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ORIGINAL CONTRIBUTIONS

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A novel copolymerizable surfactant and its application based on concentrated emulsion polymerization

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Abstract A three-arm copolymerizable surfactant (surfmer) which possesses (1) a side chain terminated with a double bond and (2) a double bond in the hydrophobic moiety was synthesized. Because, one of the double bonds was located at the end of the side chain, the hydrophilicity of the surfmer was not affected in a major way by its copolymerization with the monomer. In addition, because of its three-arm structure, its self-polymerization was greatly inhibited, but not its capability for copolymerization. The surfmer was employed to prepare polystyrene particles of uniform size via the concentrated emulsion polymerization.

Keywords Concentrated emulsion · Surfactant · Polystyrene

Introduction

In emulsion polymerization, surfactants are usually employed to generate micelles and to stabilize the latexes. Particularly in the concentrated emulsion polymerization [1–3], the surfactants are employed in high concentrations, usually 10–20 wt% of the continuous phase. However, it is difficult to remove the remaining surfactant from the final product, resulting in potential harm to the environment and human health [4]. In order to avoid these negative features, reactive surfactants [5–14] were employed, which participating in the polymerization process became constituents of the final products. Covalent binding of the surfactants to the polymers obtained from emulsion polymerization is expected to improve some properties of the resulting latexes [15]. The reactive surfactant may be an initiator or a transfer agent (known as INISURF or TRANSURF). More frequently, it acts as a comonomer, known SURFMER, polymerizable or copolymerizable surfactants.

The surfmers usually contain reactive double bonds. The double bonds can be introduced as unsaturated alkyl chains or as styrene moieties [8]. An important characteristic of surfmers is their copolymerization capability with other monomers. Guillume [14] found that the surfmer $CH_2=CHCONH(CH_2)_{10}COONa$ had no copolymerization reactivity, but self-polymerized to generate polyelectrolytes. Homberg [8] examined the surfactants of aliphatic-poly(ethylene oxide) type and found that the double bonds within the aliphatic chains exhibited a high activity for copolymerization, while those located at the hydrophilic end exhibited no reactivity. In contrast, the double bonds on the styrene moieties provided relatively high copolymerization abilities with other monomers, such as styrene, acrylic acid, and butyl acrylate. The long hydrophilic moiety inhibited the self-polymerization, thus promoting the copolymerization activity. Schoonbrood [16] studied the copolymerization of styrene with two surfmers based on maleic acid in batch emulsion polymerizations. It was found that both surfmers copolymerized well with styrene and their partial conversion was higher than that of styrene.

Soula [17] compared two preparation procedures of reactive surfactants. The first one involves the initiation of anionic polymerization of ethylene oxide by an alkyl silanolate. Once the ethylene oxide is fully consumed, the anion is condensed on a styrenic alkyl bromide. Then, the hydroxyl is recovered by a reaction of deprotection. The second one, on the contrary, starts from the hydrophobic end group. This anionic polymerization is initiated by vinyl benzyl alcoholate. Both butylene oxide and ethylene oxide are polymerized successively. It was found that the second procedure gives good control of both hydrophobicity and hydrophilicity.

In this research, a novel surfmer was prepared. This surfmer possesses a side chain with a double bond at the end, which is expected to have a high copolymerization activity because (1) it has high freedom to react with monomer; (2) the bulk main chain impedes the self-polymerization. Another advantage of the double bond located at the end is that its reaction does not affect the hydrophilicity of the surfmer in a major way, which thus can survive on the surface of the droplets of the emulsion. The new surfmer was employed to prepare latexes via the concentrated emulsion polymerization of polystyrene.

Experimental

Materials

Styrene (St, AR), was purchased from Tianjin Chemical Manufacturer No.6, China, and the azobisisobutyronitrile (AIBN, CP), provided by Shanghai Reagent Manufacturer No.4, China, was recrystallized from methanol. Dodecennyl succinic anhydride (DDSA) was provided by Fluka and *N*-methylglycine (sarcosine) by MERK. Glycidyl methacrylate (GMA), potassium peroxydisulfate (KPS, AR), hydroquinone, chloroform, methanol, and sodium hydroxide were provided by Beijing YI LI Chemical Co. Ltd. The water used was distilled and deionized.

Synthesis of the reactive surfactant

The reactive surfactant was prepared using the following 3 steps shown in Scheme 1.

Step A. Sarcosine and sodium hydroxide (1/1 mol mol^{-1}) generated sodium sarcosine.

Step B. Sodium sarcosine reacted with DDSA (1/1.1 mol ratio), through a ring-opening addition in a mixture of dioxane and water (7/3 v/v), and the product was dissolved in ether and precipated with cold acetone. The product was a mixture of two isomers.

Step C. The product obtained in step B was dissolved in dioxane at 60 °C and GMA was added dropwise. After the addition of GMA (1.2 mol/mol of product of step B), a reaction was conducted for 5 h at 60 °C, in the presence of a small amount of methyl benzoic acid as catalyst. Each of the two isomers of step B produced a surfmer, which have the structures as shown in Fig. 1.

Polymerization

The homo-polymerization of the surfmer

Small amounts of surfmer (0.4 g) and potassium peroxydisulfate (0.01 g) were dissolved in water and the mixture was heated at 50 °C for 24 h; subsequently, the system was dried in a vacuum oven.

