

Synthesis of Nanosized Poly(ethyl acrylate) Particles via Differential Emulsion Polymerization

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ABSTRACT: Nanoparticles of poly(ethyl acrylate) were synthesized via a semibatch differential emulsion polymerization method with potassium persulfate as the initiator and sodium dodecyl sulfate as the surfactant. The effects of the reaction temperature, aging time, and surfactant/initiator/monomer ratios on the polymer particle sizes were in-

vestigated. Poly(ethyl acrylate) with particle sizes of less than 20 nm was synthesized under mild conditions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1609–1614, 2006

Key words: nanoparticles; nanotechnology; particle size distribution; synthesis

INTRODUCTION

Nanosized polymer particles have attracted great interest because of their attractive properties arising from the dimension effect and the surface/volume ratio effect. They have potential applications in various fields, such as catalysts, colorants, pesticides, lubricants, electrophotography, biosensors, and microelectromechanical systems.¹ The common methods for preparing nanosized polymers include molecular assembly, template chemistry, dendrimer polymerization, mechanical pulverization, and microemulsion polymerization, among which microemulsion polymerization is the most widely used method.^{2–5} Ozer et al.⁶ synthesized methacrylate-based polymer nanoparticles by microemulsion polymerization. The resulting polymers had viscosity-average molecular weights of 6×10^5 to 1.25×10^6 , the average diameters of the polymer particles were 20–40 nm, and the monomer conversions were 55–85%. Capek and Juranicova⁷ studied the free-radical microemulsion polymerization of alkyl methacrylate. They proposed that the strong dependence of the reaction rate on the monomer concentration resulted from the different locations of the reaction loci (in the interface or in the core of the monomer-swollen micelles or particles) and the gel effect; the average number of radicals per particle, the number of particles, and the coemulsifier efficiency of the monomer increase with an increase in the

alkyl chain length of the monomer. Xu et al.⁸ studied the growth of polymer nanoparticles in microemulsion polymerizations initiated with γ rays. Ming et al.⁹ carried out the microemulsion polymerizations of styrene, butyl methacrylate, butyl acrylate, methyl methacrylate (MMA), and methyl acrylate with a modified microemulsion polymerization process. At a high polymer/surfactant weight ratio ($\geq 9:1$), relatively concentrated (10–30 wt %) latex and small (10–20-nm) particle diameters were attained. He et al.¹⁰ studied the microemulsion polymerization of MMA by a differential addition process; a particle diameter of less than 20 nm was achieved under mild reaction conditions.

Much research has been done on the microemulsion polymerizations of various alkyl methacrylates, except for ethyl acrylate (EA). EA is an important component in latex paints and adhesives because of its low polymer glass-transition temperature. However, it has rarely been studied and is not well understood.¹¹ Capek et al.¹² investigated the microemulsion polymerization of alkyl acrylates initiated by ammonium peroxydisulfate. They found that the reaction rate strongly depended on the EA monomer concentration, and the particle size and number increased with an increase in the conversion; the final conversion and particle size were 90% and 38 nm, respectively. Bhowal et al.¹³ investigated the emulsion and microemulsion polymerizations of EA with a turbid emulsion system of EA, sodium dodecyl sulfate (SDS), and water with monomer/surfactant (M/S) ratios of 10 and 40. A nanoparticle with a diameter of 35 nm was obtained at a conversion of 95%. The major disadvantage of microemulsion polymerization is the requirement of a large amount of a surfactant for the stabili-

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zation of the monomer droplets. The purpose of this article is to investigate the synthesis technique for nanosized poly(ethyl acrylate) under mild conditions.

EXPERIMENTAL

Materials

EA (99%), MMA (99%), SDS (70%; containing ca. 25% tetradecylsulfate, sodium salt, and ca. 5% hexadecylsulfate sodium salt), cetyltrimethylammonium bromide (CTAB), and potassium persulfate (KPS; >99%; American Chemical Society reagent) were used as supplied by Aldrich Chemical Co. (Milwaukee, WI). The critical micelle concentration (cmc) of SDS in water was reported to be 3×10^{-3} mol/L (0.864 g/L) at 25°C and 4.2×10^{-3} mol/L (1.21 g/L) at 80°C.¹⁴ 1-Pentanol (>99%; American Chemical Society reagent), from Aldrich Chemical, was used as a cosurfactant.

