

# Functional Polymers for Colloidal Applications. VII. Aggregate Formation of Lipophile-Modified Polyacrylates in Aqueous Solutions

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## SYNOPSIS

Water-soluble copolymers, poly(dodecyl acrylate-coacrylic acid) (PDA), are synthesized by copolymerizing different ratios of dodecyl-acrylate/acrylic acid. Their aqueous solutions are transparent. The plots of  $I_1/I_3$  (the intensity ratio of pyrene emission at 374 nm and 385 nm) and of surface tension as a function of polymer concentrations are combined to verify the existence of the aggregates of PDAs. It is found that the aggregations begin to form at concentrations below that of the polymer transfer to the air-water interface. The plots of  $I_1/I_3$  as a function of polymer concentration shows that the polymers with a higher ratio of dodecyl acrylate form polymer aggregates at lower concentrations. The hydrophobicity of the inner core of polymer aggregates is close to that of sodium dodecyl sulfate (SDS). Polymer solutions of PDA 30, PDA 30L, and PDA 15, show significant solubilization ability to pyrene. (The molar ratio of dodecyl acrylate/total acrylates is 30%, 30%, and 15% for PDA 30, PDA 30L, and PDA 15, respectively. L, low molecular weight.) The solubilization ability increases with the increase in polymer concentration and degree of substitution of dodecylamine. The intensity ratio of the excimer emission to monomer emission of pyrene ( $I_e/I_m$ ) increases with increasing polymer concentration, roughly parallel to the increase in the amount of pyrene solubilized. However, the  $I_e/I_m$  at a fixed pyrene concentration ( $I_e/I_m^*$ ) decreases with increasing polymer concentration. These phenomena are interpreted in terms of the amount of pyrene solubilized and the size and concentration of the polymer aggregates. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

For ABA, three block-type, water-soluble copolymers such as poly(ethylene oxide-propylene oxide-ethylene oxide), the polymer chains form aggregates<sup>1-4</sup> in aqueous solution that is transparent. However, for a water-soluble polymer such as polyacrylic acid, the polymer chain is well-expanded in aqueous solution.<sup>5-8</sup> When the backbone of such a water-soluble polymer is grafted with long-chain hydrophobic groups, the polymer then consists of both hydrophobic and hydrophilic groups and forms aggregates as a result of the intermolecular and/or intramolecular hydrophobic interactions. Thus, such

a polymer can be regarded as polymerized surfactant, and its property in solutions is expected to be an intermediate between a surfactant and a water-soluble polymer so as to form aggregates in aqueous solution.

In previous studies, poly(dodecyl acrylate-coacrylic acid) (PDA) was synthesized and used as an emulsifier for emulsion and for emulsion polymerization.<sup>9</sup> It was found that the content of the hydrophobic group (dodecyl acrylate) of such a polymer significantly influences the properties of emulsion and the result of the emulsion polymerization. It is important to understand the fundamental behavior of PDA in aqueous solutions, such as aggregate formation, and the properties of such aggregates.

The ratio of intensities of the fluorescence of pyrene at different wavelengths was used to monitor

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the micropolarity,<sup>10-13</sup> and this was combined with surface tension to investigate the formation of the micelle aggregates of surfactants and the aggregates of polymers.<sup>10-18</sup> The intensity of the excimer formation in an aggregate could also be used to investigate the size or number of aggregates.<sup>14-16</sup> In this study, the fluorescence method and the surface tension method were combined to verify the formation of the aggregates of PDA. Then, the properties of the aggregates were studied by means of the intensity ratio of excimer emission of pyrene, and pyrene solubility. It was found that the hydrophobicity (the percentage of dodecyl acrylate) of PDA significantly influences the minimum concentration for aggregate formation and the properties of aggregates.

## EXPERIMENTAL

### Materials

Pyrene, purchased from Merck Chemical Co., was purified by three recrystallizations from ethanol. Acrylic acid (Ishizu), dodecyl acrylate (Fluka), benzoyl peroxide (Kokusan), *n*-butyl mercaptan (Tokyo, Kasei), were used as supplied.

