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ORIGINAL CONTRIBUTION

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Surfactants with transfer agent properties (transurfs) in styrene emulsion polymerization

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Abstract Styrene emulsion polymerization has been carried out at 70 °C using 2-2′ Azobis (2 methyl, N-(2 hydroxyethyl) propionamide as initiator and thiol-ended surfactants (I) $HS\text{-}C_{11}\ H_{22}\text{-}\ (OCH_2\ CH_2)_nOH$ with n from 17 to 90 units. The kinetics of monomer conversion, the evolution of particle size, particle size distribution, molecular weight, and molecular weight distribution have been studied. After washing the final latex, the incorporation yield of the surfactant moieties in the particles has been measured. Most of the experiments have been carried out in batch; complementary experiments used semi batch or seeded process. In some experiments the two functions of transfer agent and surfactants have been decoupled using either dodecylmercaptan (oil soluble) or thioglycolic acid (water soluble) as transfer agent and the bromine ended precursor of (I) as surfactant. The discussion of the results is chiefly oriented towards both the molecular weight distribution and the incorporation of the surfactant to the latex.

Key words Surfactants – polystyrene – emulsion polymerization – amphiphilic thiol – transfer agents

Introduction

The use of reactive surfactants in emulsion polymerization is becoming increasingly popular. The purpose is to covalently bind the surfactant molecule to the surface of the latex particle; this results in improved properties in terms of latex stability and water rebound after film formation. A lot of work, described in a recent review [1], has been carried out using mainly anionic and non ionic surfactant.

A pioneering work has been reported by Greene and Sheets [2] concerning the surface functionalization of a seed latex of styrene-butadiene copolymer, with sodium acrylamido stearate. The coverage of the surface can be varied from 20 to 80% while, correspondingly, the grafting yields of the surfactant were between 100 and 70%. The latex with a high coverage level displays excellent stability versus electrolytes and also versus shear floculation. Using an anionic surfactant carrying a styrenic function, Fitch and Tsaur were able to prepare latex with a very high surface charge density [3]. However, another study using acrylic surfactant showed the formation of water soluble polymers which may cause the floculation of the latex [4]. A recent study from the group of Lehigh University [5] did compare the behavior of an allylic surfactant with its hydrogarated equivalent. The latter behave as an usual surfactant, as expected, but the allyl derivative caused the retardation of the polymerization. Industrial interest has been paid to non ionic polymerizable surfactants [6], although in such case, where the pioneering work has been done by Ottewill [7], large amounts of surfactant (at least 3% of the monomer) are necessary to get both a good enough stability and control of the particle size.

A lot of work has been devoted to the surfactants carrying an initiator group (INISURFS). Peroxide compounds

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have been used, chiefly in Russia [8]; more recently, azo compounds have attracted the interest of several groups [9, 10]. However, it has been shown that in all cases, the efficiency of the radicals produced by such initiators is extremely low [10], although latex with good properties can be obtained. Surprisingly, in some cases, the particles size is almost not dependent on the amount of inisurf [9]. In such cases, however, there is no special reason to produce water soluble polyelectrolytes able to cause the floculation of the latex.

However a third possibility has been neglected. It is the use of transfer reaction. Although one piece of work has been carried out under the direction of Pr. Fitch [12], nothing has been published in the open literature. The work of Fifield involves a thiol-ended alkylsodium sulfonate $HSC_{10}H_{22}SO_3Na$, which can be used to produce a stable polystyrene latex in the presence of azocyano-valeric acid as initiator. Again here, the particle size is almost independent of the amount of surfactant. In seeded experiments, this surfactant allows to prepare a latex with a high charge density (up to more than 5 microcoulomb/cm^2).

Thus, the present paper describes, at least from our knowledge, the first attempt to use a nonionic surfactant carrying a transfer agent (TRANSURF) in emulsion polymerization. Mercaptans are often used in emulsion polymerization to get the molecular weight of the polymer under control. The transfer constant of the thiol containing molecule is generally very high, around 20 [13]. Then, we have chosen to introduce a thiol function at the end of the hydrophobic part of a family of non ionic surfactant molecules, and used them in emulsion polymerization of styrene. Starting with 11-Bromo undecanol, we first attach a polyethylene oxide (PEO) sequence through catalytic polymerization of ethylene oxide from the alcohol end group, and then we replace the Bromine with a thiol group by the thiazonium salt route. So the structure of our TRANSURFS is as follow

$$HS-C_{11}H_{22}-O(CH_2-CH_2-O)_nH$$

with n in between 17 and 90.

Experimental

Materials

The styrene (Prolabo) is purified before use upon vacuum distillation. Water is deionized through ion-exchange resins. The initiator, 2-2′-azobis (2-methyl, N(2 hydroxyethyl)-propionamide) is a commercial product (VA 86 of Wako). 11-Bromo undecanol is used as received (Aldrich).

