Inifer surfactants in emulsion polymerization

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ABSTRACT

Thiol-ended non-ionic surfactants, used in combination with t-butyl hydroperoxide are components of a redox system able to initiate the emulsion polymerization of styrene, as well as control the molecular weight by transfer. Most of the surfactants remain as side products in the water phase, while multimodal molecular weight distributions of polymer are observed depending on the structure of the surfactant, the conversion of the monomer and the process used for feeding the reactor. The maximum incorporation yield of these reactive surfactants in the polymer is around 40%.

INTRODUCTION

The term "inifer" has been introduced by J.P. Kennedy about compounds able to work both as coinitiators and transfer agents using BCl_3 as coinitiator[1] in the cationic polymerization of isobutene. Later on the term has been used in radical polymerization for thiouram compounds[2]. We think that this term may also be applied to the system described in this paper where radical emulsion polymerization of styrene is carried out in the presence of a redox system containing t-butyl hydroperoxide and a thiol containing surfactant. The thiol function is able to react with the t-butyl hydroperoxide to produce radicals initiating the polymerization according to reaction (1) :

$$tBuOOH + RSH \rightarrow H_2O + tBuO^\bullet + RS^\bullet \qquad (1)$$
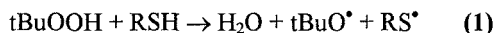
At the same time, the thiol is a very efficient transfer agent, its transfer constant being as high as 10-20 whatever the structure of the thiol[3].

In addition, in the present case, the thiol group is attached to the hydrophobic end of a non ionic amphiphilic surfactant. The behavior of these surfactants (TRANSURFS) in the emulsion polymerization of styrene is described in another paper[4,5] where the initiator was a water soluble azo compound. Some features of the behavior of the same redox system where the thiol function is at the end of a water soluble oligomer of polyethylene oxide have also been described[5,6].

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EXPERIMENTAL

• The synthesis of the TRANSURFS has been described previously[5]. The starting material is Bromo 11 undecanol which is an initiator in the polymerization of ethylene oxide ; it results an amphiphilic precursor of the surfactant having a poly (ethylene oxide) (PEO) hydrophilic sequence of lenght n (between 17 and 90). Then the bromine end group of the hydrophobic hydrocarbon sequence is reacted with thiourea to give the thiol function after hydrolysis. The formula is $HSC_{11}H_{22}O (CH_2-CH_2O)_n-H$.

• Experimental method of the emulsion polymerization and of the characterization of the polymer and latexes have been also described previously[4,6].

RESULTS AND DISCUSSION

A set of batch polymerization experiments have been carried out for 24h at 60°C using the recipe as folllows : water 90g., styrene 10g., transurf 2g. and tBuOOH 0.09g. The final data of the resulting polymer are reported in Table I (runs 1-4)

Except in one case (run 3) high conversion can be reached with limited amounts of floc. This amount of floc is increasing with increasing hydrophilicity of the surfactant. Small particle size is obtained. However the particle size distribution (PSD) is becoming broader when the hydrophilicity is higher. As shown in fig. 1, some aggregates are obviously formed in run 4 as shown by electron microscopy where small particles of 108nm diameter can be observed. While in run 3, the particle diameters are observed to be in between 200 and 400nm (fig. 2).
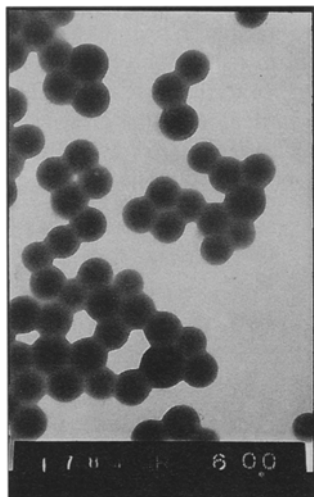

Then it seems that the actual trend is to produce smaller particles upon increasing the hydrophilicity of the surfactant ; but then the number of surfactant molecules has been decreased, because their molecular weight has been increased, the total weight of surfactant being constant in all the experiments. Most probably, upon increasing conversion there is not enough surfactant for the steric stabilization of all the particles. So some aggregation and floculation will take place.

