



Preparation of transparent polystyrene nano-latexes by an UV-induced routine emulsion polymerization

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ABSTRACT

Transparent polystyrene (PS) latexes were prepared by photo-polymerization of a routine styrene (St) emulsion with a surfactant concentration of 0.4 wt% and a monomer concentration of 10 wt%, by using UV light as well as a hydrophilic photo-initiator. The entire polymerization could be performed within 1–2 h and display a conversion higher than 90%. The particle sizes could be tuned in the range of 20–40 nm. The formation mechanism for these of nano-sized latex particles was attributed to an in situ formation of PS chains with terminal hydroxyl groups. The presence of the hydroxyl-functionalized polymer chains seemed to promote a colloidal stability of the small latex particles and prevent coagulation even at low surfactant concentrations.

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1. Introduction

Polymer nano-particles with sizes of 10–100 nm have attracted great interest in the field of colloidal and materials science. They have various applications in a broad range of fields, such as optics, catalysis, microelectronics, coatings, adhesives, biology, medicines, etc. [1–6]. Though microemulsion [7–10] polymerization is a well-established technique for the production of nano-particles with very small sizes and a narrow particle size distribution, it suffers from the disadvantage of a high surfactant concentration. Such a high level of surfactant is often not acceptable for economic or performance reasons and thus limits its applications. For example, a high surfactant leaves residues or contaminants in the chemical reaction media, both of which have to be removed, thus resulting in increased costs. Among the efforts to address this problem, the most ideal solution would be to add new chemistries or techniques to routine emulsion systems, and thereby achieved a nano-latex with a low level of surfactant. Some impressed investigations have been led along this route. Pusch and co-workers [11,12] used a pulsed electron beam as the initiation method in the synthesis of the transparent nano-sized latexes (20–60 nm). For most acrylate ester monomers except styrene (conversion below 20%), surfactant

concentration varying between 0.15 and 1.2 wt% and a monomer concentration of 10 wt% concentration were achieved. The strategy used by these authors was to produce a high flux of radicals as a result of a decomposition of water with the high frequency pulsed electron beam irradiation. This resulted in the formation of low molecular weight hydroxyl-functionalized polymer chains that enhance a colloidal stability to the small latex particles and prevented coagulation even at low surfactant concentration. For certain partly hydrophilic monomers, Bhawal et al. and Pokhriyal et al. [13–16] explored the emulsion polymerization of ethyl acrylate, and was able to yield stable translucent nano-sized latexes (30–50 nm). Moreover, similar observations has been reported for the emulsion copolymerization of 2-ethylhexylacrylate/acrylonitrile and butylacrylate/acrylonitrile systems; Pusch and van Herk [17] investigated the seeded emulsion polymerization of vinyl acetate (VAc) in the presence of polydivinylbenzene (PDVB) seed latexes and obtained a transparent double-layer seed latex with particle sizes of 30 nm at a monomer concentration of more than 10 wt% and a surfactant (SDS) concentration of 2 wt%.

The abovementioned researches are based on the monomers with varying degree of hydrophilic, and very few studies have involved completely hydrophobic monomer such as styrene. Monteiro and de Barbeyrac [18] obtained a PS nano-latex with particle sizes of 30–80 nm, through conventional emulsion in the presence of a reverse addition-fragmentation transfer (RAFT) agent with a low chain transfer constant to styrene. The main strategy involved the production of a radical from the fragmentation of the RAFT agent [19], which would exit the particles and reenter another

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micelle to create new particles during the nucleation period. This significantly increased the number of latex and decreased their size. Zhang et al. [20] reported on a novel method of using microwave radiation to prepare surfactant-free PS nano-spheres with sizes below 100 nm where the polystyrene nano-particles were stabilized by the ionic groups generated from the decomposition of the persulfate initiator and chemically bonded to the polymer chain end. These authors also found that the particle size decreased dramatically when an acetone/water mixture was used as the dispersion medium [21]. Despite some recent progresses, obtaining PS nano-particle through conventional emulsion polymerization remains a big challenge.

UV light has become a useful tool for initiating polymerization due to certain significant advantages [22–25], and this method has been applied to emulsion polymerization [26,27]. The polymerization can be easily varied by controlling the light intensity and the time of irradiation. Another advantage is that the radical flux is independent of temperature, whereas in chemical initiation a certain temperature is necessary for the significant decomposition of the initiator, e.g. peroxides. During the last decade, our group has explored the use of UV light as a polymerization tool and interesting results have been achieved [28–31]. The aim of this work was to extend the photo-polymerization into the preparation of transparent styrene nano-latexes. The strategy was to use a specific photoinitiator with hydroxyl groups, which was expected to produce hydroxyl terminated polystyrene as a macromolecular surfactant. Moreover, it was expected that strong UV radiation would produce high flux radicals facilitating an increase in the number of loci. The results were exceptional: we not only obtained transparent latex, but also found that the particle size could be as small as 24 nm and that the final polystyrene chains each has one terminal hydroxyl group. We believe that this simple fabrication method and the involved strategy will lead the way towards new kinds of emulsion polymerization and nano-materials.

