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Water expandable polystyrene (WEPS)
Part 2. In-situ synthesis of (block)copolymer surfactants

J.J. Crevecoeur[1], L. Nelissen*, P.J. Lemstra

Eindhoven Polymer Laboratories (EPL), Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract

In Part 1 of this series (Polymer 1999;40:3685), the concept for the preparation of expandable polystyrene (PS) applying water as a blowing agent was presented. In order to achieve this goal, water was emulsified by means of a commercially available surfactant (sodium bis(2-ethylhexyl)sulfosuccinate) in a prepolymerised styrene/PS mixture. This mixture was subsequently suspended in water and polymerisation was continued to complete conversion. This procedure resulted in spherical PS beads containing tiny water droplets which were capable of expanding the material upon heating above its glass transition temperature. In certain cases (especially at high surfactant concentrations), miscibility problems between the surfactant and the PS matrix caused unstable systems during polymerisation. For this reason, a new technique was developed to synthesise in-situ amphiphilic copolymers with good miscibility in the PS matrix. This novel route to incorporate very finely dispersed water into polystyrene is described in this paper. This procedure also has potential for the preparation of amphiphilic species with other applications, e.g. as detergents, dispersants, in the enhanced oil recovery, etc., since a very simple radical copolymerisation is applied, whereas the syntheses of most surfactants require a relatively complicated reaction sequence. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Expandable polystyrene; Water; Blowing agent

1. Introduction

In our previous study, we introduced the concept for the preparation of water expandable polystyrene (WEPS) [1] via the partial polymerisation of the continuous phase of an inverse emulsion (water-in-styrene) followed by a suspension polymerisation up to complete conversion of the prepolymerised mixture. During polymerisation, destabilisation of the inverse emulsion can take place as a result of phase separation between the surfactant and the continuous phase. This phase separation is originating from the continuously decreasing miscibility of the aliphatic part of the surfactant and the continuous phase, which changes in composition from styrene to polystyrene (PS) during polymerisation.

Considering this aspect, the ideal surfactant for our specific system is composed of a very hydrophillic (ionic) headgroup and a PS tail as hydrophobic part. In this paper, a new strategy for the synthesis of polymeric amphiphiles via the (block)copolymerisation of styrene and a hydrophillic monomer, e.g. sodium styrene sulphonate (SSS), [2–7] is presented. A procedure for the in-situ synthesis of such amphiphilic (block)copolymers with the aid of a phase transfer catalyst (PTC) [8–10] is introduced and applied for the preparation of WEPS beads.

The use of a PTC is essential in the proposed procedure in order to establish reaction between the incompatible comonomers.

2. Experimental

2.1. Materials

The styrene monomer, manufactured by Shell and supplied by Bredase Polystyreen Maatschappij (B.P.M.), was used without distillation from the inhibitor *tert*-butylcatechol (11–17 ppm). The initiators dibenzoylperoxide (DBPO) (active content, 75%; water, 25%) possessing a halflife ($t_{1/2}$) at 90°C of 75 min [11] and *tert*-butylperoxybenzoate (TBPB) with $t_{1/2}(120°C) = 70$ min [11] were supplied by Akzo Nobel Chemicals. The initiator dilauroylperoxide (97% purity) with $t_{1/2}(79°C) = 60$ min [11], was supplied by Aldrich. The monomer 4-vinylbenzenesulfonic

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* Corresponding author.

[1] Present address: DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands.

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Table 1
Preparation of P(S-SSS) copolymer, formulation in parts by weight SSS, sodium styrene sulphonate; DLPO, dilauroylperoxide; TOMAC, trioctylmethylammonium chloride

Component	Content
Styrene	13.63
Water	114.53
SSS	11.46
DLPO	0.17
TOMAC	2.26

acid sodium salt (SSS) was supplied by Fluka. Deuterated dimethyl sulfoxide (DMSO) (purity, 99.9% and 0.05% v/v tetra methyl siloxane), solvent for the nuclear magnetic resonance (NMR) experiments, was supplied by Cambridge Isotope Laboratories. The PTCs tetrapentylammonium bromide (TPAB) and trioctylmethylammonium chloride (TOMAC) were supplied by Fluka and Aldrich, respectively. Both were used as received.