The synthesis of the surfactants, described in detail elsewhere [14], is carried out in two steps. In the first one, the Bromo undecanol is used as initiator in a catalytic polymerization of ethylene oxide, with a catalyst prepared upon reaction of triisobutylaluminium with dry silica and then reacted with an excess of Bromo undecanol to give a silica-supported aluminum alcoholate. The ethylene oxide molecules are then inserted into the Al-O bond. A fast exchange reaction takes place between the alcoholate and the alcohol molecules in the toluene solution so that all the Bromo undecanol molecules are chain ends and, in addition, all the growing molecules are expected to grow at the same rate, so that a Poisson distribution of the molecular weight is expected. This catalytic polymerization, applied to the synthesis of more simple surfactants from fatty alcohol initiators, has been shown to actually produce a Poisson distribution, at least for short polyethylene oxide sequences [15]. Some perturbation may be caused by the complexation of silica residues from the support, when the polyoxyethylene sequence is long, so that analysis of the molecular weight distribution by liquid chromatography cannot be carried out safely.

The product is an amphiphilic molecule which is a bromo ended surfactant precursor of the actual TRANSURF. In a second step, this brominated precursor is reacted with thiourea, and after hydrolysis the thiol ended molecule is obtained and characterized by NMR analysis (Bruker AG 250 Mhz). Surface tension measurements are used to determine the critical micellar concentration (CMC) of these surfactants. These CMC values are respectively 82.5 and 150 mg/l for $n = 17$ and 40. These values are rather close to the molar values given in the literature [16] for ethoxylated nonylphenol. Smaller values have been obtained for long PEO sequences. However, here again the measurements are probably perturbed by complexed silica residues.

Emulsion polymerization

Styrene emulsion polymerization is carried out under nitrogen atmosphere in a batch process in a glass reactor thermostatted at 70 °C with water circulating in a jacket around the reactor, using a recipe including 10 g of styrene, 2 g of Transurf, 0.115 g of VA86 and 90 g of water. The reactor is equipped with a stirrer working at 250 rpm and with a sampling valve in the bottom.

Particle size measurements

Average particle size number (D_n) and size distribution were characterized using both dynamic light scattering and transmission electron microscopy.

Quasi elastic light-scattering experiments have been carried out using the Brookhaven BI 8000.

Transmission electron micrographs were taken with a Hitachi HU 12 electron microscope. A specimen for the observation was made by putting a drop of a highly diluted sample of the latex on a carbon-coated nylon grid followed by air-drying.

Surfactant incorporation measurements

Incorporation yield is calculated from theoretical and experimental molar ratio of polyethylene oxide molecules and styrene units. Theoretical ratio is obtained from data of the recipe after taking into account the value of final conversion. Experimental ratio is determined by N.M.R. investigation of the latex washing. The calculation is based on the area determination of aromatic (from styrene units) and oxyethylene oxide proton peaks.

Proton nuclear magnetic resonance (^{1}H-NMR) analysis was performed with a Bruker AC 250 NMR spectrometer (250 Mhz) using CDC*l*3 solution.

Results and discussion

Batch emulsion polymerizations of styrene have been carried out using various transurfs with PEO sequences containing in between 17 and 90 monomer units. In all cases, the concentration of the surfactants is higher than their CMC so that micelles are present. Data concerning the latexes obtained after 24 h are reported in Table 1.

In almost all cases high conversions have been reached with no or almost no coagulum except if the length of the PEO sequence is higher than 50 units. The particle size is strongly related to the hydrophilicity of the surfactant: it is smaller when the length of the PEO sequence is longer.

The particle size and the particle size distribution are governed by two main factors: the nucleation process and the stabilization of the particles (Scheme I). When micelles are present, as in the present case, and with a monomer of low water solubility such as styrene, a part, at least, of the nucleation obeys the micellar mechanism where the oligoradicals created in the water phase activate some of the micelles formed by the surfactant above its CMC; such activated micelles become particles. Another source of particles comes from the homogeneous nucleation mechanism, which is a self precipitation of the oligoradicals having reached a critical size (2 or 3 styrene units) [17]. These particles adsorb some surfactant to get stabilized. In the present system, where there are no charged moieties, the stabilization of the particles is exclusively a steric stabilization using the PEO sequence of the TRANSURF which is either adsorbed or grafted onto the particle surface. The stabilization is more efficient when the hydrophilic PEO sequences are the longest. On the other hand, the TRANSURF with the longest PEO sequences is more easily desorbed. Such easier desorption may explain why the amount of coagulum tends to increase when n is higher. Surface tension measurement can be used to estimate the amount of surfactant which can be adsorbed on the surface of a latex. Using a seed latex with a diameter of 341 nm and the transurf $n = 40$, it has been observed that one molecule of surfactant can cover $58\ \mathring{A}^2$ when the surface is saturated. In the case of run 2, this means that the existing particles should be able to adsorb up to about 3 g of transurf at the end of the polymerization. This result shows that not enough surfactant has been introduced in the recipe (2 g) to ensure the stabilization of the particles simply by adsorption.