### Methods

#### Synthesis of Poly(dodecyl Acrylate-Coacrylic Acid) (PDA)<sup>9</sup>

In a four-neck reaction kettle, dodecyl acrylate (35.3 g), acrylic acid (24.7 g), and *n*-butyl mercaptan (12 g), dissolved in dioxane (150 g), and benzoylperoxide (BPO) (2.4 g), was added into the reactor during 3 h at 90°C. The reactor was maintained at 90°C for another 3 h to complete the polymerization. The solvent was evaporated, and the residue dissolved

in 0.1 M NaOH solution, and the solution was adjusted to pH 9. After reprecipitation in methanol, the white solid (PDA 30) was filtered and dried in a vacuum oven at 50°C for 48 h. The conversion yield was more than 99%.

By similar procedure, PDA 30L (using *n*-butyl mercaptan, 2.4 g) and PDA 15 (using 15% of dodecyl acrylate) were synthesized (Table I).

### Fluorescence Measurements

All fluorescence measurements were recorded on a Hitachi Model F-4010 Fluorescence Spectrophotometer. The ratio of the intensity of pyrene emission at 374 nm and at 385 nm is defined as  $I_1/I_3$ . The ratio of the intensity of the maximum pyrene excimer emission (ca. 468 nm) to the maximum pyrene monomer emission (374 nm) is defined as  $I_e/I_m$ . All of the solutions for fluorescence measurements contained a buffer solution to maintain the pH at 7. For reference,  $I_1/I_3$  values for pyrene in water, *n*-hexane, and the micelle of sodium dodecylsulfate are measured to be 1.84 ( $\epsilon = 80$ ), 0.56 ( $\epsilon = 3$ ), and 1.10 ( $\epsilon = 30$ ), respectively, which are close that of the reported value.<sup>19-21</sup>

### Measurement of Surface Tension

The PDAs were dissolved in water to prepare a 1% solution, that was then serially diluted. The surface tension of these solutions was measured by using a tensiometer (Surface Tensiometer CBVP-A3).

### Solubilization Measurements

Pyrene (0.10 g) was added to a 10 mL solution of PDAs and stirred overnight. Then the solution was filtered with Gelman Sciences Sterile Acrodisc 0.2

**Table I** Composition and Behaviors of Poly(dodecyl Acrylate-Coacrylic Acid) (PDA)

Symbol	Comparative Hydrophobicity (%) <sup>a</sup>	$C_1^b$ (wt %)	Minimum <sup>c</sup> $I_1/I_3$	$I_e/I_m^d$	Solubilization to Pyrene (%) <sup>e</sup>
PDA 30	30	$5 \times 10^{-5}$	1.07	0.97	0.47
PDA 30L	30	$10^{-4}$	1.05	2.05	0.49
PDA 15	15	$5 \times 10^{-4}$	1.17	0.16	0.09
PDA 5	5	$5 \times 10^{-3}$	1.23	0	0

<sup>a</sup> The Comparative hydrophobicity is expressed by the molar ratio of dodecyl acrylate/(dodecyl acrylate + acrylic acid).

<sup>b</sup> The concentration (weight percentage) where polymer begins to form aggregates is defined as  $C_1$ .

<sup>c</sup> Pyrene concentration is fixed at  $9.8 \times 10^{-6}$  M.

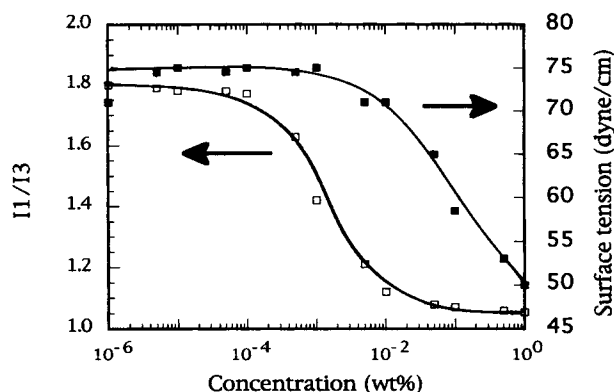
<sup>d</sup> Polymer solution (concentration, 1 wt %) was saturated with pyrene.

<sup>e</sup> Percentage based on total amount of solution; polymer concentration, 1 wt %.

$\mu\text{m}$  syringe filter. The UV absorbance of the solution was measured using Jasco Model 7850 UV spectrophotometer, and the concentration of solubilized pyrene was calculated from the calibration curve.