2.2. Preparation of P(S-SSS) (block)copolymer

A model experiment for the preparation of a P(S-SSS) (block)copolymer was performed in order to verify the validity of the proposed reaction mechanism (see Section 3).

The molar ratio styrene/SSS was 70/30 for this model experiment. The weight fractions of the different components are listed in Table 1. The mixture was polymerised in a 500 ml double-walled reaction vessel for 48 h at a temperature of 79°C.

Before characterisation with differential scanning calorimetry (DSC), the reaction product was filtered and extensively washed with water (4°C) to remove potentially present SSS monomer and poly(sodium styrene sulfonate) (PSSS) homopolymer. For the surface tension measurements, the room-temperature water-soluble fraction (possibly also containing SSS and PSSS) was used.

2.3. Preparation of WEPS beads via suspension polymerisation

The following experimental procedure was executed which resulted in PS beads containing tiny water droplets. Styrene (2700 g), 300 g water (blowing agent), 6.0 g of TOMAC as PTC, 30 g (1 wt.%) of sodium styrene sulfonate and the initiators (12.0 g of DBPO and 4.5 g of TBPB) were all mixed together in a 6.4 l reaction vessel and heated to 90°C. The mixture was polymerised in bulk for 150 min in a nitrogen atmosphere, while stirring at 800 r.p.m. Subsequently, the viscous reaction mixture was suspended, in a suspension reaction vessel of 10 l containing 5.0 l of water and 20 g of suspension stabiliser (water soluble polymer), and polymerisation was continued for 4 h at 90°C in a nitrogen atmosphere while stirring at 350 r.p.m. Subsequently, the temperature was raised to 125°C under a nitrogen pressure of 4 bar and the polymerisation was continued for another 3 h. Finally, the suspension was cooled to room temperature and the spherical beads were filtered and washed with water.

2.4. Differential scanning calorimetry

Glass transition temperatures (T_gs) were determined using a Perkin–Elmer DSC-7. The heating rate was 20°C min^{-1} and two runs were recorded. Indium was used for calibration.

2.5. Nuclear magnetic resonance (^{1}H-NMR)

A 300 MHz Varian spectroscope was used for NMR spectroscopy. Samples were measured after accumulating 64 scans at room temperature. Styrene (40 g), 40 g distilled water, 15 g SSS and 10 mol% (on SSS basis) of PTC were mixed at a stirring rate of 800 r.p.m. and a temperature of 90°C for 30 min. Subsequently, the stirrer was stopped and the system separated into two layers. A sample of the styrene layer was dissolved in deuterated DMSO at room temperature in a NMR tube. Deuterated DMSO was selected as the solvent because both monomers dissolve in DMSO.

2.6. Surface tension measurements

Surface tension measurements were performed using a Krüss K10 surface tension apparatus at a temperature of 23°C by the static Wilhelmy plate method. Surface tensions of the water-soluble fraction of the copolymer, prepared as described (not washed), PSSS homopolymer and SSS monomer, respectively, were determined in the concentration range 0–180 g l^{-1}.

2.7. Scanning electron microscopy

Scanning electron microscopy (SEM) was performed on the WEPS beads both prior to and following expansion using a Cambridge Stereoscan 200 microscope, operating at 20 kV. Compact samples were fractured at liquid nitrogen temperature and the expanded samples were cut with a razor blade. Subsequently, the samples were coated with a gold layer.

