Colloid Polym Sci 275:716–729 (1997)

ORIGINAL CONTRIBUTION

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Thiol-ended polyethylene oxide as reactive stabilizer for dispersion polymerization of styrene

Received: 26 September 1996
Accepted: 4 March 1997

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Abstract Radical dispersion polymerization of styrene in aqueous ethanol solutions was performed in the presence of a new reactive polyethylene oxide stabilizer with thiol end groups. This reactive stabilizer was compared to the more conventional poly (*N*-vinyl pyrrolidone). Particles size distribution, molecular weights and kinetics were investigated. Monodispersed polymer particles with diameter in the range 200–2000 nm were obtained depending on the amount of stabilizer used. In all cases, the polyethylene oxide (PEO) sequence of the dispersant was partly incorporated at the surface of the latex particles, but the grafting yield of polyethylene oxide chains was always limited and did not exceed 15%. Part of the stabilizer being unreacted or reacted with low molecular weight polystyrene remained in the continuous phase.

Key words Dispersion polymerization – styrene – reactive stabilizer – molecular weight – particles size – incorporation yield

Introduction

Dispersion polymerization has become increasingly popular as a technique for producing large (up to 15 μm) monodisperse polymer particles [1–3]. The critical condition for such a reaction is that the monomer and the initiator are both soluble in the polymerization medium but the medium is a poor solvent for the resulting polymer. Polymerization is thought to occur in homogeneous solution until a critical molecular weight is reached; the particles then precipitate from the solution and are stabilized by a suitable steric stabilizer. Good stabilizers for dispersion polymerization are polymer and oligomer compounds with low solubility in the polymerization medium and moderate affinity for the polymer particles [4–5].

Some of the early work on non-aqueous dispersion polymerization involved the use of a comb polymer (poly 12-hydroxystearic-acid-g-methyl methacrylate) as the stabilizer [6–8]. Block copolymers of poly (styrene-b-methyl methacrylate), poly (styrene-b-dimethyl siloxane) or poly (styrene-b-(ethylene-co-propylene)) were used by Dawkins and coworkers to stabilize the dispersion polymerization of methyl methacrylate in cyclohexane [9–12]. Recently, dispersion polymerization of styrene in aqueous ethanol solutions has been extensively studied because of the simplicity of the process for the preparation of micron size monodisperse polymer particles [13–19]. This method involved the use of a polymeric stabilizer such as poly (*N*-vinyl pyrrolidone), hydroxypropyl cellulose or poly (acrylic acid). It is believed that in these cases, hydrogen abstraction takes place which then allows grafting of the monomer in solution to occur giving birth to an amphipathic copolymer [1, 2, 15, 20]. However, it is difficult to really control the process since the exact structure and amount of the stabilizer produced are not known.

In this context, the use of suitable reactive stabilizers might be the one possible way to get a more controlled stabilization. A review of this kind of work on reactive surfactants-in-emulsion polymerization has been published recently [21]. Concerning dispersion polymerization, pioneering work in that direction has been done by Kobayashi et al., who have used poly (2-alkyl-2-oxazoline) styrenic macromonomers **1** instead of the more conventional poly (2-oxazoline) homopolymer **2** to produce monodisperse particles of polymethyl methacrylate or polystyrene in aqueous methanol solution [22, 23]. They demonstrated that a very low concentration of **1** was sufficient to prepare monodisperse polymer particles while more than 10 wt% (based on MMA) of the stabilizer **2** was necessary to produce polymer particles with narrow size distribution. Another example of this type of stabilizer is polyethylene oxide which is terminated at one end with a reactive acrylate ester group capable of undergoing polymerization [24–27]. From a general point of view, the main advantage of macromonomers is that they can produce more stable polymer particles since they act as stabilizers as well as comonomers. They are supposed to be covalently linked to the polymer particles but actually, data concerning their incorporation yield are lacking in the literature. A third example of this kind of reactive compound has recently been described [28]. Since dispersion polymerization is a radical process, another way to covalently anchor the stabilizer to the polymer particles is to make them reactive in, for example, transfer reactions. Polyvinyl acetate stabilizers with thiol end groups have been used by Yabuuchi to prepare monodispersed polystyrene particles by dispersion polymerization in polar medium. However, again, no data were given about the yield of incorporation in the latex particles.

The present paper describes our results along this line using a transfer agent equivalent of macromonomer, i.e a hydrophilic oligomer of polyethylene oxide carrying a thiol moiety at its end: POE_{113}–SH (I) ($M_w = 5000$ g/mol).

$$CH_3\text{–}(O\text{–}CH_2\text{–}CH_2)_{113}\text{–}O\text{–}CO\text{–}CH_2\text{–}SH\ . \qquad (I)$$

A few preliminary results have already been published [29], and this paper gives much more information about the system, which is otherwise more fully discussed.

The reactive stabilizer used in the present study, can be easily prepared from esterification of monomethyl ether of polyethylene oxide with thioglycolic acid as described in the experimental part. It was compared to the more conventional poly (N-vinyl pyrrolidone) (PVP) for the preparation of polystyrene in aqueous-ethanol medium. We were more precisely interested in particles size distribution, molecular weights and kinetics. Data on the incorporation yield of the reactive stabilizer are added showing that the stabilizing polyethylene oxide chains were firmly and covalently anchored to the polymer in the particles. Grafting yield, however, did not exceed 15% of the total amount of stabilizer but it appeared to be sufficient to ensure a good steric stabilization.

Experimental

Materials

Monomethyl ether of polyethylene glycol POE_{113}–OH ($M_w = 5000$ g/mol) and thioglycolic acid were supplied by Aldrich and used as received. Styrene monomer (Janssen Chimica) was purified upon distillation under nitrogen atmosphere to remove the inhibitor. 2,2′-azobis (isobutyronitrile) (AIBN from Janssen), diethyl ether (SDS), toluene (SDS) and ethanol (95% v/v from Onyx) were used as received. Poly (N-vinyl pyrrolidone) (PVP K30, $M_w = 40000$ g/mol) from Aldrich were used without further purification.

Synthesis of thiol-ended polyethylene oxide stabilizer (I)

According to Vidal and Hamaide [30], thiol-ended polyethylene oxide (I) was prepared from esterification of thioglycolic acid with monomethylether of polyethylene glycol according to Eq. (1).

$$CH_3\text{–}(O\text{–}CH_2\text{–}CH_2)_{113}\text{–}OH + HO\text{–}CO\text{–}CH_2\text{–}SH \rightarrow$$
$$CH_3\text{–}(OCH_2CH_2)_{113}\text{–}O\text{–}CO\text{–}CH_2\text{–}SH\ . \qquad (1)$$

PEO was dissolved in toluene. Water was removed by azeotropic distillation. Thioglycolic acid was added in excess (5 times) and the reaction was carried out by an azeotropic distillation followed by a gentle reflux for one night. The solvent was removed on a rotary evaporator. The product was then dissolved in chloroform and precipitated in cold diethyl ether dropwise to remove thioglycolic acid in excess and was finally placed in a vaccum oven at room temperature to remove diethyl ether residues. White product was obtained with a yield above 90%. The POE–SH was characterized by ^{1}H NMR (Fig. 1). The assignments are reported in the figure.

