Functional Polymers for Colloidal Applications. IV. Aggregate Formation of Lipophile-Grafted Water-Soluble Copolymers in Aqueous Solutions

PING-LIN KUO* and MIN-NAN HUNG

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 70101, Republic of China

SYNOPSIS

A water-soluble styrene–maleic anhydride copolymer (SMA) is derivatized with different lipophilic groups, butylamine and dodecylamine, with different degrees of substitution (5, 15, and 30%). These lipophile-grafted SMAs are water-soluble, and their solutions are transparent. A plot of I_1/I_3 as a function of polymer concentrations indicates the extent of aggregate formation. Surface tension methods also verify the existence of aggregates. It is found that the aggregates 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 concentrations for SMAs of different molecular weights derivatized with different lipophile with varying degrees of substitution show that the polymers with a higher degree of substitution and lower molecular weights aggregate at lower concentrations. Polymers substituted by butylamine form aggregates at a very high concentration, independent of the degree of substitution. These phenomena are interpreted in terms of hydrophobic interactions as in micelles formed from surfactants. The higher degree of dodecyl-substituted SMA solubilizes pyrene at higher concentrations, and these pyrene solubilized solutions show pyrene excimer emission spectra. These emission spectra are used to characterize the relative size and hydrophobicity of aggregates. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

When a water-soluble polymer is dissolved in aqueous solution, the polymer chain is well extended or well expanded.[1-4] For ABA three-block-type water-soluble copolymers, the polymer chains form aggregates[5-8] in the transparent solution. When the backbone of a water-soluble polymer is grafted with long-chain hydrophobic groups, the polymer then consists of both hydrophobic and hydrophilic groups that greatly affect both the intermolecular and intramolecular hydrophobic interactions. Thus, such a polymer can be regarded as a polymerized surfactant, and its property in solution is expected to be an intermediate between those of a surfactant and a water-soluble polymer.

In previous studies, lipophile-grafted styrene–maleic anhydride copolymers (Scheme 1) were used as dispersants.[9] It was found that the length and

content of the hydrophobic group of such a polymer significantly influence their dispersing properties. It is important to understand their fundamental properties in solutions, such as aggregate formation and the properties of such aggregates.

Photochemical technology has been widely applied to study the colloidal systems.[10-23] Strauss investigated the properties of maleic anhydride by using naphthalene derivatives as probes,[10,11] monitored the conformation of the alkylated copolymers by means of the fluorescence of the copolymers,[12] and determined the size of intramolecular micelles by fluorescence quenching.[13] Chu and Thomas studied the energy transfer of pyrene that was solubilized in the aqueous solution of the copolymer of maleic and poly(methacrylic acid).[14] Also, pyrene fluorescence has been used to investigate the microenvironment of aggregates of surfactants and polymers.[15-23] The ratio of intensities of the fluorescence at different wavelengths was used to monitor the micropolarity,[15-18] and the intensity of the excimer formation in an aggregate could be used to investigate the size or number of aggregates.[19-21] In this

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$$\left(H_2C-CH-HC-CH\right)_n$$

R : C₄H₉ - , C₁₂H₂₅ -
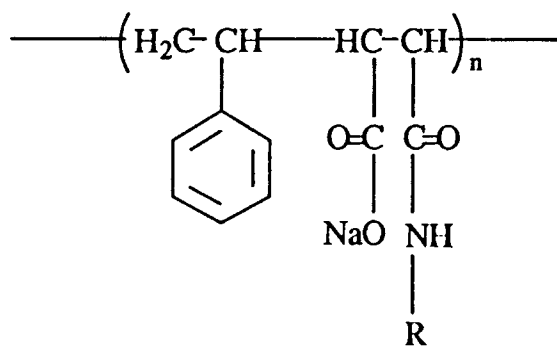
Scheme 1 The structure of lipophile-grafted SMA.

study, the fluorescence method and the surface tension method were combined to verify the formation of polymer aggregates. 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 degrees of substitution and the chain length of the lipophile significantly influence the concentration of aggregate formation and the properties of aggregates.