3. Results and discussion

3.1. Synthesis and characterisation of the amphiphilic model compound

Copolymers composed of a hydrophobic PS-rich block and a hydrophillic PSSS-rich block, were synthesised by free radical polymerisation of styrene mixed with a solution of the comonomer SSS in water. The two phases were initially dispersed exclusively by vigorous stirring. However, the formed copolymer provided an increasing stability during the course of polymerisation. The reaction

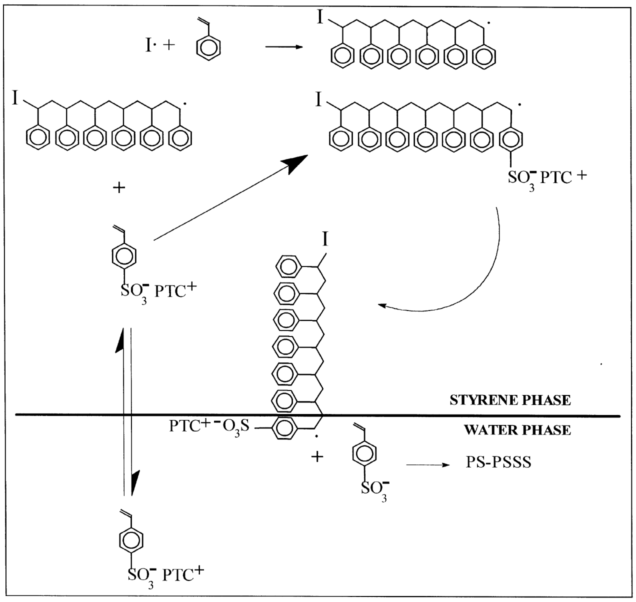

Fig. 1. Reaction mechanism for the formation of a PS/PSSS (block)copolymer via phase transfer catalysis.

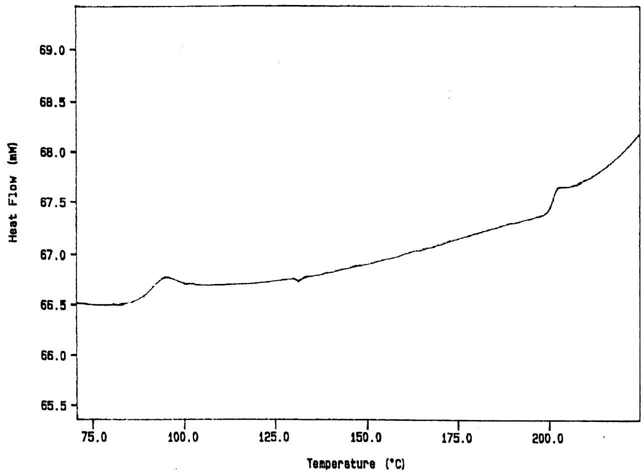

Fig. 2. Second-run DSC scan of P(S-SSS) (70/30) (block)copolymer.

mechanism of the copolymer formation is depicted schematically in Fig. 1.

The polymerisation was initiated by a conventional, styrene-soluble free radical initiator. The polystyryl free chain radical reacts with the SSS monomer which has been transported from the aqueous phase to the organic styrene phase by a PTC [8]. After the reaction between a growing PS chain and SSS monomer, the product becomes surface active and will preferably migrate to the styrene/water interface as a consequence of this. Once such a free chain radical is located at the interface, it can continue growing in the aqueous phase with SSS monomer resulting in a P(S-SSS) (block)copolymer stabilising in-situ the water-in-styrene emulsion. Note that the surface active free chain radical, obtained after reaction with a SSS monomer unit, can, during migration to the interface, possibly also react with the styrene monomer before continuation of the polymerisation in the aqueous phase. This would result in imperfections in the blocks of the copolymer, or even in random incorporation of sulfonated species in the PS chains. If this occurs, and to what degree, depends on the balance between the migration rate and the styrene polymerisation rate.

Fig. 2 shows the second heating run of a DSC scan of the synthesised amphiphilic copolymer according to the reaction mechanism presented in Fig. 1. The material possesses two T_g values at, respectively, 89 and 200°C. Since the sample was washed extensively with water, the presence of PSSS homopolymer can be excluded. This indicates that a P(S-SSS) block-like copolymer has been formed, of which each block (a styrene-rich and a sulfonated styrene-rich block, respectively) possesses a separate T_g. This supports the mechanism as proposed in Fig. 1. The somewhat low values of the T_g (literature values are 100 and 257°C, respectively) [11,12] may be the result of the low molar mass of the copolymer and/or the presence of styrene and residual water present in the sample (despite drying). No molar masses could be measured because it is, experimentally, practically impossible to determine molar masses of such amphiphilic copolymers since both blocks require different solvents and moreover, the ionic sulfonate groups are known to form clusters, disturbing molar mass determinations [5,13–17].