## RESULTS AND DISCUSSION

There are five peaks in the emission spectra of pyrene, and the emission intensity of the first peak (374 nm) and of the third peak (385 nm) is sensitive to the microenvironment. Thus, the intensity ratio of the emission at 374 nm and 385 nm ( $I_1/I_3$ ) has been used to monitor the solution behavior of surfactants and/or polymers.<sup>10-13</sup> A bigger  $I_1/I_3$  value means a greater polarity of the solution around pyrene. Therefore, the formation of the aggregates with a hydrophobic inner core can be detected by means of plotting  $I_1/I_3$  vs. polymer concentration. In Figure 1,  $I_1/I_3$  value of pyrene in a polymer solution of PDA 30 is measured as a function of polymer concentration. When the polymer concentration is below  $5 \times 10^{-5}\%$  (weight percentage, hereafter), the  $I_1/I_3$  value remains at a value of 1.8, close to that of pure water, indicating that there are no aggregates formed in this region. In the region of  $5 \times 10^{-5}\%$ – $10^{-1}\%$ , the  $I_1/I_3$  value decreases gradually down to 1.07. The decrease in  $I_1/I_3$  indicates the microenvironment around pyrene is getting less polar. It means that the polymer begins to form aggregates above  $5 \times 10^{-5}\%$ . The continuous decrease in  $I_1/I_3$  values can be interpreted as the micropolarity in the polymer aggregates becomes less and less polar due to the increase in the aggregate size, which is accompanied by a closer packing of the inner core. In Figure 1, the surface tension ( $\gamma$ ) of polymer solution



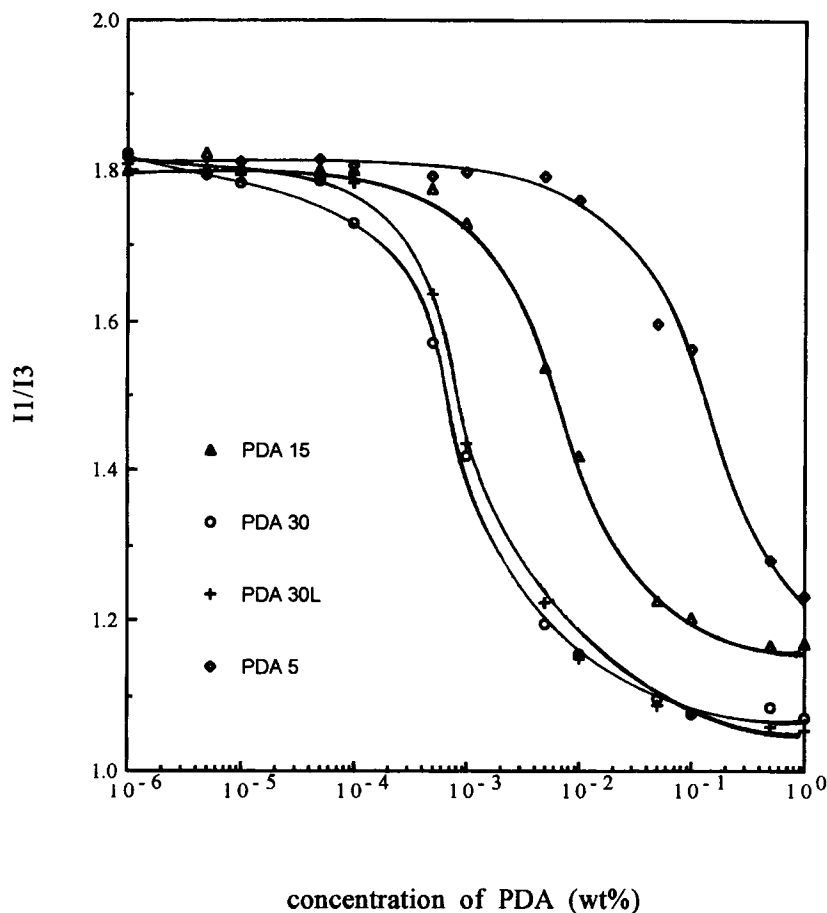
**Figure 1**  $I_1/I_3$  value ( $\square$ ) and surface tension ( $\blacksquare$ ) for the polymer solutions of PDA 30 as a function of polymer concentration. ( $[\text{Pyrene}] = 9.8 \times 10^{-6} \text{ M}$ ).

