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ORIGINAL CONTRIBUTION

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Copolymerization of styrene and reactive surfactants in a microemulsion: control of copolymer composition by addition of nonreactive surfactant

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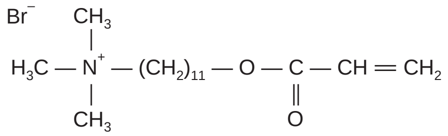
Abstract The γ-ray-induced copolymerization of styrene and the surfactant monomer (surfmer) (11-acryloyloxy)undecyltrimethylammonium bromide, **1**, – with and without the presence of the nonreactive surfactant *N*-dodecyltrimethyammonium bromide, **2**, – was studied in a single-phase (1Φ) oil-in-water microemulsion. Upon exchange of 50 weight percent of **1** against **2** the 1Φ region could be increased to higher styrene content. Upon γ-ray irradiation a copolymer is formed: this copolymer exhibits a larger styrene-to-surfmer ratio than the original monomer mixture. This allowed the styrene-to-surfmer molar ratio in the resulting polymer to be varied from 0:1 to 4.3:1. The larger styrene-to-surfmer ratio originates from the simultaneous formation of homopolymer **P-1**, which is in accordance with the Candau–Leong–Fitch model of polymerization. Further information on particle size and material properties of the copolymers, which is not accessible by other preparation methods, is also given.

Key words Microemulsion · Copolymerization · Styrene · Surfactant monomer

Introduction

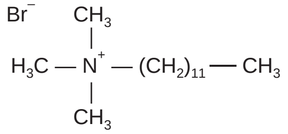
Polymerization in microemulsions represents a versatile method for the preparation of novel nanostructured materials [1–3]. As recently demonstrated, the simultaneous use of styrene as a polymerizable oil component and amphiphilic (meth)acrylates as a polymerizable surfactant (surfactant monomer, ‘surfmer’) in three-component oil-in-water (o/w) microemulsions allows amphiphilic copolymers with defined nano-structures to be prepared [4, 5]. While surfmers with the reactive unit at the hydrophobic tail end, for example, (11-acryloyloxy)undecyltrimethylammonium bromide, **1**, lead to formation of surface-functionalized, redispersable nanoparticles [4], the use of surfmers with the reactive unit near the polar headgroup (e.g. **3**) favours the formation of transparent, nanostructured and highly elastic polymer gels [5]. In principle, a variation of the styrene-to-surfmer ratio should enable the composition and material properties of the resulting copolymers to be tailored. However, up to now only microemulsions of distinct composition have been polymerized, while a systematic study of the copolymerization of styrene and surfactant monomers has not been undertaken yet. Unfortunately, a wide variation of the styrene-to-surfmer ratio is restricted by the relatively small size of the single-phase (1Φ) region of the microemulsion. Especially, it is impossible to increase the styrene content above the value determined by the solubilization limit of the oil component; however, a broader variation of the copolymer composition may be achieved, if the surfmer is partially exchanged by a nonpolymerizing surfactant. The nonpolymerizing surfactant would still be able to solubilize the oil component but would not become incorporated into the polymer. Hence the use of such surfactant mixtures should be an effective method to vary the styrene content more widely and thus to tailor the material properties of the resulting copolymers.

The purpose of this communication is to report the first attempts to copolymerize styrene and **1** in a 1Φ o/w



$$\mathrm{Br^-}\quad \mathrm{H_3C-\underset{CH_3}{\overset{CH_3}{N^+}}-(CH_2)_{11}-O-\underset{O}{\underset{\|}{C}}-CH=CH_2}$$

1



$$\mathrm{Br^-}\quad \mathrm{H_3C-\underset{CH_3}{\overset{CH_3}{N^+}}-(CH_2)_{11}-CH_3}$$

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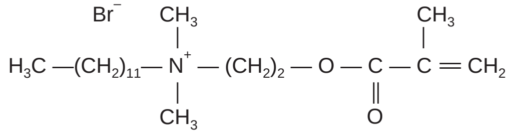

$$\mathrm{Br^-}\quad \mathrm{H_3C-(CH_2)_{11}-\underset{CH_3}{\overset{CH_3}{N^+}}-(CH_2)_2-O-\underset{O}{\underset{\|}{C}}-\overset{CH_3}{C}=CH_2}$$

3

microemulsion to form amphiphilic copolymers of controlled composition. The composition is tailored through a partial exchange of surfmer **1** by the nonpolymerizing *N*-dodecyltrimethylammoniumbromide, **2**. The phase behaviour, the formation and the composition of the resulting copolymers are reported.

