–32], and many publications include the ATRP polymerization of hydroxyethyl methacrylate (HEMA, **M1a**) [18,19] and acrylate (HEA, **M1b**) [16,17], the ATRP of the *tert*-butyldimethylsilyl protected derivatives **M2a** and **M2b** has not been described yet. Since the *tert*-butyldimethylsilyl protecting group has advantages regarding hydrolytic stability, we decided to include the ATRP of the TBDMS protected functional methacrylate **M2a** and acrylate **M2b** in our studies. Of further interest also with regard to the potential deprotection conditions, are amino functional acrylates and methacrylates being protected by the well-known BOC group.

Based on literature results reported for ATRP of acrylates and methacrylates [33–37] we used ethyl 2-bromopropionate (EBrP) as an initiator and copper bromide (CuBr) as a transition metal/halide system, and also three types of ligands DTB-bpy, PMDETA and Me_6TREN (Fig. 2) were studied to select the most effective ligand in this specific ATRP system. Considering the solubility and the relatively smooth polymerization, the ratios between the components of the ATRP reaction system were fixed at [monomer]:[initiator]:[CuBr]:[ligand] equal to 100:1:1:2 (molar ratio).

3.1. Homopolymerization of protected functional acrylates and methacrylates

3.1.1. ATRP of *M2b* in bulk

ATRP of **M2b** was carried out in bulk under conditions of [M]:[I]:[CuBr]:[L] = 100:1:1:2, using EBrP as an initiator and CuBr as catalyst. The reaction conditions used and the results received are summarized in Table 1.

The data obtained in Table 1 clearly indicated that the rates of the ATRP of **M2b** could be adjusted by application of different ligands. For example, a very fast polymerization was observed using Me_6TREN (**R1**) or PMDETA (**R2**) as ligand, and monomer conversions of 90 and 93% were obtained after 10 min or 2.5 h, respectively. Under the same conditions, however, the weaker binding ligand DTB-bpy (**R3**) gave a slower polymerization. Only 67% monomer conversion was reached after 11 h. Therefore, the polymerization rates of **M2b** decreases in the order of Me_6-TREN > PMDETA > DTB-bpy.

During the polymerization one could observe that the color of copper changed (light green for Me_6TREN; mint green for PMDETA; dark orange for DTB-bpy), and the solutions became viscous as the reaction time increased. All the polymer solutions were purified by passing through alumina columns to remove the catalyst completely before characterization by GPC. The polymer solutions were almost colorless after being passed through the alumina columns.

The GPC results in Table 1 showed that ligands Me_6TREN (**R1**) and PMDETA (**R2**) afforded polymers with low polydispersities (PD = 1.24 and 1.18), and a satisfactory agreement between experimental ($M_{n,\,GPC}$) and

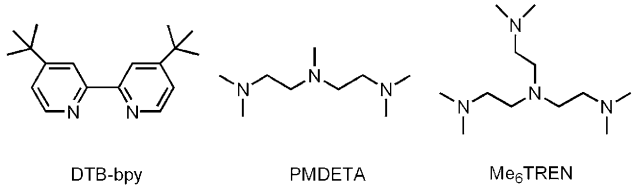

Fig. 2. Multidentate nitrogen-based ligands.

Table 1
ATRP polymerization of **M2b** using EBrP as initiator ([**M2b**]:[EBrP]:[CuBr]:[L] = 100:1:1:2, bulk, 90 °C)

No.	L	t	Y (%)	$M_{n,\ theor}$ (g/mol)	$M_{n,\ GPC}$ (g/mol)	PD (M_w/M_n)
R1	Me_6TREN	10 min	90	20,915	17,100	1.24
R2	PMDETA	2.5 h	93	21,606	17,700	1.18
R3	DTB-bpy	11 h	67	15,616	18,100	1.43

theoretical molecular weights ($M_{n,\ theor}$, predicted by the ratio of monomer to initiator and conversion). However, the ligand DTB-bpy (**R3**) gave a little higher experimental molecular weight than the theoretical value and a relatively broad distribution (PD = 1.43).

