Polymer Bulletin 61, 749–757 (2008)
DOI 10.1007/s00289-008-1000-0

Polymer Bulletin

Morphology and Characterization of Epoxy-acrylate Composite Particles

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Received: 10 April 2008 / Revised version: 31 August 2008 / Accepted: 2 September 2008

Summary

Epoxy-acrylate sample was prepared by two-stage feed emulsion polymerization. Gel permeation chromatography (GPC) and Ultraviolet-Visible (UV-Vis) spectra indicated the acrylic and styrene monomer were grafted onto epoxy resin. Transmission electron microscope (TEM) showed that epoxy-acrylate composite particles with different epoxy resin content stained by pH1.5 phosphotungstic acid (PTA) had an obvious core-shell structure, with styrene-acrylate as the core and epoxy resin as the shell. TEM micrographs also showed the acrylate cores concentrically or eccentrically were positioned inside epoxy resin shells, which was consonant with the particle structures designed. But the Epoxy Resin/Methyl Methacrylate (EP/MMA) particles showed a strange quadrangle-like structure and Epoxy Resin/Methyl Methacrylate/ Butyl Acrylate (EP/MMA/BA) particles showed a hexagon-like structure, which were different from the normal particle structures.

Keywords

Core-shell structure, Graft reaction, Epoxy-acrylate particle

Introduction

The studies of preparation, characterization, and applications of core-shell particles have been attracting more and more attentions in various aspects, such as coatings and adhesives, toughing and strengthening for plastics and reinforcement for rubber[1-3]. The preparation of core-shell particles by seeded emulsion polymerization has been attracting great interest among researchers[4-6]. So a tremendous progress in this field has been achieved.

The core-shell particles normally were prepared by adding monomers into a seeded emulsion using batch or continuous method[5-6]. Most of the researches focused on methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), vinyl acetate (VAc), butadiene and N-isopropylacrylamide[7-8], with only a few reports available on epoxy resin as the shell material[9-12]. Epoxy resin has a number of excellent performances, such as high flexibility, good weather resistance (including ultraviolet and water resistance), excellent thermal stability. Thus, it is an excellent material for the modification of paints.

If a very thin layer of epoxy resin is formed outside of the polystyrene or polyacrylate, the required properties of epoxy resin are introduced into the composite material. In this paper, a unified set of emulsion polymerization processes for the synthesis of epoxy-acrylate composite particles with styrene-acrylate as the core and epoxy resin as the shell were employed. The cores concentrically or eccentrically were positioned inside epoxy resin shells in the particles because the critical surface tension of epoxy resin is higher than that of St and BA (shown in Figure 1). Furthermore, two particular core-shell emulsoid structures of hexagon-like and quadrangle-like, which were much different from traditional spherical, dumb-bell and strawberry structures had been prepared by emulsion polymerization in this study.

Experimental

Materials

Butyl acrylate(BA,96%), Styrene(St,97%), Methyl Methacrylate(MAA,96%) and Diacetone acryl amide (DAAM) were purchased from Qingdao Reagent Company. Epoxy resin (0.38~0.45 epoxy value) was kindly provided by Jiangsu Sanmu Company. The anionic surfactant sodium dodecyl sulfate (SDS), nonionic surfactant nonylphenol polyoxyethylene ether (OP-10) and ammonium persulfate were purchased from Qingdao Chemistry Reagent Company. All materials were used without further purification.

Preparation of Epoxy-acrylate Composite Particles

The latex sample was prepared by two-stage feed emulsion polymerization in a 250ml four-necked flask, with the ingredients shown in Table 1. The first-stage mixture as indicated in Table 1(part A) was fed into the flask and was then purged with nitrogen gas and heated to 75±1°C. After polymerization at 75°C for 1h to obtain conversion of 95% or more, the second-stage feed mixture as indicated in Table 1(part B) was added at constant rate over 1.5h and the flask was then maintained at 75°C for two more hours to complete the reaction. The pH of the final latex was adjusted to 8~9 with ammonia.

