Styrene-terminated poly(vinyl alcohol) macromonomers: 2. Free-radical (co)polymerization studies and application to the functionalization of latex particles

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The kinetics of the radical-initiated solution homopolymerization of a styrene-terminated poly(vinyl alcohol) macromonomer with a degree of polymerization (*DP*) of 7–9 (A) and copolymerization with styrene (S) have been investigated at 60°C in deuterated dimethyl sulfoxide solution using azobisisobutyronitrile as initiator and ^{1}H n.m.r. as the analytical technique. It was found that the macromonomer exhibits a lower reactivity than styrene and a model monomer with $DP=0$, which was confirmed by copolymerization with styrene ($r_A=0.9\pm0.1$ and $r_S=1.3\pm0.1$). The hydrophilic macromonomer was then copolymerized onto seed polystyrene latex particles by a shot growth process, a more efficient surface yield being ensured by using polar comonomers like methyl methacrylate and acrylonitrile.

(Keywords: styrene-terminated PVA; radical (co)polymerization; latex functionalization)

INTRODUCTION

In the past decade, there has been much work on the synthesis of various types of macromonomers, mainly using anionic polymerization techniques[1] and more recently group transfer polymerization[2]. It has been clearly shown that polymerization of such macromonomers appears to be a quite versatile method for the design of comb-like polymers and especially graft copolymers exhibiting specific properties[3].

However, a good control of the composition and, more precisely, the average sequence length requires a knowledge of the kinetic parameters characterizing the reactivity of these macromonomers in polymerization. In this domain, most of the investigations have been concerned with the radical-initiated homopolymerization and copolymerization of various types of macromonomers in the presence of low-molecular-weight monomers. It is now well admitted that many parameters can affect the reactivity of macromonomers[4], especially in copolymerization, namely the nature of the polymerizable double bond and of the polymer chain, the degree of compatibility between the macromonomer and the propagating chain, the macromonomer chain length, the nature of the reaction mixture, etc.

With a view to preparing hydrophilic macromonomers exhibiting narrow molecular weight distributions, we recently described[5] the synthesis of styrene-terminated poly(vinyl alcohol) (PVA) macromonomers by aldol GTP. The purpose of this paper is to report recent data on the free-radical homopolymerization and copolymerization of such macromonomers (with the *DP* of the polymer chain between 7 and 9) with styrene. In the first part, by solution polymerization in deuterated dimethyl sulfoxide (DMSO) we investigated the radical homopolymerization and copolymerization of a well-defined macromonomer ($DP=7$–9) with styrene (S), using azobisisobutyronitrile (AIBN) as an initiator, so as to determine the relative reactivity ($k_p/\sqrt{k_t}$) and reactivity ratios, respectively; in the second part, this macromonomer was used to functionalize polystyrene latex particles using a seed polymerization process.

EXPERIMENTAL

Reagents

Anhydrous dimethylformamide (DMF), deuterated dimethyl sulfoxide (d_6-DMSO, from Spin et Techniques), deuterium oxide (D_2O from Spin et Techniques), azobisisobutyronitrile (AIBN, 98% purity, from Merck), potassium persulfate (KPS, >99% purity, from Riedel-de-Haën) and 3-(*N*,*N*-dimethyllaurylammonio)propanesulfonate (97% from Fluka) were used as received; styrene, methyl methacrylate (MMA) and acrylonitrile monomer (all 99% purity, from Janssen) were distilled under vacuum prior to use. Sodium and dipotassium hydrogenophosphate (K_2HPO_4, reagent grade, from Merck) were used as an electrolyte and a buffer, respectively. Deionized water was purged with N_2 for 1 h before use.

The syntheses of the macromonomer and the ester model monomer have already been described in detail in the first paper of this series[5]; they have been well

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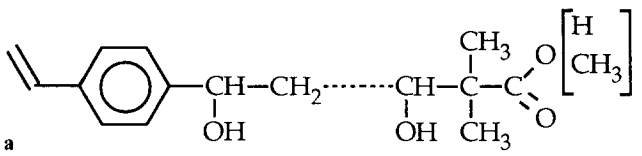
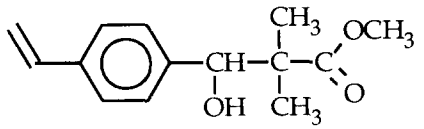
characterized by ^1H and ^{13}C n.m.r. spectroscopy and in addition by size exclusion chromatography (s.e.c.) for the macromonomer. The following formulae describe the PVA macromonomer (with $DP = 7$–9) (**a**, ester form 54 mol%) and the ester monomer methyl 2,2-dimethyl-3-hydroxy-3-(4′-vinylphenyl)propanoate (**b**, P29H), respectively:



a



b

Solution polymerization

Procedure. Polymerization experiments were performed in a three-necked, round-bottomed flask equipped with a magnetic stirrer and argon inlet. It was initially loaded with (macro)monomer(s) and most of the solvent: DMF for the model monomer (P29H) homopolymerization, and d_6-DMSO for the macromonomer homopolymerizations (*Table 1*) and for the macromonomer and styrene copolymerizations (*Table 2*). The mixture was stirred and flushed with argon for 1 h afterwards, the temperature was raised to 60°C using a thermostatted oil bath. Finally, the initiator was dissolved in a small amount of solvent and was added into the reaction mixture: this marked the beginning of the reaction. An inert atmosphere was maintained throughout the experiment.

