

# Direct Miniemulsification of Kraton Rubber/Styrene Solution. I. Effect of Manton–Gaulin Homogenizer, Sonifier, and Membrane Filtration

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**ABSTRACT:** A direct miniemulsification process was utilized to prepare an artificial latex from a Kraton® D1102 thermoplastic elastomer. The Kraton rubber was dissolved in a styrene monomer and emulsified in an aqueous surfactant solution in the presence of a costabilizer using a sonifier, a Manton–Gaulin homogenizer, and membrane filtration. Each miniemulsion droplet contained 20 wt % Kraton rubber in styrene, and, thus, the Kraton rubber particle size and size distribution can be used to estimate the droplet size and size distribution of the miniemulsion. It was found that Kraton rubber particles obtained using the Manton–Gaulin homogenizer had an extremely broad size distribution ranging from 20 nm to 2  $\mu\text{m}$ . The use of a cetyl alcohol costabilizer produced Kraton rubber particles with a narrower size distribution by lowering the interfacial tension between the

oil and aqueous phases, compared to the use of hexadecane as a costabilizer. The broad size distribution of the Kraton rubber particles could be narrowed by employing a membrane-filtration technique. However, small miniemulsion droplets remained undisturbed in the miniemulsion since they easily passed through the pores of the filter. These small droplets resulted from the sonification process conducted prior to the use of the membrane-filtration process. The Kraton rubber particle-size distribution became narrow with an increase in the sonifier duty cycle due to the viscoelastic behavior of the oil phase. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 451–464, 2003

**Key words:** dispersions; emulsion polymerization; particle-size distribution; rubber

## INTRODUCTION

Artificial latexes have been developed as water-based coatings to replace solvent-based coatings, motivated by environmental considerations. In addition, the application areas for artificial latexes have been recently expanded. For example, artificial latexes are being used in latex systems which utilize core/shell types of latex particles to solve many practical problems in areas such as sealants, self-crosslinking thermoset coatings, and impact modifiers for many polymer matrices.

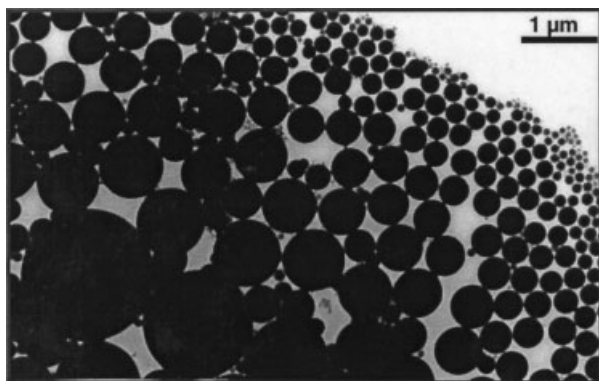
An approach to produce core/shell latexes is to use a direct miniemulsification process to prepare core latex particles which are then used as seed in an emulsion polymerization process where these particles are overcoated with the shell polymer. This approach offers the advantage that one can select any type of polymer to be used as seed and not be limited to polymers prepared by emulsion polymerization.<sup>1</sup> Both Warson<sup>2</sup> and Blackley<sup>3</sup> reviewed the various methods for the direct emulsification of polymer solutions for the preparation of artificial latexes. These

conventional emulsification methods usually result in the formation of latexes with an average particle diameter in the range of 1–10  $\mu\text{m}$  or greater, which is approximately 5–10 times larger than is the size of most commercial latexes prepared by a conventional emulsion polymerization process. This larger latex particle size can result in poor shelf stability and inferior film properties.<sup>4</sup>

It was found that a mixed-emulsifier system composed of a sodium lauryl sulfate anionic surfactant and cetyl alcohol costabilizer produced styrene emulsion droplets with diameters as small as 200 nm.<sup>5</sup> This was later termed a miniemulsion, where the smaller droplet sizes made the monomer emulsion droplets more competitive in capturing radicals generated in the aqueous phase. Miniemulsions are typically formed by subjecting the oil/water/surfactant/costabilizer system to a high shear field created by devices such as a sonifier, a Manton–Gaulin homogenizer, or microfluidizer.<sup>6</sup> This process has been further applied to the preparation of artificial latexes for use in the coatings area owing to the advantage that smaller size particles can be obtained by this process.<sup>7–10</sup>

In this study, the styrene monomer was used as a reactive solvent to dissolve the Kraton rubber instead of using a general solvent such as toluene, because Kraton rubber/styrene emulsions prepared in this

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**Figure 1** TEM micrograph of Kraton rubber particles prepared from SLS/HD = 20/80 mM with six passes through the Manton–Gaulin homogenizer at a first-stage pressure of 6000 psi and a second-stage pressure of 1500 psi.

study will subsequently be polymerized to form hybrid composite latexes. However, initial studies on this project revealed that the actual distribution of the emulsion droplets, which is reflected by the Kraton rubber particle-size distribution after stripping off styrene monomer, is extremely broad, with a diameter extending up to 2  $\mu\text{m}$  when the Manton–Gaulin homogenizer was used with a sodium lauryl sulfate and hexadecane system (see TEM micrograph in Fig. 1). These large particle sizes and broad size distribution could bring about problems such as poor emulsion shelf-life stability, inferior film-forming properties, and secondary nucleation of particles during a subsequent polymerization process.<sup>11,12</sup> Thus, the particle size should be decreased and the size distribution narrowed. Few articles have been published which systematically investigate the effects of various parameters such as the operating conditions for the homogenization device on the particle size and size distribution of artificial latexes. Therefore, in this study, the effects of different emulsification conditions such as sonification, homogenization using the Manton–Gaulin homogenizer, or membrane filtration were examined in detail.

## EXPERIMENTAL

### Materials

Kraton<sup>®</sup> D1102, a styrene–butadiene–styrene (SBS) triblock copolymer (Shell Chemical Co., Houston, TX) was used in these studies. It is composed of a polybutadiene midblock (72 wt %) and two polystyrene end blocks (28 wt %). Sodium lauryl sulfate (SLS, Aldrich, Milwaukee, WI), hexadecane (HD, Aldrich), cetyl alcohol (CA, Aldrich), lauryl alcohol (LA, Aldrich), and stearyl alcohol (SA, Aldrich) were all used as received without further purification. Deionized water was used for all experiments.

### Emulsification procedures

The HD, 80 mM, or CA costabilizer, 60 mM, was dissolved in the styrene monomer prior to dissolving the Kraton rubber in styrene; the weight ratio of the Kraton rubber/styrene was always maintained as 20/80. Kraton rubber was then added to the styrene/costabilizer solution. This solution was left to stand for 12 h and then stirred with a magnetic stirrer for 1 h so that it was completely dissolved. The styrene/costabilizer/Kraton rubber solution was slowly added to a 15 mM SLS aqueous solution with stirring using a magnetic stirrer and then further stirred for 2 h to form a crude emulsion. This crude emulsion was sonified using a Branson sonifier (Model 450, Branson Ultrasonics) at a power level of 8 and a duty cycle of 70% and then homogenized using a Manton–Gaulin homogenizer or passed through a membrane-filtration device. In the membrane-filtration process, a sonified emulsion is forced through a membrane (0.4  $\mu\text{m}$  polyester track-etch membrane, Osmonics) using 50 psi of nitrogen gas. During this process, emulsion droplets that are smaller than are the membrane pore size can pass through the pores without any interference, while slightly larger ones are squeezed as they pass through the membrane. However, droplets that are much larger than the membrane pores are broken down to smaller droplets. CA-based emulsions were homogenized without sonification unless otherwise mentioned.

