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Synthesize and characterization of new polymeric surfactants based on nonionic maleate surfmer by catalytic bulk copolymerization with methyl methacrylate

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ABSTRACT

Non-ionic maleate surfmer (M1) was prepared via ring opening reaction of maleic anhydride with hexanol followed by esterfaction with polyethylene glycol. The prepared surfmer was homo-polymerized and copolymerized with methyl methacrylate (M2) at different conditions using TiO_2 and V_2O_5 as catalysts in presence of O_2 or N_2. The chemical structure of the prepared surfmer, homo-polymer and copolymer were confirmed by FT-IR, ^{13}C and ^{1}H NMR. The molecular weights of the prepared polymers were measured using Gel Permeation Chromatography (GPC) and their thermal gravimetric analysis (TGA) was determined. TGA indicated a higher thermal stability for the copolymers M1M2TN and M1M2VO relative to the pure polymethylmethacrylate (PMMA). The interfacial tension for the prepared surfmer and the copolymer was measured. The optimum conditions which resulted in 64.2% and 63.8% conversion were 20% w/w TiO_2 in N_2 and 10% w/w V_2O_5 in O_2 at 80 °C for 4 h with M1/M2 molar ratio of 1:1.

1. Introduction

A significant number of studies have been undertaken on the polymerization of polymerizable surfactants (surfmers). Surfmers show the advantage of combining the physical behavior of surfactants with the reactivity of monomers [1–3]. A wide variety of surfmer structures that differ with respect to the polar functional groups and the location of the polymerizable moiety have been reported. Examples include anionic, cationic, zwitterionic and nonionic surfactants [4–7]. The conventional polymerizable groups that have been used include styrene, acrylic, methacrylic, and acrylamide [8–10]. The surfmers are interesting in various field of applications. Several investigations have been carried out on maleic anhydride copolymers to be used as polymeric surfactants [11–13]. It was asserted for many years that 1,2-disubstituted ethylene does not polymerized, while maleic anhydride shows only a small tendency for radical polymerization [14]. Braun et al [15] used various radical initiators to polymerize maleic anhydride; they observed partial decarboxylation and obtained a polymer which consists mainly of cyclopentanone derivatives. Heseding and Schneider [16] prepared maleic anhydride homopolymer by γ-irradiation. The polymer obtained by initiation via irradiation showed the anhydride structure without decarboxylation and discoloration. These results were in good accord with the findings from the work of Lang and coworkers [17]. Synthesized catalysts for industrial purposes consume a billion-dollar and account for the manufacture of 60% of chemicals that are utilized for most chemical transformations. Catalytic processes enable the production of many substances such as polymers, plastics, pharmaceuticals, detergents and many others [18–23]. For example, fabricated TiO_2 has been designed, synthesized and used as green catalyst for save chemical process by Shrikant et al. [24].

Polymer-inorganic catalyst have a great attention recently due to their importance in different fields. It is known that TiO_2 and V_2O_5 have good thermal and photo-catalytic activities in different chemical processes such as polymerization and environmental treatment reactions [25,26]. Also nano-TiO_2 has bioactivity behaviors and thus polymer-TiO_2 nanocomposites can be used in industrial and medical areas [27–29]. The functionality of PMMA/$CaSO_4$ nanocomposites has been studied to be used as support for gentamicin antibiotic in bone substitute material and antibiotic vehicle [30]. Maleic anhydride (MA)-copolymers have been used as polymer-drug conjugates [31,32]. These copolymers are usually prepared in organic solvents which have cytotoxicity effect. The simple maleate surfmer (i.e. the neutralized hemi ester of a fatty

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alcohol) was used to prepare seeds of polystyrene latex which were grown with a shell of film-forming polymers [33].

This investigation describes a novel method for catalytic copolymerization of nonionic maleate surfmer with methyl methacrylate using bulk polymerization technique to keep away from terrible effects of organic solvent. Copolymerization process was carried out using TiO_2 and V_2O_5 in presence of O_2 or N_2 atmosphere at different reaction temperatures, times and molar ratios of monomers. Also, the mechanism of this reaction with and without catalyst was estimated.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich Company. First of all, linear hexanol was dried using magnesium sulphate ($MgSO_4$) then distilled under atmospheric pressure. Also, maleic anhydride (MA) was refluxed with chloroform and filtered to remove any traces of maleic acid. Finally, the product was then crystallized three times from chloroform to yield white needles with a melting point of 53 °C. Polyethylene glycol 200 (PEG_{200}) and p-toluene sulphonic acid were used as received from Merck-Schuchardt. Methyl Methacrylate (MMA) was purified to remove the hydroquinone inhibitor as illustrated in previous methods [33]. TiO_2 and V_2O_5 are purchased from Sigma Company.

