(17) Halperin, A.; Alexander, S.; Schechter, I. *J. Chem. Phys.* **1987**, *86*, 6550; **1989**, *61*, 1383.
(18) Chen, Z.-Y.; Talbot, J.; Gelbart, W. M.; Ben-Shaul, A. *Phys. Rev. A* **1988**, *61*, 1376.
(19) Wang, Z.-G. *J. Phys.* (*Les Ulis, Fr.*), in press.
(20) Moore, B. G. *J. Chem. Phys.* **1989**, *91*, 1381.
(21) Prost, J. *Adv. Phys.* **1984**, *33*, 1.
(22) Halperin, A. *J. Phys.* (*Les Ulis, Fr.*) **1988**, *49*, 131.
(23) Huang, K. *Statistical Mechanics*; John Wiley: New York, 1987.
(24) Halperin, A. *Europhys. Lett.* **1987**, *4*, 439. The blob argument in this paper suggests that the interaction parameter between densely grated A and C coils scales as $\hat{\chi} \sim N_{blob}\chi_{pp}^{blob} \sim N_Z(a/d)^{5/3}\chi_{pp}^{blob}$ where N_{blob} is the number of blobs per chain and χ_{pp}^{blob} is the interaction parameter between A and C blobs. The final result of this paper follows from the assumption $\chi_{pp}^{blob} \approx \chi_{pp}$ where χ_{pp} is the corresponding monomer-monomer interaction parameter. A more rigorous analysis (Broseta, D.; Leibler, L.; Joanny, J. F. *Macromolecules* **1987**, *20*, 1935) suggests $\chi_{pp}^{blob} \sim \chi_{pp}\phi\chi^{SD}$ where $\chi^{SD} \approx 0.275$, thus leading to the result quoted in the text.
(25) Properly speaking, the term "line tension" refers to the free energy per unit length associated with the three-phase boundary. See, for example: Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Clarendon Press: Oxford, 1982. For convenience we use this term for the two-dimensional analogue of surface tension.

Fluorescence Probing of Microdomains in Aqueous Solutions of Polysoaps. 2. Study of the Size of the Microdomains

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ABSTRACT: The time-resolved fluorescence quenching method has been used to investigate the size (number of repeat units) of microdomains in solutions of poly(disodium maleate-*co*-decylvinylether) and poly(disodium maleate-*co*-hexadecyl vinyl ether) referred to as PS10 and PS16, using pyrene as the fluorescence probe and the dodecylpyridinium ion as the quencher. The shape of the decay curves reveals that the microdomains are somewhat polydisperse in size. In the case of PS10 the number of repeat units per microdomain was found to decrease nearly linearly upon increasing the degree of neutralization of the maleic acid moieties. For PS10 the number of repeat units per microdomain is nearly independent of the polysoap concentration and polymerization degree as well as of the ionic strength and temperature. For PS16, the number of repeat units per microdomain is independent of the polymerization degree but increases much with temperature. Also, it is much larger than that for PS10. Moreover the decay data for PS16 suggest that probe and quencher can rapidly migrate from microdomain to microdomain, on the fluorescence time scale. Overall the results suggest that the formation of a microdomain involves a single polysoap molecule and that several microdomains can be formed from a single polysoap molecule of high molecular weight. Such microdomains are connected by polysoap segments that may be the cause of the probe and quencher migration observed in PS16 solutions and also in PS10 solutions at 60 °C. The migrating molecules would move along these fairly hydrophobic segments.

Introduction

The term polysoap refers to alkali-metal salts of the alternating copolymers poly(maleic acid-*co*-alkyl vinyl ether).[1,2] In aqueous solution polysoaps give rise to hydrophobic microdomains,[1-10] somewhat similar to the micelles existing in solutions of soaps or surfactants at a surfactant concentration above the critical micellization concentration.

In the first part in this series,[11] pyrene fluorescence was used to probe the conformational state of polysoaps, where the alkyl group was *n*-butyl, *n*-decyl, and *n*-hexadecyl (referred to as PS4, PS10, and PS16, respectively) as well as of polymethacrylic acid and poly(maleic acid-*co*-styrene) as a function of the neutralization degree of the carboxylic groups. The same technique was used to investigate the comicellization of PS4 and alkyltrimethylammonium halide surfactants as a function of the surfactant concentration and alkyl chain length. The results clearly showed that the hydrophobic microdomains disappear upon neutralization of PS4, polymethacrylic acid, and poly(maleic acid-*co*-styrene) but persist even at full neutralization in PS10 and PS16. A compact conformation of PS10 and PS16 in aqueous solution had been previously inferred by Pefferkorn et al. from diffusion, conductivity, and viscosity measurements.[9,10]

There has been thus far few attempts to determine the number of repeat units N_c involved in a polysoap microdomain. This information is indeed rather difficult to obtain by classical techniques because polysoaps combine the complexity of polyelectrolytes and surfactant micelles. Barbieri and Strauss[8] attempted to determine N_c from potentiometric titration data and thus obtained values of 19 and 13 for PS4 and PS5 samples, respectively, of polymerization degrees (DP) much larger than these N_c values. Time-resolved fluorescence quenching (TRFQ) was later used by Hsu and Strauss[12] to determine the value of N_c in acidic solutions (pH = 4) of a sample of PS6 of DP = 1700. The low value found for N_c, 24, indicated that a single polysoap molecule can give rise to many microdomains. A different conclusion was reached by Chu and Thomas,[13a] who determined the value of N_c in a fully neutralized solution of poly(dipotassium maleate-*co*-octadecene) of DP = 24 by TRFQ. The value of N_c was found to be equal to the DP, within the exper-

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imental error. Since the same result had been previously found for polymethacrylic acid,[13b] which also forms microdomains, Chu and Thomas concluded that one polymer molecule gives rise to one microdomain. A still different conclusion was reached by Shih et al.,[14] who determined microdomain sizes using small-angle neutron scattering for a series of poly(dilithium maleate-*co*-1-alkene), with alkenes ranging from 1-octene to 1-octadecene, and of molecular weights between 6 000 and 20 000. The results suggested that several polymer molecules can associate to form a single microdomain.

