Photoinduced graft copolymerization of polymer surfactants based on hydroxyethyl cellulose

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Abstract

A novel polymer surfactant, hydroxyethyl cellulose-based copolymer, was prepared via ultraviolet (UV) irradiation by copolymerizing hydroxyethyl cellulose (HEC) with hexadecyl acrylate (HDA) and comonomer styrene (St) in aqueous solution. The purified graft copolymer was characterized by FT-IR and ^{1}H NMR, which showed that HDA and St were grafted on HEC chains under UV irradiation. Effects of UV irradiation time, pH value of the reaction solution and monomer volume percent in the feed on the chemical structure and the surface tension of graft copolymer were investigated. The result showed that the grafting of HDA on the HEC was limited by the grafting of St under UV irradiation, and the graft copolymer performed excellent surface activity when the grafting was under an appropriate conditions (i.e. both the volume percent of HDA and St in the feed were 4% (v/v), the pH value of the reaction solution was 7 and the UV irradiation time was 1 h).
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1. Introduction

Polymer surfactants are important for a variety of industrial applications in the areas of cosmetics, personal-care, food, pharmaceutics, detergents and mineral processing, and have drawn much attention in the last decades [1–5]. Compared with oligomer surfactants, polymer surfactants have many advantages such as densification, emulsification, decentralization, dissolution and film-building [5]. In 1980, a nonionic cellulose-based polymer surfactant was firstly patented by Landoll [6], which was synthesized by hydrophobically modified hydrotropic cellulose with long alkyl. Since then, besides nonionic cellulose-based polymer surfactants [7,8], ionic [9], fluorocarbon [10] and amphoteric cellulose-based polymer surfactants [11,12] have

also been synthesized subsequently, and they present many novel performances such as costless, biodegradation and peculiar emulsification [13].

Commonly, those cellulose-based polymer surfactants were synthesized by grafted alkylating agents onto the hydroxyl groups or other functional groups of cellulose and its derivatives [6–8,14]. However, the grafting degree was limited by various reasons, such as the number of functional groups, temperature and pressure condition, as well as the presence of catalyst, which led to an inferior surface activity. Fortunately, photopolymerization provides a promising and excellent approach to synthesize cellulose-based polymers without the above limits. Under ultraviolet (UV) irradiation, the side groups of cellulose or its derivatives could be decomposed into free macro-radicals which could induce copolymerization with olefin monomers [15,16]. Besides, due to the low energy of UV irradiation, the degradation of the cellulose backbone could be negligible during copolymerization and the grafting reaction was controllable [17–19]. It was found that UV irradiation has the unique ability to produce cellulose-based copolymers with improved chemical and physical properties for used as fiber, membrane, etc.

[17,20–23]. To our knowledge, there are few reports available in the open literature on synthesis of cellulose-based polymer surfactant via UV irradiation method.

In present work, a novel polymer surfactant, hydroxyethyl cellulose-based copolymer, was synthesized by copolymerizing hydroxyethyl cellulose (HEC) with hexadecyl acrylate (HDA) and comonomer styrene (St) in aqueous solution under UV irradiation. The effects of the UV irradiation time, the pH value of the reaction solution and the monomer volume percent in the feed on the chemical structure and the surface tension of the graft copolymer were investigated and discussed.

2. Experimental part

2.1. Materials

Hydroxyethyl cellulose (HEC, $\bar{M}_w = 4.65 \times 10^4$, DS = 0.9) was purchased from Tokyo Chemical Industry Co., Ltd., Japan. HDA was supplied from Shanghai Xingtu Chemical Co., Ltd., China and was treated by NaOH aqueous solution (0.5 mol/L) to remove polymerization inhibitor. Styrene was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. HCl and NaOH were of reagent grade and were used without further purification. Distilled de-ionized water was used in the experiment.