### Characterization of particle size and size distribution of Kraton rubber particles

Each emulsion droplet contains 20 wt % Kraton rubber. Therefore, the size of the Kraton rubber particles, which can be obtained after stripping off the styrene monomer, should correspond to the emulsion droplet size. Kraton rubber particles were obtained by stripping styrene from emulsions using a rotary evaporator at 50°C under a vacuum. Three or four drops of a 1% aqueous hydroquinone solution were added to 1.5 g of emulsion to prevent thermal polymerization of the styrene monomer during the stripping process. The emulsion was diluted with a 10 mM aqueous SLS solution in an emulsion to an SLS solution ratio of 1 to 1.5. Kraton particle-size analysis was then carried out using capillary hydrodynamic fractionation (CHDF Model 1100; Matec Applied Sciences). The polybutadiene phase in Kraton rubber was stained with OsO<sub>4</sub> for transmission electron microscopy (TEM; Philips Model 4T) examination.

## RESULTS AND DISCUSSION

### Homogenization with Manton–Gaulin homogenizer

The Manton–Gaulin homogenizer (Model 15M, APV Gaulin Co.) is a type of a fine clearance valve ho-

mogenizer. The homogenization process produces submicron droplets by a combination of mechanical shearing and cavitation. The model 15M which has been used in this study is composed of two stages: Large emulsion droplets are broken down into smaller ones primarily in the first stage of the homogenizer, while the homogenization process occurs in the second stage of the homogenizer which is usually operated at less than 20% of the first-stage pressure. The size distribution of the emulsion droplets is narrowed in the second stage.

A Kraton rubber/styrene solution was emulsified using a mixed-emulsifier system composed of the SLS anionic surfactant and the CA or HD costabilizer. Homogenization conditions such as the first- and second-stage homogenization pressure and number of cycles through the Manton–Gaulin homogenizer were investigated along with the effect of the type of costabilizer. The use of a high concentration of surfactants may have an adverse effect on the use of artificial latexes in coatings applications due to the presence of residual surfactants or on a subsequent polymerization of monomers which were used to dissolve polymers due to the formation of secondary particles in the aqueous phase. Therefore, the SLS concentration was limited to 15 or 20 mM. The free SLS concentration in the aqueous phase was found to be about 5.5 mM, which is below the cmc, when 15 mM SLS was employed; therefore, a 15 mM SLS concentration was used in the majority of experiments.

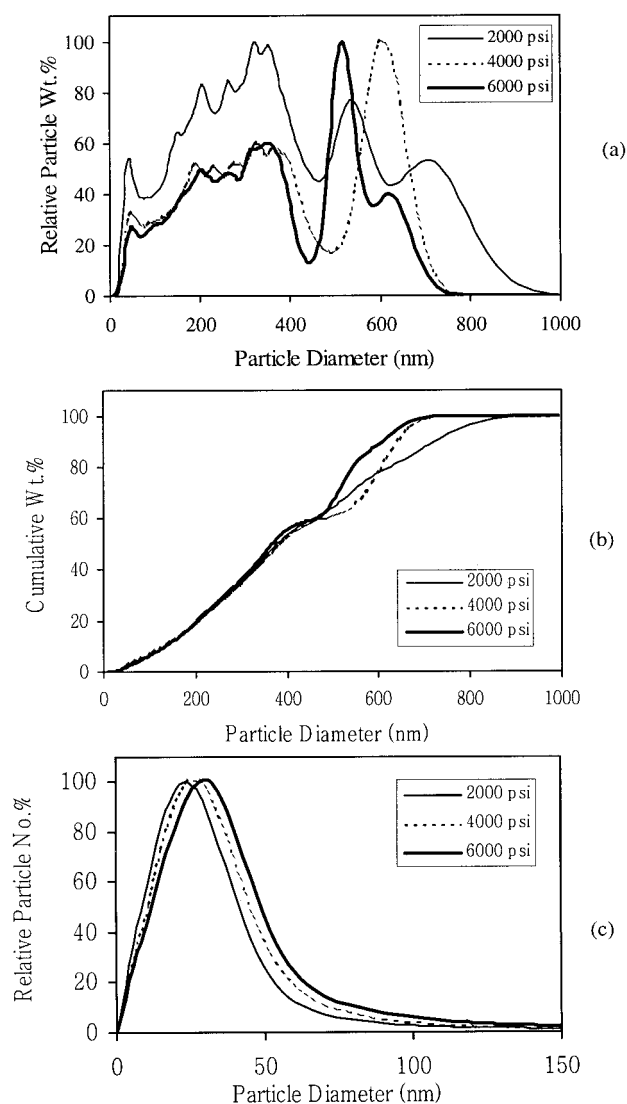
#### Effect of the first-stage pressure of the Manton–Gaulin homogenizer

As mentioned earlier, large emulsion droplets are broken down primarily in the first stage of the homogenizer. Therefore, the first-stage pressure was varied from 2000 to 6000 psi to investigate the influence of the first-stage pressure on the size and size distribution of the Kraton rubber particles. The Kraton rubber emulsions were prepared from the Kraton rubber solution in styrene using  $[SLS]/[CA] = 20/60$  mM. The crude

**TABLE I**  
Homogenization Conditions and Average Diameters of Kraton Rubber Particles as Measured by CHDF

Measurement	Experiment no.		
	XM-109	XM-108	XM-107
1st-stage pressure (psi)	2000	4000	6000
2nd-stage pressure (psi)	1500	1500	1500
No. cycles (passes)	10	10	10
SLS/CA (mM)	20/60	20/60	20/60
$D_w$ (nm)	305	306	302
$D_n$ (nm)	40	53	51
PDI	7.62	5.77	5.92

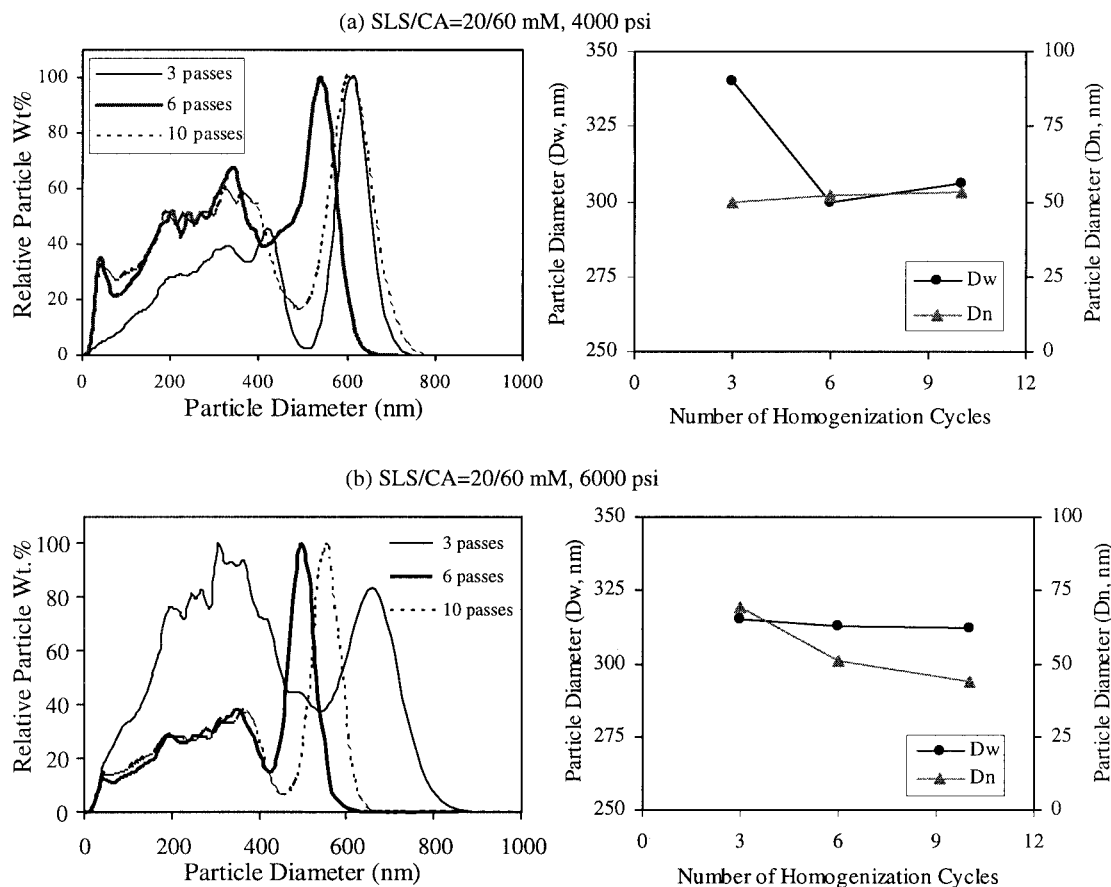
$D_n$  is the number-average diameter;  $D_w$  is the weight-average diameter; and  $PDI = D_w/D_n$



