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Amphiphilic poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) graft copolymers: synthesis and characterisation

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Abstract

Amphiphilic poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) graft copolymers (PDMAEMA-g-PCL) with various compositions and molecular weights were synthesised via a fully controlled three-step strategy. First, poly(ε-caprolactone) macromonomers (PCLMA) were prepared by ring-opening polymerization (ROP) of ε-caprolactone (CL) initiated by aluminum triisopropoxide ($Al(O^iPr)_3$), followed in a second step by quantitative esterification of PCL hydroxy end-groups with a methacrylic acid derivative. Finally, the controlled copolymerization of PCLMA and *N*,*N*-dimethylamino-2-ethyl methacrylate (DMAEMA) was carried out by atom transfer radical polymerisation (ATRP) in THF at 60 °C using CuBr ligated with 1,1,4,7,10,10, hexamethyl triethylenetetramine and ethyl 2-bromoisobutyrate as catalyst and initiator, respectively. Furthermore, PDMAEMA-g-PCL graft copolymers were reacted with methyl iodide to convert the pendant tertiary amines into quaternary ammonium iodides increasing accordingly their water solubility. Some preliminary experiments was further carried out by tensiometry and dynamic light scattering in order to shed so light on the tensioactive behaviour of these amphiphilic graft copolymers (with protonated amines or quaternary ammonium cations).

Keywords: Amphiphilic graft copolymers; Atom transfer radical polymerization; Macromonomer; Copolymerization; Tensioactive properties

1. Introduction

The discovery of new mechanisms allowing the polymerization process to be under control has paved the way to new macromolecular architectures. Recently, considerable progress has been made in the design and synthesis of new graft copolymers by metal-catalyzed radical polymerization, most of them being obtained by copolymerization of an unsaturated macromonomer with a low molecular weight vinyl comonomer [1,2]. Compared to conventional free radical polymerization, the graft copolymers obtained by atom transfer radical polymerization (ATRP) are usually more homogeneous in terms of molecular weight distribution (lower polydispersity index) and number of grafts pending along the main backbone. As far as the grafts distribution is concerned, it is dictated by the reactivity ratios of both the

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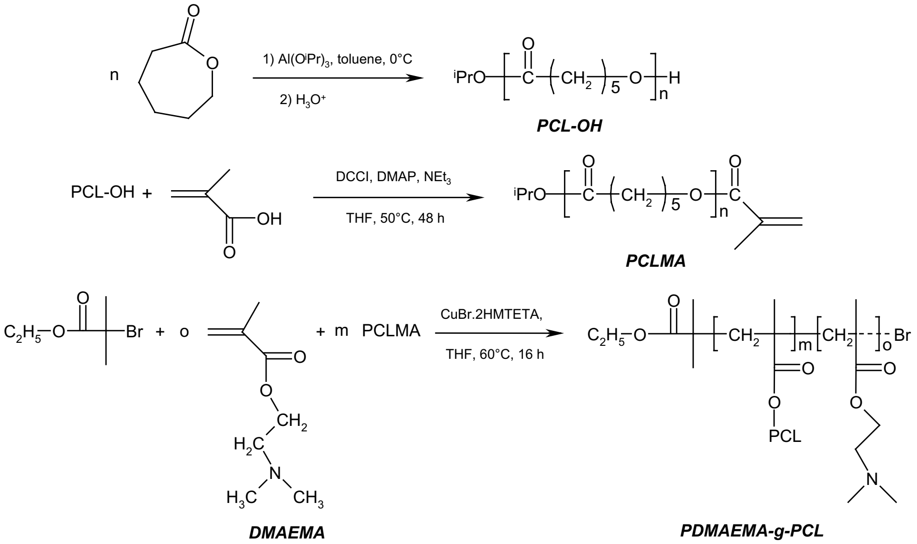
macromonomer and the low molecular weight comonomer. As a typical example Matyjaszewski et al. reported on the reactivity of (meth)acrylate-terminated polylactide macromonomers (PLAMA) in copolymerization with methyl methacrylate (MMA) in ATRP [3]. PLAMA reactivity proved to be similar to the inherent reactivity of the terminal 2-oxyethyl (meth)acrylate group, whatever the length of the attached PLA chain, attesting for the absence of diffusion control effect or simply incompatibility effect. Indeed, the two main factors that may reduce the reactivity of PLAMA compared to MMA are the kinetic excluded volume effect associated with the large size of the macromonomer relative to the free radical lifetime [4,5] and the potential incompatibility of the incoming macromonomer and grafted propagating chain due to thermodynamic repulsive interactions [6]. Furthermore in case of functionalized (macro)monomers containing for instance donor atoms such as N or O atom, their coordination to the transition-metal catalyst may also affect the reactivity ratios by either altering the electronic structure of the double bond, or simply through some mass effect [7]. In that respect, Haddleton et al. have copolymerized MMA with either various aminoethyl methacrylate monomers or poly(ethylene glycol) macromonomers (PEGMA) characterised by different molar masses, the reactivity ratio toward MMA comonomer was significantly reduced in ATRP compared to free radical copolymerisation [8]. Similarly, some of us have observed that functional monomers such as 2-hydroxyethyl methacrylate and PEGMA (with Mn of ca. 450), were preferably incorporated into growing copolymer chains with MMA by using $NiBr_2(PPh_3)_2$ and ethyl 2-bromoisobutyrate as catalyst and initiator, respectively, in toluene at 85 °C [9].

Here we aim reporting on the controlled synthesis and characterisation of new amphiphilic poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) graft copolymers (PDMAEMA-g-PCLMA) by ATRP between preformed poly(ε-caprolactone) macromonomer (PCLMA) and *N*,*N*-dimethylamino-2-ethyl methacrylate (DMAEMA) as functional comonomer. To the best of our knowledge, such amphiphilic graft copolymers with a pH and temperature sensitive water soluble poly(aminomethacrylate) backbone [10] and biodegradable aliphatic polyester grafts have never been synthesized, nor their tensioactive properties investigated by tensiometry and dynamic light scattering. It is worth mentioning that such polycations carrying a low content of hydrophobic side chains are of increasing interest for their properties in water solution and applications such as flocculants, thickening agents, latex particles, cosmetics, gene therapy, etc. [11,12]. Practically, the synthesis of PCLMA macromonomers has been first carried out according to a previously reported method [13] consisting of the controlled ring-opening polymerization (ROP) of ε-caprolactone (CL) initiated by aluminum triisopropoxide ($Al(O^iPr)_3$), followed by the quantitative esterification of ω-hydroxy groups by methacrylic acid derivatives. Then, the controlled copolymerization of PCLMA and DMAEMA was carried out by ATRP in THF at 60 °C using CuBr ligated with 1,1,4,7,10,10, hexamethyl triethylenetetramine and ethyl 2-bromoisobutyrate as catalyst and initiator, respectively (Scheme 1). PDMAEMA-g-PCL graft copolymers have also been reacted with CH_3I to convert tertiary



Scheme 1. Three-step synthesis pathway of poly(*N*,*N*-dimethylamino-2-ethyl methacrylate)-g-poly(ε-caprolactone) (PDMAEMA-g-PCL).