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Synthesis and self-association in aqueous media of poly(ethylene oxide)/ poly(ethyl glycidyl carbamate) amphiphilic block copolymers

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Abstract

New temperature sensitive AB, ABA, and BAB amphiphilic block copolymers consisting of hydrophilic poly(ethylene oxide) and hydrophobic poly(ethyl glycidyl carbamate) blocks were synthesized by anionic polymerization followed by chemical modification reactions. The self-association of the block copolymers in aqueous media was studied by UV–vis spectroscopy and dynamic and static light scattering. The obtained block copolymers spontaneously form micelles in aqueous media. The critical micellization concentration varied from 0.5 to 4 g/L depending on the copolymer architecture and composition. The influence of the temperature upon the self-association of the block copolymers was investigated. The increase of temperature did not affect the value of the critical micellization concentration, but led to the formation of better defined micelles with narrow size distribution.

Keywords: Anionic polymerization; Polyethers; Amphiphilic block copolymers

1. Introduction

The self-association of amphiphilic block copolymers in aqueous media is an entropy driven process, which in the majority of cases leads to formation of spherical micelles comprising hydrophobic core and hydrophilic shell [1,2]. The most extensively studied is the micellization of block copolymers of hydrophilic poly(ethylene oxide)—PEO and hydrophobic polyoxiranes such as poly(propylene oxide)—PPO or poly(butylene oxide)—PBO [3,4]. In the case of PEO–PPO copolymers, the micellization is a temperature dependent process [5,6], as PPO exhibit the lower critical solution temperature at a relatively low temperature [7,8]. In the majority of cases, the temperature is typically not so important for the micellization of PEO–PBO block copolymers [3,9]. For some copolymer architectures and compositions even athermal micellization was observed [10,11].

Polyglycidol—PG is a polyoxirane that carries one primary hydroxyl functional group per monomeric unit and resembles PEO by its hydrophilicity. Well defined linear polyglycidol polymers have been obtained by anionic polymerization of ethoxyethyl glycidyl ether—EEGE followed by successive mild cleavage of the protective ethoxyethyl group [12]. In recent years, various polyglycidol based random [13], block [14], star-block [15], brush-like [16], and arborescent [17–21] copolymers have been synthesized.

The hydroxyl functionality of PG opens versatile synthetic routes of selective chemical modification leading to new materials of desired physicochemical properties. Up to now only few modifications of the hydroxyl groups of the glycidol monomeric units have been performed. High molar mass PEO–PG block copolymers were modified with stearic acid aiming for rheology builders [22]. Superabsorbing hydrogels were obtained after chemical cross-linking of hydrophilic PEO–PG triblock copolymers [14,23]. Temperature sensitive copolymers with controllable cloud points have been achieved by tuned hydrophobization of high molar mass polyglycidol or PG–PEO–PG block copolymers [13,24].

Block copolymers of ethylene oxide—EO and glycidol—G of different architecture are suitable precursors for new class amphiphilic block copolymers when the hydrophilic groups of the glycidol units are reacted with hydrophobic compounds. In the present article, we investigate the synthesis of well defined di- and triblock copolymers of EO and ethyl glycidyl

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carbamate—EGC of different hydrophilic/hydrophobic balance. Their self-association properties in aqueous media is studied as a function of temperature by using UV–vis spectroscopy and dynamic and static light scattering.

2. Experimental

2.1. Materials

All solvents were purified by standard methods. $CsOH\cdot H_2O$ 99.5% (Aldrich) and *t*-BuOK 97.0% (Aldrich) were used as received. Diethylene glycol—DEG (Aldrich) was distilled under reduced pressure prior to use. Poly(ethylene glycol)—PEG of $\bar{M}_n = 12{,}000$ g/mol and $\bar{M}_w/\bar{M}_n = 1.03$ (Aldrich) and poly(ethylene glycol)monomethyl ether—MPEG of $\bar{M}_n = 11{,}000$ g/mol and $\bar{M}_w/\bar{M}_n = 1.02$ (Polysciences) were precipitated in hexane. Ethoxyethyl glycidyl ether was synthesized according to procedure described elsewhere [25] and purified by vacuum distillation. Fractions of purity exceeding 99.8% (GC) were used for polymerizations. Ethylene oxide (Aldrich) was kept over CaH_2 and distilled under vacuum prior to polymerization. Dibuthyltin dilaurate 95% (Aldrich) and ethyl isocyanate 98% (Aldrich) were used as received.

2.2. Synthesis of block copolymers

2.2.1. Synthesis of di- and triblock copolymers

Cesium alkoxides of PEG and MPEG were used as initiators for the polymerization of EEGE in order to obtain copolymers of $EEGE_nEO_mEEGE_n$ and $EEGE_nEO_m$ architectures. Details are given elsewhere [14].