2.2. Synthesis and characterization of graft copolymer

2.2.1. Graft copolymerization

Previously, it was found that the side groups of cellulose or its derivatives could be decomposed into free macro-radicals by treatment with UV light and could induced to copolymerize with olefin monomers [15,16]. In this study, HDA and St were chosen as olefin monomers to copolymerize with a hydrophilic polymer, HEC, under UV irradiation ($\lambda > 245$ nm), which provided by a high-intensity mercury lamp (250 W, Shanghai Yaming Lighting Co., China). The graft copolymerization was carried out in the HEC aqueous solution (1 wt.%). Due to the long hydrophobic chains, it causes a strong hydrophobicity of HDA and also leads a strong steric hindrance when the HDA copolymerizes with HEC. Therefore, the comonomer, St, was also added in the graft copolymerization to reduce the steric hindrance. However, cellulose or its derivatives could be degraded under UV irradiation [16,24], thus the degradation of HEC under UV irradiation was investigated firstly. The HEC aqueous solution was introduced into a reaction vessel with hydroquinol (inhibitor, 0.01 wt.% respect to the solution). The reaction system was protected by nitrogen and dispersed under vigorous stirring for 30 min. Then, the whole unit was exposed to UV irradiation at a distance of 8 cm from the reactor surface for 0, 30, 60, 120 and 180 min, respectively. The change of $\bar{M}_w$ of HEC was traced by gel permeation chromatography (GPC, Waters 515-410, US). The mobile phase was distilled de-ionized water at the flow rate of 0.6 mL/min.

The graft copolymerization was carried out as the following procedure with some variations of the ultraviolet irradiation time, the pH value of the reaction solution and the monomer volume percent in the feed. In a reaction vessel, appropriate amount of HDA and St (both the volume percent were from 0 to 8% (v/v) with respect to the HEC aqueous solution) were added into the aqueous solution of HEC (1 wt.%). The pH value of the solution was adjusted by HCl (0.01 mol/L) and NaOH (0.01 mol/L) aqueous solution ranged from 3 to 10, and measured with a pH meter (PHB-3, Shanghai Weiye Instrument Plant, China). The reaction system was protected by nitrogen and dispersed under vigorous stirring for 30 min. The whole unit was then placed in a bath maintained at a specific temperature (20–40 °C) and exposed to the UV irradiation at a distance of 8 cm for requisite time. After that, the mixed solution was separated by tap funnel to remove excessive monomer after stewing for 30 min. The lower layer of solution was precipitated by steeping in excess acetone, and then the gross polymer product (filter residue) was Soxhlet extracted with acetone for 24 h dried in vacuum at 70 °C to constant weight.

2.2.2. Characterization of graft copolymer

2.2.2.1. ^{1}H NMR measurement. The ^{1}H NMR measurements were performed on a DRX-400 Bruker spectrometer. The HEC and the graft copolymer were dissolved overnight in D$_2$O at 25 °C.

2.2.2.2. FT-IR spectroscopy. The Fourier transform infrared (FT-IR) spectra were recorded with a FT-IR Analect RFX-65A spectrometer. Samples were pressed into discs of variable thickness of potassium bromide and analyzed in transmittance. Thermal treatments of discs were carried out to eliminate the humidity from the samples. The relative contents of HDA (G_{HDA}), St (G_{St}) and –OH (G_{OH}) of the graft copolymer during the synthesis were traced with IR Scaling method [25]. The peak at 889 cm^{-1} (assigned to two non-equivalent C$_1$–O–C$_5$ bonds of cellulose [26]) could be used as internal reference, because it was unchanged when HEC was irradiated directly by UV light for a short time [18,27]. And the G_{HDA}, G_{St} and G_{OH} were then given by $G_{HDA} = A_{1710}/A_{889}$, $G_{St} = A_{1468}/A_{889}$, $G_{OH} = A_{3410}/A_{889}$, where A_{889} is the absorbed intensity at 889 cm^{-1}, A_{1710} is the absorbed intensity at 1710 cm^{-1} (assigned to C=O stretching apparently from HDA), A_{1468} is the absorbed intensity at 1468 cm^{-1} (assigned to aromatic ring stretching apparently from St) and A_{3410} is absorbed intensity at 3410 cm^{-1} (assigned to O–H deformation bands from HEC).