Fig. 1
TEM of latex from run 4 (Table I)

TABLE I
Batch emulsion polymerization of styrene at 60°C

Run	1	2	3	4	5	6
Surfactant	Inifer [a]	Inifer [a]	Inifer [a]	Inifer [a]	Precursor [b]	NP 30
n	17	40	50	90	17	30
amount g	2.01	2.0	2.0	2.0	2.06	1.03
Dodecane-thiol (g)					0.424	0.446
Thiol/Surfactant mole	1	1	1	1	1.02	1
SH/OOH	3.1	1.6	1.2	0.66	3.3	2
Conversion %	89.4	88	46.5	99.4	53	63
Floc %	1	2.8	0	8	-	-
Particle size $^{(nm)}$ QELS	174	166	310	188	233	145
Variance	-	0.0024	0.036	0.37	0.085	0.021
Particle size $^{(nm)}$ TEM Dn	150	133	273	108		
Incorporation %	33	27	-	-	-	-
Mn	10.100	10.100	8.100	30.400	2.150	2.950
Mw	212.000	686.000	140.000	533.000	9.300	138.000
Dw	157	149	297	111		

a : $HS-C_{11}H_{22}- (O\ CH_2-CH_2)_n- OH$ b : $B_r\ C_{11}\ H_{22}\ (O\ CH_2\ CH_2)_{17}\ OH$
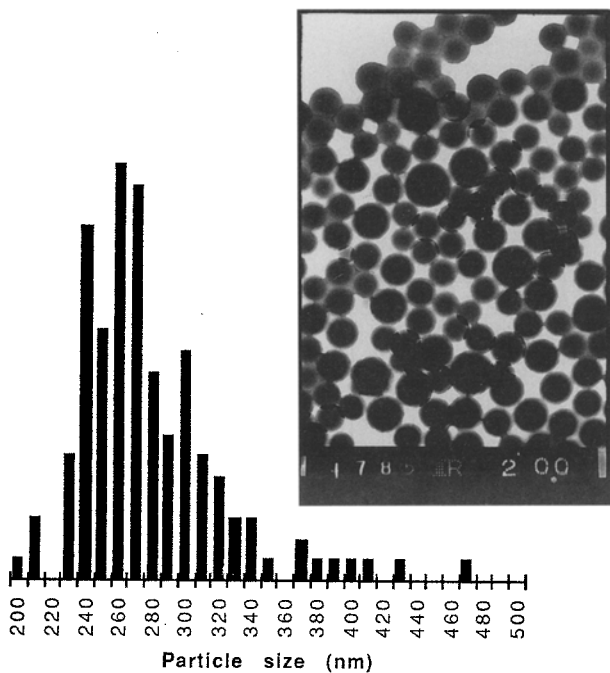
Fig. 2
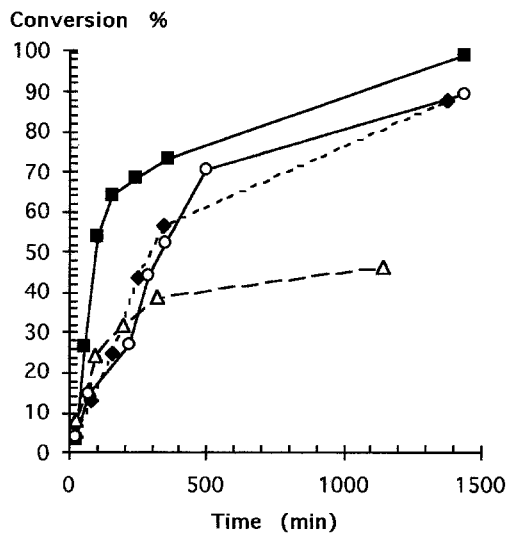TEM of latex from run 3 (Table I) and its particle size distribution


Fig. 3
Kinetics of styrene emulsion polymerization using transurfs
with n=17 (—o), 40 (---◆), 50 (---Δ) and 90 (-■-) ethylene oxide units.

As shown in fig. 3, the polymerization rate is also increasing with the hydrophilicity of the surfactant at least during the initial steps. This polymerization rate is expected to be an increasing function of the number of particles. Most probably, the nucleation rate is governed by two main factors : the rate of production of radicals, and the stabilizing ability of the surfactants. The production of radicals results from the reaction (1).

Due to the transfer constant of the surfactant, which has been estimated to be around $15^{(5,7)}$, and the rather low solubility of styrene in water, most of the t-butyloxy radicals will not react with the surfactant to give t-butyl alcohol and $RS^\bullet$ radicals

$$(CH_3)_3\, CO^\bullet + RSH \rightarrow (CH_3)_3\, COH + RS^\bullet \quad (2)$$
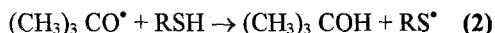
Initiation in the water phase will take place from the reaction of $RS^\bullet$ radicals from reactions (1) and (2) with monomer

$$RS^\bullet + M \rightarrow RSM_1^\bullet \qquad (3)$$

Both propagation and transfer will take place in the water phase giving $RSMx^\bullet$ radicals $(x > 1)$ and RSMxH dead molecules. Also termination will take place in the water phase

