Synthesis and kinetic studies of TiO₂/polystyrene composite particles by emulsion polymerization

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Abstract: In the presence of titanium dioxide (TiO₂) nanoparticles, emulsion polymerization of styrene with sodium dodecyl sulphate (SDS) as an emulsifier and potassium persulphate as an initiator was investigated in detail. It was shown that SDS concentration influences the morphology of the composite particles in higher degree. Moreover, the effects of operating variables such as emulsifier concentrations, initiator concentration, monomer concentration, and polymerization temperature on the kinetic features were also examined. The kinetic data showed that at conditions studied, the rate of polymerization over interval II was proportional to the 0.68 power of the initial emulsifier concentration, to the 2.2 power of the initial initiator concentration and to the 1.6 power of the initial monomer's concentration. The initiator concentration has a dominant effect on the rate of the polymerization. The appropriate conditions for polymerization were obtained when emulsifier concentration of $6.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, initiator concentration of $4.4 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, the polymerization temperature of 75 °C and the initial monomer's concentration of $0.288 \text{ mol} \cdot \text{L}^{-1}$ were used. The polymerization rate obtained is more favorable than that of the conventional emulsion approach. The experimental results can be reasonably ascribed to the nucleation mechanism of "TiO₂/SDS" micelles in the emulsion polymerization of styrene.

Key words: Composite particles; Titanium dioxide; Polystyrene; Kinetics; Emulsion polymerization

Introduction

Inorganic-organic composite particles are increasingly important and have gained much interest due to the remarkable change in properties, such as mechanical, thermal, electrical and magnetic properties, compared to pure polymer particles [1-3]. Composite particles have been achieved with different materials and different methods, such as by spray drying [4], vacuum deposition [5], phase separation [6] and in situ polymerization [7-9].

However, emulsion polymerization is a unique chemical process widely used to produce inorganic-organic composite particles with various colloidal and physicochemical properties. Because of advantages such as high reaction rate, good heat dispersion, and relatively sophisticated engineering technology in industrialization, the method has attracted extensive interest [10-14]. Chuang et al. [10] used an approach of emulsion polymerization along with ammonium persulphate initiator to encapsulate titania particles modified with γ -aminopropyl-triethoxy silane and N-phenyl- γ -aminopropyl-trimethoxy silane. Yu et al. [11, 12] studied encapsulation of titania particles by dispersing them in water using emulsifiers (SLS

and Triton X-100). De Oliveira [13] modified the surface of titania particles with isopropoxy-titanium-tri-isostearate coupling agents in the studies of their encapsulation by conventional emulsion polymerization. Viala et al. [14] encapsulated inorganic pigments such as TiO_2 or Fe_xO_y (black, yellow or red), using NP30 as emulsifier.

Although some work has been reported in the literature for the preparation of TiO_2 /polymer composite particles by emulsion polymerization, only less was concerned about the kinetics and mechanism of the emulsion polymerization of styrene in the presence of nanosized TiO_2 as inorganic particles. The emulsion polymerization is a rather complex process because nucleation, growth and stabilization of composite particles are controlled by the free radical polymerization mechanisms in combination with various colloidal phenomena. Although the nucleation period is quite short, generation of particle nuclei during the early stage of the polymerization plays a crucial role in determining the composite particle size and particle size distribution and has also a significant influence on the quality of composite particles. How to effectively control the particle nucleation process represents a very challenging task to those who are involved in this fascinating research area. The emulsifier concentration, the initiator concentration, the monomer concentration, and the polymerization temperature are the key factors that govern the particle growth stage. Here, the main interest has been devoted to study the kinetics and mechanism of emulsion polymerization of styrene in the presence of nanosized TiO_2 , which will enable us to develop a deeper insight into the phenomena occurring during the polymerization. To gain a fundamental understanding of polymerization is also a demand in designing quality composite particles that fulfill customers' requirements.