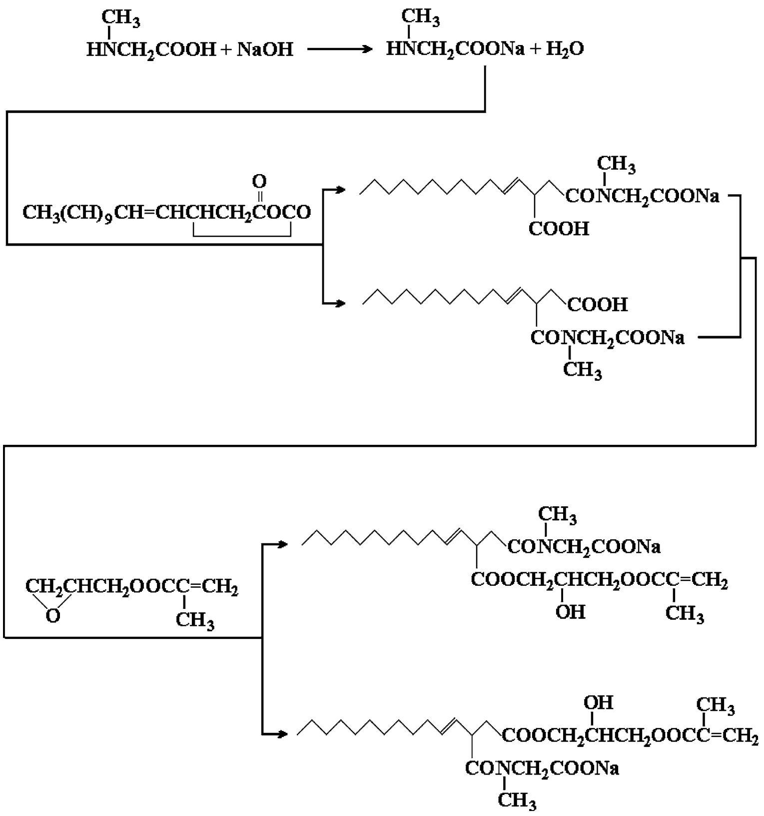
Concentrated emulsion polymerization of styrene

A concentrated emulsion in water with a volume fraction of the dispersed phase larger than 0.8, was first prepared. An aqueous solution of the surfmer (of various concentrations) was placed in a flask provided with a magnetic stirrer. The flask was sealed with a rubber septum, and the air inside was replaced with nitrogen. Styrene containing AIBN was added dropwise with stirring into the flask with a syringe, until the volume fraction of the aqueous solution acquired a predetermined value. The whole addition process lasted about 15 min, and took place at room temperature. The obtained concentrated emulsion was kept at room temperature for about 10 min, and subsequently transferred to a test tube which was subjected to polymerization at various temperatures in a water bath.

Molecular weight distribution (MWD)

Molecular weight distribution was determined by gel permeation chromatography (Waters 150 C, USA). The polystyrene obtained via the concentrated emulsion polymerization was dissolved three times in chloroform and precipitated with methanol. The purified product

Scheme 1 Preparation procedures of the Surfmer



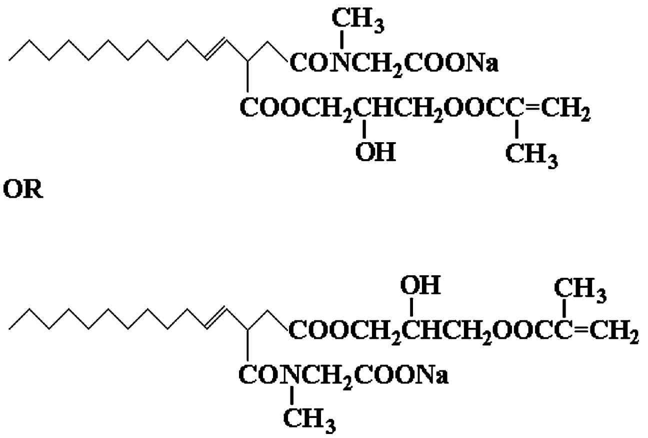


Fig. 1 Structural formula of the surfmer prepared in this work

was used as a solution in tetrahydrofuran (20 mg/10 ml) for the determination of the MWD.

Determination of the conversion

A certain amount of polymerized concentrated emulsion and a_0 grams of an inhibitor (hydroquinone) were introduced into an aluminum foil cup of weight W_0, and the mixture was dissolved in acetone, and subsequently dried in an oven at 70 °C. The conversion (in wt%) was calculated using the formula:

$$X = \frac{[(W_2 - W_0 - a_0)/(W_1 - W_0)] - A}{B} \times 100$$

where W_1 is the weight of the aluminum foil cup and emulsion, W_2 the weight of the aluminum foil, dried polymer and hydroquinone, A the weight fraction of the nonvolatile components (polymer and hydroquinone), and B the weight fraction of the monomers.

Fourier transform infra-red spectroscopy

The sample was coated onto potassium bromide as a chloroform solution and scanned with an FT-IR Shimatsu F-1000 (Japan) instrument.

Nuclear magnetic resonance (NMR)

The sample was dissolved in $CDCl_3$ and scanned with a JNM-AL300 FT-NMR JOEL (Japan) instrument, at room temperature.

Atomic absorption spectroscopy

The sample was calcined at 300 °C, and subsequently dissolved in hydrochloric acid. The sodium ion content was determined with an atomic absorption spectroscopy instrument (Hitachi Z8000, Japan).

Transmission electron microscopy (TEM)

A small amount of polymer powder was bound to a holder with an adhesive, coated with gold and examined with a HITACHI H800 (Japan) TEM instrument.

Elemental analysis

The elemental analysis was carried out using an elemental analyzer (Carloerba 1106, Italy).

Dynamic mechanical analysis (DMA)

The DMA was conducted using the Rheology Science V (USA) instrument; the frequency was 1 Hz and the heating rate was 10 °C/min.

