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Dispersion polymerization of styrene in aqueous ethanol media using poly(ethylene oxide) macromonomer as a polymerizable stabilizer

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The kinetics of dispersion polymerization of styrene with a small amount of ω-methoxy poly(ethylene oxide)$_{40}$ undecyl-α-methacrylate macromonomer (PEO-R-MA-40) in the ethanol-water media was studied. A maximum and constant rate of polymerization for this system appeared at the 18%—55% conversion of styrene to polystyrene. However, only 50% of the amphiphilic PEO macromonomer was found to be grafted in the copolymer (stabilizer) after 10 h of polymerization at 65°C. But as high as 98.5% conversion of styrene to polymer was attained. The initial rate of polymerization follows the scaling relationship, $(R_p)_i \propto [\text{PEO-R-MA-40}]_0^0$ $[\text{styrene}]_0^{0.92}$ $[\text{AIBN}]_0^{0.90}$. It increased with increasing temperature but decreased with increasing water content because of the solvency effect in the reaction medium. The molecular weight M_w of polymer increased with increasing conversion of styrene up to about 55%. It then decreased slightly towards higher conversions, leading to a broader molecular weight distribution. The activation energies for the dispersion polymerization in the initial stage (< 6% conversion) and in rate interval II were 122.3 and 66.7 kJ mol^{-1} respectively. The characterization of the monodisperse latex particles of about 250 nm in diameter was carried out by the transmission electron microscope (TEM), *FT*i.r., n.m.r. and X-ray photoelectron spectroscope (XPS). The XPS result shows that the grafted PEO macromonomers were enriched and anchored on the surface of polystyrene latex particles with a top surface composition of 28% macromonomer. © 1997 Elsevier Science Ltd.

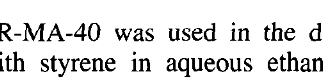
(Keywords: dispersion polymerization; poly(ethylene oxide) macromonomer; polymerizable stabilizer)

INTRODUCTION

Amphiphilic PEO macromonomers are a unique type of macromonomers. They can readily be organized to form micelles[1–3] and to proceed an unusually high rate of micellar polymerization in an aqueous medium compared with their slow solution polymerization in benzene. When they are used as polymerizable surfactants in emulsion polymerizations[4–6], the polymerizable end groups of the macromonomers are concentrated in the micellar cores to copolymerize with conventional monomers that produce stable latexes with monodisperse particles. The significant advantage of using polymerizable surfactants in emulsion polymerization is to prevent the surfactant desorption from particle surfaces[7–9], so as to attain a long-term stability of latexes.

In contrast to multiple phases existed in an emulsion polymerization, a dispersion polymerization starts from a clear homogeneous phase and it becomes a turbid heterogeneous phase in the early stage of polymerization. The reaction medium is selected to be a good solvent for both stabilizer and monomer used, but a precipitant for the formed polymer. The mechanism of dispersion polymerization is more complex and poorer understood as compared to that of emulsion polymerization. Paine and his coworkers[10–13] have made a major contribution to the dispersion polymerizaton of styrene in polar solvents. A grafting steric stabilization was found in their systems, in which hydroxypropyl cellulose (HPC), poly(N-vinyl-pyrrolidone) (PVP) or poly(acrylic acid) (PAA) was used as a stabilizer. They have confirmed, by using fluorescence quenching[10], transmission electron microscopy (TEM)[12] and a combination[13] of X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS), that the true steric stabilizer was the grafted HPC (or PVP)-polystyrene copolymer, formed *in situ*, which was anchored onto the particle surface.

We have recently synthesized an amphiphilic PEO macromonomer[3] (PEO-R-MA-40) in which a long hydrophobic chain R is inserted in between a polymerizable terminal group and PEO as shown in the following structure.



$$CH_3O(CH_2CH_2O)_{40}(CH_2)_{11}OC(=O)C(CH_3)=CH_2$$

This PEO-R-MA-40 was used in the dispersion polymerization with styrene in aqueous ethanol media. The grafted PS-PEO copolymers could readily be obtained in the

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form of monodisperse particles of stable latexes. This paper reports the details of the study.

EXPERIMENTAL

Materials

PEO-R-MA-40 was synthesized as described in the previous article [3]. Styrene from Fluka was vacuum distilled to remove inhibitor. α, α'-Azobisisobutyronitrile (AIBN) from TCI was recrystallized from methanol. Absolute ethanol and water were distilled separately before being used as a polymerization medium. Deuterated solvent D_2O and CD_3CD_2OD from Merck were used as received.