Polymerization

A mixture of SDS, KPS, 1-pentanol, and deionized water was charged into a three-necked, round-bottom, 250-mL flask that was equipped with a magnetic stirrer, a reflux condenser, and a thermometer. When the temperature in the system reached a designated level, EA was continuously added in very small drops for about 90 min; this was called a differential operation.¹⁰ After the completion of the EA addition, the reaction system was then maintained at the reaction temperature for a certain aging time.

Particle size measurement

The particle size and its polydispersity (PD) were determined by a dynamic light scattering method with a 90 Plus particle analyzer from Brookhaven Instrument Corp. (software version 3.37). The PD was defined in this instrument as follows:

$$PD = \mu / \Gamma^2 \quad (1)$$

where μ is a parameter proportional to the variance of the intensity-weighted diffusion coefficient distribution and Γ is related to the relaxation of the intensity fluctuations of the scattered light. A small PD means a narrow distribution. Before the analysis, the latexes were diluted with deionized water to minimize the particle-particle interactions.

The solid content of the polymer in the latex was determined via weighing and was calculated as follows:

$$\text{Solid content (\%)} = W_1 / W_2 \times 100\% \quad (2)$$

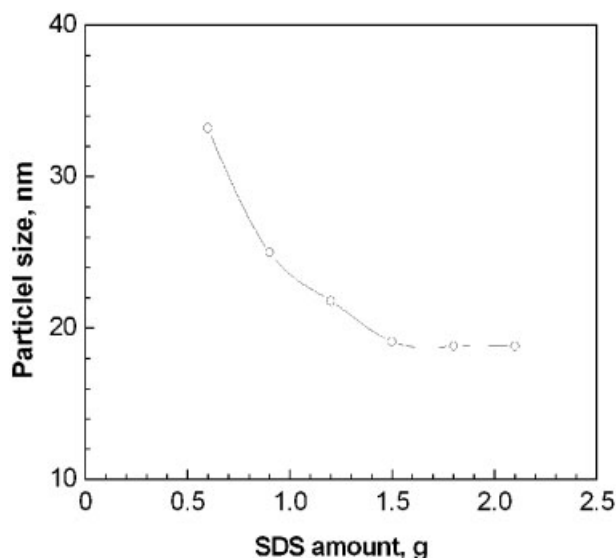


Figure 1 Effect of the surfactant amount on the particle size (EA, 15 mL; 1-pentanol, 0.2 mL; KPS, 0.08 g; SDS, varies; water, 85 mL; reaction temperature, 82°C; EA addition time, 90 min; aging time, 30 min).

where W_1 and W_2 are the weights of the polymer and latex, respectively. The conversion of EA was determined with the following equation:

$$\text{Conversion (\%)} = (W_1 - W_3) / W_4 \times 100\% \quad (3)$$

where W_3 is the total weight of KPS, SDS, and 1-pentanol and W_4 is the weight of EA. The polymer content is calculated by

$$\begin{aligned} \text{Polymer content (\%)} \\ = (\text{Conversion} \times W_4) / W_2 \times 100\% \quad (4) \end{aligned}$$

RESULTS AND DISCUSSION

Effects of the surfactant types and amount on the particle size

The effects of two types of surfactants, SDS (anionic) and CTAB (cationic), on the particle size of the resultant polymers are investigated.

The dependence of the particle size on the SDS amount is illustrated in Figure 1. The experimental data indicate that the particle size decreases with an increase in the surfactant amount from 0.6 to 2.1 g in 85 mL of water (the corresponding concentration of the surfactant is $2.45\text{--}8.58 \times 10^{-2}$ mol/L in the reaction system). The particle size decreases from 33.2 to 19.1 nm as the SDS amount increases from 0.6 to 1.5 g. Beyond the critical amount of 1.5 g (ca. 6.13×10^{-2} mol/L, M/S = 9 : 1) of the surfactant, the dependence of the particle size on the surfactant amount is insignificant. This phenomenon can be explained by the

