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Small particle size in emulsion polymerization using non-ionic stabilisers

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Abstract

Macromonomer with styrenic polymerizable group was synthetized by anionic polymerization of ethylene oxide initiated by a mixture of potassium *p*- and *m*-vinylbenzyl alcoholate. The corresponding alcohol was prepared by modified two-step method described by Bamford et al. (Polymer 1973;14:330) using vinylbenzyl chloride as a starting material. Emulsion polymerization of styrene was carried out in the presence of either a styrenic macromonomer of poly(ethylene oxide) or conventional surfactants ethoxylated alkylphenol. In all cases small particle size of less than 75 nm in diameter were produced. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Styrene; Emulsion polymerization; Non-ionic surfactant

1. Introduction

It is generally observed in emulsion polymerization that the use of non-ionic surfactants alone to stabilise the particles results in rather large sized particles [1–5]. Further, it was observed several times, that bimodal particle size distribution might be sometimes obtained [4,6] because of the partition of surfactant between the aqueous and organic phases. In such case also acceleration of the polymerization takes place during the polymerization [6,7]. For these reasons, in the industrial practice, mixture of anionic and non-ionic surfactants are preferably used to get much more monomodal or even monodispersed particle size distribution. However, if the composition of such mixtures are not well balanced, increased amounts of non-ionic surfactants result in increasing of the final particle size.

2. Experiment

2.1. Materials

Styrene from Prolabo (France) was distilled under reduced pressure and stored at 20°C under nitrogen. DMSO, $CHCl_3$, *n*-heptane, Na_2SO_4, potassium acetate, sodium hydroxide, and ethanol from Prolabo (France) were used as received. Vinylbenzyl chloride was received as a gift from Dow Chemical Co. (USA) as a mixture of *p*- and *m*-isomers, and was used as received and stored at −20°C. The initiator, potassium persulphate, and buffer, sodium bicarbonate, were commercial products of Aldrich (USA) used without any further purification. The surfactants Triton X-305 and Triton X-405 (4-*t*-octylphenol ethoxylated with 30 and 40 ethylene oxide units, respectively) were from Aldrich (USA) as 70% solution in water. Water was removed by lyophilisation. The surfactants NP-30 and NP-40 (4-*t*-nonylphenol ethoxylated with 30 and 40 ethylene oxide units, respectively) from Schering (UK) were received as solids and were used as received. Distilled and deionised water was used throughout. THF from Aldrich (USA) used in an anionic polymerization was purified, partially dried and water was completely removed by distillation from sodium–benzophenone complex under steady flow of argon using a Vigreux's column with built-in trap for condensing THF. Ethylene oxide from Merck (Germany) was distilled before polymerization directly from a steel bottle without any further purification to a glass trap with built-in calibrated cylinder for precise volume measurement. Potassium hydride from Aldrich (USA) was washed with dry heptane to remove a mineral oil, dried, and stored under argon.

2.2. Preparation of macromonomer

The macromonomer was prepared via anionic polymerization of ethylene oxide initiated by potassium vinylbenzyl alcoholate. The corresponding vinylbenzyl alcohol was prepared as follows: A suspension of fine-powdered potassium acetate (40 g; 0.4075 mol) in 130 ml of DMSO,