Dispersion polymerization

The monomer solution of 80 g was introduced into a conical flask with a magnetic stirrer. The formulations for the dispersion polymerization of styrene are given in *Table 1*. The clear feed solution was repeatedly degassed and then purged with nitrogen at below 5°C. The feed solution under nitrogen atmosphere started to polymerize after it was placed in a water bath at 65°C with a magnetic stirring rate at 700 rpm. A syringe was used to withdraw about 5 ml of the polymerized solution through a rubber septum at different polymerization intervals. A small amount of hydroquinone was mixed with the drawn samples to terminate the polymerization. About 3 ml of each polymerized solution was weighed precisely for solid content determinations. After drying in a vacuum oven, the polymer was washed with water until it was free of unreacted PEO macromonomers as identified by GPC. The conversions of styrene and macromonomer were determined by gravimetry[14–18] and ^{1}H n.m.r. method[4,6,19], respectively. The remaining 2 ml solution was used for the morphology study of the particles by TEM.

The polymerization was also carried out in the mixed deuterated ethanol and water directly in the n.m.r. tubes and it was monitored by a Bruker AMX 500 (500 MHz)spectrometer. At different time intervals, the tubes were quenched to 0°C before they were measured at 25°C. The extent of styrene and PEO-R-MA-40 conversions was monitored by the disappearance of the corresponding terminal vinyl protons with reference to the ω-methoxy protons in the ^{1}H n.m.r. measurements[6]. The experiments were run with a 45 s pulse delay time at a near 75° pulse angle and the spectra were obtained by accumulating 8 scans. This method is in very good agreement with the gravimetric method.

Molecular weight and its distribution

The average molecular weights of polymers and their distributions were determined by gel-permeation chromatography (GPC). The measurements were performed on a Waters 600E liquid-chromatography system equipped with a Waters 410 differential refractometer as a detector. Two 10μ Phenogel columns (500 A and linear, 300 × 7.8 mm) were used in series. The HPLC grade THF which contained 0.25 wt% 2,6-di-*tert*-butyl-*p*-cresol as a stabilizer was used as an eluent at a flow rate of 0.8 ml min^{-1} at an ambient temperature. The molecular weights of the polymers were obtained from the calibration line using polystyrene standard samples supplied by Polyscience.

Table 1 Formulations for the dispersion polymerization

System	Standard recipe	Experimental variations
Styrene (wt%)	10	5–15
PEO macromonomer (wt%)	1	0.1–2
AIBN (mM)	12	6–30
Water/ethanol(10/90 vol)(wt%)	89	0–25[a]
Temperature(°C)	65	60–70

[a] Vol.% of water in water/ethanol media.

Particle size

A JOEL JEM-100CX transmission electron microscope (TEM) was used to examine the particle morphology of the polymer latexes. The particles were stained by phosphotungstic acid (PTA). Two to three drops of each latex were added to a 2 ml of 0.2% PTA aqeous solution, and the mixture was well mixed with a Vortex mixer. A drop of this mixture was then put on a copper grid coated with a thin layer of Formvar. The sizes of latex particles were determined directly from each transmission electron micrograph.

Characterization of polymer particles by FTi.r. and ^{1}H n.m.r.

The infrared (i.r.) spectrum for the PEO-grafted polystyrene was obtained from a Perkin-Elmer 1600 series *FT*i.r. using a KBr pellet. The proton n.m.r. spectrum was recorded with a Bruker ACF (300 MHz) spectrometer using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. The experiment was run by accumulating 100 scans for the composition analysis of the polymer.

Particle surface analysis by XPS

The water-washed and dried polymer powders were further vacuum-dried for two days before they were analyzed by X-ray photoelectron spectroscopy (XPS). The surface analysis was carried out in a VG ESCALAB Mk II Spectrometer with a Mg Kα X-ray source (1253.6 eV) and with an energy analyzer set at a constant retardation ratio of 40. The X-ray source was run at a reduced power of 120W (12 kV and 10 mA). The powder samples were mounted on the standard sample studs by means of double-sided adhesive tape. The pressure in the analysis chamber during the measurements was maintained at or lower than 10^{-8} mbar. To compensate for surface charging effects, all binding energies were referenced to C(1s) neutral carbon peak at 284.6 eV. The peak area for the calculation of oxygen and carbon compositions were corrected by experimentally determined instrumental sensitivity factors (0.296 for C(1s) and 0.711 for O(1s)). The fraction of PEO-R-MA-40 grafted on the particle surface of polystyrene, based on the pure macromonomer (also measured by XPS), can be calculated from the following equation[13]:

$$\text{Fraction of PEO} - \text{R} - \text{MA} - 40 \text{ on particle surface}$$
$$= \frac{\text{O in particle surface}(\%)}{\text{O in PERO} - \text{R} - \text{MA} - 40\%} \quad (1)$$