Results and discussion

Characterization of the surfmer

Infrared spectroscopy

The infrared spectrum (a) in Fig. 2 is that of the surfmer (mixture of the isomers). In the spectrum, the wide peak between 3,400 and 2,500 cm^{-1} can be assigned to the associated –OH groups. The peak at 1573.44 cm^{-1} can be assigned to the sodium salt, and the peak at 1635.21 cm^{-1} to the double bonds. In step C, the ester groups formed through the reaction between the carboxylic acid and epoxy group, gave rise to a peak at 1722.37 cm^{-1} . A saturated ester should exhibit a peak at 1,730 cm^{-1} ; being, however, conjugated with a terminating double bond, the peak was shifted to a lower wave number.

Elemental analysis

The results of the elemental analysis are listed in Table 1, and the content of sodium was determined by atomic absorption spectroscopy.

The results are comparable to the theoretical values.

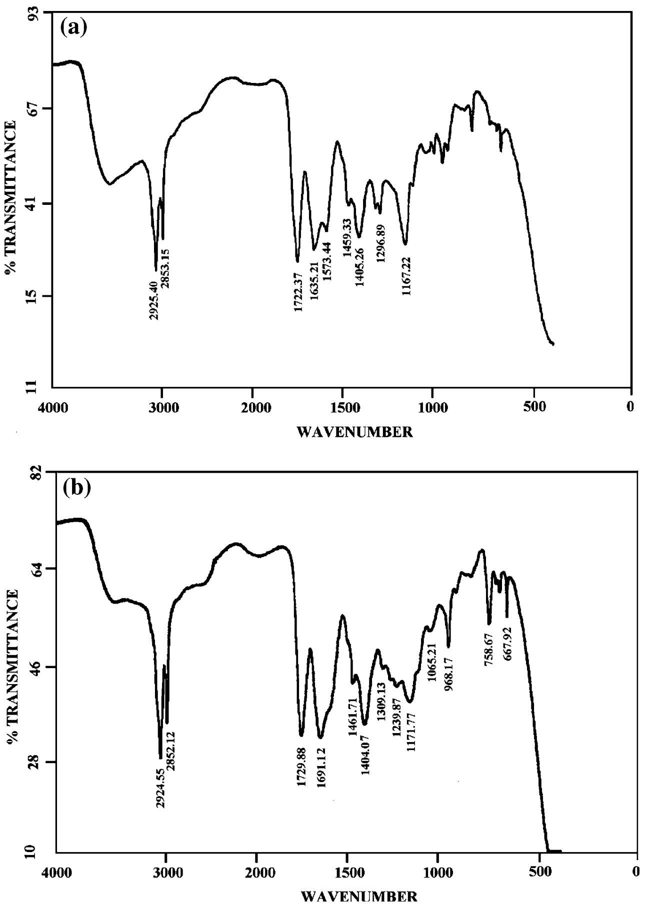


Fig. 2 Fourier transform infra-red spectroscopy spectrum. **a** Surfmer, **b** self-polymerized surfmer

NMR

The NMR spectra of the intermediate and final products are presented in Figs. 3 and 4, respectively.

In both spectra, the peaks between 35.495 and 35.554 ppm can be assigned to the carbon in – $\underline{C}H_2$–CH = CH– near a double bond, and demonstrate the presence of a double bond in the hydrophobic moiety. The peaks at 128.865 and between 133.216 and 133.768 can be assigned to the carbons in $(CH_2)_9\underline{C}H = CH$ and $(CH_2)_9\underline{C}H = CH$, respectively, of the double bonds of the hydrophobic moiety of the surfmer. The peaks between 36.970 and 37.539 ppm can be assigned to the carbons in $\underline{C}H_2CON$ and $\underline{C}H_2COO$. The peaks at 51.640 and 181.232 ppm can be assigned to N $\underline{C}H_2COONa$ and

Table 1 The elemental composition of the surfmer

Content(wt%)	C	H	O	N	Na
Theoretical	60.23	7.92	24.71	2.70	4.44
Determined	58.16	8.50	–	2.25	4.11

