Ultrasonically Irradiated Emulsion Polymerization of Styrene in the Presence of a Polymeric Surfactant

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ABSTRACT: A polymeric surfactant based on carboxymethyl cellulose and alkyl poly(etheroxy) acrylate (CMC-A9) was used in ultrasonically irradiated emulsion polymerization of styrene. Polystyrene nanoparticles (30–60 nm) with high molecular weight were prepared. Compared with the conventional emulsion polymerization, the introduction of CMC-A9 in the polymerization yielded higher monomer conversion in a shorter time and under lower ultrasonic power output. A single latex particle contained only a few polymer chains with average chain numbers of 2–19. The particle size and polymer chain per particle could be controlled by changing the concentration of CMC-A9 and SDS. The effect of CMC-A9 and SDS on ultrasonically irradiated emulsion polymerization kinetics was studied. The results indicated that the ultrasonically irradiated emulsion polymerization had a similar nucleation mechanism to a miniemulsion polymerization system. This is attributed to the high ratio of radicals and a great number of smaller sizes of monomer droplets produced under ultrasonic irradiation. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 763–768, 2004

Key words: polymeric surfactant; polystyrene; ultrasonic irradiation; emulsion polymerization

INTRODUCTION

The synthesis and characterization of polymer nanoparticles, especially with narrow size dispersity, are subjects of current interest because of their large range of applications in technical and biomedical areas. Microemulsion polymerization is one of the most frequently used techniques.[1] The principle of microemulsion formation is the use of a large amount of surfactant, or mixture of surface-active agents, due to the necessity of stabilizing a large overall interfacial area, and the content of monomer is relatively low. These have restricted the potential industrial applications of microemulsion polymerization. Although emulsion polymerization has many advantages and is widely used in industry, the size of latex particles prepared by emulsion polymerization is generally between 50 and 700 nm. It is difficult to prepare latex particles with a size below 100 nm. Thus, there is a great interest in finding new ways, including new emulsion polymerization technology and new emulsifier systems, to prepare polymer nanoparticles.

Ultrasonic irradiation has been widely used in polymerization.[2–7] It has been demonstrated clearly that ultrasonic irradiation can make some polymers, monomers, solvents, and surfactants break down into free radicals that are capable of initiating polymerization.[2,8,9] The most interesting aspect of ultrasonically irradiated emulsion polymerization is that it might result in small (i.e., <100 nm) latex particles. Acoustic intensity plays an important role in ultrasonic irradiated emulsion polymerization. It affects the ratio of radicals produced and the size of monomer droplets.[2,3,6] Biggs and Grieser carried out the polymerization of styrene in water (o/w) emulsion under ultrasonic irradiation in the absence of any chemical initiator.[3] The final latex diameters were ~ 50 nm, but, the conversion of styrene was relatively low. The size of the latex particle was nonuniform and the latex particles trended to aggregate, due to the large overall interfacial area of small particles. Despite these problems, ultrasonic initiated emulsion polymerization has attracted more attention recently because of its unique advantages, such as not requiring chemical initiators, the aqueous medium, smaller latex particles, lower reaction temperature, and faster polymerization.

Surfactants are found to play a significant role in the stability of emulsion and polymerization kinetics. The conventional surfactants that have low molecular weight, such as sodium lauryl sulfate, often give bad effects on properties of the final polymer latex. Polymeric surfactants provide some unique advantages in emulsion polymerization, such as low foaming, and good chemical and mechanical stability of the la-
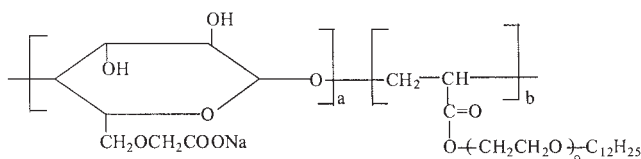
Scheme 1 CMC-based polymeric surfactants.

tex,[10–14] but their high molecular weight would lead to weakened ability to reduce the interfacial tension because of macromolecule entanglement. Few polymeric surfactants, which have both high molecular weight and low interfacial tension, have been available. We had synthesized a novel polymeric surfactant based on carboxymethyl cellulose and alkyl poly(etheroxy) acrylate (CMC-A9) by the ultrasonic method, which showed both excellent surface activity and high molecular weight.[15] These polymeric surfactants, based on CMC, can increase the latex stability against electrolytes acting as steric stabilizers and emulsifiers simultaneously in emulsion polymerizations. Moreover, polymeric surfactant could probably undergo chain scission and react with the monomer when subjected to ultrasonic irradiation.

