Colloid Polym Sci 276:402–411 (1998)
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Reactive surfactants in heterophase polymerization for high performance polymers

Part 1. Synthesis of functionalized poly(ethylene oxide)-*b*-poly(butylene oxide) copolymers as surfmers inisurfs and transurfs in heterophase polymerization

Received: 22 July 1997
Accepted: 11 December 1997

This work was supported by the Human Capital and Mobility Program of the European Union, CHRX 93 00 159

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Abstract A variety of nonionic reactive surfactants have been prepared from block copolymer precursors. These precursors are formed from a commercially available polyoxyethylene glycol monomethylether as the hydrophilic sequence of the surfactant; this product is used as initiator of ring opening anionic polymerization of butylene oxide. Finally the reactive surfactants are obtained after proper functionalization of the precursor. The reactive surfactants are an inisurf with an asymmetric azo compound, a transurf with a thiol group, and a few surfmers with acrylic, methacrylic, styrenic and α-methyl styrenic reactive groups. These compounds have been engaged in styrene emulsion or dispersion polymerization. Several of them have been found to be useful for preparing stable latices.

Key words Block-copolymers – polyethylene oxide – polybutylene oxide – reactive surfactants – emulsion polymerization – dispersion polymerization

Introduction

The covalent bonding of surfactants onto the surface of polymer particles in heterophase polymerization is expected to improve the latex stability and the properties of the films which can be formed from these lattices [1]. In a conventional emulsion polymerization, where normally one or more surfactants are involved, the surfactants are able to freely adsorb and desorb, and can therefore affect the stabilization properties of the latex chiefly under some constraints such as high shear as well as upon freezing. Also, during film formation when the polymer particles coalesce, the surfactants can migrate through the film either towards the interface where they will be concentrated, or trapped in some domains in the bulk of the film. These surfactant domains can be responsible for water rebound, poor mechanical properties, and blooming and blushing.

A solution to these problems is the chemical anchoring of the surfactants onto the surface of the polymer particles. This can be achieved by using a polymerizable surfactant (surfmer) [2, 3], which copolymerizes during the radical polymerization. One could also use a surface-active initiator (inisurf) [4–7] which is able to form surface-active radicals after decomposition. Another way is using a surfactant with transfer-active properties (transurf) [8–11].

This paper is the first in a series reporting the work done upon cooperative action of several European laboratories, in which we will describe the synthesis and use of several anionic and nonionic reactive surfactants in dispersion and emulsion polymerizations. We are interested in their reactivity and behavior during the polymerization, as well as in the properties of the latices (dispersions) obtained, and their film forming and mechanical properties.

In this publication we will describe the synthesis of an inisurf, a transurf and several surfmers, all based on the same nonionic surfactant, a poly(ethylene oxide)-*b*-poly(butylene oxide) copolymer (EO-BuO). These copolymers were prepared by anionic ring opening polymerization of butylene oxide initiated by commercial polyoxyethylene glycol monomethyl ether and their further functionalized derivatives.

Experimental procedures

Materials

Poly(ethylene glycol) methyl ether (PEO) (Aldrich, $M_n = 2000$ g/mol) was freeze-dried before use by lyophilization from a benzene solution. Tetrahydrofuran (THF) (Aldrich) was used after refluxing in an argon atmosphere in the presence of sodium benzophenone, which generates a permanent purple colour. Butylene oxide (Aldrich) was distilled over sodium hydride under argon atmosphere. The initiator potassium naphthalene was prepared by stirring potassium (Janssen Chimica) and naphthalene for 4 h in THF at room temperature.

4-*t*-Butylazo-4-cyanopentanoic acid was obtained from commercially available levulinic acid (80%, Janssen Chimica, distilled before use), sodium cyanide (p.a., Merck, Germany) and *t*-butylhydrazine hydrochloride (>95%, Janssen Chimica), as described by Macleay and Sheppard [12]. Dicyclohexylcarbodiimide (99%, Janssen Chimica) and dimethylaminopyridine (97%, Janssen Chimica) were used as received. Toluene was dried over molecular sieves (4 Å) prior to use. *p*-Toluenesulfonic acid (Janssen Chimica) was dried in an oven in vacuo at 50 °C over night.

Dichloromethane (Hays) was distilled from $CaCl_2$ and stored over 4 Å molecular sieves. Styrene (Aldrich Chem. Co), methyl methacrylate (Aldrich Chem. Co) and vinyl acetate (B.D.H.) were washed with sodium hydroxide (2 M) and water before drying over sodium sulfate (B.D.H.). Acryloyl chloride (Aldrich Chem. Co), potassium persulfate, hydroquinone (Merck), aluminium chloride hexahydrate (Fisons), calcium chloride, sodium carbonate, sodium chloride, trisodium orthophosphate, sodium sulfate (B.D.H.) and sodium hydrogen carbonate (Fluka) were used as received.

n-Isopropenyl-α, α′-dimethylbenzylisocyanate (TMI, Cytec), dibutylbis(lauroyloxy)stannate (T12, Merck), isooctane (Merck), potassium persulfate (KPS, Fluka), and $NaHCO_3$ (Fluka), were used as received. Toluene was distilled and used immediately, styrene (S) and butyl acrylate (BA) were distilled and kept at −18 °C.