Polymerization procedure

In a typical reaction, POE_{113}–SH (0.05–0.5 g) was dissolved into around 95 g of an aqueous ethanol solution ($EtOH/H_2O$: 95/5 v/v) under nitrogen atmosphere and

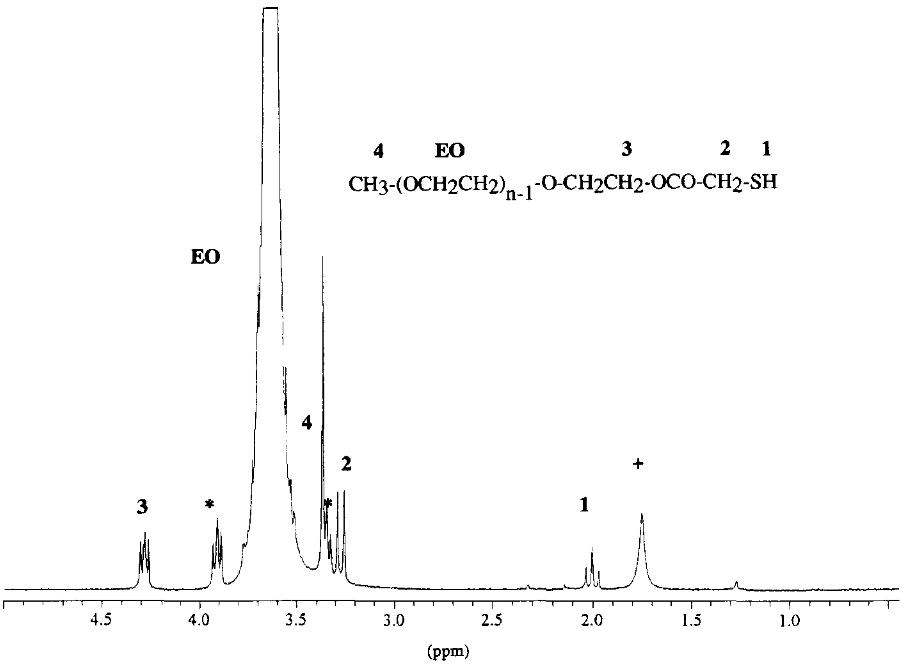


Fig. 1 ^{1}H NMR spectrum of the thiol-ended polyethylene oxide stabilizer. Small triplets (*) on both sides of the PEO resonance are due to the ^{13}C satellites. (+) is water

constant stirring (250 rpm) in a 250 ml reactor fitted with a condenser. After degassing, styrene monomer (5 g) along with the initiator (AIBN: 0.1 g) were added all at once at 70 °C. Polymerization was carried out for up to 25 h for complete reaction and small samples were taken at various times for the determination of conversion and particles size distribution.

Characterizations

The monomer to polymer conversions were determined gravimetrically. Particles size were obtained by dynamic light scattering (Brookhaven BI 8000) for intermediate samples and transmission electron microscopy (Hitachi HU 12) for the final products. One drop of the highly diluted latex solution was put on a carbon-coated nylon grid and air dried before observation. Particles size distribution was obtained from electron micrographs of negatives by measuring the diameters of 100–200 particles for each sample.

The polymer latices were made free of monomer, unreacted stabilizer, initiator and low molecular weight by-products using 3 cycles of centrifugation (30 min at 15 000 rpm)/redispersion in aqueous ethanol (95/5 v/v). The total reaction product, the recovered powder and the supernatant, were taken separately, dried under vacuum at 40 °C and weighed before characterization.

Molecular weights were determined by size exclusion chromatographic analysis (SEC) with a Waters 510 apparatus using THF as eluant at a flow rate of 1.2 ml/min and Pss gel-mixed columns. A waters R410B refractive index detector was calibrated with monodisperse polystyrene standards. Unless otherwise stated, molecular weights were determined on the latex particles after cleaning.

The incorporation yield of the stabilizer was calculated from a material balance on the total amount of dispersant collected in the washings. The calculation is based on the determination of the experimental molar ratios of ethylene oxide to styrene units by proton NMR investigation of the three different fractions (i.e. the polymer particles, the recovered powder and the supernatant). The same was done on styrene in order to determine the polymer content in the continuous phase. More details on the calculations are given in the text. Proton nuclear magnetic resonance (^{1}H-NMR) analysis was performed using a Bruker AC 250 NMR spectrometer (250 MHz) using $CDCl_3$ solutions.

Results and discussion

POE-SH as a new reactive stabilizer

Efficiency of the thiol-ended stabilizer

A first set of experiments has been carried out with the purpose to demonstrate the efficiency of the POE–SH

Table 1 Effect of the type of stabilizer on diameters and molecular weights of polystyrene particles[a]

Entry	Type of stabilizer	Particles size[b]		Molecular weights		Yield [%]
		D_n [nm]	D_w/D_n	M_w [g/mol][c]	M_w/M_n	
1	PVP	1930	1.09	23153	2.76	71
2	POE_{113}–SH	311	1.03	46375	3.81	80
3	None	/	/	Unstabilized samples	/	/
4	POE_{113}–OH					

[a] Polymerization of styrene (5 wt% based on total) was performed in a mixture of ethanol and water (95/5) at 70 °C using AIBN as initiator and 10 wt% of stabilizer (based on styrene).
[b] As determined by TEM.
[c] Weight-average molecular weight.

compounds in dispersion polymerization. In this study, we have chosen the conventional poly (*N*-vinyl pyrrolidone) stabilizer of intermediate molecular weight (PVP, $M_w =$ 40000 g/mol) as a basis of comparison since it proved to be the best stabiliser for dispersion polymerization of styrene in aqueous ethanol solutions (13). The greater importance of stabilization is suggested by several experiments. The results are summarized in Table 1.

As expected, polymerization carried out in the presence of PVP gives a stable latex with particle size in the usual range (entry 1 of Table 1). Not surprising also is the obtention of unstable particles in the absence of steric stabilizer (entry 3 of Table 1). Coalescence was uncontrolled since the solvent was selected to be a good solvent for the monomer and initiator, but a poor solvent for the polymer being formed.