reaction mechanism. At the beginning of the polymerization, the EA monomers in the water phase are attacked by free radicals produced by the decomposition of KPS and become monomer radicals, which grow in the water phase and then come out of the water phase and become primary particles after the chains reach a certain length. These particles are surrounded by SDS and continue to grow by receiving monomers from the water phase until the reaction in the particles terminates. When the SDS amount is sufficient to generate new polymer precursors and to cover them, the particle size is small. Beyond this adequate amount of the surfactant, further increasing the surfactant amount cannot significantly influence the particle size. Ouzineb et al.¹⁵ studied the effect of the SDS concentration on the particle number and the particle size in the emulsion polymerization of butyl acrylate and methacrylate and found similar phenomena. They observed that the polymer particle number continued to increase because of continual homogeneous nucleation caused by dissolved MMA for an SDS concentration greater than the cmc. They proposed that if the free surfactant above cmc in the reaction system is sufficient to stabilize the small particles produced by homogeneous nucleation, the small particles formed by homogeneous nucleation are not all driven to flocculate onto the larger particles. When the SDS concentration is below the cmc, there is very little free surfactant available to stabilize homogeneously nucleated particles, and the small particles are driven to flocculate onto the larger ones present.

The effect of the amount of surfactant CTAB used in the polymer latex on the particle size is shown in Figure 2. Similarly to the effect of SDS, the increase in

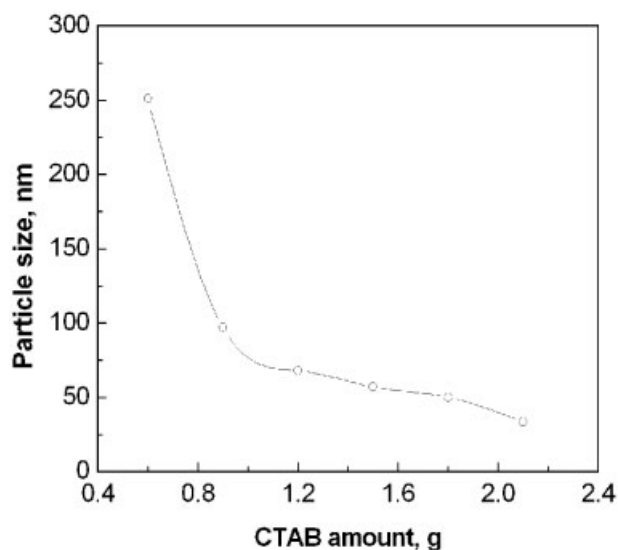


Figure 2 Effect of the CTAB amount on the particle size (EA, 15 mL; 1-pentanol, 0.2 mL; KPS, 0.08 g; water, 85 mL; reaction temperature, 82°C; addition time, 90 min; aging time, 30 min).

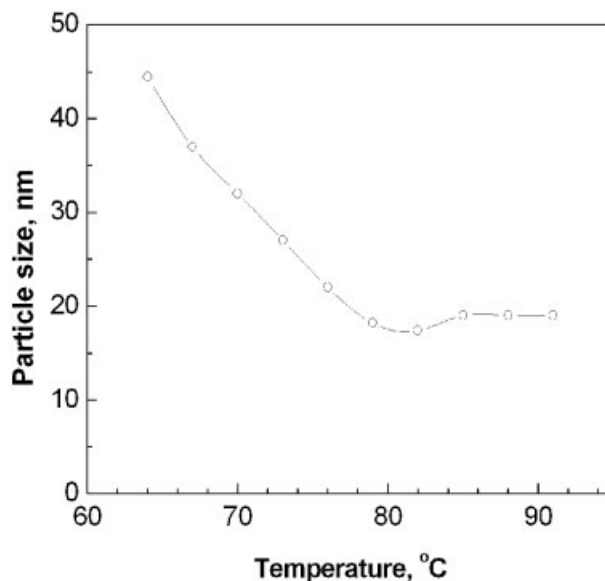


Figure 3 Effect of the reaction temperature on the particle size (EA, 15 mL; 1-pentanol, 0.2 mL; KPS, 0.08 g; water, 85 mL; SDS, 1.5 g; EA addition time, 90 min; no aging operation).

the CTAB amount also leads to a decrease in the particle size. As the amount of CTAB increases from 0.6 [surfactant/monomer (S/M) \approx 1/15] to 2.1 g (ca. S/M = 1/4), the particle size decreases from 251 to 33.3 nm. However, the particle size here is much larger than that obtained via SDS.

The results indicate that CTAB is not as good as SDS in reducing the particle size of poly(ethyl acrylate), and hereafter, SDS is used as the surfactant.