Synthesis of poly(ethylene oxide)-*b*-poly(butylene oxide) copolymers: anionic ring opening polymerization of butylene oxide

The polymerization was carried out in THF under an argon atmosphere and a complete exclusion of water. After introduction of the PEO to the THF, the potassium naphthalene initiator solution was added until a permanent light green colour was obtained. Then, polymerization was initiated by the addition of the amount of butylene oxide needed. Next, the temperature was raised and maintained at 70 °C for 18 h. The reaction was terminated by the addition of methanol. After evaporation of the solvents the polymer was purified by precipitation in heptane. The obtained copolymers were characterized by ^{1}H NMR (Bruker 250 MHz in $CDCl_3$) and by SEC (Waters, with THF as an eluant).

Synthesis of an asymmetrical inisurf: 4-*t*-butylazo-4-cyanopentanoic acid methoxy-*b*-(ethylene oxide)$_{45}$-*b*-(butylene oxide)$_9$ ester

Equimolar amounts of surfactant (26.6 g) and initiator 4-*t*-Butylazo-4-cyanopentanoic acid (2.11 g) (10 mmol each) and 100 ml of dry toluene were charged into a dry 250 ml round-bottomed flask, equipped with a drying funnel and magnetic stirrer. The contents were cooled in an ice bath. Next, dimethylaminopyridine (0.061 g) and *p*-toluenesulfonic acid hydrate (0.095 g) (0.05 equiv. each) were added, followed by addition of discyclohexylcarbodiimide (2.16 g, 1.05 equiv.). The flask was wrapped in aluminium foil, and the contents were stirred at 4 °C for two days. The dicyclohexylurea formed, as well as dimethylaminopyridinium *p*-toluenesulfonate were removed by filtration, using a fritted glass disc filter. The toluene was evaporated in vacuo: the temperature of the water bath during evaporation was kept below 30 °C. The inisurf was obtained as a slightly yellow solid ($\overline{M}_n = 2878$ g/mol). Comparing the integrals of the ester resonances at $\delta = 4.2$–4.3 ppm and 4.9–5.0 ppm to that of the butylene oxide methyl resonance at $\delta = 0.95$ ppm in the 400 MHz ^{1}H NMR spectrum indicated that the esterification was complete (yield: 28.5 g, i.e., 100%).

^{1}H NMR ($CDCl_3$) δ 0.95 (m, $C\underline{H}_3CH_2$), 1.25 (s, 9H, *t*-Bu), 1.50 (m, $CH_3C\underline{H}_2$), 1.60 (s, 3H, CH_3), 2.10–2.60 (m, 4H, CH_2CH_2), 3.40 (s, 3H, OCH_3), 3.50–3.70 (m, CH_2CH_2O and $C\underline{H}_2C\underline{H}$ $(CH_2CH_3)O$), 4.20–4.30 (m, C(O) OCH_2), 4.90–5.00 (m, C(O)OCH).

Synthesis of transurf

The EO–BuO–SH transurf was prepared by esterification of the monomethylether of the EO–BuO copolymer with an excess of mercaptoacetic acid (Aldrich) in toluene under nitrogen atmosphere. The reaction was performed under reflux for 18 h in toluene under nitrogen atmosphere, in the presence of a catalytic amount of *p*-toluenesulfonic acid. After removal of the solvent under vacuum, the product was dissolved in chloroform and purified by precipitation in a cold mixture of ether/petroleum ether (1/2, v/v). This has been done under nitrogen in order to avoid the formation of disulfide upon oxidation.

Next, the transurf was dried under reduced pressure at room temperature over night. The transurf was characterized by NMR and SEC. SEC traces of two samples (see Fig. 1) are showing either a bimodal distribution when the sample contains disulfide, or a monomodal distribution when the preparation has been carried out carefully enough.

Emulsion polymerizations of styrene

The emulsion polymerizations using the nonfunctionalized EO–BuO diblock copolymers or the transurfs were performed batchwise in a thermostated glass reactor (200 ml), under nitrogen atmosphere at 70 °C for several hours. Unless stated otherwise, the reactions were carried out with 90 g of water, 10 g of styrene (distilled before use), 0.115 g of 2-2′azobis (2-methyl, *N*(2-hydroxyethyl) propionamide (VA-86) and 0.5–2 g of the surfactant.

The kinetics of polymerization were followed upon gravimetric determination of the weight of polymer produced after a given time. After the polymerization has been completed, the coagulum which may have been formed was separated upon filtration using filter paper. Then the particles were separated upon centrifugation and then washed four times with deionized water. Particle size measurements were carried out using quasielastic light scattering (MALVERN Autosizer). The amount of surfactant grafted (both at the surface and into the particle) can be deduced from the NMR spectrum of the polymer dissolved in $CDCl_3$, by comparing the signal from the ethylene oxide protons and those from the styrene protons.

Synthesis of surfmers

Acrylated polyethylene oxide-b-polybutylene oxide copolymer

Into a 100 ml round-bottomed flask fitted with a dropping funnel and a drying tube were placed polyethylene oxide-*b*-polybutylene oxide copolymer (Run 2 of Table 1) (2 g, 7.45×10^{-4} mol) dissolved in dry dichloromethane (45 ml) and sodium carbonate (0.1 g, 9.31×10^{-4} mol). The flask was dipped into an ice bath and cooled down. A solution of acryloyl chloride (0.074 g, 9.31×10^{-4} mol) in dichloromethane (10 ml) was added dropwise to the solution. The reaction was continued for 20 h, then the solids were filtered off and the solvent evaporated. A white solid was obtained (1.89 g, 6.9×10^{-4} mol) which corresponds to a 93% yield.