Studies of the effect of a polymeric surfactant on the ultrasonically irradiated emulsion polymerization have not been performed. It would be of interest to compare results with conventional emulsion polymerizations. In this study, polystyrene nanoparticles were prepared by emulsion polymerization in the presence of a polymeric surfactant CMC-A9.

EXPERIMENTAL

Materials

Styrene (Xilong Chemical Plant, China; CP) was washed with 10 wt % NaOH aqueous solution and distilled under vacuum prior to use. Sodium dodecyl sulfate (SDS) and solvents (acetone, tetrahydrofuran, ethanol) were used as supplied from Wuhan Chemical Reagents Institute of China. The polymeric surfactant (CMC-A9) shown in Scheme 1, was synthesized by ultrasonic irradiation as described earlier[15] ($\bar{M}_w = 1.69 \times 10^5$, the average composition of block, $b = 10.1\%$).

Apparatus

Ultrasound, with a frequency of 20 kHz, was produced with a Sonics and Materials 1500 Ultrasonic Generator (USA); the power output was adjustable.

Emulsion polymerizations

The polystyrene was prepared by subjecting the mixture of styrene, CMC-A9, SDS, and water to ultrasonic

irradiation at 25 ± 2°C. The probe of the ultrasonic horn was immersed directly in the emulsion. Ultrasonic power output was kept constant. The basic recipe is listed in Table I

Measurements

Monomer conversions were determined gravimetrically. The polymerization rate R_p versus time reaction curves were obtained by derivation of the conversion versus time curves.

FTIR spectra of polymers were recorded with a Nicolet Model 560 spectrometer (USA). Each spectrum was recorded in double precision at a resolution of 2 cm^{-1} with a total of 20 scans.

The intrinsic viscosity of polymers was determined using a Ubbelohde viscometer at 24 ± 0.1°C, and THF as the solvent. The molar masses of polymer $\bar{M}_v$ can be calculated from the intrinsic viscosity.[16]

Particle size of polystyrene latex was examined by transmission electron microscopy (JEM100X, Japan). A drop of a diluted polymer emulsion was put on a carbon film supported by a copper grid and placed in the vacuum of the electron microscope after air-drying. The diameters of over 200 particles were used in the calculation of the average sizes for the samples imaged by TEM. The number-average diameter (D_n), the volume-average diameter (D_v), weight-average diameter (D_w), and the polydispersion of particle size (PDI) were calculated according to equations (1–4), where N_i is the number of particles with diameter D_i (nm)

$$D_n = \sum N_i D_i / \sum N_i \qquad (1)$$

$$D_v = \sum N_i D_i^3 / \sum N_i D_i^2 \qquad (2)$$

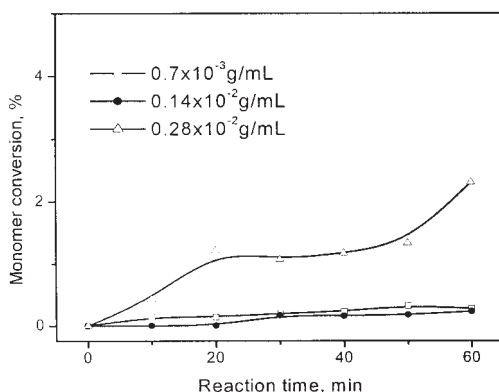$$D_w = \sum N_i D_i^4 / \sum N_i D_i^3 \qquad (3)$$

$$\text{PDI} = D_w / D_n \qquad (4)$$

where $\bar{M}_w$ was approximatively replaced by $\bar{M}_v$, and the average number of chains per particle (N_c) was estimated from the equation

$$N_c = [4/3\pi(D_v/2)^3 N_A \rho]/\bar{M}_v \qquad (5)$$

TABLE I
Basic Recipe of Emulsion Polymerization

Feed		Conditions	
Styrene (% v/v)	10	Ultrasonic power output (W)	600
CMC-A9 (×10³ g/mL)	0.7	Temperature (°C)	25 ± 2
SDS (g/mL)	0.03	Time (min)	60

Figure 1 Monomer conversion versus time curves for the ultrasonically irradiated emulsion polymerization of St at various CMC-A9 concentrations (without SDS).

and the particle number (N_p) generated per milliliter of water was calculated from the equation

$$N_p = 6y/[\pi(D_v)^3\rho] \tag{6}$$

where N_A is Avogradro's number (6.02×10^{23}), y is latex solid content (g/mL), D_v is volume-average diameter of the latex particle (m), and ρ is polymer density (g/mL).