Kinetic study. Samples were withdrawn at different reaction times and were stored at a temperature of −20°C in order to stop the polymerization.

For the P29H homopolymerization experiment, the monomer consumption *versus* time curve was established from gas chromatography (g.c.) analysis: separation was performed with a DELSI equipment DI200 on a Carbowax column (10% Carbowax 20M on Chromosorb WAW, 80/100 mesh, 1 m column length) at a temperature of 200°C and using flame ionization detection. The amount of residual monomer was calculated from the monomer and solvent peak areas according to the formula

$$[\text{monomer}]_t = \frac{(\text{monomer peak area})_t}{(\text{DMF peak area})_t} \times \frac{(\text{DMF peak area})_0}{(\text{monomer peak area})_0} \times [\text{monomer}]_0$$

Table 1 Homopolymerization recipes of a PVA macromonomer (HP0) and a model compound (HP1)

Sample	Macromonomer[a]	AIBN	Solvent
HP0	1.0143 g (0.52 mmol)	0.006 g (0.036 mmol)	4.65 g (d_6-DMSO)
HP1	0.2323 g (0.99 mmol)	0.0122 g (0.074 mmol)	5 g (DMF)

[a] For the macromonomer, the reported amount takes the residual TBA into account and the axact amount is given in parentheses

Table 2 Copolymerization recipies for styrene–PVA macromonomer mixtures

Sample	Macromonomer[a]	Styrene	AIBN	d_6-DMSO
CMS2	1.0897 g (0.56 mmol)	0.1587 g (1.5 mmol)	0.0152 g (0.09 mmol)	5.3 g
CMS3	1.2424 g (0.64 mmol)	0.0585 g (0.56 mmol)	0.0192 g (0.12 mmol)	5.5 g

[a] For the macromonomer, the reported amount takes the residual TBA into account and the exact amount is given in parentheses

The macromonomer homopolymerization experiment was carried out in d_6-DMSO which allowed direct ^1H n.m.r. analysis: the conversion was calculated from the total vinylic proton peak area (I_M) as compared to the tetrabutylammonium (TBA) protons[5] (I_{ref}: $(H_7C_3\underline{CH_2})_4N^+$, $\delta = 3.46$ ppm) (TBA was an impurity which was not consumed by the polymerization reaction). We used the following formula to calculate the conversion at time t

$$\text{conversion } (\%) = \frac{(I_M/I_{ref})_0 - (I_M/I_{ref})_t}{(I_M/I_{ref})_0} \times 100$$

Macromonomer and styrene copolymerization reactions were carried out in d_6-DMSO: the overall conversion and monomer mixture composition were directly determined from ^1H n.m.r. analysis of the reaction medium. Overall conversion was calculated according to the above formula in which I_M represents the sum of the peak areas corresponding to given vinylic protons of styrene (I_S) and macromonomer (I_A) (doublets with chemical shifts in the range 5.7–5.9 ppm, see *Figure 2*).

The monomer mixture composition was calculated from the integrations of the macromonomer (I_A) and styrene (I_S) vinylic protons according to the formula

$$f_A = \frac{I_A}{I_A + I_S}$$

where f_A represents the macromonomer mole fraction.

Functionalization of latex particles

Preparation of the polystyrene seed latex. The polystyrene seed latex was obtained by emulsifier-free polymerization of styrene using K_2HPO_4 as a buffer. Polymerization was carried out in a four-necked glass reactor equipped with a glass paddle agitator, condenser, nitrogen inlet and temperature controller. The polymerization procedure and recipe have already been reported[6]. After 7 h, conversion was found to be 99% and the latex was filtered through quartz wool and stored at 4°C. Particle size as measured by quasi-elastic light scattering (QELS) and transmission electron microscopy (TEM) was 320 nm.

Functionalization of the seed latex by the macromonomer. The seed latex was first centrifuged and redispersed so as to eliminate any residual electrolyte or initiator; then in some experiments it was post-stabilized around or below complete saturation with a zwitterionic surfactant. A given amount was purged with N_2 for 12 h, then it was pre-swelled with styrene monomer for 1 h. Concerning the addition of the macromonomer, this was performed using various procedures as detailed in *Table 3*: (i) adding first the initiator aqueous solution, then subsequently the macromonomer solution under shot or

Table 3 Latex recipes[a]