3.1.2. ATRP of *M3a*, *M3b* and *M2a* in diphenyl ether (DPE)

To further investigate the influence of the ligand on the polymerization of the interesting BOC protected amino functional monomers, the atom transfer radical polymerization of **M3a** was carried out with different ligands under the similar reaction condition as the previous ATRP of **M2b**. However, this time ATRP was performed in diphenyl ether (DPE) since the monomer is a solid. To our knowledge ATRP of this specific monomer was not reported so far. The polymerization data are summarized in Table 2.

As similarly observed for the acrylate **M2b**, the polymerization of the methacrylate **M3a** in the presence of different ligands showed that the polymerization rates decreased in the order of Me_6TREN > PMDETA > DTB-bipy. The excellent agreement between $M_{n,\ GPC}$ and $M_{n,\ theor}$ and the narrow distributions can be observed using Me_6TREN or PMDETA as ligands. However the ligand DTB-bpy resulted again a less good control of molecular weight, proved by a slightly lower molecular weight ($M_{n,\ GPC}$) than calculated and a somewhat higher polydispersity of 1.49.

The results received above lead to the conclusion that the ligand has an important influence on the rates of polymerization of functional acrylate and methacrylate, as well as on the degree of control of the polymerization. The ATRP of methacrylate **M3a** in DPE and acrylate **M2b** in bulk were both rather rapid using Me_6TREN as ligand. A high conversion was often achieved in only 10 min, giving polymers with a relative narrow distribution. The ATRP systems using PMDETA as ligand show reasonably high polymerization rates in 1–3 h and afforded polymers in high yield with quite narrow distributions. The polymerization with DTB-bpy proceeded more slowly and gave polymers with a relatively high polydispersity.

Considering that a reaction time in the range of 1–3 h is easy to control and in combination with the achieved high control regarding molecular weight and polydispersity, thus, PMDETA was chosen as ligand for further ATRP of two other functional monomers (methacrylate **M2a** and acrylate **M3b**). The results, also summarized in Table 2, showed that the $M_{n,\ GPC}$ of polymers were close to the $M_{n,\ theor}$ values and the distributions were all narrow (PD = 1.21, 1.20), confirming that PMDETA was an effective ligand for the ATRP of these functionalized methacrylate (**M2a**) and acrylate (**M3b**).

3.1.3. Kinetics of the ATRP of *M2b* and *M3a*

In order to prove the controlled character of the polymerization of **M2b** using PMDETA as ligand, the relationship between time-conversion and molecular weight-conversion was studied. In principle, the characteristics of a controlled process are revealed through a first-order kinetic plot of molecular weight and monomer conversion and a low polydispersity.

As shown in Fig. 3(A), an excellent linear relationship is seen between $\ln([M]_0/[M])$ and reaction time, obeying first-order kinetics ($R^2 = 0.995$), and indicating that the number of propagating species remained constant.

Furthermore, one can observe from Fig. 3(B), that the molecular weight increases rather linearly with conversion, and the polydispersity decrease from 1.30 to 1.18 over the same period. However, the molecular weights measured by GPC are slightly lower than the theoretical values, especially at higher conversion. It seems possible that a small amount of side reaction, such as transfer or termination (loss of bromide end group) takes place, which could be considered as breaking the kinetic chain. Nevertheless, the linear kinetics plot and the low polydispersity confirmed that the ATRP of **M2b** proceeded in a living fashion under the conditions used and with PMDETA as metal complex ligand.

