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Synthesis of well-defined and near narrow-distribution diblock copolymers comprising PMMA and PDMAEMA via oxyanion-initiated polymerization

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Abstract

In this paper, the possibilities offered by oxyanion-initiated polymerization were exploited to tailor well-defined and near narrow-distribution poly[(dimethylamino)ethyl methacrylate]-*b*-poly(methyl methacrylate) (PDMAEMA-*b*-PMMA) AB or BA diblock copolymers that were initiated by potassium benzyl alcoholate (BzOK) and controlled by the sequential addition of the alternative monomers. To clarify the living mechanism for MMA and DMAEMA, a series of MMA and DMAEMA homopolymers with near narrow molecular weight distribution were prepared in our laboratory, respectively. If not quenched, the first living moiety could be subsequently used to yield block copolymers BzO-PDMAEMA-*b*-PMMA with adding the second feed of monomer to the living system. Using reverse succeeding addition of monomers, another benzyloxy-capped diblock copolymer, i.e. BzO-PMMA-*b*-PDMAEMA was obtained. The thorough characterization of all these diblock copolymers was investigated from ^{1}H NMR measurement. The results indicated that the expected molecular structures have been obtained with a good correlation between original monomer-to-initiator molar ratios. GPC analysis showed that PDMAEMA homopolymer and the above mentioned two block copolymers possessed narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$) in the range of 1.15–1.34, while PMMA homopolymer had a little broad molecular weight distribution of 1.29–1.60. This study shows further evidence that oxyanion-initiated polymerization is a control/'living' process, not only suitable for tertiary amino-substituted methacrylates, but also for methyl methacrylate. The critical micelle concentration (cmc) of the diblock copolymer BzO-PDMAEMA-*b*-PMMA in aqueous solution was attained by surface tension measurement. The effects of different lengths of two segments and pH values on the behavior of solution were investigated.

Keywords: Oxyanion-initiated polymerization; PDMAEMA-*b*-PMMA; Amphiphilic diblock copolymer

1. Introduction

Living polymerization has been considered as one of the most powerful methods to produce amphiphilic block copolymers. There are several possible ways to combine hydrophobic and hydrophilic blocks, including sequential anionic polymerization [1,2], group transfer polymerization (GTP) [3–6], atom transfer radical polymerization (ATRP) [7,8], reversible addition-fragmentation chain transfer (RAFT) [9,10], and cationic polymerization [11,12]. As a novel living polymerization, the concept of oxyanion-initiated polymerization (OIP) was first proposed by Nagasaki's group [13,14] and developed successfully by Armes and his co-workers [15–20]. Up to now, most studies about OIP have been devoted to preparation of various of amphiphilic block copolymers and macromonomers containing tertiary amine methacrylates, such as 2-(*N*-morpholino)ethyl methacrylate (MEMA), *t*-(butylamino)ethyl methacrylate (BAEMA), 2-(*N*,*N*-dimethylamino)ethyl methacrylate (DMAEMA), 2-(*N*,*N*-diethylamino)ethyl methacrylate (DEAEMA), and so on [15]. These polymers have versatility and potential commercial applications in adhesives,

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emulsion and dispersion stabilizers and emulsifier, flocculation for water and wastewater treatment and biomaterials.

When the chemical structures of initiators were changed in OIP process, new species of block copolymers [21,22] could be gained. Wang et al. reported that potassium hydroxyl-terminated poly(ferrocenyldimethylsilane) (PFS–$CH_2CH_2CH_2O^-K^+$) was utilized as an initiator to prepare PFS-*b*-PDMAEMA. This work incorporated Fe^{2+} ions into block copolymer structures and generated a novel self-assembled supramolecular material with new physical and chemical properties [22]. Tertiary amine methacrylates were reported to integrate with some alcoholate-capped oligomers, which had narrow molecular weight distribution, for instance, monohydroxyl-capped poly(ethylene oxide) (PEO) [17,19], Pluronic (PEO–PPO–PEO) [23], and poly (propylene oxide) (PPO) [17,24]. Hyperbranched polymer or comb-like polymer with multi-hydroxyl group at their pendent groups also has been linked with DMAEMA [25,26].

The living mechanism of oxyanion-initiated polymerization was proved by two group's contributions: (1) the linear relationship of conversion to time reported by Nagasaki [14]; (2) the linear evolution of $\bar{M}_n$ vs. conversion and narrow polydispersity presented by Armes et al. [15]. Recently, Mallapragada et al. introduced benzyl bromide to terminate the living pentablock polymer PDMAEMA–PEO–PPO–PEO–PDMAEMA, and quantified by ^{1}H NMR to give strong evidence [23].