Latex	Seed latex[b] (g)	Macromonomer[c] (g)	Comonomer (g)	Initiator (g)	Addition method
LF10[d]	30 (0.861)	0.11 (0.012)	0.061 (S)	0.0314	Shot
LF17	30 (0.864)	0.116 (0.031)	0.1157 (S)	0.0034	Semicontinuous
CP4	25 (0.720)	0.116 (0.027)	0.0989 (MMA)	0.0066	Semicontinuous
LF19	15.1 (1.465)	0.037	0.226 (MMA)	0.0067	Shot
LF20	20.10 (1.400)	0.033	0.3308 (S+AN)	0.0069	Semicontinuous

[a] Styrene, S; methyl methacrylate, MMA; acrylonitrile, AN
[b] Amount of dried polymer particles in parentheses (g)
[c] Residual TBA in parentheses (g)
[d] No post-stabilization of the seed latex

semicontinuous conditions; and (ii) same procedure as (i) but also adding semicontinuously a comonomer which could be styrene, MMA or acrylonitrile.

Latex samples were withdrawn at various reaction times to control colloidal stability, particle size (QELS) and macromonomer conversion. At the end of the reaction (around 7 h), a fraction of the latex was centrifuged (12 000 rev min^{-1} over 10 min) in order to separate the serum from the particles. After drying, the serum was redissolved in D_2O and then analysed by ^1H n.m.r. so as to quantify the amounts of residual unconverted and polymerized macromonomer. Polymer particles were dissolved in $CDCl_3$ or d_6-DMSO; in this latter case, the polystyrene core was hardly soluble and therefore only the shell-polymerized phase (supposedly macromonomer-rich) was roughly analysed.

(Co)polymers and latex characterization

High resolution liquid n.m.r. spectroscopy. This was carried out with a Bruker AC200 apparatus working at 200 MHz for protons and 50.3 MHz for ^{13}C; deuterated chloroform, acetone and water were used as solvents and chemical shift values were measured in ppm in reference to tetramethylsilane (TMS) and d_4-trimethylsilyl-3-propionic acid (d_4-TSP) used as internal standards. Integration of the different peaks of the ^1H n.m.r. spectra of the copolymers allowed calculation of their mole fractions.

To analyse the latexes, dried particles were redispersed in d_6-DMSO; then a given amount of polymer particles was used in which a precise quantity of dioxane was added as internal reference (except in the case where MMA was used as comonomer). Owing to the low content of the macromonomer in the particles, around 1000 scans at 57°C were necessary for good signal to noise ratio; the areas under the peaks were measured by planimetry on suitably enlarged spectra. When the amount of water was too high, a water-suppression acquisition sequence was used.

X.p.s. analysis of latexes. X-ray photoelectron spectroscopy (X.p.s.) was performed on a V. G. Scientific X-ray Escapope apparatus using monochromatic aluminium Kα radiation (1486.6 eV) at a potential of 20 kV and an X-ray current of 30 mA. The analysed surface area was 1.2 × 1.2 mm with a depth less than 100 Å. The sample was obtained by cleaning a small amount of latex (so as to eliminate any electrolyte, residual initiator and water-soluble oligomers left in the serum) by centrifugation followed by drying under reduced pressure at low temperature.

RESULTS AND DISCUSSION

Solution homopolymerization and copolymerization with styrene in d_6-DMSO

Macromonomer homopolymerization. From free-radical homopolymerization kinetic results, according to the relationship giving the decrease in monomer concentration as a function of time and taking into account initiator consumption, the graph representing $\ln([M]_0/[M]_t)$ or $\ln(1/1-x)$ *versus* $(1-e^{-k_d t/2})$ allows, from the slope, the calculation of $k_p/\sqrt{k_t}$.

$$\ln([M]_0/[M]_t) = \ln(1/1-x)$$
$$= 2(k_p/\sqrt{k_t})\sqrt{(f[I]_0/k_d)}(1-e^{-k_d t/2})$$

where $[M]_0$ and $[M]_t$ are monomer concentrations (initial and at time t, mol l^{-1}), x is the monomer conversion, k_p and k_t are, respectively, the propagation and termination rate constants (l mol^{-1} s^{-1}), f is the initiator efficiency, k_d is the initiator decomposition rate constant (s^{-1}) and $[I]_0$ is the initial initiator concentration (mol l^{-1}).

The constant k_d has been evaluated as 1.2×10^{-5} s^{-1} for AIBN at 60°C in DMSO (6.21×10^{-5} s^{-1} for AIBN at 71.2°C in DMF, with an activation energy of 140 kJ mol^{-1})[7].