**Figure 2** Weight- and number-average particle diameter distributions for the Kraton rubber particles (after stripping off styrene monomer) prepared at different first-stage pressures: 2000, 4000, and 6000 psi, while maintaining the second-stage pressure constant at 1500 psi.

emulsion that resulted from mixing the oil phase and aqueous phase using a magnetic stirrer was then passed 10 times through the Manton–Gaulin homogenizer while varying the first-stage pressure from 2000 to 6000 psi while keeping the second-stage pressure constant at 1500 psi.

Table I summarizes the homogenization conditions and average diameters of the Kraton rubber particles after stripping off the styrene monomer. The size distributions are shown in Figure 2. It can be seen from Table I that the size distributions of the Kraton rubber particles are very broad (PDI values ranging from 5.77 to 7.62). However, the average diameters ( $D_w$  and  $D_n$ ) remain almost constant as the first-stage pressure of the homogenizer was varied from 2000 to 6000 psi. However, if the size distributions of the Kraton rubber



**Figure 3** Weight distributions of the Kraton particles (obtained after monomer stripping) prepared from the emulsions withdrawn after three, six, and ten passes through the Manton–Gaulin homogenizer and the average particle diameter obtained by varying the number of homogenization cycles: (a) 4000 psig without sonification; (b) 6000 psig with sonification.

particles shown in Figure 2 are examined, it can be seen that the distributions were affected by the variation of the first-stage pressure. The first-stage homogenization pressure had a pronounced effect on the large particle size population (diameters over 400 nm) and had little effect on the small particles. The population of the large particles over 500 nm shifted to a larger size range with a decrease in the first-stage homogenization pressure [Fig. 2(a)], while the population of the small particles with diameters under 500 nm remained constant, as determined from the cumulative weight distribution shown in Figure 2(b).

From these results, it is seen that only specifying an average diameter does not accurately depict the size characteristics of latex particles with a broad size distribution. Only the size distribution can reflect the actual characteristics of latexes with a broad size distribution.

#### Effect of the number of homogenization cycles

Samples of emulsions XM-107 and 108 were withdrawn at 3, 6, and 10 passes through the Manton–Gaulin homogenizer and the size and size distribution

of the Kraton rubber particles after stripping off the styrene monomer were measured by CHDF. The results are shown in Figure 3. It is observed that the population of large Kraton rubber particles (over 500 nm in diameter) shifted upward at 10 passes through the homogenizer in both cases (XM-107 and 108) due to recombination and coalescence of emulsion droplets by an excessive energy input. This trend was not reflected in the average particle diameter as mentioned earlier. The weight-average diameter of the Kraton particles remained almost constant for the emulsion droplets prepared at different numbers of homogenization cycles through the homogenizer at a first-stage pressure of 6000 psi as shown in Figure 3(b). In contrast, the number-average diameter for the same sample kept decreasing with an increase in the number of homogenization cycles. However, the weight-average diameter of the Kraton particles formed at a first-stage pressure of 4000 psi were greatly decreased after six passes through the homogenizer and then remained constant as shown in Figure 3(a). These observations indicate that most of the large droplets in a crude emulsion are broken up in the early stages of homogenization (e.g., after three passes) if sufficient

energy input is provided to the system, as was the case of a first-stage pressure of 6000 psi. In addition, smaller droplets which contribute to the lowering of the number-average diameter are continuously generated during the homogenization process and increase as the number of homogenization cycles increases, as can be seen in Figure 3(b).

In conclusion, excessive energy input during the homogenization process resulting from a greater number of homogenization cycles (or longer homogenization time) causes emulsion droplets to recombine and coalesce. Very small emulsion droplets which are continuously formed during the homogenization process consume larger amounts of surfactants by generating a larger total surface area. This process makes the larger emulsion droplets unstable and coalescence is accelerated over longer homogenization cycles or at a later stage in the homogenization process. This means that longer homogenization times will produce an emulsion with a very broad size distribution. Therefore, a shorter homogenization time with a sufficiently high homogenization pressure is desirable to obtain an emulsion with a relatively narrower size distribution.

#### **Effect of a costabilizer on the size distribution of Kraton rubber particles**

In a miniemulsification process, a mixed-emulsifier system which is composed of an ionic surfactant such as SLS and a costabilizer such as a long-chain alkane (e.g., HD) or a long-chain alcohol (e.g., CA) were used to obtain stable and small droplets ranging from 50 to 500 nm in diameter by suppressing Ostwald ripening (i.e., retarding monomer diffusion from smaller droplets to larger ones). The principal function of the costabilizer is to increase the stability of the oil droplets by reducing the rate of diffusive degradation.<sup>13</sup> It has been postulated that, for long-chain alcohols, additional stabilization may be provided by the formation of interfacial barriers (intermolecular complex) to droplet coalescence.<sup>14</sup> It was reported by Shinoda and Friberg that the primary role of the short-chain alcohol in the stabilization of microemulsion systems prepared with a mixed emulsifier is to cause a large depression in the interfacial tension between the oil phase and the water phase.<sup>15</sup> Miller et al.<sup>16</sup> and Goetz<sup>17</sup> also showed that the emulsion droplet size decreased with an increasing CA concentration. In addition, Miller et al. suggested that the CA behaves as a surfactant, lowering the oil/water interfacial tension.<sup>18</sup> All these results were obtained by measuring only the average droplet size using light scattering or CHDF. Therefore, it could not be explained how the size distribution of the emulsion droplets was changed. However, analyzing the Kraton rubber particles obtained from the Kraton rubber/styrene emul-

sion can exactly reflect the initial droplet-size distribution. Therefore, the use of this system will be a good model to investigate the effect of long-chain alcohols on the size and size distribution of emulsion droplets.

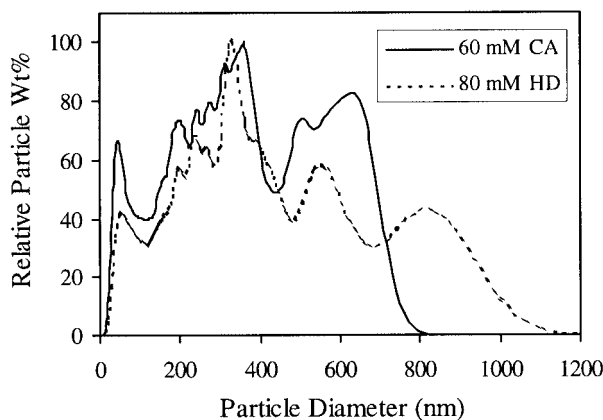
#### **Comparison of two costabilizers: HD and CA**

HD and CA are the typical costabilizers used in miniemulsion systems. It was reported that the droplet size of a toluene miniemulsion prepared using HD as the cosurfactant is much smaller than that of a corresponding emulsion prepared using CA. CA miniemulsions have exhibited some instabilities during aging due to the limited solubility of CA in water.<sup>16,17</sup> However, CA may offer a benefit that results from the presence of a hydroxyl group: CA can reside in the interface between the oil and water phases due to the presence of the hydrophilic hydroxyl group which can reduce the interfacial tension, while HD is always inside the oil droplets. To investigate the difference between HD and CA as costabilizers in detail, miniemulsions were prepared with 20 mM SLS using 80 mM HD or 60 mM CA which were dissolved in the styrene monomer prior to dissolving the Kraton rubber. The emulsions were homogenized using the Manton-Gaulin homogenizer at a first-stage pressure of 6000 psi and a second-stage pressure of 1500 psi with six passes through the Manton-Gaulin homogenizer.

