

Synthesis and self-assembly of amphiphilic maleic anhydride–stearyl methacrylate copolymer

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Abstract

Amphiphilic maleic anhydride–stearyl methacrylate (MA–SMA) random copolymer was synthesized via the free radical copolymerization and its amide was prepared through the MA moieties being reacted with morpholine. Polymers obtained were characterized by GPC and ¹H NMR. The aggregating behaviors of copolymers were investigated by first dissolving them in tetrahydrofuran (THF) and then adding water to induce association of the long alkyl chains and observed over the range of copolymer concentrations from 0.028 to 0.22 wt% and water content from 5.32 to 34.85 wt%. Resultant aggregates show new potential application in the fields of drug delivery systems, microcapsules and so on.

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1. Introduction

Amphiphilic molecules have received considerable attention due to their ability to self-assemble in bulk and in solution forming a range of different morphologies (e.g. spheres, rods, lamellae and large compound vesicles) and sizes through weak non-covalent interactions (hydrogen bonding, π – π interaction, van der Waals, coordination, and charge-transfer interaction) [1–7]. Amphiphilic micellar systems have very interesting particular properties, so they have many potential applications in areas such as micro-reactors, microcapsules, and drug delivery systems, encapsulation of various kinds of guest molecules [8–12]. Many investigations had begun on the thermodynamic and kinetic aspects that induced morphogenesis [13–15]. And many factors were found to alter the aggregation architectures, for example, temperature, solvent, concentration [16], solvent composition and water content [17], and pH [18], among other factors [19].

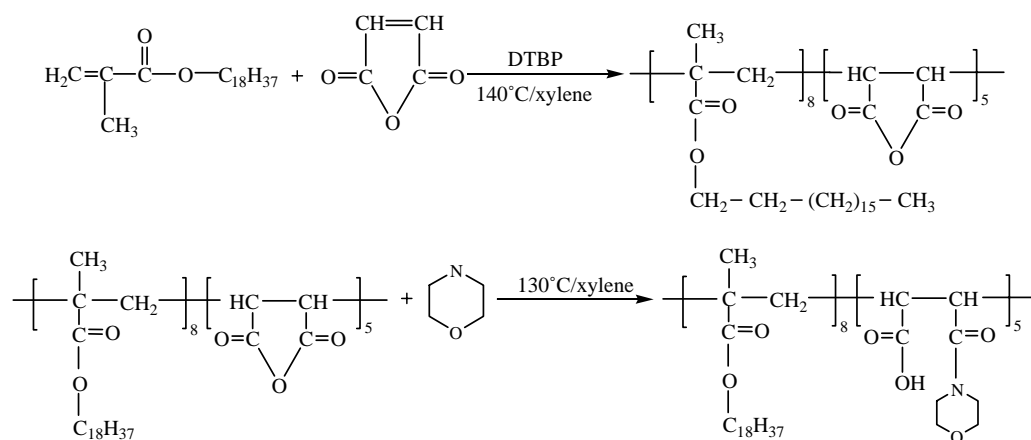
Maleic anhydride (MA) is an excellent monomer which can provide reactive anhydride or carboxylic groups, and amphiphilic molecules can be obtained easily via

the copolymerization of MA and hydrophobic monomer. Recently, extensive studies have been performed on the radical copolymerization of MA with other monomer and the self-assembly of their copolymers [20–27]. For example, Stover et al. [20] studied that the self-assembly of lightly cross-linked, swellable poly(divinylbenzene-*alt*-maleic anhydride) microgels at the oil–water interfaces of a propyl acetate–water suspension. Li et al. [21] prepared a well-defined block copolymer having alternating maleic anhydride/styrene segments and polystyrene segments and studied the self-assembly aggregating behavior of its hydrolyzed amphiphilic product in water. Li et al. [22] also reported on the synthesis of a diblock copolymer containing a block of alternately structured maleic anhydride with 4-vinylbenzyl chloride (VBC) and PVBC block. It was found that the copolymer can form stable inverse micelles in THF after the MA moieties being reacted with 2-mercaptoethyl amine. In general, the studies mentioned above mainly focused on the self-assembly of alternate copolymers or diblock copolymers containing one alternate block and other hydrophobic block.