The homopolymerization kinetics of the model monomer (P29H) and macromonomer were established and the results are presented in *Figure 1* from which the initial slope values were determined. The $k_p/\sqrt{k_t}$ ratios were then calculated and these are reported in *Table 4* together with those of styrene and *p*-formylstyrene, as obtained under the same conditions in earlier work[6]. It is clearly shown that the macromonomer exhibits a lower reactivity than the low-molecular-weight styrene derivatives. Such an effect is difficult to explain since it can be caused by an increase in k_t or a decrease in k_p: the former hypothesis seems unrealistic since the termination reaction between two hindered macroradicals should be disfavoured. On the contrary,

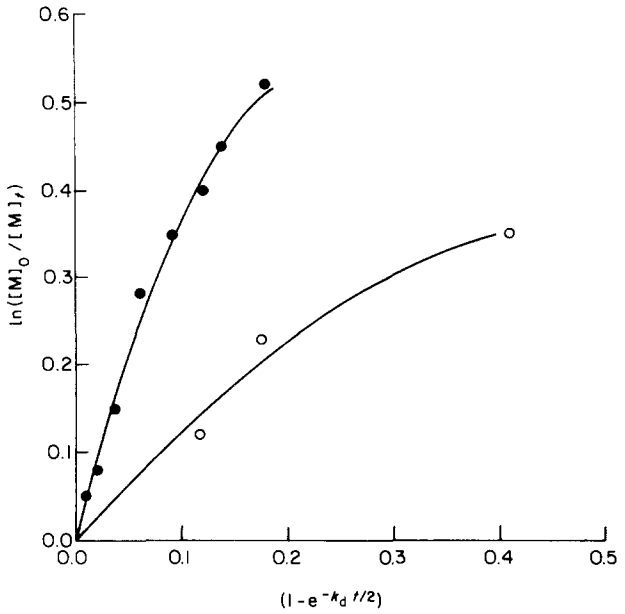


Figure 1 Semilogarithmic variation of the monomer consumption $\ln([M]_0/[M]_t)$ *versus* the decomposition rate of the initiator: (○) PVA macromonomer; (●) model monomer

Table 4 Comparison of the relative reactivity ($k_p/\sqrt{k_t}$) of the macromonomer ($DP = 7$–9) with the relative reactivities of various styrene derivatives

Monomer	Slope[a]	$k_p/\sqrt{k_t}$ $(mol^{-1/2}\,l^{1/2}\,s^{-1/2})$
p-Formylstyrene	8.0	0.135
P29H	3.15	0.065
Styrene	2.03	0.042
Macromonomer	1.0	0.027

[a] From $\ln([M]_0/[M]_t)$ curve

the propagation reaction between a highly branched macroradical and a terminal double bond bearing a polymer chain is probably more affected (owing to steric hindrance around the radical locus) than in the case of the low-molecular-weight monomers. This was shown and extensively discussed by Tsukahara *et al.*[8] for the radical polymerization behaviour of styrene macromonomers having methacryloyl or vinylbenzyl end groups (with molecular weights of 4400 and 4980, respectively) and interpreted in terms of diffusion control of the macromonomer polymerization.

Macromonomer and styrene reactivity ratios. A preliminary study was directed towards selecting a suitable and precise analytical method for following the consumption of each monomer; ^{1}H n.m.r. was found to be most appropriate and *Figure 2* gives an example of the vinylic region of the spectrum corresponding to a styrene–macromonomer reaction mixture and shows the presence of two well-separated doublets belonging to each monomer. Using this technique, it was possible to estimate with good precision the variation of the macromonomer mole fraction in the monomer mixture (f_A) with conversion. Two copolymerization kinetics were accurately followed using the experimental conditions reported in *Table 2*. The relatively low initial weight concentration in macromonomer (around 15%) should not raise the viscosity of the reaction medium too much, therefore preventing diffusion control of the macromonomer addition as recently shown by Radke and Müller[9]; the normal time–conversion curves obtained in both experiments seem to support this assumption.

From the graph representing f_A as a function of conversion x (*Figure 3*), the initial slope gives F_A, i.e. the initial instantaneous copolymer composition (macromonomer mole fraction), according to the formula

$$\left(\frac{df_A}{dx}\right)_{t=0} = f_{A0} - F_{A0}$$

Therefore the slope estimation allows us to calculate F_{A0}. From the f_{A0} and F_{A0} values corresponding to the CMS2 and CMS3 experiments, the monomer reactivity ratios were estimated with a relatively large error since only two initial monomer compositions were considered. The values obtained are $r_A = 0.9 \pm 0.1$ and $r_S = 1.3 \pm 0.1$.

These copolymerization parameters suggest that the relative reactivity of the macromonomer (as defined by $1/r_S$) towards the polystyryl radical is decreased although the molecular weight of the polymer chain is not large (600). This behaviour confirms the tendency reported in the literature and particularly in the case of copolymerizations of styrene-terminated poly(ethylene oxide) with styrene: Niwa *et al.*[10] found $r_A = 0.86$ and $r_S = 1.20$ for a macromonomer with a molecular weight of 2140 and Hamaide *et al.*[11] found $r_A = 1.04$ and $r_S = 1.18$ for a macromonomer with a molecular weight of 236.

