

# Drop deformation, breakup, and coalescence with compatibilizer

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The effect of copolymers on the breakup and coalescence of polybutadiene (PB) drops in polydimethylsiloxane (PDMS) is studied using a four-roll mill flow cell. Copolymers are produced at the interface by a reaction between functionalized homopolymers. They reduce the interfacial tension and thus enhance breakup; they also inhibit coalescence of drops. Under the conditions of our experiments, the latter effect is much more significant than the former. For example, the addition of copolymer sufficient to reduce the interfacial tension by only 3% relative to the bare interface value is found to reduce the critical capillary number  $Ca_c$  for coalescence by a factor of 6. The critical capillary number for coalescence in the absence of copolymer is also measured for the first time. It is found to scale with the drop radius  $a$  as  $Ca_c \sim a^{-0.82 \pm 0.03}$  and with the viscosity ratio  $\lambda$  as  $Ca_c \sim \lambda^{-0.41 \pm 0.06}$ . © 2000 American Institute of Physics. [S1070-6631(00)01203-4]

## I. INTRODUCTION

Surfactants or copolymers are commonly used to make emulsions and stabilize drops suspended in an immiscible medium. The role of surfactant is thought to be two-fold: lowering the interfacial tension (thereby facilitating breakup) and preventing coalescence. Many experimental studies of drop breakup have been reported,<sup>1</sup> though few<sup>2-4</sup> have focused on the effects of surfactant. There have been no quantitative experimental investigations of the coalescence of two drops in a shear flow, as far as we are aware, either with or without surfactant. In the present paper, we report on the effect of copolymer surfactant on droplet breakup and on what we believe to be the first quantitative experimental data for the coalescence of two equal size drops in a velocity gradient. Our most surprising result is the quite dramatic effect of copolymer in inhibiting coalescence.

## II. EXPERIMENTAL PROCEDURES

The experiments were carried out in a miniaturized version of the computer-controlled four-roll mill first developed by Bentley and Leal.<sup>5</sup> The current system can achieve shear rates between  $10^{-3}$  and  $8.7 \text{ s}^{-1}$ , thus allowing both breakup and coalescence to be studied for drop diameters from several microns to several hundred microns. A detailed description of this apparatus will appear elsewhere. The suspending fluid was polydimethylsiloxane (PDMS,  $M_n = 116\,500$ ), and the drops were a series of different molecular weight polybutadienes (PB) chosen to provide a range of viscosity ratios (Table I). Under the conditions of the present experiments, both the drop and suspending liquid behaved as Newtonian fluids. All experiments were performed at  $22 \pm 0.1 \text{ }^\circ\text{C}$ .

The coalescence experiments were carried out by first breaking a drop at the stagnation point into a pair of equally sized drops. The two drops were then separated along the symmetry axis of the four-roll mill (using pure extensional

flow) while maintaining the center of mass of the two-drop pair at the stagnation point (see Fig. 1). The flow was stopped when the center-to-center distance between the drops was two drop diameters. The rollers were then reversed to bring the drops back together. The coalescence data reported here are for a single mixed-type flow, with a flow-type parameter<sup>6</sup> of  $\alpha = 0.9$ . Although this flow differs only slightly from the pure extensional flow that was used to separate the drops, the difference was enough to avoid head-on collisions. In fact, the initial configuration corresponds to a constant value of the dimensionless offset distance  $d/a$ , as shown in Fig. 1. The decision to avoid head-on collisions for this initial study was made because it is a singular case in the sense that the critical capillary number for coalescence is infinite, independent of the drop size or the viscosity ratio between the drop and the suspending fluid.