Effect of the reaction temperature

The experimental results for the effect of the reaction temperature on the particle size are shown in Figure 3, which indicates that the particle size decreases with an increase in the reaction temperature from 64 to 82°C. However, if the reaction temperature is further increased after 82°C, the particle size does not decrease further or even increases slightly. This may be explained by the effect of temperature on the initiator-decomposition, chain-propagation, and chain-termination reactions. At the low temperature range, with an increase in the reaction temperature, the decomposition rate of the initiator is accelerated, and more free radicals are generated, which promote the formation of more particles; in turn, the average particle size is decreased. On the other hand, with an increase in the free radicals caused by an increase in temperature, the radical termination rate increases. When the temperature reaches a certain level, the contribution of increasing temperature to the increase in the radical concentration and then to the decrease in the particle size

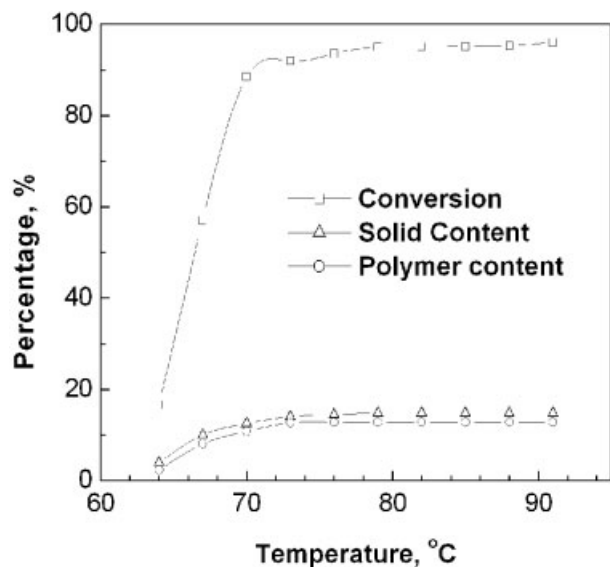


Figure 4 Effect of the reaction temperature on the solid content, conversion, and polymer amount (EA, 15 mL; 1-pentanol, 0.2 mL; KPS, 0.08 g; water, 85 mL; EA addition time, 90 min; no aging operation).

may be offset by the increase in the radical termination rate.

Figure 3 also indicates that when the temperature is below 65°C, the particle size is as high as 44.5 nm; when the temperature is around 80°C, the particle size is less than 20 nm (17.4 nm at 82°C). In comparison with 38 nm, the smallest poly(ethyl acrylate) particle size reported in the literature¹⁴ obtained via emulsion polymerization, the particle size has been significantly reduced in this work.

Figure 4 indicates the effect of the reaction temperature on the reaction conversion. The results reveal that the monomer conversion, solid content, and polymer amount increase from 16.6, 3.9, and 2.3% to 93.6, 14.5, and 12.8%, respectively, with an increase in the reaction temperature from 64 to 76°C. When the reaction temperature is above 79°C, there is no significant effect of the reaction temperature on the conversion, the solid content, and the polymer amount obtained.

Effect of the aging time

The effects of the aging time on the monomer conversion and the particle size are shown in Figures 5 and 6. The results indicate that the aging time significantly influences the polymer particle size and monomer conversion. A longer aging time favors a higher monomer conversion, which promotes the formation of larger particle sizes. A similar phenomenon was observed by Capek et al.¹² During the aging time, particle nucleation is not a significant process, and the monomer is consumed mainly to increase the particle size. With an increase in the monomer conversion

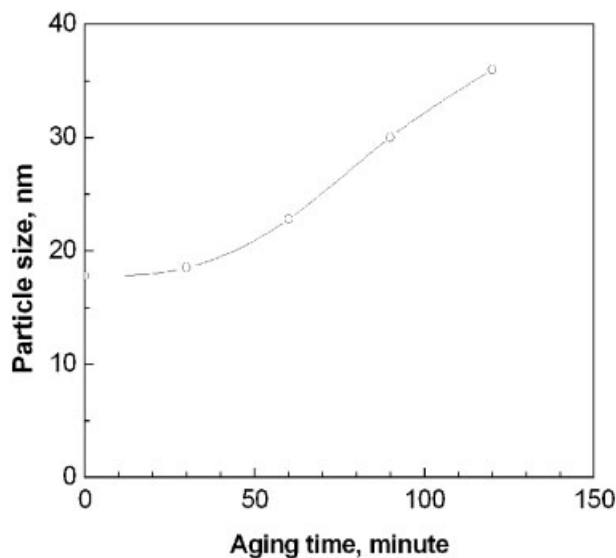


Figure 5 Effect of the aging time on the particle size (EA, 15 mL; 1-pentanol, 0.2 mL; KPS, 0.08 g; SDS, 1.5 g; water, 85 mL; reaction temperature, 82°C; EA addition time, 90 min).

from 96.1 to almost 100% when the aging time increases from 0 to 120 min, the particle size is approximately doubled, that is, from 17.4 to 36 nm, as shown in Figures 5 and 6. This phenomenon suggests that some coalescence between particles possibly happens. An aging time of 30 min is suitable for obtaining a poly(ethyl acrylate) with a particle size of 19.1 nm, at which 97.8% EA conversion is reached, as indicated in Figures 5 and 6.