2. Experimental section

2.1. Materials

Styrene (St) from Beijing Chemical Reagents Company, China, was vacuum-distilled to remove trace inhibitor. Cetyltrimethylammonium bromides (CTAB), potassium peroxydisulfate (KPS) from Beijing Chemical Reagents Company (China), 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (HHPMP) from Insight High Technology Co. Ltd. (Beijing, China), and 2,2-dimethoxy-2-phenylacetophenone (BDK) from Ciba Special Chemicals Ltd (Hong Kong, China) were used as-received. Their chemical structures of HHPMP and BDK are shown in Fig. 1.

2.2. UV initiated polymerization

A typical emulsion recipe, consisting of 0.2 g CTAB, 0.2 g (20 mM) the photoinitiator HHPMP, 5 g styrene; 45 g water was employed. A pre-emulsification of St, CTAB, the HHPMP and water was carried out for 30 min in a flask with stirring at a speed of 400 rpm. When BDK was used as the photoinitiator, it was first dissolved in the monomer and then added to the reaction mixture. The polymerization was conducted for 150 min in a reactor with

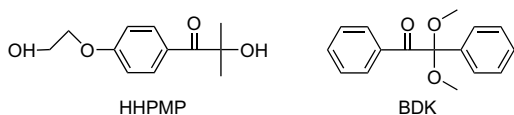


Fig. 1. Chemical structures of the UV light initiators.

a quartz cap as shown in Fig. 2. The UV source used was a 375 W high-pressure mercury lamp and the light intensity varied by changing the distance between the reactor and the lamp. During the UV irradiation, stirring and a nitrogen purge were maintained at ambient temperature. The reaction was quenched by adding 40 ppm of hydroquinone. The product latex was discharged into a separatory funnel to separate a precipitate and to collect stable latex. The conversion was determined gravimetrically by using methanol as the deposited solvent. The kinetics of the reaction was studied by withdrawing aliquots at regular time interval.

2.3. Conventional polymerization

A typical chemically initiated emulsion polymerization was performed in a 100 mL glass reaction vessel equipped with a Teflon stirrer, reflux cooler, and gas inlet. First 42 mL of deionized water and 0.5 g of CTAB were charged to the vessel, mixed at 400 rpm, purged with nitrogen, and heated to 80 °C for 30 min. Subsequently 5 g of St was added. The mixture was stirred for 45 min, allowing the monomer to emulsify. After formation of the emulsion, it was initiated with 0.115 g of KPS dissolved in 3 mL of water and polymerization was carried out for 3 h.

2.4. Characterization

The polystyrene particle sizes were determined by dynamic light scattering using a Malvern Zetasizer NanoZS apparatus with a laser of 633.0 nm wavelength at 25 °C. Before the analysis the latexes were diluted with deionized water to minimize the particle–particle interactions. The size of the PS latexes size was also examined in a HITACHI H-800 transmission electron microscope (TEM). One drop of latex diluted in 1 mL of deionized distilled water was placed on a grid after which one drop of 10% phosphotungstic acid (PTA) aqueous solution was added, and the grid was dried overnight. The molecular weight and distribution were analyzed at room temperature on a Waters GPC515-2410 system with Styragel (HT3_HT5_HT6E) columns using THF as an eluent solvent. The transmission measurements providing information on the latex transparency were conducted on a GBC Cintra 20 UV-vis spectrophotometer using a quartz cuvette of a 1 cm optical path length. The chemical structures of the polymer were confirmed with a Bruker AV 600 MHz ¹H NMR using CDCl₃ as the solvent.

3. Results and discussions

3.1. Comparison of three initiating systems

Fig. 3 displays four photos of which (a) shows the emulsion state before polymerization. In order to evaluate application, a control chemical initiation polymerization was conducted with a surfactant

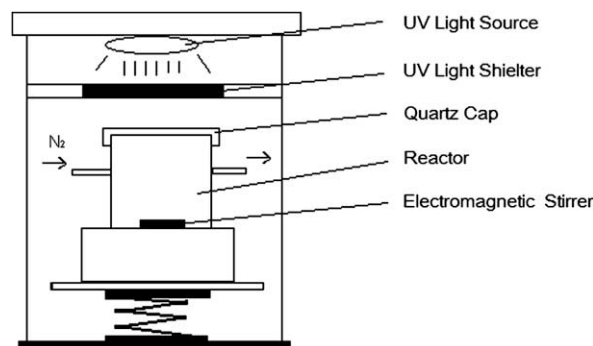


Fig. 2. A schematic representation of the UV initiated polymerization reacting set-up.