Results and discussion

Effect of emulsifier concentration on the morphology

Figures 1(a) and 1(b) show images of the resultant particles prepared with the SDS concentration of $1.7 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ and $3.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, respectively. It can be seen that some of the TiO_2 particles escaped from the oil phase and dispersed in the continuous phase as bare TiO_2 particles. Nano- TiO_2 particles tend to agglomerate obviously. These observations could lead to the conclusion that not all of the nano- TiO_2 particles were encapsulated in the polystyrene (PS) particles in the course of the emulsion polymerization. Figure 1(c) and 1(d) show the images of the resultant particles prepared with the SDS concentration of $5.2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ and $6.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, respectively. The composite particles have a smooth surface and spherical shape, with an average diameter of about 180 nm. The central black spot and translucent part in a composite particle are TiO_2 particles and PS, respectively. No bare TiO_2 particles could be observed besides the composite particles. The morphology of the particles revealed that the modified TiO_2 particles acted as the core for deposition of the PS that formed the shell. It could be verified that the TiO_2 particles were encapsulated in the polymer phase. The images also show that the dispersibility and dispersion stability of the composite particles were optimum.

The dispersion stability of inorganic particles in the aqueous phase during emulsification and encapsulation polymerization is the major obstacles in successfully applying conventional emulsion polymerization as an encapsulation method [15]. The low concentration of the SDS could not provide enough of a spatial

barrier among particles, so it also could not provide dispersion stabilization of TiO_2 in aqueous phase. In contrast, increasing the SDS concentration (for example, $5.2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$), could be favorable for providing better dispersion stabilization in aqueous phase, and could offer good spatial stabilization for the dispersion of TiO_2 particles as well.

Fig. 1. TEM micrographs of composite particles with different emulsifier concentration (a) $1.7 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, (b) $3.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, (c) $5.2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, (d) $6.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

In conventional emulsion polymerization, the principal site of particle nucleation is either in the aqueous phase or in the monomer swollen micelles. There were no monomer-containing micelles because the concentrations of SDS emulsifier were lower than the CMC ($8.7 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) [16]. In the presence of inorganic particles dispersed in the aqueous phase, an additional site can be the surface of particles [15]. However, the competition between these mechanisms can lead to both free polymer particles containing no inorganic particles and unencapsulated inorganic particles, in addition to the encapsulated ones. In this polymerization, the number of nano- TiO_2 particles was much higher than that of the monomer droplets, so the principal site of particle nucleation was either in the aqueous phase or on the surface of TiO_2 particles.

The morphology of the particles revealed that the mechanism in the formation of composite particles using the SDS could be: SDS molecules absorbed onto the nano- TiO_2 particle surfaces, which formed the so-called TiO_2/SDS micelles, and monomer molecules were collected on the surfaces of TiO_2/SDS micelles,

polymerization was initiated when the water-soluble initiating radical entered a micelle that contained nano-TiO₂ particles. As the polymerization proceeds, additional monomer molecules were transferred from the monomer droplets to the growing micelles through the water medium. When a critical chain length was achieved, these oligomeric radicals became so hydrophobic that they exhibited a strong tendency to be absorbed onto the TiO₂/SDS micelles monomer droplets. As a consequence, TiO₂/SDS micelles were successfully transformed into particle nuclei and TiO₂/Polystyrene composite particles were formed. At the same time continued to propagate by acquiring the reactant species from time, these oligomeric radicals might collide each other and continue to propagate by reacting with monomer molecules, thus the free polymer particles containing no inorganic particles were formed.

Effect of emulsifier concentration on the polymerization rate

Figure 2 shows the effect of initial emulsifier concentration (E) on the monomer conversion versus time curves at 75 °C. The initial emulsifier concentration was varied from 3.5×10^{-3} to $7.8 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, whereas the initial initiator concentration, the initial monomer concentration, nano-TiO₂ charge and deionic water dosage were fixed at $4.44 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $0.2881 \text{ mol} \cdot \text{L}^{-1}$, 1.0 g and 250 mL, respectively. As expected, the monomer conversions increased with increasing SDS concentration. In the experiments, when a lower SDS concentration of $5.2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (0.6CMC) was used, 50% conversion was obtained after 75 min, whereas 50% conversion was obtained after only 30 min reaction time by using higher SDS concentrations of $7.8 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (0.9CMC).