$$RSMx^\bullet + RS^\bullet \rightarrow RSMxSR \qquad (4)$$

Nucleation will take place upon capture of $RSMx^\bullet$ radicals by the micelles of surfactant (micellar nucleation), or upon self nucleation when x becomes larger than a critical value z (homogeneous nucleation). Micellar nucleation should be more important in the case of run 1 due to the lower value of the CMC of the corresponding surfactant. Homogeneous nucleation should be more and more important with the availability of water soluble surfactant. Then it can be concluded that in the present system, the kinetics are dominated by the homogeneous nucleation, because the rate is increasing with the hydrophilicity of the surfactant.

The reasons for the limitation of the conversion in run 3 are not known. It may be caused by some impurities in the corresponding surfactant ; it may be due also to a more rapid consumption of the actual initiator, owing to the specific value of the SH/OOH ratio. However, data about the consumption of either the thiol compound or the hydroperoxide are not yet available.

Most of the surfactant residues remain in the water phase ; thorough washing has been applied only to samples with narrow enough particle size distribution. The incorporation yield of the surfactant actually bound to the particle is 33% or 27% respectively for n = 17 and 40. These values represent both the efficiency of the initiator and the consumption by transfer of the surfactant adsorbed to the surface of the particle. Obviously this second part is expected to be higher for the less hydrophilic surfactant. Then 60 to 80% of the surfactant seems to be consumed by side reactions in the water phase : production of water soluble polystyrene oligomers through termination or transfer reactions or by termination between two $RS^\bullet$ radicals. The importance of these side reactions is expected to be the highest for the more hydrophilic surfactants. These side products are not efficient to stabilise the particles so that the production of flocs and aggregates will increase at high conversion, chiefly with these more hydrophilic surfactants.

The molecular weight distributions (MWD) obtained in runs 1-4 are illustrated by the size exclusion chromatographs (SEC) shown in fig. 4. These distributions are very broad and indicate the existence of several populations of polymers ; among them one corresponds to oligomers rather than polymers ; that population is more important in run 1 for the more hydrophobic surfactant ; it may be suggested that these oligomers might correspond to captured oligoradicals experiencing transfer reaction with adsorbed surfactant soon after their capture by particles.
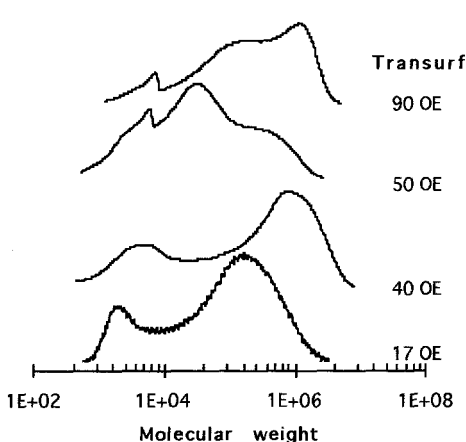

Fig. 4

SEC diagram of the final latex obtained using transurfs with 17, 40, 50 and 90 ethylene oxide units.
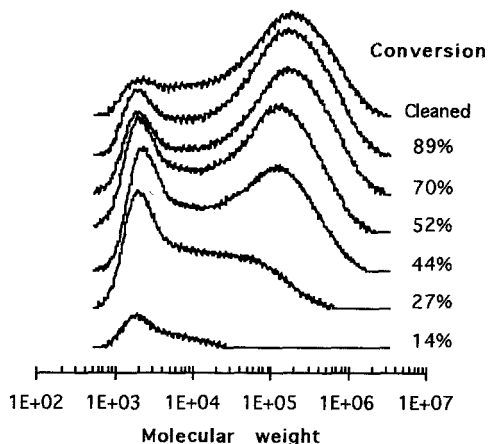
Fig. 5

SEC diagram of polymer latex prepared in the presence of transurf with n = 17 at increasing conversion (bath process).