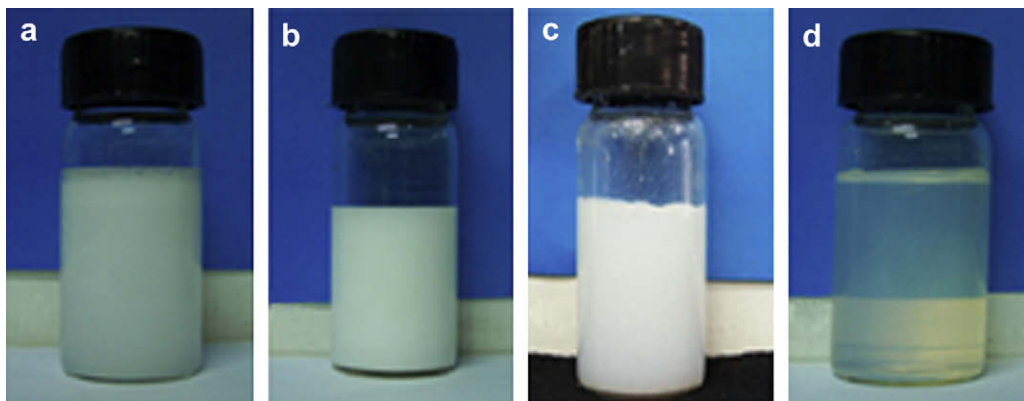


Fig. 3. Photos of (a) the styrene emulsion before polymerization, (b) the PS latex with KPS as thermal initiator and a CTAB concentration of 1 wt%, (c) the PS latex initiated by BDK with a CTAB concentration of 0.4 wt%, and (d) the PS latex initiated by HHPMP with a CTAB concentration of 0.4 wt%.

concentration of 1 wt%, and the resulting PS latex can be seen in Fig. 3(b). It was clear that the chemically initiated PS was opaque and a subsequent TEM measurement indicated that the particle size was around 90 nm. Between the two photoinitiators, i.e. the water-soluble HHPMP and the oil-soluble BDK (chemical structure is shown above), only the former gave rise to a transparent latex (Fig. 3(d)). The latex obtained when using BDK, on the other hand, was opaque (Fig. 3(c)). The particle sizes were 60 nm and 28 nm for the BDK-initiated and HHPMP-initiated latex, respectively, as shown in Fig. 4. These results demonstrate that by using the water-soluble photoinitiator containing hydroxyl groups, transparent nano-scale PS latex could be fabricated.

The polymerization evolution of the two UV-induced systems is exhibited in Fig. 5. The polymerizations were completed within 150 min for both systems, and the achieved conversion was 95% and 89%. When HHPMP was used as an initiator, the turbid white emulsions became transparent after only 30 min of polymerization which corresponds to ~35–40% conversion under constant stirring. Such a transition was not observed for the BDK-initiated polymerization at the equivalent conditions. The maximum polymerization rate in the HHPMP system was 0.015 mol/L/min, which was approximately twofold that of the BDK system, 0.008 mol/L/min. The fact that it was possible to obtain both smaller particles and higher polymerization reactivity for the HHPMP system could be explained from two aspects: (1) **large number of loci** – the water-soluble HHPMP mainly stayed in water phase, whereas, contrarily, the oil-soluble photoinitiator BDK in the monomer droplets and monomer-swollen micelles. Very little thus remained in the water phase. It has been proved [32,33] that the amount of initiator dissolved in the water phase plays a decisive role in an emulsion polymerization procedure with an oil-soluble initiator.

Once under UV irradiation, HHPMP could directly engender numerous radicals directly, whereas BDK needed to be continuously supplied from the oil phase. Ultimately, this gave rise to more loci and a faster polymerization rate for the HHPMP system. (2) **In situ formed co-surfactant with the period** – when irradiated by UV light, HHPMP decomposed into a radical with a hydroxyl group, which could initiate polymerization. This led to the formation of a large number of polymer chains capped with OH. In micro-emulsion polymerization, hydroxyl-functional molecules like 1-pentanol are often added to the recipes as a co-surfactant to reduce the particle size [34]. In this work, the in situ formed end-hydroxyl functionalized PS, predominantly presented on the latex surface acted as a co-surfactant and decreased the diameter to 28 nm. Inversely, for the BDK system, no such hydrophilic groups were present and thus only big particles were obtained. In addition, when more hydrophilic initiator KPS was used, no transparent dispersion was obtained. It is probably because that the addition of KPS would increase the ionic strength of the system, which may decrease the stability of the formed nano-latexes, and that the end group generated by KPS cannot act as a co-surfactant.