More surprising is the result obtained using the unmodified (polyethylene glycol) monomethylether from which POE_{113}–SH was synthesized (Eq. (1)). Polymerization carried out with POE_{113}–OH resulted in massive coagulum (entry 4 of Table 1). Now, if one takes into consideration the fact that polyethylene glycol contains active sites for chain transfer of radicals, a graft steric stabilizer should be formed *in situ* by hydrogen abstraction as it is the case for PVP and stable particles should be obtained. Actually, the formation of graft by chain transfer to POE cannot be denied and has been described in the literature [24]. However, the author of that study pointed out that stabilization was succesful only under specific conditions. Moreover, the latices thus obtained were rather coarse even if polyethylene glycol of molecular weight of at least 6000 g/mol was used. Clearly, the length of the polyethylene oxide chain and its concentration are important parameters in determining the stability of the polymer particles. For example, if the polystyrene fragment of the graft has a very low molecular weight compared to the POE fragment, then the graft may be too soluble, particularly in good solvents for POE, and may not adsorb onto the particle surface as a steric stabilizer, resulting in an unstabilized polymerization (i.e. infinite particle size). But also critical may be the rate of formation of the stabilizing graft copolymer and the grafting probability of the stabilizer. Indeed, the theory of steric stabilization predicts that the steric repulsive energy governing particle size is dependent upon the concentration of stabilizing polymer in the adsorbed layer which in turn is determined by the amount of graft available (i.e. the probability of grafting) and the affinity of the polymer for adsorption to the particle surface [31]. If one considers that grafting occurs in solution by chain transfer to stabilizer, then the probability of grafting can be estimated using standard kinetic laws of radical polymerization as described in Ref. [20]. Chain transfer to POE can be approximated by the chain transfer constant for ethylene glycol as being 2×10^{-4}, and we can find, using the other known constant values of the literature [32] that probability of polystyrene grafting to POE is approximatively of 0.2 chain in 100, which is of the same order of magnitude as that for grafting to PVP [33]. Nevertheless, in this approach, we must also consider the stabilizing ability of the stabilizer. Indeed, with a molecular weight of only 5000 g/mol in comparison to the molecular weight of PVP ($M_w = 40\,000$ g/mol), the highly hydrophilic POE–OH homopolymer is expected to have a poor affinity for the hydrophobic surface of the nanoparticles and, therefore, to be a poor stabilizer. Such hypothesis could account for the above experimental observation and it is then clear that polyethylene oxide homopolymer could not prevent uncontrolled coalescence during precipitation when compared to PVP in the same conditions.

On the contrary, when the new reactive stabilizer POE–SH is used instead of POE–OH, a very stable dispersion is obtained with very low particles size as shown in Table 1 (entry 2). After sedimentation by centrifugation, the particles can easily be redispersed by gentle shaking. In that case, it is likely that the difference in stabilization is due to difference in the grafting mechanism. Indeed, since POE–SH compounds contain a powerful active site for chain transfer, the terminal thiol group in addition to the labile hydrogens of the POE units, a grafting reaction between the polystyrene radicals and the transfer agent will take place, giving rise to chemically linked polyethylene oxide chains to the polymer as it will be evidenced later on. As a matter of fact, the transfer constant of POE–SH has been measured as being close to 15 [34], i.e. close to the value which can be predicted from model compounds [32]. Then the same calculation as that presented above can be done, and we find that the probability of polystyrene grafting to POE–SH is of 60 chains in 100, that is 300 times far higher than the probability of grafting to POE–OH. So, the new reactive stabilizer definitively proved to be more efficient than the corresponding unmodified polythylene glycol for dispersion polymerization of styrene in polar medium because of its higher transfer efficiency.

Effect of stabilizer concentration

Data about the influence of stabilizer concentration have already been reported in the preliminary publication [29]. As shown in Table 2, the average particle size increased from 311 to 2280 nm decreasing the stabilizer concentration. In all cases, the dispersions are very stable with no floc formation even if the POE–SH concentration is below 1 wt% vs. monomer. Particles size distribution is narrow even at very low stabilizer concentration.

All these results prove once again that the thiol-ended stabilizer is a very efficient stabilizer for the dispersion polymerization of styrene since very low concentrations of POE–SH with a relatively low molecular weight ($M_w = 5000$ g/mol) are sufficient to ensure the colloidal stability of the growing particles. On the contrary, the conventional poly (*N*-vinyl pyrrolidone) of higher molecular weight ($M_w = 40\,000$ g/mol) needs almost 10 wt% based on the monomer for the preparation of micron size monodisperse polystyrene particles [13]. It is quite clear that the molecular weight of the stabilizer is a critical parameter as explained in the beginning of the paper. Even for macromonomers stabilizers, it is agreed that too low a molecular weight will not be sufficient to stabilize the particles while too high a molecular weight will lead to less efficient polymerization to the macromonomer which could lead to an unstable latex [24, 25]. Nevertheless, the opposite is observed using the new thiol-agent stabilizer. In the present study, the differences between the two stabilizers may be explained as follows. In the dispersion polymerization of styrene using conventional non-reactive dispersants, the particle is stabilized mainly by the adsorption of the stabilizer on the particle surface though some minor part may also be grafted. The amount of grafted or adsorbed stabilizer on the polymer surface is small and the rest of the stabilizer exists in solution [35]. In dispersion polymerization using the reactive stabilizer, however, the thiol-ended polyethylene oxide dispersant gives polymer particles having chemically bonded stabilizer chains and, hence, a low concentration of the low molecular weight stabilizer POE–SH is sufficient to stabilize the polymer particles.

Concerning the decreased particles size with increased POE–SH concentration, we propose that it is the consequence of the larger number of stabilizing polymer molecules being able to stabilize a higher surface area and, hence, produce smaller particles. This explanation is in accord with the theories of particle formation proposed by Barrett [1]. Concurrently with the decrease in size, molecular weights increase with broadening in the molecular weight distribution in accordance to the inverse correlation between particle size and molecular weights already observed in the literature for other kinds of systems. A rational explanation can be given if one considers that particles growth, in dispersion polymerization, is governed by two competiting mechanisms: adsorption of monomer and oligomeric radicals from the continuous phase and subsequent particle phase polymerization or accretion of dead polymer obtained by termination in the continuous phase [14]. The molecular weights from particles phase polymerization are usually higher than those from solution polymerization because the termination rate is reduced by

Table 2 Effect of stabilizer concentration on particle size and molecular weights[a]

Entry	Stabilizer content[b]	Particles size[c] D_n	D_w/D_n	Molecular weight M_w[d]	M_w/M_n	Yield [%]
A	10	311	1.03	46375	3.81	80
B	5	2052	1.1	28274	2.59	77
C	3	2280	1.02	23524	2.44	73

[a] Polymerization of styrene (5 wt% based on total) was performed in a mixture of ethanol and water (95/5) at 70 °C using AIBN as initiator.
[b] Wt% of styrene.
[c] As determined by TEM.
[d] Weight-average molecular weight.

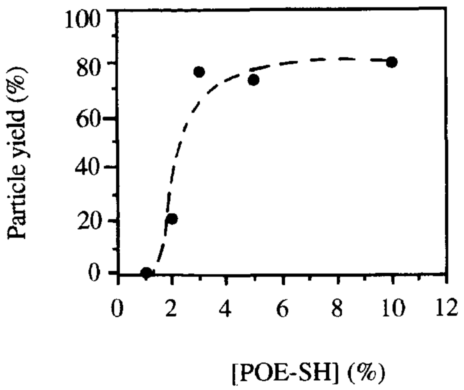


Fig. 2 Effect of POE_{113}–SH concentration on particle yield

the viscosity of the monomer/polymer particle medium (the so-called gel effect). Thus, the smaller particles tend to have higher molecular weights since a higher proportion of particle-phase polymerization occurs because solution-initiated oligomeric radicals are captured more efficiently due to the greater surface area of the particles.

Also dependent on the stabilizer concentration are the polymerization rate and the final conversion as shown in Ref. [29]. The lower the stabilizer concentration, lower are the polymerization rate and the final conversion as illustrated in Fig. 2.