2.2.2.3. Surface tension measurements. The surface tension (γ) of graft copolymers solution (0.3 wt.%) was measured using a Wilhelmy instrument and Platinum sheet (BZY-1, Shanghai Hengping Instrument & Meter Factory, China) at 23 ± 0.5 °C, after the solution was prepared for 12 h. The Platinum sheet was rinsed with de-ionized filtered water and burnt on the alcohol lamp to remove impurity before using. The γ values reported in this work were mean values of three replications.
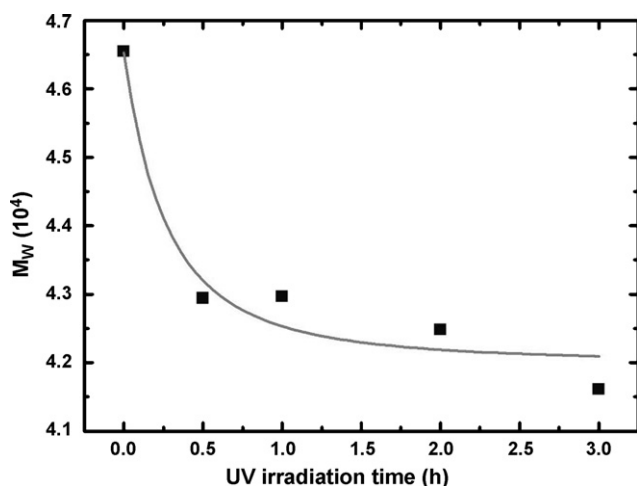
Fig. 1. Molecular weight of HEC vs. UV irradiation time.

Fig. 2. FT-IR spectra of (a) HEC and (b) the graft copolymer.

3. Results and discussion

3.1. Degradation and graft copolymerization of HEC

Since the side groups of HEC could be decomposed by treatment with UV light into free macro-radicals [16], the $\bar{M}_w$ of HEC is traced with different UV irradiation time to measure the degradation of HEC. A significant change is observed in the $\bar{M}_w$ of HEC, when altering the UV irradiation time, as shown in Fig. 1. The $\bar{M}_w$ of HEC decreases as the UV irradiation time is increased. A rapid decrease from 4.65×10^4 to 4.30×10^4 is observed under 0.5 h UV irradiation and then, the degradation slows down and the $\bar{M}_w$ shifts to a constant value (4.15×10^4) in further prolonged irradiation time. It indicates that the degradation of HEC is very slight, which confirms that the degradation of HEC under UV irradiation occurred on its side groups instead of skeleton structure [18]. Induced by the UV irradiation, these reactive sites of the cellulose substrate may become as starting points for the graft copolymerization with HDA and St [15]. Since the Q value (measure of the resonance stabilization of monomers) of HDA is close to that of St [28], it is easy to copolymerize HDA and St on the cellulose substrate simultaneously. Fig. 2 shows the FT-IR spectra of the graft copolymer synthesized under UV irradiation for 1 h with 6% HDA and 4% St in the HEC solution (pH 4.0). The appearance of a sharp absorption peak at $1710 \, cm^{-1}$ is attributed to C=O stretching vibration of ester moieties of HDA. Two media absorption peaks at 1605 and $1468 \, cm^{-1}$ are attributed to aromatic ring stretching vibration of St. The above strong bands are, however, absent in the IR spectrum of the HEC (curve a in Fig. 2). It indicates that HDA and St have been successfully grafted on the HEC chains. The introduction of the HDA and St on HEC chains is further confirmed by the ^{1}H NMR spectra of HEC and the graft copolymer. As shown in Fig. 3, in the spectrum of graft copolymer, the peaks at range 7.2–7.5 ppm are related to the protons of double bonds of aromatic ring from St and the peaks at 0.9, 1.4, 1.6 and 3.9 ppm are corresponded to the protons of methyl group from HDA. Those peaks are absent in the ^{1}H NMR spectrum of HEC. In contrast, the peaks at 2.1 and 4.6 ppm are disappeared after
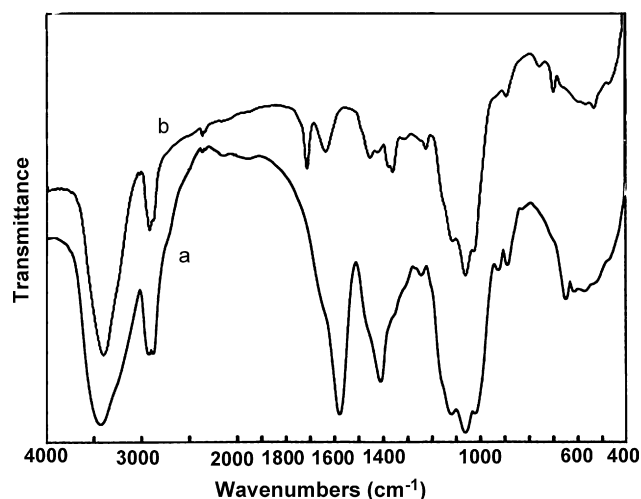
UV irradiation, which suggests that the side groups –OH of HEC and the –H of C_1 (as shown in Fig. 3) are decomposed under UV irradiation. Both the FT-IR spectroscopy and ^{1}H NMR spectra suggest that the monomer HDA and comonomer St have been grafted on HEC chains under UV irradiation.