In order to track the mechanism of this system, the particle size, PDI, number of latex particles, and molecular weight of PS latexes during the polymerization course for both HHPMP and BDK systems (as comparison) were measured and listed in Table 1. These data indicate that there existed very significant differences between these two systems: 1) the number of particles of the HHPMP system is 1–2 order higher than the BDK system, 2) for the HHPMP system the variations of particle size and polymer molecular weight are totally reverse to BDK system, and 3) the number of radicals per latex particle is less than that of BDK system [35,36]. These results further support the interpretation above, that is, since

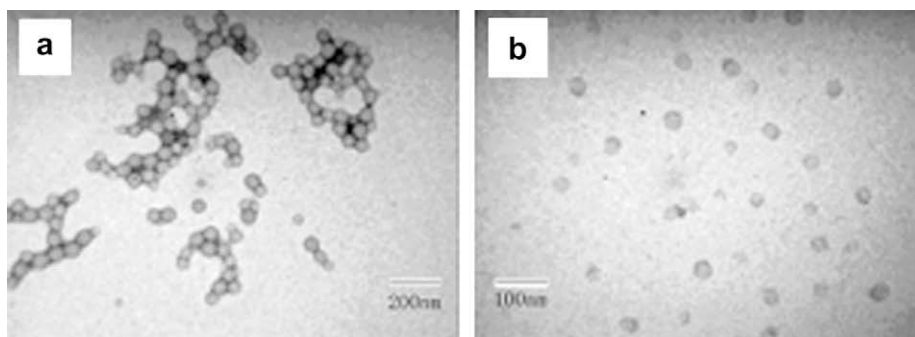


Fig. 4. TEM micrographs of PS latex particles. (a) Initiated by 20 mM BDK with 0.2 g CTAB, and (b) initiated by 20 mM HHPMP with 0.2 g CTAB.

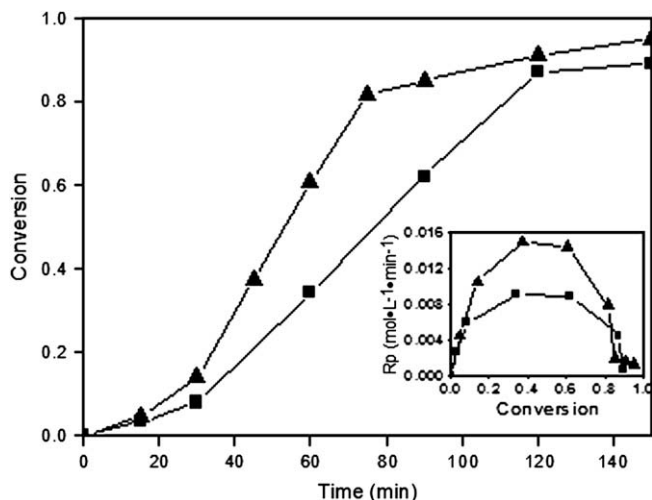


Fig. 5. The effect of the two photoinitiators HHPMP (▲) and BDK (■) on the conversion and the rate of polymerization. Photoinitiator concentration: 20 mM, CTAB: 0.2 g; light intensity: 8000 $\mu\text{W}/\text{cm}^2$.

HHPMP mainly distributed in water phase and micelles, whereas BDK in the monomer droplets and monomer-swollen micelles, under UV radiation, HHPMP system would produce more free radicals than BDK, which, in turn, resulted in higher polymerization rate, lower molecular weight and much more loci number as well as lower number of radicals per latex particle. While reverse change of two systems in particle size come from in situ formed hydroxyl group ended PS as a co-surfactant with time.

The effect of the HHPMP concentration on the particle sizes, transparency and polymer molecular weight of the latexes were followed and compared with a controlled sample from a BDK system. The results are listed in Table 2. With an increasing concentration of HHPMP, from 1 mM to 20 mM, the latex diameter decreased from 37 nm to 28 nm, and concurrently the transparency increased. It could also be observed that the molecular weight of PS decreased with an increasing HHPMP concentration. These results could be explained as follows: with an increasing HHPMP concentration, the radical flux produced under UV light irradiation increased, which resulted in, on the one hand, the decrease in the PS molecular weight (an increase in the numbers of PS chains). On the other hand, more loci were generated which led to a decrease in the latex diameter. In addition, the BDK system displayed a higher

Table 1
The particle size, PDI, number of latex particles, and molecular weight of PS latexes during the polymerization course.