As we can know literatures, oxyanion-initiated polymerization was only conducted to those monomers of tertiary amino-substituted methacrylate, which possessed heteroatom at β-position in the ester moiety. These monomers were believed to facilitate the alcoholate initiation [14]. Significantly, however, studies of oxyanion-initiated polymerization (OIP) for most of common methacrylates have been neglected and the mechanism is still elusive. Only a few efforts have been done by Mallapragada et al., who prepared a random copolymer of DMAEMA and poly(ethylene glycol)-methyl ether methacrylate (PEGMEMA) initiated by potassium *t*-butoxide [27]. For MMA homopolymerization via OIP, a very broad molecular weight distribution was observed ($\bar{M}_w/\bar{M}_n > 2.5$) [16]. Moreover, the range of molecular weight in the related literature was not discussed.

The main objective of this work is to use sequential oxyanion-initiated polymerization for the preparation of amphiphilic block copolymers containing both PMMA and PDMAEMA blocks, and further understand the nature of the living chemistry. The effects of additional sequence of monomers on the structure and composite of the AB or BA block copolymers were investigated in details. This polymerization system has potential application for designing novel amphiphilic polymethacrylate syntheses.

2. Experimental

2.1. Materials

2-(*N*,*N*-Dimethylamino)ethyl methacrylate (DMAEMA), methyl methacrylate (MMA) and tetrahydrofuran (THF) were purchased from Shanghai Chemical Reagent Co., China. The monomers were passed through a basic alumina column, respectively, to remove the inhibitor and dried over CaH_2, then distilled in vacuum. THF was initially dried over potassium hydroxide and then refluxed over sodium wire for 3 days before use. Potassium hydride (KH, Aldrich) was stored in mineral oil and washed with THF in an inert atmosphere when was used. Benzyl alcohol was dried by CaH_2 for 12 h and distilled under reduced pressure. All polymerizations were carried out under a dry argon atmosphere.

2.2. Syntheses of PMMA and PDMAEMA homopolymers

The detailed process of polymerization can be described in previous literatures [15,24]. The polymerization reactor was a 100 ml round-bottom flask with a rubber septum and a magnetic bar, which was dried at 150 °C for 12 h and flamed in vacuum to eliminate moisture before use. In a preweighed flask with a magnetic bar, dry THF and washed dry KH powder were added. Benzyl alcohol equivalent to the molar amount of KH was added via a syringe needle to the flask. The reaction solution was stirred at 0 °C for 0.5 h to yield potassium benzylate (BzOK). A required amount of MMA monomer was added to the reactor. The reaction was carried on 0.5 h at 25 °C water bath before being quenched with methanol. The solvent was removed with a rotary vacuum distillatory. The product was purified by repeated precipitation into cold *n*-hexane for the removal of unreacted monomer. The samples were dried in a vacuum oven at 40 °C for 3 days. The overall conversions of monomers were greater than 92%.

A series of PDMAEMA homopolymer initiated by BzOK were prepared according to the previous literatures [15,28].

2.3. Syntheses of AB and BA diblock copolymer initiated by BzOK

The polymerization procedures of PDMAEMA-*b*-PMMA and PMMA-*b*-PDMAEMA were similar to that of above method. BzOK was prepared in THF at 0 °C for 0.5 h, the first monomer was added to the reactor and the polymerization proceeded at 25 °C for 0.5 h. Afterward, the second monomer was added to the flask and the reaction carried on 0.5 h at the same temperature before quenched with methanol. The accurate recipes are summarized in Table 1.

Table 1
Recipes of syntheses of PDMAEMA-*b*-PMMA and PMMA-*b*-PDMAEMA diblock copolymers with the different addition orders. The first monomer was initiated by potassium benzyl alcoholate followed by the second monomer addition

Sample ID	KH (mmol)	BzOH (mmol)	The first monomer/mmol	The second monomer/mmol
BDM-1	1.65	1.61	DMAEMA/16.20	MMA/15.89
BDM-2	1.10	1.02	DMAEMA/22.12	MMA/11.21
BDM-3	1.25	1.18	DMAEMA/35.10	MMA/11.70
BMD-1	3.67	3.49	MMA/36.75	DMAEMA/36.35
BMD-2	1.21	1.11	MMA/12.15	DMAEMA/24.80
BMD-3	3.63	3.42	MMA/54.60	DMAEMA/36.10