CA can migrate from the interior of the emulsion droplets to the droplet surface due to the presence of its hydrophilic hydroxyl groups, while HD remains inside the emulsion droplets. The presence of hydroxyl groups on the surface of the emulsion droplets would result in a decrease in the interfacial tension and would influence the size and size distribution of the emulsion droplets. In this way, the primary role of the CA in this Kraton miniemulsion system would be as a secondary surfactant acting to reduce the interfacial tension, rather than acting to retard Ostwald ripening, as would be the case when HD was used as costabilizer.

Kraton particle-size distribution results are shown in Figure 4. As expected, the size distribution of the Kraton rubber particles prepared with 80 mM HD was very broad with a tail extending up to 1.2  $\mu\text{m}$ . However, in the case of 60 mM CA, the size distribution is narrower and the upper bound in the distribution is 800 nm. These results indicate that CA is a more suitable costabilizer compared to HD for the emulsification of Kraton rubber/styrene mixture.

The above results can be further confirmed by an aging experiment for each emulsion as described below. Each emulsion was placed in a test tube and left undisturbed on a shelf at room temperature. A small sample of each emulsion was then withdrawn with a disposable glass pipette from the top and middle layers of the test tube as a function of time. Four test tubes



**Figure 4** Weight-size distribution of the Kraton rubber particles prepared with 20 mM SLS using 60 mM CA or 80 mM HD.

were prepared for each emulsion. Each test tube was discarded after sampling because the sampling process may induce mixing of the emulsion inside the tubes. The droplet size was measured by dynamic light scattering (NICOMP 370).

As the emulsion droplets have a lower density than that of the dispersion medium (water), they will tend to accumulate at the air/liquid interface under the influence of gravity. According to Stokes' law as shown in eq. (1), the rate of creaming is proportional to the square of the droplet size ( $D$ ). Therefore, large droplets will accumulate in the top layers at a faster rate with aging time:

$$\text{Creaming rate} = (D^2/18\eta)(\rho_p - \rho_m)g \quad (1)$$

where  $D$  is the diameter of emulsion droplets;  $\eta$ , the viscosity of the water phase;  $\rho_p$  and  $\rho_m$ , the densities of the emulsion droplets and the water phase, respectively; and  $g$ , the gravitational constant.

Results are shown in Figure 5. It is seen that the droplet sizes obtained from the top layers of the test tubes for the HD system greatly increased, to a size more than  $1 \mu\text{m}$ , only after 2 days of aging. However, the droplet diameter obtained from the top layer of the CA system was 650 nm, which was much smaller than that of the HD system. This indicates that large droplets over  $1 \mu\text{m}$  were not formed in the CA system during the homogenization stage. After 4 days of aging, the emulsion droplet size for the middle layer decreased very slightly, due to a loss of large droplets in the middle layer.

#### Effect of the type of fatty alcohols on the Kraton rubber particle-size distribution

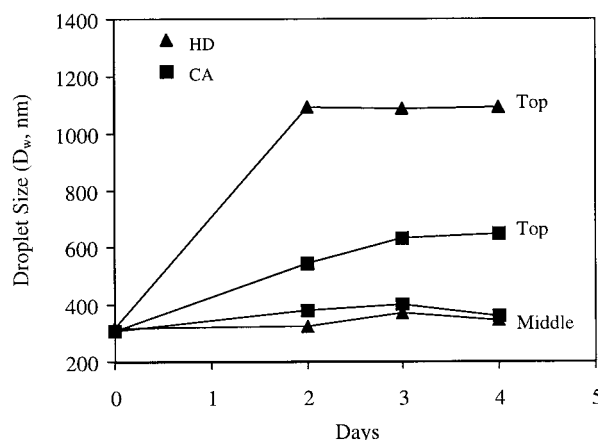
In the previous section, it was found that the use of CA as a costabilizer had a pronounced effect on reducing the Kraton rubber particle size. Thus, in an

attempt to elucidate the influence of the fatty alcohol on interfacial phenomenon, interfacial tension measurements were carried out using a drop-volume method.<sup>19</sup> Four costabilizers, HD (C16), LA (C12), CA (C16), and SA (C18), were examined. Each costabilizer was dissolved in the styrene monomer prior to dissolving the Kraton rubber. The molar concentration ratio of SLS to the costabilizer was 15–30 mM, based on the aqueous phase. The 15 mM SLS aqueous was pumped into a 20 wt % Kraton rubber solution in styrene at a flow rate of 0.015 mL/min through a capillary (with a radius of 0.2785 cm) immersed in the Kraton/styrene solution. The interfacial tension ( $\gamma$ , dynes/cm) was calculated using the following equation:

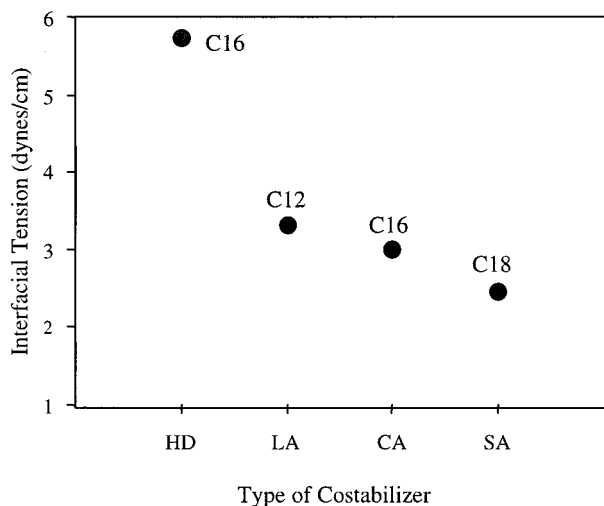
$$\gamma = \frac{V(\Delta\rho)gF}{r} \quad (2)$$

where  $V$  is the volume of an individual droplet ( $\text{cm}^3$ );  $\Delta\rho$ , the density difference between the aqueous phase droplet (15 mM SLS aqueous solution) and the surrounding oil phase (20 wt % Kraton rubber solution in styrene) ( $\text{g}/\text{cm}^3$ );  $g$ , the gravitational constant;  $F$ , a correction factor; and  $r$ , the capillary radius.

Figure 6 illustrates the effect of the type of costabilizer on the interfacial tension between the aqueous phase and the oil phase (20 wt % Kraton rubber solution). The interfacial tension for the HD system was the highest, as expected, which explains why the HD system exhibited a broader size distribution of Kraton rubber particles as shown in Figure 4. The interfacial tensions for the fatty alcohols decrease with an increasing carbon chain length. These are in a good agreement with previous emulsion stability test results using costabilizers with different alcohol chain lengths.<sup>20</sup> However, Lack showed a contradictory result in which the interfacial tension increased with an



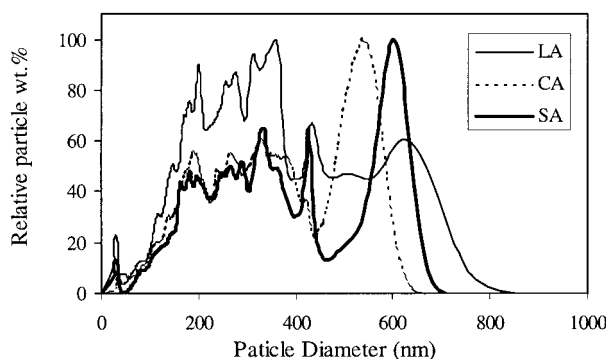
**Figure 5** Emulsion droplet size as a function of aging time as determined by light scattering for the emulsions withdrawn from the top and the middle layers of the test tubes.