Experimental

Materials

The polymerizable surfactant **1** was prepared according to methods described in the literature [6]. For purification, the surfactant was recrystallized 5 times from acetone with a small amount of dry ethanol. The homopolymer of **1** (**P-1**) was prepared by polymerization in a micellar solution and polystyrene (PSt) was prepared by microemulsion polymerization using **2** as a surfactant. **2** (Fluka, Neu-Ulm, Germany) with a purity of 99% was used as received. Styrene (Aldrich, Steinheim, Germany) was freshly distilled before use in order to remove the inhibitor and oligomeric impurities. Hydroquinone (Merck, Darmstadt, Germany) was used as received. Milli-Q_{PLUS} water was used for all experiments.

Polymerization

Polymerization in a microemulsion was performed in closed glass tubes at 25 °C. The transparent samples were treated with ultrasonic radiation shortly before use in order to remove small gas bubbles. No attempts were made to remove dissolved oxygen because purging of the samples with an inert gas would have been accompanied by partial evaporation of the styrene from the microemulsion. ^{60}Co γ radiation was used for the polymerization. The dosage was 0.44 kGy/h (1Gy = 1 J/kg = 100 rad).

Methods

The clear 1Φ regions of the microemulsion at 25 and 60 °C were determined visually by titrating styrene into water/surfactant mixtures in screw-capped glass tubes. Each sample was thoroughly homogenized using a Vortex mixer and thermostated in a water bath. The phase diagram at 60 °C was determined with styrene, to which a few parts per million of hydroquinone were added in order to prevent thermal polymerization.

The copolymer composition was determined using Fourier transform infrared (FTIR) spectroscopy. The ratio, y, of the band intensities of the C=O stretching mode of the homopolymer **P-1** at 1728 cm^{-1} and the C-H out-of-plane bending mode of the aromatic ring in PSt at 698 cm^{-1} was determined. From this ratio the relative composition of the copolymers was calculated using a calibration curve obtained from mixtures of the two homopolymers in different ratios x. This calibration curve could be fitted by a straight line following the expression $y = -0.31 + 0.08x$. The spectra were measured using a Perkin-Elmer Paragon 1000 spectrometer. The preparation of the samples was carried out by dropping a methanolic solution of the sample onto a KBr pill and evaporating the solvent in vacuo. The spectra were baseline-corrected and normalized using appropriate spectrometer software.

Particle sizes were determined at a temperature of 25 ± 0.1 °C using a goniometer system with an ALV5000e correlator (ALV, Langen, Ar ion laser; λ = 488 nm). For details see Ref. [7].

Results and discussion

Phase behaviour

Partial phase diagrams of the water/**1**/styrene and water/**1**/**2**/styrene systems with 1:1 weight ratio of **1** and **2** are shown at 25 and 60 °C in Fig. 1. It can be seen that transparent and fluid 1Φ regions only exist near the water edge of the triangle. For the system with the 1:1 mixture of **1** and **2**, this region is larger than for the system with **1** only. This is not surprising because the water/**2**/styrene system is known to exhibit a 1Φ region of a similar size [8]. Figure 1 also indicates that for both systems the 1Φ region at 25 °C is larger than that at 60 °C, but the difference between the two systems is more pronounced at 60 °C than at 25 °C. The improved solubilization of styrene upon addition of **2** is more clearly shown in Fig. 2. For the 1:1 weight mixture of the two surfactants, the molar solubilization ratio of styrene to surfactant is not simply the average of the values found for the pure surfactants **1** and **2**, but is clearly higher. This is especially observed for a total surfactant concentration in the microemulsion above 10 wt% and clearly indicates a mixing of the surfactants.

Polymerization

Polymerization was carried out using γ radiation. This type of radiation is advantageous because it penetrates the sample homogeneously, initiates polymerization at room temperature and prevents additional initiator compounds being needed. All samples were irradiated in closed glass tubes at 25 °C using a dose of 52 kGy. Previous studies had shown that such a dose is sufficient

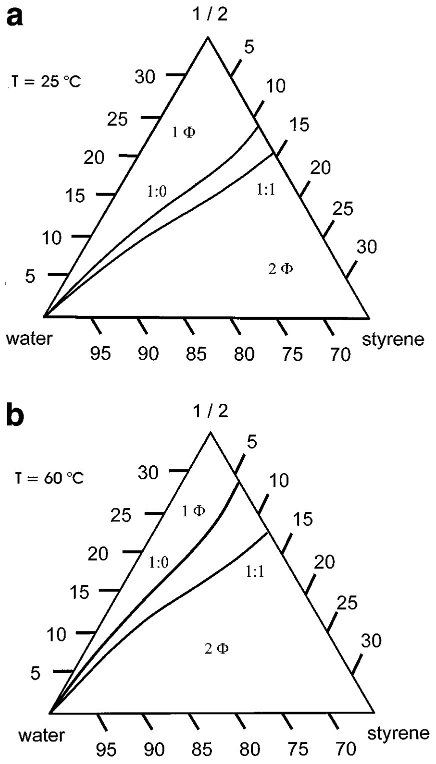

Fig. 1 Partial phase diagrams of the water (11-acryloyloxy)undecyltrimethylammoniumbromide **1**/styrene and water/**1**/*N*-dodecyltrimethylammonium bromide 2 (in 1:1 weight ratio)/styrene systems at **a** 25 °C and **b** 60 °C (*1Φ* and *2Φ* denote single- and two-phase regions)