2.4. Characterization

The FTIR spectrum was recorded on a Nicolet Magna 550 FT-IR spectrometer. ^{1}H NMR spectra were recorded on an INVOA-400 nuclear magnetic resonance instrument, $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. ^{1}H NMR spectra were used to estimate the molecular weight ($\bar{M}_n$) of homo- and copolymers by comparing the aromatic protons of benzyloxy group with the aliphatic protons of three methyloxy group in PMMA or six dimethylamino protons in PDMAEMA. Samples were dissolved in $CDCl_3$ approximately 10 mg/ml and measured at ambient temperature 20 °C.

Gel permeation chromatography (GPC) was performed in the mixed solvent of THF with 2% triethylamine (flow rate: 1.0 ml/min) at 30 °C using a Shimadzu LC-10A liquid chromatograph system, equipped with a Shimadzu LC-10AD pump, three polystyrene gel columns (Shodex K-803, 804 and 805) and refractive index/ultraviolet dual detectors. Standard narrow polydispersity polystyrene was used in the calibration. The molecular weight distributions of all polymer samples were recorded by GPC measurement.

Surface tension measurements were carried out by a JZHY-180 surface tensiometer (Chengde Experimental Instrument Co., China) equipped with a platinum ring. The aqueous stock solutions of the copolymers were prepared by dissolving the pure copolymers in deionized water, and adjusted the solution at desired pH value using diluent hydrochloric acid. A series of aqueous polymer solutions with different concentrations were prepared by diluting the stock solution, holding the same pH with hydrochloric acid. All measurements were carried out at 20 ± 1 °C, and the obtained values were checked gradually through measurement of the surface tension of dionized water (72–73 mN/m). The effects of different pH values and the length of PDMAEMA block on the surface tension were studied.

3. Results and discussion

3.1. Synthesis and characterization of PMMA and PDMAEMA homopolymers

Two kinds of near narrow-distribution, low molecular weight homopolymers with benzyloxy-capped and block length-controlled PMMA and PDMAEMA were obtained via oxyanion-initiated polymerization using potassium benzyl alcoholate (BzOK) as an initiator. Armes et al. studied the synthesis and characterization of the DMAEMA homopolymers [15]. Through this way, our group prepared BzO-PDMAEMA homopolymers with different PDMAEMA lengths and narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$) in the range of 1.15–1.28, and investigated the behaviors of these polymers in aqueous solution at various pH values and temperatures [28].

An attempt of preparation of PMMA homopolymer initiated by benzyloxy anion has been conducted in our laboratory. The appropriate reaction condition and different molar ratios of MMA monomer to initiator are important for achieving well-controlled oxyanion polymerization. We have found that the initiation of MMA monomer by BzO^-oxyanion could be performed. Table 2 summarizes the compositions, molecular weights, molecular weight distribution of MMA homopolymers.

The molecular weights of PMMA homopolymers were obtained by the results of ^{1}H NMR. From Table 2, one can observe that the $\bar{M}_n$ calculated by ^{1}H NMR spectra are in good agreement with those of theoretical data corresponding to the monomer/initiator ratios. GPC measurements showed the polydispersity ($\bar{M}_w/\bar{M}_n$) of PMMA. In the scope of our experimental conditions, the resulted PMMA possessed near narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.29 - 1.44$) at lower degree of polymerization (units 10–20, theoretically), while there was a little broad PDI (1.36–1.60) at higher degree of polymerization (units 30–40). This fact suggested that ordinary methacrylate monomers could be performed by the living polymerization in definite condition.

The composition of the benzyloxy-capped PMMA was confirmed by FTIR spectroscopy and ^{1}H NMR. From the FTIR spectrum of PMMA homopolymer (BM-2) as shown in Fig. 1, we can see that the strong carbonyl band at 1730 cm^{-1} is attributed to the ester group (C=O) of PMMA. The bands of $-CH_2-$ and α-CH_3 can be found at 3000–2800 cm^{-1}. And 1600 cm^{-1} can be attributed to the band of phenyl group.