Copolymers were produced at the drop interface by reaction between end-functionalized PB and PDMS. In the present experiments, this was done outside the flow cell. A small amount (0.02% to 0.44% by weight) of PDMS-HN<sub>2</sub> (PDMS,  $M_n = 27\,000$ , with single amino end groups) was mixed with an inert PDMS ( $M_n = 62\,700$ ) in a small vial. A drop of either PB-COOH or PB with 0.4% of PB-2COOH was introduced into the vial with a syringe and allowed to react at room temperature for about 10 min. This produces a "salt-like" complex of PB-COO-+NH<sub>3</sub>-PDMS (no covalent bond is formed) at the interface that we refer to as the "copolymer."<sup>1</sup> The copolymer concentration at the interface was controlled by the concentration of PDMS-NH<sub>2</sub> in the vial. The PB drop with copolymer at the interface was then transferred via pipette into the flow cell. We took care that very little PDMS ( $\sim 10 \text{ mg}$ ) from the vial was loaded into the flow cell with the PB drop.

Since we had no means of directly measuring the concentration of copolymer at the interface, we characterized the copolymer concentration by measuring the interfacial tension

TABLE I. Material characteristics.

Sample	Source	$\mu$ (Pa s)	$M_n$
PDMS	Rhone Poulenc	9.6	62 700
PDMS	United Chemical	57.4	116 500
PDMS-NH <sub>2</sub>	United Chemical	1.9	27 000
PB	Aldrich	0.72	1800
PB	Aldrich	2.8	3000
PB	Aldrich	5.5	5000
PB-2COOH	Aldrich	73	4200
PB	Polymer sources	12.9	13 400
PB	Polymer sources	34	18 000
PB-COOH	Polymer sources	125	10 000

of each drop. This was done in the flow cell by turning on a weak flow and monitoring the drop deformation  $D_f \equiv (L - W)/(L + W)$ , where  $L$  and  $W$  are the length and width of the deformed drop, respectively. For weak flows ( $D_f \ll 1$ ),  $D_f = 2 \text{Ca} (19\lambda + 16)/(16\lambda + 16)$ , where the capillary number  $\text{Ca} \equiv \dot{\gamma} \mu_s a / \Gamma$ , and  $\dot{\gamma}$  is the strain rate,  $\mu_s$  the viscosity of the suspending liquid,  $a$  the drop radius, and  $\Gamma$  the interfacial tension. This technique for measuring the interfacial tension is known to give reliable results, even when there is surfactant at the interface, provided the drop deformation is within the linear regime. In our measurements,  $D_f$  was kept between 0.05 and 0.15 for which we observed good linearity between  $D_f$  and  $\text{Ca}$ .

After loading a drop, we monitored the deformation per unit strain rate  $D_f / \dot{\gamma}$ . Initially,  $D_f / \dot{\gamma}$  decreased with time (up to 50% in one hour). However, the rate of decrease slowed with time to the point of being insignificant over the time scale of an experiment (tens of minutes). All our results were obtained after the initial period of rapid change. There are at least two possible reasons for this initial time dependence. First, the PDMS that initially surrounds the drop is from the vial and has a different viscosity (9.6 Pa s) from that of the PDMS (57.4 Pa s) in the flow cell. Second, the reaction between the NH<sub>2</sub> and COOH groups is reversible so that it may require some time to reach a new equilibrium in the

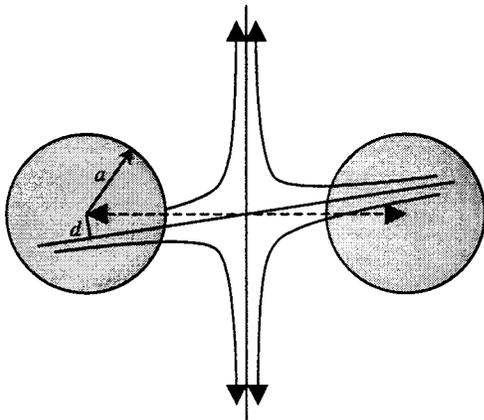


FIG. 1. Flow geometry. A single drop is split into two drops that are separated along the dashed lines with outward arrows. The drops are then directed toward each other in a flow field with a flow axis inclined slightly with respect to the horizontal direction. The center of the drop is offset from the symmetry axis of the inward flow by a distance  $d$ . The drop radius is  $a$ .