is also plotted as a function of the polymer concentration.  $\gamma$  begins to decrease at  $\sim 10^{-3}\%$  and remains at a constant value above 0.5%. This indicates that the polymer begins to transfer to the air–water interface at  $10^{-3}\%$  and ceases to transfer above 0.5%. The behaviors of lipophile-grafted polyacrylic acid in solution can be summarized from the results of  $I_1/I_3$  value and  $\gamma$  as follows:

1. The polymer begins to form aggregates at a very low concentration ( $5 \times 10^{-5}\%$ ) similar to that of surfactants.
2. The polymer forms aggregates before it starts to transfer to the air–water interface.

For surfactants, the molecules transfer to the interface before the micellar formation. This indicates that the tendency for PDA to transfer to the interface is smaller than that of surfactants.

The plots of  $I_1/I_3$  value vs. polymer concentration for acrylic copolymers composed of different ratios of dodecyl acrylate or with different molecular weight (PDA 5, PDA 15, PDA 30, PDA 30L) are shown in Figure 2. (The molar ratio of dodecyl acrylate/total acrylates is 5%, 15%, and 30% for PDA 5, PDA 15, and PDA 30, respectively. All of them are random copolymers.) At very low polymer concentration,  $I_1/I_3$  values are  $\sim 1.8$  for all of the four polymers. This value is close to that of water. It means that no aggregates of polymer formed in solution at this concentration. The  $I_1/I_3$  value begins to decrease at concentrations of about  $5 \times 10^{-5}\%$ ,  $10^{-4}\%$ ,  $5 \times 10^{-4}\%$ , and  $5 \times 10^{-3}\%$  for PDA 30, PDA 30L, PDA 15, and PDA 5, respectively. This means that the four polymers begin to form aggregate at these four corresponding concentrations. (The concentration where the polymer begins to form aggregates is defined as  $C_1$ .) For PDA 5,  $I_1/I_3$  decreases continuously and gradually up to 1%; but for PDA 15, PDA 30, and PDA 30L, the  $I_1/I_3$  value ceases to decrease above the concentration of 0.5%, 0.1%, and 0.1%, respectively. This means that for PDA 5, the micropolarity of the inner core of aggregates keeps decreasing as the polymer concentration increases as a result of the continual increase in the size of the aggregate so that the inner cores of the aggregates become more hydrophobic. However, for PDA 15, PDA 30, and PDA 30L, the hydrophobicity of the inner core of aggregates remaining constant above 0.5% or 0.1% indicates a saturation in the growth of the aggregates. From the above results, the ease in which these four polymers form aggregates in aqueous solution is PDA 30  $\approx$  PDA 30L > PDA 15 > PDA 5. This trend can be interpreted as



**Figure 2**  $I_1/I_3$  value as a function of polymer concentration for PDA 15, PDA 30, PDA 30L, and PDA 5 ( $[\text{Pyrene}] = 9.8 \times 10^{-6} \text{ M}$ ).