RESULTS AND DISCUSSION

General aspects

The PEO macromonomer was not only a comonomer but also acted as a stabilizer in the dispersion polymerization of styrene using AIBN initiator in the ethanol-water medium. Owing to the low concentration of PEO macromonomer was used in the system, the homopolymerization of styrene and the copolymerization of styrene with the PEO Macromonomer might have been coexisted. As a result, both polystyrene and its copolymer (the real stabilizer) were produced simultaneously. *Figure 1* shows the respective conversion of styrene and PEO macromonomer versus time for the standard recipe shown in *Table 1*. It is noted that the styrene conversion curve shows a sigmoidal shape as for emulsion polymerization, whereas the macromonomer conversion curve is more like the one for solution polymerization. The conversion of styrene could reach to 98.5% after 10 h of polymerization in contrast to only 50% for PEO macromonomer. It seems that the PEO macromonomer did not form micellar structures, but it copolymerized with styrene randomly in the continuous phase. When the copolymer grew to a critical length at which it was no more soluble in the reaction medium, it either coagulated with other insoluble polymer to form a new particle or was captured by existed particles. As a result of the hydrophilic nature of PEO, the copolymer should be anchored and enriched on the particle surface where the PEO groups extended towards the continuous phase to provide a steric stabilization to the particle.

By plotting the derivatives of *Figure 1*, the disappearance rates of styrene (R_p) and PEO macromonomer (R'_p) at their respective conversions are shown in *Figure 2*. It shows that the polymerization rate of styrene increased rapidly to the maximum at about 18% conversion, leveling off from 18% to 55% conversion it then decreased sharply on further increasing conversion. These three polymerization rate intervals are very similar to those observed in the emulsion polymerization[20].

The dispersion polymerization began in the homogeneous solution. The growing oligomers were formed at a certain extent of polymerization in the continuous phase which became a non-solvent for them. They started to coagulate owing to the insufficient PEO groups attached to the surface of particles. The unstable particles coalesced with one another or/and captured graft copolymers with PEO pendant groups. Thus the latex particles became sterically stabilized when a sufficient amount of PEO groups anchored on the particle surface. This can happen in the early stage (5%–10% conversion) of polymerization for some systems[15,21]. Beyond that, the particle number remains rather constant as the stabilized particles refrain from coalescence with one another. In the present system, the stabilized latex particles seem to be produced only at a much higher styrene conversion (> 18%). This may be caused by the relatively shorter chain length of PEO-R-MA-40 used compared with the stabilizer HPC, PVP, or PAA in the other dispersion polymerization system[21].

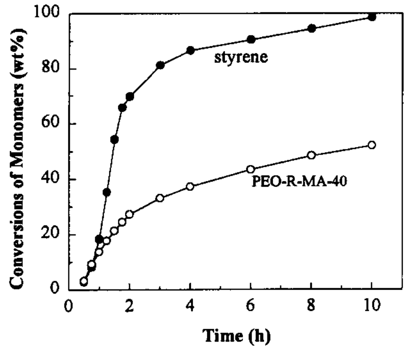

Figure 1 The conversions of styrene and macromonomer to polymers in the dispersion polymerization using the standard recipe shown in *Table 1*

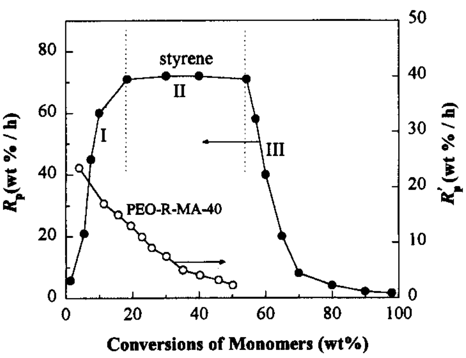

Figure 2 The disappearance rates of styrene (R_p) and macromonomer (R'_p) and their respective conversions