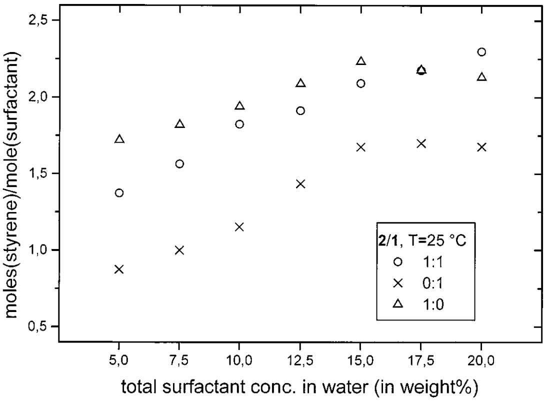

Fig. 2 Plot of the molar solubilization ratio of styrene/surfactant versus the surfactant concentration at 25 °C

to cause nearly complete polymerization [4]. After polymerization, the samples were transparent and more viscous than before. This contrasts with the water/**2**/styrene system of comparable styrene content, which turns highly turbid upon polymerization [8–11]. The polymer was separated by flocculation in 2-butanol, while the nonpolymerizable surfactant **2** was soluble in that solvent. The precipitated polymer was dried in a vacuum, swelled in water for 1 day, filtered and repeatedly rinsed with clean water in order to leach out the water-soluble homopolymer **P-1**. The same cleaning was carried out with toluene in order to dissolve any PSt which might have formed eventually. The experiments showed that the main product was a copolymer of styrene and **1**, which was soluble neither in water nor in toluene. **P-1** was always found as a side product, while PSt was never observed. The copolymer was a hard and brittle material. Since it could be swelled in organic solvents such as dimethylsulfoxide and redispersed in alcohols such as ethanol, we assume that core–shell nanoparticles with hydrophilic shells were formed, as demonstrated recently [4].

Copolymer composition

The characteristic data of the samples investigated are shown in Table 1. The composition of the copolymer was analysed using FTIR spectroscopy. Details are given in the Experimental part. Typical spectra of two styrene/**1** copolymers of different composition are shown in Fig. 3. It can be seen that the bands of the C=O stretching mode of **P-1** and the out-of-plane bending mode of the aromatic ring of PSt are well suited for the determination of the comonomer ratio. The relative copolymer composition is plotted versus the corresponding monomer composition in Fig. 4. In all samples, the total surfactant concentration was 10% (w/w), while the **2/1** surfactant weight ratio was either 1/1 or 0/1. Two main results were found. Firstly, the use of **2/1** mixtures allows copolymers with higher styrene content to be prepared than by the use of **1** alone, i.e. our concept of tailoring the copolymer composition through exchange of reactive **1** by nonreactive **2** works. The main reason is that **2/1** mixtures are able to solubilize more styrene than **1** alone. Secondly, the styrene-to-**1** molar ratio in the copolymer is always higher than in the original monomeric microemulsion. This is consistent with the Candau–Leong–Fitch model [12] of polymerization. Radical chain growth is mainly initiated in the micellar droplets

Table 1 Characteristic data of the samples investigated

Weight ratio **1/2**	Molar ratio styrene/**1** in the microemulsion	Molar ratio styrene/**1** in the copolymer	R_h(nm)
1/0	0.88/1	1.48	10.0
1/1	1.41/1	3.63	11.0
1/1	1.75/1	3.92	12.6
1/1	2.34/1	4.13	14.7
1/1	2.87/1	4.27	21.4