^{1}H NMR ($CDCl_3$) $\delta = 0.93$ (m, 67.5H), 1.4–1.5 (m, 46H), 2.0 (m, 11H), 3.3–3.8 (m, 524H), 5.8– 6.5 (m, 3H).

Microanalysis ($C_{129}H_{255}O_{56}$) Mwt.: 2701.99; Calculated C 57.6%, H 9.71%; Found: C 57.1%, H 9.2%.

Methylmethacrylate isocyanate surfmer

A block copolymer (from Run 3 in Table 1) was reacted with a five-fold excess of methacryloyl isocyanate (MAI

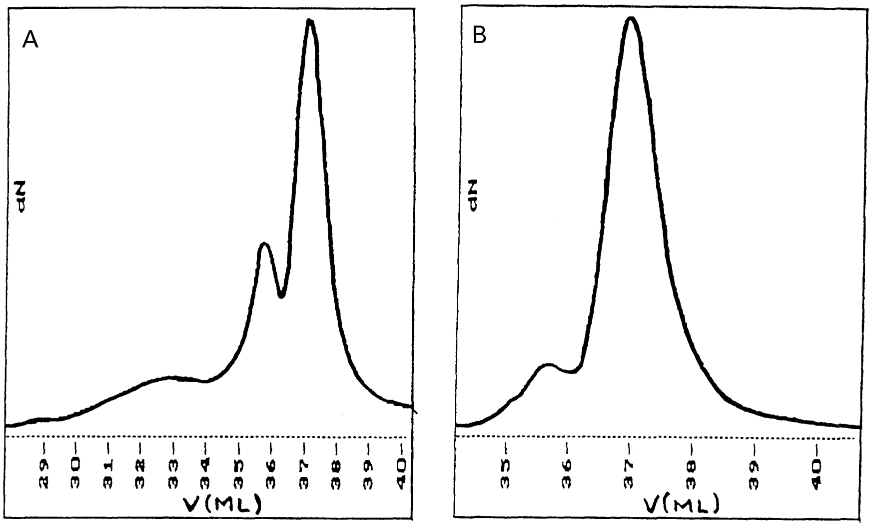


Fig. 1 SEC traces of transurfs: (a) purified sample and, (b) sample containing disulfide

Table 1 Block copolymers data

Run	PEO [g]	THF [ml]	BuO [g]	Conversion [%]	$(BuO)_m$ [NMR]	M_n	M_w/M_n
1	36	43	13.4	80	8.5	–	–
2	88.5	70	33.7	76	9.3	2730	1.05
3	96.1	72	38.9	61	8.4	2370	1.05
4	101	97	43.5	80	10.5	2620	1.10
5	167	41.8	137.1	82	12.2	2540	1.13

Table 2 Styrene polymerization using block copolymers from Run 3 (Table 1)

Block copolymer					
Amount (g)	2	0	1	1	0.5
SDS (g)	0	0.05	0.12	—	0.12
Initiator (g)	0.115 (VA 86)	0.115 (VA 86)	0.115 (VA 86)	0.075 (KPS)	0.115 (VA86)
Conversion %	86	100	97.5	100	87.5
Coagulum %	8.5	5.8	1	2.7	8
Particle size (nm)	338	585	93	229	102

from SNPE Chimie). The reaction was carried out 3.5 h at 40 °C and then overnight at room temperature. The excess of MAI was neutralized with methanol, and the product was purified through precipitation with petroleum ether. The functionalization yield is almost 100%. As for the other compounds, the structure was checked with NMR (Brucker, 250 MHz). The number average molecular weight was measured as 3050 g/mol (calculated 2730 g/mol).

Dispersion polymerization using the methacrylate isocyanate surfmer

The dispersion polymerizations were carried out using a batch process in ethanol-water (70/30 by volume). Azobisisobutyronitrile (AIBN-Janssen Chimica) was used as the free radical initiator (2 wt% based on monomer) and styrene (Aldrich) was added in quantities such that the polystyrene content was 10% (W/W) at 100% conversion.

The amount of stabilizer added was 3.1% by weight with respect to the quantity of styrene. The reaction was carried out under nitrogen atmosphere for 24 h at 70 °C with a total volume of 180 ml in the reactor which was stirred at 250 rpm. The size of the particles was determined by a Disk Centrifuge Photosedimentometer analysis (BI-DCP Brookhaven particle sizer). ^{1}H NMR (Bruker 250 MHz) is used to determine the extent of grafting of the reactive surfactant from comparison of the integral of signals coming from polystyrene and the polyethylene oxide sequence of the surfactant.

Styrenic surfmer

The third surfmer prepared was a styrenic compound. It was simply produced upon killing of the living block copolymer with a stoichiometric amount of vinylbenzyl chloride (VBC from Dow Chemical). The purification of the product was similar to that of the nonfunctionalized copolymer, i.e. dissolution in chloroform and precipitation in a mixture of ether–petroleum ether.