Once the stabilized polymer particles were formed, they were swollen by styrene monomer because of he monomer partition in both continuous and particle phases[22,23]. The polymerization continued to occur in the particles as long as they could continuously capture radicals formed in the continuous phase[22,24]. Owing to the constant particle numbers existed in rate interval II, the polymerization rate was determined by the monomer concentrations both in the continuous phase and in particles. A higher rate of polymerization can be obtained if the oligomeric radical lifetime in particles is prolonged. In the present system, the high rate of styrene polymerization was maintained in rate interval II. It indicates that the stabilized particles were main loci of styrene polymerization in this stage. During this rate interval, styrene dissolved in the continuous phase continued to partition in the growing latex particles so as to maintain the monomer concentration in the particles. After about 55% conversion, the rate of styrene polymerization decreased continuously because of the styrene concentration decreased both in the particles and in the continuous phase.

In terms of molar basis, the concentration of PEO-R-MA-40 used in the dispersion system was very much smaller than that of styrene, i.e., 1:195. It is thus inferred that PEO-R-MA-40 was mainly copolymerized with styrene rather than to proceed homopolymerization. The loci of copolymerization of PEO-R-MA-40 with styrene mainly occurred in the continuous phase as for a typical solution polymerization. The disappearance rate of PEO-R-MA-40 decreased continuously with its increasing conversion as also shown in *Figure 2*.

Figure 3 shows the molecular weight M_w of polymers as produced and its molecular weight distribution (M_w/M_n) as a

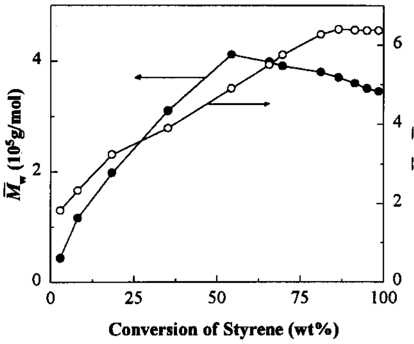

Figure 3 The molecular weight M_w of polymer and its distribution (M_w/M_n) as a function of styrene conversion. Polymer samples were washed with water until free of the unreacted macromonomer as identified by GPC

function of styrene conversion. M_W increased steadily to about $4 \times 10^5 \, g \, mol^{-1}$ with increasing conversion of styrene up to about 55%, and then it decreased slightly on further polymerization. This result is consistent with the view that the growth of polystyrene chains was mainly in sterically stabilized particles during rate interval II. The polydispersity of M_w/M_n also increased gradually from about 3 to 5 at about 20% to 55% conversion of styrene respectively. It further increased to about 6.5 at about 85% conversion and it seems to remain unchanged thereafter. This implies that lower molecular weight polymer/copolymer might also be produced during the entire course of the dispersion polymerization. The similar trend has also been observed for the systems[14,15,25–27] stabilized by a methacryloyl-terminated PEO-MA macromonomer or HPC.

Kinetics of polymerization

Effect of initial PEO-R-MA-40 concentration. The initial rate of styrene polymerization was not affected by the macromonomer concentration investigated (0.1–2 wt%). This is caused by the very low PEO-R-MA-40 concentration used as compared with for instance, the molar ratio of PEO-R-MA-40 to styrene was 1:195 when 1 wt% macromonomer and 10 wt% styrene were used in the polymerization. In fact, the concentration of PEO-R-MA-40 used varied from 4.9×10^{-4} M to 9.9×10^{-3} M. Within this low concentration range of PEO-R-MA-40, the polymerization characteristics remained the same as shown in *Figure 1*. Similar results were also reported for the systems[16,28,29] using PVP, sodium dodecylsulfate, poly(ethylene glycol) (PEG) and 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate (AOT) as non-polymerizable stabilizers.

Effect of initial concentrations of styrene and initiator. Owing to the very low concentration of PEO-R-MA-40 used, the rate of styrene polymerization may be approximated as the overall rate of polymerization for this system. Hence,

$$(R_p)_i = -\frac{d[\text{styrene}] + d[\text{PEO} - \text{R} - \text{ma} - 40]}{dt} \simeq \frac{d[\text{st}]}{dt} \tag{2}$$

$$= k_{11}[\text{st}^{\bullet}][\text{st}] + k_{21}[\text{PEO} - \text{R} - \text{MA} - 40^{\bullet}][\text{st}]$$

$$\simeq k_{11}[\text{st}^{\bullet}][\text{st}] = k_p[\text{st}\bullet][\text{st}] \tag{3}$$

where the very low PEO-R-MA-40°] is neglected and k_p is the rate constant for the styrene polymerization.

