

The amphiphilic block copolymers of 2-(dimethylamino)ethyl methacrylate and methyl methacrylate: Synthesis by atom transfer radical polymerization and solution properties

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Received 17 June 2005; received in revised form 8 September 2005; accepted 13 September 2005

Available online 3 October 2005

Abstract

Amphiphilic di- and tri-block copolymers of poly(methyl methacrylate) (PMMA) and poly(2-dimethylamino)ethyl methacrylate (PDMAEMA) have been synthesized by atom transfer radical polymerization (ATRP) at ambient temperature (35 °C) in the environment-friendly solvent, aqueous ethanol (water 16 vol%) using CuCl₂/o-phenanthroline as the catalyst. The PDMAEMA blocks are contaminated with ethyl methacrylate (EMA) residues to the extent of 1–2 mol% of DMAEMA depending on the length of the PDMAEMA block. The EMA forms through the autocatalyzed ethanolysis of the DMAEMA monomer and undergoes random copolymerization with the latter. The rate of ethanolysis is unexpectedly greater in the aqueous ethanol than in neat ethanol, which has been attributed to the higher polarity of the former than of the latter. In contrast to the ethanolysis no hydrolysis of DMAEMA in the aqueous ethanol medium could be detected for 133 h. The block copolymers form micelles in water. Their solubility and CMC in neutral water have been studied. Dynamic light scattering (DLS) studies reveal that for a fixed degree of polymerization (DP) of the PMMA block the hydrodynamic diameter of the micelles in methanolic water (water 95 vol%) increases at a faster rate with the DP of the PDMAEMA block when it is much greater than that of the PMMA block compared to when it is less than or close to that of the latter.

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Keywords: Atom transfer radical polymerization; Amphiphilic block copolymer; Block copolymer

1. Introduction

Amphiphilic block copolymers have great application potential e.g. in the stabilization of latex particles [1], emulsions [2], dispersions [3], separations [4] and also as drug and gene delivery vehicles [5–7]. Poly(2-dialkylamino)ethyl methacrylates (PDAAEMA) as the constituents of amphiphilic block copolymers have attracted interest. When the alkyl is methyl the polymer is hydrophilic, whereas when it is ethyl the character of the polymer changes from hydrophobic to hydrophilic as the pH of the medium is lowered to the acidic region [8–10]. Micelles of the A–B–C tri-block copolymer comprising of polyethylene glycol as one end block (block A) and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) as the other end block (block C) and poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) as the centre block (block

B) have been studied for the stabilization and the controlled release of the hydrophobic drug, dipyrindamole [10]. Diblock copolymers with PDMAEMA as the hydrophilic block and poly(alkyl methacrylates) as the hydrophobic blocks have been studied as dispersion polymerization stabilizers [11]. On the other hand, the solution properties of the PMMA–PDMAEMA di-block copolymers and their micelles have been characterized in detail [12,13]. Such polymers were prepared earlier by the classical living anionic or the group transfer polymerization [12–14].

After the advent of atom transfer radical polymerization (ATRP) it has been the method of choice for the synthesis of block copolymers by virtue of its insensitivity towards moisture or other protic compounds, greater tolerance towards functional groups in monomers or initiators as well as impurities [15–18]. Matyjaszewski et al. were the first to report the ATRP synthesis of di- and tri-block copolymers of MMA and DMAEMA at 90 °C in dichlorobenzene using CuBr/4,4'-di(5-dinonyl)-2,2'-bipyridine (dNbpy) as the catalyst [19]. Subsequently, Hadjleton et al. synthesized di- and tri-block copolymers of *n*-butyl methacrylate (nBMA) and DMAEMA in toluene at 90 °C using

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CuBr/N(*n*-propyl)2-pyridylmethanimine as the catalyst and studied some aspects of their aggregation behavior in aqueous solution [20].

On the other hand, in recent years aqueous alcohols (methanol, ethanol, isopropanol) have attracted interest as the medium of polymerization [8–10,21–29]. This is because the polymerization can be carried out at ambient temperature at reasonably fast rates and the solvents are environment-friendly. However, methanol is reported to be an unsuitable medium for the ATRP of DMAEMA and other *t*-amine methacrylates such as DEAEMA and 2-(diisopropylamino)ethyl methacrylate (DiPAEMA) inasmuch as these monomers undergo transesterification reaction with methanol at rates which are comparable with the rates of polymerization leading to the formation of statistical copolymers with MMA [24]. On the other hand, transesterification is insignificant in *i*-propanol due to steric reasons [24]. Matyjaszewski et al. used aqueous *i*-propanol (10% water by volume) as the medium for the ATR block as well as random and gradient copolymerization of nBMA, DMAEMA and DEAEMA at 25 °C [9].