EXPERIMENTAL

Materials

Pyrene, purchased from Merck Chemical Co., was purified by three recrystallizations from ethanol. Styrene–maleic anhydride copolymer (SMA) (Aldrich Chemical Co.) and sodium dihydrogen phosphate ($Na_2PO_4 \cdot 2H_2O$, Junsei Chemical Co.) were used as supplied. The addition of n-alkylamines to SMA follows the procedure of the previous paper.[9] The prepared lipophile-grafted SMAs were neutralized by adjusting the pH of the aqueous solution to 9.0 and then precipitated in acetone. The prepared copolymers were further purified by reprecipitation in H_2O/acetone to remove the unreacted alkylamine completely and dried at 60°C under vacuum for 48 h. In the H'-HMR spectra of these copolymers (dissolved in D_2O), the existence of the CH_3— of the alkyl group (δ = 0.9 ppm) illustrates that the alkylamine has been introduced in the polymer backbone. The peak area of CH_3— (δ = 0.9 ppm) and that of the benzene ring of styrene (δ = 7.2 ppm) were used to determine the degree of substitution of alkylamine.

Methods

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 and 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 of pyrene monomer emission (374 nm) is defined as I_e/I_m. All the solutions for fluorescence measurements contained a buffer solution to maintain the pH at 7. For references, I_1/I_3 values for pyrene in water, n-hexane, and the micelle of sodium dodecylsulfate were determined to be 1.84 (ϵ = 80), 0.56 (ϵ = 3), and 1.10 (ϵ = 30),[24] respectively, which are close to the reported values.[25,26]

Solubilization Measurements

Pyrene, 0.10 g, was added to a 10 mL solution of a polymer and stirred overnight. Then, the solution was filtered with a Gelman Sciences Sterile Acrodisc 0.2 μm syringe filter. The UV absorbance of the solution was measured using a Jasco Model 7850 UV spectrophotometer and the concentration of solubilized pyrene calculated from the calibration curve shown in Figure 1.

RESULTS AND DISCUSSION

The ratio of intensities of the emission of pyrene at 374 and 385 nm, called I_1/I_3, has been widely used to detect the polarity of a microenvironment in aggregates of surfactants and/or polymers.[15-18] The

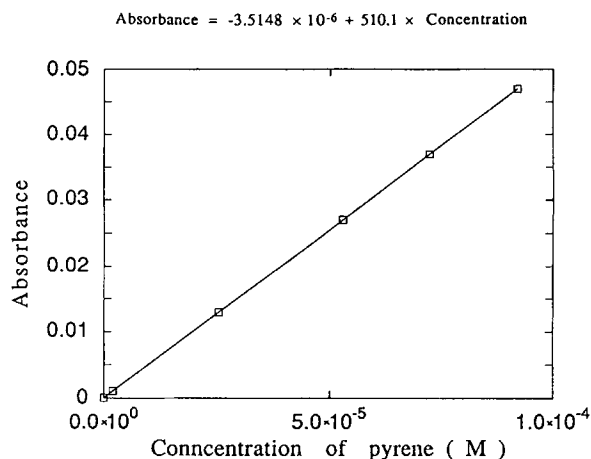Absorbance = -3.5148 × 10⁻⁶ + 510.1 × Concentration

Figure 1 Calibration curve of UV absorbance vs. concentration for pyrene.

greater I_1/I_3, the greater the polarity of the solution around pyrene. Therefore, the formation of the aggregates with a hydrophobic inner core can be monitored by a plot of I_1/I_3 vs. polymer concentration. In Figure 2, I_1/I_3 of pyrene in a polymer solution of $C_{12}N30$-8500 is measured as a function of polymer concentration. When the polymer concentration is below $10^{-5}\%$ (weight percentage, hereafter), the I_1/I_3 remains at a value of 1.7, close to that of pure water, indicating that there is no aggregate formed at these concentrations. In the region of $10^{-5}\%$–1%, I_1/I_3 decreases gradually down to 1. The decrease in I_1/I_3 indicates that the microenvironment around pyrene is getting less polar and that the polymer begins to form aggregates above $10^{-5}\%$. 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. If the surface tension (γ) of polymer solution is plotted as a function of the polymer concentration, γ begins to decrease at ca. $10^{-3}\%$ 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 behavior of lipophilic-grafted SMA in solution can be summarized as follows: (a) The polymer begins to form aggregates at a very low concentration ($10^{-5}\%$). (b) The polymer forms aggregates before it starts to transfer to the air–water interface. Phenomenon (a) is similar to that of surfactants but phenomenon (b) is different.

