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European Polymer Journal 39 (2003) 1013–1018

EUROPEAN POLYMER JOURNAL

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Polymerization of sodium acrylate in inverse-suspension stabilized by sorbitan fatty esters

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Received 16 April 2002; received in revised form 24 September 2002; accepted 26 September 2002

Abstract

This paper is devoted the synthesis of poly(sodium acrylate) by an inverse-suspension polymerization technique. Ammonium persulfate, ethylcellulose and toluene were used as initiator, suspending agent, and continuous organic phase, respectively. Two surfactants, sorbitan monooleate (SMO) and sorbitan monostearate, were used as the suspension stabilizers. The effect of the initiator concentration as well as the type and concentration of the surfactant on the polymer molecular weight and solution viscosity was investigated. Participation of the unsaturated surfactant (SMO) in the free radical polymerization was recognized to be the main reason of enhancement of the average molecular weight and viscosity of the products. A similar effect was observed when the polymerization reactions were run in the presence of air. In the latter conditions, however, an inhibition effect of atmospheric oxygen resulted in substantially decreased solution viscosity. Meanwhile, it was found that higher polymers were obtained when the as-synthesized beads were dewatered and hardened in methanol rather than in acetone.

Keywords: Sodium acrylate; Inverse-suspension polymerization; Surfactant; Sorbitan monooleate; Sorbitan monostearate

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1. Introduction

Sodium acrylate (SA) and its polymer (PSA) are soluble in aqueous media. SA can be polymerized by four methods; bulk (solid state), solution, inverse-emulsion and inverse-suspension [1].

Inverse-suspension polymerization is defined as a dispersion of water-soluble monomer in a continuous organic matrix. The advantage of inverse-suspension over other methods is that a fine powdery product is obtained and the particle size can be easily controlled by controlling the reaction conditions. In recent years, the inverse-suspension polymerization method has been successfully used to prepare water soluble/swellable products, e.g., thickeners, flocculating agents and superabsorbent hydrogels [2,3].

Emulsifier levels are typically 2–5 wt.% of the organic phase and are below the critical micelle concentration. The dispersion is thermodynamically unstable and requires both continuous vigorous agitation and the addition of a low hydrophilic–lipophilic balance stabilizer. The latter forms a condensed electrically neutral interfacial layer and prevents coalescence. The monomer droplets are typically 1–100 μm in diameter and are controlled predominantly by the Weber number of the mixture. The polymerization is often initiated chemically by free radical azo or peroxide species; these can be located either in the dispersed (aqueous) or continuous (organic) phase. If water-soluble initiators are employed, each particle contains all the reactive species and therefore behaves like an isolated micro-batch polymerization with the kinetics proceeding according to the solution mechanism. Oil-soluble initiators are, however, more common because they generate higher molecular

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doi:10.1016/S0014-3057(02)00352-X

Table 1
The mainreported works on the inverse-suspension polymerization of SA

Entry	Initiator	Suspending agent	Particle diameter	Remarks	Ref.
1	KPS[a]	Span 60	–	SAP[b]	[2]
2	KPS	Span 80	50–500 μm	SAP	[3]
3	KPS	Span80	300 μm	SAP	[4]
4	KPS	PVP[c]	150–300 μm	–	[5]
5	KPS	PVP	100–350 μm	VAC[d]/NVP[e] (85/15) comonomer mixture used	[6]
6	KPS	Alkenyl succinate	1–100 μm	–	[7]
7	APS[f]	Sulfonated polyolefin	0.3–2 mm	–	[8]
8	APS	METAC[g]	0.21 mm	Viscosity of 0.5% Soln., 456 mPa s	[9]
9	–	Styrene glycerol methacrylate	290 μm	–	[10]
10	ACVA[h]	Span 60	–	SAP	[11]
11	ACVA	Span 60	–	SAP	[12]
12	KPS	Ethylcellulose	2 mm	SAP	[13]

[a] Potassium persulfate.
[b] Superabsorbent polymer product.
[c] Poly(vinylpyrrolidone).
[d] Vinyl acetate.
[e] *N*-vinylpyrrolidone.
[f] Ammonium persulfate.
[g] 2-methacryloxyethyl trimethyl ammonium chloride.
[h] 4,4′-Azo bis(4-cyanovaleric acid).

weights and offer better thermal stability and reactor control [2–4].

Applications of PSA, as a water-soluble polymer, are ranged from thickening of aqueous systems to wastewater treatment as flocculant [1]. Superabsorbent polymers consumed in personal healthcare products and agriculture are mainly based on PSA homopolymers or copolymers [3,4].