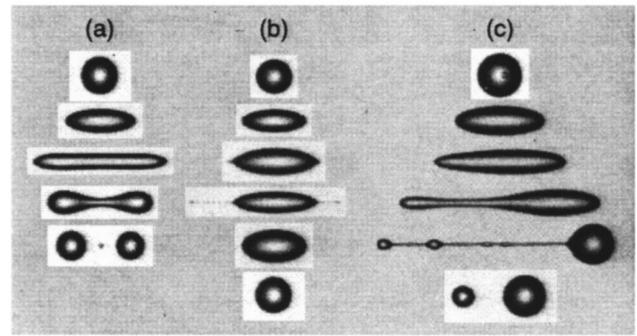


FIG. 2. Different modes of drop breakup for different concentrations of copolymer at the interface. Time proceeds from top to bottom for each case with the flow commencing immediately after the top image was obtained. (a) Capillary modes—no surfactant. Flow was stopped after the third image. Initial drop diameter = 88  $\mu\text{m}$ . (b) Tip streaming—modest copolymer concentrations. Flow was stopped after the fifth image. Initial drop diameter = 89  $\mu\text{m}$ . (c) Asymmetric end pinching—higher copolymer concentrations. Flow was stopped after the fourth image. Initial drop diameter = 107  $\mu\text{m}$ . Drop materials: PB ( $M_n = 5000$ ) with 0.4% of PB-2COOH added and copolymers generated at the surface by reaction with a mixture of PDMS ( $M_n = 62\,700$ ) and 0.17% of PDMS-NH<sub>2</sub>. Medium: PDMS ( $M_n = 116\,500$ ).

flow cell. In any case, once the equilibrium state has been reached, the copolymer behaves essentially as though it were an insoluble surfactant. This is consistent with our experimental data as we shall see below, and also with thermodynamic estimates of the equilibrium amounts of the copolymer in the bulk.

### III. DROP DEFORMATION AND BREAKUP

We first examine the effect of copolymers on drop deformation and breakup in steady, purely extensional flow. We report results for low and high viscosity ratios  $\lambda = \mu_d / \mu_s$ , where  $\mu_d$  and  $\mu_s$  are the viscosities of the drop and surrounding liquid, respectively. At a low viscosity ratio of 0.10, we observed three typical types of breakup, as shown in Fig. 2: (a) capillary modes characteristic of drops with very low copolymer concentrations or no surfactant at all;<sup>6</sup> (b) tip streaming at modest copolymer concentrations, where the interfacial tension was reduced from its value without copolymer by less than about 10%; and (c) asymmetric end pinching at higher copolymer concentrations. Similar breakup modes were reported by Janssen<sup>2</sup> for small molecule surfactant systems.

Both Janssen<sup>2</sup> and De Bruijn<sup>3</sup> have suggested that different modes of breakup are caused by the redistribution of the surfactants/copolymers at the interface. This is confirmed in our experiments by examining the values of the interfacial tension of the drops before and after breakup. For the case of tip streaming shown in Fig. 2 (b), the interfacial tension of the single large drop after tip streaming has increased from its original value of 3.7 mN/m to a final value of 4.0 mN/m. This final value is the same as for a drop without copolymers and indicates that nearly all of the copolymer was swept off with the small tip-streamed drops. If the flow is reversed, the very small satellite drops readily recombine with the large drop, and the original interfacial tension is then recovered.