RESULTS AND DISCUSSION

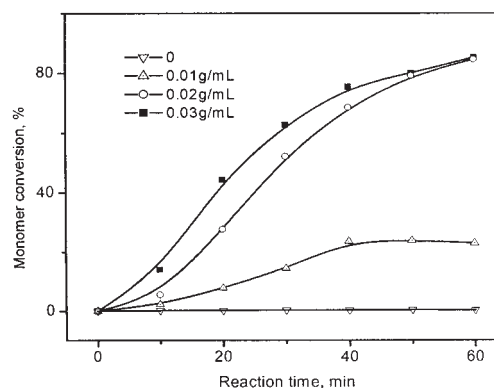### Ultrasonically irradiated emulsion polymerization

Because CMC-A9 has high molecular weight and long molecular chains, which may rupture to form macromolecular radicals under ultrasonic irradiation, it could serve not only as a surfactant but also as an initiator. Without any chemical initiator and any other surfactants added, CMC-A9 was used as emulsifier in ultrasonically irradiated emulsion polymerization of styrene. Time–styrene conversion curves are shown in Figure 1. Obviously, monomer conversion is very low in this reaction. Thus, if only using polymeric surfactant CMC-A9, ultrasonic irradiation cannot initiate styrene efficiently to polymerize it.

The emulsion polymerization of styrene, using SDS as emulsifier, can be successfully performed under ultrasonic irradiation.[2,3] In the presence of CMC-A9, SDS was added as initiator and emulsifier. As expected, with the increase of SDS concentration, monomer conversion improved greatly (as shown in Fig. 2). Thus SDS, that may be the source of radicals, plays an important role in the ultrasonically initiated emulsion polymerization. The FTIR spectra, of polymers prepared by using 10 vol % St, 0.03 g/mL SDS by ultrasonically irradiated and conventional emulsion polymerization (with initiator potassium sulfate), respectively, are shown in Figure 3. These spectra are similar. For the spectrum of the polymers prepared by ultrasonically irradiated emulsion polymerization, new peaks at 1244 and 1214 cm^{-1}, due to the stretching of S—O—C, are clearly observed. It may indicate that SDS is broken down into radicals under ultrasonic irradiation, which initiates styrene polymerization. Stoffer et al.[4] proved that the source of these free radicals mainly came from the degradation of SDS under ultrasonic irradiation in the aqueous medium.

In ultrasonically irradiated emulsion polymerization, it has been reported that SDS serves as emulsifier and initiator. However, the conversion of styrene in ultrasonically irradiated emulsion polymerization was low at short times.[3] This result was also obtained in our study, as shown in Figure 4: using only SDS, the conversion of styrene was below 40% within 60 min.

Because it has been reported that the dense absorbed layer of some water-soluble polymers [e.g., hydroxyl propyl cellulose (HPC), CMC] on fine particles shows a strong protective action against flocculation of the particles, CMC was added during ultrasonically emulsion polymerization in a comparison with the polymeric surfactant CMC-A9. Figure 4 shows that their effect on the emulsion polymerization of styrene is not similar: the conversion of styrene even decreases by using CMC at a lower concentration. When CMC-A9 is added to the ultrasonically irradiated emulsion polymerization, the conversion of styrene improves greatly, especially at a higher concentration of CMC-A9 (Fig. 4). This observation is most likely due to the difference in the number and size of micelles, and the stability of emulsion. Because CMC-A9 is used as a stabilizer, as well as an emulsifier, as the CMC-A9 concentration is elevated, the number of micelles and small monomer droplets would also increase. Thus, the rate of nucleation and the number of nucleating particles are expected to increase, resulting in higher monomer conversion and a larger amount of

