Polystyrene latex particles obtained by emulsifier-free emulsion polymerization and their interaction with bentonite

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Abstract: Polystyrene latex particles were prepared by using an emulsifier-free emulsion polymerization with two ionic initiators: potassium persulfate (KPS) and 2,2'-azobis(2-amidinopropane)dihydrochloride (AIBA). The purpose of this study was to obtain polystyrene latex with a good stability in time, a high surface charge density and a small particle size (between 100 and 1000 nm). We used two distinctive molar concentrations for both initiators: 5.5 mM and 55 mM based on aqueous phase. The analysis showed that in the case of KPS initiator the latexes stability was better. With AIBA as initiator smaller latex particles can be achieved. A high surface charge density was measured for large initiator concentration. We achieved satisfying results with both initiators, the optimal condition of polymerization depending on the subsequent utilization of the latex. The SEM images showed that latexes containing bentonite and latexes with no clay have similar size.

Keywords: polystyrene; emulsifier-free; emulsion polymerization; anionic initiator (KPS); cationic initiator (AIBA).

Introduction

Emulsifier-free (surfactant-free or soap-free) emulsion polymerization is one of the methods used to obtain latex particles with a good stability and a polydispersity index of almost 1 (monodisperse particles). It has the unique advantage which is lacking in surfactants that leads to a much cleaner particle surface. The emulsifier-free emulsion polymerization can provide more information than the classical emulsion polymerization due to fewer possible interactions amongst components. At the same time, the latex is easy to be prepared and well characterized particles are obtained. As a result, the emulsifier-free emulsion polymerization is used in academic mediums and in biomedical fields [1-4].

Although there are other studies on the emulsifier-free emulsion polymerization of styrene with potassium persulfate (KPS) and 2,2'-azobis(2-amidinopropane)dihydrochloride (AIBA) initiators [5-16], there is no consensus with regards to the variation of the average size of obtained latex particles with the concentration of the initiator [17] and there is not enough information on the stability and surface charge of latex particles, both with direct implications on coagulation and particles coalescence during the polymerization process.

The results comparison with those in literature is just informative, due to different methods of synthesis and preparation of samples for analysis. In most cases, different substances were added to maintain the desired reaction conditions, and resulted latexes were dialyzed. We analysed the properties of crude latexes, in order to use them as models for studying interaction with layered silicate. Therefore, the preparation is significantly different.

We have developed our own experimental method in order to achieve a good stability, a high surface charge density for latex particles and average particle diameters between 100 and 1000 nm. Preliminary results for latex particles interaction with bentonite are also discussed.

Results and discussion

Latex particles characterization

In the first group of experiments we studied the effects of temperature, polymerization time and initiator concentration on particle size, surface charge density and latexes' stability in time.

Tab. 1. The recipe and average particle diameter of polystyrene latex with KPS.

Sample	KPS ^a , mM	Temperature, ° C	Polymerization time, hour, minute	Average diameter, nm
K1	55	80	2h	475.8
K2	55	80	2h 30min	836.2
				172.8 (after 7 months)
K3	55	80	3h	915.7
				510.4 (after 2 weeks)
K4	55	70	24h	316.4
K5	55	70	24h	414.8
K6	55	70	24h	439.9
K7	5.5	70	24h	450.9
K8	5.5	70	24h	349.3

^a Molar concentration based on aqueous phase (25 ml)

The polymerization recipes and the average sizes of the resulted particles are given in Table 1 and Table 2. The styrene monomer amount was 1.8 g for all polymerizations (0.69 M based on water charge).

As seen in Figure 1, AIBA leads to much smaller particles the size of which is not affected by parameter variations.

The polystyrene latexes with KPS initiation

The K1, K2 and K3 samples were created at a temperature of 80 °C, a constant initiator concentration of 55 mM and different polymerization times. The analysis results show that the particle diameter increases with reaction time (Table 1 and Figure 1).