α-Methylstyrenic surfmer

In a water-jacketed glass reactor of 200 ml, the block copolymer (5 g, 1.9×10^{-3} mol from Run 1 of Table 1) was dissolved in 36.4 g of toluene. To this mixture T12 was added (0.012 g, 1.9×10^{-5} mol) as a catalyst for the reaction between the isocyanate group of TMI and the terminal, secondary hydroxyl group of the block copolymer (from Run 2 of Table 1). This mixture was then heated to 60 °C and left to homogenize. Then TMI was added (0.417 g, 2.0×10^{-3} mol), and this was heated to 75 °C and left to react during 24 h. After this a few drops of an aqueous solution of NH_3 were added to neutralize any unreacted isocyanate groups. Upon cooling a white, waxy solid separated from the solution. Toluene was removed by rota-evaporation. To the remaining waxy solid a few milliters of iso-octane were added and this mixture was stirred at ca 80 °C. This was left for 10 min, after which the iso-octane layer was decanted. This procedure was repeated eight times. With ^{1}H NMR it was checked whether the waxy product contained any reacted TMI groups (presence of signal of vinylic protons). No difference was observed in the ratios of the vinylic signals at 5.1 and 5.35 ppm on the one hand, and the ethyl proton signals on the other hand between the sixth and the eighth cycle of cleaning, indicating that no free TMI was left. The efficiency of the reaction was ca 96% according the signals of the vinyl protons and the $-CH_3$ protons of the butylene groups.

Critical micelle concentration of the α-methylstyrenic surfmer

The critical micelle concentration (cmc) was determined by measuring the surface tension of an aqueous solution of the product in water. The cmc, obtained from intersection of two straight lines, is approximately 0.02 mM, i.e. noticeable lower than for the precursor (see below in Fig. 2).

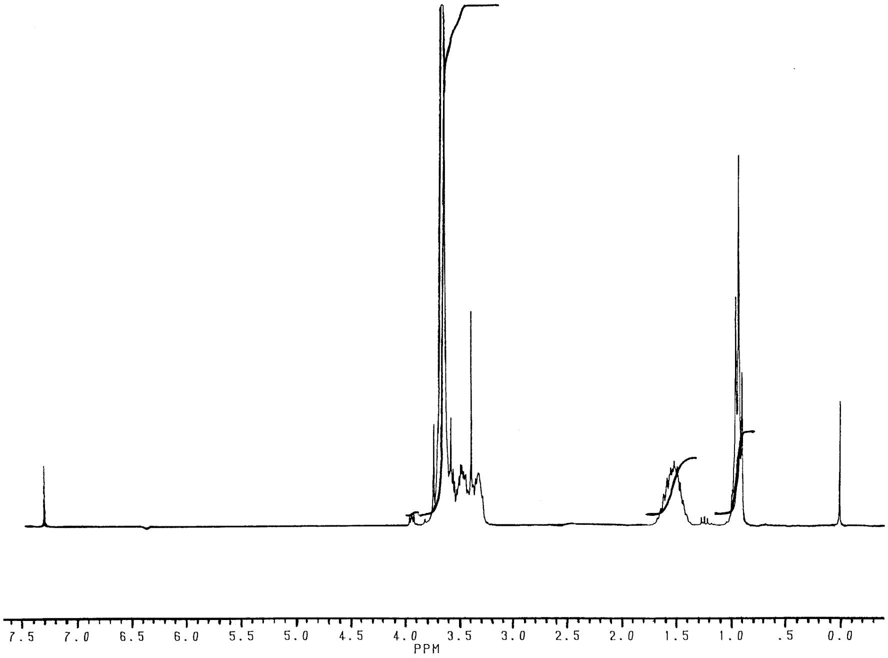


Fig. 2 Surface tension curve for a precursor block copolymer (Sample 2 of Table 1)

Emulsion polymerizations with the α-methyl styrenic surfmer

Two emulsion polymerizations were carried out with the synthesized surfmer, one in batch with S at 10% solids, and the second in a semi-continuous mode with a 50/50 mixture of S and BA at 30% solids, a recipe which has also been used to screen some anionic surfmers [17, 18]. Recipe for the first reaction: S 30 g, water 270 g, KPS 0.073 g, $NaHCO_3$ 0.16 g, surfactant 0.299 g. Reaction temperature was 60 °C, just below the Krafft temperature of the surfmer. For the second reaction the reactor was charged with 153 g water, 0.3 g KPS, 0.3 g $NaHCO_3$, and 0.1 g surfmer. This mixture was heated to 60 °C and stirred at 250 rpm. At this temperature 2.5 g S and 2.5 g BA were added over a period of five minutes, and this was left to react during 10 min. Subsequently 47.5 g of S, 47.5 g of BA, 0.3 g of KPS, 0.3 g $NaHCO_3$, 0.9 g surfmer and 81.6 g water were added at a constant rate during four hours under constant purging with nitrogen. Both reactions were followed with gravimetry.

Results and discussion

Block copolymer precursors

Because the polymerization of ethylene oxide may cause some problems of safety at the laboratory scale, we have decided to use polyethylene oxide with one alcohol chain end to initiate the polymerization of butylene oxide. The latter, owing to its higher molecular mass, is easier to handle. On the other hand, good steric stabilization may be achieved if the length of the polyoxyethylene sequence is large enough [13]. Further, a large length for that sequence displays a could point at a higher temperature so that there is less limitation for a further emulsion polymerization. So a length of 45 units ($M_n = 2000$) has been chosen.