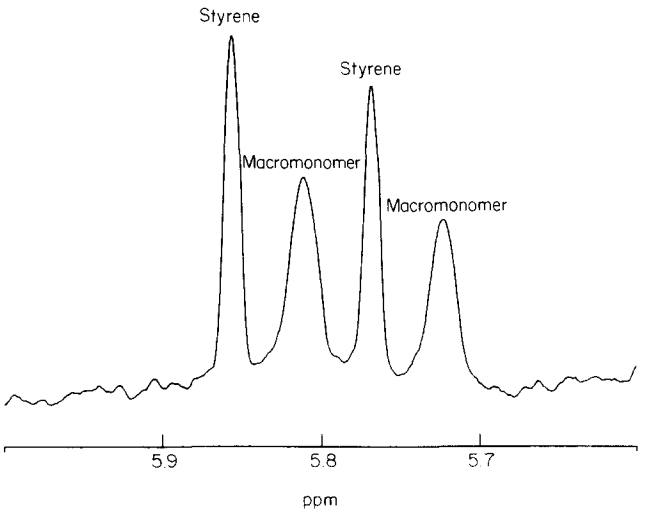


Figure 2 Part ^{1}H n.m.r. spectrum (200 MHz) of the styrene–macromonomer reaction mixture during copolymerization CMS3 (enlarged between 5.6 and 6.0 ppm)

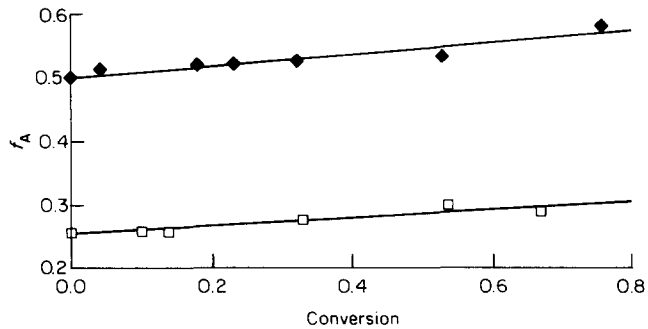


Figure 3 Variation of the comonomer feed composition f_A *versus* conversion (A = macromonomer): (◆) $f_{A0} = 0.26$ (CMS2); (□) $f_{A0} = 0.42$ (CMS3)

(Co)polymer characterization. From the copolymerization experiments, the formed copolymers were recovered upon precipitation in water in order to eliminate residual monomer and traces of tetrabutylammonium fluoride, then filtered and dried under vacuum. They were found to be highly soluble in DMSO, DMF and THF–methanol mixtures, and insoluble in water, chloroform, acetone, pure methanol and pure THF.

Copolymers were first analysed by ^{1}H n.m.r. in d_6-DMSO and *Figure 4* shows a spectrum of sample CMS3; by integration of the aromatic proton resonances (6–7.5 ppm) (corresponding to both monomers) and the C*H*OH proton resonance (corresponding to the macromonomer alone), the copolymer compositions were calculated for the two copolymer samples. Values of 20 and 30 mol% were obtained for samples CMS2 and CMS3, respectively. These values can be compared to the theoretical values (based on the above determined r_{ij} and numerical integration of the copolymerization equation) of 23 and 47 mol%, respectively; the noticeable difference in the case of the latter sample was ascribed to the important uncertainty in discriminating the C*H*OH domain.

Copolymers were also characterized by ^{13}C n.m.r. as illustrated in *Figure 5*, which shows the general spectra of the two samples.

Functionalization of polystyrene seed latex by the macromonomer

Based on a knowledge of its reactivity in homopolymerization and copolymerization, the functionalization of polystyrene seed particles by a PVA macromonomer was investigated in order to design hair-like particles consisting of poly(vinyl alcohol) chains bearing a terminal reactive group.

The high water solubility of the macromonomer with $DP > 5$ motivated us to select a functionalization process suitable in the case of water-soluble and reactive monomers and favouring an efficient incorporation onto hydrophobic particles[12]. A core–shell polymerization process was selected and various recipes were tried so as to optimize the incorporation of macromonomers with $DP = 7$–9: (i) by adding the macromonomer in one shot or semicontinuously; and (ii) by using comonomers with various polarities so as to control the amphiphilicity of the water-originated oligomers and then to increase their subsequent rate of capture by the particles. Styrene was first used, then MMA and acrylonitrile.

Moreover, the presence of TBA residues in the macromonomer (which was used as a hydrolysing agent for recovering the PVA chain during its synthesis[5]) induced, as evidenced in preliminary experiments, the flocculation of latex particles during the synthesis. This organic cation exhibits an amphiphilic character and a recent paper[13] reported the ability of such ions to destabilize oil–water emulsions at very low concentrations (10^{-3} mol l^{-1}). In order to prevent such a problem, post-stabilization of the seed was imparted using a sulfobetaine-type zwitterionic surfactant which was found to provide strong protection against flocculation by monovalent and divalent salts[14]. A concentration ensuring surface coverage below complete saturation was used to avoid secondary particle nucleation.