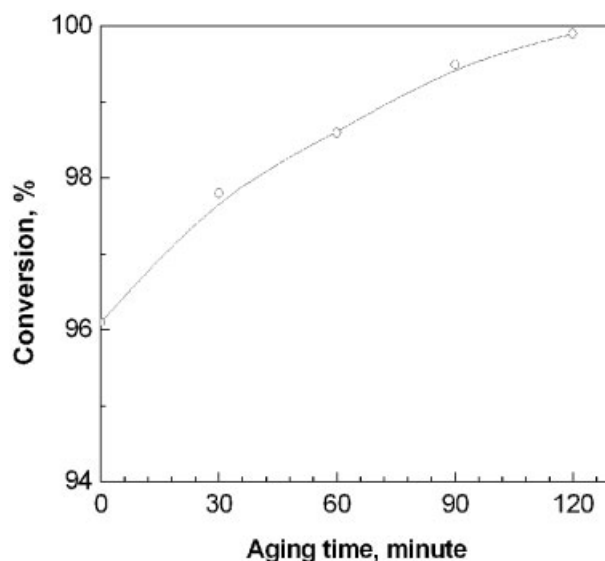


Figure 6 Effect of the aging time on the monomer conversion (EA, 15 mL; 1-pentanol, 0.2 mL; KPS, 0.08 g; SDS, 1.5 g; water, 85 mL; reaction temperature, 82°C; EA addition time, 90 min).

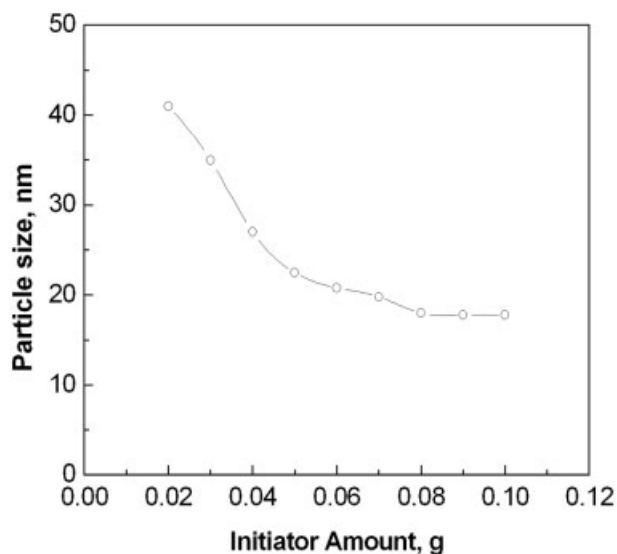


Figure 7 Effect of the initiator amount on the particle size (EA, 15 mL; 1-pentanol, 0.2 mL; KPS, varies; SDS, 1.5 g; water, 85 mL; reaction temperature, 82°C; EA addition time, 90 min; aging time, 30 min).

Effect of the initiator amount

The effect of the initiator amount on the particle size is shown in Figure 7, which indicates that increasing the initiator concentration in the reaction system helps with decreasing the particle size. This is because increasing the initiator amount leads to an increase in the free-radical number in the reaction system. As a result, more free radicals attack the monomer molecules to form more active sites, and this results in a smaller particle size at a given monomer amount. However, similarly to the effect of the reaction temperature discussed previously, with an increase in the radicals, the radical termination rate also increases, and this may offset the effect of the increase in the initiator amount used in the reaction and result in relatively constant active sites. This may be the reason that the particle size does not decrease when the KPS amount is above a certain level, which is 0.08 g [monomer/initiator (M/I) \approx 173 : 1] in this system.