Fig. 2 depicts the ^{1}H NMR spectrum of BM-2. The characteristic chemical shift of phenyl group can be

Table 2
Compositions, molecular weights, and molecular weigh distributions of a series of BzO-PMMA homopolymers

Sample ID	Polymer chemical formula (theoretical)	[KH]/[BzOH]/[MMA] (molar ratios)	$\bar{M}_n$ (g mol^{-1})		$\bar{M}_w/\bar{M}_n$[a]
			Theor.	Actual[b]	
BM-1	BzO-PMMA$_{10}$	1/1/9.98	1100	1300	1.29
BM-2	BzO-PMMA$_{10}$	1/1/10	1100	1200	1.32
BM-3	BzO-PMMA$_{10}$	1/1/9.89	1100	1230	1.41
BM-4	BzO-PMMA$_{20}$	1/0.99/19.78	2100	2020	1.44
BM-5	BzO-PMMA$_{20}$	1/1/19.81	2100	2100	1.35
BM-6	BzO-PMMA$_{30}$	1/1/29.63	3100	3060	1.36
BM-7	BzO-PMMA$_{30}$	1/1/29.61	3100	3080	1.59
BM-8	BzO-PMMA$_{40}$	1/1/39.98	4100	4300	1.52
BM-9	BzO-PMMA$_{40}$	1/1/39.85	4100	4020	1.60

[a] As measured by GPC in THF.
[b] As measured by ^{1}H NMR in CDCl$_3$.

observed ($\delta=7.2$–7.4 ppm). The methylene protons of benzyl appear at $\delta=5.0$ ppm. The signals of ester protons group of PMMA is clearly visible at $\delta=3.6$ ppm. The backbone methylene protons (peak c) appear in the range $\delta=1.7$–2.0 ppm and the α-methyl protons (peak a) at $\delta=0.8$–1.2 ppm. These data confirm that the oxyanion polymerization of MMA has been achieved successfully.

3.2. Synthesis and characterization of benzyloxy-capped AB and BA diblock copolymers

To further demonstrate the mechanism of the polymerization similar to that of living anion process, block copolymers of hydrophilic DMAEMA (monomer A) and hydrophobic MMA (monomer B) were prepared by sequential addition. We employed these two methacrylates as the first and the second monomer, respectively, to synthesize AB and BA diblock copolymers with different block lengths and linking sequences. Fig. 3 shows a representative reaction scheme for the synthesis of AB and BA diblock copolymer via oxyanion-initiated polymerization.

The first monomer was added to the reactor containing BzOK with magnetic stirring at 25 °C for 0.5 h, and then the second monomer was injected into the flask. The reactants were stirred continuously for 0.5 h before quenched. The resulting products of benzyloxy-capped PDMAEMA-*b*-PMMA and PMMA-*b*-PDMAMA with different lengths of PMMA and PDMAEMA are shown in Table 3. The polymers are denoted as BzO-PDMAEMA$_m$-*b*-PMMA$_n$, where *m* and *n* stand for the theoretical number-average degrees of polymerization of the PDMAEMA and PMMA blocks, respectively. The block copolymer BzO-PMMA$_m$-*b*-PDMAEMA$_n$ was prepared by the reverse addition of two monomers with the similar procedure.

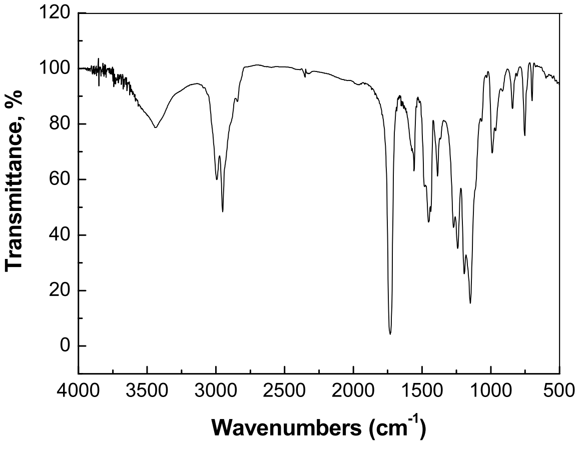

Fig. 1. FTIR spectrum for BzO-PMMA$_{10}$ (BM-2 in Table 2).

The incorporation of both monomers was confirmed by proton NMR spectroscopy. The molecular weights of each block were also calculated by ^{1}H NMR analysis. The protons of phenyl in benzyloxy group were considered as a labeled compound in the ^{1}H NMR analysis. The chemical shift scale was calibrated on the basis of the peak of TMS. The composition was calculated by integrating the aromatic protons of the phenyl ($\delta=7.2$–7.4 ppm) and the aliphatic protons of the six dimethylamino protons of DMAEMA units ($\delta=2.2$–2.4 ppm), as well as three methoxy protons of MMA units ($\delta=3.6$–3.8 ppm). The typical ^{1}H NMR spectra of BzO-PDMAEMA$_{20}$-*b*-PMMA$_{10}$ and BzO-PMMA$_{10}$-*b*-PDMAMA$_{20}$ are shown in Fig. 4(A) and (B).