Most work on inverse-suspension polymerization of sodium acrylate has reported in patent literature. The main reports are summarized in Table 1. Sorbitan fatty esters, especially sorbitan monostearate, SMS (Span 60) and sorbitane monooleate, SMO (Span 80) are the surface-active agents frequently used in dispersion polymerization reactions as stabilizers [2–4,11,12].

Traditionally, type and amount of main reactants and basic chemical components as well as the process conditions are studied in the investigations of dispersion polymerization systems. To the best of our knowledge, there is no report on the effect of type of sorbitan fatty esters on the PSA prepared from inverse-suspension polymerization. Do the surfactant type and amount affect fundamental properties of the PSA product? This article is a systematic attempt to empirically answer the question.

2. Experimental

2.1. Materials

Acrylic acid (Fluka), sodium hydroxide (Merck) and ammonium persulfate (APS, Merck) were used without further purification. Ethylcellulose NC 200 (Hercules), SMS (Span 60, Aldrich), SMO (Span 80, Aldrich), and commercial grade toluene were used as received.

2.2. Preparation of SA monomer solution (aqueous phase)

SA monomer was prepared by gently dropping sodium hydroxide solution (0.4 mol NaOH and 52.0 g distilled water) to acrylic acid (0.4 mol) under cooling (ice-bath). The acid–base reaction was potentiomerically monitored to achieve a complete neutralization. Just before polymerization, a defined amount APS initiator was dissolved in the monomer solution under nitrogen bubbling.

2.3. Preparation of organic phase

Ethylcellulose (3.00 g) was poured in pre-warmed toluene (233.0 g) in a 600-ml beaker. A defined amount of SMO or SMS was added to toluene (10.0 g) in a 100-ml beaker. Then the surfactant solution was added to the ethylcellulose solution under stirring.

2.4. Inverse-suspension polymerization

In a four-necked flask equipped with a mechanical (propeller-type) stirrer, reflux condenser, a dropping funnel and a thermometer the organic solution was charged. In a thermostated water bath, the reactor was heated (under a mild stream of nitrogen) to reach

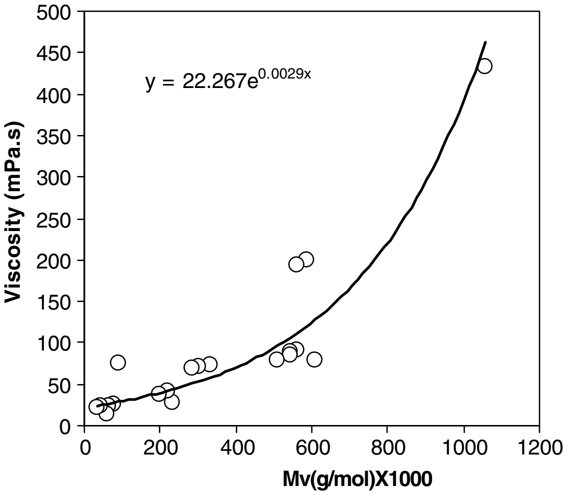


Fig. 1. Brookfield viscosity-average molecular weight plot for PSA in distilled water (0.50 wt.%, 25 ± 0.1 °C, LV viscometer, spindle #2, rpm 60).

75 ± 0.1 °C. The monomer solution was added dropwise to the organic phase, while the agitation speed was set at 400 rpm. After 30 min, the reactor was cooled in an ice-bath. The organic supernatant was decanted and the product was washed with toluene (3 × 100 ml) to eliminate the emulsifier. The particles were then poured into 800 ml acetone or methanol to dewater and harden for 2 h. The white fine particles were dried at room temperature for 24 h.

2.5. Molecular weight and viscosity measurement

The polymer solution viscosity was measured in distilled water (0.50 wt.%) at 25 ± 0.1 °C with a LV Brookfield viscometer (spindle #2, rpm 60). Average molecular weight of PSA samples was calculated according to an empirical viscosity–molecular weight equation derived from a viscosity-M_v plot obtained using PSA samples with different molecular weights (Fig. 1) (Eq. (1)) [14].

$$\text{Viscosity (mPa s)} = 22.3\exp(0.000003\text{MW}) \qquad (1)$$

3. Results and discussion

As summarized in Table 1, SA has been polymerized in inverse-suspension using persulfate or azo initiators. Sorbitan fatty esters are used in several cases as suspending agents. We used surfactants SMO and SMS in combination with ethyl cellulose as a bead stabilizer that protect the particles from adhering to each other through formation of a thin layer around individual beads [3]. Larger beads form when ethyl cellulose is used alone [13]. All the experiments were run under the same conditions except the type and amount of the fatty ester.