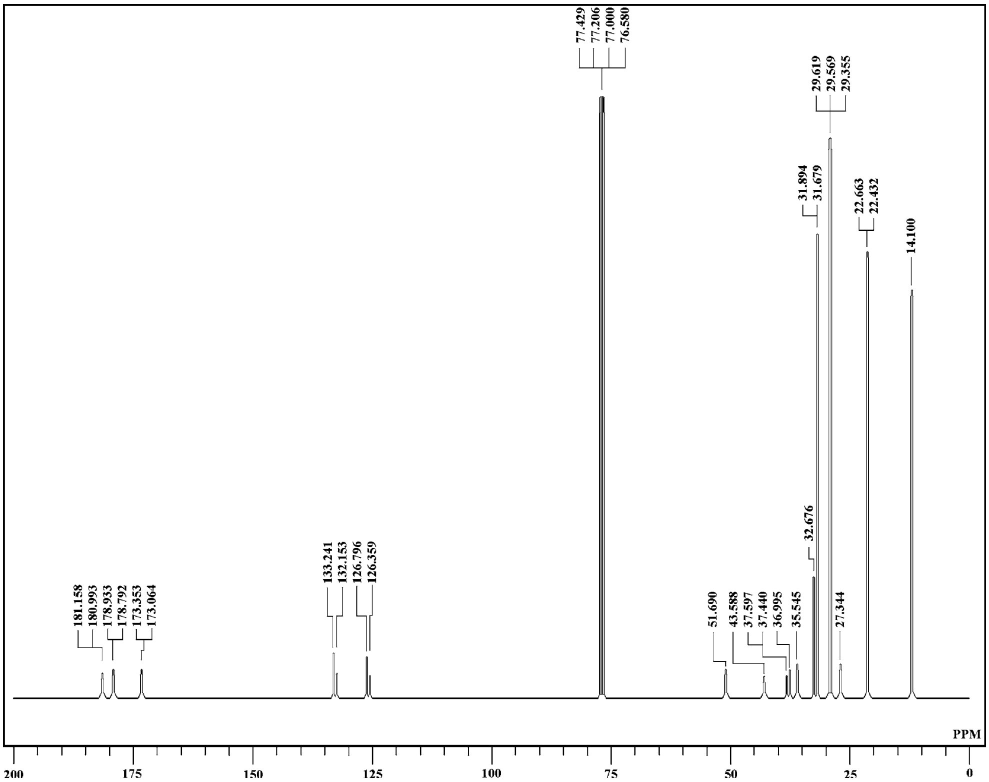


Fig. 3 Nuclear magnetic resonance spectrum of the surfmer intermediate

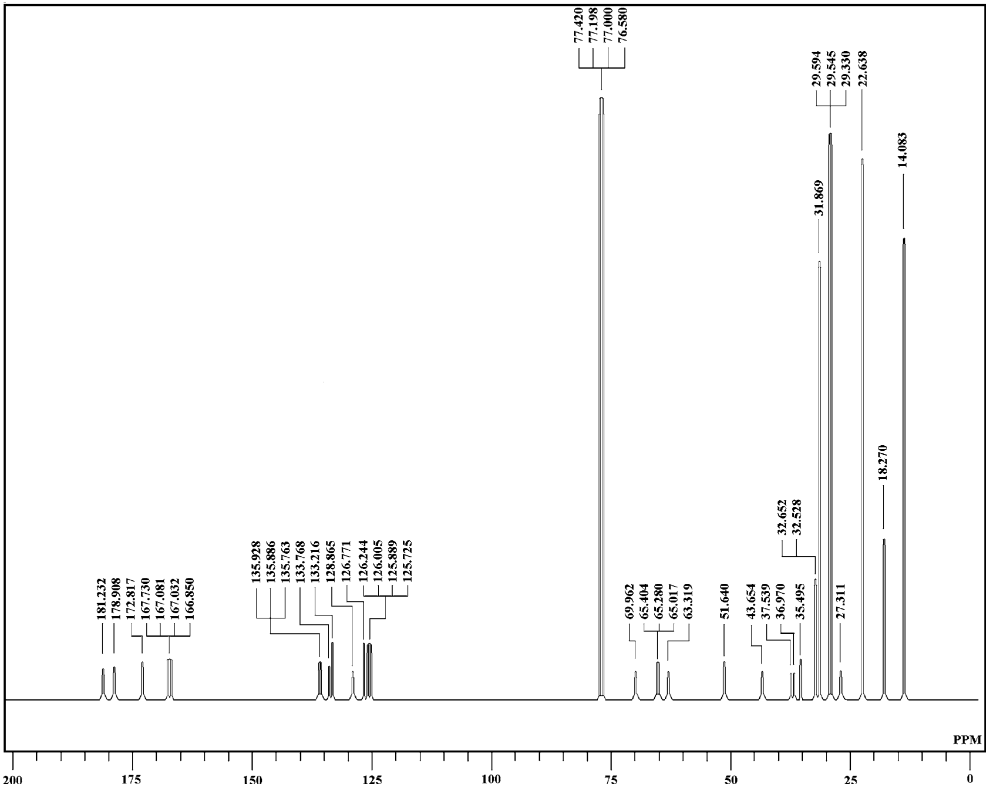


Fig. 4 Nuclear magnetic resonance spectrum of the surfmer

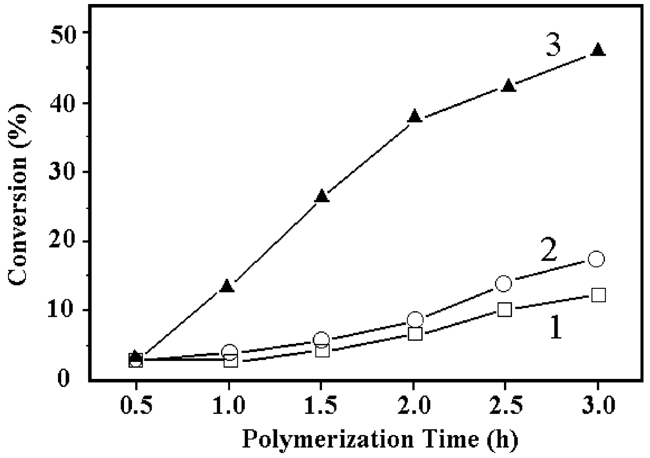


Fig. 5 Plot of polymer conversion against polymerization time. Polymerization temperature: *1* 55 °C, *2* 65 °C, *3* 75 °C. Surfmer concentration: 0.005 g/g styrene. Volume fraction of the dispersed phase $\Phi = 0.8$