In the heterogeneous polymerization, the growing oligomeric or polymeric radicals would coiled up, once they were insoluble in the reaction medium. The normal bimolecular termination between propagating radicals became more difficult. Under such a circumstance, the termination may be carried out mainly by chain transfer reactions. At a steady state, the rate of termination (R_{tr}) is equal to the rate of initiation (R_i) as related by equation (4),

$$k_{tr}[\text{st}^{\bullet}][\text{X}] = 2fk_d[\text{AIBN}] \tag{4}$$

where X could be monomer, polymer, initiator and other species. Further, equation (5) is obtained by combining equations (3) and (4).

$$(R_p)_i = 2fk_p \frac{k_d}{k_{tr}} \frac{[\text{AIBN}][\text{st}]}{[\text{X}]} \tag{5}$$

where f, k_d, k_p, and k_{tr} are the AIBN efficiency and the rate constants for AIBN decomposition, propagation and termination of styrene polymerization, respectively.

The log plot of *Figure 4* shows that the initial rate of polymerization increased linearly with the increase of the initial concentration of styrene and AIBN respectively. The following scaling relationship is thus obtained.

$$(R_p)_i = K[\text{styrene}]_o^{0.92}[\text{AIBN}]_o^{0.90} \tag{6}$$

The respective exponent value of 0.92 and 0.90 are close to unity as would be expected from equation (5). This means that the dispersion polymerization of styrene for the present system was most likely to proceed as a solution polymerization in the early stage (< 10% conversion). Baade *et al.*[30] reported a power law dependence of unity on the monomer concentration in the dispersion polymerization of acrylamide using sorbitane monooleate as a stabilizer. In contrast, the exponent value for the initiator concentration of dibenzoyl peroxide was found to be 0.80 for he dispersion polymerization of styrene using PEO-MA stabilizer[25].

Effect of solvent compositions. The composition of the reaction medium (ethanol-water) also affected the rate of the dispersion polymerization of styrene as shown in *Figure 5*. The initial (< 6% styrene conversion) rate $(R_p)_i$ decreased with increasing the volume fraction of water in the reaction medium. This is attributed to the solvency

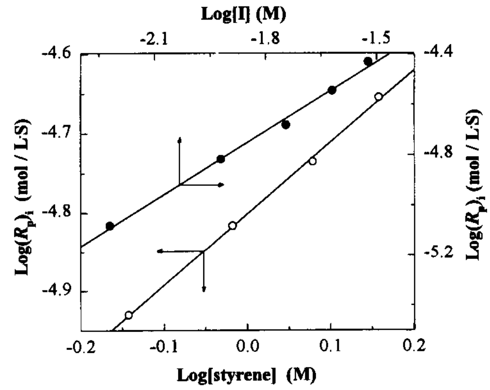

Figure 4 The effect of concentrations for both styrene and AIBN on the rate of styrene polymerization, $(R_p)_i$. The formulations are listed in *Table 1*

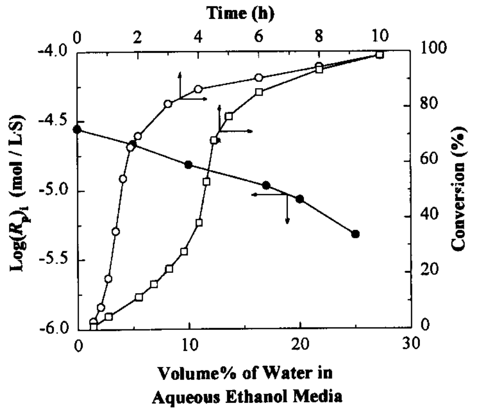

Figure 5 The effect of water-ethanol composition on the rate of styrene polymerization. ○:10% water and 90% ethanol by volume, □:25% water and 75% ethanol by volume, ●: the initial (< 6% styrene conversion) rate versus the volume fraction of water in the water-ethanol mixture

effect on the initiator. The partition of the oil-soluble initiator AIBN in the continuous phase and in formed particles would vary with the water content in the continuous phase. AIBN became less soluble in the continuous phase with increasing water content. This led to lower $(R_p)_i$. It is also reflected in the different conversions of styrene as shown in *Figure 5*.