We think that the change in polymerization rate with the POE–SH concentration is to be regarded more as a result of the change in size of polymer particles than as a particular property of the reactive stabilizer. Actually, it is well known that the kinetics of solution polymerization is not affected by transfer reactions since the generated radicals can reinitiate polymerization. It remains that when a large amount of thiol is used, most of the radicals are lost in solution due to more transfer and termination reactions. To escape this termination reaction, the oligomeric radical must be captured by the particles. If the conditions are so that there is a large number of particles, then the surface available for the capture of radicals will be important and also the part played by the polymerization inside the particles. Then, a strong acceleration of the polymerization can take place. On the contrary, the larger the particles size, smaller is the total surface area of the particles for a given amount of polymer and greater is the possibility of solvent-phase polymerization that means termination of the oligomer radicals by recombination in the continuous phase, which results in decrease in the rate of dispersion polymerization.

Thus, already now, considering our first results, stabilization clearly appears to be the mechanistically critical factor which controls particle size and molecular weight in dispersion polymerization. In particular, the amount of reactive dispersant proved to be an important parameter and it can be concluded that the final particle size and distribution are largely determined by the ability of the stabilizer to maintain the colloidal stability of the growing particles.

Particle growth and mechanism

The mechanism of the process is of considerable interest, particularly with respect to the formation of monodisperse vs. polydisperse particles and in the control of particle size. For that purpose, particle growth was followed by dynamic light scattering during the synthesis of polystyrene particles using POE–SH as stabilizer.

As demonstrated in Ref. [29], there is a linear relationship between the conversion and the whole volume of the particles that indicates that the number of particles is essentially constant from even the earliest stages of the reaction. As shown, the particle number increases abruptly from the start of the polymerization up to 5–10% conversion and, at the end of this interval, stable polymer particles are observed. Therefore, nucleation must take place in those early stages where the particle number has reached its final value, in agreement with the behavior already assumed in the study of dispersion polymerization in the presence of macromonomers [36].

Indeed, as POE–SH compounds contain active sites for chain transfer to radicals, they are able to produce *in situ* graft copolymers (POE–g–PStyr) chemically linked to the polymer particles as well as macromonomers through copolymerization. The probability of grafting is high and a relatively large amount of graft is available at the beginning of the reaction for effective stabilization of the polymer beads. Stabilization is attributed to extended alcohol-soluble polyethylene oxide chains which are convalently and strongly bonded to the polymer in the latex particles. Then, particle growth proceeds in two loci, namely, the continuous phase, especially at the beginning of polymerization and the monomer-swollen polymer particle phase. As discussed earlier, the contribution of heterogeneous polymerization is expected to increase with increasing particle fraction or with decreasing particle size so that particle growth is greatly influenced by the initial critical size. The smaller the diameter of the particles, the more effective is the particles-phase polymerization mechanism. It results in higher polymerization rates and higher molecular weights of the polymer.

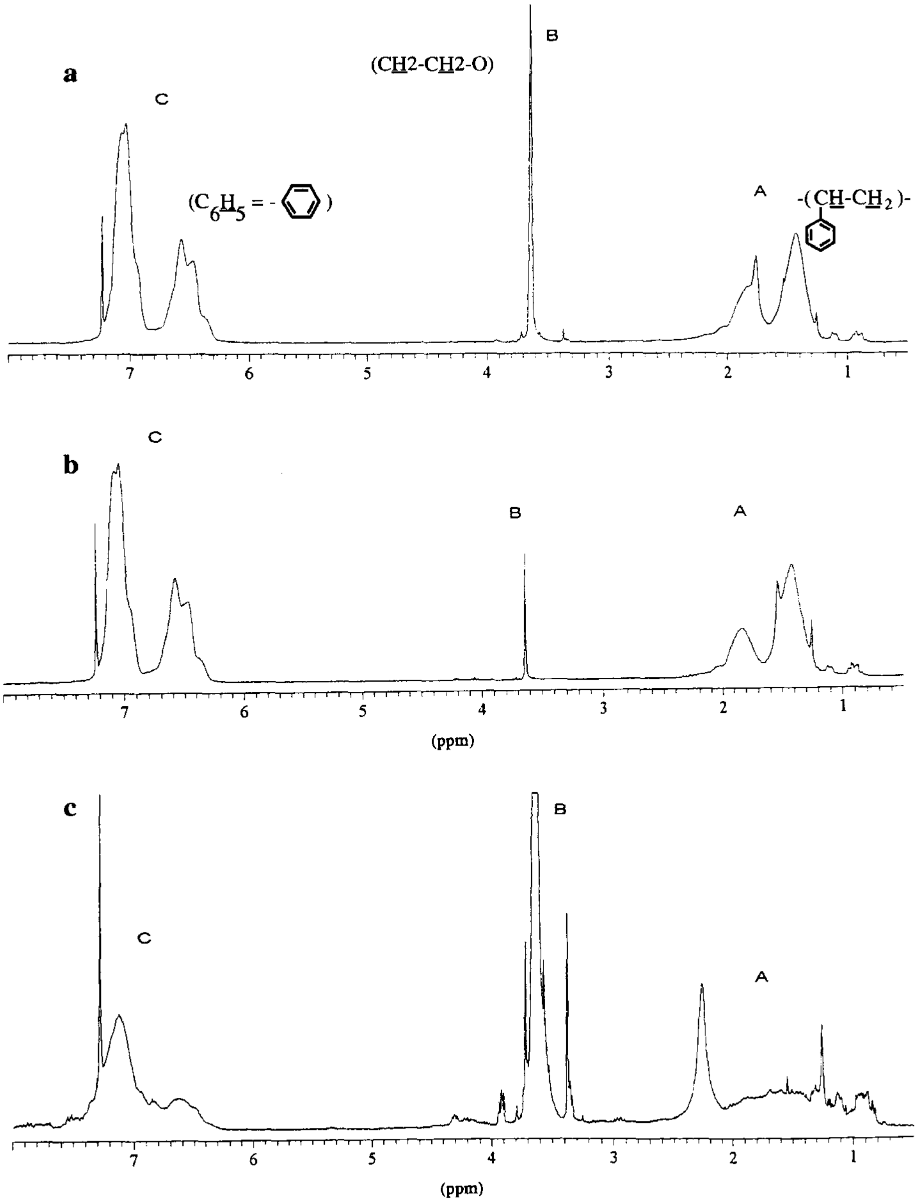
Therefore, the formation mechanism of monodisperse polystyrene particles in the present system is not very different from the mechanism in the presence of PVP. What is clearly different is the control of particle size and particle size distribution. As the thiol-ended stabilizer is very efficient in dispersion polymerization, a large number of stabilized particles, i.e. low particle size, are obtained. The efficiency of the reactive stabilizer is the direct consequence of the high reactivity of the stabilizer. Nevertheless, the capacity of the stabilizer to form graft copolymers with a sufficiently high degree of grafting of the copolymers has still to be proved. So, quantitative NMR analysis of the stabilizer in the latices is carried out in order to determine experimentally the exact amount of grafted stabilizer.