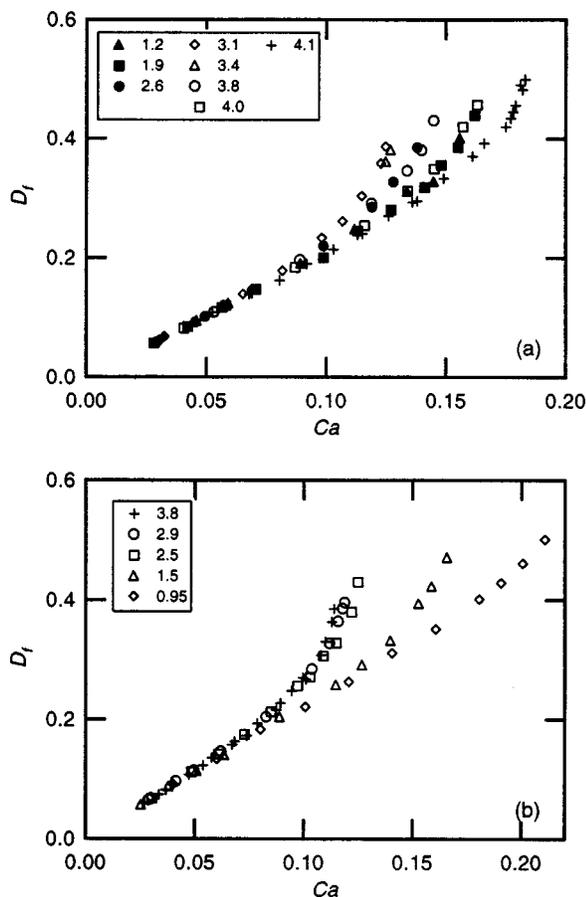


FIG. 3. Drop deformation parameter versus capillary number. (a) Low viscosity ratio ( $\lambda=0.10$ ). Drop: PB ( $M_n=5000$ ) with 0.4% of PB-2COOH added and copolymers generated at the surface by reaction with a mixture of PDMS ( $M_n=62\,700$ ) and 0.17% of PDMS-NH<sub>2</sub>. (b) High viscosity ratio ( $\lambda=2.2$ ). Drop: PB-COOH ( $M_n=10\,000$ ) with copolymers generated at the surface by reaction with a mixture of PDMS ( $M_n=62\,700$ ) and 0.17% of PDMS-NH<sub>2</sub>. Legends indicate interfacial tension in mN/m for each dataset. Lower surface tension corresponds to higher copolymer concentration at the interface.

This is consistent with the copolymer acting as an insoluble surfactant. For the case of asymmetric end pinching shown in Fig. 2(c), the smaller of the two final drops has a lower interfacial tension (1.5 mN/m, diam=53  $\mu\text{m}$ ) than the larger drop (2.6 mN/m, diam=103  $\mu\text{m}$ ), indicating that the concentration of copolymer was greater at the smaller curvature end prior to breakup. The interfacial tension of the original drop was 1.9 mN/m. Again the copolymer acts as an insoluble surfactant in the sense that none is lost in the breakup process. If the broken drops are coalesced by reversing the flow, the interfacial tension returns to the value of the original drop. We may note, however, that a copolymer mass balance based on the assumption that the amount of copolymer on the drop surface is linearly related to the decrease in interfacial tension relative to the clean interface value of 4.0 mN/m, is only accurate to about 10%. This is most likely due to the fact that the assumption of linearity is only valid at low copolymer concentrations. Finally, at a higher viscosity ratio of 2.2, only the normal capillary breakup was observed, even when the copolymer concentration coverage was quite high. There was, however, still a weak nonuniformity in copoly-

mer concentration evident in the values of the interfacial tension of the different daughter drops.

Further insight into the effects of copolymer on drop breakup can be gained by examining our measurements of drop deformation versus capillary number. In Fig. 3(a), we show  $D_f$  vs  $Ca$  for low viscosity ratio drops ( $\lambda=0.10$ ) with different copolymer concentrations (as characterized by the interfacial tension). The final data point on each curve corresponds to the maximum value of  $Ca$  for which a steady drop shape is possible. For larger values of  $Ca$ , droplet breakup occurs before a steady droplet shape is achieved. Drop breakup occurs either by tip streaming [Fig. 2(b)] or by asymmetric stretching [Fig. 2(c)]. The critical capillary number for breakup is largest for the sample without any copolymer ( $\Gamma=4.1$  mN/m). As small amounts of copolymer are added ( $\Gamma=4.0, 3.8, 3.4,$  and  $3.1$  mN/m), the critical capillary number initially *decreases*. However, as even more copolymer is added ( $\Gamma=2.6, 1.9,$  and  $1.2$  mN/m), the trend reverses and the critical  $Ca$  for breakup moves toward larger values.