Figure 3 shows the plots of I_1/I_3 vs. polymer concentration for the low molecular weight SMA (8500) substituted with different percentages of dodecylamine (12N5-8500, 12N15-8500, 12N30-8500). At very low polymer concentrations, I_1/I_3 ratios are ca.
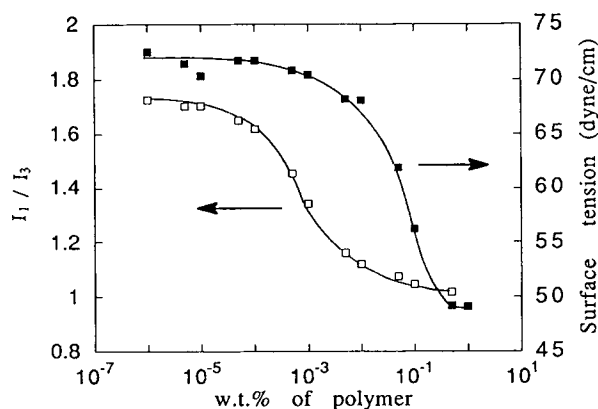
1.75 for all of three polymers. This value is close to that of water, which means that no aggregates of polymer are formed in solution at this concentration. I_1/I_3 begins to decrease at concentrations of about 10^{-5}, 10^{-4}, and $10^{-3}\%$ for 12N30-8500, 12N15-8500, and 12N5-8500, respectively, which indicates that the three polymers begin to form aggregates at these three corresponding different concentrations. The concentration where the polymer begins to form aggregates is defined as C_1. For 12N5-8500 and 12N15-8500, I_1/I_3 decreases gradually up to 0.5%, but for 12N30-8500, the decrease in I_1/I_3 begins to slow down above the concentration of $10^{-2}\%$. This means that for 12N5-8500 and 12N15-8500 the micropolarity of the inner core of aggregates keeps decreasing as the polymer concentration increases. The continual decrease in micropolarity can be interpreted to be a result of the continual increase in the size of the aggregates so that the inner cores of the aggregates become more hydrophobic. However, for 12N30-8500, the hydrophobicity of the inner core of the aggregates increase slowly above $10^{-2}\%$, indicating a saturation in the growth of the aggregates. From the above results, the ease with which these three polymers form aggregates in aqueous solution is $C_{12}N30 > C_{12}N_{15} > C_{12}N5$. As seen in Figures 3 and 4, the values of I_1/I_3 that these polymers can reach are around 1.0, below that of SDS micelles (1.1), which means the inner core of the polymer aggregates is even more hydrophobic than that of SDS micelles and is dependent on the molecular weight of the polymer.

For the SMA with a molecular weight of 18,000 and substituted by 30, 15, and 5% of dodecylamine (hereafter, 12N30-18000, 12N15-18000, 12N5-18000), the plots of the I_1/I_3 value vs. polymer concentration are shown in Figure 4. For each plot, a similar trend as in Figure 3 can be observed; thus, a sharp decrease in I_1/I_3 is observed for 12N30-18000, 12N15-18000, and 12N5-18000 at ca. 10^{-4}, 10^{-3}, and 5–$10^{-2}\%$, respectively, which corresponds to the concentration at which each polymer begins to form aggregates. These concentrations (C_1) are significantly higher than those of the corresponding 12N30-8500, 12N15-8500, and 12N5-8500 polymers (Fig. 3). From Figure 4, the ease of polymer aggregation is $C_{12}N30$-18000 $> C_{12}N15$-18000 $> C_{12}N5$-18000. Comparing Figures 3 and 4, it can be concluded that polymers with lower molecular weights and with a higher degree of substitution of dodecylamine form aggregates more readily than do the other polymers studied.