The alcoholic chain end is first changed into the corresponding potassium alcoholate, through transfer with naphthalene potassium. The alcoholate is then used to initiate the anionic polymerization of butylene oxide. A few typical data are reported in Table 1. Rather high yields have been obtained for the polymerization of butylene oxide, so that up to about 200 g of block copolymers can be obtained in one run. A typical NMR spectrum is shown in Fig. 3. There are chiefly three groups of absorbances, around $\delta = 0.95$ (CH_3 of butylene oxide), 1.50 (CH_2 of the ethylgroup of butylene oxide) and 3.4–3.7 (backbone of both sequences). Molecular weights from SEC have been calibrated with polystyrene standards using universal calibration with $K = 1.9 \times 10^{-3}$ and $a = 0.73$. The initial polyoxyethylene used for the initiation of the polymerization of butylene oxide had a number average molecular weight of 2000 g/mol and a polydispersity index of 1.05. Such a low value of the index was approximately constant during the polymerization, which shows the character of living anionic polymerization. Surface tension measurements (Fig. 2) show the (cmc) of a sample from Run 2 to be 0.06 mM/l. From the slope, the area occupied per molecule at the interface air/water is calculated to be 114 Å^2. No cloud point has been observed below 100 °C. Surface tension measurements have also been carried out in order to determine the coverage of polystyrene latex particles at saturation. Using a monodisperse latex with a diameter of 93 nm and a solid content of 1.30% it was observed that the area covered by one molecule of surfactant is 61 Å^2 which shows a strong adsorption of this kind of surfactant onto the polystyrene surface.

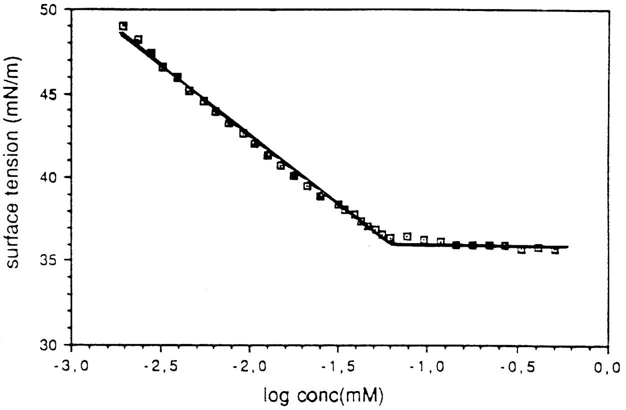


Fig. 3 Proton NMR spectrum of the block-copolymer (Sample 4 of Table 1)

Then these surfactants were used in styrene emulsion polymerizations in the presence of a nonionic water soluble azo initiator (VA 86) at 70 °C. A rather long inhibition period (about 5 h was first observed with some coagulum formation. This was thought to be a problem of nucleation, so that some SDS was introduced. This results in a high yield of polymer with small particles (93 nm) and some coagulum (1%). If, instead of the azo initiator, one uses KPS, a rapid polymerization without induction period was observed giving a 100% yield and particles of moderate size (230 nm) with a small amount of coagulum (2.7%).

Although a high conversion may be reached, the stability of the latex is not persistent. As shown in Fig. 4, using the same stabilizing system including 0.12 g of SDS and a block copolymer from Run 5, there is a trend for the formation of more coagulum at later stages of the polymerization. The conversion indicated in Fig. 4 are given without taking into account the coagulum formed. Hence, one can explain the apparent decrease in conversion for

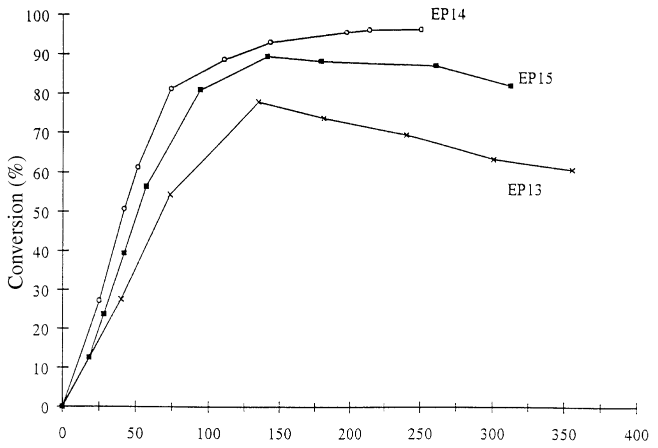


Fig. 4 Influence of surfactant concentration (Sample 5 from Table 1) on styrene conversion in the presence of a small amount of sodium dodecyl sulfate (SDS): Polymerization experiment no. 13: SDS 0.12 g block copolymer (0.5 g); Experiment no. 14: SDS 0.12 g block copolymer 1 g; Experiment no. 15: SDS 0.06 g block copolymer 1 g

long times. Further the particle size distribution is rather broad.

It may be concluded that the nonfunctionalized block copolymers are rather poor stabilizers, and some SDS needs to be added to control the nucleation.

Inisurfs

The first reactive surfactant tested was the asymmetric inisurf obtained from the diblock copolymer of Run 3 as indicated in the experimental section. The polymerization of styrene was performed at 50 °C using 9 g of styrene, 90 g water and 1.634 g (0.6%) of inisurf.

From earlier work it was known that azo-type surface-active initiators having the initiating moiety attached to the hydrophilic part of the surfactant show extremely low initiator efficiencies [3]. The reason for this is that the azo moiety is located on the outside of the micelles. As a consequence, radical generation occurred in the water phase, where the concentration of monomer (styrene) is low. As a result of this and also due to anchoring by the surfactant moiety, termination through geminate recombination is dominant, probably even for asymmetrically substituted inisurfs, having one surface-active group and one *t*-butyl group attached to the azo moiety [14].

Therefore, it was decided to attach an asymmetrically substituted azo-type initiator to the hydrophobic part of the surfactant. This compound was prepared in quantitative yield by esterification of the ethylene oxide-butylene oxide block copolymer surfactant with 4-*t*-butylazo-4-cyanopentanoic acid. The CMC of this inisurf, determined with bubble tensiometry, was with 1.5×10^{-3} mol/l, slightly higher than before fucntionalization.