Qualitative and quantitative evidence of grafting

Because of the greater importance of stabilization in dispersion polymerization, we were more specifically interested, in that section, in the characterization of grafting of the reactive stabilizer with the purpose to establish the concentration of polyethylene oxide stabilizing chains.

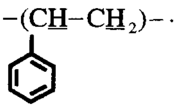
The evidence of grafting is given by proton NMR analysis of the polymer particles. First, the latices were made free of residual monomer, initiator and ungrafted stabilizer by repeated centrifugation/redispersion cycles in ethanol as described in the experimental part. After each centrifugation, the supernatant above the precipitated polymer particles was removed and the particles redispersed into fresh dispersion medium by gentle shaking. Then, samples of the different phases, i.e. the polymerization product, the recovered powder and the supernatant were characterized by ^{1}H NMR spectroscopy (Fig. 3).

Fig. 3 Proton NMR characterization of (a) polymerization medium, (b) cleaned polymer particles, and (c) extracted products



Qualitatively, ^{1}H NMR analysis of the three samples shows the presence of polystyrene characterized by the aromatic protons at 6.5–7 ppm ($C_6\underline{H}_5$–) and the vinylic protons between 1 and

2 ppm



$-(C\underline{H}-C\underline{H}_2)-\cdot$

But, it also proves the presence of POE in the three samples with the peak resonance at 3.65 ppm ($-C\underline{H}_2-C\underline{H}_2-O-$) attributed to ethylene oxide units (Fig. 3). Indications on the attributions are given in the same figure. We can see in Fig. 3b that, even after cleaning, some POE compounds still remain in the polymer phase. That part of the stabilizer surely corresponds to grafted POE–SH unextracted during the recovering procedure because it is chemically linked to the polymer particles. It seems from the relative NMR intensities of the different peaks that the amount of grafted stabilizer is low as it will be proved quantitatively in the next section, and actually NMR analysis indicates that the cleaned product corresponds mainly to polystyrene with some minor amount of grafted POE–SH.

The other part of the stabilizer which has been extracted under cleaning is contained in the supernatant as proved by the NMR spectrum in Fig. 3c. It may be free unreacted thiol agent but also eventually copolymers of polyethylene oxide and polystyrene with a few styrene units, the presence of which is also identified in the spectrum in Fig. 3c.

So, NMR analysis proved, without any ambiguity that the chain transfer agent has distributed itself between the continuous and polymer phases. The unextractable part of the stabilizer, still contained in the polymer phase, is supposed to be grafted to the latex beads since it remains anchored in the particles even after three cycles of centrifugations/redispersions into fresh alcohol. The extractable part of the thiol-agent stabilizer is presumed to be free unreacted compound lost in the continuous phase or eventually, copolymer with only traces of styrene. Quantitative informations on the repartition of polystyrene and POE–SH in the different fractions will be given later on.

Another experimental evidence of the presence of the stabilizer in both the latex particles and the supernatant was otherwise given by steric exclusion chromatography analysis (SEC) of the three different samples. SEC diagrams are reported in Fig. 4.

While the SEC diagram of the latices before cleaning shows a broad high molecular weight peak with a shoulder at a lower molecular weight, the SEC diagram of the cleaned polymers exhibits a similar shape with a decrease in the contribution of the lowest molecular weight peak to the overall signal. It results a shift of the curve toward higher molecular weights with a diminution of the relative intensity of the lowest molecular weight peak (Figs. 4a and b). Now, if one consider the values of the molecular weights associated to the two signals, it appears that the higher molecular weight peak does correspond to polystyrene from polymerization inside particles while the lower molecular weight peak probably corresponds to either unreacted stabilizer or to the relatively low molecular weight polystyrene obtained by transfer to the stabilizer in the continuous phase. The diminution of the relative intensity of the lowest molecular weight peak indicates that the corresponding products have been extracted during cleaning of the latices as supported by further analysis.

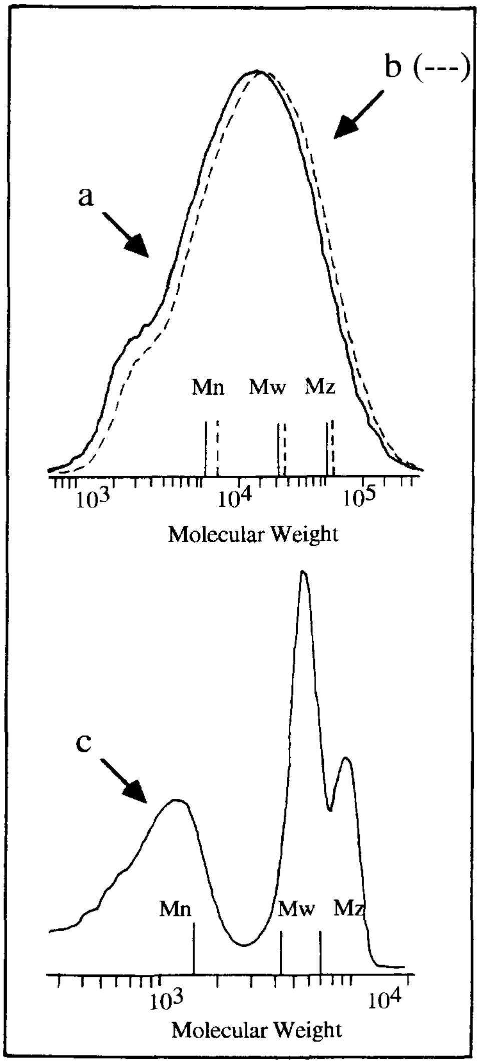


Fig. 4 SEC chromatograms of (a) polymerization product, (b) cleaned polymer particles, and (c) extracted products

Indeed, low molecular weight peaks in the range 400–15000 g/mol are observed in the SEC diagram of the extracted compounds (Fig. 4c). The lower molecular weight peak ($M_w = 1000$ g/mol) probably corresponds to free polystyrene terminated in the continuous phase, presumably by transfer to the stabilizer or to the solvent. Very similar results have been obtained in the case of dispersion polymerization stabilized by macromonomers [37]. The intermediate MW peak ($M_w = 5700$ g/mol), with a weight average molecular weight very close to that of the stabilizer, does correspond to the thiol compound not reacted or reacted with a very small number of styrene molecules. While the highest molecular weight peak ($M_w = 10000$ g/mol) can be assigned either to a disulfide (by-product of the POESH synthesis) or a product of termination by coupling after a very few steps of propagation.

So, SEC analysis corroborates the results obtained by NMR spectroscopy. The latex particles contain low and high molecular weight products. The higher MW product is polystyrene from polymerization inside particles while the lower MW compounds correspond to grafted or not grafted POE, part of which is extractable under cleaning. In addition, steric exclusion chromatography definitively attests for the presence of oligomers of styrene, free unreacted stabilizer and presumably also POE sequences with only traces of styrene in the supernatant.

Now, in order to yield more insights on the grafting mechanism and to determine which part of the stabilizer effectively contributes to stabilization of the particles, a quantitative approach is necessary to estimate the amount of stabilizer and polymer contained in the different phases.

For that purpose, we calculated the fraction of both POE–SH and polystyrene contained in the cleaned latex beads and the continuous phase and established a material balance as follows.