Since the hydrophobic groups are on the polymer (not just mixed) as illustrated by the NMR spectra,
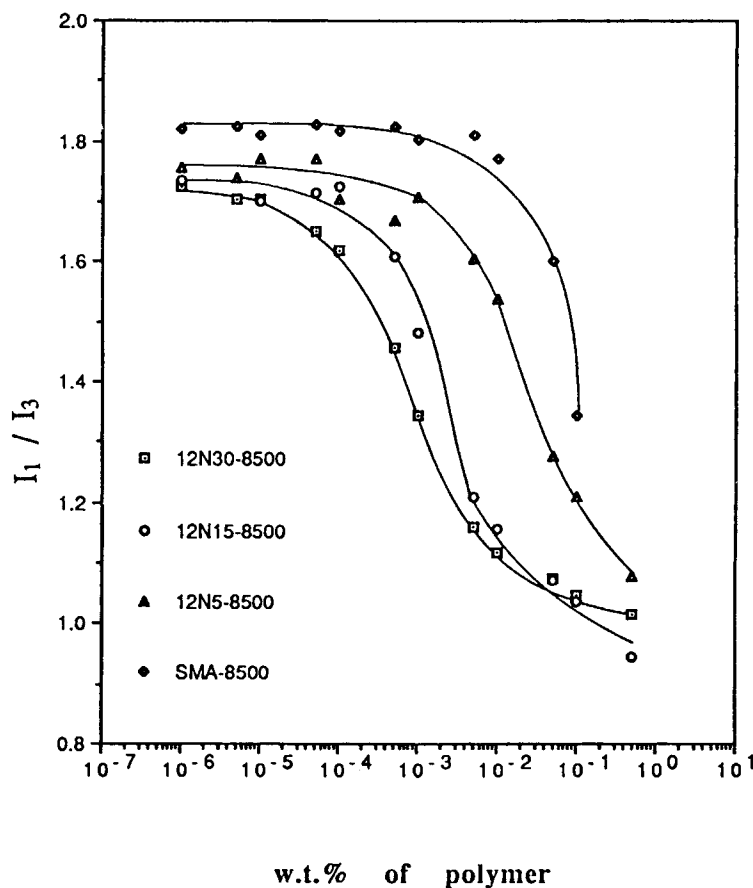

Figure 2 $(-\square-)$ I_1/I_3 value and $(-\blacksquare-)$ surface tension of polymer ($C_{12}N30$-8500) solutions as a function of polymer concentration. [Pyrene] = 9.81×10^{-6} M.

Figure 3 I_1/I_3 value as a function of polymer concentration for differently lauryl-grafted SMA (8500). [Pyrene] = 9.81 × 10^{-6} M.

these phenomena can be interpreted as follows: (a) The greater the polymer is derivatized with lipophilic moieties, the greater the hydrophobic interaction among polymer chains, which causes the polymer to form aggregates more readily. (b) The polymer chains of lower molecular weight can be more closely packed together because aggregation exerts less deformation strain on the polymer, thus making hydrophobic interaction stronger and the formation of aggregates easier.

A plot of I_1/I_3 vs. polymer concentration is shown in Figure 5 for SMA substituted by 5, 15, and 30% of butylamine (4N5, 4N15, and 4N30). The C_1 concentrations are all ca. $10^{-2}\%$ and are independent of the degree of substitution of butylamine. This C_1 is close to that of SMA-18000 and is much higher than for the SMA substituted by dodecylamine (Table I). Also, I_1/I_3 never goes below 1.5, which means the microenvironment detected by pyrene is still very polar, an indication that the aggregate is not closely packed. It can be concluded from these results that SMAs substituted with a short-chain

lipophile cannot form aggregates efficiently and the increase in the degree of substitution does not improve the aggregation properties.