With the comparison of the two ^{1}H NMR spectra, we have found that almost all chemical shift peaks attributed to the protons of BzO-PDMAEMA$_{20}$-*b*-PMMA$_{10}$ in Fig. 4(A) were as like as those of protons in BzO-PMMA$_{10}$-*b*-PDMAEMA$_{20}$ in Fig. 4(B). This fact suggests that diblock copolymers with the same target molecular weight, but different linking order, for both PDMAEAM and PMMA blocks, can be synthesized by varying the monomer-feeding order. The molecular weights of two blocks calculated by ^{1}H NMR are very close to those theoretically corresponding to the molar ratios of monomer to initiator as shown in Table 3. This result indicates that the feeding sequences of DMAEMA and MMA monomers have less influenced on the chemical structure and composition of desired copolymers in oxyanion-initiated polymerization. We conclude

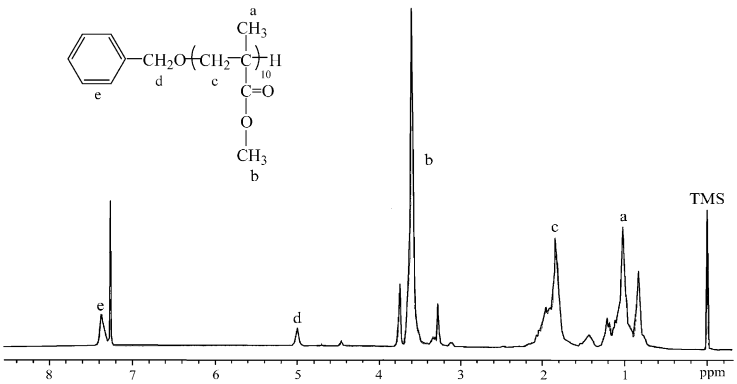

Fig. 2. ^{1}H NMR spectrum of BzO-PMMA$_{10}$ (BM-1 in Table 2) at 20 °C in CDCl$_3$.

that the mechanism should possess the feature of living anion polymerization. The method can be extended to other methacrylate monomers and provide potential applications.

The tracks of GPC confirm the formation of diblock copolymer with the sequential addition and the polydispersities in the range from 1.13 to 1.34. Fig. 5 shows the GPC profile of BMD-2 and BM-2. The peak (b) of the diblock copolymer moved towards higher molecular weight side comparing to the first block PMMA homopolymer (peak a). There is no detectable homopolymer contaminated in the block copolymer, indicating that the second monomer DMAEMA has reacted with the living anions of first moiety PMMA.

3.3. Surface tensions of PDMAEMA-b-PMMA diblock copolymers

At pH 7.0, the effects of different block lengths on the surface tension were investigated in Fig. 6 by choosing two of the diblock copolymers, i.e. PDMAEMA$_{10}$-*b*-PMMA$_{10}$ and PDMAEMA$_{30}$-*b*-PMMA$_{10}$. The surface tension was measured against air saturated with water vapor by platinum ring method. The temperature was maintained at 20 °C. The surface tension varies from the increasing concentration of diblock copolymer. In the case of equal block length (PDMAEMA$_{10}$-*b*-PMMA$_{10}$), the surface tension shows a sloping decrease. The limiting surface tension is approximately 49 mN/m, and cmc of 0.69 g/l. When the DMAEMA units are as three times as MMA units, the surface tension declines sharply to 53 mN/m at the concentration of 0.08 g/l. The cmc of PDMAEMA$_{30}$-*b*-PMMA$_{10}$ is only 0.063 g/l. These results indicate that the surface activity of both diblock copolymers mainly depend on influence of hydrophobic chain (PMMA block). These experimental phenomena are in good agreement with the report by Báñez