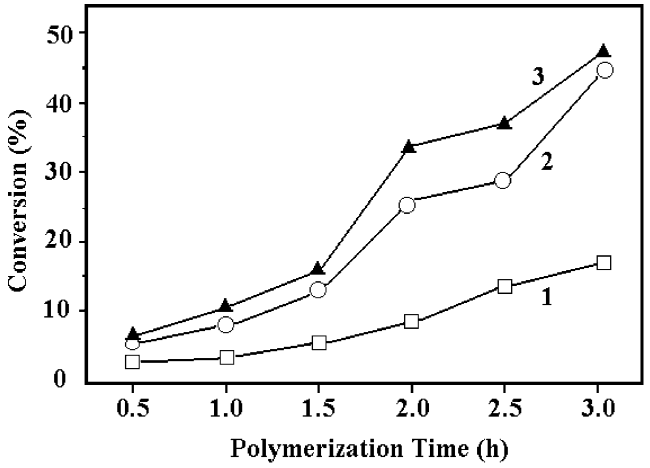


Fig. 6 Plot of polymer conversion against polymerization time. Surfmer concentration (g/g St) *1* 0.005, *2* 0.01, *3* 0.015. Volume fraction of the dispersed phase $\Phi = 0.8$

– $\underline{C}OONa$, respectively, and provide evidence for the sodium salt. The four peaks at 166.850, 167.032, 167.08 and 167.730 ppm, can be attributed to the four different carbons in –CH $\underline{C}ON$ (two isomers, each possessing a *cis* and a *trans* structure).

By comparing the final product with the intermediate one, one can see that a hydroxyl group was formed and a terminating double bond was introduced. The presence of –OH is indicated by the peak at 69.962 ppm, which can be assigned to the carbons of $–CH_2\underline{C}H(OH)CH_2–$, and that of the terminating double bond by the peaks at 125.889 ppm and between 135.763 and 135.928 ppm, which can be assigned to the carbons of $\underline{C}H{=}C(CH_3)$ and $CH{=}\ \underline{C}(CH_3)$, respectively.

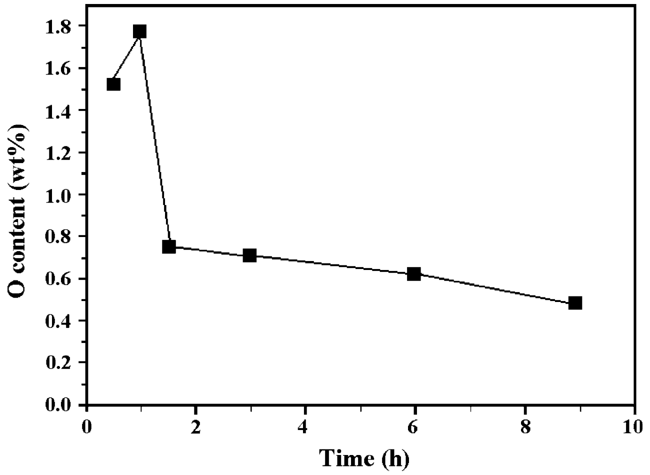


Fig. 7 The oxygen content of the products at different polymerization times

Self-polymerization of the surfmer

The self-polymerization of the surfmer could be followed in the IR spectrum (b) of Fig. 2. Indeed, after self-polymerization, the peak of the ester, originally at 1722.367 cm^{-1}, was shifted to 1729.832 cm^{-1} . As already mentioned, the peak of an independent ester is located at 1730 cm^{-1} ; however, when conjugated with a terminating double bond, it should be shifted to 1722.367 cm^{-1} (spectrum b, Fig. 2). Its shifting back from 1722.367 to 1729.832 indicates the disappearance of a fraction of the terminal vinyl groups, and this provides evidence for self-polymerization.

Copolymerization with styrene

Polymerization rate

Figure 5 presents the conversion-time relationship at various polymerization temperatures. Figure 6 provides a relationship between conversion and amount of surfmer and shows that the greater the amount of surfmer, the higher is the polymerization rate. The surfmer affected the polymerization rate because of the "gel effect". Indeed, the greater the amount of surfmer, the smaller the size of the droplets of the concentrated emulsion and hence the higher the resistance to the mobility of the growing polymer chains. As a result, the rate of termination by coupling decreased with decreasing size of the droplets. This gel effect accelerated the polymerization rate and increased the molecular weight.

The polymerization rate of the surfmer was determined by measuring the content of oxygen in the