Sample	Conversion	D (nm)	PDI	N_p (cm^{-1})	Number of radicals per latex particle	M_n	M_w	
HHPMP	0.047	88	0.521	3.05×10^{16}	0.1	1.5×10^4	3.9×10^4	
	0.14	49	0.513	5.07×10^{16}		2.1×10^4	5.1×10^4	
	0.37	41	0.316	1.07×10^{17}		3.4×10^4	8.7×10^4	
	0.61	32	0.267	2.34×10^{17}		4.6×10^4	1.3×10^5	
	0.85	30	0.236	1.24×10^{17}		3.6×10^4	1.3×10^5	
	0.91	29	0.251	2.66×10^{17}		4.6×10^4	1.3×10^5	
	0.95	28	0.225	1.69×10^{17}		3.0×10^4	1.2×10^5	
	BDK	0.034	45	0.282	2.3×10^{15}	0.2	1.3×10^5	3.2×10^5
		0.080	45	0.156	3.0×10^{15}		9.9×10^4	2.3×10^5
0.21		48	0.114	4.5×10^{15}		5.9×10^4	1.7×10^5	
0.34		55	0.070	4.1×10^{15}		3.7×10^4	1.3×10^5	
0.62		56	0.032	5.4×10^{15}		4.8×10^4	1.3×10^5	
0.87		57	0.053	8.4×10^{15}		5.1×10^4	1.3×10^5	
0.89		60	0.059	8.2×10^{15}		4.8×10^4	1.3×10^5	

Table 2
Particle size, PDI, transmission and molecular weight of the PS latexes.

Sample	Particle size (nm)	PDI	Transmission latex (%)			M_n	M_w/M_n
			550 nm	650 nm	750 nm		
20 mM BDK	76	0.047	0.5	8	27	3.0×10^4	5.62
1 mM HHPMP	37	0.253	12	32	50	1.6×10^5	3.81
10 mM HHPMP	30	0.899	32	53	67	2.6×10^4	5.0
20 mM HHPMP	28	0.225	46	69	82	3.0×10^4	4.92

molecular weight and larger size as compared to the HHPMP system under equivalent conditions. The reason behind this has been interpreted earlier.

3.2. Effect of CTAB concentration

Fig. 6 demonstrates the effect of the CTAB concentration on the conversion and the rate of polymerization under the conditions with a fixed photoinitiator concentration and the light intensity (20 mM and 8000 $\mu\text{W}/\text{cm}^2$, respectively). For a CTAB concentration of 0.6 wt%, the polymerization could be completed within an hour, whereas a concentration of 0.3 wt% led to an un-complete polymerization with a 60% end-conversion. When taking into account that the rate of polymerization began to fall just after a conversion of 40%; a possible interpretation is that the available surfactant in the system became almost exhausted at this point.

The conversion vs. the polymerization rate curves showed that with an increasing the CTAB concentration, the rate of polymerization increased. This can be attributed to variations in the number of the loci. A higher concentration of surfactant generates more number of micelles which are initiated and then converted into particles. Hence the rate of polymerization increases.

For a conventional emulsion polymerization, the size of a micelle or particle usually decreases with an increasing surfactant concentration. However, from Table 3, it can be seen that the particle size did not decrease but rather increased slightly with increase in surfactant concentration. Moreover, when the concentration was higher than 0.5 wt%, there was a drop in size. These results are unusual and cannot be explained by one-step micelle nucleation. Similar results were observed by Gan [8] as well as Pokhriyal et al. [14] too, and were in these cases interpreted by homogeneous nucleation. However, the

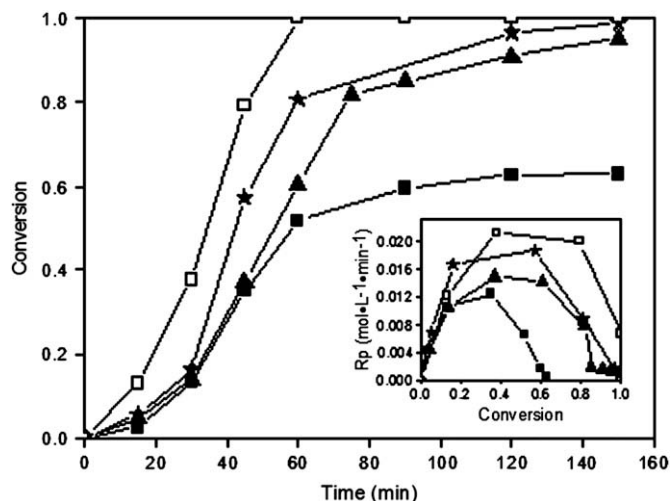


Fig. 6. The effect of the CTAB concentrations on the conversion and the rate of polymerization. 0.3 wt% (■), 0.4 wt% (▲), 0.5 wt% (★), and 0.6 wt% (□). St: 5 g, HHPMP: 20 mM, light intensity: 8000 $\mu\text{W}/\text{cm}^2$.

Table 3

Particle size, PDI, transmission, and molecular weight of the PS latexes for varying CTAB concentrations.