**Figure 6** Effect of the type of costabilizer on the interfacial tension between the aqueous phase and the oil phase: water phase, 15 mM SLS solution; oil phase, 20 wt % Kraton rubber solution in styrene.

increase in the alcohol chain length and explained this phenomenon by the hypothesis that higher interfacial tensions give more "rigid" interfacial complexes and thus more stable emulsions.<sup>21</sup> He dissolved the fatty alcohol in the aqueous phase along with the SLS surfactant and used a spinning drop interfacial tensiometer for his measurements. It is still uncertain whether the initial location of the fatty alcohol may alter the trend in interfacial tensions with the hydrocarbon chain length.

The CHDF size distributions of the Kraton rubber particles obtained after stripping the styrene from the Kraton rubber emulsions are shown in Figure 7. As can be expected from the interfacial tension results presented in Figure 6, the LA system produced the broadest size distribution among the three fatty alco-



**Figure 7** Weight-average particle diameter distributions for the Kraton particles (after monomer stripping) prepared from different fatty alcohols: [SLS]/[fatty alcohol] = 15/45 mM (for the emulsification of Kraton rubber); each emulsion was homogenized with three passes through the Manton-Gaulin homogenizer at a first-stage pressure of 6000 psi and a second-stage pressure of 1500 psi.

**TABLE II**  
Average Diameters of Kraton Rubber Particles as Measured by CHDF

Measurement	Experiment no.			
	XM-133	XM-134	XM-135	XM-136
SLS/CA (mM)	15/0	15/15	15/30	15/60
Kraton rubber particles				
$D_w$ (nm)	254	262	263	267
$D_n$ (nm)	49	56	58	51
PDI <sup>a</sup>	5.18	4.68	4.53	5.24

The average diameters of the Kraton rubber particles were obtained by stripping off the styrene monomer from the emulsions.

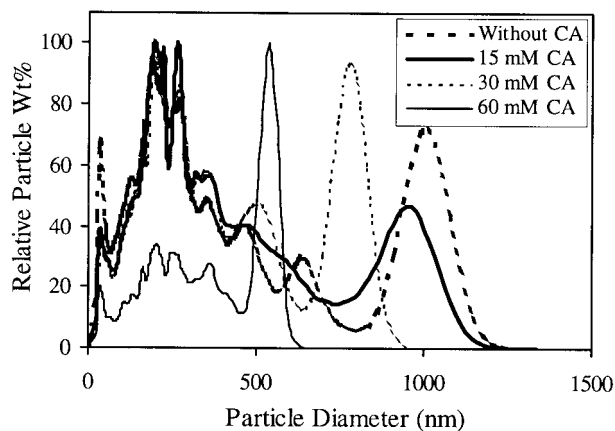
$$^a \text{PDI} = D_w/D_n$$

hol costabilizer systems investigated with a tail extending up to 850 nm. The size distribution obtained using CA as the costabilizer was narrower. These results are in good agreement with those obtained from the interfacial tension measurements. However, in the case of the SA system, 45 mM SA could not be completely dissolved in the styrene due to its lower solubility in styrene. Thus, this result falls in between the CA and LA systems. From these results, it can be concluded that CA is a more suitable costabilizer for the direct emulsification of Kraton rubber/styrene solution compared to any of the other fatty alcohols.

#### Effect of different CA concentrations on the Kraton rubber particle-size distribution

Emulsions were prepared using different CA concentrations (0, 15, 30, and 60 mM) with 15 mM SLS. The emulsions were subjected to 3 min of sonification at a power level of 8 and a duty cycle of 70% and then homogenized with three passes through the Manton-Gaulin homogenizer at a first-stage pressure of 6000 psi and a second-stage pressure of 1500 psi. Kraton rubber particles were obtained after stripping off the styrene monomer, and their sizes were determined by CHDF.

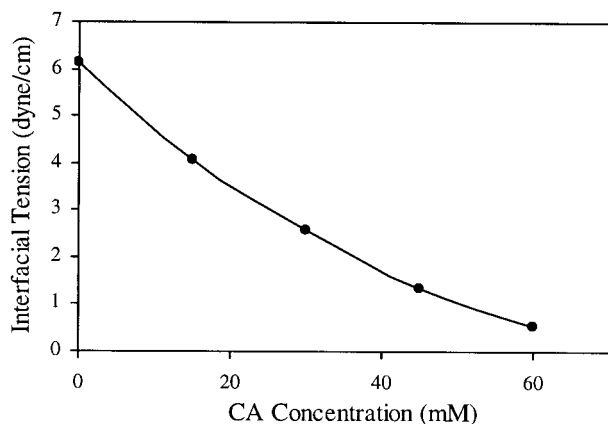
As mentioned previously, CA acts to lower the interfacial tension between the aqueous phase and the emulsion droplets. Thus, it can be expected that the size distribution of the Kraton rubber particles will be influenced by the CA concentration. The average diameters of the Kraton rubber particles are listed in Table II. No differences in particle diameters were observed for the emulsions formed with different CA concentrations. However, it can be seen clearly from the weight distribution shown in Figure 8 that CA acts to lower the interfacial tension and, hence, reduce the particle size. The population of large Kraton rubber particles over 500 nm shifts further to the lower-size ranges with an increase in the CA concentration. In the case where CA was not utilized for the emulsification,



**Figure 8** Size distribution of Kraton rubber particles prepared using different CA concentrations (0, 15, 30, and 60 mM); emulsions were sonified for 3 min and then homogenized with three passes through the Manton–Gaulin homogenizer at a first-stage pressure of 6000 psi and a second-stage pressure of 1500 psi.

a tail composed of large Kraton particles extends up to 1.3  $\mu\text{m}$ .

These results can be further confirmed by measuring the interfacial tension with different CA concentrations. Interfacial tensions between a 15 mM SLS aqueous solution and a Kraton rubber/styrene solution containing CA were measured using the drop-volume method as described in the previous section. Results are given in Figure 9. As can be seen from Figure 9, the interfacial tension decreased with increasing CA concentration from 0 to 60 mM, the same trend as found when using a regular ionic surfactant. The slope for the interfacial tension curve decreases with increasing CA concentration. The reason for this phenomenon is thought to be that the surface of the oil



**Figure 9** Interfacial tensions between the aqueous phase (15 mM SLS) and the oil phase (Kraton rubber/styrene/CA) at different CA concentrations (0, 15, 30, 45, and 60 mM); the drop-volume method was used and the aqueous phase was pumped through a capillary into the oil phase at a flow rate of 0.015 mL/min.

**TABLE III**  
Interfacial Tension Between the Aqueous Phase (15 mM SLS) and the Oil Phase (Kraton Rubber/Styrene/CA), as Measured by the Drop-volume Method

Measurement	Control <sup>a</sup>	T-1	T-2	T-3	T-4
CA concentration (mM)	0	45	60	0	60
SLS concentration (mM)	0	0	0	15	15
Interfacial tension (dyne/cm)	35.06	26.74	21.41	6.14	0.53

<sup>a</sup> Interfacial tension between Kraton rubber solution and pure deionized water.

phase became more saturated with CA at a higher CA concentration and relatively larger amounts of CA reside inside the oil phase.