Recently, we reported the ambient temperature ATRP of MMA in the environment-friendly solvent aqueous ethanol in which PMMA is soluble in the composition range, $6 \leq \text{water} \leq 30$ volume percent [29]. PDAAEMA and many other hydrophilic polymers are also soluble in aqueous ethanol. The method, therefore, presents an opportunity for the convenient synthesis of amphiphilic block copolymers with PMMA as the hydrophobic block in this environment-friendly solvent. In this paper we present the ATRP synthesis of di- and tri-block copolymers of DMAEMA and MMA at ambient temperature in aqueous ethanol. The block copolymers have been characterized which included a study of the transesterification of DMAEMA with ethanol and aqueous ethanol. The micellar dimensions of the block copolymers are also reported.

2. Experimental section

2.1. Materials

MMA (BDH) was washed with 5% NaOH solution followed by distilled water, dried over CaCl₂ and distilled under reduced pressure. It was stored under nitrogen atmosphere at –15 °C. DMAEMA (98%, Aldrich) was distilled under vacuum. CuBr (98%, Aldrich) and CuCl (98%, BDH) were purified by washing with corresponding acids (10% HCl or HBr in water) followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere. Absolute ethanol (Bengal Chemical and Pharmaceutical works, India) was refluxed for 2 h with Mg wire and distilled. Commercial distilled water was redistilled over alkaline permanganate. *o*-Phenanthroline (*o*-phen, 99.5%, E Merck), and ethyl 2-bromoisobutyrate (EBiB, 97%, Aldrich) were used as received. The difunctional initiator, 1,2-bis(bromoisobutyryloxy) ethane (BiBE), was synthesized using a literature procedure [30].

2.2. The molecular weights (MW) and their polydispersity indices (PDI)

These were measured by GPC at room temperature using a Waters model 510 HPLC pump, a Waters series R-400 differential refractometer and Waters Ultrastaygel columns of 10,000, 1000, 500 Å pore size which were preceded by a prefilter. HPLC grade THF (Spectrochem, India) mixed with triethylamine (5 vol%) was used as the eluent at a flow rate of 1 ml/min. Before injection into the GPC system the polymer solutions were passed through a silica gel column using THF as the eluent to free them from Cu salts. They were then filtered through a prefilter–filter combination system compatible with organic solvents. Waters poly (methyl methacrylate) standards were used for calibration.

2.3. Homo polymerization of DMAEMA

A typical procedure for the ATRP synthesis of PDMAEMA is as follows. In a nitrogen purged reaction vessel (15 ml) provided with a B-19 standard joint were taken CuBr (33 mg, 0.23 mmol) and *o*-phen (92 mg, 0.46 mmol). Deoxygenated (nitrogen purged) ethanol (4 ml), water (1 ml) and DMAEMA (4.66 g, 29.7 mmol) were next added into the vessel under nitrogen. The vessel was then closed with a rubber septum, which was secured by Cu wire. The admixture was sonicated for 2 min. A deep brown solution was obtained. The vessel was then placed in a thermostated water bath maintained at 35 °C. EBiB (0.035 ml, 0.23 mmol) was next introduced into the vessel using a gas-tight syringe which was purged with nitrogen. The polymerization was continued for 4 h. The polymerization mixture was then diluted with acetone (3 ml) and poured into excess petroleum ether. The polymer was purified by passing its solution through a silica gel column using THF as the eluent. The polymer so purified was isolated and dried in a vacuum oven at 45 °C for 48 h and weighed. Conversion was 98%. The M_n and PDI of the polymer were 19,700 and 1.28, respectively.

For kinetic studies, aliquots (1.5 ml) were withdrawn from time to time from the reaction vessel using gas tight syringes and poured into petroleum ether. The polymer was isolated and dried as above.

2.4. Homo polymerization of MMA

It is similar to that described above and published earlier [29].

2.5. Synthesis of PMMA-*b*-PDMAEMA di-block copolymer

A representative example is as follows. A monofunctional PMMA macroinitiator was prepared using the EBiB initiator and the CuCl/*o*-phen catalyst with the following recipe: MMA (4.7 g, 47 mmol), EtOH (4.2 ml), H₂O (0.8 ml), CuCl (58.16 mg, 0.587 mmol), *o*-phen (232.45 mg, 1.174 mmol), EBiB (0.088 ml, 0.587 mmol). The polymer was purified as described above. The polymer (0.467 g,

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