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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.

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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 ^1H 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.

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