Convincing evidence for the validity of the proposed reaction mechanism was obtained by surface tension measurements. According to this mechanism, amphiphilic block-like copolymers are prepared during the described model experiment. Such copolymers should evidently be surface active in contrast with random or alternating copolymers. This means that surface tension measurements can provide information about the molecular structure of the copolymer. In Fig. 3, the surface tension of the water-soluble fraction of the copolymer is depicted versus its concentration, together with those of SSS monomer and PSSS homopolymer. This figure clearly shows a substantial reduction of the surface tension by the copolymer. The sulfonated styrene monomer is also slightly surface active, but to a much smaller extent, and the PSSS homopolymer hardly possesses any surface activity. This means that the decrease in surface tension by the water-soluble fraction of the copolymer cannot be attributed to the potential presence of sulfonated monomer and homopolymer. Moreover, it confirms the validity of the mechanism as proposed in Fig. 1, since the surface activity can only be explained by the organisation of a block-like copolymer at the surface.

Although the concentrations at which surface activity is observed (Fig. 3) are relatively high on a weight basis, the molar concentrations are evidently orders of magnitude lower.

A crucial step in the reaction sequence as presented in Fig. 1 is the transfer of SS$^-$ to the organic phase. That this

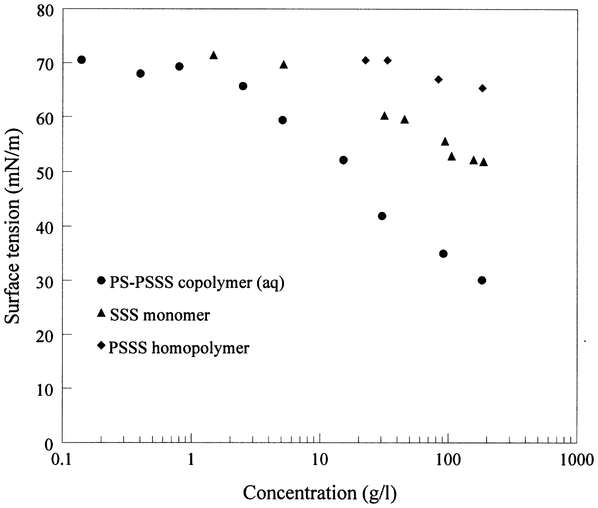

Fig. 3. Surface tension as a function of concentration for, respectively, PSSS homopolymer, SSS monomer and the water-soluble fraction of the P(S-SSS) (block)copolymer.

transfer actually takes place was demonstrated by NMR spectroscopy.

Styrene, a solution of SSS in water and a PTC were intensively stirred at 90°C for 10 min. After this mixing period, the stirrer was stopped and a sample of the clear styrene (upper) layer was taken and cooled to room temperature. In some cases, a small fraction of dissolved water phase separated from the solution upon cooling. This was due to the higher solubility of water in styrene at 90°C than at room temperature. In these cases, the sample was stored until a clear styrene solution was macroscopically separated. This solution was dissolved in deuterated DMSO and transferred to a NMR tube. DMSO was selected as the solvent because both styrene and SSS are soluble in DMSO.

In Fig. 4(a), the ^{1}H-NMR spectrum of the styrene fraction of a mixture without PTC (reference measurement) is shown. According to expectations, no doublet corresponding to SSS is observed in this spectrum. In Fig. 4(b), the ^{1}H-NMR spectrum of the styrene fraction of a mixture containing TPAB as PTC is presented. In this spectrum, the presence of SSS in the organic styrene phase is clearly