CTAB concentration	Particle size (nm)	PDI	Transmission latex (%)			M_n	M_w/M_n
			550 nm	650 nm	750 nm		
0.3 wt%	24	0.616	64	79	87	4.5×10^4	3.87
0.4 wt%	28	0.225	46	69	82	3.0×10^4	4.92
0.5 wt%	32	0.192	43	65	78	1.3×10^4	3.86
0.6 wt%	30	0.184	44	64	77	2.2×10^4	3.95

monomers in these systems were hydrophilic, not hydrophobic styrene.

A plausible explanation consists in precursor particles firstly being formed according to the coagulation nucleation [37,38]. These precursor particles constituted the primordial latex particles with a single (or at most, a few) free radical species inside, and they were stabilized by several surfactant molecules. The formation of these precursor particles was obtained by either homogeneous nucleation or, possibly, micelle nucleation. Such particles differed from the true latex particles in at least two important respects: they presented a colloidal instability and a very slow polymerization rate. After the formation of the precursor particles, they underwent the coagulation with other precursor particles or the true latex particles to form the mature latexes. The precursor particle coagulation events are favored over coagulation events between two primary particles as the concentration of dissolved surfactant decreases.

As showed in Table 4, when both systems was in nucleation stage (conversion of 14%), the number of particles per milliliter was 5.07×10^{16} at the surfactant concentration of 0.4 wt%, while the number increased to 1.08×10^{17} as the surfactant concentration became to 0.6 wt%. However, after that, when the conversion exceeded 80% (when the polymerization nearly to be completed), the number of particles per milliliter for the 0.6 wt% system was smaller than that of the 0.4 wt% system. This may be an experimental proof of the coagulation mechanism due to the unexpected variation of the number of particles. At higher surfactant concentration, more fractions of precursor particles were formed. Thus collisions between precursor and latex particles become more and more frequent and larger latex particles were formed. The number of particles decreased as the result of coagulation, especially at high conversion for the concentration of dissolved surfactant decreased.

The variation in polydispersity index (PDI) could also reflect this tendency. The PDI dropped from 0.616 to 0.184 when the CTAB concentration increased from 0.3 wt% to 0.6 wt%. By increasing the

Table 4

The particle size, PDI, number of latex particles, and molecular weight of PS latexes during the polymerization course of different surfactant concentrations.

Sample	Conversion	D (nm)	PDI	N_p (cm^{-3})	Number of radicals per latex particle	M_n	M_w
0.4 wt% CTAB	0.047	88	0.521	3.05×10^{16}	0.1	1.5×10^4	3.9×10^4
	0.14	49	0.513	5.07×10^{16}		2.1×10^4	5.1×10^4
	0.37	41	0.316	1.07×10^{17}		3.4×10^4	8.7×10^4
	0.61	32	0.267	2.34×10^{17}		4.6×10^4	1.3×10^5
	0.85	30	0.236	1.24×10^{17}		3.6×10^4	1.3×10^5
	0.91	29	0.251	2.66×10^{17}		4.6×10^4	1.3×10^5
	0.95	28	0.225	1.69×10^{17}		3.0×10^4	1.2×10^5
0.6 wt% CTAB	0.13	139	0.395	1.08×10^{17}	0.25	1.7×10^4	4.1×10^4
	0.38	–	–	–		2.3×10^4	5.7×10^4
	0.79	33	0.198	7.3×10^{16}		3.6×10^4	7.3×10^4
	1.00	31	0.210	1.2×10^{17}		3.3×10^4	7.2×10^4
	1.00	35	0.212	1.6×10^{17}		3.1×10^4	7.3×10^4
	1.00	36	0.197	1.1×10^{17}		2.6×10^4	7.2×10^4
	1.00	30	0.184	6.8×10^{16}		2.2×10^4	6.7×10^4

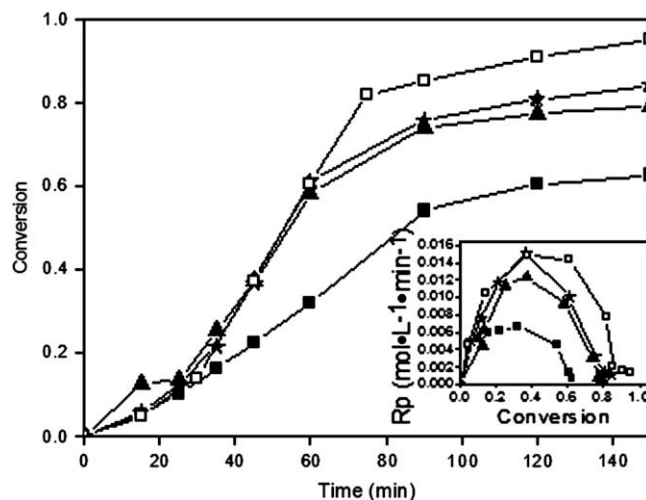


Fig. 7. The effect of various light intensities on the conversion and rate of polymerization. 1300 $\mu\text{W}/\text{cm}^2$ (■), 3000 $\mu\text{W}/\text{cm}^2$ (▲), 5000 $\mu\text{W}/\text{cm}^2$ (★) and 8000 $\mu\text{W}/\text{cm}^2$ (□). St: 5 g, HHPMP: 20 mM, CTAB: 0.4 wt%.