Recent theoretical work predicts<sup>7-9</sup> that the addition of a small amount of surfactant causes increased deformation at a fixed value of  $Ca$ , and hence a reduction in the critical capillary number for breakup. (Note that the simple effect of a reduction in the equilibrium interfacial tension is incorporated into the capillary number, and thus into the data in Fig. 2.) This is consistent with our observations when the amount of added copolymer is small [ $\Gamma=3.8, 3.4,$  and  $3.1$  mN/m in Fig. 3(a)]. It is caused by a decrease in interfacial tension at the tips of the drops arising from the nonuniform concentration of copolymer at the interface. This allows higher curvature at the ends of the drop and a tendency for the tip of the drop to be stretched out farther than a drop at the same  $Ca$ , but with no surfactant. This effect is compensated to some degree by Marangoni stresses and by simple dilution. The latter effect corresponds to the increase in average interfacial tension due to the increase of surface area as the drop deforms and the concentration of any insoluble surfactant at the interface is decreased. Marangoni stresses decrease the tangential velocity at the interface. This has two effects: the first is to decrease the surfactant concentration gradients due to a decrease in the effective interfacial Peclet number, and thereby decrease the tip stretching effect; the second is to increase the local shear stress, which will tend to increase deformation in a manner similar to an increase of the viscosity ratio for a clean drop with  $\lambda < O(1)$ . The actual flow curve depends on the competition between tip stretching, dilution, and Marangoni effects. At low copolymer concentrations and low viscosity ratios, where the copolymer is both compressible and relatively mobile, the copolymer distribution becomes highly nonuniform; this leads to an increase in deformation at a given capillary number. At higher copolymer concentrations, beyond the range of the linear relationship between interfacial concentration and tension used in the simple theory,<sup>7</sup> the interfacial tension becomes increasingly sensitive to small changes in the surfactant concentration, and Marangoni stresses then tend to immobilize the interface with only very small gradients of the concentration. Recent theoretical work<sup>10,11</sup> for  $\lambda=1$  indicates that dilution effects then become increasingly important and largely com-