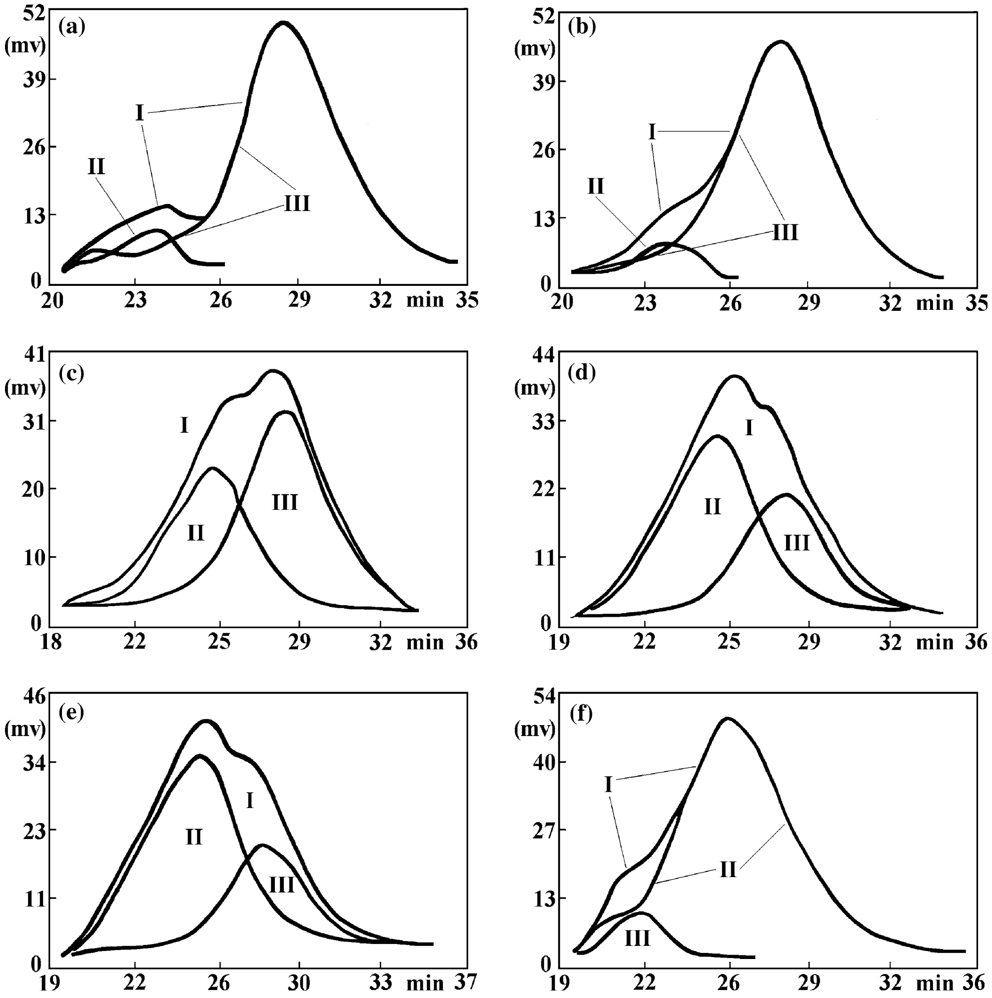


Fig. 8 Gel permeation chromatography traces of samples for various polymerization times and for a surfmer content of 0.02 g/ml St. **a** 0.5 h, **b** 1.0 h, **c** 1.5 h, **d** 2.0 h, **e** 2.5 h, **f** 3.0 h

Table 2 Parameters for the peaks of PS/surfmer copolymer

Time of polymerization (h)	Position of the peak (min)	Area fraction of the peak	M_n	M_w	M_w/M_n
0.5	28.44	0.925	28,743	91,477	3.18
1.0	28.24	0.927	29,876	107,615	3.60
1.5	27.84	0.593	35,142	215156	6.12
2.5	27.54	0.404	34,215	159,153	4.65
3.0	27.75	0.321	28,705	139,768	4.87

Table 3 Parameters for the peaks of PS homopolymer

Time of polymerization (h)	Position of the peak (min)	Area fraction of the peak	M_n	M_w	M_w/M_n
0.5	23.37	0.075	223,027	581,158	2.61
1.0	24.05	0.073	161,589	415,909	2.57
1.5	24.71	0.407	102,999	583,495	5.67
2.5	24.86	0.596	77,435	445,402	5.75
3.0	24.71	0.679	64,412	494,107	7.67

Table 4 Gel content of samples (wt%) as a function of the amount of surfmer (g/ml St)

Amount of surfmer (g/ml St)	0.005	0.010	0.015	0.020
Gel content (wt%)	1.75	3.21	4.38	5.02

Table 5 Sodium content determined by atomic absorption spectroscopy (wt%)

Surfmer concentration (wt% in water)	2%	4%	6%	8%
Raw product	0.021	0.058	0.071	0.094
Alcohol washed product	0.016	0.037	0.040	0.052

product at different times, and the results are plotted in Fig. 7.

Table 6 Copolymerized fraction of the surfmer (wt%)

Surfmer concentration (wt% in water)	2%	4%	6%	8%
copolymerized fraction	76.2	63.8	56.4	55.3

One can notice that after a short induction time, the oxygen content increased dramatically to a maximum and then decreased rapidly to a low level. Because styrene contains no oxygen, the change in the oxygen content must be caused by the relative content of surfmer in the product. The polymerization rate of the surfmer is expected to be more rapid than that of styrene because the former possesses two double bonds. For this reason the oxygen content in the early stages has increased rapidly. After most of the surfmer polymerized, via both homopolymerization and copolymerization, the oxygen content decreased because of the polymerization of styrene. From the change in the oxygen content, one