3.2. Effect of UV irradiation time on the chemical structure and surface tension of the graft copolymer

By using the IR Scaling method, the relative contents of HDA (G_{HDA}), St (G_{St}) and –OH (G_{OH}) on the graft copolymer during the synthesis can be traced. In order to investigate the influence of the UV irradiation time, the other variables are fixed during the graft (the pH value is 4, the volume percent of St and HDA is 6 and 4%, respectively). As shown in Fig. 4, the G_{OH} decreases with the increase of the UV irradiation time (Fig. 4d), while both of G_{HDA} and G_{St} are gradually increased (Fig. 4b and c). The results indicate that with the decomposition of –OH groups from HEC, the monomers of HDA and St
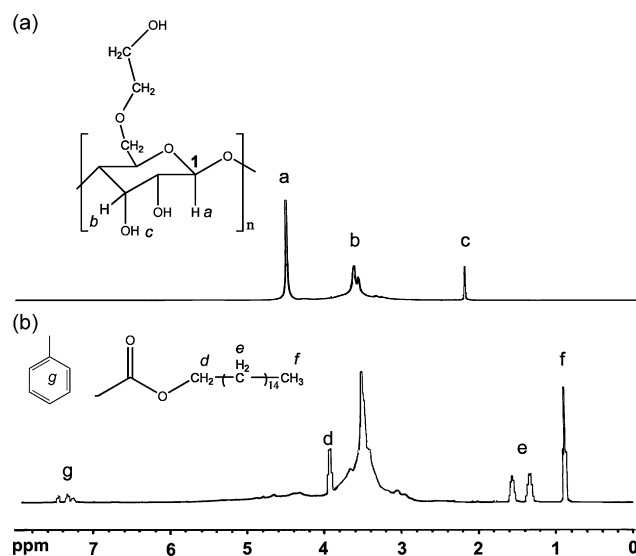