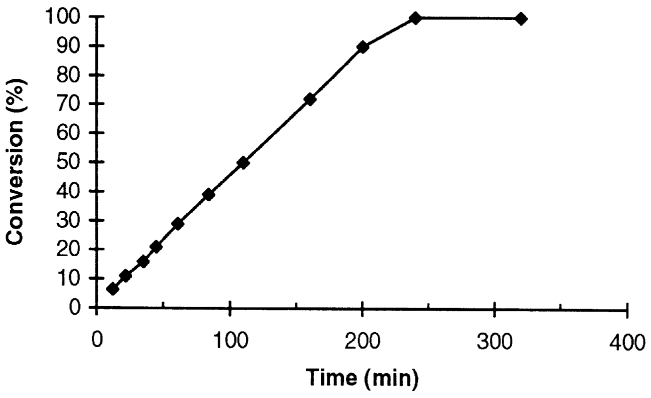


Fig. 5 Styrene conversion versus time in emulsion batch polymerization containing: Transurf 0.5 g (SEC trace in Fig. 1a), SDS 0.12 g, VA 86 0.115 g

The use of this inisurf in ab initio emulsion polymerization of styrene resulted in a stable, monodisperse latex ($d = 115$ nm). Experiments to determine K_a and the yield of incorporation of the block copolymer will be reported separately.

Transurfs

As indicated in the experimental section, the synthesis and the characterization of the transurf obtained upon reaction of the diblock copolymer with mercapto acetic acid must be carried out upon rigorous exclusion of oxygen, otherwise a part of the thiol terminated transurf can be dimerized through oxidation to the disulfide. However, a high yield of purified material (i.e. 75%) can be obtained. This material with no disulfide has been used in emulsion polymerization of styrene. Using 0.5 g of transurf and 0.12 g of SDS, in the presence of a water soluble azo initiator (VA 86), a rapid polymerization was observed as shown by the conversion curve in Fig. 5 at 70 °C. An average particle size of 142 nm was found, but the dispersion was not really monodisperse. A rather high grafting yield of the transurf (i.e. 64%) was observed.

This yield has been increased using a seeded experiment. A polystyrene seed of 93 nm has first been produced at 66 °C using the following recipe: water: 1500 g, SDS 2.5 g, $NaHCO_3$ 1.2 g, Styrene 169 g and KPS 1.11 g. Then, using 100 g of the seed latex at a concentration of 1.3 wt.%, a swelling process was carried out using 0.41 g of styrene, 0.02 g of azobis isobutyronitrile, and 0.141 g of transurf. The polymerization was carried out at 70 °C and was almost completed (95% yield) after 215 min. The particle size was increased to 102 nm. The grafting yield of the transurf was 79%.

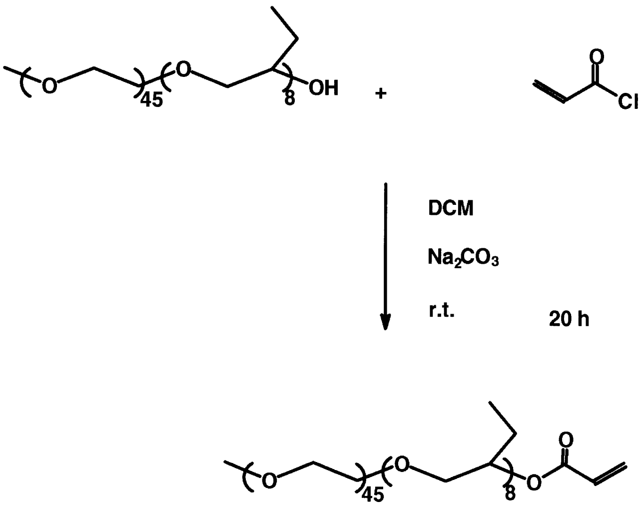
Acrylic surfmer

The first surfmer which was produced from the non functionalized block copolymers was an acrylated compound. Fig. 6 shows the reaction scheme of the condensation of acryloyl chloride with the block copolymer.

This esterification seemed straightforward, however much care had to be taken. The solvent was freshly distilled and dried to avoid traces of water during the reaction, and the temperature was kept below 4 °C. Sodium carbonate was used as a base to trap the acid chloride produced during the reaction. The use of this base allowed us to use a complete non-aqueous work up avoiding emulsification problems [15]. The resulting product was a tacky material, which was difficult to purify. Nevertheless, microanalytical and NMR data showed that the crude material had a reasonable purity. Therefore, this surfmer was used as isolated without any further purification. In the ^{1}H NMR spectrum a complex signal in the region of 6 ppm appeared. This can be further analysed as a doublet of doublets at 5.8 ppm, two doublets at 6.0 ppm, and again a doublet of doublets at 6.2 ppm corresponding to the three protons of the acrylate function, and having the right area. Thus, it can be deduced that the acrylation was achieved.

Surface tension of solutions of the precursor block copolymers and the acrylated counterpart solutions were measured. Both amphiphilic species have their cmc at very similar concentrations, as expected. It has been reported previously that the major effect on cmc is the polyethylene oxide chain length, rather than small changes in the hydrophobic tail [15]. However, the acrylated species has a slightly higher cmc, which may be due to the presence of the acrylate function at the end of the hydrophobic tail. This may make the tail slightly more hydrophilic than its nonreactive counterpart.