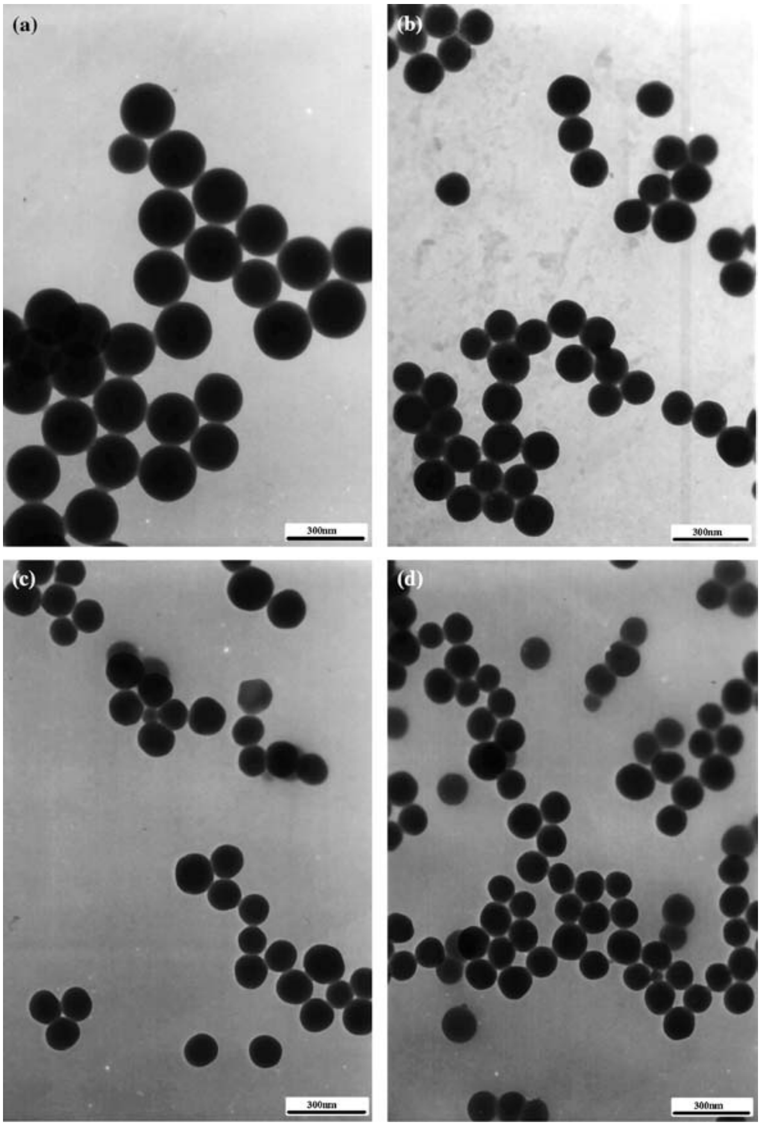


Fig. 9 The TEM micrographs of the particles prepared with various contents of surfmer. Surfmer content: **a** 0.1, **b** 0.2, **c** 0.3, **d** 0.4 g/20 ml styrene, volume fraction of the dispersed phase $\Phi = 0.8$, polymerization temperature: 65 °C, time: 28 h

Table 7 Particle diameter D_w (wt average) and D_n (number average) (μm) for various surfmer contents

Amount of surfmer (g/100 ml)	D_w	D_n	D_w/D_n
0.1	0.202	0.196	1.0285
0.2	0.200	0.189	1.0625
0.3	0.186	0.177	1.0549
0.4	0.158	0.147	1.0812

can conclude that a large fraction of the surfmer was consumed during the initial stages of polymerization.

Gel permeation chromatography (GPC)

Figure 8 presents the GPC traces of samples for different polymerization times. All the traces (denoted as I) were split into two individual peaks (denoted II and III). In the system styrene-surfmer, there are three possible products: the homopolymers of styrene and surfmer, and the copolymer of styrene/surfmer. Because of steric hindrance, the amount of surfmer homopolymer is small. For this reason the two peaks should be assigned to the styrene homopolymer and to the copolymer. The fractions of the areas of the peaks and the corresponding molecular weights are listed in Tables 2 and 3, respectively.

It is worth noting that the relative area of peak II increases, and that of peak III decreases with time. Peak III with the lower molecular weight should be assigned to the copolymer because (1) as concluded in the previous section, the surfmer is consumed rapidly in the early stages of polymerization; (2) the relative area fraction of the peak III decreases in time (see Table 2);

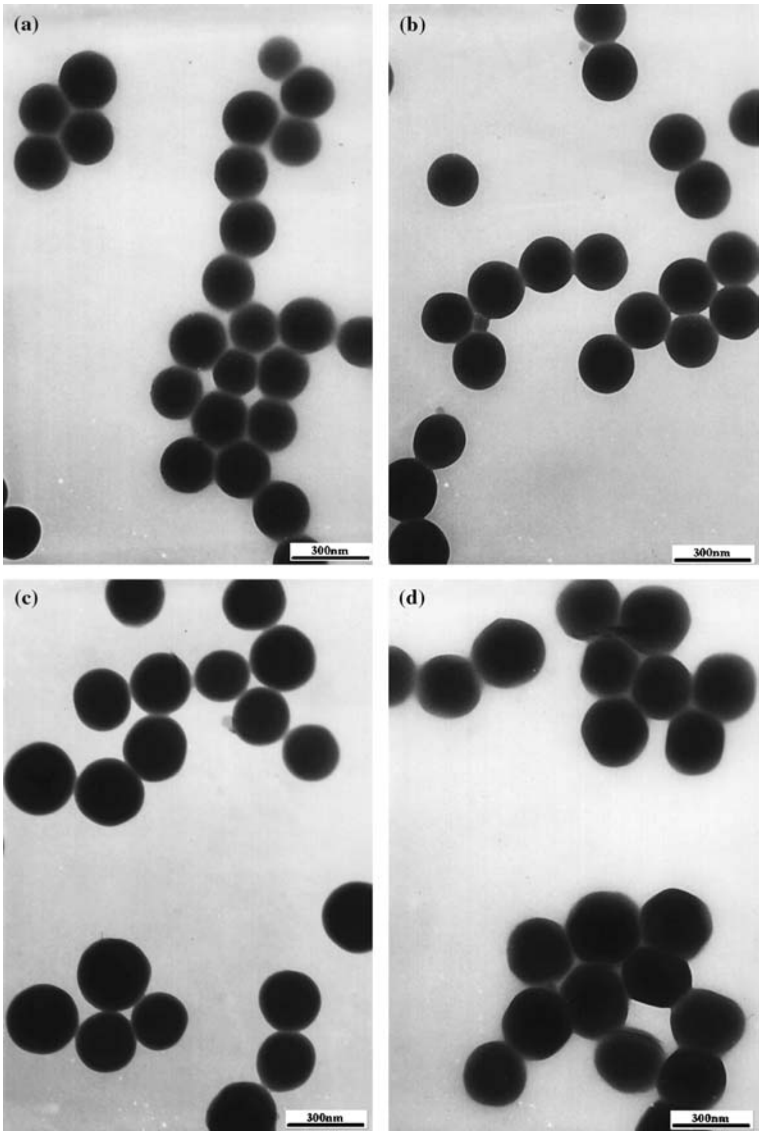


Fig. 10 TEM micrographs of particles for various volume fractions of the dispered phase (Φ). Surfmer concentrations: 0.02 g/ml styrene; polymerization temperature: 50 °C, polymerization time: 30 h