In the case of a polymerization longer than 3 h, the particles sizes were measured with dynamic light scattering (DLS) technique and we obtained a size distribution

between 10 nm and 1000 nm.

Tab. 2. The recipe and average particle diameter of polystyrene latex with AIBA.

Sample	AIBA ^b , mM	Temperature, ° C	Polymerization time, hour	Average diameter, nm
A1	55	80	6	148.3
A 2	55	80	24	145.9 (one month)
A 3	55	80	24	144.9
A 4	55	80	24	299.5
A 5	55	80	24	109.3 (4 months)
A 6	55	80	24	125
A 7	55	80	24	180.15
A 8	55	70	24	221.8
A 9	55	70	24	148.7
A 10	5.5	70	24	148.9
A 10	55	60	24	73.4
				272.2

^b Molar concentration based on aqueous phase (25 ml)

Fig. 1. Comparison of the average particle size (DLS) of K1÷K8 samples and A1÷A10 samples.

Other authors showed that at 70 °C, the average particle size increases for approximately 9 h, after which the size remains constant [12]. Even if the polymerization is faster at 80 °C, we assume that it is still in progress after 3 h. To verify this hypothesis, we repeated the DLS measurements after two weeks (sample K3) and after seven months (sample K2). Both samples exhibited a pronounced decrease in particle size, which confirms that the reaction had not been complete after three hours of polymerization. We concluded that the reduction in particle size is

the consequence of the system's physical stabilization in time. This was confirmed by zeta potential analysis. For the K3 sample, after 3 h, the measured diameter was 915.7 nm and zeta potential was -60.1 mV. After 2 weeks, the diameter decreased to 510.4 nm, while the zeta potential increased in absolute value to -88.4 mV. It is known that stability of emulsions increases with the decrease in particle size and with the increase in absolute value of zeta potential. The high stability of the samples K1, K2, K3 was confirmed by a macroscopic observation in time. The latexes remained white, opaque with a milky appearance even after 12 months. There was a slight deposition of precipitate, the volume of which was less than 10% of the total volume of latex after 6 months. Although these latexes have a good stability and a high surface charge density, after seven months we have observed a dimensional decrease and loss of monodispersity, as seen in Figure 2 (b) (image taken after 7 months).

The polystyrene latex particles obtained with KPS are known to be practically monodisperse systems, but we could not find any study in the literature investigating the stability in time of this property. Our experimental observations show that the monodispersity of latex particles obtained with KPS is affected by time.

Fig. 2. SEM images of K2 sample: (a) the latex after a polymerization time of 2 h and 30 min, (b) the latex after 7 month.

Tab. 3. Data obtained at different initiator concentrations, a polymerization time of 24 h and a temperature of 70 °C.

Sample	KPS, mM	Zeta Potential, mV	Average diameter, nm
K4	55	-78.6	316.4
K5	55	-62.2	414.8
K7	5.5	-42.7	450.9
K8	5.5	-51.4	349.3

Other authors had repeated DLS and TEM measurements after ten months [16] for latexes with no monomer removal. Their results are different than our observations, in their measurements the size was not affected by time. Unfortunately, the available data about this subject is limited, and we could only assume that the big differences

in DLS and SEM analysis were caused by the fact that we used a shorter polymerization time. The high stability of latexes in time is confirmed in the study mentioned above.

Fig. 3. Zeta potential and diameters for different concentrations of KPS.