It is well known that surfactants have solubilization properties[27-30] because they form micelles in aqueous solution,[31] where the hydrophobic inner core of the micelles[32-34] solubilizes organic compounds. It is found that polymer solutions of SMA with a high substitution of dodecylamine, $C_{12}N15$-8500, $C_{12}N30$-8500, and $C_{12}N30$-18000, show significant solubilization ability to pyrene (Table I). This can be attributed to be the fact that those polymers form aggregates like micelles in aqueous solution. The solubilization ability increases with polymer concentration for each polymer (Fig. 6). This trend is similar to that observed for surfactants.[27-30] The increase in solubilization can be attributed to an increasing aggregate concentration (like micelle concentration) and/or in the size of the aggregates. Also, with a given molecular weight polymer, the solubilization ability increases with increasing substitution of dodecylamine ($C_{12}N30$-8500 > $C_{12}N15$-
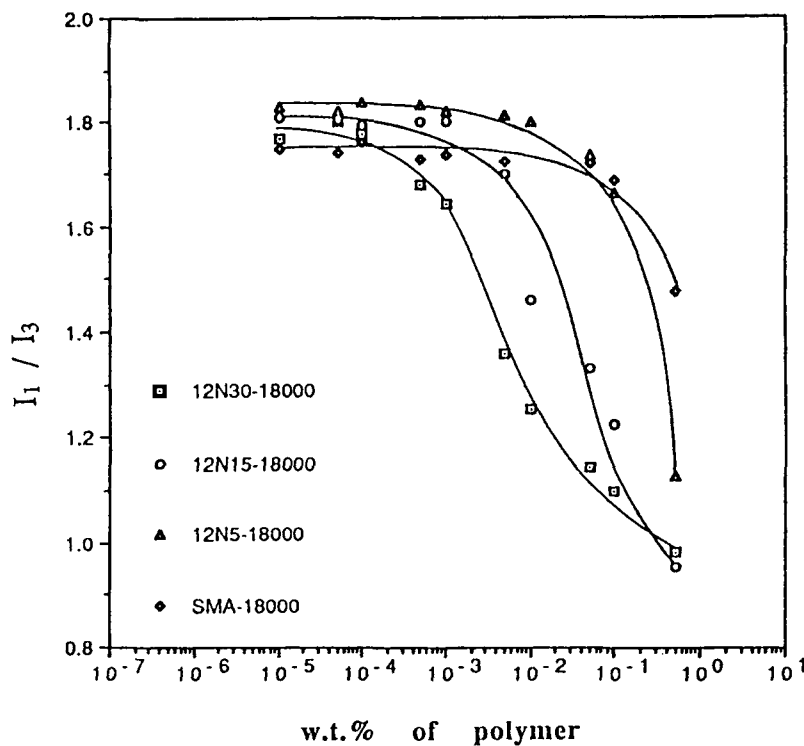
Figure 4 I_1/I_3 value as a function of polymer concentration for differently lauryl-grafted SMA (18,000). [Pyrene] = 9.81 × 10^{-6} M.
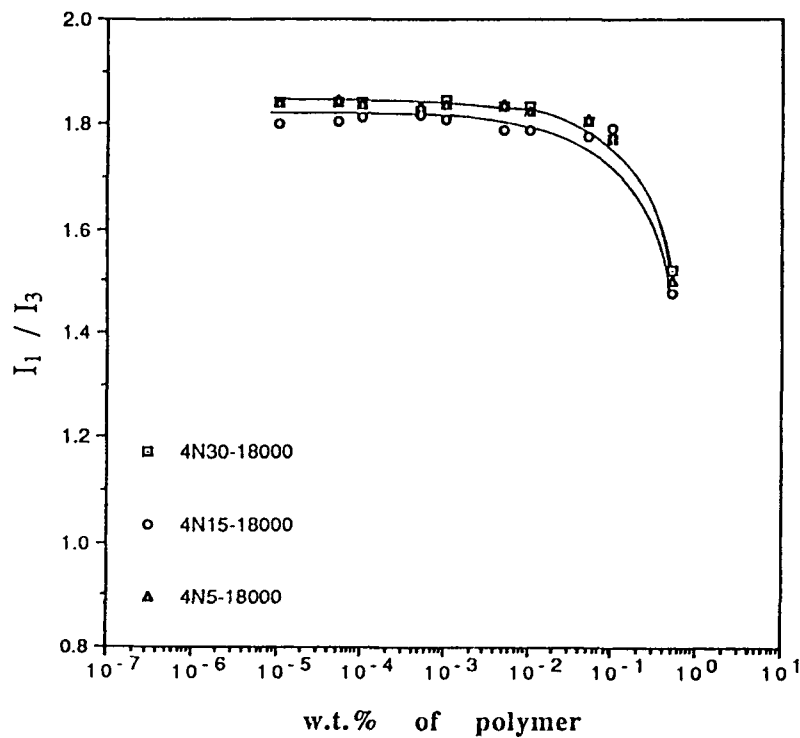
Figure 5 I_1/I_3 value as a function of polymer concentration for differently butyl-grafted SMA (18,000). [Pyrene] = 9.81 × 10^{-6} M.

Table I Composition of Lipophile-grafted SMAs and the Behaviors of Their Aggregates

Symbols	M.W.	Substituted Lipophile	Degree of Substitution[a] (%)	C_1^b (wt %)	I_1/I_3	I_e/I_m^c	Solubilization in Pyrene[d] (%)
12N5-8500	8500	Dodecylamine	5	10^{-3}	1.196	—	0.026
12N15-8500	8500	Dodecylamine	15	10^{-4}	0.972	0.393	0.630
12N30-8500	8500	Dodecylamine	30	10^{-5}	0.896	0.610	0.883
12N5-18000	18000	Dodecylamine	5	5×10^{-2}	1.270	—	0.004
12N15-18000	18000	Dodecylamine	15	10^{-3}	1.184	—	0.031
12N30-18000	18000	Dodecylamine	30	10^{-4}	0.894	0.607	0.768
4N5-18000	18000	Butylamine	5	10^{-2}	1.426	—	—
4N15-18000	18000	Butylamine	15	10^{-2}	1.316	—	—
4N30-18000	18000	Butylamine	30	10^{-2}	1.155	—	—