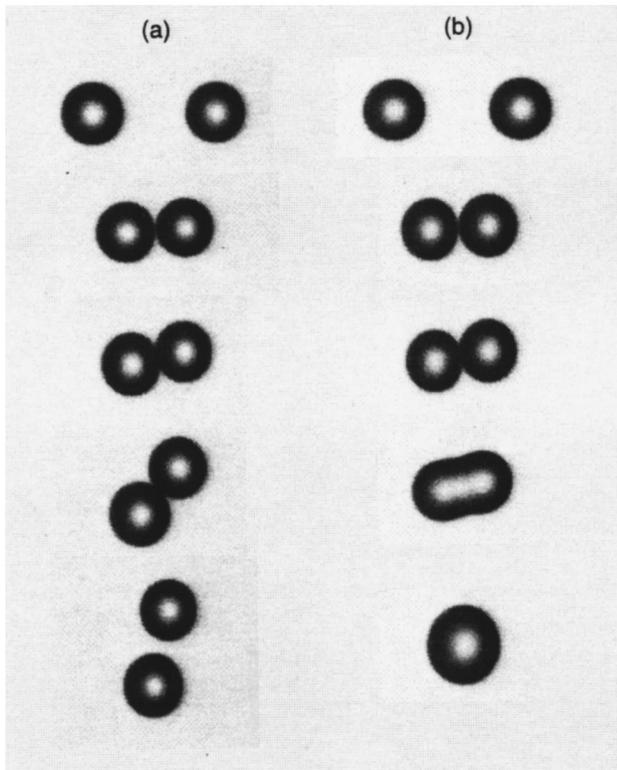


FIG. 4. Time sequence of two drop coalescence experiments without copolymer: one above and the other below the critical capillary number  $Ca_c \approx 0.012$ . (a) Coalescence does not occur for  $Ca=0.013 > Ca_c$ . (b) Coalescence occurs for  $Ca=0.0086 < Ca_c$ . Drops are PB ( $M_n=5000$ ) and  $70 \mu\text{m}$  in diameter.

pensate the increased deformation due to the tip stretching effect. Based on our data, these effects apparently lead to a reversal of the trend toward increased deformation with increased copolymer coverage.

Figure 3(b) shows deformation curves for drops with a higher viscosity ratio of  $\lambda=2.2$ . In this case, the critical capillary number for breakup *increases* monotonically as the copolymer concentration is increased. We believe this is a consequence of the reduced flow within the drop at higher  $\lambda$ . This leads to a decreased mobility of copolymer at the interface. The measured values of the interfacial tension of the daughter droplets after breakup of these higher viscosity ratio drops is much more uniform than shown earlier for the lower viscosity ratio case. Thus, the decreased mobility of copolymer at the interface leads to more uniform copolymer coverage during flow. With more uniform copolymer coverage, the dilution of copolymer concentration when the drop is stretched becomes more important. The enhancement of the dilution effect with increased copolymer concentrations then leads to a decrease in deformation at fixed capillary number, as also predicted theoretically for insoluble surfactants.<sup>7</sup>

#### IV. COALESCENCE

We now turn our attention to the effect of copolymer on the coalescence of two drops. First we consider the case of coalescence without copolymer. In Fig. 4 we show images

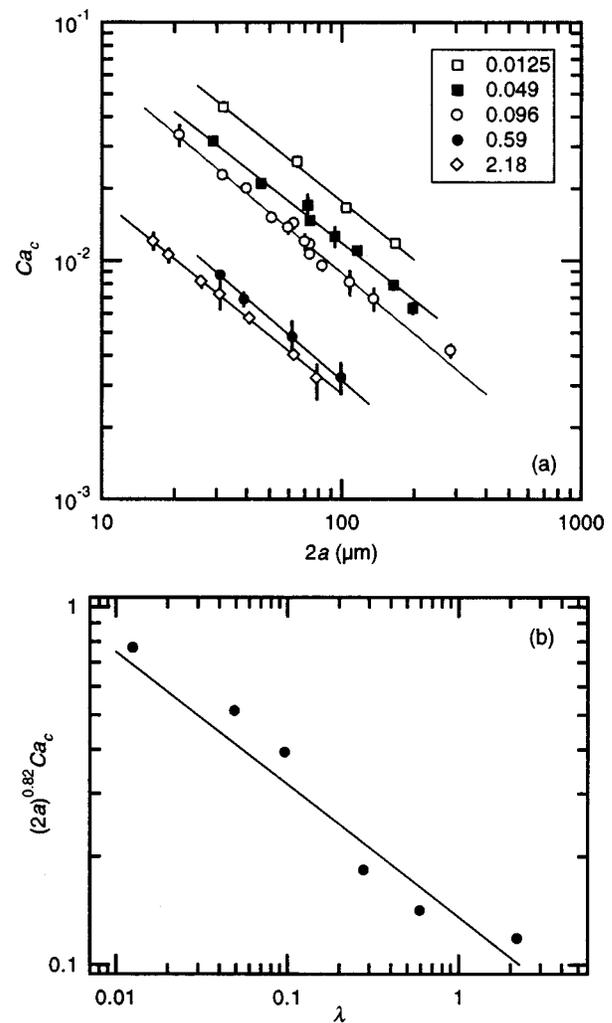


FIG. 5. Coalescence of drops without copolymer. (a) Critical capillary number  $Ca_c$  versus drop diameter  $2a$  for different viscosity ratios (indicated in the legend). The data are fit to power laws with a mean exponent of  $-0.82 \pm 0.03$ . Drop: PB ( $M_n=5000$ ). (b) Dependence of coalescence on viscosity ratio  $\lambda$ . The data are fit to a power law with an exponent of  $-0.41 \pm 0.06$ . Drop: PB with various  $M_w$  (see Table I).