Figure 3 shows the effect of initial emulsifier concentration on the polymerization rate. The line shown on the graph is a linear least square fit to the whole data on the ln–ln scale. All the data points on the graph can be approximated by a single line with a slope of 0.68 and a correlation coefficient of 0.995, which falls within the range of prediction of Smith-Ewart theory [17]. That is, the reaction order with respect to the emulsifier concentration was determined

$$R \propto [E]^{0.68} \quad (1)$$

Fig. 2. Curves of conversion vs time at different emulsifier concentrations.

Fig. 3. Effect of emulsifier concentrations on polymerization rate.

The influence of sodium dodecyl sulphate (SDS) on the rate of decomposition of $\text{K}_2\text{S}_2\text{O}_8$ initiator in aqueous solution was investigated [18]. It was found that SDS molecules in the micelle state do not contribute to the acceleration of $\text{K}_2\text{S}_2\text{O}_8$ decomposition. Decomposition of $\text{K}_2\text{S}_2\text{O}_8$ in aqueous solution is accelerated by “free” molecules of emulsifier in monomolecular dispersed state.

In all cases the used concentration region of emulsifier was lower than its CMC. Furthermore, by enhancing the SDS concentration, the observed rate of polymerization increased because with increasing the emulsifier concentration more so-called TiO_2 /SDS micelles, which are considered as the main loci of polymerization, were formed. So the rate of polymerization throughout the entire process became higher. One can expect, therefore, that the higher the content of SDS in the emulsion, that is, the higher the number of TiO_2 /SDS micelles, the faster the polymerization rate.

Effect of KPS concentration on the polymerization rate

Figure 4 shows the effect of initial KPS concentration (I) on the monomer conversion versus time curves with other parameters fixed. It is clear from the graph that the conversion and stationary rate of polymerization increases with the KPS concentration. In the experiments, when a low KPS concentration of $2.9 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ was used, less than 20% conversion was obtained after 60 min, whereas 30% conversion was obtained after only 30 min reaction time by using high KPS concentrations of $4.4 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. At the three higher initiator concentrations, the conversion curves do not show a typical “sigmoidal shape” for conventional emulsion polymerization. A deviation was observed at high initiator concentrations, which could be explained by the suppression of the first interval.

In order to explain the experimental findings, it should be borne in mind that the initiator concentration has two opposite effects on the conversion in emulsion polymerization. First, increasing KPS concentration increases the number of sulphate ions involved in more nucleation loci, which leads to higher conversion. Second, enhancing the KPS concentration also increases the ionic strength of the aqueous phase, which results in larger particles [19]. Thus, it seems that the two opposite effects of the initiator KPS competed with each other under the experimental

conditions. The suppression of the rate for high initiator concentration can be attributed to a decrease in initiator efficiency. Initiator efficiency decreases with increasing the initiator concentration in the aqueous phase, due to enhancement of radical termination in the aqueous phase [20, 21].

Similarly, the graph of the polymerization rate against initial initiator concentration in $\ln$ – $\ln$ scale can be plotted. All the data points in the graph can be approximated by a single line with a slope of 2.2 and a correlation coefficient of 0.997, which differs from the exponent (0.4) found by Smith and Ewart for styrene [17]. The primary cause for deviating from the ideal polymerization system may be the addition of titanium dioxide, which causes the initiator efficiency to decrease. That is, the reaction order with respect to the initiator concentration was determined

$$R \propto [I]^{2.2} \quad (2)$$

Fig. 4. Curves of conversions vs time at different initiator concentrations.

Effect of monomer concentration on the polymerization rate

Figure 5 shows the effect of initial monomer concentration (M) on the monomer conversion versus time curves with other parameters fixed. It is clear from the graph that the conversion and equilibrium conversion of polymerization increase with the styrene concentration increasing from 0.09602 to 0.2881 mol·L⁻¹, whereas the equilibrium conversion of polymerization decreases with the styrene concentration of 0.3841 mol·L⁻¹. At the lower styrene concentration (0.09602 mol·L⁻¹), the conversion curve shows a typical “sigmoidal shape” for conventional emulsion polymerization. In present emulsion polymerization, the monomer is partitioned among three locations: monomer droplets, the aqueous phase, and TiO₂/SDS surface. For a sparingly water soluble monomer, such as styrene, the monomer concentration in the water phase is negligible. It is well known that the higher the monomer concentration in the emulsion, the more monomer molecules diffuse to the surface of TiO₂/SDS, the faster the polymerization rate, the higher the value of monomer conversion. As the monomer concentration increases to a definite value, at a constant emulsifier concentration, the polymerization rate no longer increased, so the lower value of monomer conversion was obtained [22].