3.1. Effect of initiator concentration

The effect of the initiator concentration on the polymer molecular weight is shown in Fig. 2. Brookfield viscosity, mPa s (*cP*), is decreased with increasing the initiator concentration. This well-known behavior may be explained with the following relationship [15]:

$$X_n = k_p[\mathrm{M}]/(fk_dk_t[\mathrm{I}])^{1/2} \qquad (2)$$

X_n, f, [M], and [I] respectively represent number average degree of polymerization, initiator efficiency factor, molar concentration of monomer and initiator. The parameters k_p, k_d and k_t stand for corresponding rate constants of propagation, initiator dissociation, and termination, respectively. Since there is a proportional relationship between molecular weight (or X_n) and viscosity [15,16], diminished trends were observed in solution viscosity versus APS amount, in the experiments applying either SMS or SMO. It is also obvious from the Fig. 2 that higher polymers were obtained when methanol was used as a dewatering non-solvent. It means the soluble components including oligomers dissolve more easily in methanol rather than in acetone. So, methanol was recognized to be a preferable non-solvent for dewatering and hardening the PSA beads obtained from the inverse-suspension polymerization.

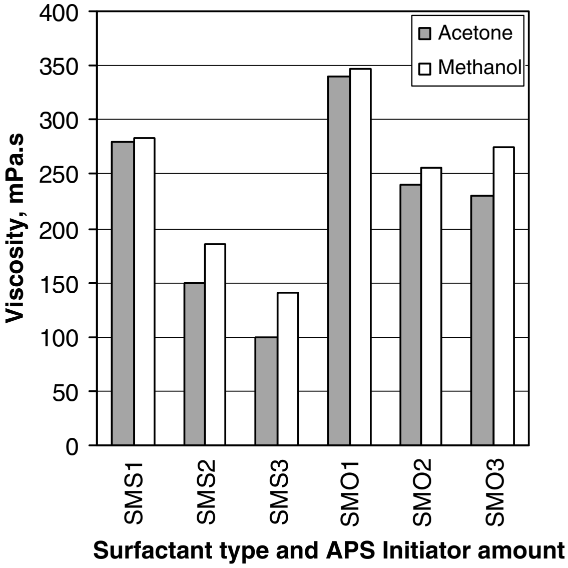


Fig. 2. Effect of the initiator concentration, surfactant type, and dewatering non-solvent on solution viscosity of the PSA products (surfactant, 0.211 wt.% of organic phase). Numbers 1, 2, and 3 denote APS concentration as 0.019, 0.038, and 0.076 weight percent of aqueous phase, respectively.

3.2. Effect of surfactant type

Effect of the type and concentration of surfactant was studied at a fixed concentration of the initiator. As shown in Fig. 3, higher molecular weight polymers were obtained when SMO was used as the suspension stabilizer rather than SMS. On the other hand, no considerable variation in molecular weight was observed when different concentration of SMS was applied. Conversely, the concentration of SMO surfactant remarkably affected the molecular weight of the PSA product, so that the higher is SMO concentration, the greater is the polymer molecular weight. The source of this obvious difference is related to the chemical structural difference between these two surface-active agents. The molecular structure of SMO and SMS is shown in Scheme 1.

The surfactant SMO contains an additional double bond. It has four allylic hydrogen atoms that can involve chain transfer reactions. The labile allylic hydrogen atoms may easily be abstracted by a reactive free radical. Therefore, SMO may firstly react with primary radicals, $R_i^{\cdot}$ (Scheme 2) (Eq. (3)).

$$R_i^{\cdot} + \text{SMO} \rightarrow \text{SMO}^{\cdot} \quad (k_1) \tag{3}$$

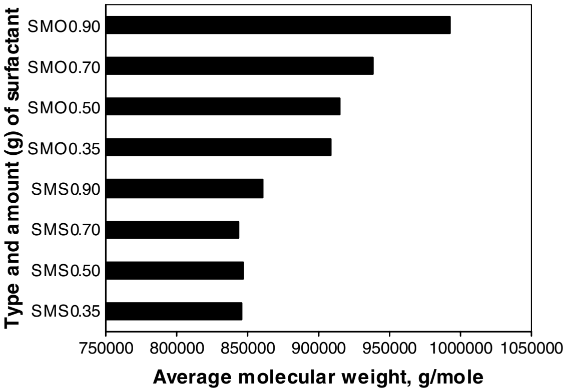
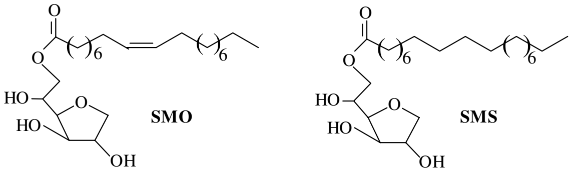