A washing process has been carried out to separate the serum and the surfactants molecules simply adsorbed onto the surface of the latex. It has been applied only to the monodisperse latexes. In two cases (runs 2 and 4), the particle size measured after this washing process has been increased significantly, most probably because some floculation took place. This limited floculation means that the particles were partly stabilized by the adsorbed surfactant which has been desorbed by the washing process. On the other hand, after the washing process, a part of the

Table 1 Styrene emulsion polymerization data

Run	1	2	3	4	5	6
n	17	40	50	75	75	90
Conversion %	88.5	96.5	94.5	88	91	86.5
Coagulum %	0	1.2	0.8	10.2	4.4	10
Particle size nm	363	242	309	217	210	164
Variance	0.23	0.02	0.17	0.023	0.025	0.023
Washed latex particle size	–	283	–	252	213	159
Variance	–	0.023	–	0.020	0.023	0.019
Transurf Incorporation %	–	26.8	–	25.8	25.2	8.7
Mn	6200	14 900	14 000	16 500	18 300	10 150
Mw	300 000	840 000	425 000	974 000	770 000	580 000

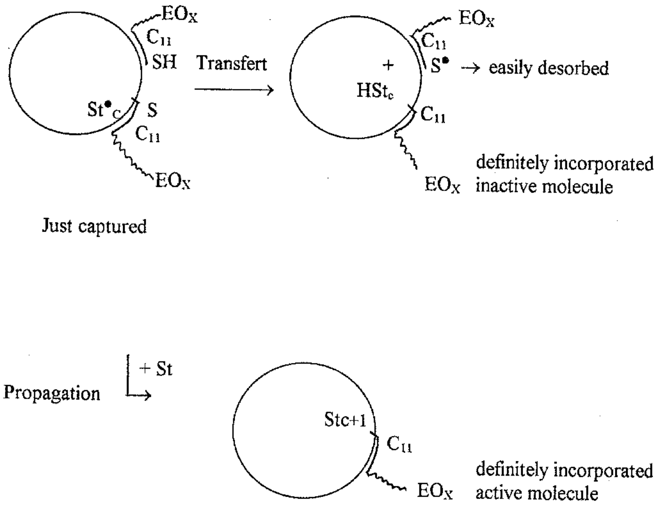
Scheme I Nucleation of the particles

mHS–C_{11} – $EO_n \rightarrow$ micelle (aggregation number m)
VA86 $\rightarrow$ 2 $R^{\bullet}$ (primary radical)
$R^{\bullet}$ + styrene(S) $\rightarrow$ $RS^{\bullet}$initiation (in water phase)
$RS^{\bullet} + xS \rightarrow\ \rightarrow RS_x^{\bullet}$
$RS_x^{\bullet}$ + micelle $\rightarrow$ active particle (micellar nucleation)
$RS_x^{\bullet} + S \rightarrow\ \rightarrow RS_c^{\bullet}$ c: critical size for precipitation
L $\rightarrow$ active particle (homogeneous nucleation)
active particle + Transurf $\rightarrow$ adsorption for stabilization
p active particles $\rightarrow$ limited floculation if not enough stabilized

Scheme II Behavior of Transurf HSC_{11} EO_x in the water phase

Primary radical $R^{\bullet}$ + styrene (St) $\rightarrow$ $RSt^{\bullet}$
$R^{\bullet}$ + Transurf $\rightarrow$ RH + $^{\bullet}SE_{11}(EO)_x$ ($I^{\bullet}$)
$Rst^{\bullet}$ + Transurf $\rightarrow$ RStH
$^{\bullet}SC_{11}EO_x$ + St $\rightarrow$ $(EO)_x$ C_{11} $SSt^{\bullet}$
$(EO)_x$ C_{11} $SSt^{\bullet}$ + Transurf $\rightarrow$ $I^{\bullet}$ + $(EO)_x$ C_{11} $SStH_1$ +
water soluble
+ St $\rightarrow$ $(EO)_x$ C_{11} $SSt_2^{\bullet}$ captured

Scheme III



surfactant remains attached to the latex. That part which is supposed to be grafted is around 25% except when the PEO sequence is the longest where it decreases to only 9%. The fact that the smallest particles are obtained even with a low amount of the more hydrophilic surfactant shows that the steric stabilization efficiency of the grafted surfactant is very high. The smallest transurf molecules, although more easily adsorbed and more easily grafted are less efficient, because the length of their hydrophilic PEO sequence is too short.

The smallest particles obtained with the more hydrophilic surfactants are highly monodisperse (the variance being around 0.02), while the largest are more polydisperse (variance around 0.2). Narrow distributions are generally associated with a short nucleation period followed by regular growth without neither floculation nor secondary nucleation during the process. However, rapid floculation may take place during the nucleation period if the precursor particles are not well stabilized. That might be the case for the longest transurfs which are more difficult to be adsorbed on hydrophobic surfaces.

Most of the surfactant remains soluble in the water phase. This is especially true for the more hydrophilic surfactant, although it is able to stabilize the largest surface area of latexes. NMR analysis of the water soluble material shows that there are very few styrene units in it. The molar ratio between the PEO sequence and styrene is 2.5, which means that only 40% of the transurf molecules have reacted with one styrene unit.

When more than one styrene unit has been added, the corresponding radical becomes hydrophobic enough to be definitely incorporated in the latex. A large part of the transurf remains in the water phase, possibly due to the high reactivity of the thiol group; when it is still in the water phase, the transurf is prone to react as a transfert agent which stops the growth of the oligoradicals in the water phase. On the other hand, if it is adsorbed at the surface of the latex, it is also prone to react very easily with the entering radicals, and the new radical can be desorbed before having reacted with monomer. These possibilities are illustrated in schemes II and III, and can explain why a rather small part of the transurf is incorporated in the latex. On the other hand, it is not so certain that, once incorporated, the transurf causes a definite stabilization of the particles, because they can be buried in the particle during their growth. More arguments should be given in that discussion if the kinetics of consumption of the transurf were known. Unfortunately, we have been limited to only following the kinetics of monomer conversion.