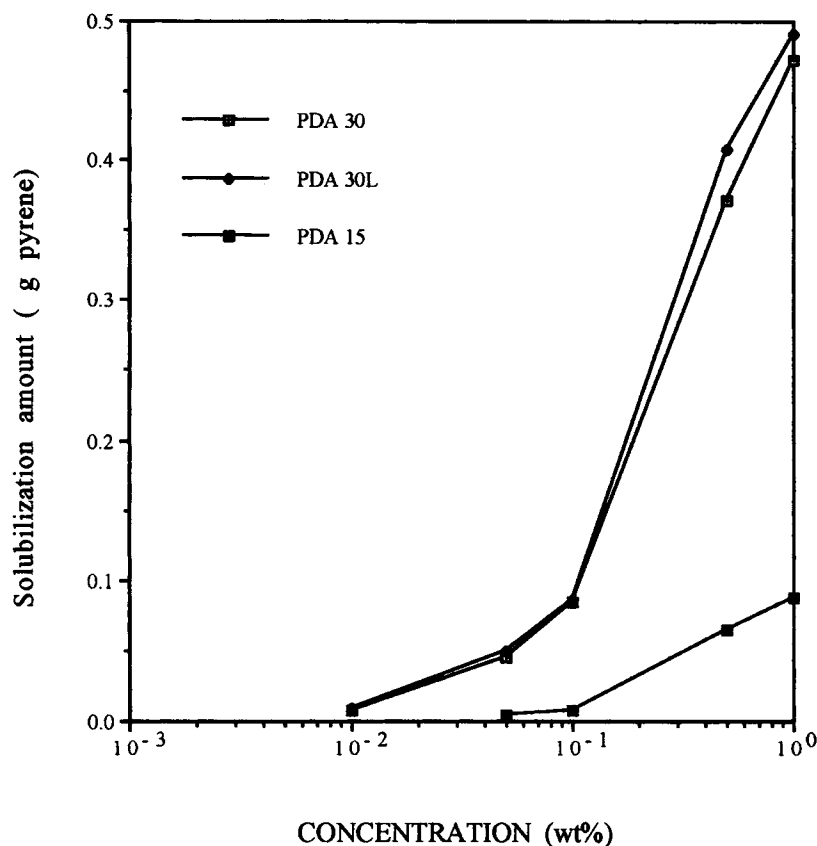
the greater the polymer is composed of hydrophobic moieties the greater the hydrophobic interaction among polymer chains, which causes the polymer to form aggregates more readily.

As seen in Figure 2, the values of  $I_1/I_3$  that PDA 30 or PDA 30L can reach are around 1.05, close to that of SDS micelles (1.1), which means the inner core of the polymer aggregates is similarly hydrophobic as are SDS micelles, independent of the molecular weight of the polymer. The minimum  $I_1/I_3$  value that a polymer can reach is: PDA 30  $\approx$  PDA 30L < PDA 15 < PDA 5 (Table I). It means that a polymer with a higher hydrophobic moiety can form aggregates easily due to higher hydrophobic interaction in the inner core.

It is well known that surfactants have solubilization properties<sup>22-25</sup> because they form micelles in aqueous solution,<sup>26</sup> where the hydrophobic inner core of the micelles<sup>27-29</sup> solubilized organic compounds. In this study, it is found that polymer so-

lutions of PDAs show significant solubilization ability to pyrene (Table I). This is also evidence that those polymers form aggregates like micelles in aqueous solution. The solubilization ability of PDAs increases with polymer concentration for PDA 30 and PDA 30L. This trend is similar to that observed for surfactants.<sup>19</sup> The increase in solubilization can be attributed to an increase in aggregate concentration (like micelle concentration) and/or in the size of the aggregates. Also, with a given percentage of polymer substitution, the solubilization ability changes very little with the decrease in molecular weight (PDA 30L  $\approx$  PDA 30). The solubilization ability for PDA 15 is smaller than that for PDA 30L or PDA 30, and is not sensitive to the increase in polymer concentration.

Surfactants with higher hydrophobicity form micelles more readily (lower critical micelle concentration),<sup>30</sup> and show a greater solubilization ability.<sup>22-25</sup> The results from Figure 2 (or Table I) and