amount of surfactant, the enhanced coagulation led to average the particle size to a certain extent. This was due to smaller particles having less colloidal stability and thus they strived to become larger, which lead to the decrease of the PDI. In addition, the PS molecular weight fell from 4.5×10^4 g/mol to 1.3×10^4 g/mol when the surfactant concentration increased from 0.3 wt% to 0.5 wt%, after which it rose to 2.2×10^4 g/mol for a surfactant concentration of 0.6 wt%.

The surfactant concentration is important factor on which emulsion polymerization and microemulsion polymerization are distinguished. In conventional emulsion polymerization, the surfactant concentration is low, e.g., about 4 wt%, based on monomer weight. For the microemulsion polymerization, on the other hand, surfactant concentration is high, normally equal to monomer concentration or even higher. Kuo et al. [9] obtained PS microemulsion using UV-light initiation with a surfactant concentration as high as 150% (based on the monomer), and their latex size was approximately 40 nm. In our system, the surfactant concentration corresponded to only 0.4% of the total weight and 4% with respect to the styrene monomer, and we are able to obtain a similarly sized latex (or even somewhat smaller) to that of the microemulsion polymerization. The method presented in this paper is thus extremely promising for producing nanolatex with low surfactant contents.

3.3. Effect of light intensity

Fig. 7 displays the conversion and rate of the St polymerization plotted against the UV intensity in. From figure, it can be seen that the polymerization rate increased with increasing UV intensity; for examples, with a light intensity of 1300 $\mu\text{W}/\text{cm}^2$, and after polymerized for 150 min, the conversion was only 63%, whereas a light

Table 5

Particle size, PDI, transmission, and molecular weight of the PS latexes under different light intensities.

Light intensity ($\mu\text{W}/\text{cm}^2$)	Particle size (nm)	PDI	Transmission latex (%)			M_n	M_w/M_n
			550 nm	650 nm	750 nm		
1300	43	0.206	45	67	79	2.4×10^4	3.62
3000	31	0.406	36	59	74	2.0×10^4	3.79
5000	30	0.300	44	66	79	2.4×10^4	3.59
8000	28	0.225	46	69	82	3.0×10^4	4.92

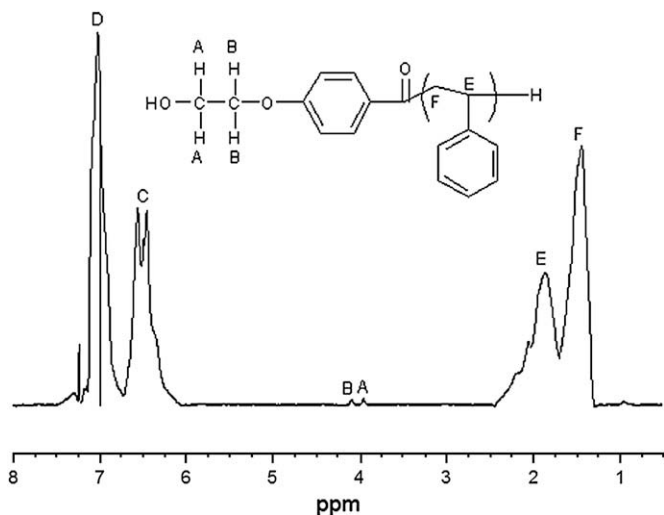


Fig. 8. The ^1H NMR spectrum of PS initiated by 20 mM HHPMP, with 0.4 wt% CTAB and a light intensity of $8000 \mu\text{W}/\text{cm}^2$.

Table 6

The effect of the photoinitiator concentrations on the number of hydroxyl groups and the number of styrene units per chain.

Initiator concentration	Number of hydroxyl per chain	M_n	Total areas of A and B	Total areas of the phenyl hydrogen
1 mM	0.6	1.6×10^5	0.0016	5.08
10 mM	1.0	2.6×10^4	0.017	5.07
20 mM	0.6	3.0×10^4	0.020	6.43

intensity of $8000 \mu\text{W}/\text{cm}^2$ rendered a possible conversion as high as over 95%. However, this trend became less obvious for light intensity above than $3000 \mu\text{W}/\text{cm}^2$. These results are easily understandable. For a fixed photoinitiator concentration, a stronger UV irradiation leads to a higher flux of primary radicals, which increases the rate of polymerization. However, if the primary radical concentration is too high, a combined termination between free radicals become inevitable (very common in UV-initiated polymerization system), which counteract the positive effect.