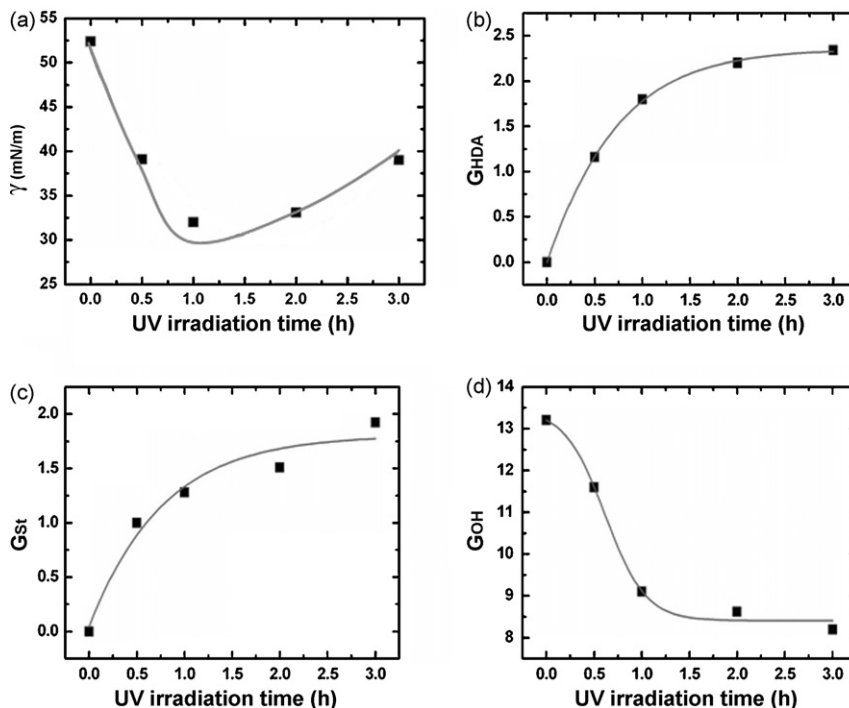Fig. 3. ^{1}H NMR spectra of (a) HEC and (b) the graft copolymer.

Fig. 4. Effect of UV irradiation time on the surface tension and the chemical structure of the graft copolymer (the pH value is 4, the volume percent of St and HDA is 6 and 4%, respectively); the surface tension (a), the HDA content (A_{1710}/A_{889}) (b), the St content (A_{1468}/A_{889}) (c) and the –OH content (A_{3416}/A_{889}) (d) vs. UV irradiation time are shown, respectively.

are grafted on the HEC substrate gradually. The similar results have also been reported in other articles [21,22,29]. The γ of graft copolymer solution decreases to 32.1 mN/m after 1 h polymerization (Fig. 4a) because the hydrophobic HDA and St are grafted on the hydrotropic HEC (Fig. 4b and c), which provides the copolymer with amphiphilic properties [30]. But the γ increases with increasing polymerization time after going through a minimum value. It is due to that when lengthening the UV irradiation time, the continued decrease of content of hydrotropic –OH groups (Fig. 4d) and the increase of the amount of the hydrophobic segments (Fig. 4b and c) result in the graft copolymers have a preference of associating in the aqueous solution to distributing on the surface of the solution [31].

3.3. Effect of pH value on the surface tension of the graft copolymer

Acidic natural and alkaline pH values of 3, 4, 6, 8.5 and 10 were selected to study the effect of pH on the γ of graft copolymer solution which synthesized at a constant volume percent of St (6%) and HDA (4%) under UV irradiation for 1 h (Fig. 5). The γ of graft copolymer is found very sensitive to pH value, whereas the γ firstly decreases with increasing pH value and reaches a minimum value of 30.0 mN/m when pH is about 7 and then, it increases with further increasing pH value. The reason of the variation of the γ with the pH value might be that the macro-radicals are inclined to degrade HEC chains rather than induced grafting reaction when the pH value is higher than 10 or lower than 4 [32,33].

3.4. Effect of monomer volume percent in the feed on the chemical structure and the surface tension of the graft copolymer

Amphiphilic polymers are constituted of hydrophobic and hydrophilic segments. Their physical properties mainly depend on the chemical composition and the balance between hydrophobic and hydrophilic moieties [34]. In present work, since the graft copolymer is synthesized by grafting hydrophobic HDA and St
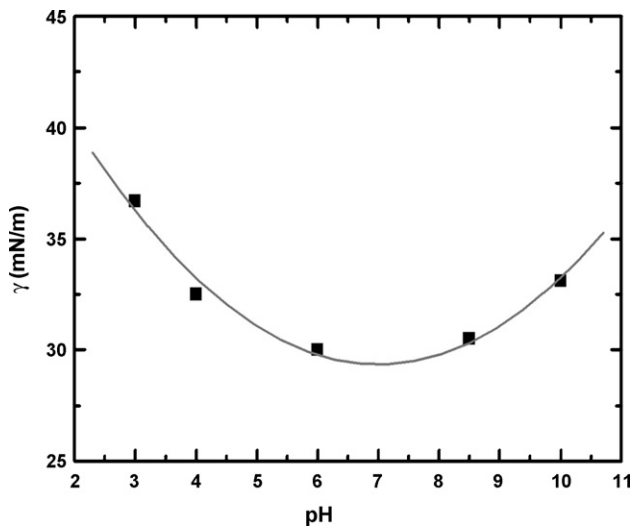