Sample Characterization

GPC: The epoxy-acrylate latex was prepared by two-stage emulsion polymerization, in which the styrene-acrylate latex was prepared in first-stage. The styrene-acrylate latex and epoxy-acrylate latex are demulsified with methanol, washed 5 times with deionized water followed by drying at 50°C under a vacuum oven for 24h to obtain the composite copolymers. The GPC was obtained from Agilent 1100 series measurement by running 0.5% composite copolymer in tetrahydrofuran (THF) at 35°C. THF was used as the eluent phase. The elution volume was converted to apparent molecular weights using narrow distribution polystyrene standards.

UV-Vis Spectra: In the GPC experiment, elution polymer from 5min~7min for the styrene-acrylate latex and epoxy-acrylate latex were samplinged and analyzed for the UV-Vis detector, respectively. The UV-Vis spectra were obtained from CARY UV-Vis-detector with the scan rang from 190nm to 400nm.

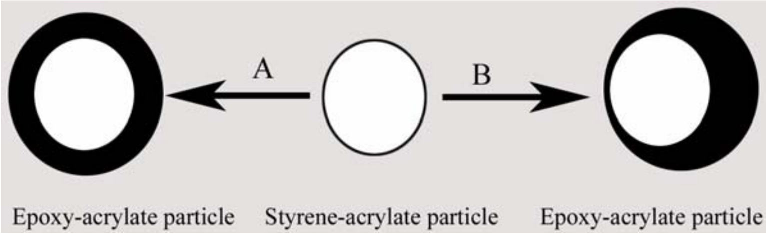


Figure1. Scheme for epoxy-acrylate composite particles: (A) cores concentrically positioned inside epoxy resin shells, (B) cores eccentrically positioned inside epoxy resin shells.

Table1. Typical Recipe for Synthesis of Epoxy-acrylate Composite Latex

Materials	Part A /g	Part B /g
BA	33	
St	36	
MAA	2.5	
DAAM	1.0	0.5
Epoxy resin(E-44)		14~28
SDS+OP-10	3	
$NaHCO_3$	0.2	
$(NH_4)_2S_2O_8$	0.4	
Deionized water	70	

TEM: The morphology of the latex particles was examined with a JEOL 100 U TEM. The staining with PTA was carried out as follows: the latex was first diluted to 1000 times and then, the same volume for both latex and PTA (3%) solution (pH=1.5) were mixed for 3min. A copper microscope grid was dipped into the mixture, put on a filter paper, and then dried at room temperature.

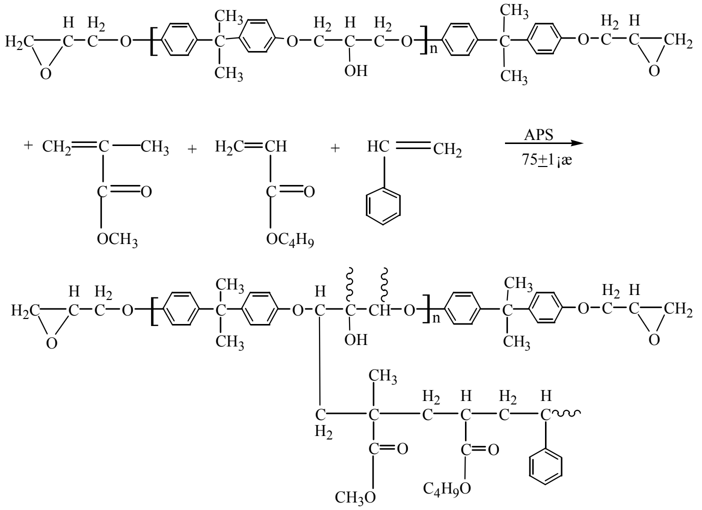
Results and Discussion

GPC

Figures 2 is typical representative of the GPC measurements for the styrene-acrylate latex, epoxy resin, and epoxy-acrylate latex using the RI detector. For the curve of styrene-acrylate latex, the peak corresponds to a molecular weight of about 40, 000, which can be taken as the GPC of the copolymer of styrene and acrylic monomer. In the curve of epoxy-acrylate copolymer the first peak corresponds to a molecular weight of more than 56,000, which can be taken as the GPC of the copolymer, including the epoxy-acrylate graft copolymer and the ungrafted acrylic copolymer. The second peak corresponds to a molecular weight of about 1,000. By comparing the peak of epoxy resin with the second peak of epoxy-acrylate latex, they have not only the same outflowing time, but also the similar molecular weight. As a result, the second peak is obviously the GPC of the ungrafted epoxy resin.