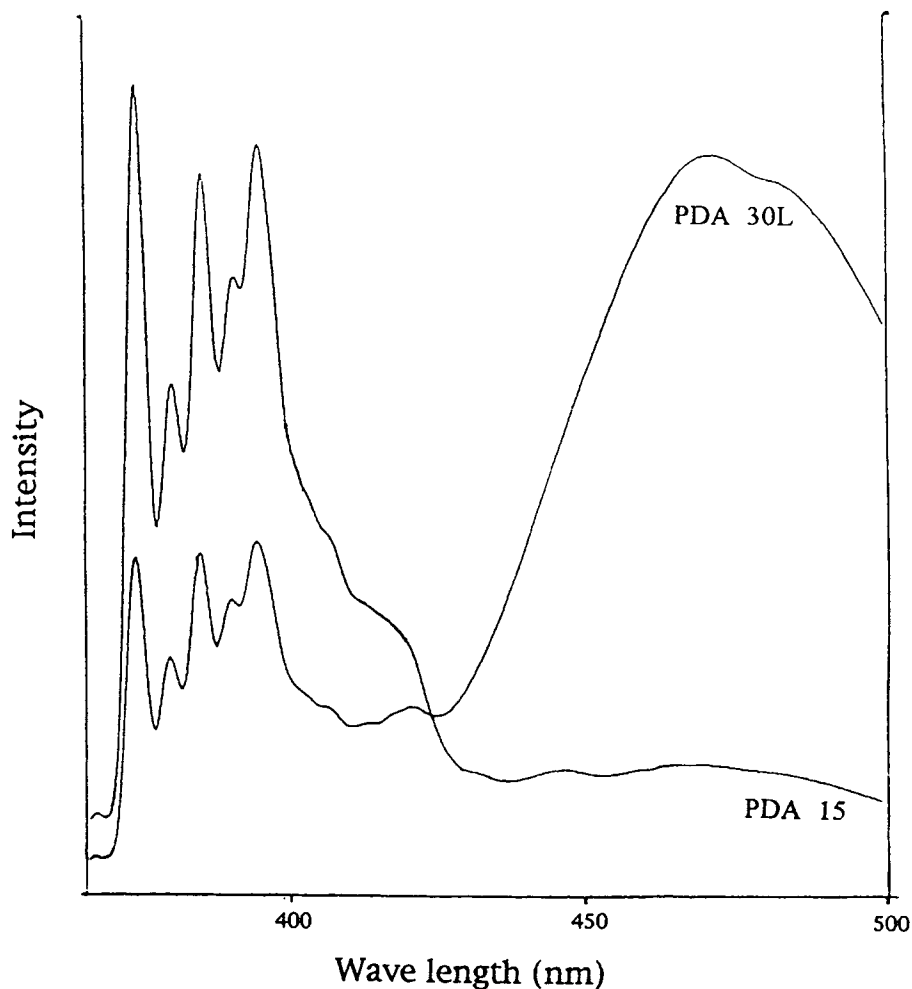


**Figure 3** The solubilization amount of pyrene (g/100 g of polymer solution) as a function of polymer concentration in the solution of PDA 30, PDA 30L, and PDA 15.

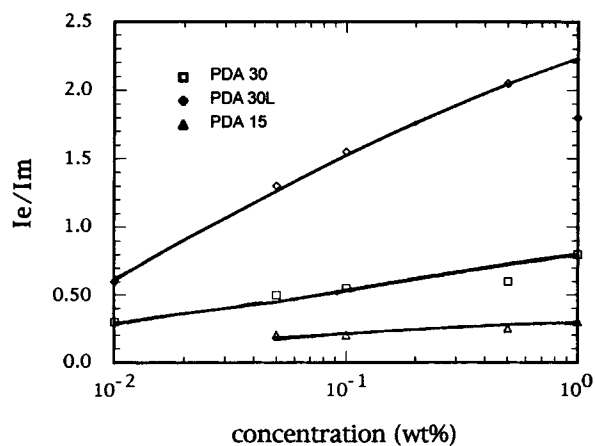
Figure 3 indicate that the greater the substitution of polymer with dodecyl, the greater hydrophobicity of the aggregation (the linear  $I_1/I_3$  value), and concomitantly the greater the solubilization ability. These phenomena for lipophile-grafted polymers are similar to those for surfactants, and the behaviors of these polymer aggregates probably can be interpreted in terms of micelles.

When pyrene is solubilized in the aggregates of surfactants or polymers above a certain concentration, it forms excimers.<sup>31-32</sup> As the local concentration of pyrene increases, the intensity of the excimer emission increases, since the probability is higher for the excited pyrene ( $\text{Py}^*$ ) to collide with a ground-state pyrene to form the excimer ( $\text{PyPy}^*$ ).<sup>33-37</sup> Therefore, the intensity ratio of the excimer emission to monomer emission ( $I_e/I_m$ ) of pyrene can be used to monitor the local concentration of pyrene in an aggregate, and the behavior of the aggregate. It was found that pyrene solubilized in the polymer solutions of PDAs shows strong excimer emission (Fig. 4). Figure 5 shows that  $I_e/I_m$  increases with