Table 2
ATRP of **M3a**, **M3b** and **M2a** in DPE (0.5 g/ml (monomer/solvent)) ([M]:[EBrP]:[CuBr]:[L] = 100:1:1:2, 90 °C)

No.	M	L	t	Y (%)	$M_{n,\ theor}$ (g/mol)	$M_{n,\ GPC}$ (g/mol)	PD(M_w/M_n)
R4	**M3a**	Me_6TREN	10 min	94	21,733	21,100	1.26
R5	**M3a**	PMDETA	1.5 h	93	21,504	20,400	1.23
R6	**M3a**	DTB-bipy	7 h	90	20,816	18,700	1.48
R7	**M3b**	PMDETA	2.5 h	50	10,944	9120	1.25
R8	**M2a**	PMDETA	3 h	92	22,666	21,300	1.20

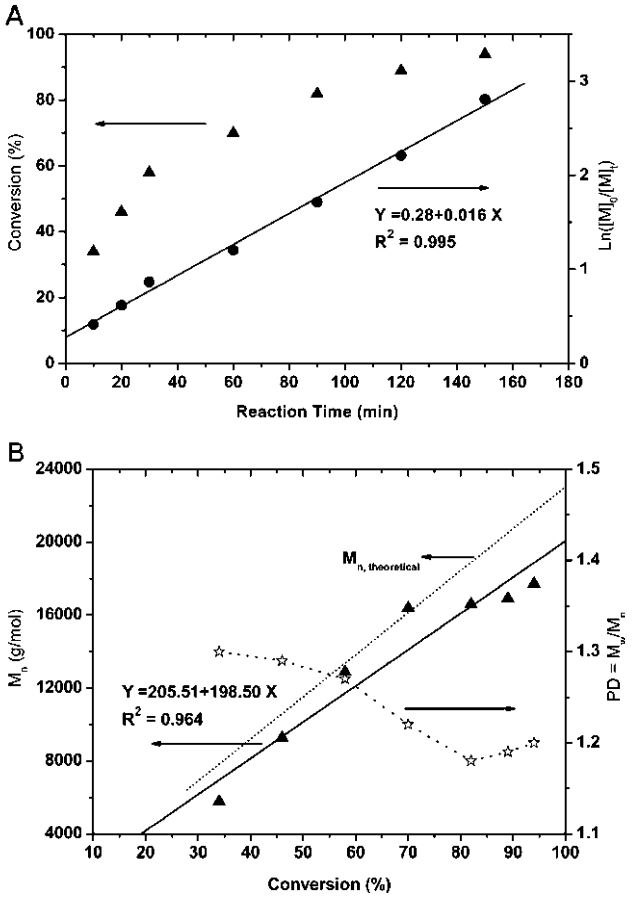

Fig. 3. (A) Kinetics plot of the ATRP of **M2b** using PMDETA as ligand ([**M2b**]:[EBrP]:[CuBr]:[L] = 100:1:1:2, bulk, 90 °C). (B) Effect of conversion during the ATRP of **M2b** on the PD and molecular weight using PMDETA as ligand.

The kinetics of **M3a** polymerization was investigated as well using PMDETA as a ligand. The living character of the polymerization was proved also for that monomer by a linear relationship between $\ln([M]_0/[M])$ and reaction time (Fig. 4(A)), and also by the linear increase of the molecular weight with monomer conversion and the low polydispersities (Fig. 4(B)).

The ATRP of **M3a** proceeded quite fast, a monomer conversion of 93% was obtained after 1.5 h (Fig. 4(A)). However, it performed with high control over molecular weight as demonstrated by the excellent agreement between the molecular weights measured by GPC and the theoretical values of the received polymers and also demonstrated by the low polydispersities obtained.

*3.2. Block copolymerization by ATRP using a polystyrene (**Pst**) macroinitiator system*

ATRP of styrene has been investigated extensively [38–40]. We wanted to use a bromide terminated well-defined polystyrene chain as part of the initiating system to prepare block copolymers having the functional acrylates and methacrylates in the second block. For this, styrene was polymerized by ATRP in bulk using DTB-bpy as reported in the literature [38]. A **Pst** macroinitiator with $M_{n,\ GPC} = 5900$ g/mol was obtained for the further block copolymerization of **M2a**, **M2b**, **M3a** and **M3b**. The macroinitiator had a polydispersity of 1.19 and was achieved in a yield of 68%. From NMR spectroscopy $n = 62$ was determined which means that it was calculated that 62 repeat units of polystyrene chain contain one bromide group which results in $M_{n,\ NMR} = 6619$ g/mol. This NMR molecular weight is in reasonable good agreement with the molecular weight value of GPC results indicating a high bromide end group content necessary for successful chain extension.