Effect of polymerization temperature. The effect of temperature on the dispersion polymerization of styrene is shown in *Figure 6*. As expected, the rate of polymerization was faster at higher temperatures. According to equation (5), the effect of temperature on the initial rate of polymerization depends on the ratio of the three rate constants $\frac{k_p k_d}{k_{tr}}$. Relating these rate constants with three Arrhenius-type equations, one obtains

$$\mathrm{Ln}(R_p)_i = \mathrm{Ln}C - E_a/RT \qquad (7)$$

where C is proportional to $[\mathrm{I}]_o[\mathrm{M}]_o$. The overall activation energy for polymerization (E_a) is related to the activation energies for propagation (E_p), termination (E_{tr}), and decomposition of initiator (E_d) in the simple form of $E_a = E_p + E_d - E_{tr}$.

By plotting the polymerization rate at the initial stage (<6% conversion) and in rate interval II against $1/T$, the respective activation energies are 122.3 and 66.7 kJ mol^{-1} as obtained from the gradients of the linear plots of *Figure 7*. The much lower activation energy for the interval II polymerization means that the polymerization mainly proceeded in the stabilized particles at this stage[31].

Characterization of polymer particles

Morphology of latex particles. Stable latexes were readily prepared by the dispersion polymerization of styrene using PEO-R-MA-40 macromonomer as a polymerizable stabilizer. The TEMs for the latex particles at different conversions of styrene are shown in *Figure 8*. Pictures c and d show the final latex particles at 98.5% conversion under different magnifications. The spherical particles were monodisperse and their sizes are around 250 nm in diameter. In fact, the nearly monodisperse latex particles were already formed in the vicinity of 18% conversion as can be seen from *Figure 8a*. Unlike other systems[12] stabilized by higher molecular weight HPC, PVP or PAA, no layers of PEO-R-MA-40 stabilizer around latex particles can be discerned from *Figure 8d*. Perhaps the hydrophilic chain length of the present PEO macromonomer is not long enough for the clear TEM observation.

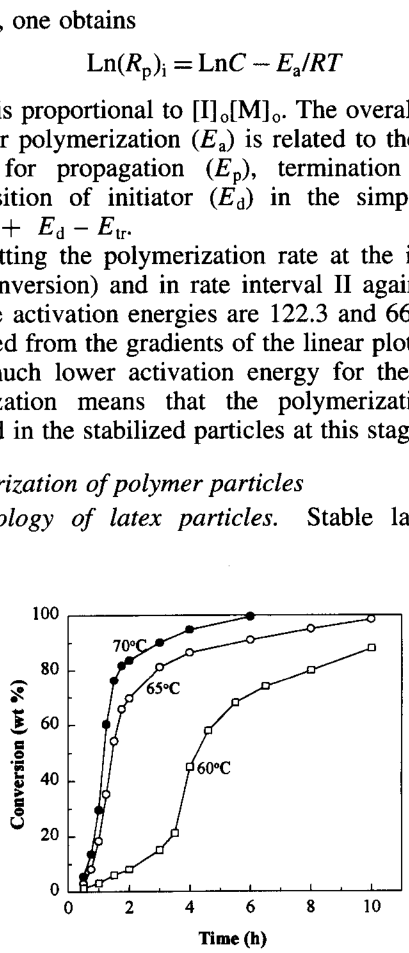

Figure 6 The effect of temperature on the dispersion polymerization of styrene using the standard recipe shown in *Table 1*

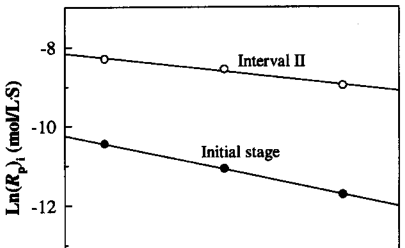

Figure 7 The Arrhenius plots for the effect of temperature on the polymerization rate

Characterization by FTi.r., ^{1}H n.m.r. and X-ray photoelectron spectroscope (XPS). All samples before measurements by *FT*i.r., ^{1}H n.m.r. and XPS were washed with distilled water for one to two weeks and dried in vacuum at room temperature until the GPC showed no unreacted PEO-R-MA-40 macromonomer existed in the final products. *Figure 9a* shows the *FT*i.r. spectrum of the product. The absorption peak at 1110 cm^{-1} caused by the asymmetrical stretching of C-O-C is clearly observed, indicating that the grafted copolymer indeed existed in the final product. The strong absorption peaks appeared at 3024 cm^{-1} and 2922 cm^{-1} arise from the stretching of aromatic C-H and CH_2. The peaks observed at 757 cm^{-1} and 697 cm^{-1} are caused by the deformation of five adjacent hydrogen atoms in the benzene ring.