UV-Vis Spectra Analysis

UV-Vis spectra of outflowing latex for the first peak (outflowing time from 5min to 7min) in epoxy-acrylate latex were analyzed in order to confirm whether the acrylic monomer had grafted onto epoxy resin. In the UV curve only the epoxy parts in the composite copolymer can be detected when the wavelength was 284nm[9], which was based on the fact that the epoxy resin had a strong absorption at this wavelength due to the bisphenol A structure while the styrene-acrylate copolymer was almost transparent. UV curves of styrene-acrylate latex and epoxy- acrylate latex outflowing from the GPC experiment at the first peak were shown in Figure 3. In the UV-Vis spectra there was a sharp peak at 282nm of epoxy-acrylate latex while in the styrene-acrylate latex there was not the sharp one, indicating that the acrylic monomers had grafted onto the epoxy resin. Graft reaction and reaction mechanism between epoxy resin and acrylate was proved by Woo and Toman[13] through ^{13}C-NMR. A ^{13}C-NMR spectroscopy analysis showed that the most probable grafting locations on epoxy resin molecular chains were adjacent carbon of aether bond and tertiary carbon. In this study the graft reaction between epoxy resin and acrylate was analyzed by GPC and UV-Vis spectra, and the approximate structure for this composite polymer was supposed as following:



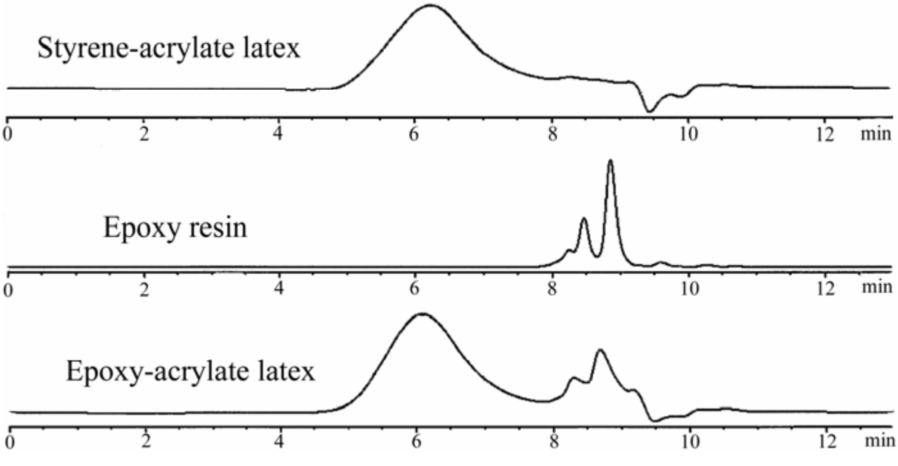


Figure2. GPC of the styrene-acrylate latex, epoxy resin, and epoxy-acrylate latex

TEM Micrograph of Latex

Core-shell particles are produced through seeded emulsion polymerization, styrene-acrylate as seeds and epoxy resin grafted onto them. Figure 4 shows typical TEM micrographs of the resulting particles with spherical structures. Figure4 (a) is epoxy-acrylate particles that were not stained and Figure4 (b) is epoxy-acrylate particles that were stained with PTA. It was found that the particle size was between 150~250nm. Only the particle size and morphology can be seen when it is not stained, and the structure can not be present[14]. But in most of the case, the researchers are interested in the outboard of the particle. As a result, it is necessary to apply the electron-staining technique to distinguish the inboard and outboard of the particle. Figure 4 (b) shows