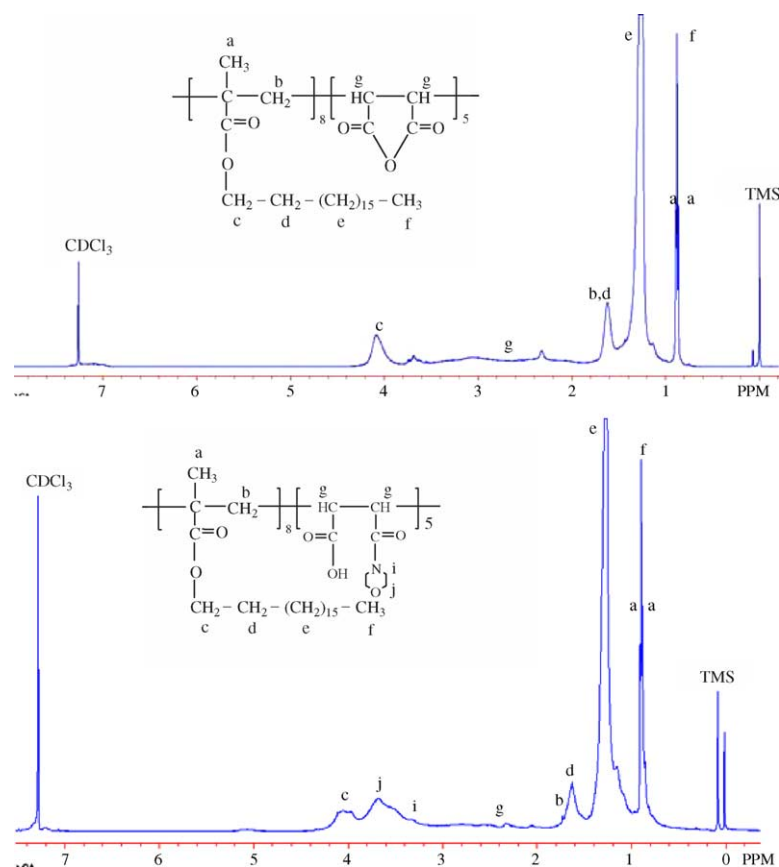
Stearyl methacrylate (SMA) is an interesting monomer because it has a pendent long alkyl side chain which can form crystalline domain [28]. Many studies have appeared in the literature concerning the micelle properties of copolymers consisting of a PSMA block. Hadjichristidis et al. [29] reported on the synthesis of polystyrene-*b*-polystearyl methacrylate (PS-*b*-PSMA) using anionic polymerization high-vacuum techniques. And it was found that the copolymer could self-assemble into aggregates in organic solvents.

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Scheme 1. Synthesis procedure of P(MA-co-SMA) and its amide.

Fig. 1. ^1H NMR spectra of P(MA-co-SMA) and the amide of P(MA-co-SMA).

The copolymer of MA and SMA should combine the reactive anhydride property of MA and crystalline property of SMA together. The polymeric micelles formed from MA and SMA copolymer are of interest in further chemical or biological modification. If the hydrophilicity of the resultant copolymer was regulated through amination, the self-assembly behaviors of it would be changed. The synthesis of MA-co-SMA was first reported by Gargallo et al. [30]. In Gargallo's work, an alternating (1:1) copolymer of MA-co-SMA was synthesized

Table 1
Molecular weight and molecular weight distribution of copolymers

Copolymer	M_n^a (g/mol)	M_w/M_n^a
P(MA-co-SMA)	3.1×10^3	1.45
Amide of P(MA-co-SMA)	4.3×10^3	1.34

^a M_n determined by GPC.

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