[a] Degree of substitution is defined as $(-CONR)/(-COONa) + (-CONR)$.
[b] The concentration (weight percentage) for polymer begins to form aggregates.
[c] Polymer solution (concentration: 1 wt %) was saturated with pyrene.
[d] % based on total amount of solution; polymer concentration: 1 wt %.

8500); with a given percentage of polymer substitution, the solubilization ability increases with decreasing molecular weight ($C_{12}N30$-8500 > $C_{12}N30$-18000) (Table I).

Surfactants with higher hydrophobicity form micelles more readily (lower critical micelle concentration)[35] and show a greater solubilization ability.[27-30] The results from Figures 3 and 4 and Table
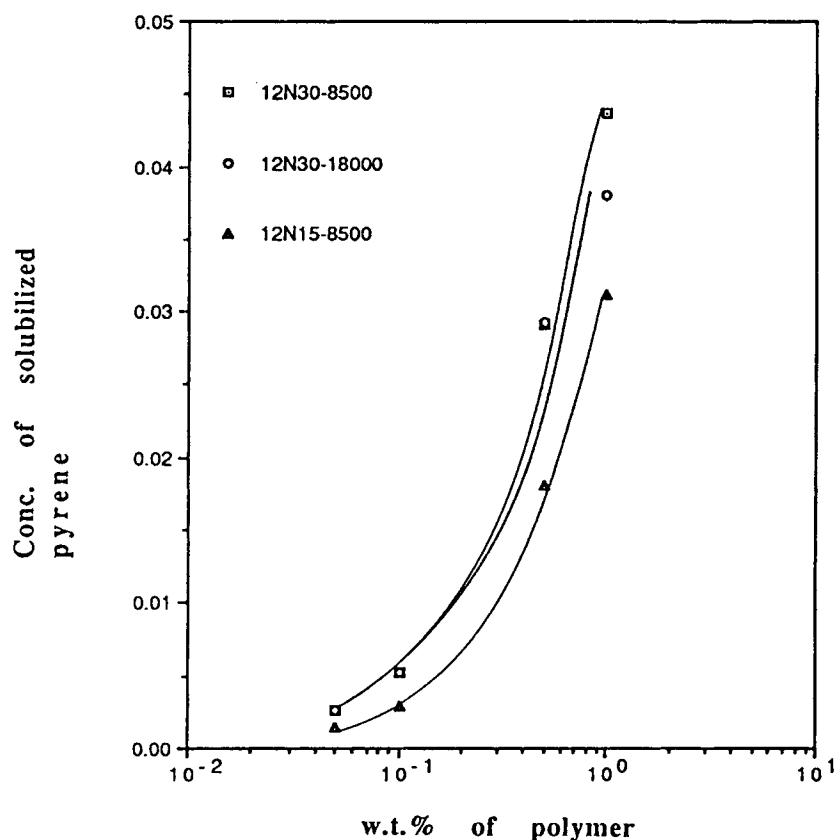

Figure 6 The concentration of solubilized pyrene as a function of polymer concentration in the solution of differently lipophile-grafted SMA ($C_{12}N30$-8500, $C_{12}N30$-18000, $C_{12}N15$-85000).