It should be noted that for a temperature of 80 °C and a polymerization time of 24 h the reproducibility of results was poor for 4 repeated samples. Therefore, we used a polymerization temperature of 70 °C, considering that if the polymerization reaction will be slower then it will affect to a smaller degree the reproducibility of experiments. Thus, K4, K5, K6 samples were made at a concentration of 55 mM of initiator, and samples K7 and K8 at a concentration of 5.5 mM., while the temperature was maintained at 70 °C, and the polymerization time was 24 h. The obtained latexes were white, opaque, with a milky aspect, but some of the samples have presented a small amount of coagulum. Also, the stability in time was poorer than for K1, K2 and K3 samples. We observed separation of phases starting after an interval of time between few days and one month. An interesting result was that the particle sizes did not vary that much with KPS amount (Fig 1, K4-K8 samples). More data was obtained from zeta potential measurements. The results for samples K4, K5, K7 and K8 are presented in Table 3 and Figure 3. Figure 3 shows a good correlation between the particle diameters and zeta potential. A decrease of average particle size and an increase of zeta potential values illustrated once more the tendency of the systems to stabilize. Moreover, a more pronounced instability in time for systems with low concentration of initiator, K7 and K8, is confirmed by decrease of zeta potential in absolute value.

The polystyrene latexes with AIBA initiation

Latex with a milky aspect was obtained after at least 6 hours of polymerization; a shorter time yields separated phases.

Even if the average particle size was smaller in the case of AIBA (Figure 1), the morphology of latexes was quite different, we obtained more polydisperse polystyrene particles, and the stability of latexes was more deficient than for KPS.

The A1-A6 samples were created at 80 °C temperature and at 55 mM initiator concentration, while the polymerization time varied between 6 h and 24 h. Figure 1 shows no big difference in the average particle size among the samples. The stability in time was better for samples resulted from a polymerization time of 24 h than for those obtained after a polymerization time of 6 h. A large amount of coagulum was found in most of experiments. The SEM micrographs of A1 sample (after one month) and A4 sample are presented in Figure 4. In both cases we achieved polydisperse spherical particles.

Fig. 4. SEM images of A1 sample (a) and A4 sample (b).

Fig. 5. SEM images of A9 sample: (a), (b) the latexes were not diluted; (c), (d) the latexes were diluted (1:1 latex to distilled water).

When we changed the temperature to 70 °C, for 55 mM initiator concentration, we obtained more stable latexes after 24 h polymerization time (A7 and A8 samples). The samples had a high polydispersity.

Tab. 4. Data obtained at different initiator concentrations and temperatures polymerization, while the polymerization time was 24 h.

Sample	AIBA, mM	Temperature, °C	Zeta Potential, mV	Average diameter, nm
A 6	55	80	69.2	221.8
A 8	55	70	77.6	148.9
A 9	5.5	70	1.23	73.4
A 10	55	60	70.4	272.2

Fig. 6. Correspondence between zeta potential and average diameters for different AIBA concentrations and temperatures, while the polymerization time was maintained at 24 h.

For a concentration of 5.5 mM of AIBA, we obtained a small amount of coagulum, the latex was white, opaque, with milk-like aspect, but we did not obtain reproducible results from DLS measurement. The polydispersity seems to be very high for these samples. The A9 sample had an average particle size of 73.4 nm. After a week the sizes were dispersed between 5 nm and 200 nm. The sample exhibits an interesting particularity. In Figure 5, (a) and (b), it can be seen that the particles are agglomerated and deformed, with a non spherical shape. When we have diluted the sample, Figure 5 (c) and (d), spherical particles are seen, but they seem to be formed by groups of elementary particles. A possible explanation for particle grouping is the loss of positive charges in the amidinium groups due to hydrolysis which is more pronounced for low concentrations of initiator. In other words, the particle coalescence is caused by an electrostatic destabilization of the system. The

loss of positive charges is clearly shown in the zeta potential measurements (Table 4 and Figure 6). When we changed the initiator concentration from 55 mM to 5.5 mM, we obtained a dramatic decrease in zeta potential value from 77.6 mV to 1.23 mV.

The surface charge density does not appear to be affected by a change in temperature. Small differences were observed in the values for a temperature between 60° C and 80° C. The increase in particle size at 60° C (A10 sample) has been attributed to a slow polymerization rate which results in not enough free radicals in the system. Additionally, the stability in time for A10 sample was low and considerable amount of coagulum was obtained.