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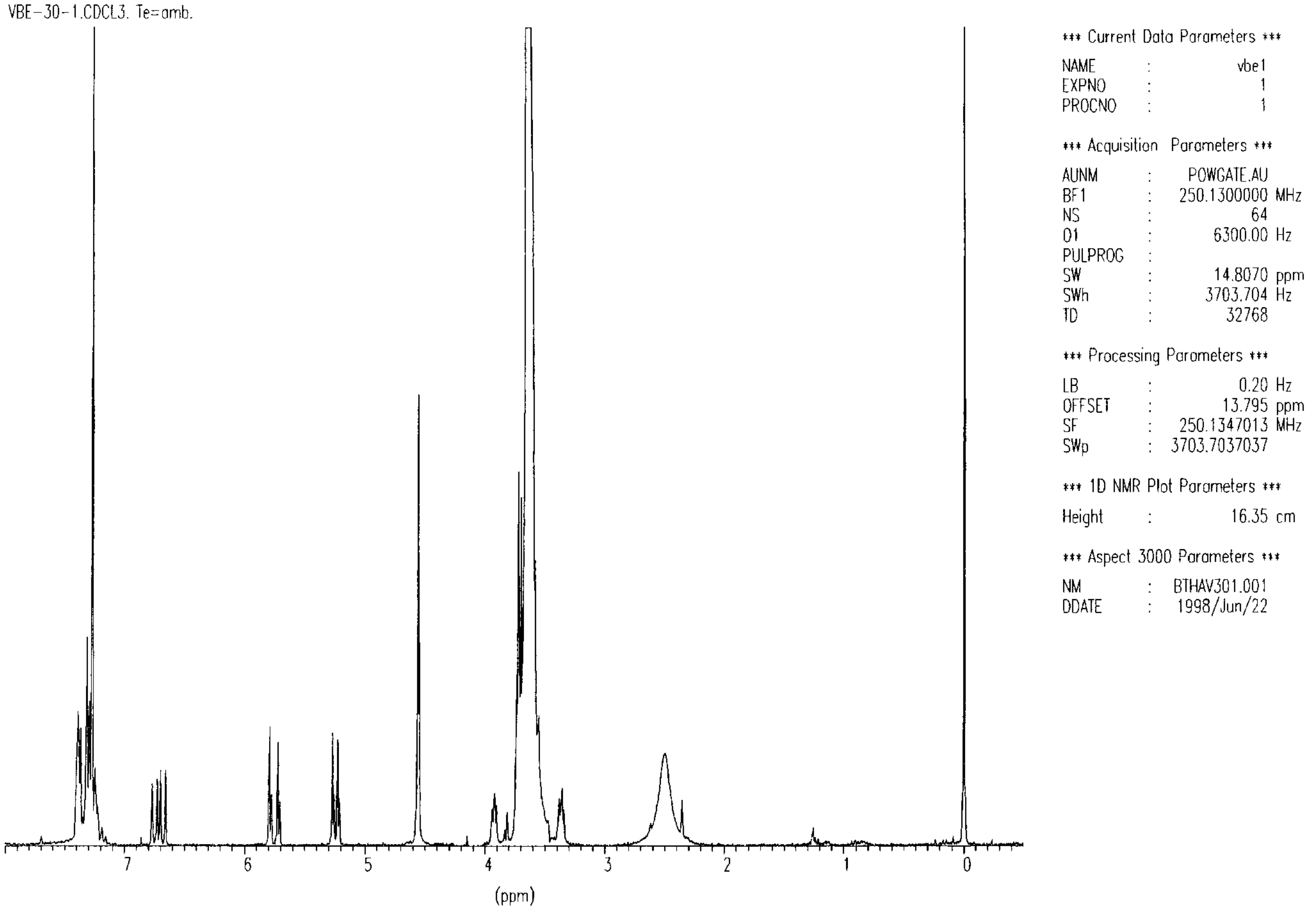

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Fig. 1. NMR spectrum of the macromonomer.

preheated to 40°C was placed into a 250 ml one-neck, round-bottomed flask. The suspension was stirred by magnetic stirrer at medium rate. Then, vinylbenzyl chloride (50 ml; 0.3519 mol) was added dropwise. The colourless suspension initially turned to dark blue, then to dark brown and the reaction mixture was stirred overnight. After completion of the reaction, in the flask a very fine suspension of potassium chloride and unreacted acetate was found. The reaction mixture was filtered and the precipitate was repeatedly washed with DMSO. To the filtrate 500 ml of water was then added and the separated oil was extracted with five 50 ml portions of $CHCl_3$. The extracts were dried over anhydrous Na_2SO_4 and the solvents were evaporated to give almost colourless viscous oil. This oil was then dissolved in 150 ml of ethanol and treated with a solution of sodium hydroxide (24 g; 0.6 mol) in 25 ml of water. The solution was slowly heated and kept under reflux for 0.5 h. After cooling down to room temperature 500 ml of water was added. The diluted reaction mixture was again extracted with five 50 ml portions of $CHCl_3$ and dried over Na_2SO_4 overnight in a refrigerator. After evaporation of solvent a yellowish oil was obtained and was then purified by fraction distillation under vacuum using Vigreux's column. A small amount of hydroquinone was added to prevent polymerization of vinylbenzyl alcohol at an elevated temperature. The fraction distillation gave pale yellow oil which was stored at -20°C where it solidified to an almost white solid. The anionic polymerization of ethylene oxide to prepare a macromonomer was carried out as follows: A 250 ml three-necked, round-bottomed flask equipped with pressure sensor was used. Vinylbenzyl alcohol (3.41 ml; 25 mmol) was dissolved in 50 ml of stirred, freshly distilled dry THF. Then, potassium hydride (0.97 g; 24.2 mmol) suspended in a small amount of THF was added. When the evolution of H_2 was finished, the reaction mixture was heated up to 30°C and became dark brown. The flask was evacuated and the pressure was registered. Ethylene oxide (37.4 ml; 0.75 mol) was then very carefully added and the addition rate was adjusted so the pressure inside the flask remained moderate, and during its addition the temperature inside the flask gradually increased. After dissolving, the reaction mixture was slowly heated up to 50°C and the internal pressure was closely watched to prevent overpressure and the reaction mixture was stirred for another 48 h. Polymerization was quenched by a methanol–hydrochloric acid mixture. The cooled mixture was filtered and the filtrate was added dropwise to 10 times excess of *n*-heptane. The procedure was repeated