First, for every sample of the different phases, we determined the experimental molar ratio R of styrene units to polyethylene oxide from the NMR spectra of the samples as

$$R = \frac{b/5}{a/(4 \times 113)} \tag{2}$$

where a and b are respectively, the area of the peak resonance at 3.65 ppm ($C\underline{H}_2$–$C\underline{H}_2$–O) and 7 ppm

($C_6\underline{H}_5$ = – ) ·

The assignments are reported in Fig. 3.

Then, the massic ratio A = Styr.units/POE–SH will be given by the following equation:

$$A = \frac{\text{Styr.units}}{\text{POE–SH.}} = R \times \frac{104}{5000}\,, \tag{3}$$

where 104 and 5000 are, respectively, the molecular weights of styrene and polyethylene oxide. Notice that the styrene units involved in this calculation represents styrene constituting the polymer. Therefore, in the following, PS (polystyrene) will replace Styr.units.

Now, if we take into account the solid content τ in a given medium, one has

$$\tau = \text{POE–SH} + \text{PS}\,. \tag{4}$$

Thus, by combining Eqs. (3) and (4), one finds for each medium

$$\text{PS (wt\%)} = \frac{A \times \tau}{A+1}\,, \tag{5}$$

$$\text{POE–SH (wt\%)} = \frac{\tau}{A+1}\,. \tag{6}$$

Let us now design the three media by

1. initial dispersion after polymerization,
2. recovered powder after centrifugation, and
3. solid content of the supernatant.

Then, taking into account that the overall solid content should be constant, one can write the relation (7), where the indices 1, 2 and 3 represent (see above) the three media.

$$\tau_1 = \tau_2 + \tau_3\,. \tag{7}$$

From Eqs. (6) and (7), it follows:

$$\frac{\text{POE–SH}_2}{\text{POE–SH}_1} = \left(\frac{\tau_2}{A_2+1}\right) \times \left(\frac{A_1+1}{\tau_1}\right) = \left(\frac{\tau_1-\tau_3}{\tau_1}\right) \times \left(\frac{A_1+1}{A_2+1}\right)\,, \tag{8}$$

$$\frac{\text{POE–SH}_3}{\text{POE–SH}_1} = \left(\frac{\tau_3}{A_3+1}\right) \times \left(\frac{A_1+1}{\tau_1}\right) = \left(\frac{\tau_3}{\tau_1}\right) \times \left(\frac{A_1+1}{A_3+1}\right)\,. \tag{9}$$

Equations (8) and (9) also write:

$$\frac{\text{POE–SH}_2}{\text{POE–SH}_1} \times 100 = (100 - \tau_{\text{alcoholsoluble}}) \times \left(\frac{A_1+1}{A_2+1}\right)\,, \tag{10}$$

$$\frac{\text{POE–SH}_3}{\text{POE–SH}_1} \times 100 = \tau_{\text{alcoholsoluble}} \times \left(\frac{A_1+1}{A_3+1}\right)\,, \tag{11}$$

where $\tau_{\mathrm{alcoholsoluble}} = 100 \times (\tau_3/\tau_1)$ is the solid percent extracted from the latex dispersion during cleaning.

Thus, knowing τ_1 and τ_3 from weighing and A_1, A_2, and A_3 from NMR measurements, Eq. (10) allows to estimate the incorporation yield of the stabilizer in the cleaned polymer particles, whereas Eq. (11) gives the percentage of stabilizer present in the continuous phase.

Similarly, from Eq. (3), we obtain the incorporation yield of polymer in the particles (Eq. (12)) and the percentage of polymer in the supernatant (Eq. (13)).

$$\frac{\mathrm{PS}_2}{\mathrm{PS}_1} \times 100 = \left(\frac{A_2}{A_1}\right) \times \left(\frac{\text{POE–SH}_2}{\text{POE–SH}_1}\right) \times 100\,, \tag{12}$$

$$\frac{\mathrm{PS}_3}{\mathrm{PS}_1} \times 100 = \left(\frac{A_3}{A_1}\right) \times \left(\frac{\text{POE–SH}_3}{\text{POE–SH}_1}\right) \times 100\,. \tag{13}$$

Results of this analysis are given in Table 3 for different amounts of stabilizer.

From the values reported in Table 3, one can also control the validity of the method. Indeed, material balance of the POE–SH and the PS can be calculated separately. This is done by adding the percent formed in medium 2 and 3 for each of the two compounds. One sees in Table 3 that the results are very satisfactory for polystyrene. The results are also satisfactory in case A and B for POE–SH. The only case where a noticeable difference with the theoritical value of 100 appears, is in case C for POE–SH. This is due to the low amount of stabilizer used in this experiment.

Results of Table 3 show that, as expected, the major part of polystyrene (95%) is located in the latex particles. However, low amount of polymer (5%) is also contained in the supernatant. As shown previously, these macromolecules left in solution are probably oligomers of styrene constituted of around 10 styrene units, eventually associated to the reactive dispersant. They are obtained by transfer to the stabilizer and termination in the continuous phase. The relatively high concentration of those low molecular weight species is surely due to the high probability of chain transfer to POE–SH discussed in POE–SH as a new reactive stabilizer section. Indeed, only 1 wt% of soluble compounds is usually found using more conventional stabilizers like HPC or PVP which have a lower chain transfer constant than the thiol-ended stabilizer [33].

More interesting data are obtained from the analysis of the reactive stabilizer. We demonstrate in Table 3 that, whatever is the initial POE–SH content, the incorporation yield of the stabilizer in the polymer particles is rather poor, limited to 14%. As a consequence, a large part of the dispersant is found in the continuous phase. We do not know whether it is free unreacted thiol agent or grafted stabilizer with a small number of styrene units. Nevertheless, this fraction (90%) of the dispersant, lost in the polymerization medium, does not contribute to steric stabilization of the latices since its removal does not affect the stability of the dispersion. After cleaning, the particles can be easily redispersed with no change in their size. The relatively large amount of POE–SH found in the continuous medium constitutes another evidence that mercapto groups are very efficient transfer agents, but certainly consumed too fast so that a large fraction of stabilizer is lost initially rather than being captured by the existing particles by transfer or termination.

Considering now the incorporation yield of the stabilizer in the polymer particles, we showed that between 10% and 14% of the initial POE–SH is grafted onto the latex beads. So, it appears that the grafting yield does not depend much on the initial POE–SH concentration. Consequently, as the amount of POE–SH in the feeds decreases, the weight of grafted stabilizer (in wt% of polystyrene), also decreases as reported in Table 4. Despite the very low values of grafted stabilizer obtained in cases B and C for low initial amounts of stabilizer, the particles remain stable. Nevertheless, it is clear that as particles size

Table 3 Incorporation yield of polystyrene and thiol-ended stabilizer into the latex particles and material balance[a]

Entry	POE–SH[b]	Polym. yield [%]	$\mathrm{POE_{113}}$-SH[c]			Polystyrene[d]		
			particle[e]	Serum[f]	Total	Particle[e]	Serum[f]	Total
A	10	80	9.4	92.3	101.7	95.2	4.85	100.05
B	5	77	14.4	83.6	98.0	94.0	6.1	100.1
C	3	73	10.3	84.9	95.2	95.9	4.4	100.3

[a] Polymerization of styrene (5 wt% on total) was performed in EtOH/H_2O (95/5: v/v).
[b] Wt% of styrene.
[c] Wt% of the total amount of stabilizer.
[d] Wt% of the total amount of polystyrene.
[e] In medium 2.
[f] In medium 3.