Block copolymers—$EO_mEEGE_nEO_m$ were obtained using sequential polymerization of EEGE and EO initiated by potassium alkoxide of diethylene glycol. Schlenk tube equipped with teflon seals, teflon sealed ampoules and high vacuum (10^{-4} bar) were used for the polymerizations. Stock solution of *t*-BuOK (0.026 g, 2.3×10^{-4} mol) in 10 mL of DMSO was prepared at room temperature in a calibrated ampoule. 1.4 mL of the stock solution containing 3.34×10^{-5} mol *t*-BuOK was added dropwise under vacuum to the polymerization ampoule containing diethylene glycol (0.125 g, 1.18×10^{-3} mol) dissolved in another 5 mL of DMSO. The reaction mixture was stirred at room temperature and occasionally slightly heated for 1 h under vaccum in order to remove the released *t*-BuOH. The EEGE monomer (6.8 g, 4.7×10^{-2} mol or 13.7 g, 9.4×10^{-2} mol for $DP_{EEGE} = 40$ and $DP_{EEGE} = 80$, respectively), was added and the polymerization continued for 48 h at 60 °C. After taking a sample for analysis, the temperature was lowered to 0 °C and EO (12.5 mL, 0.25 mol) was transferred under vacuum to the ampoule. The EO was polymerized initially at room temperature (24 h), then at 40 °C (48 h) and finally at 65 °C (24 h).

2.2.2. Deprotection of the ethoxyethyl groups

EO/EEGE copolymer was dissolved in acetone (polymer concentration was 150 g/L). Oxalic acid dissolved in water was added and after 1 h of stirring at room temperature the reaction mixture was neutralized with aqueous solution of $Ca(OH)_2$. The molar ratio [EEGE]:[oxalic acid]:[$Ca(OH)_2$] was 1:0.5:1. The suspension formed by insoluble calcium oxalate was removed by filtration and the polymer solution was concentrated under reduced pressure. The polymer was dialyzed against deionised water. The resulting EO/G copolymers were dried under reduced pressure at 50 °C.

2.2.3. Chemical modification of copolymers of ethylene oxide and glycidol with ethyl isocyanate

While maintaining dry conditions, ethyl isocyanate was added to a DMF solution of EO/G block copolymers and dibutyltin dilaurate (DBTL) catalyst at room temperature (polymer concentration in DMF was 150 g/L). The molar ratio [glycidol units]:[DBTL]:[ethyl isocyanate] was 1:0.02:2. The reaction leading to block copolymer of ethylene oxide and ethyl glycidyl carbamate was carried out at 40 °C for 48 h. DMF was exchanged with water via dialysis for 12 h. The water was evaporated under vacuum. The residue was dissolved in small amount of methylene chloride and precipitated in diethyl ether. After several precipitation procedures the final product was dried under vacuum.

2.3. Measurements

2.3.1. NMR

^{1}H NMR spectra were recorded at 25 °C on a Varian Unity-Inova spectrometer operating at 300 MHz. $CDCl_3$ and D_2O were used as solvents.

2.3.2. Size exclusion chromatography (SEC)

The setup for SEC measurements consisted of differential refractive index detector Δn-1000 RI WGE DR Bures and a multiangle laser light scattering (MALLS) detector DAWN EOS from Wyatt Technologies. Four PSS SDV columns of nominal pore sizes 1×10^5, 1×1000, 2×100 Å were used for measurements in THF. THF was used as a mobile phase in the case of homopolymers of EO, EEGC, EGC and their block copolymers. Also four PSS GRAM columns of nominal pore sizes 1×3000, 1×1000, 1×100, and 1×30 Å were used for measurements in DMF with 5 mmol/L LiBr. DMF was used as a mobile phase in the case of PG and its block copolymers with EO. Measurements were preformed at 30 °C for THF and at 45 °C for DMF/LiBr. The nominal flow rate of the eluent was 1 mL/min. The specific refractive index increment (d*n*/d*c*) of polymer samples was measured at 30 °C using a differential refractive index detector Δn-1000 RI WGE DR Bures from Wyatt Technologies. SEC results were collected and evaluated by ASTRA software from Wyatt Technologies and WINGPC software from PSS.

2.3.3. Dynamic light scattering (DLS)

DLS measurements were performed on a Brookhaven BI-200 goniometer with vertically polarized incident light of wavelength $\lambda = 632.8$ nm supplied by a helium–neon laser operated at 75 mW and a Brookhaven BI-9000 AT digital autocorrelator. Measurements of scattered light from the