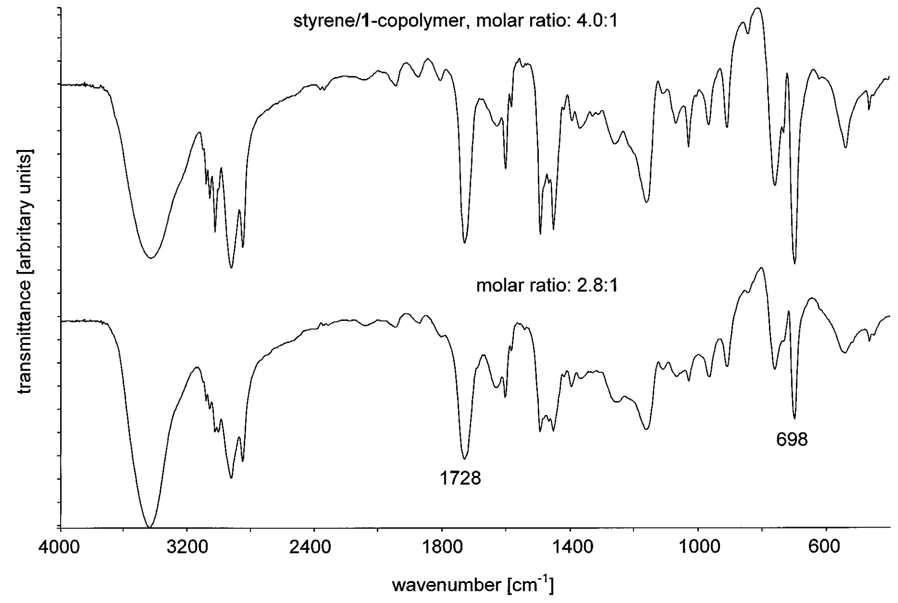

Fig. 3 Fourier transform IR spectra of two copolymers of styrene and **1** prepared in a microemulsion of styrene/**1** with molar ratios of 4.0:1 and 2.8:1. The bands at 698 and 1728 cm^{-1} were evaluated for determining the composition of the polymer

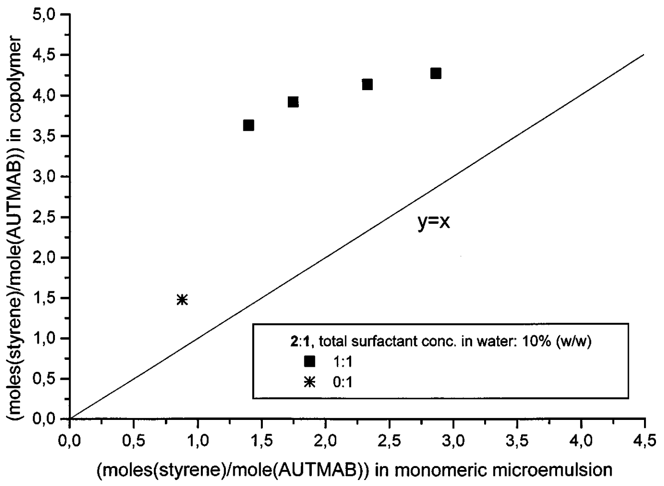

Fig. 4 Plot of styrene/**1** molar composition of the copolymer versus the styrene/**1** molar composition of the monomeric microemulsion. The **2**/**1** weight ratio was either 0:1 or 1:1

containing styrene in the core. Polymerization takes place within the droplets and leads to copolymers of styrene and **1**. During polymerization, additional styrene is supplied from non-initiated micellar droplets, which causes the styrene content in the copolymer to increase. Simultaneously, more and more empty (i.e. styrene-free) micelles are formed, in which only homopolymerization of **1** can take place; therefore, at the end, a mixture of copolymer (with higher styrene content than in the original monomer mixture) and homopolymer of **1** is obtained. As also shown in Fig. 3, the excess styrene in the copolymer decreases with increasing styrene content in the monomer microemulsion. The reason might be that a higher styrene content in the microemulsion reduces the number of empty micelles at the end of the reaction so that an increasing amount of surfmer **1** is copolymerized instead of forming the homopolymer **P-1**. This should result in a decrease in homopolymer formation that still has to be confirmed experimentally. The hydrodynamic radii, R_h, of the polymerized particles were determined using light scattering and values are listed in Table 1. It is not surprising that a higher styrene content in the copolymer results in larger R_h values; however the particle sizes increase more strongly than the styrene content. The reason might be that with increasing styrene content the copolymers are increasingly less stabilized by the hydrophilic shell and tend to agglomerate and form larger particles.

Conclusions

Our studies indicate that the partial replacement of surfmer **1** by nonreactive surfactant **2** increases the 1Φ region of the water/**1**/styrene microemulsion. This allows copolymers of **1** and styrene to be prepared with considerably higher styrene content than in a system without **2**. If a 1:1 weight mixture of **1** and **2** is present in the monomeric microemulsion, a variation of the styrene content allows copolymers with a styrene-to-surfactant molar ratio from 0:1 (homopolymer of **1**) to 4.3:1 to be prepared without formation of a turbid solution. The present studies indicate that for a 2:3 weight mixture of **1** and **2** the situation is different: a turbid solution is formed, if the styrene-to-surfmer weight ratio in the monomeric system exceeds 3. The reason is that with decreasing content of **1** the copolymer becomes increasingly hydrophobic and is therefore less stabilized by the copolymerized **1**. Nevertheless, polymerization in a microemulsion represents a versatile method to prepare amphiphilic copolymers of tailor-made composition which cannot be prepared by any other polymerization method.

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