I indicate that the greater the substitution of polymer with dodecylamine and/or the lower molecular weight of polymer the greater the aggregation and, concomitantly, the greater the solubility properties. These phenomena for lipophile-grafted polymers parallel those for surfactants; therefore, the behavior 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 excimer.[36,37] As the local concentration of pyrene increases, the intensity of the excimer emission increase, since the probability is higher for the excited pyrene (Py^*) to collide with a ground-state pyrene to form the excimer ($PyPy^*$).[38-42] Therefore, the intensity ratio of the excimer emission to monomer emission of pyrene can be used to monitor the local concentration of pyrene in an aggregate, thus monitoring the behavior of the aggregate. Figure 7 shows that I_e/I_m increases with increasing polymer concentration, roughly parallel to the increase in the amount of pyrene solubilized (Fig. 6). However, the I_e/I_m at a fixed pyrene concentration (Ie/Im^*) decreases with increasing polymer concentration. The phenomena of I_e/I_m^* can be easily inte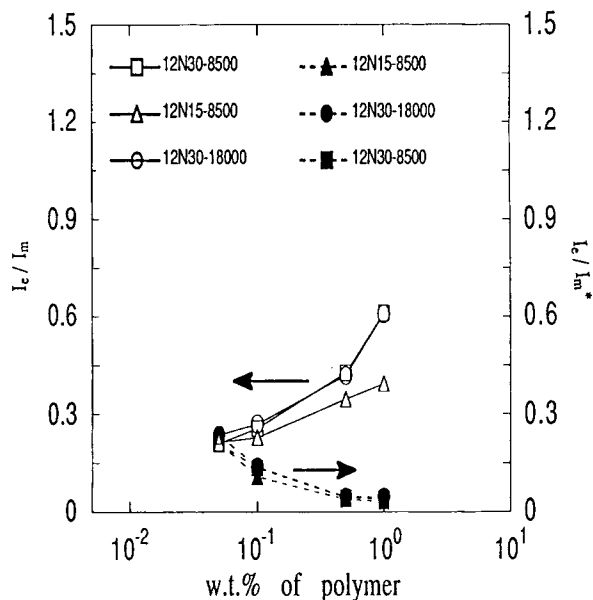rpreted. At a given pyrene concentration, the local concentration of pyrene decreases as the size and/or the amount of polymer aggregate increases. An increase in polymer concentration increases (a) the amount of pyrene solubilized and (b) the amount and size of the polymer aggregates. The former favors excimer formation, and the latter does not. Therefore, the increase of I_e/I_m with increasing polymer concentration indicates that the increase in pyrene solubilization can outweigh the increase in size or amount of aggregates.

Figure 7 also shows that when a polymer is saturated with pyrene I_e/I_m increases with the increasing substitution by dodecylamine ($C_{12}N30$-8500 > $C_{12}N15$-8500), independent of the chain length of the polymer ($C_{12}N30$-8500–$C_{12}30$-18000). Again, this is due to the increased ability to solubilize pyrene, which increases the local concentration of pyrene. However, when the pyrene concentration in polymer aggregates is maintained at the same level, $I_e I_m^*$ is almost independent of the degree of substitution and polymer chain length.

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 SMA begins to form aggregates in aqueous solution at a very low concentration ($10^{-5}\%$), 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 even more hydrophobic than that of SDS micelles and is independent of the molecular weight of polymer. The polymers with lower molecular weight and with higher degree of substitution of dodecylamine form aggregates more readily than do the other polymers studied. SMAs substituted with a short-chain lipophile cannot form aggregate efficiently, and the increase in the degree of substitution does not improve the aggregation properties. Polymer solutions of SMA with a high substitution of dodecylamine, $C_{12}N15$-8500, $C_{12}N30$-8500, and $C_{12}N30$-18000, show significant solubilization ability to pyrene. The solubilization ability increases with increasing 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

Figure 7 Variation of I_e/I_m (—□—, —○—, —△—) maximum pyrene concentration solubilized by polymer and of I_e/I_m^* (—■—, —●—, —▲—) pyrene concentration fixed at $2.69 \times 10^{-3}M$, $2.67 \times 10^{-3}M$, and $1.41 \times 10^{-3}M$ for 12N30-8500, 12N30-18000, and 12N15-8500, respectively, as a function of polymer concentration, for differently lipophile-grafted SMA.

of the amount of pyrene solubilized and the amount and size of the polymer aggregates.