Fig. 5. Effect of the pH value of the reaction solution on the surface tension of the graft copolymer, while the volume percent of St is 6%, HDA is 4%, and under UV irradiation for 1 h.
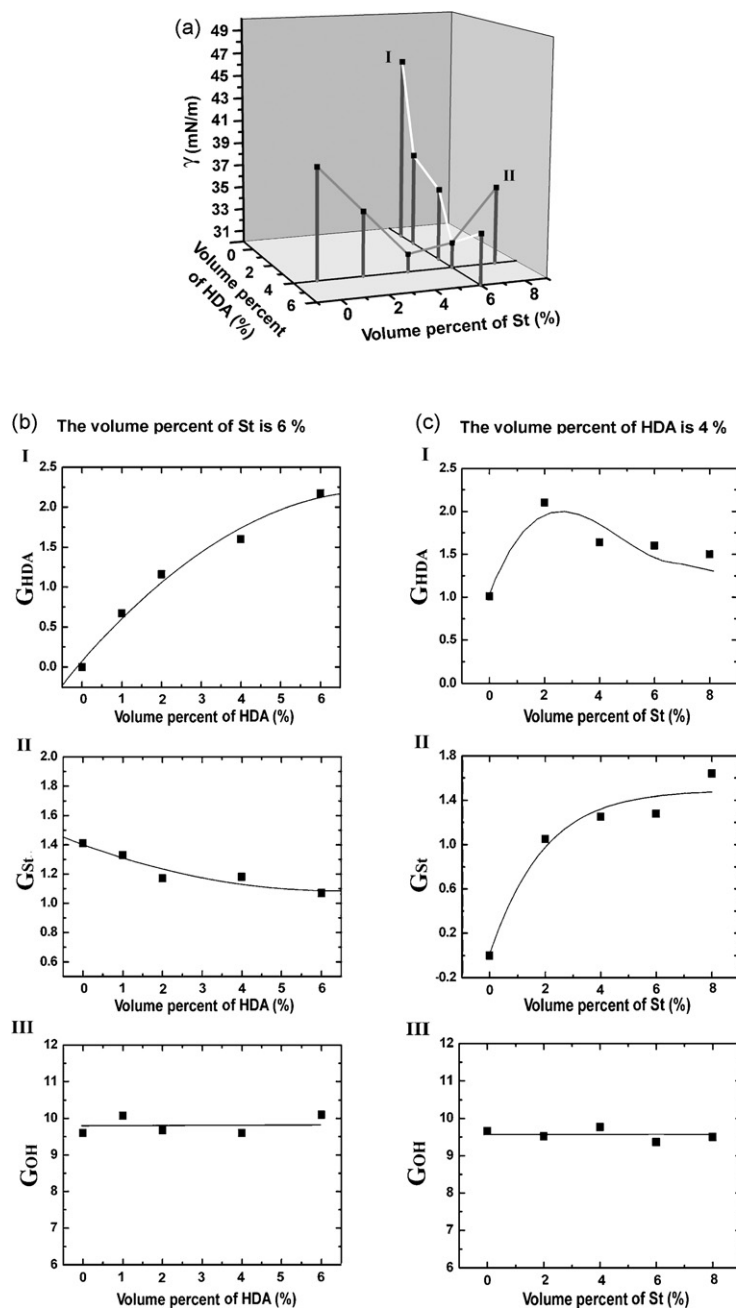
Fig. 6. Effect of monomer volume percent on the surface tension and the chemical structure of the graft copolymer (the pH value is 4 and under UV irradiation for 1 h). The surface tension vs. the volume percent of HDA (aI) and the volume percent of St (aII), and the HDA content G_{HDA} (bI, cI), the St content G_{St} (bII, cII) and the –OH content G_{OH} (bIII, cIII) vs. the volume percent of HDA and St are shown, respectively.

on the hydrotropic HEC, the monomer volume in the feed may make intense influence on the chemical structures and surface tension of the graft copolymer [17,29,35].