The proton n.m.r. spectrum as shown in *Figure 9b* is another evidence to confirm that the PEO macromonomer was grafted onto the polystyrene backbone by the dispersion polymerization. The proton peak of the OCH_2CH_2O group appears at δ3.64 ppm. The peak at δ6.3–7.2 ppm indicates the presence of the phenyl groups in polymers. The overall

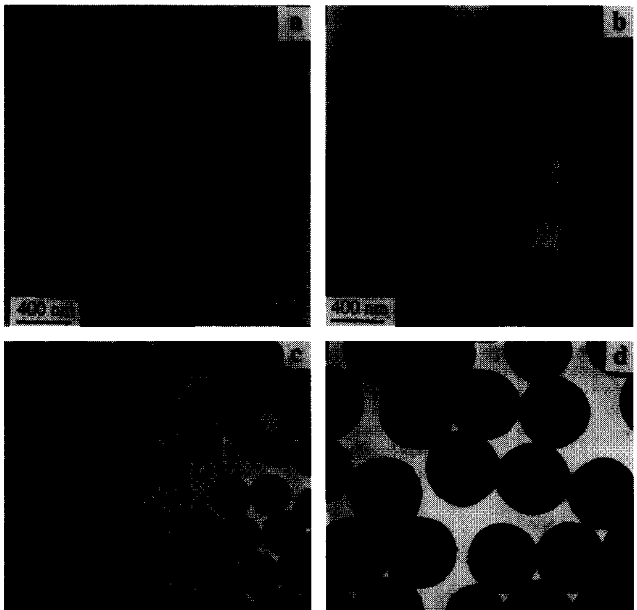

Figure 8 TEMs for latex particles at different conversions. Pictures a and b are for samples at 18.4% and 54.3% conversions respectively; c and d are for sample at 98.5% conversion under different magnifications