Hybrid systems characterization

In the second group of experiments we have studied the effect of initiator type on the interactions between polystyrene latexes and bentonite.

For this purpose, we used latexes with a high surface charge density, good appearance, a milky consistency and good stability in time. Optimal polystyrene latexes obtained with KPS were prepared with two recipes: one with an initiator concentration at 55 mM, 3 h polymerization time and a temperature at 80 °C and one with a 5.5 mM initiator concentration, a polymerization time of 24 h and a temperature of 70 °C.

In the case of polystyrene latexes obtained with AIBA, the optimal conditions are 55 mM initiator concentration, 24 h polymerization time and 70 ° C temperature.

SEM images of latexes with 5 wt % bentonite (based on the solid content) are presented in Figure 7 and Figure 8.

Fig. 7. SEM images of PS latexes and hybrid systems: (a), (b) K7 sample; (c), (d) K7 sample with 5 wt.% bentonite.

The silicate particles obtained with and without the clay appear to have comparable sizes. Differences are observed in particle morphology.

Polystyrene latex particles with KPS initiation obtained without clay are spherical with a smooth surface, as is seen in Figure 7, (a),(b). Apparently the hybrid clay-latex particles have a smooth surface too. At a closer look we can see that hybrid clay-latex particles are deformed. Other studies showed that particles have nonspherical shapes with smooth surfaces when the clay platelets have been completely encapsulated inside the latex particles [18]. This could be the reason for the shapes observed in Figure 7, (c), (d), but it is unlikely that the clay platelets could have been encapsulated by the simple process of mixing them with the latex. Further investigations are needed to confirm this hypothesis.

Hybrid particles obtained from the mixture of polystyrene latex particles with AIBA initiation and an aqueous bentonite, are spherical, but their surface is rugged as if covered with clay 8(c). In the corners of SEM image in Figure 8, (d), large, separated areas of bentonite can be seen.

The results are quite surprising. We have expected stronger interactions between clay and latexes obtained with AIBA due to compatibility between positive amidinium groups around polystyrene particles and negative charge of silicate platelets. Instead we observed stronger interactions between the clay and KPS latexes where both platelets and polystyrene particles have negative charge. Further studies are needed to explain these results.

Fig. 8. SEM images of PS latexes and hybrid systems: (a), (b) A8 sample; (c), (d) A8 sample with 5 wt % bentonite.

Experimental part

Materials

The Styrene monomer was purchased from Sigma-Aldrich and was distilled under vacuum at 60 °C and 40 mmHg before used.

The initiators, potassium persulfate and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (Aldrich), and the bentonite (Aldrich) were used as received.

Distilled water was the dispersion medium for all experiments.

Latex particles preparation

The polymerizations were carried out in an all-glass reactor with cylindrical shape and a magnetic Teflon stirrer. A typical preparation technique is as follows: the initiator (KPS or AIBA) was dissolved in 25 ml of distilled water and 1.8 g of styrene monomer was added in the reactor under stirring and purged with nitrogen gas for 10-15 minutes. Then the reactor was closed (it has interchangeable lids perfectly fitting the body) and was immersed in a thermostatic oil bath. The reactions were conducted at 60 - 80 °C and were stopped after 2 - 24 hours. The system was slowly cooled to attain the room temperature with continuous stirring.

Hybrid systems preparation

After the latexes attained the room temperature (20-23 °C), a suspension of 1 wt % bentonite in distilled water was added and mixed with a magnetic stirrer for 10-15 minutes. The amount of the clay was calculated to be 5 wt % based on the total solid content.

Equipment

Particle size and zeta potential measurements were performed with a Malvern Zetasizer Nano ZS ZEN 3600. For a constant ionic background, the samples were diluted with 0.001 M NaCl solution (0.1 ml latex to 25 ml solution).

The morphologies of latex particles were observed with an ESEM Philips XL 30 at an accelerating voltage of 20 kV.

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