Fig. 3. Influence of sorbitan fatty ester surfactant type (SMS and SMO) and concentration (0.148, 0.211, 0.296 and 0.380 wt.% of the organic phase) on molecular weight of the PSA products, at a fixed initiator concentration (0.019 wt.% of aqueous phase). Methanol was used as the non-solvent for dewatering the as-synthesized products.



Scheme 1.

This SMO radical can either inactivate by reacting with a hydrogen source (e.g., solvent) or propagate the monomer (Eqs. (4) and (5)).

$$\text{SMO}^{\cdot} + \text{H—C} \rightarrow \text{Inert} \quad (k_2) \tag{4}$$

$$\text{SMO}^{\cdot} + \text{M} \rightarrow R_p^{\cdot} \quad (k_3) \tag{5}$$

Macroradicals ($R_p^{\cdot}$) may either react with monomer or with SMO (Eqs. (6) and (7))

$$R_p^{\cdot} + \text{M} \rightarrow R_{p+1}^{\cdot} \quad (k_4) \tag{6}$$

$$R_p^{\cdot} + \text{SMO} \rightarrow \text{SMO}^{\cdot} \quad (k_5) \tag{7}$$

where $k_5 \ll k_4$, because of the high steric hindrance effect in the SMO structure. This also gives a long lifetime of SMO radicals to increase the possibility of reaction with initiator radicals (aqueous phase) and decreasing the efficiency of bimolecular termination (Eq. (8)).

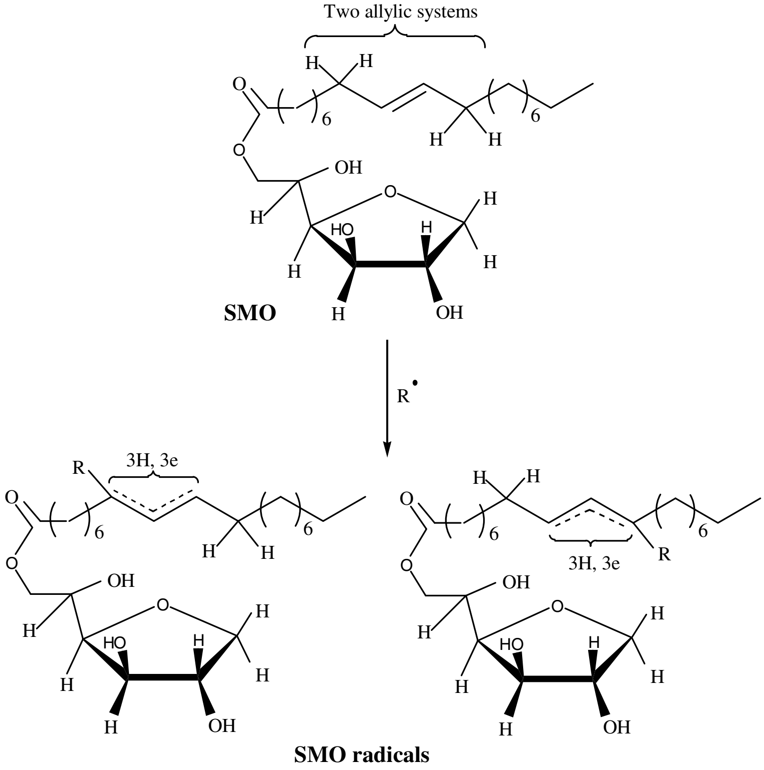
$$\text{SMO}^{\cdot} + R_i^{\cdot} \rightarrow \text{Dead polymer} \tag{8}$$

Here, since the Eqs. (4), (6) and (8) are of importance [17], SMO decreases the concentration of initiating radicals and macroradicals. Therefore, according to Eq. (2), the polymer molecular weight increases with in situ decreasing overall concentration of initiator, [I]. In the case of SMS surfactant, such an interactive process cannot be occurred due to lack of the structural unsaturation.