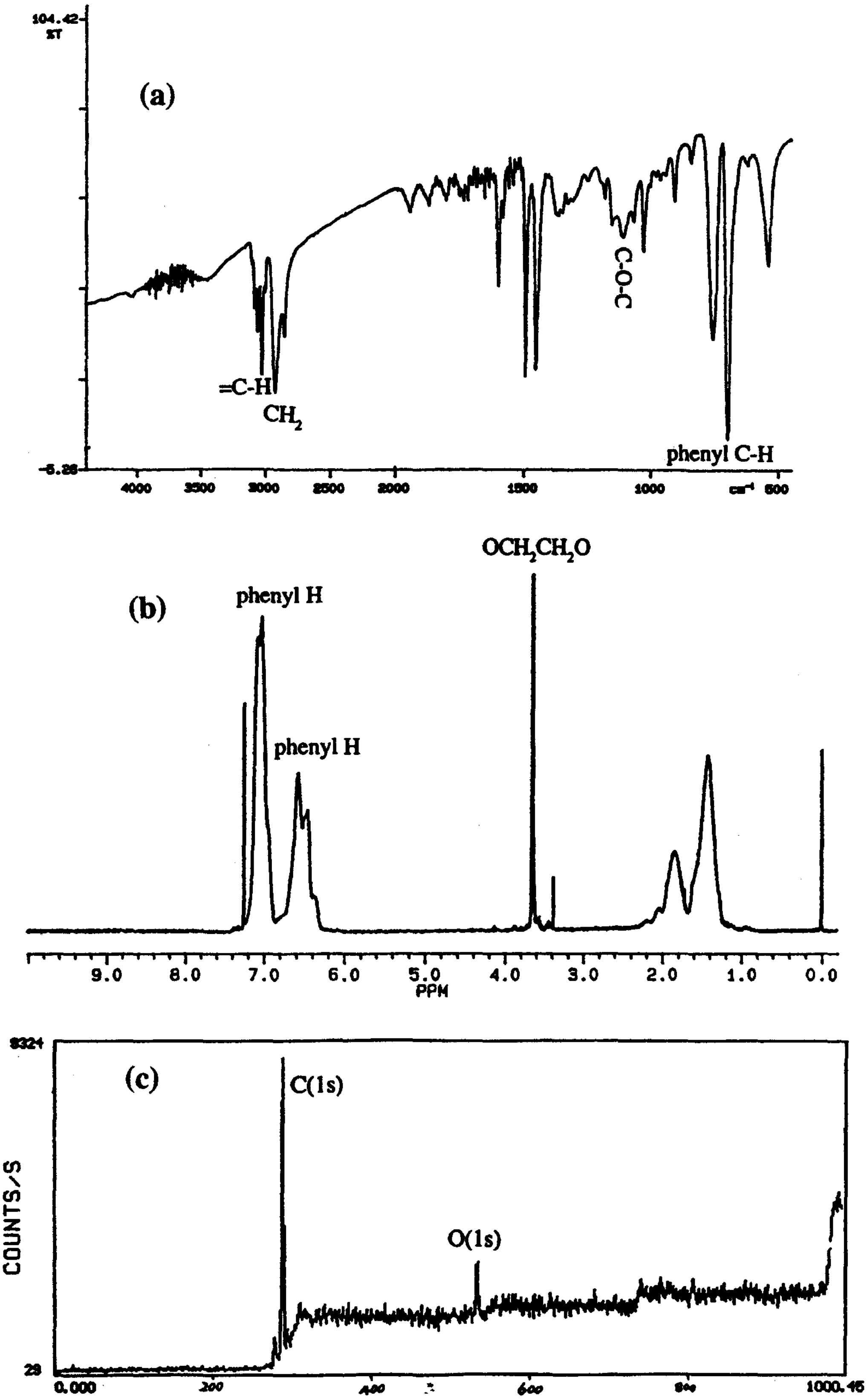

Figure 9 Characterization of a final polymer. a, *FT*i.r. spectrum; b, ^{1}H n.m.r. spectrum; c, XPS spectrum (wide scan)

content of the grafted PEO-R-MA-40 macromonomer in the final polymer was calculated from the ratio of phenyl protons to oxyethylene protons[4,6,19]. It is 4.8 wt% based on the weight of polymers as produced.

The composition on the particle surface was analyzed by a X-Ray Photoelectron Spectroscope (XPS). XPS uses X-ray to irradiate the particle surfaces and generate photoelectrons whose energy is characteristic of each element present in a certain depth of the sample surface. The sampling depth is defined as the depth from which 95% of the signal arises. It is approximately 3 times the escape depth of the electron (the electron mean free path). Since the escape depth is about 2.3 nm[32,33], XPS probes the top 7.5 nm or so of the surface. *Figure 9c* shows the XPS wide scan spectrum with a strong carbon peak together with a weak oxygen peak in the polymer powder. The atomic concentrations can be calculated based on these peak areas and the surface composition of the particles can be estimated from equation (1). The result indicates that the top surface composition for the latex particles constituted about 28% PO macromonomer. This supports the view of the patchy model[13] that only a fraction of a particle surface covered by a stabilizer is sufficient to stabilize the latex particles.

CONCLUSIONS

The dispersion polymerization of styrene using 0.1 − 2 wt% PEO-R-MA-40 macromonomer as a steric stabilizer in the mixed ethanol-water media was studied. A critical point of styrene conversion appeared around 18%, at which the polymerization rate reached to the maximum. Thereafter, the maximum rate of polymerization remained almost constant up to about 55% conversion. The initial rate of polymerization follows the scaling relationship of $(R_p)_i \propto [\text{PEO-R-MA-40}]_0^0\ [\text{styrene}]_0^{0.92}\ [\text{AIBN}]_0^{0.90}$. The activation energies were found to be 122.3 and 66.7 kJ mol^{-1} for the polymerization in the initial stage and in rate interval II respectively. In rate interval II, the polymerization proceeded mainly in the sterically stabilized latex particles. The spherical and monodisperse particles around 250 nm in diameter were obtained for the final stable latexes. The average composition of the grafted PEO-R-MA-40 in the particles was 4.8 wt%. In terms of the top surface composition, it was 28% PEO-R-MA-40 that was enriched on the particle surface of the latexes.

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