Another population corresponds to very high molecular weights ; it is much less important in run 3 where the conversion was low ; then it may be suggested that it correspond chiefly to molecules formed at high conversions when most of the transfer agent has been consumed. This is confirmed by following the evolution of the SEC diagram at increasing conversions, as shown in fig. 5 (run 1). The high molecular weight (MW) population does appear late and becomes more and more dominant.
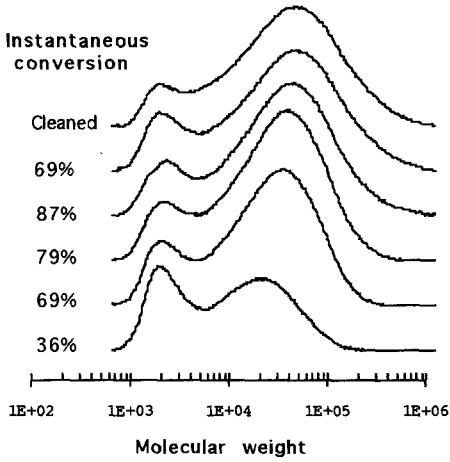
Instantaneous
conversion

Cleaned

69%

87%

79%

69%

36%

1E+02   1E+03   1E+04   1E+05   1E+06

Molecular weight

Fig. 6

SEC diagram of polymer latex prepared in
the presence of transurf with n = 17 in a
semi-continuous process at different times.

The same conclusion is valid for
run 2 (fig. 6) ; however in that case, the
high MW population is observed much
sooner and an intermediate population is
clearly visible at intermediate steps. This
intermediate population seems to be
more important with the highly
hydrophilic surfactants ; in such cases,
the surface density of the adsorbed
surfactants may be lower so that the
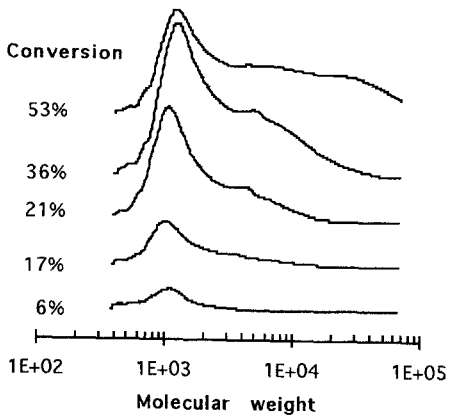transfer is less important.

Conversion

53%

36%

21%

17%

6%

1E+02   1E+03   1E+04   1E+05

Molecular weight

Fig. 7a

SEC diagram of polymer latex prepared in
the presence of dodecyl mercaptan and the
bromine ended precursor of transurf with
n = 17

Conversion

63%

25%

12%

3%

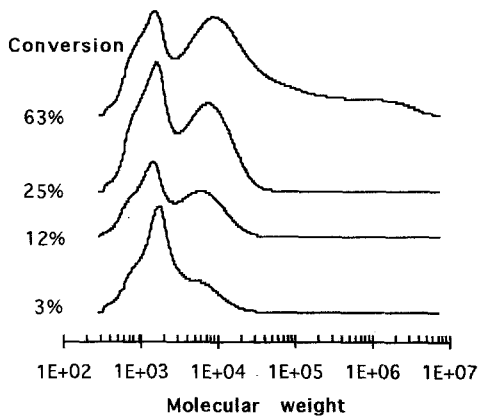1E+02   1E+03   1E+04   1E+05   1E+06   1E+07

Molecular weight

Fig. 7b

or commercial non ionic surfactant
NP30 at increasing conversion

When instead of a batch process, one uses a semicontinuous process with continuous feeding of both monomer and inifer surfactant, important modifications are observed as shown by the results obtained with n = 17 surfactant. In that case, the initial recipe included 90% of water, 10% of styrene and of the inifer, and all the hydroperoxide. The emulsion of the remaining components (9g styrene and 1.82g inifer in 10.46g water) was fed at a rate of 0.8 ml/hour. Smaller monodisperse particles were obtained with a diameter of 99nm ; more than 40% of the surfactant was incorporated in the particles. Moreover, the MWD was much narrower all along the process, as shown in fig. 6, and corresponds to much smaller MW. The shift toward higher MW is much less pronounced. The semicontinuous process improve significantly the efficiency of the inifer in both the transfer reaction and the particle stabilization.

Finally, two comparative experiments (run 5 and 6 of Table I) have been carried out to estimate the combination of the functions played by the inifer surfactant. In these experiments, the surfactants were either the brominated precursor of the n = 17 inifer surfactant, or the commercial non-ionic nonylphenol ethoxylated (NP30) in the presence of dodecylmercaptan.

The kinetic study shows that, when the surfactants are not transfer agents, the redox system is less efficient : the initial rates as well as the conversion after 24h are lower. As shown in fig. 7 (a and b) the molecular weights are much lower, again with bimodal MWD and again with production of the higher MW at the higher conversions. However, the transfer efficiency is much higher, this behaviour is certainly caused by a different partition of the thiol component which is much more in the organic part of the system. For that reason, it is less efficient as a component of the redox system and more efficient as a transfer agent versus the growing polymer in the particles.

Aknowledgment

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