Similarly, the graph of the polymerization rate against initial monomer concentration in ln–ln scale can be plotted. All the data points in the graph can be approximated by a single line with a slope of 1.6 and a correlation coefficient of 0.998, which differs from the exponent (1.0) found by Smith and Ewart for styrene [17]. That is, the reaction order with respect to the monomer concentration was determined.

$$R \propto [M]^{1.6} \quad (3)$$

Fig. 5. Curves of conversion vs time at different monomer concentrations.

Effect of temperature on the polymerization rate

The conversion-time data as a function of temperature for the emulsion polymerization of styrene initiated by KPS in the presence of TiO_2 are displayed in Figure 6. As expected, the initial rate of polymerization increases with increasing temperature. Moreover, the equilibrium conversion increased from 60 to about 80% with temperature increasing from 65 to 80 °C at polymerization time of 160 min. This is mainly due to the increase in the radical number and the rate coefficients for radical entry and exit which increases the particle formation rate and the polymerization rate with increasing temperature. Generally, the equilibrium conversion is a result of the consumption of initiator and/or immobilization of monomer and initiator within the micelle aggregates. The transformation of the high-coverage polymer particles to lower coverage polymer particles with increasing temperature could be one of possible explanations for the increase in the equilibrium conversion.

Variations of the rate of polymerization with conversion are illustrated in Figure 7. The curve of the polymerization rate versus conversion has a parabolic shape. In the classical emulsion polymerization of hydrophobic monomers (e.g., styrene), the rate of polymerization increases in interval I, and reaches the constant (maximum) value in interval II and then decreases in interval III [23]. In the microemulsion polymerization, two non-stationary-rate intervals appear, and in the miniemulsion four non-stationary-rate intervals appear. Curves of conversion vs conversion rate at different temperatures are presented in Figure 7, which did not apparently show the classical constant rate period in Interval II. Nevertheless, these polymerization rate data are more favorable than that of the conventional emulsion approach. This

behavior has been extensively studied in detail by means of calorimetry [24, 25]. It has been proposed that the rate of polymerization increases during Interval II because the number of particles also increases on account of the occurrence of homogeneous nucleation once micelles have disappeared. Moreover, constant rate periods have not often been directly observed experimentally in the literature because the techniques used to perform kinetic studies are not real-time and rates of polymerization cannot be measured directly.

According to Arrhenius equation [26], the $\ln R$ as a function of $1/T$ for the emulsion polymerization of styrene are displayed in Figure 8. It is evident that the temperature has a strong effect on the polymerization rate. The line shown on the graph is a linear least square fit to the whole data. All the data points on the graph can be approximated by a single line with a slope of -8.76 and a correlation coefficient of -0.992 , as shown in Figure 8. The apparent activation energy estimated from the maximum rates, however, was found to be $72.7 \text{ kJ}\cdot\text{mol}^{-1}$.

Fig. 6. Curves of conversion vs time at different temperatures.

Fig. 7. Curves of conversion vs conversion rate at different temperatures.

Fig. 8. Effect of temperatures on polymerization rates.