The reaction conditions and the results received for the block copolymer formation based on this **Pst** macroinitiator are given in Table 3. The ATRP was carried out in DPE at 90 °C. Similar to the homopolymerization, the block copolymerization rates of methacrylates **Pst-*b*-P2a** (54%) and **Pst-*b*-P3a** (72%) were somewhat higher than those of the corresponding acrylates **Pst-*b*-P2b** (40%) and **Pst-*b*-P3b** (50%) after the same reaction time (3 h). The experimental molecular weights as determined by GPC of the block copolymer were in general lower than the theoretically calculated molecular weights. One reason for this deviation might be that the poly(methyl methacrylate) calibration used in GPC analysis might not be fully valid for those block copolymers with segments of different polarity. The polydispersities of block copolymers are slightly increased compared to that of the first block, but are still rather low (PD = 1.28–1.36).

The molar mass distributions (from GPC curves) of the macroinitiator and different block copolymers are given in Fig. 5. The resulting molar mass distributions are monomodal, indicating successful chain extension of the **Pst** macroinitiator chains and the increase in molar mass can be taken as further prove for successful block copolymer formation. In addition, no significant homopolymer formation of the functional acrylates and methacrylates was observed, indicating the high initiator efficiency of the bromide functional **Pst** chain and a high control of block copolymerization.

The compositions of the block copolymers were characterized by proton NMR spectroscopy. Unfortunately, the methyl and methylene groups from the bromide end groups were overlapped by the broad signals of $-CH_3$ and $-CH_2-$ groups of the repeat units from acrylates and methacrylates. Therefore, the number average molar mass of block copolymers could not be calculated from the NMR spectra. Nevertheless, the peaks of the repeating units within both blocks were clearly identified. A proton NMR spectrum of a block copolymer, namely **Pst-*b*-P2a**, as an example, is shown in Fig. 6(A). The aromatic units from the polystyrene block can be assigned to the peak of 6.1–7.1 ppm, and the block of **P2a** is represented by the peaks at 0.02 ppm ($-CH_3$, **3**), 0.82 ppm ($-CH_3$, **4**), 3.68 ppm ($-CH_2-$, **2**) and 3.88 ppm ($-CH_2-$, **1**). In addition, the proton NMR