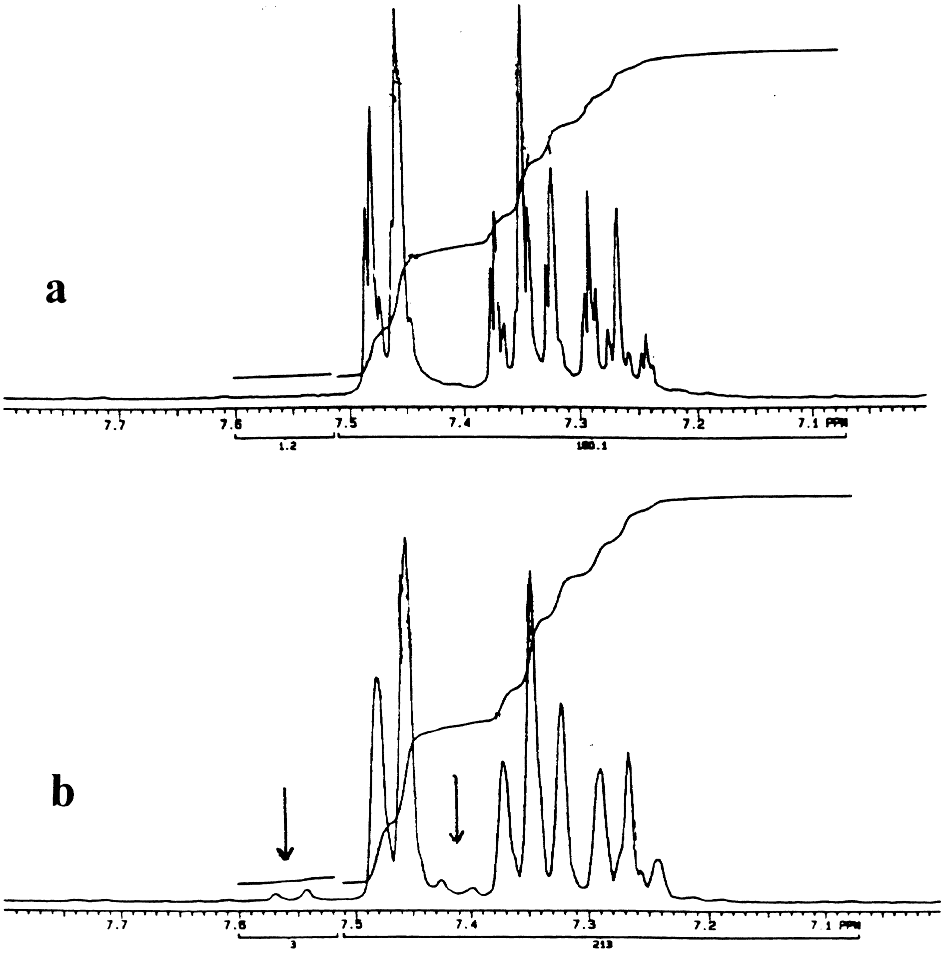

Fig. 4. Aromatic region of the ^{1}H-NMR spectrum of the styrene phase of a styrene/water/SSS mixture after 10 min of stirring at 90°C, (a) in the absence and (b) in the presence of the PTC tetrapentyl ammonium bromide (TPAB).