Figure 2 Monomer conversions versus time curves for the ultrasonically irradiated emulsion polymerization of St at various SDS concentrations.
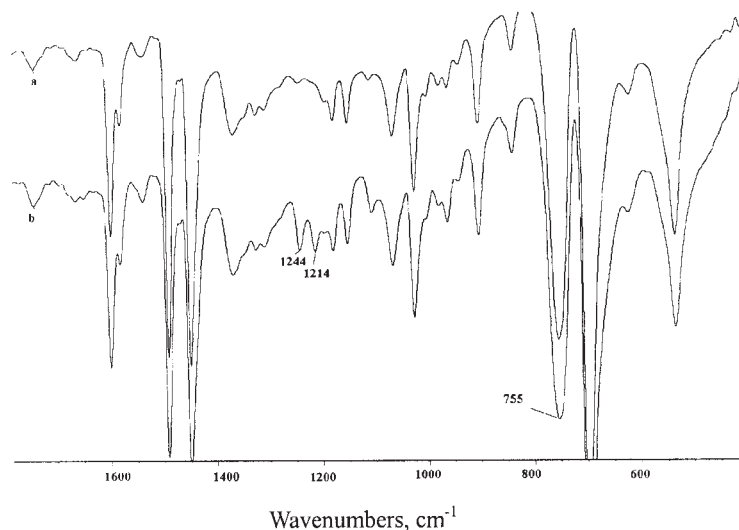
Figure 3 FTIR spectra of PS polymerized by (a) conventional emulsion polymerization, (b) ultrasonically irradiated emulsion polymerization.

latex. This gives an indication that CMC-A9 is a very effective emulsifier and stabilizer.

The effect of the ultrasonic power output on emulsion polymerization, in the presence of 0.7×10^{-3} and 1.4×10^{-3} g/mL CMC-A9, is shown in Figures 5 and 6, respectively. From Figure 5, we see that the conversions are improved with the increase of ultrasonic power output when the concentration of CMC-A9 is 0.7×10^{-3} g/mL. However, with 1.4×10^{-3} g/mL CMC-A9 (Fig. 6), high conversion can be obtained even when the ultrasonic power output is quite low. Thus, the higher concentration of CMC-A9 added into the emulsion polymerization could increase the monomer conversion in a shorter time at lower ultrasonic power output. It is possible that the higher CMC-A9 concentration corresponds to the formation of a large number of particles and the nucleation process is very rapid, so that ultrasonic power output may have less effect on ultrasonically irradiated emulsion polymerization.

In Figures 7 and 8, the rates of polymerization R_p versus reaction time are given at various concentrations of CMC-A9 and SDS, respectively. The rates R_p were obtained by derivation of the conversion versus time curves. It is clear that the same phenomena occur in that there are obviously only two stages in ultrasonically irradiated emulsion polymerization of styrene. Compared with the conventional emulsion polymerization mechanism of three stages for the process, under ultrasonic irradiation there is no period at which the rate of polymerization is constant. This phenomenon is also observed in miniemulsions. It may indicate that the ultrasonically irradiated emulsion polymerization has a similar nucleation mechanism with the miniemulsion polymerization system, where monomer droplets are known to be the major locus of nucleation.
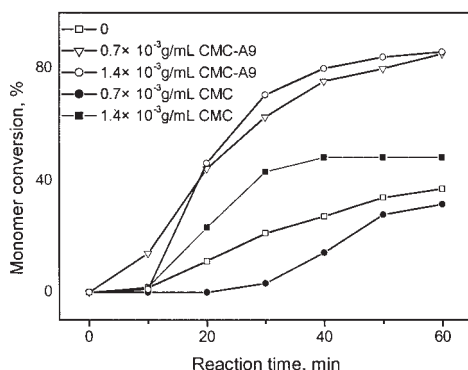
Figure 4 Monomer conversion versus time curves for the ultrasonically irradiated emulsion polymerization of St (St = 8 mL, [SDS] = 0.03 g/mL).
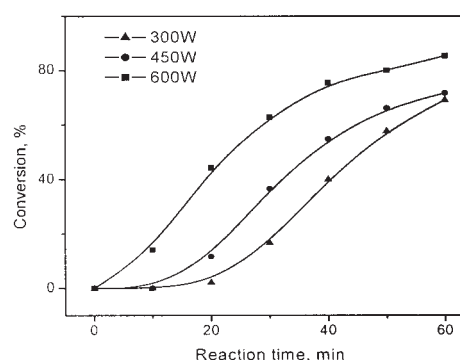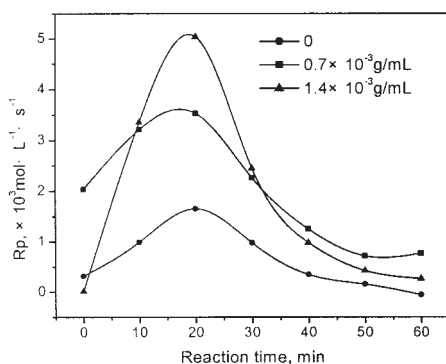

