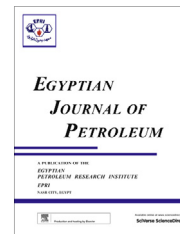




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FULL LENGTH ARTICLE

Synthesis and characterization of high molecular weight hydrophobically modified polyacrylamide nanolatexes using novel nonionic polymerizable surfactants

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Abstract In this article, nine hydrophobically modified polyacrylamides (HM-PAM) nanolatexes, were synthesized by copolymerizing the acrylamide monomer and novel polymerizable surfactants (surfmers). The reaction was carried out by inverse microemulsion copolymerization technique. The copolymerization was initiated by redox initiators composed of potassium peroxodisulphate and sodium bisulfite. The emulsion was stabilized using mixed tween 85 and span 80 as nonionic emulsifiers. The prepared HM-PAMs were classified into three groups according to the surfmers used in the copolymerization. The chemical structures of the prepared HM-PAMs were confirmed by FT-IR, ¹H NMR and ¹³C NMR. The thermal properties were estimated with the thermal gravimetric analysis (TGA). The size and morphology of the prepared latexes were investigated by the dynamic light scattering (DLS) and the High Resolution Transmission Electron Microscope (HRTEM). Finally, the molecular weights of the prepared copolymers were determined by the GPC and the viscosity average molecular weight method. They were situated between 1.58×10^6 and 0.89×10^6 .

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1. Introduction

The water-soluble hydrophobically modified polyacrylamide (HMPAM) has been extensively investigated in the last thirty years. Research interest stems mainly from two areas: solutions and hydrogels. Interest in HMPAM solutions has arisen primarily from controlling viscosity at different shear rates (rheology) in many technologies. A useful strategy for enhanced control of rheology in these systems takes advantage of HMPAM which build viscosity through transient polymer association [1]. Therefore, these systems have received a great

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deal of attention due to their unique rheological characteristics and applications, such as cosmetics, coatings, drilling fluids, and chemically enhanced oil recovery [1–9]. HMPAM consists of a water-soluble polymer containing a small number of hydrophobic groups. Over the years, several classes of associative polymers have been developed: depending on the method of synthesis, the hydrophobes can be end-attached (telechelic polymers) or distributed either statistically or as small blocks in the hydrophilic polymeric backbone (multisticker polymers). They are usually obtained either by chemical modification of a precursor polymer or by free-radical copolymerization of the appropriate monomers. However, a major drawback in the latter process comes from the insolubility of the hydrophobic co-monomer in water. This problem can be overcome by carrying out the polymerization reaction in a mixture of solvents where both monomers are soluble [5,10–12] or by using a micellar polymerization technique in which the presence of a surfactant in the micellar state ensures solubilization of the hydrophobe in the aqueous medium [2,7,13]. The latter process was shown to lead to multiblock copolymers in which the hydrophobic blocks are of tunable length and number, according to the experimental conditions [3,5,7,14–17]. The design of such materials with controllable rheological properties is quite attractive, although the low solid contents achieved at full conversion (a few wt%) may restrict their potential applications.

However, polymerization reactions in inverse emulsions or microemulsions are choice methods for the synthesis of high molecular weight, water-soluble polymers in the form of latexes, that is, water-swollen polymer particles dispersed in an organic, continuous phase [18–20]. The advantages of the techniques are the high solid contents (25–35 wt%) with low viscosities of the dispersions, good handling, and storage facilities. The microemulsions are isotropic, transparent or translucent, and thermodynamically stable multicomponent fluids, normally composed of an aqueous component, an oily component, an amphiphile as surfactant, and frequently a co-surfactant (usually an alcohol of intermediate chain length). The unique properties of the microemulsions such as lower viscosity, greater stability and transparency due to uniformly dispersed smaller droplets have made them attractive media for polymerization [21–25]. Since 1980s, a new polymerization method was developed: inverse microemulsion polymerization and it has become an attractive way to produce high molecular weight water-soluble polymers. Therefore, inverse microemulsion polymerization has recently attracted considerable attention and become an increasingly growing field of research in water-soluble polymer synthesis. Up to now many water-soluble polymers have been prepared by inverse microemulsion polymerizations, most of them are AM-based ones. Some investigators [26] prepared two types of water-soluble polymers through an inverse microemulsion polymerization route: (i) copolymers of acrylamide with sodium-2-acrylamido-2-methylpropanesulfonate and (ii) copolymers of acrylamide and sodium acrylate hydrophobically modified with an amphiphilic monomer, and obtained stable, clear microlatexes of moderate particle size containing up to 25% high molecular weight polymer in the medium.