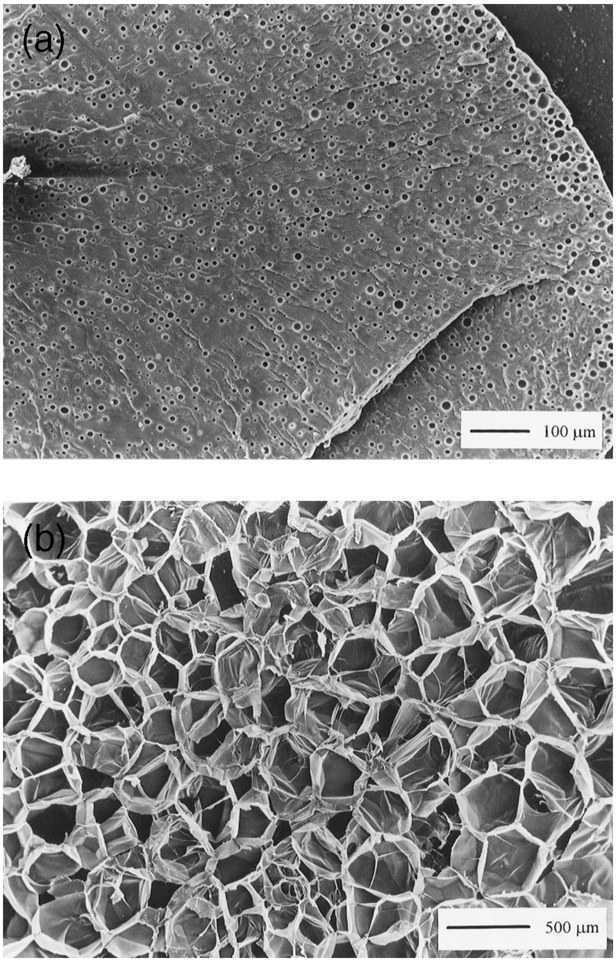

Fig. 5. SEM micrographs of (a) a compact WEPS bead and (b) an expanded WEPS bead.

demonstrated by the appearance of the characteristic SSS doublets (between 7.38–7.44 ppm and 7.53–7.58 ppm, respectively). This proves that the assumed mechanism of transfer of SSS from the aqueous to the organic phase by a PTC is valid. Consequently, it is very reasonable to assume that copolymerisation between styrene and SSS occurs. Note that the tetrapentylammonium counter ion is, of course, also present in the measured sample, but its signals appear in the low ppm range and are consequently not observed in Fig. 4(b).

3.2. Application of amphiphilic copolymerisation for the preparation of WEPS

The described strategy to synthesise amphiphiles via radical copolymerisation was applied in-situ for the preparation of expandable PS beads containing water as the blowing agent. This was achieved by a two-step polymerisation process; respectively, the bulk polymerisation of an inverse emulsion of water in styrene up to a conversion of approximately 50%, and a suspension polymerisation of this viscous reaction mixture up to complete conversion. During the prepolymerisation, the in-situ synthesised amphiphilic copolymer stabilised the emulsified water droplets. That this actually occurred was observed visually by the progressive decrease in droplet size and the increase of emulsion stability during the course of reaction.

Fig. 5(a) shows a SEM micrograph of a fractured WEPS bead, prepared via the two-step polymerisation procedure described, applying 1 wt.% of SSS. This micrograph reveals a very fine and homogeneous dispersion of water droplets (size approximately 5 μm) in a PS bead with a size of 2 mm. This favourable dispersion of water droplets could be established thanks to the stabilisation of the in-situ synthesised block-like P(S-SSS) copolymers. The small water droplets inside the beads are capable of expanding the material by heating it above its T_g. Fig. 5(b) shows the foam structure of a WEPS bead expanded in hot air (135°C). From this micrograph, it is clear that a regular foam structure with a fairly fine cell size (approximately 100 μm) was achieved in this manner. The relative increase in volume as a result of expansion amounted to a factor of 24. The concept of synthesising an amphiphilic copolymer for the preparation of WEPS beads has some advantages with respect to the use of commercially available surfactants like sodium bis(2-ethylhexyl)sulfosuccinate. The most important one is the perfect compatibility of the amphiphile with the polymer matrix, since the hydrophobic part of the copolymer consists of PS. This increase in compatibility also results in a higher expandability, which is possibly caused by a more homogeneously distributed interfacial tension. This might reduce the probability of cell rupture and consequently improve foam stability [18].

4. Conclusions

A reaction mechanism for the preparation of amphiphilic block (or semi-block) copolymers consisting of polystyrene (PS) and poly(sodium styrene sulphonate) (PSSS) via phase transfer catalysis was introduced. Characterisation of such copolymers by DSC and surface tension measurements confirm the proposed reaction mechanism for the synthesis of block-like copolymers. These blocks or semi-blocks respectively represent sulfonate-rich and sulfonate-poor parts.

The strategy to prepare amphiphilic block-like copolymers was applied in-situ for the preparation of water expandable polystyrene beads (WEPS). The beads contained a fine and homogeneously distributed dispersion of water droplets after suspension polymerisation. Expansion of these beads in hot air (135°C) resulted in a relative volume increase by a factor of 25 and a homogeneous and fairly fine foam structure.

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