The kinetics of the styrene conversion are illustrated in Fig. 1. The whole rate seems quite related to the particle size, as is normal in emulsion polymerization, the higher rate corresponding to the smaller particle size. On the other hand, one observes acceleration of the polymerization up to a rather high conversion, at least in some cases. This fact probably does not correspond to a long nucleation period, because the corresponding particles are rather monodisperse; then, it might be due to somes deviation from the ideal 0–1 case (case II of Smith–Ewart [6]). The presence of the transurf might cause the average number of radicals in the particles to be higher than 0.5, if after a transfer reaction, the new radical is not desorbed (scheme III).

Another special and more specific feature of the transurf is related to the molecular weight distribution. The data reported in Table 1 point out the very high polymolecularity of the molecules with a trend to increase the number average molecular weight Mn when the PEO

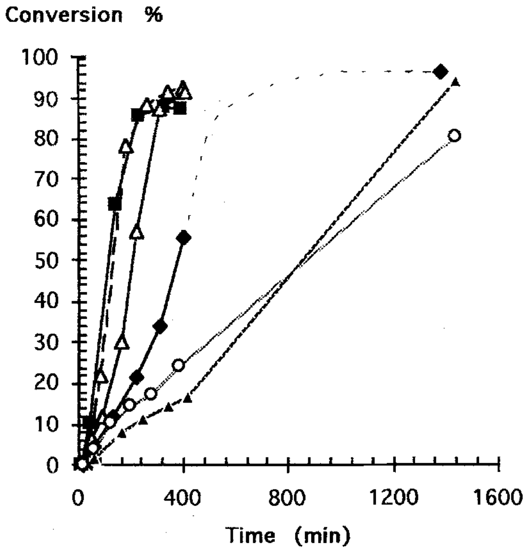


Fig. 1 Conversion versus time is styrene emulsion polymerization in the presence of transurfs with 17 (-○-), 40 (-◆-), 50 (-△-), 75 (-△- and --△--) or 90 (-■-) ethylène oxide units in the hydrophilic sequence

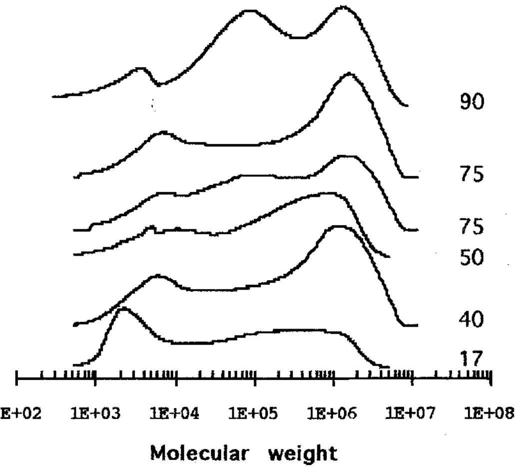


Fig. 2 Size exclusion chromatograms (SEC) of final latexes obtained from styrene emulsion polymerization in the presence of transurfs with 17, 40, 50, 75 or 90 ethylene oxide units

sequence is longer. Further insight into the molecular weight distribution is given by the SEC diagrams shown in Fig. 2 for the set of final polymers. There are at least two and even three families of polymers with molecular weight varying from a few hundreds to near 10^7.

In order to get a better understanding of the behavior of the transurfs, comparative studies have been carried out with a few different systems: for that purpose the brominated product separated after the first step of the synthesis of the transurf is used, either alone or with a thiol, the latter being either hydrophobic (dodecylmercaptan) or hydrophilic (thioglycolic acid). The data concerning the molecular weights of the polymers obtained in these comparative experiments are reported in Table 2 and point out the dramatic broadening of the molecular weight observed when the surfactant is the transurf.

As shown in Fig. 3, upon replacing the transurf by just its brominated precursor, there is no visible change in the styrene conversion curves. However, the final particle size becomes smaller (138 nm instead of 164 nm). The washing process causes floculation of these small particles. Their stability is limited as shown also by the larger amount of coagulum and the broadness of the particles' size distributions (polydispersity index).

The most striking difference is in the molecular weight distribution (MWD), which becomes narrower and shifted towards the highest molecular weight. As shown in Fig. 4, the MWD of the polymer prepared in the presence of the transurf is trimodal, and the two distributions corresponding to the lower molecular weight are attributed to some effect of the transurf; the third one might correspond to molecules formed in the absence of transurf, because it corresponds to the distribution obtained with just the precursor (in the absence of thiol).

When the brominated precursor is used as surfactant, but in the presence of small thiol molecule, again a monomodal distribution is finally obtained, which is broader if the small thiol molecule is water-insoluble; but both distributions seem to correspond to the central part of the trimodal distribution in the case of the transurf (Fig. 5).