It is evident from Table 5 that when the light intensity increased from $1300 \mu\text{W}/\text{cm}^2$ to $8000 \mu\text{W}/\text{cm}^2$, the latex diameter decreased from 43 nm to 28 nm. The increase in light intensity resulted in faster nucleation and a broader constant rate interval (Fig. 7). This led to a larger number of loci, and the particle size of the resulting latex thus became smaller. These results demonstrate that the light intensity plays a very important role in the

preparation of nano-scale transparent latex, since only a high radical flux can generate large enough number of loci in order to obtain small particles.

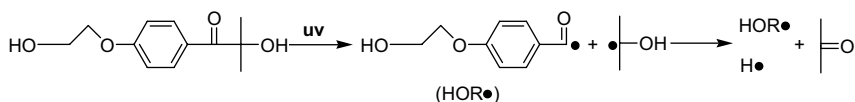
3.4. NMR

The PS structure data was obtained by ^1H NMR and can be seen in Fig. 8. The hydroxyl hydrogen peak occurred at about 2 ppm, but the characteristic peak was somewhat hidden by the strong peak corresponding to the hydrogen at the E site (according to the figure). Therefore, the hydrogen peak corresponding to sites A and B (that appeared at 3.966 ppm and 4.094 ppm) were used to calculate the number of $-\text{OH}$. As shown in the structural formula, the mole ratio of hydroxyl to the total number of A and B hydrogens was 1–4. Hence the number of hydroxyls could be calculated based on this relationship and the total area of peaks A and B. The peaks C and D represented the phenyl hydrogen, and the total peak areas could thereby provide the number of styrene units in the PS.

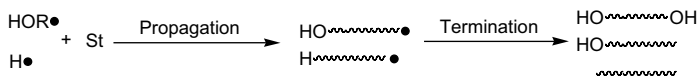
Relevant data from the ^1H NMR spectrum as well as calculated results are listed in Table 6. The data demonstrate that the average number of hydroxyls per chain was 0.6 for the 1 mM HHPMP (high molecular weight), and 1.0 for the 10 mM HHPMP system (low molecular weight). These results imply that in average sense, 50–100% PS polymer chains had a terminal hydroxyl groups, depending on the photoinitiator concentration. When the HHPMP concentration is 20 mM, the number of hydroxyl per chain decreased to 0.6, which indicated that the initiation role of hydrogen free radicals arose at high HPPMP concentration.

Based on the above results above, a plausible scheme for reaction and stabilizing mechanisms was devised: As can be seen in Scheme 1, under UV irradiation, one HHPMP molecule decomposed into two free radicals, one with a hydroxyl and the other an isopropanol radical. The radical containing the hydroxyl group could initiate the styrene polymerization, and form a hydroxyl group terminated PS chain free radical. This latter would further release a hydrogen free radical, thus resulting in the formation of a PS chain free radical. At room temperature, the PS chain free radicals would terminate by coupling to form three different PS chains. On average, the number of hydroxyl groups each chain can possess is less than one due to the chain transfer. Moreover, with high concentration of the initiator (20 mM in this work), the transfer to the hydroxyl group would become obvious and decrease the number of hydroxyl groups per chain to less than one (probably corresponding to stability of the radical by an adjacent oxygen atom). It is reasonable to expect that both the surfactant molecules and the hydroxyl ends of the polystyrene chains were present on the particle surface, as shown in Scheme 2, and that they played a similar role to that of the co-surfactant molecules in the stabilization.

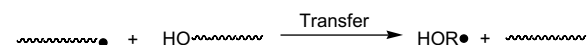
Formation of the Radicals



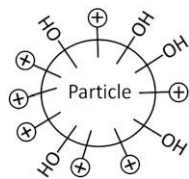
Propagation and Termination



Chain Transfer



Scheme 1. The mechanisms of polymerization with initiation by HHPMP.



Scheme 2. The co-stabilization of a polystyrene latex particle by the in situ formed end-hydroxyl PS.

4. Conclusion

An UV initiated emulsion polymerization of styrene (St) yielded transparent polystyrene (PS) latexes at a surfactant concentration of 0.4 wt%, monomer concentration of 10 wt% and with a hydrophilic photo-initiator. The entire polymerization could be completed within 1–2 h give rise to a conversion above 90%, and the particle sizes could be tuned within the range of 20–40 nm. The size of the nano-latexes was measured by TEM and DLS. The large number of loci created by the high radical flux in the UV-initiated system as well as the in situ formed hydroxyl-functionalized PS chains (resulting from radicals with OH groups) give rise to small particles. The hydroxyl-functional PS chains were believed to have enhanced the colloidal stability of the nano-latex, by acting as a cosurfactant similar to in microemulsion polymerizations. ^1H NMR analysis of the reaction products confirmed the existence of covalently bonded hydroxyl groups on the PS chains.

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