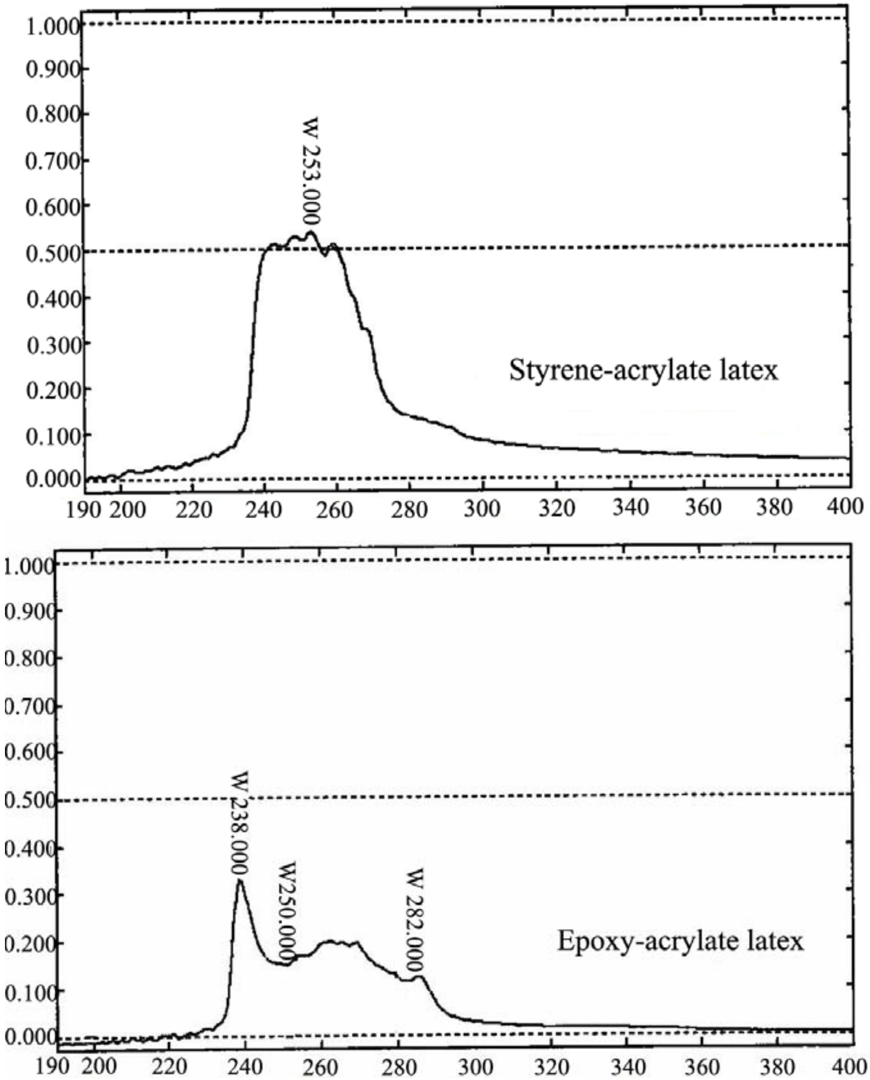
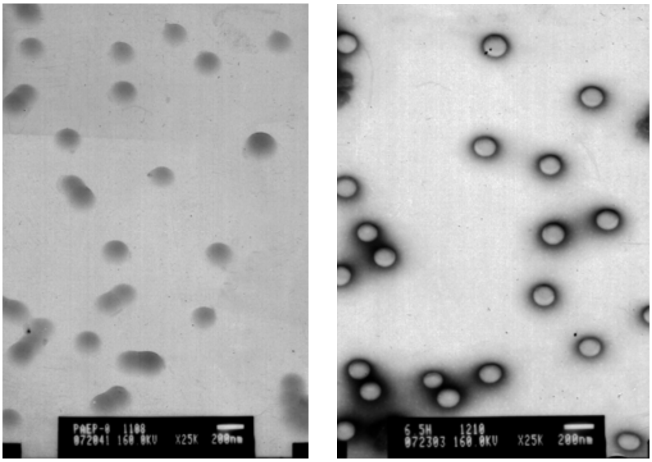


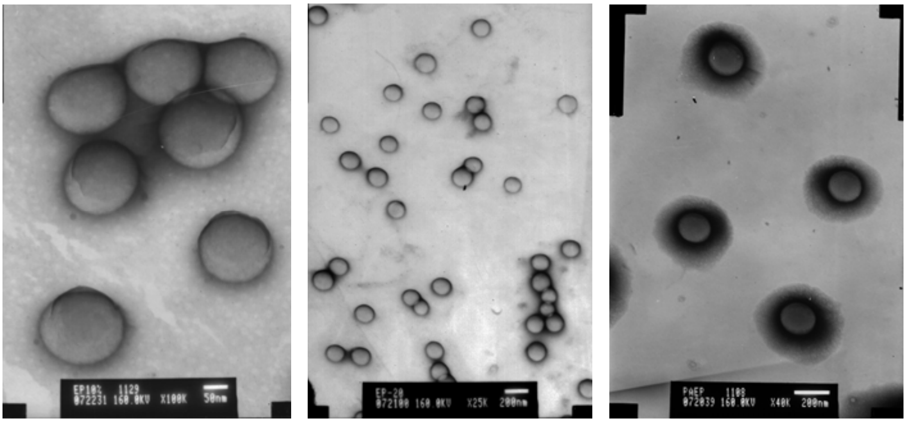
Figure3. UV-Vis spectra of styrene-acrylate latex and epoxy-acrylate latex