Figure 5 Monomer conversion versus time curves at various ultrasonic power outputs ([CMC-A9] = 0.7×10^{-3} g/mL).
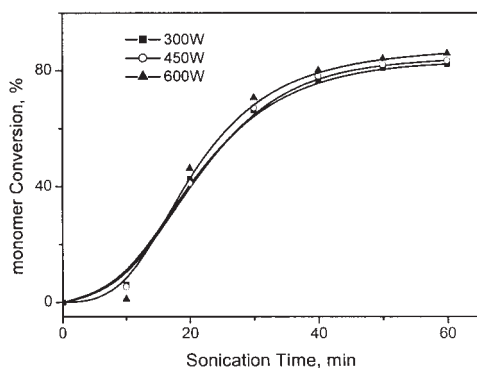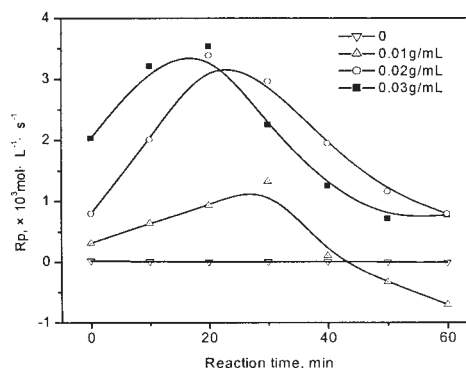
Figure 6 Monomer conversion versus time curves at various ultrasonic power outputs ([CMC-A9] = 1.4×10^{-3} g/mL).

Figure 8 R_p versus time curves for the ultrasonically irradiated emulsion polymerization of St at various SDS concentrations.

When an ultrasound wave passes through a liquid medium, a large number of microbubbles (called cavitated bubbles) form and grow and then collapse. The collapsing of the cavitated bubbles can generate high local temperatures up to 5000 K, high local pressures up to 500 atm, and a very violent shearing action, which results in the formation of free radicals and production of a high concentration of small monomer droplets. In conventional miniemulsion or microemulsion polymerizations, these conditions may require the use of high levels of added surfactants. Thus, under ultrasonic irradiation, there are large numbers of very small monomer droplets, having high surface area, that will result in these droplets becoming the locus of polymerization. This result should lead to the formation of small latex particles, which is proved by the characterization of the latices as discussed below.

As shown in Figures 7 and 8, at various concentrations of CMC-A9 and SDS, polymerization rate versus time data are obtained. Although the increased concentration of surfactants, CMC-A9 or SDS, both lead to higher maximum rate, the effects of CMC-A9 and SDS on the polymerization process are different. When the

concentration of SDS is constant, at various concentrations of CMC-A9, the maximum rate is observed at approximately the same reaction time of 20 min, and the lengths of nucleation period for systems with various CMC-A9 concentrations are nearly the same. This indicates that CMC-A9 plays a more important role on the stabilization of small monomer droplets. When CMC-A9 concentration is kept constant at 0.7×10^{-3} g/mL, the reaction time at which maximum rate arrives shortens with the increase of SDS concentration (Fig. 8). This relates to the larger number of radicals produced by the cleavage of SDS when SDS concentration increases, resulting in a much shorter nucleation process.

Characterization of the latexes

The representative electron micrograph of one polystyrene latex, obtained by ultrasonically irradiated emulsion polymerization, is shown in Figure 9. The size of the latex particles is in the range of 30–60 nm, which is much smaller than when polymerized by conventional emulsion using the same emulsifier. Under ultrasonic vibration, a large number of small

Figure 7 R_p versus time curves for the ultrasonically irradiated emulsion polymerization of St at various CMC-A9 concentrations.