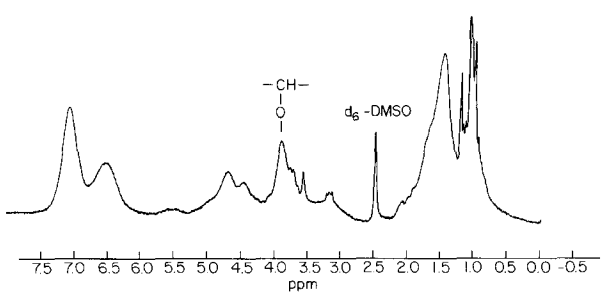


Figure 4 ^{1}H n.m.r. spectrum (200 MHz) of the CMS3 copolymer in d_6-DMSO (350 K)

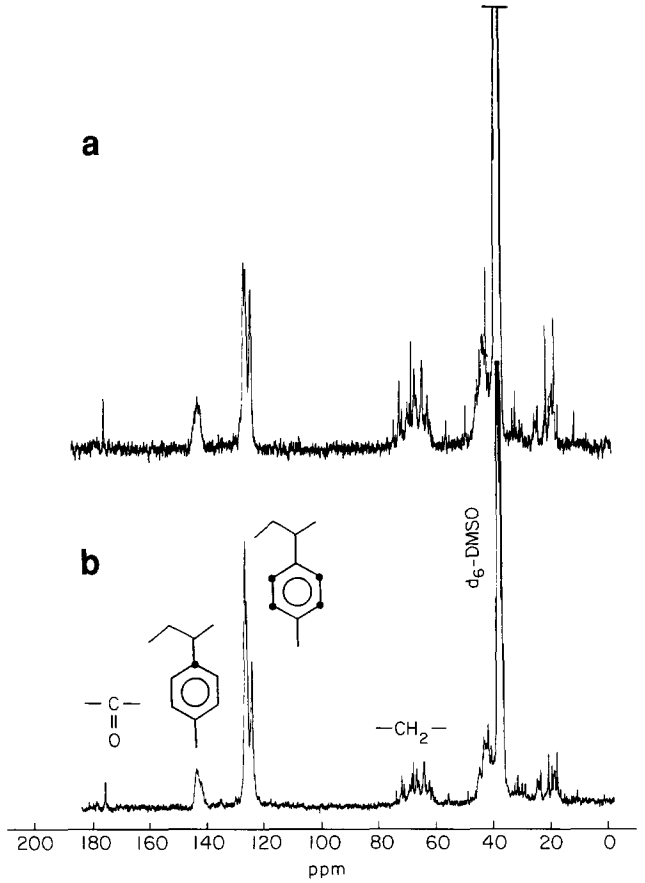


Figure 5 ^{13}C n.m.r. spectra (50.3 MHz) of CMS3 (a) and CMS2 (b) copolymers in d_6-DMSO

Results are reported in *Table 5* giving the fractions of polymacromonomer left in the aqueous phase after centrifugation of the final latexes (as quantified using ^{1}H n.m.r., see *Figure 6*) together with the particle sizes of these latexes.

In spite of the selected process a major problem clearly arises, i.e. the water-phase polymerization of the macromonomer as revealed for the LF10, LF17 and CP4 experiments. It was indeed found that a large quantity of polymacromonomer is formed in the aqueous phase (or poorly physically adsorbed onto the seed particles) whether the macromonomer is added either in one shot or even semicontinuously onto the pre-swelled particles just after the introduction of the initiator solution. No significant difference was found whether styrene or methyl methacrylate was used as comonomer.

This result is tentatively explained by estimating the expected concentrations of both monomers in the aqueous phase where polymerization starts using the partition coefficients of the comonomers between the organic and aqueous phases and assuming that all the

Table 5 Functionalization of polystyrene seed particles[a] by PVA macromonomer (M): effect of experimental variables on macromonomer conversion and particle size

Latex	Comonomer	$\frac{[M]}{[M]+[comonomers]}$	Amount of converted macromonomer in aqueous phase (mol%)	Particle size by QELS (nm)
LF10	Styrene	0.21	95	–
LF17	Styrene	0.15	40[b]	350
CP4	MMA	0.16	95	350
LF19[c]	MMA	0.027	20	348
LF20	Styrene + acrylonitrile	0.015	5	353

[a] Diameter = 325 nm
[b] The remainder is mostly macromonomer
[c] Partially flocculating aggregates can be easily redispersed