Finally, it should be pointed out that the chain transfer to SMO would have a very complex effect on molecular weight. Consideration of reactivity ratios for copolymerization of acrylates with 1,2-substituted olefins [18] suggests that chain transfer to a molecule such as SMO is more likely than copolymerization [19]. So, the chain transfer event would reduce the chain length for the propagating chain. But it would also lead to the formation of stable allylic radicals (Scheme 2) which would have a much lower potential for re-initiation of new polymer chains and could, therefore, reduce the steady-state radical concentration with consequent increase in the kinetic chain length.

3.3. Effect of atmospheric oxygen

To study the influence of oxygen on the polymerization and product, the same polymerization system was run, but in air, at a fixed surfactant type. The unrestricted access of atmospheric oxygen to the reaction mixture resulted in PSA products having very low viscosity (Fig. 4). Molecular oxygen, a well-known inhibitor of free-radical polymerization reactions [15], imposes a retardation period (10–20 min) to the reaction. Such inhibited reactions were recently studied in the case of SA polymerization in solution [14] and SA-based hydrogel synthesis [20].



Scheme 2.

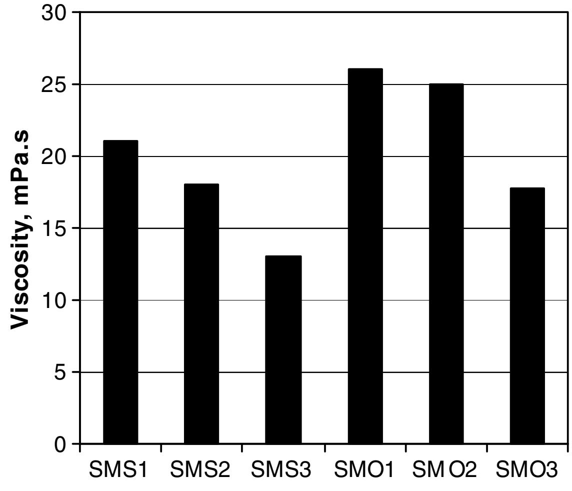


Fig. 4. Effect of the initiator concentration and type of surfactant on solution viscosity of the PSA products obtained from inverse-suspension polymerization in the presence of atmospheric oxygen, at a fixed surfactant concentration (0.211 wt.% of organic phase). Numbers 1, 2, and 3 denote APS initiator as 0.019, 0.038, and 0.076 weight percent of aqueous phase, respectively.

In the present experiments, when the reactions were continued for a longer time (more than 30 min) to compensate the retardation period, the final PSA products were found to contain insoluble/swellable fractions (the gel content was negligible). It can be attributed to formation of crosslinked and/or highly branched/entangled chains in the presence of oxygen. During the inhibition process, O=O, as a competitive comonomer, reacts with the monomer radical forming a peroxy radical.

$$R_i^{\cdot} + M \rightarrow R_iM^{\cdot} \quad (k_6) \tag{9}$$

$$R_i^{\cdot} + O_2 \rightarrow R_iOO^{\cdot} \quad (k_7) \tag{10}$$

$$R_iOO^{\cdot} + M \rightarrow \text{Polymeric peroxides and hydroperoxides} \tag{11}$$

Addition of monomer to the peroxy radical ($R_iOO^{\cdot}$) is much slower than to the normal polymer radical ($R_iM^{\cdot}$), resulting in suppression of the normal propagation reaction and formation of a polyperoxide chain altering in end group between monomer and peroxy radicals. Each peroxide or hydroperoxide link might be a potential source of free radicals for initiating polymerization. As a result, the concentration of initiating radicals would increase, leading to decreased degree of polymerization, according to Eq. (2). Nevertheless, in such a system that is much more complicated, a similar trend was observed in the effect of the surfactant type; i.e., SMO results in a polymer with higher solution viscosity than SMS (Fig. 4). This observation reconfirms our above explanation on the discrimination of SMS and SMO behaviors in this polymerization system.

4. Conclusion

We showed that the kind of sorbitan fatty ester can affect substantially fundamental properties of PSA prepared from inverse-suspension polymerization of SA. Higher molecular weight polymers were achieved when SMO was used as the surfactant, in comparison with SMS. This result obtaining even from the reactions run in the presence of air was attributed to a mechanism involving abstraction of allylic hydrogen atoms of SMO. Under an inert atmosphere and during a short time (30 min), fine PSA beads (mesh 40–60) with high molecular weight ($\sim 10^6$ Dalton) can easily be prepared using the oleate ester, while the stearate ester results in a lower molecular weight polymer under the same conditions.

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