Table 4 Surface analysis of the grafted latex particles from results of Table 3

Entry	Particles size [nm]	POE_{113}–SH conc		Surfacic grafted amount		$\sigma/\pi\langle s^2\rangle$
		Feed[a]	Surface[b]	$1/\sigma$[c]	σ[d]	
A	311	10	1.2	0.08	13	0.64
B	2052	5	1.05	0.43	2.3	0.11
C	2280	3	0.4	0.19	5.2	0.25

[a] Wt% of styrene.
[b] Wt% of polystyrene particles.
[c] Molecules per unit area (molecules/nm^2).
[d] Area per molecules (nm^2/molecules).

change with the POE–SH concentration, the POE chain content on the surface, which is the real parameter to take into account for the latex stability, will change too. Indeed, from the specific surface area of the latex particles and the grafted amount per unit area ($1/\sigma$), the area occupied per grafted chain, σ, can be evaluated. σ may be compared to the projected area of a random coil located at the surface. Taking a value for the radius of gyration $\langle s^2\rangle^{1/2}$, of 2.55 nm for POE of molecular weight of 5000 in water [38], the projected area $\pi\langle s^2\rangle$ equals 20.4 nm^2.

Results of Table 4 show that, for the three samples, the grafted POE chains occupy a surface smaller than the projected area $\pi\langle s^2\rangle$ of the coil. The low value of $\sigma/\pi\langle s^2\rangle$ comprised between 0.1 and 0.67 suggests that the polymer chains have an extended conformation normal to the surface, as one would expect for terminal anchoring of the stabilizer in good solvent. In addition, one can see that the larger particles contain the greatest amount of grafted molecules per unit area. As expected, higher stabilizer content are needed to stabilize big particles. Consequently, the POE segments adopt in that case, an even more extended configuration as supported by the values of Table 4 (entry B and C).

Although the grafting yield remains lower than 15% whatever is the particles size, the proof is given that low amount of stabilizer is sufficient to ensure the steric stabilization of the latex beads. If one considers the precedent results, we may say that the high efficiency of the thiol ended stabilizer is probably due to the extended conformation of the polyethylene oxide chains which is the direct consequence of the relatively great amount of grafted molecules per surface units calculated by quantitative NMR analysis.

Comparison between POE–SH and PVP

Particles size and molecular weights

In the following, the ability of the reactive dispersant to stabilize the latex particles was compared with that of PVP. First, we demonstrate that the new reactive stabilizer gives, in the same conditions, a better control of particle size distribution and a lower size than the usual polymeric stabilizer polyvinyl pyrollidone. An illustration is proposed in Fig. 5 with TEM micrographs of two polystyrene samples prepared with the two different types of stabilizers according to recipes of Table 1. The corresponding particle size histograms are given in Fig. 6. Concurrent with the size decrease, higher conversions and molecular weights are obtained with broadening in the molecular weight distribution (Table 1).

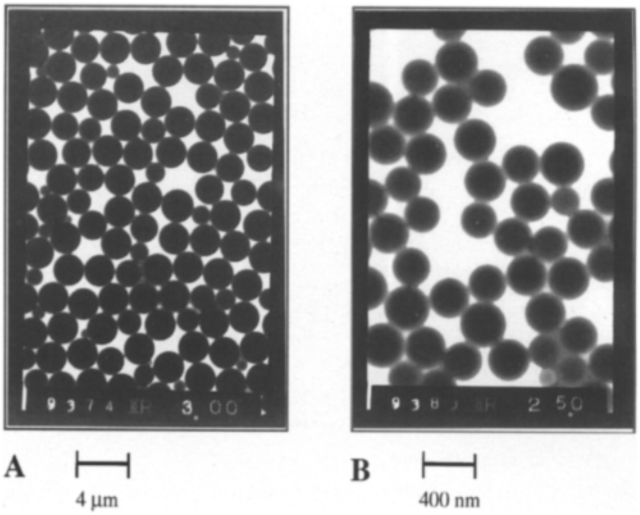


Fig. 5 TEM micrographs of polystyrene particles prepared in aqueous ethanol solution as a function of the type of stabilizer. (A) entry 1, (B) entry 2 of Table 1

If it is assumed that POE–SH compounds can undergo transfer reactions with a relatively high probability, it is likely that a greater amount of grafted steric stabilizer could be formed in the case of POE–SH giving rise to a greater number of stabilized nuclei in comparison to PVP. Then, stabilization of small polymer particles is more probable in the former case so explaining the formation of a large number of particles with a lower size. The high values of conversion are the direct consequence of

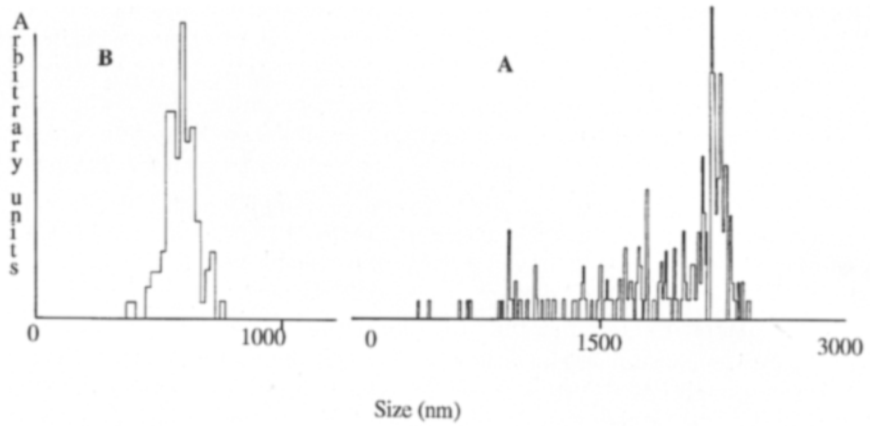


Fig. 6 Particles size histograms of PStyr. particles prepared in aqueous ethanol solutions as a function of the type of stabilizer. (A) entry 1, (B) entry 2 of Table 1

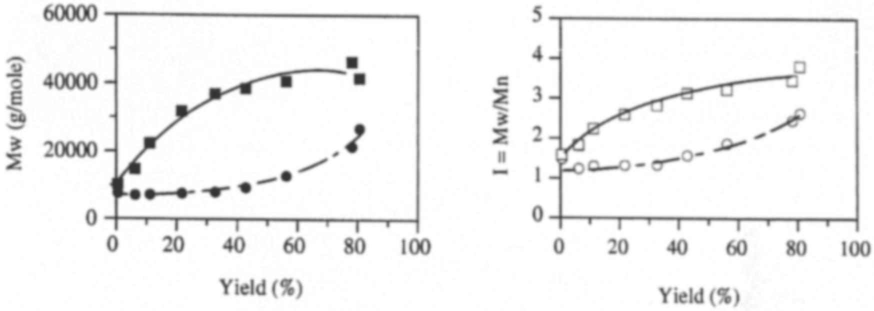


Fig. 7 Weight-average molecular weights (M_w) and polymolecularity index (M_w/M_n) vs. polymerization yield for the two different types of stabilizers. (●, ○) PVP and (■, □): POE–SH

this large number of particles which can offer, in further steps of the process, a surface area large enough for efficient capture of the newly growing radicals, that means particles remain for a longer period in a regim of oligomer capture and solid-phase polymerization.