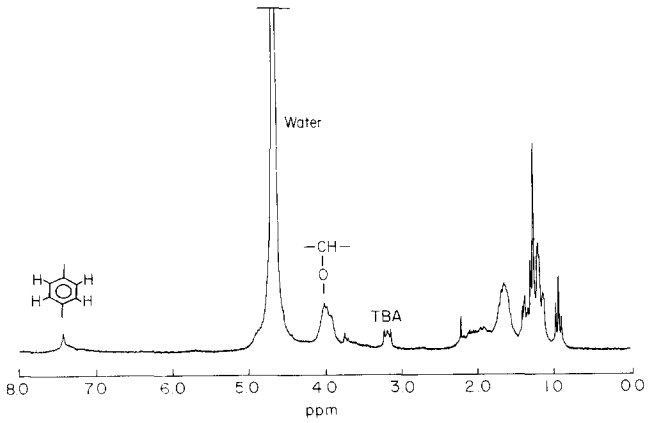


Figure 6 ^{1}H n.m.r. spectrum of dried serum of LF10 latex in D_2O

macromonomer is located in the aqueous phase. These coefficients were reported to be nearly 0.0002 for styrene[15] and 0.05 for MMA[16]. The value for styrene is too low to ensure enough molecules in the aqueous phase (for the experiments performed with styrene), which suggests the formation of a pure homopolymer of the macromonomer. On the contrary, using MMA as comonomer and considering the amount given in the CP4 recipe, values of 1.7 and 7.2 mmol l^{-1} can be deduced, respectively, for MMA and the macromonomer in the aqueous phase; however, the low surface incorporation yield obtained for the CP4 run seems to indicate that the oligomers from the water phase exhibit too high a hydrophilicity to be captured by the seed particles.

Finally, we tried to overcome this water-phase polymerization with a better control of the aqueous phase comonomer composition by changing the comonomer feed composition and also by substituting MMA with acrylonitrile, a polar monomer with a higher water solubility[17] (in the range of 80 g l^{-1}) and whose oligomers are probably more readily captured by the particles. The data corresponding to such experiments (LF19, LF20) clearly show that a higher surface yield is ensured since the amounts of macromonomer recovered in the latex sera are quite low. In the first experiment (LF19), the estimated concentrations of MMA and macromonomer in the aqueous phase are 7.5 and 4.7 mmol l^{-1}, respectively. This composition (around 60 mol% in MMA) would lead to more MMA-rich oligomers that are probably more easily captured by the seed particles: the amount of converted macromonomer left in the aqueous phase is indeed only 20%. This quantity is even decreased (5%) with acrylonitrile (LF20): the same explanation holds, the partition towards water for this monomer being more favourable than for MMA. Hence the above approach to estimating the aqueous phase concentrations of the monomers seems correct in this system and is a suitable guide for controlling the macromonomer polymerization at the particle loci.

Moreover, such an incorporation method was found to be quite reproducible since the same surface yield (95%) was obtained using a recipe duplicating the LF20 experiment. In addition, the particle size increase as obtained by QELS is nearly the predicted value assuming complete conversion in the particles and electron microscopy did not show any secondary particle nucleation, indicating that the shell growth mechanism[18] of the seed latex particles occurred exclusively.

More work was performed in order to characterize directly the presence of the macromonomer at the particle surface. The techniques used were ^{1}H n.m.r. and X.p.s.

With the first method, the principle consisted in dispersing the dried latex particles (separated after centrifugation to eliminate the serum) in d_6-DMSO, a solvent which was found partially to swell the polystyrene-based particles within a thickness of shell representing 5 to 7% of the particle radius[19]; therefore, the macromolecules located in this outer layer are more accessible and mobile than those in the interior of the particle.

This procedure was applied to the functionalized latex. *Figure 7* shows the ^{1}H n.m.r. spectrum of latex LF20, and the observation of a resonance peak around 4 ppm clearly shows (in comparison with the PS seed blank sample) the presence of protons corresponding to CHO groups belonging to the poly(vinyl alcohol) chain. The analysis was pursued in order to quantify the amount of macromonomer covalently bound at (or near) the particle surface. In the case where MMA was used as comonomer (LF19 sample), it was first found that the macromonomer/MMA weight ratio was close to the theoretical value deduced from the recipe (i.e. 0.17). However, remembering that only 20% of the polystyrene seed is accessible (and using aromatic protons as the internal standard), it was estimated that 25 to 30% and 30 to 35% of the overall amounts of MMA and