2.2. Synthesis of the non-ionic maleate surfumer (M1)

The maleate surfmer as shown in Scheme 1 was prepared in two steps. First, the preparation of the hemiester of maleic anhydride via ring opening reaction. Maleic anhydride (0.1 mol) was placed in one necked flask and 0.12 mol of hexanol was added and then the reaction mixtures stirred at 80 °C for one hour. Heptane was added to the reaction mixtures and stirred to dissolve the hemiester. This process was repeated three times. The hemiester was dissolved in ethylacetate and washed three times with saturated NaCl solution to remove unreacted hexanol. Ethyl acetate was evaporated and the prepared hemiester was collected [34].

The second step is the preparation of maleate surfmer (maleate diester) by esterification of 0.1 mol of the hemiester with 0.12 mol of PEG_{200}. The reaction was performed in an appropriate amount of xylene in presence of 1% p-toluene sulphonic acid as a catalyst. When the reaction completed, the solvent was distilled off under reduced pressure. Unreacted polyethylene glycol was removed by dissolving the reaction product in isopropanol and then washes with a solution of 5% sodium carbonate. Isopropanol was then distilled off under reduced pressure in a rotary evaporator. The produced diester surfmer ($MANS_{200}$) was left to dry overnight on anhydrous sodium sulphate and will be denoted as M1 in discussion.

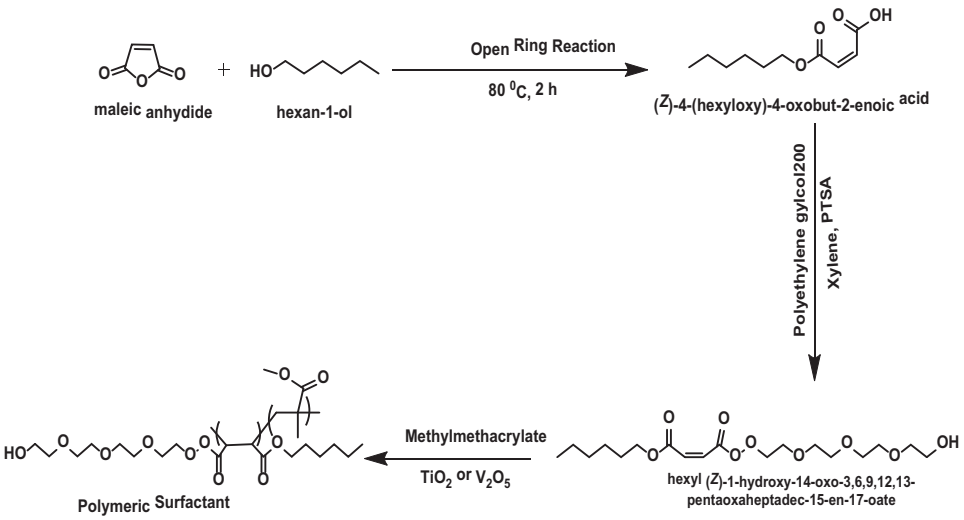
2.3. Non-catalytic and catalytic bulk homo-polymerization of M1

3.6 g of the prepared nonionic maleate surfmer (M1) was placed into polymerization tube of 20 ml capacity with and without catalyst. The reaction tube was sealed under a dry flow of nitrogen gas and then placed in a thermostat adjusted at 80 °C for 8 h. After cooling to room temperature, the tube was carefully opened and the content was dissolved in acetone under occasional shaking. The solution was filtered to remove the catalyst (in case of presences of catalyst). The polymer produced was precipitated by adding the solution into a calculated amount of methanol and then filtered, washed and dried under vacuum at 40°.

2.4. Non-catalytic and catalytic bulk copolymerization of M1 and M2

Surfmer monomer (M1) 3.6 g and previously purified MMA (M2) 1.0 g with molar ratio of 1:1 was mixed in test tube of 20 ml capacity, then the catalyst samples TiO_2 or V_2O_5 or were added with different weight percent (2,10 and 20 wt%) with respect to the total monomers weight. Dry nitrogen or oxygen were passed through the reaction mixture then the reaction test tube was tightly closed and put in adjusted water bath at the required temperatures (60, 80 and 100 °C) for different times (2, 4, 8 and 12 h) and different molar ratios (1:2 and 2:1). When the polymerization completed, the test tubes were cooled to 25 °C, opened and the produced copolymer was dissolved in acetone and filtered to remove the catalyst. This copolymer was precipitated by running in methanol then filtered and dried under vacuum at 40 °C till constant weight. Maleate surfmer monomer (M1) also copolymerized with MMA in absences of catalyst in N_2 and O_2 atmosphere for comparison. The conversion% of the prepared polymer for each experiment was calculated by the following equation:

$$\text{Conversion } \% = \left(\frac{\text{weight of copolymer}}{\text{total weight of monomers}}\right) \times 100$$



Scheme 1. Preparation of $MANS_{200}$ surfmer (M1) and its copolymer.

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