Effect of the monomer amount

The EA amount in the reaction system also affects the particle size of the resultant polymer. The experimental results are shown in Figure 8, which indicates that an increase in the EA consumption results in an increase in the particle size. When the monomer amount is 10 mL (S/M \approx 1/6 w/w), the particle size is 17.4 nm. However, when the monomer amount is 25 mL, the particle size reaches 29.6 nm. When the monomer amount is greater than 25 mL, the particle size will increase dramatically with a further increase in the monomer amount; for example, when 30 mL of EA

(S/M ratio \approx 1/18) is added, the particle size increases to 71 nm. Therefore, a larger EA amount results in a larger particle size, and this may possibly be offset if the surfactant amount is increased to an adequate level and/or the agitation is enhanced in the reaction system.

Particle size distributions

The particle size distribution is not investigated here. However, a representative example of the particle distribution is illustrated in Figure 9; it has a z-average diameter of 18.4 nm and a PD of 0.179 (provided by the 90 Plus particle analyzer).

CONCLUSIONS

The synthesis of nanosized poly(ethyl acrylate) has been studied via a differential microemulsion polymerization method. This method is suitable for obtaining poly(ethyl acrylate) with a particle size smaller than 20 nm. The effects of the reaction conditions, such as the reaction temperature, aging time, surfactant amount, initiator amount, M/S ratio, and surfactant type, on the particle size have been investigated. The optimum temperature is 80–85°C for the lowest poly(ethyl acrylate) particle size. A long aging time favors an increasing particle size and an increasing monomer conversion. An increase in the surfactant amount and initiator amount leads to a small particle size. A higher monomer amount results in a larger particle size at a given surfactant amount. The anionic surfactant SDS is favorable for producing nanoparticles of poly(ethyl

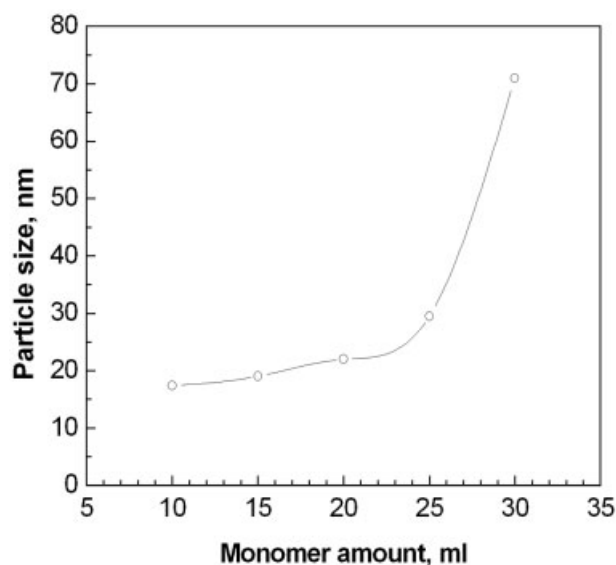


Figure 8 Effect of the monomer amount on the particle size (EA, varies; 1-pentanol, 0.2 mL; KPS, 0.08 g; SDS, 1.5 g; water, 85 mL; reaction temperature, 82°C; addition time, 90 min; aging time, 30 min).

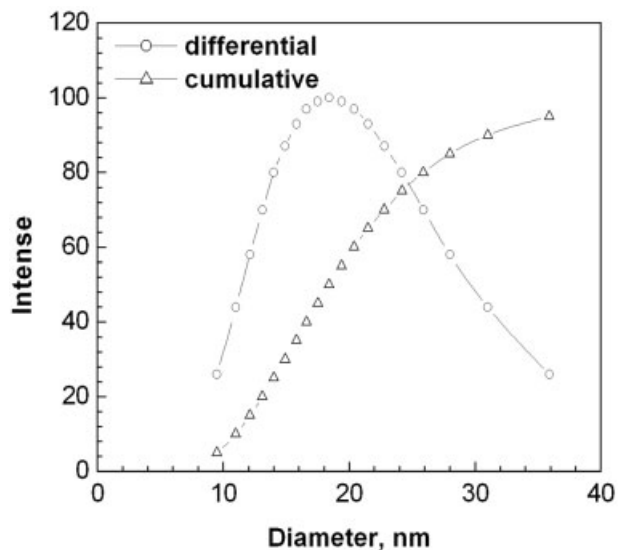


Figure 9 Typical distribution of the particle size (z-average diameter = 18.7 nm; PD = 0.179).

acrylate) in comparison with the cationic surfactant CTAB. There exist typical conditions (i.e., M/S = 9 : 1, M/I = 173 : 1, and aging time = 30 min) under which poly(ethyl acrylate) particles with a size of 19 nm can be achieved.

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