REFERENCES

1. P. Molyneux, *Water-soluble Synthetic Polymers: Properties and Behavior*, CRC Press, Boco Raton, FL, 1984, Vols. I and II.
2. R. L. Davison, *Handbook of Water-soluble Gums and Resins*, McGraw-Hill New York, 1980.
3. N. J. Turro and K. S. Arora, *Polymer*, **27**, 783 (1986).
4. N. J. Turro and K. S. Arora, *J. Polym. Sci.*, **25**, 243 (1987).
5. D.-Y. Chu and J. K. Thomas, *Macromolecules*, **17**, 2132 (1984).
6. M. Ikemi, N. Odagiri, S. Tanaks, I. Shinohara, and A. Chiba, *Macromolecules*, **14**, 34 (1981).
7. M. Ikemi, N. Odagiri, S. Tanaka, I. Shinohara, and A. Chiba, *Macromolecules*, **15**, 281 (1982).
8. C. Price, *Pure Appl. Chem.*, **55**, 1563 (1983).
9. P.-L. Kuo and S.-C. Ni, to appear.
10. U. P. Strauss and G. Vesnaver, *J. Phys. Chem.*, **79**, 1558 (1975).
11. U. P. Strauss and G. Vesnaver, *J. Phys. Chem.*, **79**, 2426 (1975).
12. U. P. Strauss and M. S. Schlesinger, *J. Phys. Chem.*, **82**, 1627 (1978).
13. J. L. Hsu and U. P. Strauss, *Polym. Master. Sci. Eng.*, **57**, 603 (1987).
14. D.-Y. Chu and J. K. Thomas, in *Polymers in Aqueous Media, Performance through Association*, J. E. Glass, Ed., American Chemical Society, Washington, DC, 1989, p. 325.
15. N. J. Turro and P.-L. Kuo, *Langmuir*, **1**, 170 (1985).
16. K. P. Ananthapadmanabhan, E. D. Goddard, N. J. Turro, and P.-L. Kuo, *Langmuir*, **1**, 352 (1985).
17. N. J. Turro and P.-L. Kuo, *J. Phys. Chem.*, **90**, 837 (1986).
18. U. Khuanga, B. K. Selinger, and R. Mcdonald, *Aust. J. Chem.*, **29**, 1 (1976).
19. N. J. Turro and P.-L. Kuo, *J. Phys. Chem.*, **91**, 3321 (1987).
20. P. Lions, J. Lang, C. Strazielle, and R. Zana, *J. Phys. Chem.*, **86**, 1019 (1982).
21. K. L. Mittal, *Micellization, Solubilization, and Microemulsion*, Plenum Press, New York, 1976, Vols. I and II.
22. P.-L. Kuo, M. Okamoto, and N. J. Turro, *J. Phys. Chem.*, **91**, 2934 (1987).
23. N. J. Turro and P.-L. Kuo, *J. Phys. Chem.*, **90**, 4204 (1986).
24. C. M. Drain, B. Christiusin, and D. Mauzerall, *Proc. Natl. Acad. Sci. U.S.A.*, **86**, 6959 (1989).
25. D. C. Dong and M. A. Winnik, *Can. J. Chem.*, **62**, 2560 (1984).
26. N. J. Turro and P.-L. Kuo, *Langmuir*, **1**, 170 (1985).
27. P. H. Elworthy, A. T. Florence, and C. B. MacFarland, *Solubilization by Surface-active Agents*, Chapman and Hall, London, (a) 1986, p. 68; (b) 1986, p. 90.
28. A. A. Green and J. W. McBain, *J. Phys. Chem.*, **51**, 286 (1947).
29. J. W. McBain and M. E. L. McBain, *J. Am. Chem. Soc.*, **58**, 2610 (1936).
30. W. D. Harkins et al., *J. Phys. Chem.*, **53**, 9 (1949).
31. L. A. Singer, in *Solution Behavior of Surfactants*, K. Mittal and E. Fendler, Eds., Plenum Press, New York, 1980, Vol. I. p. 73.
32. E. W. Anacker and H. M. Ghose, *J. Phys. Chem.*, **67**, 1713 (1963).
33. B. W. Barry, J. C. Morrison, and G. Russell, *J. Colloid Interface Sci.*, **33**, 554 (1970).
34. P. Becher, *J. Phys. Chem.* **64**, 1221 (1960).
35. M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, New York, 1978, p. 93.
36. K. S. Arora and N. J. Turro, *J. Polym. Sci.*, **25**, 243 (1987).
37. W. G. Herkstroeter, P. A. Matic, S. E. Hartman, J. L. R. Williams, and S. Farid, *J. Polym. Sci.*, **21**, 2473 (1983).
38. H. T. Oyama, W. T. Tang, and C. W. Frank, *Macromolecules*, **20**, 474 (1987).
39. H. Pownall and L. Smith, *J. Am. Chem. Soc.*, **95**, 3136 (1975).
40. N. J. Turro, M. Aikawa, and A. Yekta, *J. Am. Chem. Soc.*, **101**, 772 (1979).
41. M. Tachiya, *J. Chem. Phys.*, **76**, 340 (1982).
42. F. Quina, E. Abuin, and E. Lissi, *Macromolecules*, **23**, 5173 (1990).