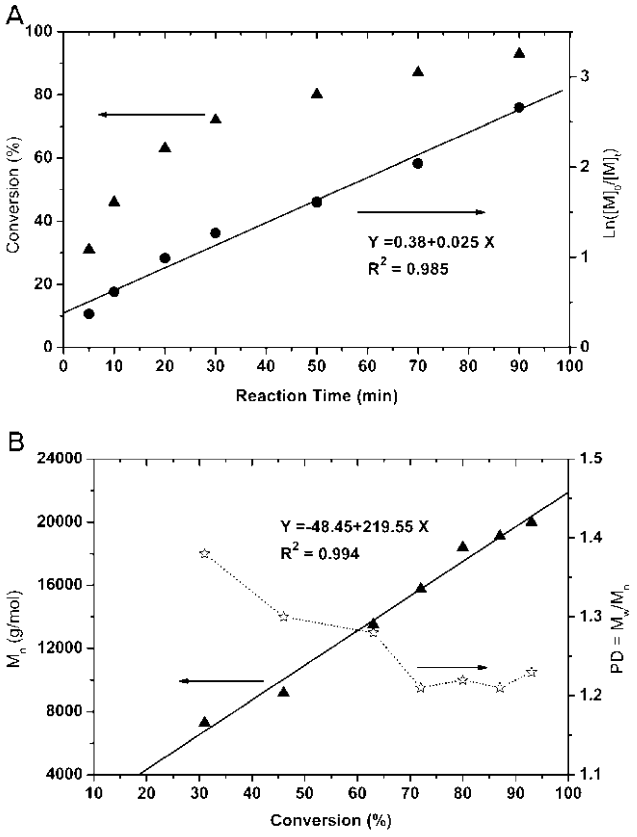

Fig. 4. (A) Kinetics plot of the ATRP of **M3a** in DPE (0.5 g/ml (monomer/solvent)) using PMDETA as ligand ([**M3a**]:[EBrP]:[CuBr]:[L] = 100:1:1:2, 90 °C). (B) Effect of conversion during the ATRP of **M3a** in DPE (0.5 g/ml (monomer/solvent)) on the PD and molecular weight using PMDETA as ligand.

spectrum of the block copolymer **Pst-*b*-P3a** is shown in Fig. 6(B). The signals of the main chain of the block copolymer **Pst-*b*-P3a** can be clearly observed by the broad peaks at 6.20–7.15 ppm (–Ar), 5.58 ppm (NH, **3**), 3.99 ppm (–CH_2–, **1**), 3.36 ppm (–CH_2–, **2**), and 1.44 ppm (–CH_3, **4**).

Therefore, we can conclude that diblock copolymers which contain a polystyrene block and a block of hydroxy and amino functional poly(acrylate) or poly(methacrylate) with TBDMS or BOC protective groups, were successfully synthesized by ATRP having good control over the block length and achieving narrow molecular weight distribution.

3.3. Deprotection of the polymers

The TBDMS and BOC groups in homopolymers and block copolymers were removed under acid condition [41,42]. The ^{1}H NMR spectra of amphiphilic block copolymers **d(Pst-*b*-P2a)** and **d(Pst-*b*-P3a)**, obtained from the deprotection, are shown in Fig. 7. Compared to the proton spectra of the protected block copolymers **Pst-*b*-P2a** and **Pst-*b*-P3a** (Fig. 6), the peaks of TBDMS and BOC protective groups have disappeared, being replaced by the new signals of free function hydroxy or amino group.

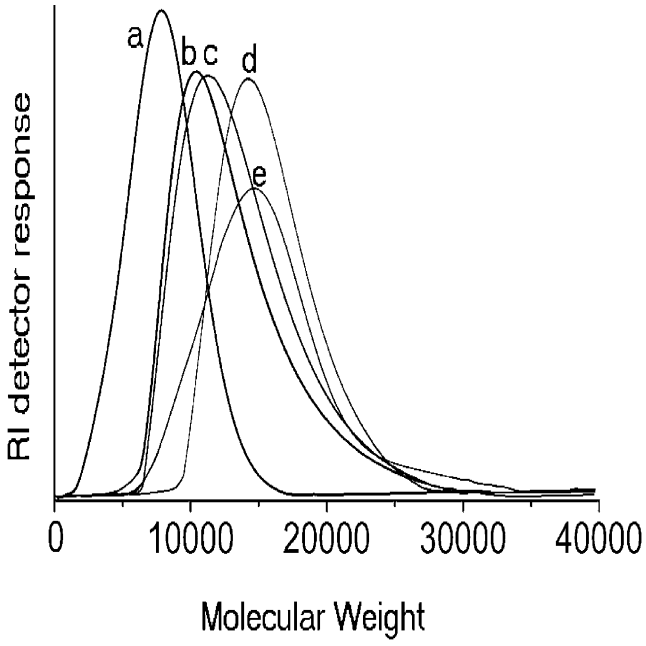

Fig. 5. Molar mass distribution of macroinitiator **Pst** and block-copolymers as determined by GPC evaluation (a, **Pst**; b, **Pst-*b*-P2a**; c, **Pst-*b*-P2b**; d, **Pst-*b*-P3a**; e, **Pst-*b*-P3b**).