us the epoxy-acrylate particles stained by pH1.5 PTA. It can be seen there are obvious core-shell structures for epoxy-acrylate particles. Although some of the particles conglutinate with each other, they are distinguished clearly. It also can be seen in Figure 4(b) that the dumbbell-shape mentioned in Figure 4 (a) is two contiguous particles in fact.



(a) **(b)**

Figure4. TEM micrographs of latex: (a) no stain, (b) stained by PTA



(a) **(b)** **(c)**

Figure5. TEM micrographs of epoxy-acrylate latex: (a) 10% of Epoxy content, (b) 20%of Epoxy content, (c) 40% of Epoxy content.

In order to confirm whether the stained component in the shell is epoxy resin, TEM micrographs for epoxy-acrylate particles with different epoxy resin content, but the same content of other components were investigated. TEM micrographs of epoxy-acrylate particles with 10%, 20% and 40% of epoxy resin are shown in Figure 5 (a), (b) and (c), respectively. It is found in micrograph (a) that the shells are thin and do not completely enwrap the cores, which seem like something that is adsorbed on the particle surface. For micrograph (b) and (c) the core-shell structures for the epoxy-acrylate particles are obvious, which are composed of light cores and dark shells. With the increasing content of epoxy resin, the dark shells became thicker, especially the shell in micrograph (c), which shows the more obvious core-shell structures. It was also found that the diameters for light cores were all between 150nm~170nm, despite the increase of epoxy resin content. So it was deduced that the increasing shells were related to epoxy resin content. As a result, the reason for not completely enwrapping shell in micrograph (a) was that the epoxy resin content was too little to enwrap the cores completely.

It was reported in the literature[15] that only the BA is stained when the pH1.5 PTA was applied to stain Butyl Acrylate/ Methyl Methacrylate(BA/MMA) particles, only the BA was stained while the MMA was not. So the staining mechanism of PTA was applied to analyze the particle structure of Methyl Methacrylate/Epoxy resin (MMA/ EP), EP/MMA and EP/MMA/BA.

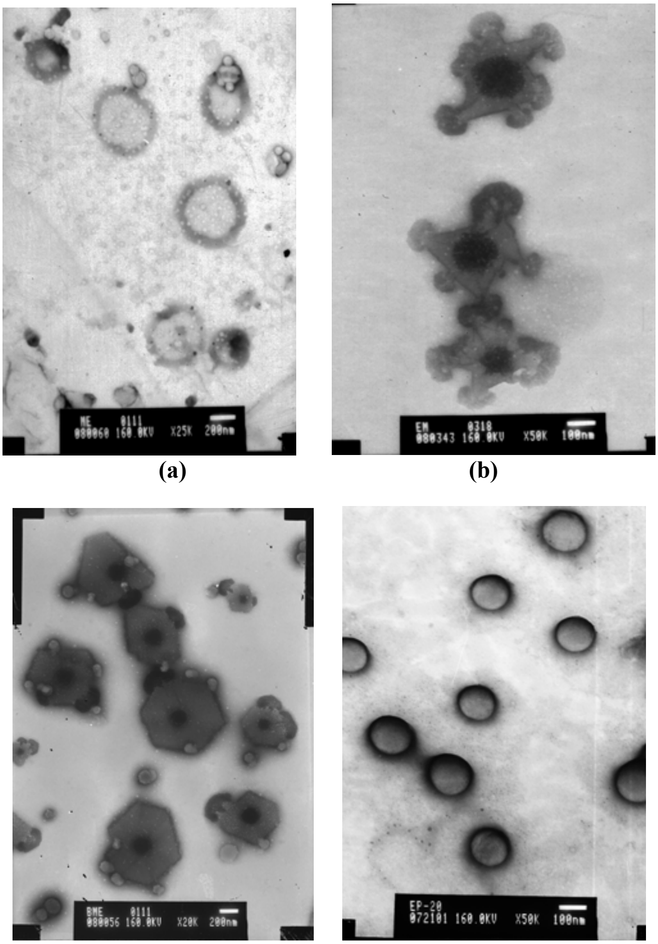
The micrographs of MMA/EP, EP/MMA and EP/MMA/BA particles are shown in Figure 6(a), (b) and (c) respectively. They are obviously core-shell particles. MMA/ EP latex showed spherical core-shell structure and the shell was black and the core was light while the shell was light and the core was black in EP/MMA particles. According to the staining mechanism of PTA, the stained black component was supposed to be epoxy resin because MMA could not be stained by pH1.5 PTA. For EP/MMA/BA particles shown in Figure 6(c), it showed a three-layer structure, where the black shell was BA and the black core was epoxy resin and the light middle layer was supposed to be MMA. It was further proved that epoxy resin can be stained by pH1.5 PTA. Consequently, it was concluded that epoxy resin formed the shell in the epoxy-acrylate composite particles. However, for the EP/MMA and EP/MMA/BA particles, the shells are quadrangle-like structure and hexagon-like structure, which are obviously different from the normal particle structures, such as spherical structure, dumb-bell structure and strawberry structure. The reason for the formation of quadrangle-like and hexagon-like structures is required further research.