Conclusions

The initial rate of polymerization increases with increasing SDS concentration, KPS concentration, styrene concentration and polymerization temperature. In particular the initiator concentration has a dominant effect on the rate of the polymerization. The appropriate conditions for polymerization were obtained when emulsifier concentration of $6.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, initiator concentration of $4.4 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, the polymerization temperature of 75°C and the initial monomer's concentration of $0.288 \text{ mol} \cdot \text{L}^{-1}$ were used. The three rate intervals typical for the emulsion polymerization are not obvious at the temperature we used. The polymerization rate data are more favorable than that of the conventional emulsion approach. In the emulsion polymerization, the effects of the monomer and the initiator concentration do not follow the Smith-Ewart theory. The experimental results can be attributed to the nucleation mechanism of “ TiO_2/SDS ” micelles in the emulsion polymerization of styrene. However, the mechanism and kinetics of the polymerizations are extremely complicated and additional research work need to be done in future. Finally, the apparent activation energy of the emulsion polymerization was $72.7 \text{ kJ} \cdot \text{mol}^{-1}$ and the rate of polymerization R , at 75°C was expressed by

$$R = k [E]^{0.68} [I]^{2.2} [M]^{1.6}$$

Experimental part

Materials

The monomer styrene, was analytically pure grade and was supplied by the Tianjin Chemical Reagent Co. (Tianjin, China). To remove inhibitor, the styrene was washed with a 5% (w) sodium hydroxide solution followed by a deionized water washing. TiO_2 particles with an average particle size close to 35 nm were used as core materials, and produced according to the literature [27]. Sodium dodecyl sulphate (SDS), potassium persulphate (KPS), CaCl_2 , anhydrous ethanol and NaOH were all analytically pure and were supplied by the Beijing Chemical Reagent Co. (Beijing, China).

Polymerization procedure

In a typical synthesis, 1 g of TiO_2 powder, 0.25 g SDS ($3.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) and 250 mL of deionized water were poured into a 500 mL four-necked flask. Then the whole system was agitated by ultrasonic cleaner (KQ-250DB, Kunshan, China) for about 30 min at room temperature. After that, the flask was equipped with a mechanical stirrer, thermometer, reflux condenser, and a nitrogen gas inlet and outlet. Then the flask was immersed into a 75 °C water bath and the nitrogen gas was bubbled through the solution for deoxygenation. The stirring speed was fixed at 250 rpm. After 30 min, 7.5 g styrene was poured into the reaction flask and stirred for 15 min. Then 300 mg KPS was added into the reactor. The polymerization was carried out at 75 °C for 4.5 h. The reaction product was poured into a 5% (w) CaCl_2 solution that had the same volume as the slurry, and the mixture was then stirred thoroughly. The resultant particles were separated from the slurry by vacuum filtration. The filter cake was washed with deionized water five times and anhydrous ethanol two times. Finally, the resultant particles were dried in a vacuum oven at room temperature for 24 h and then were used for characterization.

Conversion of monomer and polymerization rate

The conversion of monomer (C/%) was determined by means of the conventional gravimetric method. Samples were withdrawn at regular intervals and were discharged into a weighing beaker containing a little hydroquinone to inhibit further polymerization. Then they were dried in vacuum till a constant weight at about 60 °C. The weight of the withdrawn sample or dried sample was known from the weight difference of the beaker before and after sampling or drying. The percentage conversion was calculated using the following equation:

$$C\% = ((M_3 - M_1) - M_5 - M_4) \times 100\% / (M_2 - M_1) \times d \quad (4)$$

where M_1 (g) is the mass of empty bottle, M_2 (g) is total mass of empty bottle and emulsion, M_3 (g) is total mass of empty bottle and dry sample after vacuum drying, M_4 (g) is the mass of inhibitor, M_5 (g) is the mass of initiator and TiO_2 , and d (%) is the mass ratio of monomer in emulsion.

The polymerization rate was calculated using the following equation:

$$R = (C_2\% - C_1\%) \times M_0 / (t_2 - t_1) \quad (5)$$

where M_0 ($\text{mol} \cdot \text{L}^{-1}$) is the initial monomer concentration, $C_1\%$ is conversion of monomer at polymerization time t_1 (s) and $C_2\%$ is conversion of monomer at polymerization time t_2 (s).

Characterization

The morphology of the resultant particles was observed by transmission electron microscopy (TEM, Jeol-1200 EX, Japan). Samples for TEM were dispersed in deionized water in an ultrasonic bath for 10-30 min and a drop of diluted dispersion was put on a carbon film supported by a copper grid.

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