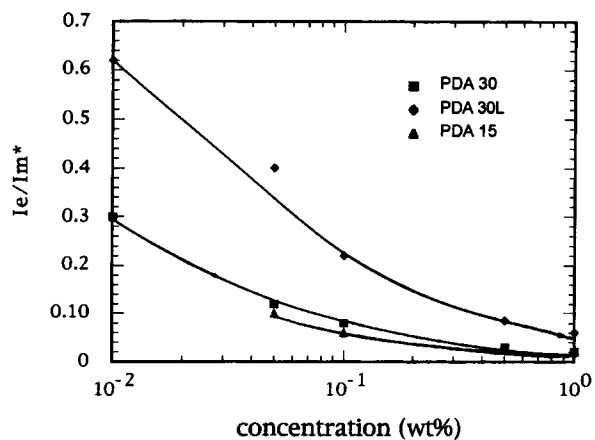
increasing polymer concentration, roughly parallel to the increase in the amount of pyrene solubilized (Fig. 3). An increase in polymer concentration increases: the amount of pyrene solubilized or the amount and size of the polymer aggregates. The former favor excimer formation, and the latter reversely decrease the excimer formation. Therefore, the increase of  $I_e/I_m$  with increasing polymer concentration indicates that the increase in pyrene solubilization can outweigh the increased in size or amount of aggregates. Figure 5 also shows that when a polymer is saturated with pyrene,  $I_e/I_m$  increases with the decreasing  $M_w$  and with the increasing hydrophobicity of PDA (PDA 30L > PDA 30 > PDA 15). Again, this is because of the increased local concentration of pyrene. In Figure 6, the  $I_e/I_m$  at a fixed pyrene concentration ( $9.8 \times 10^{-6}$  M), called  $I_e/I_m^*$ , decreases with increasing of polymer concentration. The phenomena of  $I_e/I_m^*$  in Figure 6 can be interpreted, i.e., at a given pyrene concentration, the local concentration of pyrene decreases as the size and/or the amount of polymer aggregate in-



**Figure 4** The excimer emission of pyrene in the polymer solution (1%) of PDA 30L, and PDA 15 that solubilized pyrene with the amount of 0.49 g, and 0.088 g per 100 g of polymer solution, respectively.



**Figure 5** Variation of  $I_e/I_m$ , maximum amount of pyrene solubilized by polymer, as a function of polymer concentration ( $\square$ ,  $\diamond$ ,  $\triangle$ , for PDA 30, PDA 30L, and PDA 15, respectively).



**Figure 6** Variation  $I_e/I_m^*$  ( $\blacksquare$ ,  $\blacklozenge$ ,  $\blacktriangle$ ), (pyrene concentration to be fixed at  $9.8 \times 10^{-6}$  M) as a function of polymer concentration ( $\blacksquare$ ,  $\blacklozenge$ , and  $\blacktriangle$ , for PDA 30, PDA 30L, and PDA 15, respectively).

creases, as a result of the increased polymer concentration.

## CONCLUSION

From the plot of  $I_1/I_3$  and surface tension as a function of polymer concentration, it is found that a lipophile-grafted polyacrylic acid (e.g., PDA 30) begins to form aggregates in aqueous solution at a very low concentration ( $5 \times 10^{-5}\%$ ), which is far below the concentration for it to start to transfer to the air-water interface ( $10^{-3}\%$ ). At high polymer concentration the inner core of the polymer aggregates is as hydrophobic as that of SDS micelles, and is independent of the molecular weight of polymer. The polymers with higher degree of substitution of dodecylamine form aggregates more readily than the other polymers studied.

Polymer solutions of PDA 30, PDA 30L, and PDA 15, show significant solubilization ability to pyrene. The solubilization ability increases with the increase in polymer concentration and degree of substitution of dodecylamine. The intensity ratio of the excimer emission to monomer emission of pyrene ( $I_e/I_m$ ) increases with increasing polymer concentration, roughly parallel to the increase in the amount of pyrene solubilized. However, the  $I_e/I_m$  at a fixed pyrene concentration ( $I_e/I_m^*$ ) decreases with the increase of polymer concentration. These phenomena are interpreted in terms of the amount of pyrene solubilized and the size and concentration of the polymer aggregates.