from two typical coalescence experiments. In each experiment, two equal size ( $70 \mu\text{m}$  diam) PB drops were positioned in the flow device, as explained above, and then driven toward each other at a fixed capillary number in the four-roll mill with flow-type parameter  $\alpha=0.9$ .<sup>6</sup> As the drops come together, they rotate due to the initial offset from a head-on trajectory. Whether they coalesce or separate depends on whether the fluid film between them drains to a minimum thickness  $\delta$  that is within the range of the attractive van der Waals force.<sup>12</sup> For a fixed initial *dimensionless* offset  $d/a$  and viscosity ratio  $\lambda$ , the minimum *dimensionless* film thickness  $\delta/a$  depends only on the capillary number  $Ca$ . Since  $\delta/a$  decreases monotonically with decreasing  $Ca$ , coalescence will only occur for  $Ca$  below a critical value  $Ca_c$  that depends on  $\lambda$ ,  $d/a$ , and the drop size  $a$ . In Fig. 4(a),  $Ca=0.013 > Ca_c \approx 0.012$ , and there is no coalescence. In Fig. 4(b),  $Ca=0.086 < Ca_c$  and coalescence occurs.

The scaling of the critical capillary number  $Ca_c$  with drop diameter  $2a$  is shown in Fig. 5(a). The data were ob-

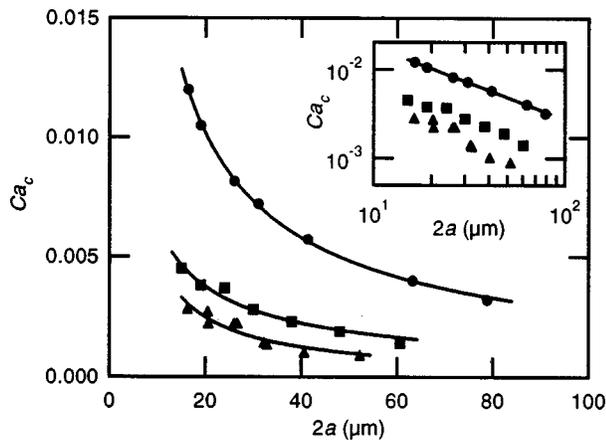


FIG. 6. Effect of copolymer on the critical capillary for coalescence. Top curve: no copolymers ( $\Gamma=3.8$  mN/m). Middle curve: ( $2.5$  mN/m  $< \Gamma < 3.5$  mN/m). Bottom curve: ( $\Gamma=3.7$  mN/m). Inset: The same data plotted in double logarithmic format.

tained for the case of no copolymer with a fixed offset  $d/a$  and viscosity ratios  $\lambda$  ranging from 0.0125 to 2.18. Each dataset is well fit by a power law. The exponents range from  $-0.79$  to  $-0.86$  with a mean of  $-0.82 \pm 0.03$ . This exponent is higher than the exponent of  $-\frac{2}{3}$  predicted by existing scaling arguments for simple shear flow,<sup>12</sup> however, the latter does not take account of the time dependence of the hydrodynamic force between the pair of drops as they rotate in the flow. A revised version of this theory will be reported shortly from our group.

The dependence of coalescence on the viscosity ratio is shown in Fig. 5(b), where we show  $(2a)^{0.82}Ca_c$  as a function of viscosity ratio  $\lambda$ . The factor  $(2a)^{0.82}$  is applied so that  $Ca_c$  for different drop diameters can be compared. Once again, the data seem to show power law behavior (though not as clearly) as expected from the simple scaling theories. However, the power of  $-0.41 \pm 0.06$  is not as steep as the existing theoretical prediction of  $-\frac{2}{3}$ ,<sup>12</sup> possibly again due to the assumptions built into the theory.