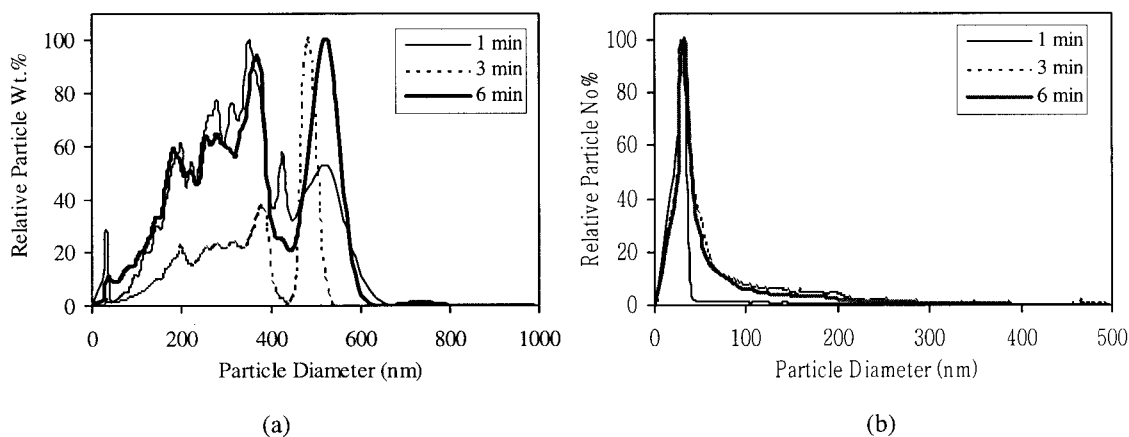
To investigate the role of CA as a surfactant, interfacial tensions were determined for the various systems where CA or SLS was not added. Results are given in Table III. The interfacial tension for the control was 37.62 dyne/cm. As can be expected, the interfacial tension decreased greatly with the addition of 15 mM SLS (T-3). In addition, the presence of only 45 or 60 mM CA should also reduce the interfacial tension (T-1 or T-2) by 8.32 or 13.65 dyne/cm compared to the control. If it is considered that one of the guidelines to select an emulsifier is its ability to reduce the interfacial tension by 5 dyne/cm,<sup>22</sup> then these observations indicate that CA is not as effective as is SLS, but still should act as a surfactant. As it was suggested that the primary role of a short-chain alcohol in the stabilization of microemulsion systems is to lower the interfacial tension between the oil phase and water phase,<sup>15</sup> then it is implied that the major role of CA in the direct miniemulsification of any polymer solution is also to reduce the interfacial tension by acting as a surfactant rather than to suppress Ostwald ripening<sup>23–25</sup> as a costabilizer.

However, there is another explanation for the role of CA as observed in the emulsification of the polystyrene/benzene solution, reported by Chu and Maw.<sup>26</sup> They suggested that the increase in the viscosity of an external phase (water phase) resulted in a reduction of particle size of polystyrene artificial latices, based on the observation that the viscosity of the external phase increased with an increase of CA concentration in the SLS/CA system. They did not measure the interfacial tension. It is still thought that the decrease of the interfacial tension is a direct cause for the reduction of the particle size even though the viscosity of the external phase decreased when the CA concentration increased.

### Sonification

In ultrasonic equipment, high shear is produced by passing the mixture of phases through an area where





**Figure 10** (a) Weight- and (b) number-average particle-diameter distributions of Kraton rubber particles prepared using different sonification times: power level = 8, duty cycle = 70%; [SLS]/[CA] = 15/45 mM.

an ultrasonic field is developed. The effect of the acoustical energy generated by ultrasonic equipment is to produce rapid local variations in the pressure applied to the system, and as a result, cavitation occurs. In this situation, a very high local shear is produced as well as a fairly energetic shock wave.<sup>27</sup> Thus, the mechanism for ultrasonic emulsification is primarily that of cavitation.<sup>28</sup> A sonifier is generally very easy to use. However, it may produce an emulsion with a broad size distribution because the extent of the energy input can differ depending on the distance from the sonifier tip. Emulsions were prepared under different sonification conditions without a further homogenization step, and the size and size distribution of Kraton rubber particles were then measured by CHDF.

#### Effect of sonification time

The sonification time was varied from 1 to 6 min at a power level of 8 and a duty cycle of 70%. Size-distribution results obtained by CHDF analysis are shown in Figure 10. It can be seen that the number- and weight-average particle diameter distributions are completely different from each other. This indicates that the number of small particles below 50 nm is much greater than that of the larger particles which have a more pronounced effect on the weight distribution. Eventually, this generation of a large number of small particles as a result of sonification resulted in a broadening in the size distribution of Kraton rubber particles. The weight-average size distributions presented in Figure 10(a) show that 1 min of sonification produced Kraton rubber particles with a broader size distribution. The population of large Kraton rubber particles over 500 nm shifted down to a smaller size range when the sonification time was increased from 1 to 3 min and increased again to a larger size range at 6 min of sonification. These results are very similar to

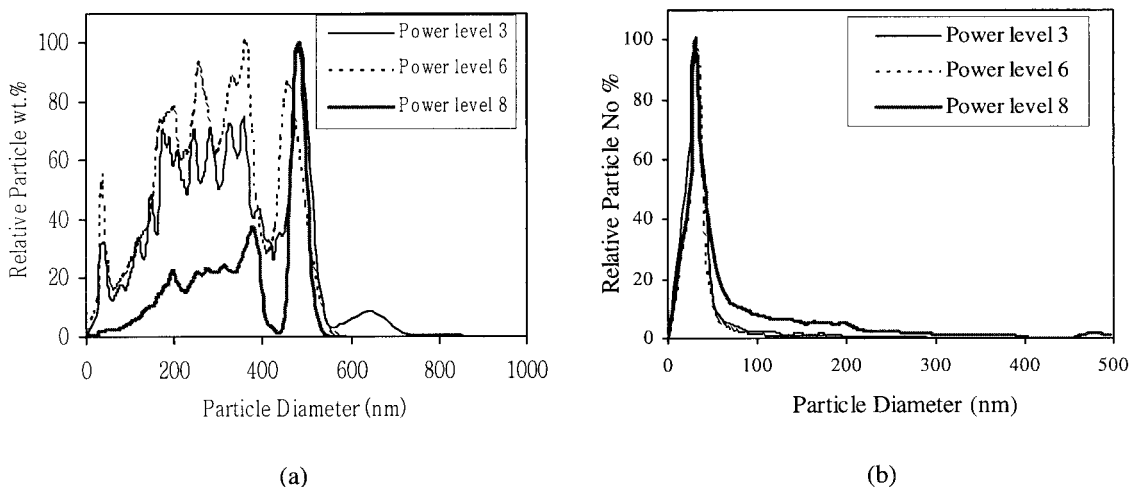
those obtained from the variation of the number of homogenization cycles shown in Figure 3 and can be explained by an increasing coalescence of emulsion droplets when excessive energy is supplied to the system at longer sonification times.

#### Effect of sonification power level

The power level of the sonifier was varied from 3 to 8 to determine the effect of the input energy on the Kraton particle size and size distribution at a constant sonification time. The sonification time and duty cycle were held constant at 3 min and 70%, respectively. The results are shown in Table IV and Figure 11. The weight- and number-average diameters show that larger Kraton rubber particles were obtained at the highest sonifier power level (8). The population of large particles over 500 nm shifted to a larger size range at a power level of 8 compared to a power level of 6, as can be seen from Figure 11(a). It is clear that the coalescence and recombination of droplets took place at the higher power level (8). Larger Kraton rubber particles over 600 nm were formed at the lowest power level (3), where the emulsion droplets were not properly broken down due to insufficient energy input.

**TABLE IV**  
Average Kraton Rubber Particle Sizes Produced Under Different Sonifier Power Levels

Particle diameter	Power level		
	3	6	8
Kraton particle diameter (nm)			
$D_w$ (nm)	258	253	280
$D_n$ (nm)	57	54	97
PDI	4.53	4.69	2.99



**Figure 11** (a) Weight-average and (b) number-average particle-size distributions for the Kraton rubber particles prepared at different sonifier power levels (3–8): sonification time = 3 min at a duty cycle of 70%; [SLS]/[CA] = 15/45 mM.