It is interesting to follow the change in MWD all along the polymerization process. The SEC traces of the four

Table 2 Molecular weight of the latex in comparative experiments using surfactants with 90 ethylene oxide units

Surfactant	Transurf	Precursor	Precursor	Precursor
Thiol	no	no	$C_{12}H_{25}SH$	HS CH_2 COOH
Mn	10160	677000	106000	69100
Mw	578000	1875000	323000	148400
Coagulum %	10	16	16	21
Particle size nm	229	170	167	159
Polydisperisty(a) index	0	0.9	0.6	3

(a) From measurement with the Coulter "Nanosizer" apparatus

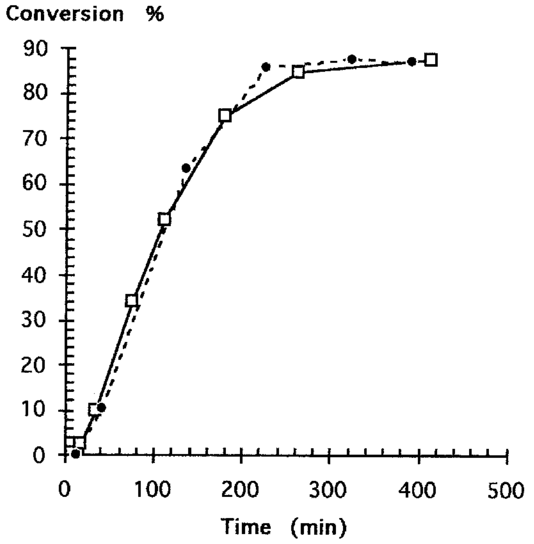


Fig. 3 Kinetic of styrene emulsion polymerization in the presence of surfactants with 90 ethylene oxide units Transurf –□–, Brominated precursor (--○--)

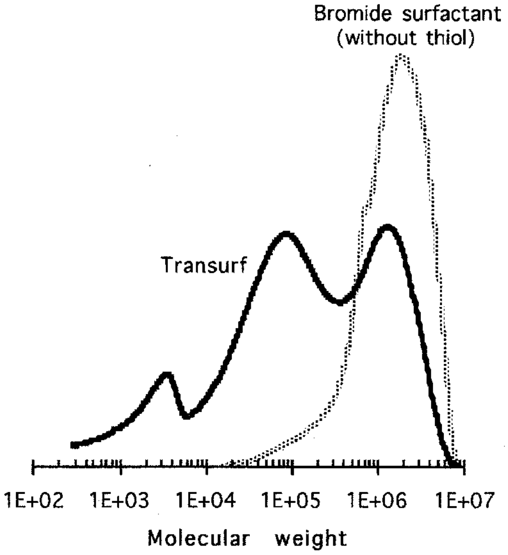


Fig. 4 SEC diagrams of polymers obtained using the bromine-ended and thiol-ended (transurf) surfactants

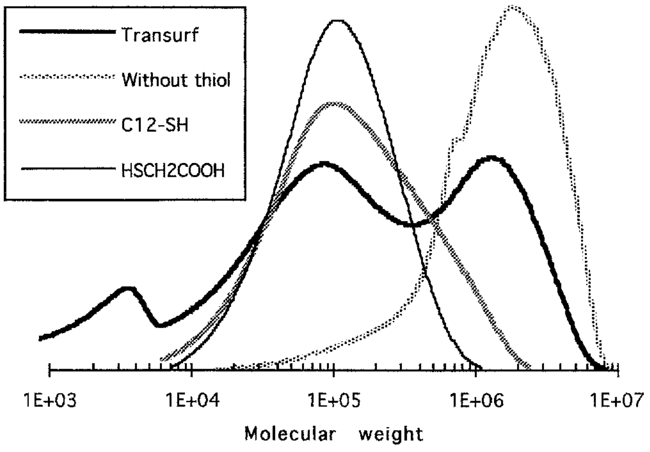


Fig. 5 SEC diagrams of final polymers of the comparative experiments (Table 3) using the transurf (thiol-ended surfactant) or its brominated precursor alone or in the presence of dodecylmercaptan or of thioglycalic acid

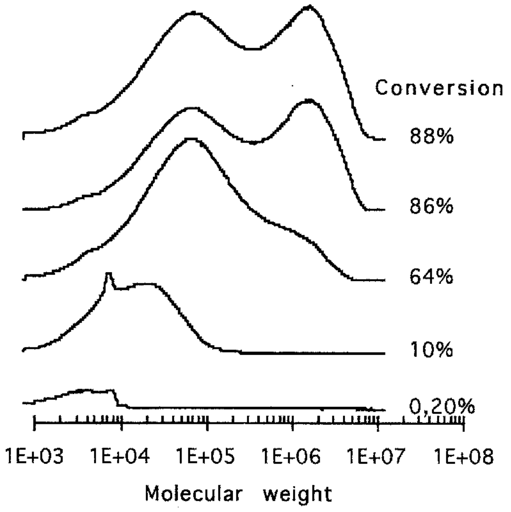


Fig. 6 SEC diagrams of polymers prepared using the transurf ($n = 90$) at various conversions

comparative experiments are shown in Figs. 6–9. In the case of the transurf, the first distribution of very low molecular weight is observed at low conversion during the nucleation period; it does not grow too much during that process. The central distribution is observed as soon as particles are present; it increases progressively and is shifted towards higher molecular weight up to its final position at around 10^5. The third population appears only at rather high conversion at a position near that of the polymerization carried out in the absence of thiol. So, this third distribution corresponds to what one can obtain with a non-ionic surfactant without high transfer activity. he latter is observed in Fig. 7 for the brominated precursor; it is a monomodal distribution with little change all along the process. When dodecanethiol is present (Fig. 8), the distribution is also monomodal but broad, and begins with rather high molecular weight, progressively shifting towards lower molecular weight. The thiol is mainly in the monomer droplets and enters the polymer particle chiefly after diffusion through the water phase; for thermodynamic reasons, its diffusion is slower than that of the monomer; although its transfer constant is very high at 20.7 [7], it does not compensate for the difference in the