Kinetics

In the previous section, a special attention has been paid to the final polymerization yield, particle size and molecular weights of the polymer. Correlations were established and coherent explanations were proposed to account for our results. However, the mentioned values are subject to many changes during the polymerization and further insights into the mechanism of the process could be obtained by looking at those changes. In this section, the molecular weight and molecular weight distribution were investigated as a function of conversion and conversion as a function of time.

At first, as it has been demonstrated in our preliminary work [29], the conversion/time curves for the dispersion polymerization of styrene in ethanol–water medium with the two kinds of stabilizers have two different aspects.

While for PVP, the kinetic curve is nearly linear up to 40–50% conversion and then slowly levels off, the curve for the reactive stabilizer exhibits a sigmoidal shape. After a short inhibition period, the polymerization was highly accelerated around 1 h with the maximum rate and after 20–30% conversion, it gradually decreases. It is to be noted in particular that the polymerization carried out in the presence of POE–SH proceeded faster than that with PVP. Simultaneously, the molecular weight of both the PVP and POE–SH stabilized polymer particles was determined by SEC in THF solvent and plotted against conversion as shown in Fig. 7.

It can be seen that, in the presence of PVP, both the molecular weight and the molecular weight distribution increase as the reaction proceeds. Nevertheless, this contrasts strongly with the results that are obtained in ethanol/water systems with hydroxypropylcellulose as stabilizer where a sharp increase in molecular weight during the course of the reaction was observed [1]. Although there is some increase in the molecular weight of the polymer with increased conversion, in the present case, there is clearly no pronounced gel effect in the classical sense. The molecular weight results are consistent with the kinetic behavior reported above, where the polymerization rate was found to be nearly constant or just slightly increasing during the course of the reaction. The early work on the kinetics of dispersion polymerization of methyl methacrylate in *n*-dodecane with particle sizes usually in the submicron range suggested that once the particle nuclei have formed, they adsorb monomer and sweep up most of radicals in the continuous phase. Polymerization occurs mainly within the monomer swollen particles. The gel effect was found to be very significant and the molecular weights of the final polymers were on the order of 10^6. In the system discussed here, the particle nuclei are indeed swollen with monomer but only to a minor extent. During polymerization, most of the monomer remains in the reaction medium and the gel effect is almost entirely absent. This is an illustration of the competition between solution polymerization and heterogeneous polymerization in the dispersion polymerization process. Indeed, a study on the partitioning of styrene between the polymer and continuous phases during the dispersion polymerization of styrene in pure ethanol showed that most of the monomer resides in the continuous phase [39]. Actually, the styrene concentration and the solvent composition of our system are not exactly the same as those of the study mentioned here due to the presence of 5 wt% of water in alcohol; but we may consider that in our conditions, the amount of styrene in the polymer particle is rather low. So, the relatively low monomer concentration in polymer particles and the low particle number density (large particle size) obtained in the presence of PVP, may explain the slow polymerization rate and low molecular weights of the final products. At low conversion, the continuous phase is rich in monomer and initiator and thus, the solution polymerization dominates the reaction resulting in slow rates and low molecular weights polymers since the limited amount of monomer in the polymer particles is shared by a large number of oligomeric radicals. At higher conversions the particle fraction is increasing and a heterogeneous polymerization mechanism becomes dominant. The termination rate is then reduced and higher molecular weights polymers are formed at higher polymerization rates as evidenced on the kinetic curves. It is probable that if different monomer levels were used, other effects on particle size and molecular weights would be observed. As a matter of fact, Vanderhoff and co-authors showed that the monomer concentration in the polystyrene particles increases with increasing initial styrene concentration [39]. Consequently, larger gel effect should be expected to take place with larger amount of styrene.

Using the POE–SH stabilizer, it is seen that the molecular weight of the particulate polymer increases initially and then levels off at around 40% conversion as illustrated in Fig. 7. If it is assumed that polymerization is taking place within the particles as proposed in the previous section, then a significant portion of the growing particle must be polymer and the Tromsdorff restrictions should pertain. Now, the molecular weight results as well as the kinetic curves do not indicate any autoacceleration or gel effect as expected. A possible explanation is that frequent chain transfer is occurring during polymerization in the solvent with not enough initiation and propagation reactions for causing the oligoradicals to be captured by existing particles or to nucleate new particles. The presence, in the continuous phase, of low molecular weight POE and PStyr compounds definitively attests this hypothesis. Consequently, the gel effect expected to take place may be undetected in the present case due to polymerization in the continuous phase which masks an increase in the rate of polymerization expected to occur within the particles. One has to keep in mind, in the present study, that the reactive stabilizer acts not only as a stabilizer but also as a transfer agent. Thus, it is supposed to be located in the particle shell and the continuous phase as well, and to influence the growth reaction within the particles less. Another possible explanation is the presence of a limited amount of ethanol within the particles. Ethanol is a rather effective transfer agent which may favor the exit of radicals from particles, then returning in the surrounding medium. Finally, transfer reaction to the POE–SH simply adsorbed may also cause similar effect.

Conclusion

A new reactive polyethylene oxide stabilizer carrying thiol-end groups (POE–SH), was used successfully in radical dispersion polymerization of styrene to produce stable monodisperse latices. Comparison with the more conventional poly (*N*-vinyl pyrrolidone) stabilizer (PVP) showed that the POE–SH compounds give lower particles size and higher molecular weight polymers with higher conversions. The high stabilizing efficiency of the thiol-agent stabilizer is presumed to be the consequence of the high probability of transfer to the stabilizer in the continuous phase. Indeed, the terminal SH group of POE–SH, with a chain constant transfer 10000 times higher than that of PVP, is a very efficient transfer agent. Consequently, a high number of stabilizing molecules will be formed initially, resulting in a large number of stabilized nuclei, i.e. lower particles size. Then, further particles growth occurs either within the particles or by a mixed particle/solution mechanism. So, stabilization appears to be a determining step in particles formation which controls ultimately particle size, size distribution, molecular weight and molecular weight distribution.

Like PVP, the new reactive dispersant functions as a steric stabilizer which can prevent flocculation and aggregation of the particles being formed. But, in the case of POE–SH, even very low concentrations are sufficient to stabilize the latices since the thiol-ended stabilizer is covalently and firmly attached to the polmer particles. We showed by quantitative NMR analysis that the grafted amount of POE chain on the surface is limited to 15%. However, further analysis also demonstrate that the POE molecules have an extended conformation normal to the surface. Consequently, the absolute POE chain content on the particles surface is relatively high enough to ensure a good steric stabilization.

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