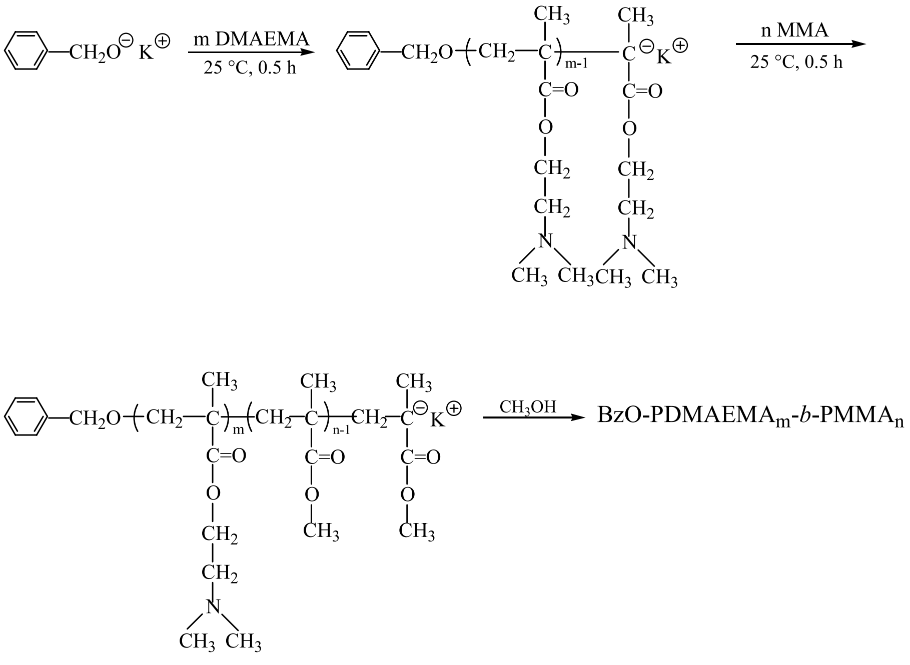

Fig. 3. A representative reaction scheme for the synthesis of BzO-PDMAEMA$_m$-*b*-PMMA$_n$ diblock copolymer via oxyanion-initated polymerization. The reverse addition order was used to prepare BzO-PMMA$_m$-*b*-PDMAEMA$_n$ diblock copolymer.

Table 3
Characteristic data of benzyloxy-capped PDMAEMA$_m$-*b*-PMMA$_n$ and PMMA$_m$-*b*-PDMAEMA$_n$

Sample ID	Polymer chemical formula (theoretical)	$\bar{M}_n$ of PDAMEMA block (g mol^{-1})		$\bar{M}_n$ of PMMA block (g mol^{-1})		$\bar{M}_w/\bar{M}_n$[a] of final copolymer
		Theor.	Actual[b]	Theor.	Actual[b]	
BDM-1	BzO-PDMAEMA$_{10}$-*b*-PMMA$_{10}$	1570	1550	1000	980	1.24
BDM-2	BzO-PDMAEMA$_{20}$-*b*-PMMA$_{10}$	3140	2900	1000	550	1.19
BDM-3	BzO-PDMAEMA$_{30}$-*b*-PMMA$_{10}$	4710	5000	1000	1090	1.34
BMD-1	BzO-PMMA$_{10}$-*b*-PDMAEMA$_{10}$	1570	1490	1000	950	1.13
BMD-2	BzO-PMMA$_{10}$-*b*-PDMAEMA$_{20}$	3140	2820	1000	910	1.24
BMD-3	BzO-PMMA$_{15}$-*b*-PDMAEMA$_{10}$	1570	1470	1500	1200	1.25

[a] As measured by GPC in THF.
[b] As determined by ^{1}H NMR in CDCl$_3$.