The block copolymers showed different solubility behavior in polar and non-polar solvent before and after deprotection. In detail, the block copolymers (**Pst-*b*-P2a**, **Pst-*b*-P2b**, **Pst-*b*-P3a**, **Pst-*b*-P3b**) including the macroinitiator polystyrene (**Pst**) dissolve in non-polar solvent such as diethyl ether and diphenyl ether, but all of them precipitate in polar solvent like methanol/water (1:1, *v*:*v*). Among them block copolymers (**Pst-*b*-P3a**, **Pst-*b*-P3b**) and **Pst** are also precipitate in pure methanol. However after deprotection all the deprotected block copolymers (**d(Pst-*b*-P2a)**, **d(Pst-*b*-P2b)**, **d(Pst-*b*-P3a)**, **d(Pst-*b*-P3b)**) are soluble in methanol, but precipitate in diethyl ether. The large difference of the solubility between the deprotected block copolymers (**d(Pst-*b*-P2a)**, **d(Pst-*b*-P2b)**, **d(Pst-*b*-P3a)**,

Table 3
Block copolymerization of **M2a**, **M2b**, **M3a** and **M3b** by ATRP using polystyrene (**Pst**) as macroinitiator in DPE (0.5 g/ml (monomer/solvent)) ([M]:[**Pst**]:[CuBr]:[PMDETA] = 100:1:1:2, 90 °C)

No.	M	*t* (h)	*Y* (%)	$M_{n,\ theor}$ (g/mol)	$M_{n,\ GPC}$ (g/mol)	PD (M_w/M_n)
Pst-*b*-P2a	**M2a**	3	54	19,817	12,000	1.32
Pst-*b*-P2b	**M2b**	3	40	15,834	12,500	1.34
Pst-*b*-P3a	**M3a**	3	72	23,127	16,800	1.28
Pst-*b*-P3b	**M3b**	3	50	17,382	14,300	1.36

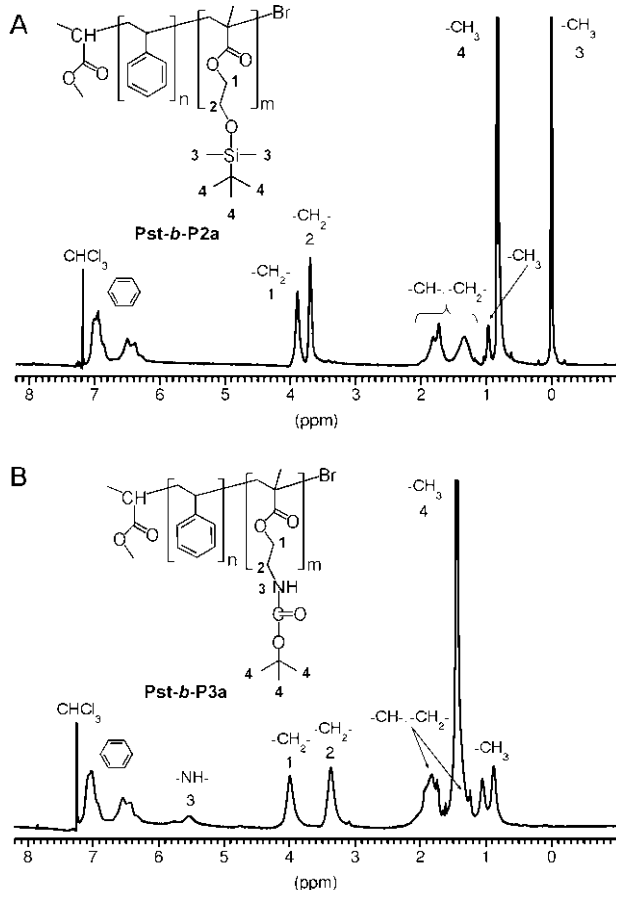

Fig. 6. ^{1}H NMR spectra of the protected block copolymers **Pst-*b*-P2a** (A) and **Pst-*b*-P3a** (B) in $CDCl_3$.