#### Effect of sonifier duty cycle

The effect of the sonifier duty cycle on the size distribution of the Kraton rubber particles was then investigated. The idea for this experiment was that the surfactant molecules present in the system should require a specific time period to reach an equilibrium state between the droplet surface and the aqueous phase. At shorter duty cycles, surfactant molecules would have a longer time to attain equilibrium before the next sonification cycle begins, while at longer duty cycles, the surfactants would have a shorter time to reach equilibrium. The sonification conditions and results are listed in Table V. For example, a duty cycle of 10% means that the sonifier is on during 10% of the sonification time and off during the remainder of the sonification time. Thus, the sonification time was controlled so that the actual sonification time interval, when the sonifier is on, is equal for the experiments with different duty cycles. Therefore, the amount of

energy input applied to the systems is the same for each experiment.

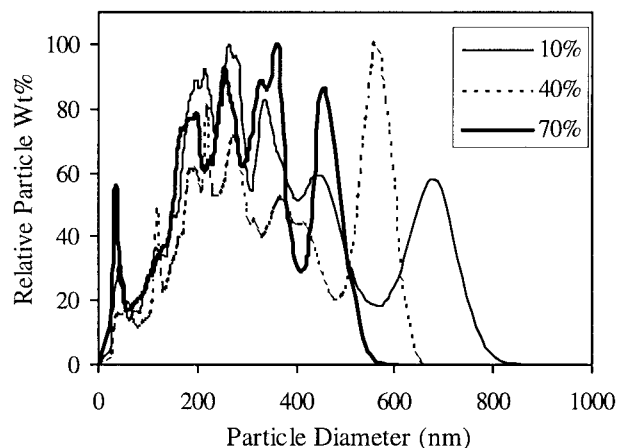
In Table V, the average diameters,  $D_w$  and  $D_n$ , of the Kraton particles decreased slightly at a duty cycle of 70%. However, the average diameters listed in Table V do not show any trend as the duty cycle was increased. On the contrary, the size distributions shown in Figure 12 (determined by CHDF) do show the effect of the duty cycle. The upper bound in the weight-size distribution shifts down to a smaller size range and the distribution becomes narrower with an increase in the duty cycle. It is difficult to explain this phenomenon simply by the time period which is needed for the surfactant to reach an equilibrium state between the aqueous phase and the surface of the droplets.

The most likely explanation for the observed phenomenon can be found from the behavior of the oil droplets. The oil phase is not a pure monomer but

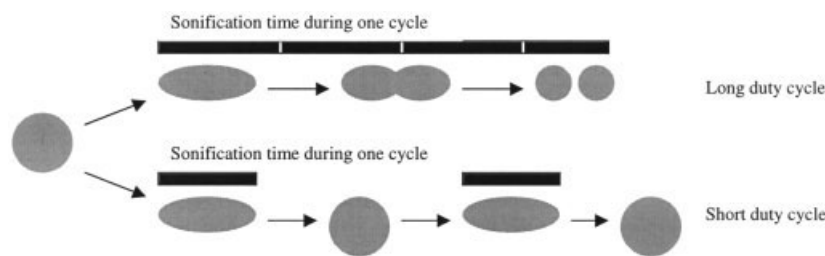
Measurement	Duty cycle (%)		
	10	40	70
	Power level		
	6	6	6
Sonification time (min)			
Set <sup>a</sup>	21.0	5.25	3.00
Actual <sup>b</sup>	2.10	2.10	2.10
Kraton particle diameter			
$D_w$ (nm)	262	262	253
$D_n$ (nm)	63	68	54
PDI	4.16	3.85	4.69

<sup>a</sup> Set: the sonification time including the time period while the sonifier is off.

<sup>b</sup> Actual: set  $\times$  duty cycle/100.



**Figure 12** Weight-average diameter distributions for the Kraton rubber particles prepared using different sonifier duty cycles (10, 40, or 70%): sonification = 3 min at a power level of 6; [SLS]/[CA] = 15/45 mM.



**Figure 13** Schematic representation for the process to break emulsion droplets using different sonifier duty cycles.

contains 20 wt % Kraton rubber. Kraton rubber chains are entangled inside the emulsion droplets, and thus a certain amount of energy is required to form two droplets from one large droplet by separating the entangled polymer chains. This energy is much higher than that needed to disrupt small monomer molecules. In addition, its behavior is also viscoelastic. It is envisioned that there are three scenarios for the process to break emulsion droplets containing polymer chains. First, there exists a relaxation time which is needed to respond to an external shear stress, due to viscoelastic behavior. If the actual sonification time is shorter than is the relaxation time for the polymer chains, emulsion droplets cannot be broken. Second, if the actual sonification time during one cycle is not sufficiently long (i.e., a shorter duty cycle), even though the sonification time length is longer than the relaxation time, a droplet may elongate but polymer chain disentanglement is not completely attained. Thus, the emulsion droplet recovers its original shape as soon as the sonification stops. This process is repeated for shorter duty cycles during the whole sonification period. Therefore, it is difficult to break down the emulsion droplets to smaller ones. Finally, in contrast, if the actual sonification time during one cycle is sufficiently long (i.e., a longer duty cycle), the large droplets can be broken down to smaller ones as schematically depicted in Figure 13. In conclusion, a longer duty cycle is preferred to obtain smaller emulsion droplets with a narrower size distribution in the case where polymer solutions are emulsified.

### Membrane filtration

Direct miniemulsification using a membrane-filtration process to form uniform submicron particles has been used to prepare a model polystyrene latex with a very narrow size distribution for fracture studies and for the investigation of polymer chain interdiffusion during film formation.<sup>29</sup> In this process, the emulsions should first be sonified to break any oil phase down into smaller droplets. The sonified emulsion is then forced through the membrane pore using 50 psi of nitrogen gas. The emulsion that was used in Mohammadi et al.'s process contained 7 wt % polystyrene in cyclohexane as an oil phase. They obtained uniform

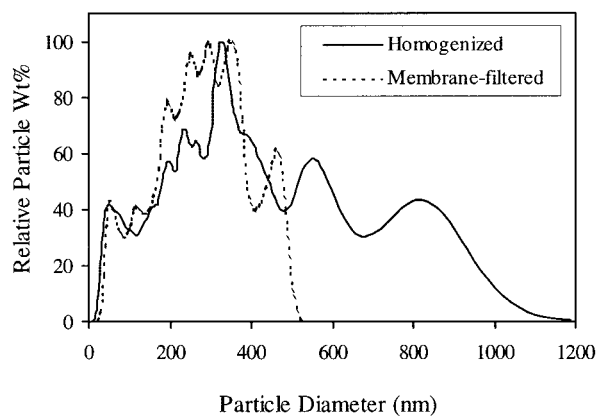
latex particles with a PDI of 1.1 after stripping off the cyclohexane. However, the current system which contains 20 wt % Kraton rubber is more viscous, resulting in causing difficulties in obtaining a narrow size distribution compared to Mohammadi et al.'s case. A microporous glass membrane has also been used to form micron-size uniform droplets and eventually to prepare uniform microspheres.<sup>30–33</sup>

The oil phase containing 20 wt % Kraton rubber is relatively rigid compared to a pure monomer and should be properly emulsified using a device such as a sonifier or rotor-stator homogenizer. In the membrane-filtration process, smaller droplets can pass undisturbed through the pores in the membrane. Therefore, only droplets with diameters which are larger than the membrane pore size can be affected by the membrane-filtration process. The resulting droplet size is influenced by a number of passes (cycles) through the membrane filter and the membrane pore size. In this study, polyester track-etch membrane filters with a narrow pore-size distribution (Osmonics) were used. Emulsions were first prepared by sonification at a power level of 8 and a duty cycle of 70% for 10 min, and the sonified emulsions were then forced through the membrane filter under a nitrogen pressure of 50 psi.