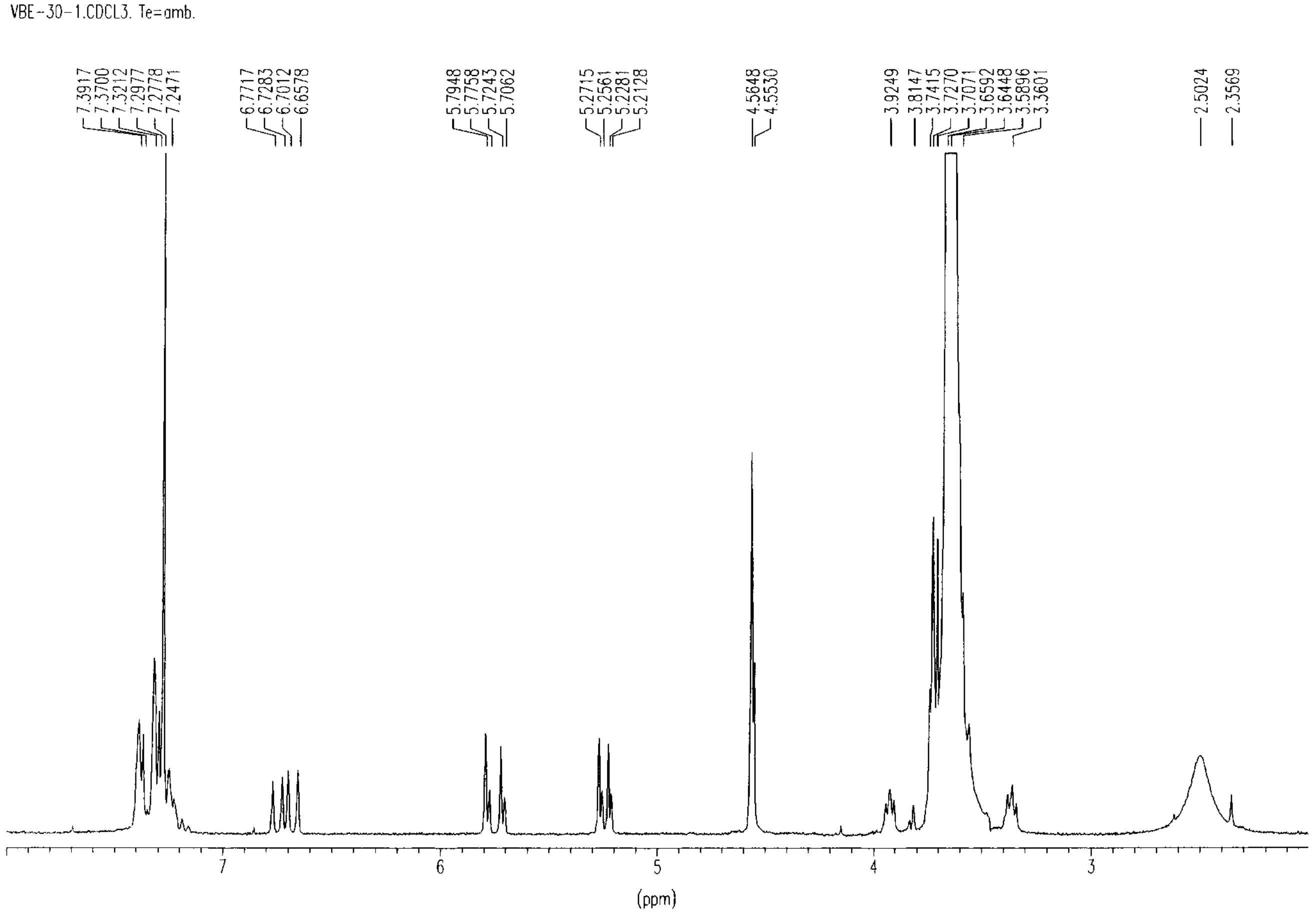

Fig. 1. (*continued*)