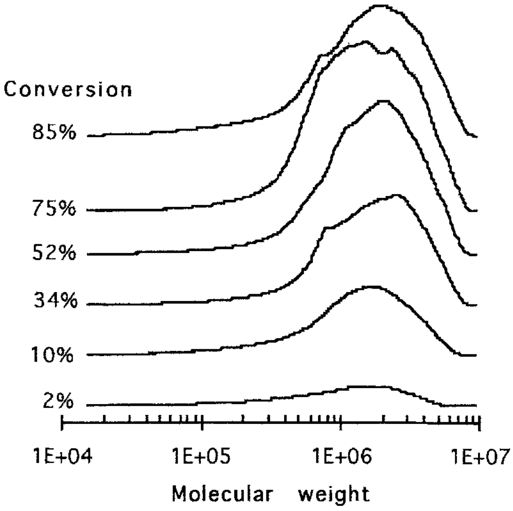


Fig. 7 SEC diagrams of polymers prepared using the bromine-ended precursor ($n = 90$) as surfactant

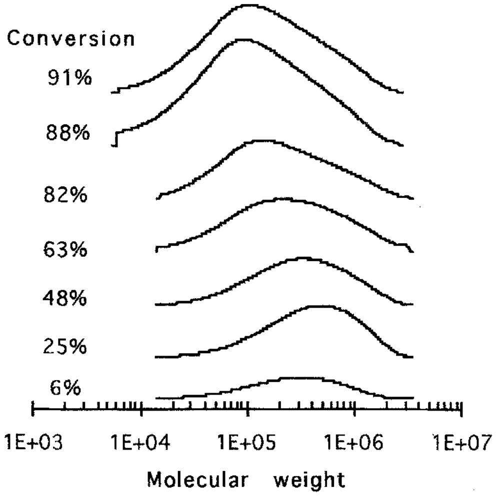


Fig. 8 SEC diagrams of polymers prepared in the presence of dodecylmercaptan and the bromine-ended precursor ($n = 90$) as surfactant

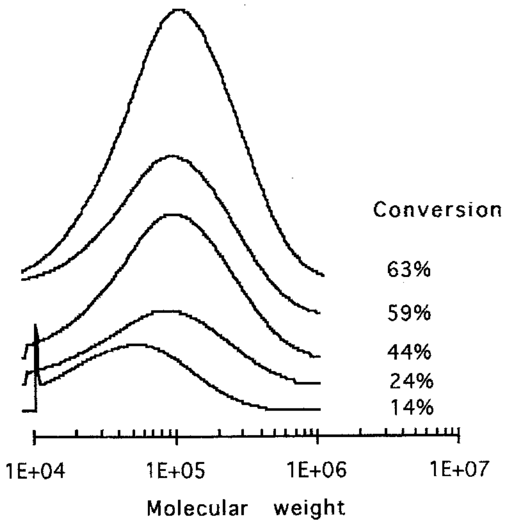


Fig. 9 SEC diagrams of polymers prepared in the presence of thioglycalic acid and the bromine-ended precursor ($n = 90$) as surfactant

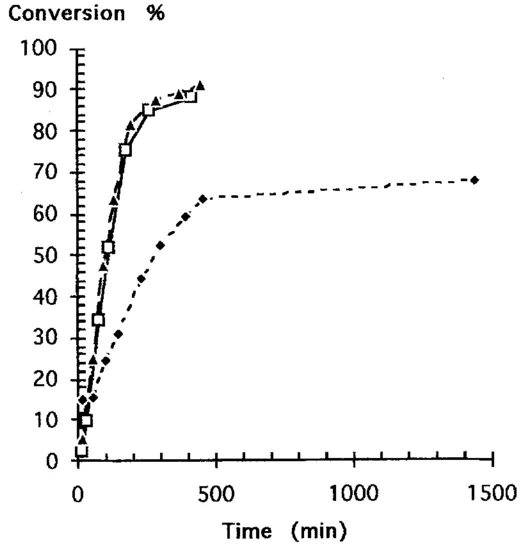


Fig. 10 Kinetics of styrene emulsion polymerization using the bromine-ended precursor ($n = 90$) as surfactant, alone (–□–) or in the presence of dodecylmercaptan (--△--) or of thioglycolic acid (--◆--)

diffusion rates, so that the transfer process become more efficient when the monomer concentration in the particles begin to decrease. A narrow distribution is observed when thioglycolic acid is used in addition to the surfactant precursor (Fig. 9), with some limited shift towards higher molecular weight. Thioglycolic acid is water soluble and is expected to work quickly in the water phase. However there is no evidence for a population of low molecular weight products. In between 24 and 63% conversion, no change in the MWD can be observed. The value of the molecular weight indeed indicates that transfer reactions take place; on the other hand, as shown in Fig. 10, the thioglycolic acid system causes a rather important decrease of the polymerization rate and, in addition, the yield is limited; one possible event is that transfer reaction takes place in the water phase causing the probability of termination in the water phase to increase. Competition between a capture of the radicals by the particles and their termination in the water phase might explain the slower polymerization rate and the limitation of the conversion.