Fig. 6 Scheme of the synthesis of the acrylated surfmer



(I)

Preliminary experiments in emulsion polymerization were carried out using these emulsifiers, namely the nonreaction precursor and the surfmer, at 80 °C. Three different monomers were used, styrene (S), methyl methacrylate (MMA) and vinyl acetate (VA). The recipe had a 30% solid content with 2 wt.% of surfactant based on monomer. The initiator was potassium persulfate. In both emulsion polymerization processes, the conversion of S was very low all along the reaction with a conversion limited to a few percent after 4 h.

The resulting lattices looked very thick although they did not seem to have coagulated or flocculated.

The MMA lattices coagulated completely during the reaction, both with the nonreactive and the reactive emulsifier. In the case of VA, stable lattices were obtained in both cases, but these were not stable to addition of electrolyte.

Methacryloyl isocyanato surfmer

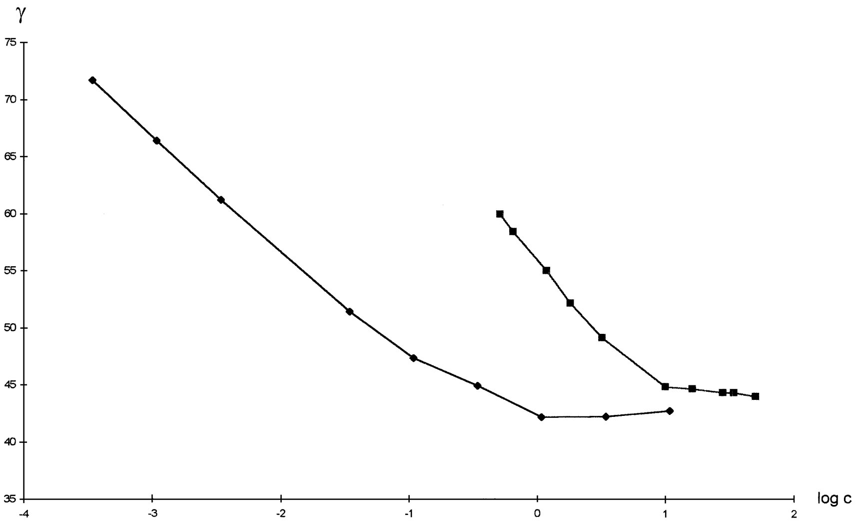
This surfactant was tested only in styrene dispersion polymerization and not in emulsion polymerization. In dispersion polymerization, a high conversion was obtained with no coagulum. The particle size was 905 nm and the particle size distribution was rather large ($D_w/D_n = 1.08$). Although the grafting yield was quite limited at only 3.5%. The stabilization might be due chiefly to the formation of adsorbed species (15.6% of the engaged surfmer) which can be separated from the particles upon washing. The washed particles lost their stability in water.

Styrenic surfmer

The styrenic surfmer produced upon killing the living block copolymer of P (EO) b(BO) with VBC displays a cmc somewhat lower than that of non-functionalized block copolymer surfactant, at 0.13 mM/l. As shown in Fig. 7, it is strongly adsorbed on the surface of polystyrene, the apparent cmc reaches 1.69 mM/l, so that the surface area covered by one molecule of surfmer is only 33 Å^2.

This surfmer has been used to obtain total coverge of a seed latex. First, the seed latex was produced using

Fig. 7 Surface tension measurement for the styrenic surfmer. CMC measurement in pure water (◆) and in the presence of a polystyrene latex (■)



a neutralized sodium salt of a hemiester of maleic anhydride, described elsewhere [16]. The seed latex itself was obtained in two steps: first a batch process led to a seed with an average particle size of 100 nm at 10% solid contents; then that seed was grown to 208 nm in average with a new charge of surfactant, at 40% solid centents.

After this step, a shot process was used to introduce a new charge of monomer together with the styrenic surfmer. A stable latex resulted, but the particle size had increased up to 405 nm so that limited flocculation must have taken place.

α-Methylstyrenic surfmer

The gravimetric data of the emulsion polymerization of both the styrene in batch and styrene-co-butyl acrylate in semi-continuous process are shown in Fig. 8.

It can be seen that in both reactions the polymerization rates are very low, and the conversions are not higher than 10%. The reason for this is very likely the phase-inversion that seemed to occur in both reactions. In the first reaction, after seven hours, the product seemed to consist of two phases, one oily phase and a latex phase with latex particles with a very large particle diameter and a specific conductivity of about 500 μS/cm. The latter number is probably an artefact due to the fact that it was not possible to separate the latex phase from the oily phase completely. In the semi-continuous reaction we also observed phase-inversion, but in this case no separate latex phase was observed. The conductivity of the product after 5 h (one hour after the feeding was stopped) was about 0.6 μS/cm, lower than that of the doubly distilled water that was used.