We now examine the effect of copolymer on coalescence. In Fig. 6, we plot  $Ca_c$  versus drop diameter  $a$ . The top curve shows coalescence data for drops without copolymers and follows the same power law as in Fig. 5(a). The lower curve was obtained with a very small amount of added copolymer (i.e.,  $\Gamma$  is reduced only from the bare interface value of 3.8 mN/m to a value of 3.7 mN/m) and is significantly lower. Different drop diameters were obtained by breaking the bigger drops into smaller drops. As a result, the smaller drops have less copolymer coverage than the larger drops and the interfacial tension must increase accordingly. Of course, for the lowest curve in Fig. 6, the change in  $\Gamma$  relative to the clean surface value is very small, and we were unable to measure  $\Gamma$  accurately enough to distinguish these expected changes. The value  $\Gamma=3.7$  mN/m reported in the figure caption is that measured for the initial (largest) drop. The middle curve in Fig. 6 was obtained with a larger initial copolymer concentration,  $\Gamma=2.5$  mN/m. In this case, there was a significant and measurable increase in  $\Gamma$  as we move from right to left along the curve (i.e., from the largest to the

smallest drop for which  $\Gamma=3.5$  mN/m). Nevertheless,  $Ca_c$  was found to exhibit a power law dependence on drop size very similar to that shown by drops with no copolymer. This insensitivity of  $Ca_c$  to copolymer coverage is intriguing, though we are currently unable to offer any explanation. It is also unclear to us why the critical Capillary number is increased slightly with the increase of copolymer coverage between the two lower curves in Fig. 6. These issues will be explored in future studies.

We currently have no direct measurement of the actual copolymer concentration at the drop surface. Of course, the measured interfacial tension values provide a qualitative basis for comparison of different cases, provided the surface coverage is not so low that the change in  $\Gamma$  is below the resolution limits of our measurements. We may also obtain a crude estimate for the surface coverage by assuming that the reaction rate for producing copolymer is diffusion limited, and then determining the total amount of reactive polymer that can reach the interface by diffusion in the available reaction time, which was approximately 600 s, as noted earlier. To make this estimate, we use a diffusivity of  $5 \times 10^{-12}$  m<sup>2</sup>/s (chosen arbitrarily to be between the self-diffusion coefficients for PDMS with  $M_n=27000$  and  $M_n=62700$ <sup>13</sup>) and assume a uniform initial concentration of reactant in the bulk fluids. Assuming that any reactive chain that gets to the interface will react, we find a surface coverage of only about  $0.1R_g^{-2}$  for drops prepared with 0.02% of PDMS-NH<sub>2</sub> (we estimate  $R_g$  to be  $10$  m<sup>-8</sup>).<sup>14</sup> This is the “low concentration” system shown in Fig. 6, where the measured  $\Gamma$  was reduced from the bare drop value of 3.8 mN/m to approximately 3.7 mN/m. Figure 2(a) indicates that the critical capillary number for breakup was hardly changed at this value of  $\Gamma$ . However, the critical capillary number for coalescence was only one-sixth of the bare polymer value (Fig. 6). We believe that the inhibition of coalescence is a consequence of a decrease in the rate of film drainage due to Marangoni stress gradients on the interfaces within the thin film region. Although the magnitude of these stress gradients will be extremely small at such a low surface coverage of the PDMS-PB copolymer, the capillary numbers for coalescence are only order  $10^{-2}$ – $10^{-3}$ , which means that it takes only a very tiny contribution from the Marangoni stresses to dominate viscous stresses and inhibit drainage of the thin film. This observation appears to be qualitatively consistent with a recent theoretical proposal.<sup>15</sup>

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