On the other hand, when the brominated precursor is used in the presence of either thioglycolic acid or dodecylmercaptan, there is no production of a high molecular weight population at the end of the process, as when the transurf itself is used (Fig. 4).

This probably means that the consumption of these two thiol containing compounds is quite regular owing to their partition between the particles and the water phase which remain equilibrated up to the end of the process.

A few attempts have been carried out to improve the incorporation yield of the transurfs. Instead of using a batch process, three different two-step experiments have been performed. In a first experiment only 20% of the monomer and of the transurf ($n = 75$) have been introduced in the first step in the batch. After 94 min of batch polymerization an emulsion with 10% of the water phase and 80% of the monomer and of the transurf have been introduced at a rate of 2ml/h during 9 h. As shown in Fig. 11a, the instantaneous conversion was not very high so that accumulation of monomer took place and the molecular weight distribution remains quite broad (Fig. 11b); however, a population with intermediate molecular weight is progressively built, showing that the transfer reaction was working. This results in a final monodisperse latex (particle diameter 173nm, variance 0.021). However, the incorporation yield was limited to 14.4% instead of 25% for a simple batch process.

In a second experiment a polystyrene seed latex with a particle diameter of 72 nm and solid content of 9.7% has been produced in the presence of sodium dodecylsulfate (SDS) and $K_2S_2O_8$ as initiator; after washing through an ion exchange resin, this seed has been engaged in a semi batch emulsion polymerization process using the water soluble azo initiator and a transurf with 40 EO units. Although, again, the instantaneous conversion was limited (Fig. 12), no crop of new particles has been produced and the final diameter (90 nm) did correspond to the expectation. However, during the washing process, floculation take place showing that the initial charges of the seed have been probably burried.

In the third experiment, the seed (99 nm), 120 g with 5% solid contents) produced in conditions similar to the previous one was swollen with styrene (1.84 g) containing 1% of azobis isobutyronitrile, in the presence of 2.29 g of

Fig. 11 Semi batch emulsion polymerization of styrene in the presence of transurf with 75 ethylene oxide units **a)** Instantaneous conversion versus time; **b)** SEC diagrams evolution at various instantaneous conversion

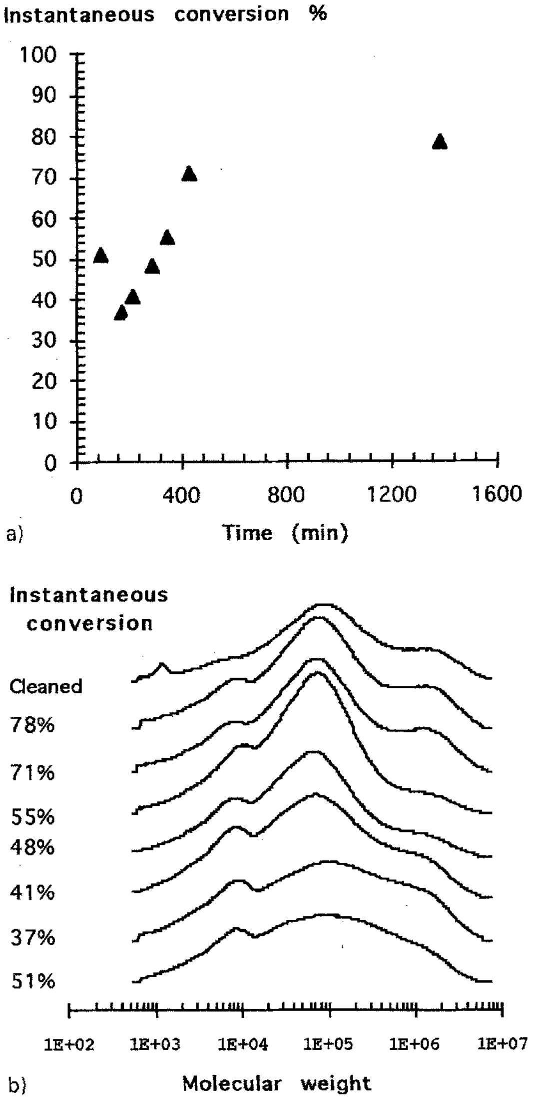
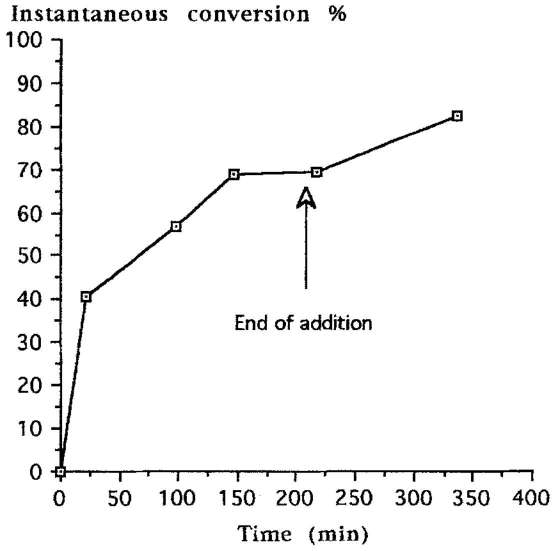