two times and a solvent was evaporated. Finally, the product was dried by lyophilisation from concentrated toluene solution to give brown solid that is stored at −20°C. The brown colour was brought about by the impurities in vinylbenzyl alcohol, but no effect on the polymerization was observed. The macromonomer was characterised through size exclusion chromatography using Waters 600 pump equipped with two Shodex KF 805L and one Shodex KF 803L columns in a series with Waters 410 differential refractometer and Waters 996 photodiod array detector using a polystyrene calibration standard, temperature 45°C, 700 psig, flow rate of THF 1 ml/min, and `millennium` software. The polymolecularity was estimated to be 1.07 and the average number of ethylene oxide units was reached to be as much as 28. On the contrary, the ^{1}H NMR experiment recorded using a BRUKER AMX 250 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard showed the number of ethylene oxide units to be 32 (see Fig. 1). The difference between the number of ethylene oxide units calculated from the NMR and SEC measurements comes from the use of the polystyrene calibration standards in SEC measurements. ^{1}H NMR in $CDCl_3$: $\delta_{\mathrm{Ar}}(-\mathrm{C_6}H_4-) = 7.247-7.392$ (bm); $\delta_{\mathrm{Vin}}(\mathrm{CH_2{=}C}H-) = 6.658-6.772$ (dd); $\delta_{\mathrm{Vin}}(\mathrm{C}H_{\mathrm{a}}\mathrm{H_b{=}CH}-) = 5.706-5.795$ (dd); $\delta_{\mathrm{Vin}}(\mathrm{CH_a}H_{\mathrm{b}}\mathrm{{=}CH}-) = 5.213-5.272$ (dd); $\delta_{\mathrm{Bnz}}(-\mathrm{C_6H_4}-\mathrm{C}H_2-) = 4.553-4.565$ (s); $\delta_{\mathrm{PEO}}(-\mathrm{C}H_2\mathrm{C}H_2\mathrm{O}-) = 3.590-3.742$ (b); $\delta_{\mathrm{OH}}(-\mathrm{O}H) = 2.502$ (b).

2.3. Emulsion polymerization

The emulsion polymerization were carried out in a double-walled glass reactor (250 ml) fitted with a condenser, a mechanical stirrer with glass paddles (425 rpm), and a nitrogen supply. The reactor was purged before the polymerization for at least 45 min with a slow stream of nitrogen. Simultaneously, the reactor was heated up to 60°C. A macromonomer or a surfactant solution was introduced, and then styrene was added. The resulting milky emulsion was purged with nitrogen for 5 min, and then an initiator solution was added. Starting the polymerization, the nitrogen stream was then stopped. The kinetics of emulsion polymerization were followed by gravimetry of aliquot samples after drying in a hot-air oven. For polymer characterisation, molecular weight of the polymers dissolved in a HPLC-grade THF from Aldrich (USA) was measured by SEC.

Table 1
Results of emulsion polymerization of styrene of basic recipe: 15 g of styrene, 150 g of water, 0.2342 g of potassium persulphate, 0.033 g of sodium bicarbonate; 60°C; 425 rpm

Run	1	2	3	4	5	6
Stabiliser	VBE	VBE	Trit. X-305	Trit. X-405	NP-30	NP-40
Amount (g)	7.5	3.75	7.5	7.5	7.5	7.5
Particle diameter (nm)	62.2	75.1	61.5	44.2	49.3	47.3
$M_n \times 10^3$ (g mol^{-1})	—	—	240	420	380	350
M_w/M_n	—	—	2.8	2.6	2.9	3.4

Particle size was measured by quasielastic light scattering (MALVERN Autosize).

3. Results

We have recently been interested to stabilise latex with polyoxyethylene macromonomers. Such compounds are not surfactants by themselves, being chiefly hydrophilic, except if the reactive group is attached to a hydrophobic moiety [8]. Surprisingly we do observe, in the polymerization of styrene, the formation of quite small particles. The amount of macromonomer used was rather high, because in order to get a good steric stabilisation, we wanted to obtain a high density of graft poly(ethylene oxide) sequences. However, using about the same amount of more conventional non-ionic surfactants, very similar results have been obtained. The corresponding data are reported in Table 1, while Fig. 2 displays the kinetic conversion curve of the same experiments.