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## REFERENCES

1. D.-Y. Chu and J. K. Thomas, *Macromolecules*, **17**, 2142 (1984).
2. M. Ikemi, N. Odagiri, S. Tanaka, I. Shinohara, and A. Chiba, *Macromolecules*, **14**, 34 (1981).
3. M. Ikemi, N. Odagiri, S. Tanaka, I. Shinohara, and A. Chiba, *Macromolecules*, **15**, 281 (1982).
4. C. Price, *Pure & Appl. Chem.*, **55**, 1563 (1983).
5. P. Molyneux, *Water-Soluble Synthetic Polymers: Properties and Behavior*, Vols. I and II, CRC Press, Boca Raton, 1984.
6. R. L. Davison, ed., *Handbook of Water-Soluble Gums and Resins*, McGraw-Hill, New York, 1980.
7. N. J. Turro and K. S. Arora, *Polymer*, **27**, 783 (1986).
8. N. J. Turro and K. S. Arora, *J. Polym. Sci.* **25**, 243 (1987).
9. P.-L. Kuo, S.-C. Ni, and C.-C. Lai, *J. Appl. Polym. Sci.*, **45**, 611 (1992).
10. N. J. Turro and P.-L. Kuo, *J. Phys. Chem.*, **90**, 837 (1986).
11. U. Khuanga, B. K. Selinger, and R. McDonald, *Aust. J. Chem.*, **29**, 1 (1976).
12. N. J. Turro and P.-L. Kuo, *Langmuir*, **1**, 170 (1985).
13. R. Zana, *Surfactant Solutions*, Marcel Dekker, New York, 1987.
14. N. J. Turro and P.-L. Kuo, *J. Phys. Chem.*, **91**, 3321 (1987).
15. P. Lions, J. Lang, C. Strazielle, R. Zana, *J. Phys. Chem.*, **86**, 1019 (1982).
16. K. L. Mittal, *Micellization, Solubilization, and Microemulsion*, Vols. I and II, Plenum Press, New York, 1976.
17. P.-L. Kuo, M. Okamoto, and N. J. Turro, *J. Phys. Chem.*, **91**, 2934 (1987).
18. N. J. Turro and P.-L. Kuo, *J. Phys. Chem.*, **90**, 4205 (1986).
19. C. M. Drain, B. Christiusin, and D. Mauzerall, *PNAS*, **86**, 6959 (1989).
20. A. D. C. Dong and M. A. Winnik, *Can. J. Chem.*, **62**, 2560 (1984).
21. N. J. Turro and P.-L. Kuo, *Langmuir*, **1**, 170 (1985).
22. P. H. Elworthy, A. T. Florence, and C. B. MacFarlane, *Solubilization by Surface-Active Agents*, Chapman and Hall, London, 1986a, p. 68; 1986b, p. 90.
23. A. A. Green, J. W. McBain, *J. Phys. Chem.*, **51**, 286 (1947).
24. J. W. McBain, M. E. L. McBain, *J. Am. Chem. Soc.*, **58**, 2610 (1936).
25. W. D. Harkins, *J. Phys. Chem.*, **53**, 9 (1949).
26. L. A. Singer, in *Solution Behavior of Surfactants*, K. Mittal and E. Fendler, eds., Plenum Press, New York, 1980, Vol. I, p. 73.
27. E. W. Anacker and H. M. Ghose, *J. Phys. Chem.*, **67**, 1713 (1963).
28. B. W. Barry, J. C. Morrison, and G. Russell, *J. Colloid Interface Sci.*, **33**, 554 (1970).
29. P. Becker, *J. Phys. Chem.*, **64**, 1221 (1960).
30. M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, 1978, p. 93.
31. K. S. Arora and N. J. Turro, *J. Polym. Sci.*, **25**, 243 (1987).
32. W. G. Herkstroeter, P. A. Martic, S. E. Hartman, J. L. R. Williams, and S. Farid, *J. Polym. Sci.*, **21**, 2473 (1983).
33. H. T. Oyama, W. T. Tang, and C. W. Frank, *Macromolecules*, **20**, 474 (1987).
34. H. Pownall and L. Smith, *J. Am. Chem. Soc.*, **95**, 3136 (1975).
35. N. J. Turro, M. Aikawa, and A. Yekta, *J. Am. Chem. Soc.*, **101**, 772 (1979).
36. M. Tachiya, *J. Chem. Phys.*, **76**, 340 (1982).
37. F. Quina, E. Abuin, and E. Lissi, *Macromolecules*, **23**, 5173 (1990).

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