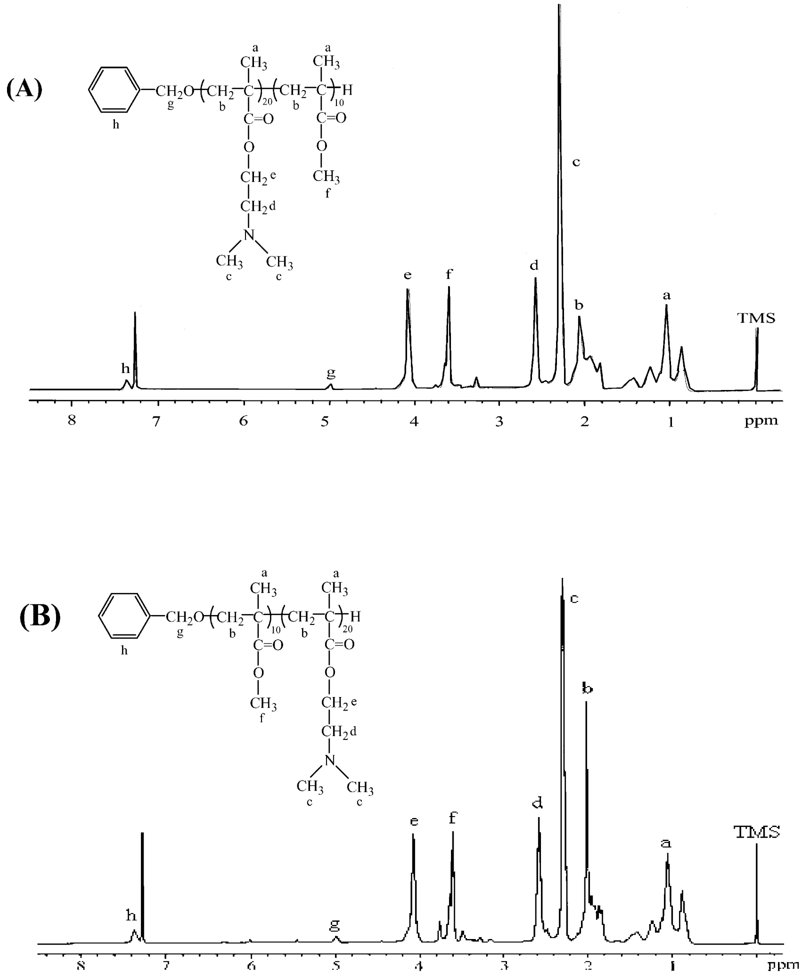

Fig. 4. ^{1}H NMR spectra of (A) BzO-PDMAEMA$_{20}$-*b*-PMMA$_{10}$ (BDM-2 in Table 3) $\bar{M}_{n(NMR)} = 3450$ g mol^{-1} and (B) BzO-PMMA$_{10}$-*b*-PDMAEMA$_{20}$ (BMD-2 in Table 3) $\bar{M}_{n(NMR)} = 3730$ g mol^{-1}. ^{1}H NMR measurements were performed at 20 °C in CDCl$_3$.

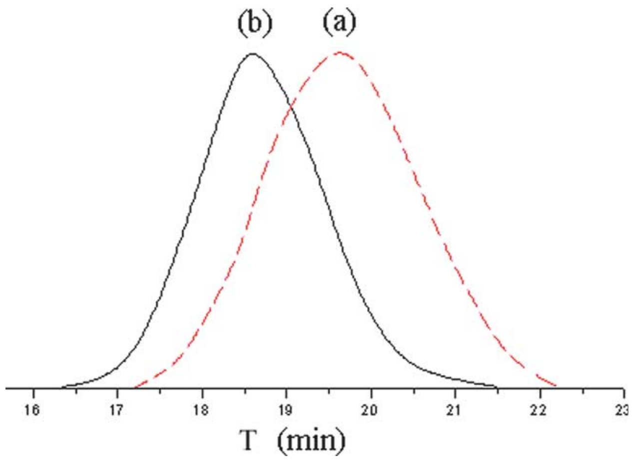

Fig. 5. Typical GPC plots showing (a) the first block BzO-$PMMA_{10}$, (b) BzO-$PMMA_{10}$-*b*-$PDMAEMA_{20}$ diblock copolymer (BMD-2 in Table 3) prepared by sequential addition. All these polymers were initiated by potassium benzyl alcoholate.

et al., who prepared short hydrophobic *n*-alkyl (C_{12}, C_{16}) end-group C_{12}-PDMAEMA, C_{16}-PDMAEMA and dimethysiloxane-2-(dimethylamino)ethyl methacrylate PDMS-PDMAEMA, PDMS-PDMAEMA-PDMS via oxyanion polymerization. They studied surface activities of these block copolymers and proposed that the hydrophobic chain imparted higher surface activity than that of DMAEMA homopolymer, the higher molecular weight DMAEMA chains reduced inefficient packing at the air-water interface [18,20].

The degree of protonation of the PDMAEMA chain and the hydrophilic–hydrophobic balance of the diblock copolymer also affect the surface activity. Surface tension studies were carried out on BzO-$PDMAEMA_{30}$-*b*-$PMMA_{10}$ copolymer at different pH media. Fig. 7 depicts the surface tension vs. concentration curves at two solutions with pH values of 3.0 and 7.0. The limiting surface tension at pH 3.0 was 68 mN/m, while at pH 7.0 the corresponding value was 53 mN/m. This result can be explained by the postulate that dimethylamino group facilitate to be protonated at pH 3 and generate the large amount of cationic polyelectrolyte. The electrostatic interaction between the polymer chains, which resulting from more cations, makes less micelle formation in water. On the other hand, the higher solubility of copolymer in acidic media reduces the adsorption of copolymer at the air-water interface.