TEM micrograph in Figure 6(d) showed the core-shell particles which were designed in Figure 1. The formation of such eccentric structure presumably was due to the interfacial tension between the hydrophilic acrylate particle and the hydrophobic epoxy resin. At the initial stage of polymerization with the addition of epoxy resin, a thin layer of epoxy resin shell was deposited in the form of small particles on the acrylate surface through copolymerization. So the symmetric distribution of epoxy resin around the acrylate cores formed. However, as shown in Table 2, the surface tension for epoxy resin is bigger than that of PSt and PMMA[16-19], so the epoxy resin shell tends to contract the surface area so as to reduce the interfacial tension, which lead to the asymmetric distribution of epoxy resin around the cores.

Conclusion

1. The core-shell epoxy-acrylate composite latex was prepared by seeded emulsion polymerization.

2. GPC and UV-Vis spectra indicated the graft reaction between acrylate and epoxy resin took place. MMA/EP and EP/MMA particles stained by pH 1.5 PTA indicated that the pH1.5 PTA can stain epoxy resin. Epoxy-acrylate particles showed an obvious core-shell structure.
3. TEM micrographs showed that acrylic monomer formed the core and epoxy resin formed the shell in epoxy-acrylate particles with different epoxy resin content. TEM micrographs also indicated the acrylate cores were concentrically or eccentrically situated inside epoxy resin shells, which was consonant with the particle structures designed.
4. It was found that EP/MMA particles had a quadrangle-like structure and EP/MMA/BA particles had a hexagon-like structure, which were obviously different from the normal particles.



(a) (b)

(c) (d)

Figure6. TEM micrographs of different latex: (a) MMA/EP, (b) EP/MMA, (c) (c) EP/MMA/BA, (d) Epoxy-acrylate latex

Table2. Surface tension ($\gamma_{s\text{-}g}$), interface tension ($\gamma_{s\text{-}water}$) and contact angle (*Θ*)of monomer and epoxy resin to water[16-19]

Sample	Contact angle Θ	$\gamma_{s\text{-}g}$ (mN/m)	$\gamma_{s\text{-}water}$ (mN/m)
H_2O	70.5	17.1	—
PMMA	76.5	27.3	19.61
PSt	92.5	16.45	10.59
Epoxy resin	66.0 [a]	44	37.04 [b]

a: tested according to the method introduced in the literature[19];

b: $\gamma_{s\text{-}water(epoxy\ resin)}$ is calculated according to the following equation:

$\gamma_{s\text{-}g(epoxy\ resin)} = \gamma_{s\text{-}water(epoxy\ resin\ )} + \gamma_{s\text{-}g(water)} \cos\Theta$ [19]

Acknowledgements. The authors would like to thank the Korea Institute of Industrial Technology for the financial support of this project.

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