The effect of monomer percent in the feed on the surface tension and the chemical structure of the graft copolymer are shown in Fig. 6. For progressive increasing HDA volume percent in the feed with a constant volume percent (6%) of St in the reaction system, the HDA segment on the graft copolymer (G_{HDA}) increases (Fig. 6bI), while the G_{St} decreases slightly (Fig. 6bII) because it is limited by increasing content of HDA. The γ decreases from 46 mN/m to a minimum value of 32.1 mN/m

as the content of HDA is increased from 0 to 4% (Fig. 6aI). This is because of hydrophobically modifying hydrotropic HEC, the graft copolymers are easy distributed on the surface of the aqueous solution [30]. The similar result has also been reported in other systems [36,37]. But the γ becomes ascending as the feed volume percent of HDA is increased continuously. That is caused by the increase of the hydrophobic segment of HDA on the graft copolymer (Fig. 6bI), which results in the polymer surfactants tends toward associating in the aqueous solution instead of distributing on the surface of the aqueous solution [31].

Fig. 6c shows the effect of St content in the feed on the chemical structure of graft copolymer at a constant HDA of 4%. The G_{St} generally increases (Fig. 6cII) with progressive increasing the volume percent of St in the mixed monomer system, whilst the G_{HDA} firstly increases with increasing St and reaches a maximum when the volume percent of St is 2% (Fig. 6cI), which is attributed to the introducing of St reduces the steric hindrance between HDA monomers and leads the grafting copolymerization of HDA on HEC chains more easy. But when the volume percent of St in the feed is exceeded to 2%, the grafting copolymerization of HDA may be limited by the competition of St [38]. The γ decreases with increasing the volume percent of St after it reaches the minimum of 32.1 mN/m at 4% St content, and then increases with further increase in the volume present of St (Fig. 6aII). It confirms that appropriate amount of St makes HDA (long chain) grafting on HDA chains more easily (Fig. 6c), and the content of HDA and St in the feed play an important role on both the chemical structure and the surface tension of graft copolymer [30,31].

The G_{OH} is almost a constant (Fig. 6bIII and cIII) when the content of two monomers are changing in the feed, which suggests that content of –OH groups on HEC chain is only influenced by UV irradiation time (Fig. 3d).

4. Conclusions

UV irradiation was applied in the first time for synthesis of cellulose-based polymer surfactants. HEC may be degraded slightly under UV irradiation and engenders free macro-radicals which could induce HEC to copolymerize with the monomers HDA and the comonomer St. The chemical structure of graft copolymers is strongly influenced by the irradiation time and the two monomers volume percent in the feed. By lengthening the UV irradiation time, the G_{OH} decreases, while both the G_{HDA} and the G_{St} increase gradually. When the HDA increases in the feed with a constant St of 6%, the G_{HDA} increases, while the G_{St} only decreases slightly. In contrast, with the increase in volume percent of St with a constant HDA of 4%, the G_{St} increases gradually, while the G_{HDA} increases firstly and then, decreases after through the maximum at 2% St. The G_{OH} is not affected by the change of the two monomers content in the feed.

The graft copolymer synthesized by UV irradiation shows excellent surface activity. The surface tension (γ) of graft copolymer is not only influenced strongly by monomer volume percent in the feed, but also by the pH value of the reaction solution. The γ could get a minimum value (about 30.0 mN/m) when both the volume percent of HDA and St are 4%, the pH value is 7 and the UV irradiation time is 1 h.

Acknowledgments

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