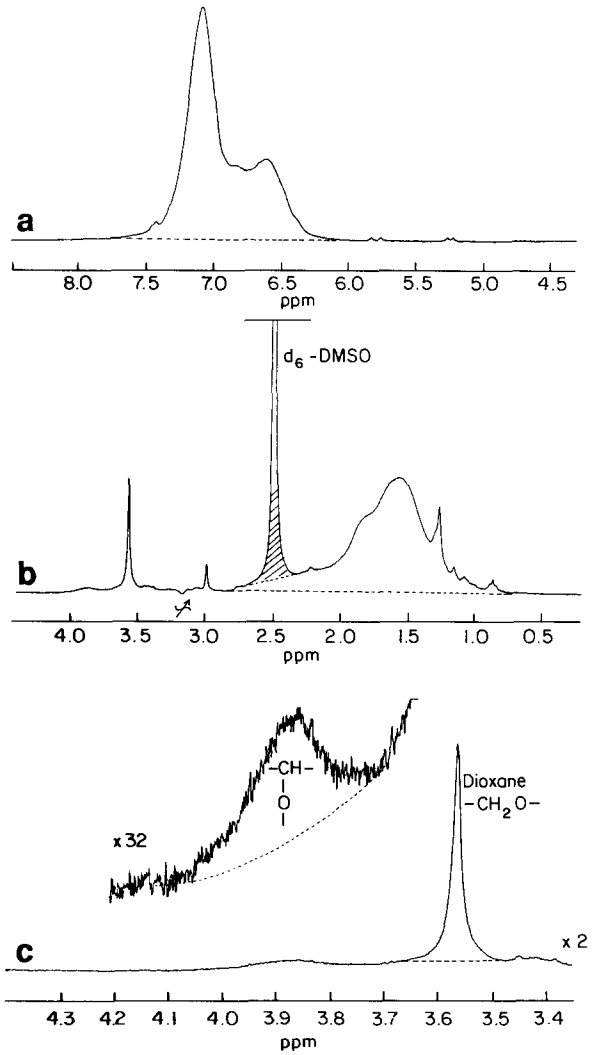


Figure 7 ^{1}H n.m.r. spectrum (200 MHz) of dried particles (latex LF20) swollen in d_6-DMSO at 57°C (water-suppression sequence): (a) aromatic resonances from styrene units; (b) aliphatic resonances (CH_2CH) from styrene and acrylonitrile; (c) enlargement of vinyl alcohol (CH(OH)) and dioxane (CH_2O) resonances

Table 6 Elemental ratios and various C ratios from X.p.s. analysis of seed (LPS7) and functionalized (LF20) latexes

	Elemental ratios (%)			C1s area ratios (%)	
Latex	C	O	N	C–C/C–H	C–O
LPS7	96	4	–	–	–
LF20	83.8	11.6	4.6	85	15

macromonomer, respectively, are detected; this value for the macromonomer is lower than that deduced from the serum analysis (80% in the particles) and might indicate that some of these monomers are not accessible (especially the MMA which could have diffused more deeply into the particles).

In the case where acrylonitrile was used as comonomer together with styrene (LF20 sample), the same procedure using dioxane as the internal standard leads to about 90% of the macromonomer being incorporated in the shell layers of the seed particles, which is close to the value deduced from the serum analysis (95%). It seems that this method, based on the preferential swelling of the shell layers of the functionalized latex particles (in our case using d_6-DMSO), provides useful information on the fate of the second-stage copolymerized material.

Such a result was confirmed by comparing an X.p.s. analysis of the cleaned functionalized latex (LF20) with that of the seed latex (LPS7). Results shown in *Table 6* give the elemental ratios in C, O and N. It is found that these three elements are detected in LF20 with the proportions 83.8, 11.6 and 4.6%, respectively, whereas in the blank sample (LPS7) oxygen is only present at a lower proportion, i.e. 4%. In this latter case, the presence of oxygen arises from the surface sulfate charges (originating from initiator decomposition) and eventually some carboxyl end groups covalently bind to the particle surface during the latex synthesis. Hence, the higher atomic proportion in O determined for the functionalized latex suggests the presence at the particle interface of many C–O structural species, presumably from the chemically anchored poly(vinyl alcohol) chains belonging to the macromonomers. This is clearly confirmed through a detailed analysis of the carbone region (C1s) which shows the contribution of the C–O at a higher binding energy (1.7 eV) corresponding to the ether carbon[20]. As indicated in *Table 6*, this second peak, after deconvolution of the C1s core levels, corresponds to an atomic proportion of about 15%, which is largely superior to the theoretical value, around 2%, if considering a homogeneous distribution of the styrene–acrylonitrile–macromonomer terpolymer in the shell regions of the final particles.

From both analytical methods it may be concluded that the poly(vinyl alcohol) macromonomer has been preferentially copolymerized at or near the particle surface; however, there is no precise indication as to what extent the PVA hydrophilic chains are expanded out into the aqueous phase.

CONCLUSIONS

The kinetic study of the solution homopolymerization in DMSO of a poly(vinyl alcohol) macromonomer (with $DP=7$–9) by ^{1}H n.m.r. showed that the PVA relative reactivity is significantly lower than that of styrene and that of an ester monomer model. In copolymerization with styrene, the obtained reactivity ratio ($r_S=1.3\pm0.1$ and $r_A=0.9\pm0.1$) confirmed such a behaviour (macromonomer addition slightly disfavoured); however, the copolymerization drift with conversion is not important, at least under the reported experimental conditions. This study was investigated with only one type of macromonomer which is obviously not sufficient for characterizing the kinetic behaviour of all such compounds.

This macromonomer was used to functionalize polystyrene latex particles using a shot growth process. Efficient incorporation (>80%) was obtained when it was polymerized in the presence of monomers like acrylonitrile or MMA (more polar than styrene) and provided that the feed composition was not too rich in the hydrophilic macromonomer. This can be explained by a polymerization mechanism in which the water-initiated oligomers play a predominant role and must exhibit an amphiphilic structure favouring their capture by the existing particles. The characterization of the final particles by ^{1}H n.m.r. and X.p.s. analyses gave further evidence for the presence of hydrophilic PVA chains at or near the surface, which confirms that the second-stage

polymerization mainly occurred in the shell regions of the seed particles.

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