4. Conclusions

The oxyanion-initiated polymerization of MMA has been carried out with potassium benzyl alcoholate (BzOK) in THF at 25 °C. Using PMMA as the first living block, a narrow distribution and well-defined diblcok copolymer has been synthesized by feeding sequence of the second monomer DMAEMA. Another diblock copolymer could be synthesized by reverse addition of monomers, only by the sequential addition of DMAEMA followed by MMA. The results of GPC analyses showed these copolymers had comparative narrow polydispersities ($\bar{M}_w/\bar{M}_n < 1.25$). ^{1}H NMR measurement confirmed that the actual molecular mass of both PDMAEMA and PMMA sections for each copolymer were very close to those corresponding to the monomer/initiator ratios, suggesting a high initiator efficiency for both monomers. These results imply that oxyanion-initiated polymerisation possess the substantial feature of living anion polymerization. It can be extended to other methacrylate monomers.

Surface tensiometry studies showed that a good surface activity occurred in the diblock copolymer PDMAEMA-*b*-PMMA with equal length of hydrophobic and hydrophilic chains at neutral media. Acidic media lead to higher charge

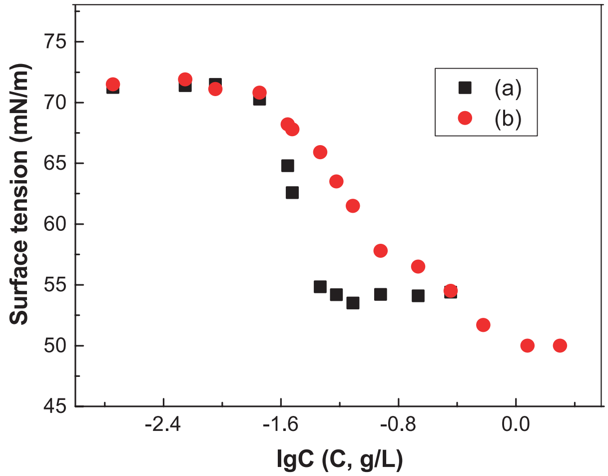

Fig. 6. Surface tension curves as a function of polymer concentration for (a) BzO-$PDMAEMA_{30}$-*b*-$PMMA_{10}$ (BDM-3 in Table 3), cmc = 0.063 g/l and (b) BzO-$PDMAEMA_{10}$-*b*-$PMMA_{10}$ (BDM-1 in Table 3), cmc = 0.69 g/l. All the measurements were carried out at 20 °C and pH = 7.0.

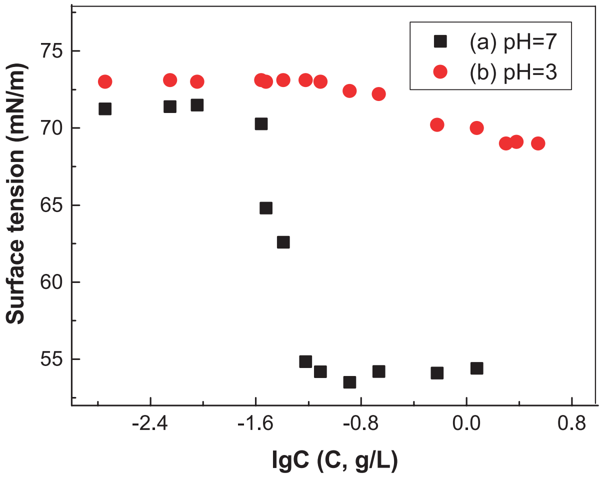

Fig. 7. Surface tension curves as a function of polymer concentration for BzO-$PDMAEMA_{30}$-*b*-$PMMA_{10}$ (BDM-3 in Table 3), measured at (a) pH = 7.0, cmc = 0.063 g/l; (b) pH = 3.0, cmc = 1.585 g/l. All the measurements were carried out at 20 °C.

density of poly(DMAEMA) and lower surface activity. The aggregation of the diblock copolymer solutions at different conditions was studied by various experimental methods and will be reported elsewhere.

Acknowledgements

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