Table 8 Particle diameter (μm) and its dispersion for various volume fractions of the dispersed phase (Φ)

Φ	D_w	D_n	D_w/D_n
0.75	0.1946	0.1842	1.0565
0.80	0.2151	0.2106	1.0214
0.85	0.2514	0.2420	1.0388
0.90	0.2561	0.2426	1.0394

(3) the steric hindrance of the surfmer prevents the generation of high molecular weight species. As a result, peak II with a higher molecular weight should be assigned to the styrene homopolymer. The molecular weight of homopolymers decreased with time because of the polymerization of surfmer, which thus became less effective in emulsification. As a result, some droplets of the concentrated emulsion coagulated and this weakened the gel effect.

Gel formation via the middle double bonds

The surfmer has two double bonds, one at the end of the side chain, and the other in the hydrophobic moiety. A small fraction of the surfmer contributed to the generation by cross-linking of a gel. The gel content of the samples for various amounts of surfmer, determined as the insoluble in tetrahydrofuran, is listed in Table 4.

The copolymerized fraction of the surfmer

The surfmer can either self-polymerize or copolymerize with St. The Na content of the products for various surfmer concentrations is listed in Table 5, from which the fraction of copolymerized surfmer could be determined (Table 6). Table 6 shows that the higher the concentration of surfmer, the lower is its copolymerized fraction. This occurred because a high surfmer concentration favors its self-polymerization.

Morphology of the particles

Figure 9 presents the electron micrographs of particles for different concentrations of surfmer. The average particle size and the dispersion are listed in Table 7. It is clear that the higher the concentration of surfmer, the smaller the particle size. The dispersion D_w/D_n indicates that the particles are essentially mono-dispersed. The small deviation from mono-dispersion was caused by the coagulation of a small fraction of the droplets.

The volume fraction (Φ) of the dispersed phase of the concentrated emulsion affected the particle size (Fig. 10, Table 8), which increased with increasing Φ, because the amount of surfmer per unit weight of dispersed phase decreased. One should note that as expected when Φ = 0.9, the shape of the particles was no longer spherical, but polyhedral.

The dynamic mechanical property

Figure 11 presents the dynamic mechanical analysis (DMA) curves of tangent of loss angle against temperature. Curves 2, 3, and 4 exhibit two peaks; one located around 100 °C (denoted I) and the other between 70 and 80 °C (denoted II). From the preceding discussion, two types of segments are expected to be detectable in the system: the homopolymer polystyrene and the styrene/surfmer copolymer. Because the surfmer contains a long aliphatic chain, its glass transition temperature should be lower than that of polystyrene. For this reason, the peak at higher temperatures (peak I) should be assigned to the polystyrene homopolymer. One can notice that peak I decreases and peak II increases with increasing surfmer content. The decrease of peak I is probably due to the incorporation of surfmer molecules into the homopolymer chains; the increase of peak II is probably a result of a higher degree of cross-linking. Curve 1 has only one peak because the content of surfmer was too low to generate a detectable amount of copolymers.

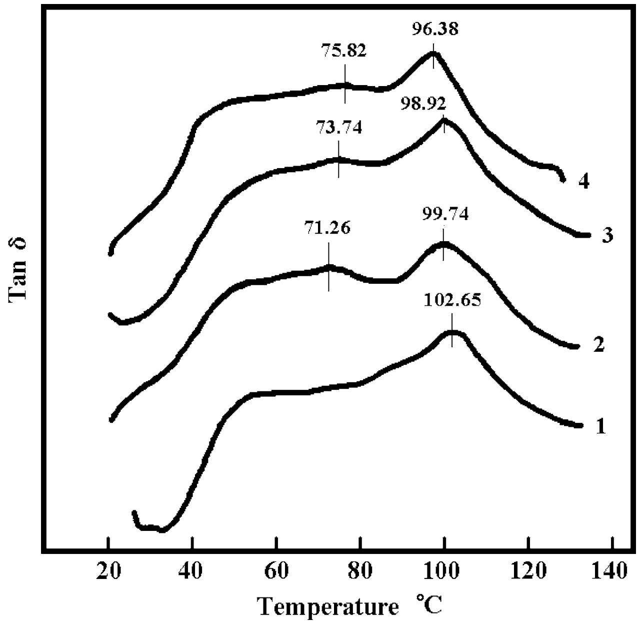


Fig. 11 DMA curves for various surfmer contents Surfmer content: (1) 0.1, (2) 0.2, (3) 0.3, (4) 0.4 g/20 ml styrene; volume fraction of the dispered phase Φ = 0.8, polymerization temperature: 65 °C, polymerization time: 28 h

Conclusion

A polymerizable surfactant (surfmer) was synthesized and employed to prepare latexes via the concentrated emulsion polymerization of styrene. This surfmer possesses a weak tendency for self-polymerization and a high copolymerization ability with styrene, because of its three-arm structure, a double bond at the end of a side chain and a double bond in the hydrophobic moiety. Because the polymerizable groups were located in a side chain and in the hydrophobic moiety of the surfmer, its hydrophilicity was little affected after polymerization. Polystyrene particles with uniform size distribution were thus prepared.

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