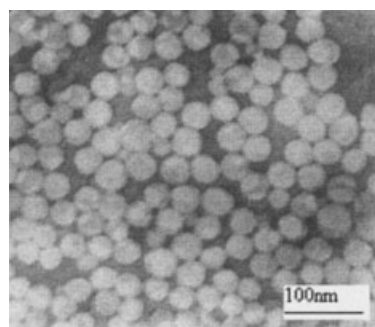**Figure 9** TEM of latices polymerized by ultrasonically irradiated emulsion polymerization with 0.7×10^{-3} g/mL CMC-A9.

monomer droplets with high surface area are produced by the violent shearing action of ultrasound, and added surfactants prevent these small droplets from aggregating. At the same time, a high concentration of radicals is produced by ultrasonic cavitation. The radicals are easy to be captured by the small droplets because of their large surface areas, and most of the droplets will be nucleated. Thus, smaller latex particles will be produced. It is believed that ultrasonically irradiated emulsion is a promising technique for preparing polymer nanoparticles.

The characteristics of the final latices, obtained with different CMC-A9 concentrations, are listed in Table II (SDS concentration: 0.03 g/mL). With the increase of CMC-A9 concentration, a significantly larger number of latex particles with higher molecular weight are obtained. The small particle sizes and high molecular weights suggest few polymer chains per particle. The average chain numbers per particle decrease from 15.5 to 2.6 with the increasing CMC-A9 concentration from 0 to 1.4×10^{-3} g/mL. Similar results are obtained by changing the SDS concentrations (as listed in Table III).

In ultrasonically irradiated emulsion polymerization, because of small particle size, it is likely that the particles will contain either zero or one radical at any time. Increasing the surfactant level could increase the number of micelles formed or assist in the stabilization of small monomer droplets; therefore, both can result in a decrease of particle size, and a decrease of radical number per particle, resulting in higher molecular weight polystyrene. As far as SDS is concerned, it not only serves as an emulsifier, but also could be ruptured to produce radicals under ultrasonic irradiation, thus serving as an initiator: the former effect of SDS improves the molecular weight of polystyrene, while the latter reduces it when SDS concentration goes up. Nonetheless, the molecular weight of polystyrene is elevated with increasing concentration of SDS, as listed in Table III. It may indicate that SDS serves mostly as an emulsifier in this case.

CONCLUSION

In this work, we investigated the application of polymeric surfactants based on CMC-A9 as emulsifiers

TABLE II
Characteristics of the Final Latices Obtained with Different CMC-A9 Concentrations[a]

[CMC-A9] (g/mL)	D_w (nm)	PDI	N_p ($\times 10^{-14}$/mL)	$\bar{M}_\eta$	N_c
0	55.0	1.44	9.5	2.19E6	15.5
0.7×10^{-3}	41.4	1.18	36.2	4.81E6	3.6
1.4×10^{-3}	37.8	1.15	43.5	4.93E6	2.6

[a] [SDS] = 0.03 g/mL.

TABLE III
Characteristics of the Final Latices Obtained with Different SDS Concentrations[a]

[SDS] (g/mL)	D_w (nm)	PDI	N_p ($\times 10^{-14}$/mL)	$\bar{M}_\eta$	N_c
0.01	63.0	1.60	3.40	2.68E6	18.7
0.02	55.3	1.18	13.77	4.31E6	9.8
0.03	41.4	1.18	36.19	4.81E6	3.6

with SDS in ultrasonically irradiated emulsion polymerization. High molecular weight ($>10^6$) polystyrene nanoparticles of 30- to 60-nm diameters were prepared. Higher concentrations of CMC-A9, added to the emulsion polymerization, increased the monomer conversion in a shorter time at lower ultrasonic power output. The curve of the polymerization rate versus time showed two stages, without a constant rate period, which was similar to miniemulsion polymerizations. This finding was discussed in terms of the monomer droplet nucleation. The high ratio of radicals produced, and a greater number of smaller size monomer droplets, have been attributed to the use of ultrasonic irradiation and the effect of the polymeric surfactants, which increase the monomer droplets surface area and the entry rate of radicals into the particles.

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