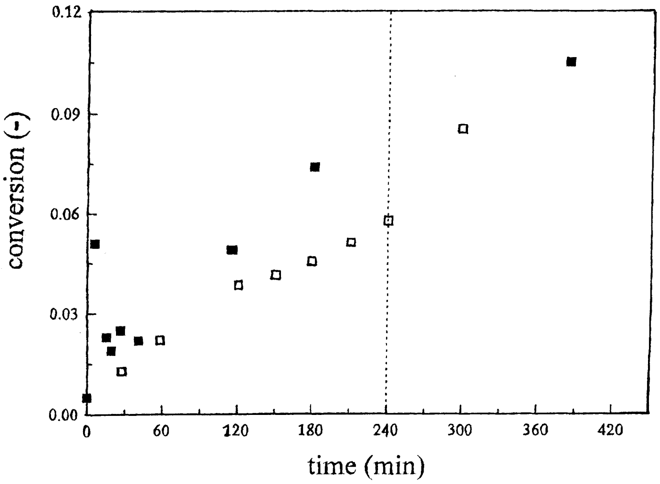


Fig. 8 Conversion versus time of the two emulsion polymerizations using the α-methylstyrenic surfmer: batch polymerization of styrene (■), and semi-continuous copolymerization of styrene and butyl acrylate (□)

Due to this phase inversion the radicals derived from the persulfate dissolved in the now disperse aqueous phase cannot effectively initiate polymerization in the continuous monomer/polymer phase, and this causes the very low rate of polymerization.

This tendency to lead to phase inversion could be a result of the fact that for this particular emulsifier the hydrophilic-lipophilic balance is such that O/W emulsions are not stable (HLB value too low) or that the reactions were carried out too close to the Krafft temperature of the surfactant. On the other hand, it is also possible that the surfmer itself can stabilize the monomer emulsions, but that as soon as the reaction starts it reacts very rapidly with both S and BA leading to high surfmer conversions. In that case the HLB-value might change and become even lower. This would be in agreement with the fact that the inversion was not observed at the beginning, but after some time during the reaction. Whatever this may be, it is clear that it is not only important to have the right polymerizable group in the surfmer [2, 3, 18, 19], but also that the surface-active properties of the surfmers are appropriate.

In conclusion, it was possible to synthesize a surfmer consisting of a block copolymer of butylene oxide and ethylene oxide and an α-methyl styrene group, by reacting *n*-isopropyl-α, α′-dimethylbenzyl isocyanate with the secondary terminal hydroxyl group of the block copolymer. This resulted in a yield of about 96%. Emulsion polymerizations carried out with this surfmer indicated that the hydrophilic–lipophilic balance of the surfmer may not be correct, as phase inversion was observed both in a batch reaction with styrene at 10% solids as well as in a semi-continuous reaction at 30% solids with styrene and butyl acrylate.

We believe that the α-methyl styrene isocyanate moiety adds too much hydrophobicity to the BO sequence. Work is in progress to add it directly to the hydrophilic PEO sequence.

General conclusions

The synthesis of block copolymers of ethylene oxide-*b*-butylene oxide has been carried out with living anionic polymerization of butylene oxide initiated by a commercial product of polyethylene oxide. These block copolymers were used directly in styrene emulsion polymerizations, but cannot give very stable lattices. In addition, some anionic surfactants are needed to control the nucleation. In the absence of these anionic surfactants long induction periods are observed.

After proper functionalization such as condensation reaction with azocarboxylic compounds or thioglycolic acid, inisurfs and transurfs can be prepared giving, when used in emulsion polymerization, very stable and monodisperse lattices with excellent stability.

Surfmers have also been prepared either by condensation reactions with acrylic acid chloride, methacryloyl isocyanate and α-methylstyrenic isocyanate derivatives, or through direct killing of the living polymerization with compounds carrying a labile halogen atom such as vinyl benzyl chloride. In some cases, stable lattices can be formed with these surfmers, but the hydrophilic–lipophilic balance needs to be adjusted to be able to produce stable lattices with any of the monomers or combinations that have been assessed.

References

1. Guyot A, Tauer K (1994) Adv Polym Sci 111:43
2. Ottewil RH, Satgurunathan R (1987) Colloid Polym Sci 265:845
3. Davies SP, Palluel ALL, Westby MJ, Bromley CA (1990) Makromol Chem Macromol Symp 35/36:509
4. Ivanchev SS, Pavljuchenko VN, Byridina NA (1987) J Polym Sci Part A: Polym Chem 25:47
5. Kusters JMH, Napper DH, Gilbert RG, German AL (1992) Macromolecules 25:7043
6. Tauer K, Goebel KH, Kosmella S (1990) Makromol Chem 31:107
7. Tauer K, Kosmella S (1993) Polym Int 30 (2):253
8. Yabuuchi N (1994) Polym Prepr (Am Chem Soc, Div Polym Chem) 35(1):807
9. Vidal F, Guillot J, Guyot A (1995) Polym Adv Technologies 6:473
10. Vidal F, Guillot J, Guyot A (1995) Colloid Polym Sci 273:999
11. Vidal F, Guyot A (1995) New J Chem 19:1081–1088
12. Macleay RE, Sheppard CS, US Pat 3,931,143 (1976) Chem Abs 1976, 84:122 581
13. Filet A, Guillot J, Hamaide T, Guyot A (1995) Polymers Adv Technologies 6:465
14. Kusters JMH (1994) PhD Thesis, University of technology, Eindhoven
15. Ferguso P, Sherrington DC (1993) Polymer 34:3281
16. Goux A, Guyot A (1997) J Appl Polymer Sci 65:2289
17. Unzue MJ, Schoonbrood HAH, Asua JM, Montoya-Goni A, Sherrington DC, Stahler K, Goebel KH, Tauer K, Sjoberg M, Holmberg K (1997) J Appl Polym Sci 66:1803
18. Schoonbrood HAS, Unzue MJ, Beck O, Asua JM (1997) Macromolecules 30:6024
19. Schoonbrood HAS, Asua JM (1997) Macromolecules 30:6034