Fig. 12 Seeded emulsion polymerization of styrene. Semi continuous addition of monomer in the presence of transurf with 40 ethylene oxide units. Instantaneous conversion versus time. The arrow indicate the end of the addition



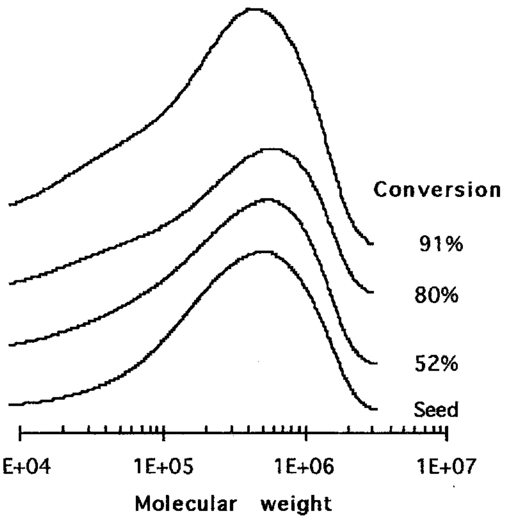


Fig. 13 SEC diagram of the seed and of the polymer produced at various conversions after having swollen the seed with styrene containing azobis isobutyronitrile, in the presence of the transurf with 40 ethylene oxide units

transurf ($n = 40$) dissolved in 4 g of water. Polymerization was carried out at 70 °C up to more than 90% conversion. The final size was 129 nm, as expected, with narrow particle size distribution (variance 0.021) and the observed change in molecular weight distribution showed that the transurf has been efficient as a transfert agent (Fig. 13). However, the incorporation yield remains limited to 17.6%.

In all these experiments, the amount of transurf has been calculated so as not to produce micelles which might induce a second nucleation. Most of the transurf is initially adsorbed on the surface of the particles in dynamic equilibrium with the serum around the particles. When radicals are produced inside the particles or are captured from the serum, they can easily undergo a transfer reaction with the adsorbed thiol; the new radical may easily be desorbed and be destroyed in the water phase, leading to the production of water soluble compounds (scheme III). The definite incorporation of the stabilizing moiety from the transurf involves that, after the transfer reaction, a set of propagation will take place so that the growing radical cannot be desorbed.

Conclusions

In the presence of a water soluble azo initiator, the thiol-ended reactive surfactants are able to give monodisperse latex particles in styrene emulsion polymerization. However, at variance from what can be expected, the yield of incorporation of the surfactant residue in the latex particle remains rather limited whatever the structure of the surfactant (hydrophilic-lipophilic balance) or the process used for the polymerization (batch, semi batch, seeded). Polymodal molecular weight distributions are obtained, according to the local concentration of the surfactant at the surface of the particles. Decoupling the surfactant function from the transfer function however shows that the stability of the particles is better when both functions are incorporated in the same transurf molecule.

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References

1. Guyot A, Tauer K (1994) Adv Polymer Sci 111:45
2. Greene BW, Sheetz DP (1990) J Colloid Interf Sci 32:90–96
3. Tsaur SL, Fitch RM (1987) J Colloid Interf Sci 115:450
4. Guillaume JL, Pichot C, Guillot J (1990) J Polym Sci Chem Ed 28:137
5. Urquiola MB, Dimonie VL, Sudol ED, El Aasser MS (1992) J Polym Sci Chem Ed 30:2619–1631
6. Palluel AL, Westby MJ, Bromley CWA, Davies SP, Backhouse AJ (1990) Malromol Chem Macromol Symp 35/36:509
7. Ottewill RH, Satgurumathan R (1988) Colloid Polym Sci 265:843–266:547
8. Ivanchev SS, Pavljuenko VN, Byrdina NA (1987) J Polym Sci Chem Ed 25:47
9. Tauer K, Wedel A, Morozova EM (1992) Makromol Chem 193:1387
10. Tauer K, Kosmella S (1993) Polymer Internat 30:253
11. Kusters IMH, Napper DH, Gilbert RG, German AL (1992) Macromolecules 25:7043
12. Fifield CC, Ph.D. Thesis University of connecticut 1985, University Microfilms International 5869 (1992) Ann Arbor, Michigan USA
13. Brandrup J, Immergut EH (1989) Polymer Handbook 3rd Ed. Wiley II 94–133
14. Hamaide T, Vidal F (1995) Polymer Bulletin 35:1
15. Hamaide T, Jacquier V (to be published)
16. Shick MJ (1967) "Non ionic surfactants": Surfactant Science Serie Vol 1 Marcel Dekker Inc. New York
17. Maxwell IA, Morrison RB, Napper DH, Gilbert RG (1992) Makromol Chem 193:303
18. Smith MV, Ewart RH (1948) J Chem Phys 16(6): 592
19. Vidal F, Gilbert RG (to be published)