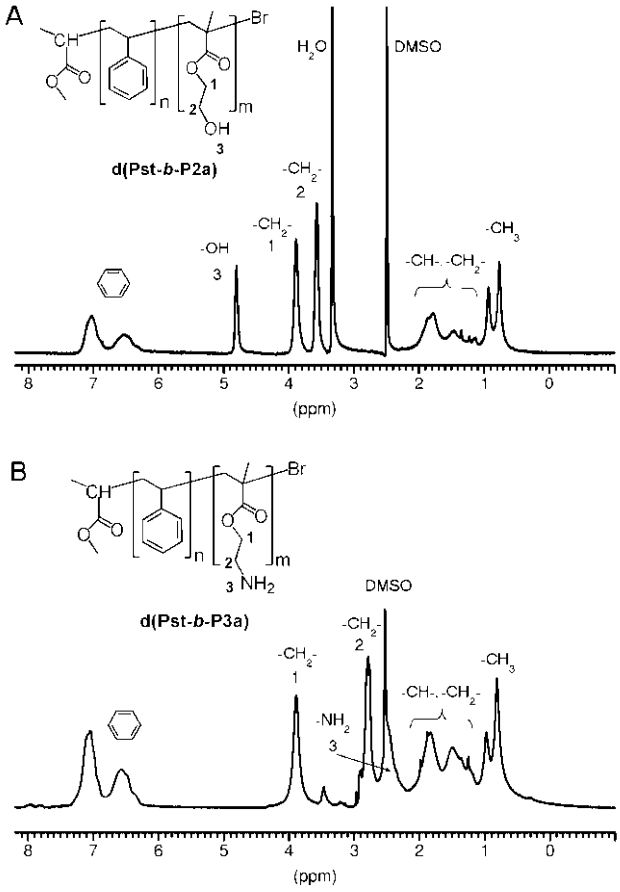

Fig. 7. ^{1}H NMR spectra of the deprotected block copolymers **d(Pst-*b*-P2a)** (A) and **d(Pst-*b*-P3a)** (B) in DMSO.

d(Pst-*b*-P3b)) and the macroinitiator polystyrene (**Pst**) demonstrate the successful chain extension using the macroinitiator (**Pst**) and the formation of real block copolymer by ATRP.

The study of the physical property of these amphiphilic block copolymers, containing a hydrophobic block polystyrene and a hydrophilic hydroxy or amino functional (meth)acrylate block will be the subject of future investigations. The functionalization with these functional groups (–OH, $–NH_2$) opens possibilities for further modification of the polymers.

4. Conclusion

ATRP of the TBDMS protected hydroxyethyl acrylate **M2b** and methacrylate **M2a** and the BOC protected amino functional acrylate **M3b** and methacrylate **M3a** was successfully performed achieving high control over molecular weight and molecular weight distribution. It was further shown in more detail for the TBDMS and BOC protected samples **M2b** and **M3a** that the type of ligand has an important influence on the polymerization rate and the polydispersity. The polymerization rates decreased in the order of Me_6TREN > PMDETA > DTB-bpy. Among the ligands used the lowest polydispersity of the resulting polymers in a suitable reaction time frame was received from the PMDETA ligand system. Kinetic studies confirmed that the ATRP of **M2b** and of **M3a** with PMDETA as a ligand proceeded in a living fashion.

A halogen-terminated polystyrene **Pst**, obtained by ATRP with a narrow molecular weight distribution, was successfully used as macroinitiator for the ATRP polymerization of the protected acrylates **M2b**, **M3b** and methacrylates **M2a**, **M3a** to give the corresponding of block copolymers. Strong differences in the solubility of the block copolymers after deprotection compared to the protected samples proved the amphiphilic nature of these products.

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