The highest conversion is observed for NP-40 (Run 6), while it is lowest for Triton X-405 although the initial rates are comparable. The curve for Triton X-305 and NP-30, which have the same length of an ethoxylated sequence, are practically superimposable. In case of macromonomers, dividing by two the amount of stabiliser results in lower rate but slightly higher conversion.

Considering the particle size, the difference between Triton X-305 and X-405 is much more pronounced than for NP-30 and 40. Possible explanation for the difference in the two series of surfactants is likely to be caused by the broadness of the distribution of the ethoxylated sequence. In contrast, dividing by a factor two of the amount of macromonomer do not cause a too important increase of the particle size.

Of course, the weight ratio of surfactant to styrene is quite high in these experiments. However, the corresponding molar ratios are only about two or three times, what was reported, for instance, by Piirma and Chang [2]. Another difference between the macromonomer and the

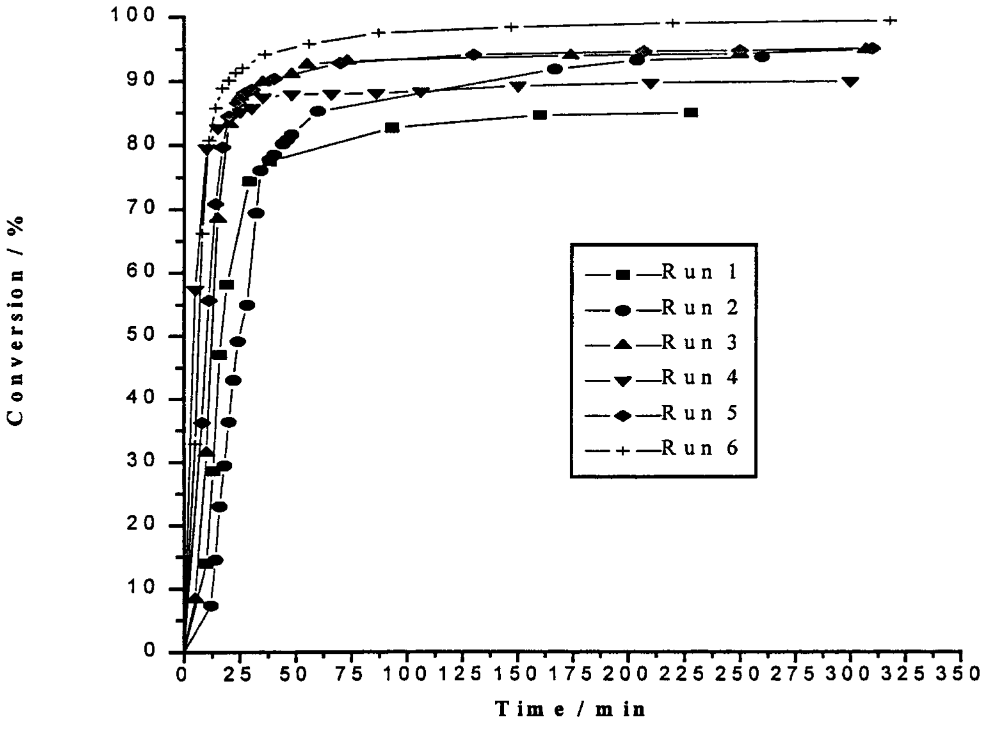

Fig. 2. The conversion-time dependencies for emulsion polymerization of styrene using different nonionic stabilisers.

conventional surfactants is the solubility of the resulting polymer. The samples obtained by using macromonomer are not soluble in THF, and then, their molecular weight cannot be measured. Obviously this is because of the high transfer constant of the benzylic proton of the macromonomer [9], which combined to the fact that termination in styrene radical polymerization takes place exclusively by coupling, well explains the cross-linking of the polymer. The usefulness of macromonomer used in our experiments is represented by much higher coagulation and precipitation stability in comparison with a non-ionic surfactants. When the sample is being precipitated, resistance against the precipitation showed in failed attempts to precipitate final polymer emulsion with ethanol. The only result was a slight increase of particle size of the emulsion (92.5 nm instead of 62.2 nm for Run 1, and 113.2 nm instead of 75.1 nm for Run 2).

Acknowledgements

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