### Comparison of size distributions for the membrane-filtered emulsion and the Manton–Gaulin homogenized emulsion

An emulsion was first prepared by sonification at a duty cycle of 70% and a power level of 8 using SLS/HD = 20/40 mM and then filtered through 0.4- $\mu$ m membrane filter for 15 passes. A second emulsion was prepared by the Manton–Gaulin homogenizer using SLS/HD = 20/80 mM. The styrene was removed from these emulsions by vacuum-distillation and Kraton rubber particle sizes and size distributions were determined by CHDF.

Figure 14 presents the results showing the size distributions of all Kraton rubber particles prepared from the membrane-filtration process and the Manton–Gaulin homogenizer. As mentioned earlier, Kraton rubber particles formed by the Manton–Gaulin homogenizer showed a very broad size distribution with



**Figure 14** CHDF weight-size distribution of Kraton rubber particles prepared from the membrane-filtered emulsion formed with SLS/HD = 20/40 mM and the homogenized emulsion formed with SLS/HD = 20/80 mM.

a tail extending up to 1.2  $\mu\text{m}$ . However, it can be seen that large particles over 500 nm were eliminated when using the membrane-filtration process.

#### Effect of the membrane pore size on the size distribution of Kraton rubber particles

The membrane-filtration process affects particles with diameters larger than the membrane pore size. Particles with diameters smaller than the pore size are not significantly influenced by the filtration process, and, thus, the number-average diameter and a number-size distribution remain almost unchanged.

Sonified emulsions, which were prepared under the same conditions described in the previous section, were filtered five times through a 0.4- $\mu\text{m}$  polyester track-etch membrane filter and then 10 times through a 0.2- $\mu\text{m}$  filter. The styrene monomer was stripped off as soon as the samples were withdrawn. The Kraton rubber particle-size distribution was then determined using CHDF. The experimental conditions utilized and the results obtained are listed in Table VI and Figure 15. The weight-average Kraton rubber particle diameters decreased by going through each process step; first, sonification; second, membrane filtration

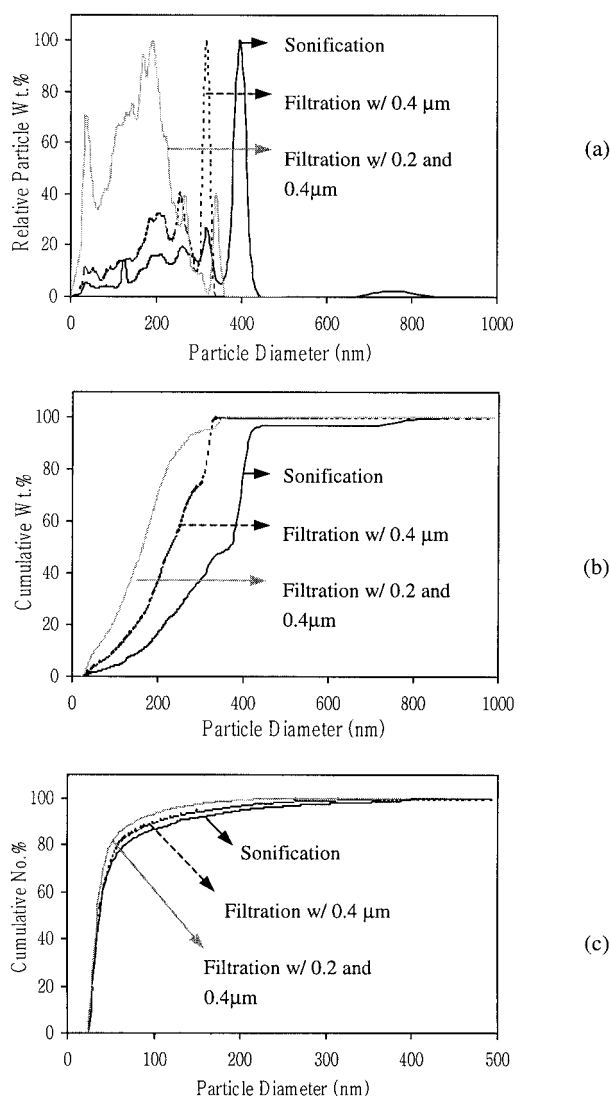
with five passes through the 0.4- $\mu\text{m}$  filter; and third, membrane filtration with 10 passes through the 0.2- $\mu\text{m}$  filter. This indicates that particles larger than the membrane pore size were eliminated from the emulsion using the membrane-filtration process. This result is again confirmed by the CHDF size distribution as shown in Figure 15(a). It can be seen that most particles larger than 300 nm in diameter were removed after the emulsion was passed through the 0.2- $\mu\text{m}$  membrane filter. The larger upper bound in the size distribution, compared to the membrane pore size, indicates that the larger emulsion droplets were squeezed and then passed through the membrane filter. However, the number-average diameters of Kraton rubber particles decreased very slightly as they went through each step. In addition, the number-size distribution in Figure 15(b) remained almost unchanged. It can be inferred from these observations that the emulsion droplets with diameters smaller than the membrane pore size were not affected by the membrane-filtration process and they passed through the filter without interference.

## CONCLUSIONS

The Manton–Gaulin homogenizer supplied a greater amount of energy to the Kraton rubber/styrene system than did any other devices tested (sonifier and rotor-stator homogenizer), and, thus, the Kraton rubber/styrene solution was emulsified within a very short time period (within 1 cycle, ca. 17 s). However, very small Kraton rubber particles with diameters less than 50 nm were continuously generated during this process as the number of homogenization cycles was increased, while the population of large Kraton rubber particles over 500 nm shifted to a larger size range at higher number of cycles (10 passes) due to the coalescence of emulsion droplets. At a lower first-stage pressure of the homogenizer, Kraton rubber particles were reduced in size due to an insufficient energy input. Therefore, a shorter homogenization time with a sufficiently high homogenization pressure is desirable to obtain an emulsion of polymer solution with a smaller size and a narrower size distribution.

**TABLE VI**  
Experimental Conditions for the Sonification/Membrane Filtration and the Resulting Average Kraton Rubber Particle Diameters

Experimental conditions	Sonification only	Sonification and 5 passes through 0.4- $\mu\text{m}$ membrane filter	Sonification, 5 passes through 0.4- $\mu\text{m}$ and then 10 passes through 0.2- $\mu\text{m}$ membrane
Kraton particle diameter (nm)			
$D_w$ (nm)	268	211	162
$D_n$ (nm)	61	55	47
PDI	4.39	3.84	3.45



**Figure 15** (a) Weight, (b) cumulative weight, and (c) cumulative number distributions of Kraton particles prepared by sonification or membrane filtration: sonification = power level of 8 and duty cycle of 70%; 0.2- or 0.4- $\mu\text{m}$  polyester track-etch membrane was used in the membrane-filtration process;  $[\text{SLS}]/[\text{CA}] = 15/45 \text{ mM}$ .

The interfacial tension decreased as the CA concentration increased and the population of large Kraton rubber particles over 500 nm continuously shifted down to a smaller size range. It was found that CA has enough surface activity to lower the interfacial tension between the oil and the aqueous phases, resulting in the decrease of the Kraton rubber particle diameter, even though it is not as effective as an anionic surfactant such as is SLS. It is thought that its role of lowering the interfacial tension is more important than is its role as a costabilizer or a swelling promotor in the emulsification of a polymer solution.

A large number of small Kraton rubber particles less than 50 nm in diameter were generated even at 1 min sonification. The population of large Kraton rubber

particles over 500 nm was located in a larger size range at a longer sonification time (6 min) due to the coalescence of emulsion droplets, as observed by varying the number of homogenization cycles. The same result was found when the power level of the sonifier was varied, that is, the highest power level (8) resulted in a larger weight-average diameter of Kraton rubber particles. As the duty cycle increased, the population of large Kraton rubber particles shifted down to a smaller-size range because of the viscoelastic behavior of the emulsion droplets.

Large emulsion droplets could be removed by the membrane-filtration process and, thus, the upper bound in the size distribution was determined by the membrane pore size. Small emulsion droplets passed through the pores on the membrane without any interaction with the membrane filter.

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