In the previous work, three groups of nonionic surfmers have been prepared based on alkenylsuccinic anhydride [27]. In this article, these surfmers should be used as co-monomers to prepare three groups of hydrophobically modified poly-

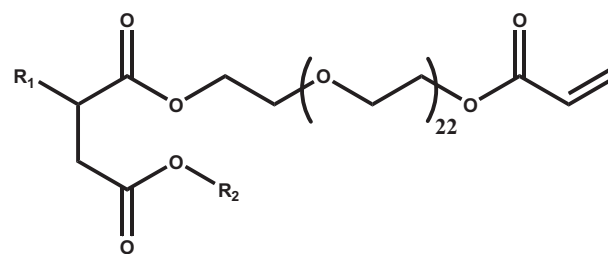


Figure 1 The general formula of the used surfmers.

acrylamides by inverse microemulsion copolymerization, which initiated by redox system (potassium peroxydisulphate and sodium bisulfite). The microemulsion will be stabilized by tween 85 and span 80 as mixed emulsifiers. The amount of the surfmers in the microemulsion should not be more than 1 mol%.

2. Experimental

2.1. Materials

Acrylamide (Am), potassium persulfate (KPS) and sodium bisulfite (NaBiS) were all of analytical grade and used as received without further purification, also solvents; methanol, ethanol and acetone. Kerosene, Sorbitan monooleate (span 80) and polyoxyethylene sorbitan trioleate (Tween 85) were technical grade. The nonionic surfmers based on alkenylsuccinic anhydride were synthesized in the previous work [27]. The general formula of these amphiphilic co-monomers (surfmers) is given in Fig. 1. These nine surfmers were divided into three groups according to the chemical structure. Their abbreviations, molecular weights and HLBs are also presented in Table 1.

2.2. Methods of preparation

The inverse microemulsion copolymerizations for a total recipe of 100 g were carried out in a 250-mL glass reactor fitted with a stirrer, a condenser, a thermometer, and a nitrogen inlet. In all the experiments, the aqueous phase/oil phase ratio and total monomers/water ratio were kept constant as 1/3 and 1/2, respectively. The emulsifier content was 11–13 wt% based on the total recipe and the HLB of the surfmer was used. The aqueous phase [AM (99 mol%) and the proper surfmer (1 mol%)] and the oil phase (kerosene, span 80 and tween 85) were emulsified at 40 °C. The redox initiators KPS ($0.05 \text{ mM} \times 10^{-3}$) and NaBiS ($0.15 \text{ mM} \times 10^{-3}$) were intro-

Table 1 Abbreviations, molecular weights and HLBs of the used surfmers.

Group	Abbreviation	Molecular weight	HLB
Group I	OSA- <i>eo</i> 22Ac (Ia)	1264	15.82
	DDSA- <i>eo</i> 22Ac (Ib)	1320	15.15
	ODSA- <i>eo</i> 22Ac (Ic)	1404	14.24
Group II	O-DDS- <i>eo</i> 22Ac (IIa)	1432	13.96
	TD-DDS- <i>eo</i> 22Ac (IIb)	1516	13.19
	OD-DDS- <i>eo</i> 22Ac (IIc)	1572	12.72
Group III	O-OS- <i>eo</i> 22Ac (IIIa)	1376	14.53
	DD-DDS- <i>eo</i> 22Ac (IIIb)	1488	13.44
	OD-ODS- <i>eo</i> 22Ac (IIIc)	1657	12.07

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