The scarcity of N_c values, the contradictory conclusions reached in the reported studies, and our interest in the behavior of polysoaps[11] were the main reasons for the investigation reported below. Using TRFQ under more stringent experimental conditions than in the previously reported studies, we have determined N_c values for PS10 and PS16 as a function of DP, concentration, neutralization degree (PS10 only), and temperature. A number of difficulties have been encountered in the analysis of the fluorescence decay curves that were not fully addressed in previous studies. The results indicate that several microdomains can arise from a single polysoap molecule and show some important differences in the behavior of classical micelles and polysoap microdomains.

Experimental Section

Materials. The sample of poly(maleic anhydride-*co*-hexadecyl vinyl ether) used to prepare the fully neutralized aqueous solutions of PS16 was the same as in part 1.[11] The polymerization degree of this polymer determined from light-scattering experiments performed on solutions in tetrahydrofuran (THF) was found to be 4000 ± 500. (Notice that this value represents a weight-average DP.) This polymer was fractionated by progressive precipitation of a THF solution in methanol. One fraction of low DP was selected for fluorescence measurements. Its DP, determined from viscosity measurements analyzed on the basis of a reported intrinsic viscosity–molecular weight relationship,[15] was found to be 140 ± 20.

Two samples of PS10 were used in the present investigation. One was prepared from the sample of poly(maleic anhydride-*co*-decyl vinyl ether) used in our previous investigation.[11] The DP of this polymer determined from light scattering of solutions in THF was found to be 1000 ± 100. A second sample of lower DP was prepared by polymerization of an equimolar solution of decyl vinyl ether and maleic anhydride in THF heated at 60 °C for 1 h using azobis(isobutyronitrile) as the initiator.[16] The polymer was purified by two precipitations of THF solutions in methanol. Its polymerization degree as determined from light scattering and viscosity measurements was 100 ± 15.

The hydrolysis of the poly(maleic anhydride-*co*-alkyl vinyl ether) samples was performed as previously described,[11] using NaOH. The fully neutralized aqueous solutions of PS16 were directly used in fluorescence probing experiments. The concentration of the stock PS16 solution was determined by dry content measurements. The solution of PS10 was further purified by successive passages through columns of anion- and cation-exchange resins (Merck, types III and I) and thus obtained in acidic form. Its concentration was determined by dry content.[11] The solutions of PS10 could thus be used to investigate the effect of the degree of neutralization. The lifetime of these solutions was limited to about 2–3 weeks, as the polyacid slowly precipitated out.

The anhydride hydrolysis is known to result in a partial degradation of the polymer. We have therefore attempted to measure the molecular weight and also to characterize the polydispersity of the polysoaps in aqueous 0.1 M KBr solution by means of HPLC using Beckman Spherogel-TSK SW 2000 and SW 4000 columns (made of silica gel grafted with a hydrophilic polymer). The chromatograms showed evidence of strong interactions between the polymers and the column packing, which prevented the determination of the above polymer characteristics. It is however likely that the DP's of the polysoaps are lower than those of their poly(maleic anhydride-*co*-alkyl vinyl ether) parents. Also all of the samples investigated are more or less polydisperse. This did not matter, however, in view of the very small effect of the DP on N_c (see below).

Methods. The N_c values, that is, the number of alkyl chains from the alkylvinylether moieties constituting a microdomain, were determined by using the time-resolved fluorescence quenching method, as in other studies of polysoap solutions.[12,13] Recall that TRFQ has been successfully used to determine the aggregation number of micelles of a large number of surfactants.[17] The method consists of the determination of the fluorescence decay curve (variation of the fluorescence intensity $I(t)$ with time t) of a probe, P, solubilized in the micelles or microdomains, in the presence of a quencher Q, under conditions such that $[P]/[M] \ll 1$ and $[Q]/[M] \simeq 1$, where [P], [Q], and [M] are the molar concentrations of probe, quencher, and micelles, respectively. The equation

$$I(t) = I(0) \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\} \quad (1)$$

where A_2, A_3, and A_4 are three time-independent adjustable parameters and $I(0)$ is the intensity at time $t = 0$, following a flash illumination of the system, is then fitted to the decay curve in order to determine the values of A_2, A_3, and A_4. This equation accounts very well for decay data in a variety of surfactant-containing systems[17-21] and of polysoap solutions.[11-13] In the case where probe and quencher do not migrate from micelle to micelle on the fluorescence time scale (i.e. migration is negligible during a time equal to a few probe fluorescence lifetimes, τ), the expressions of A_2, A_3, and A_4 are as follows

$$A_2 = k = \tau^{-1} \qquad A_3 = [Q]/[M] \qquad A_4 = k_Q \quad (2)$$

where k is the fluorescence decay rate constant and k_0 is the intramicellar quenching rate constant. Notice that k can be obtained in a separate experiment in the absence of quencher. The decay then obeys eq 1 with $A_3 = 0$ and $A_2 = k$. From the value of A_3 and of the weighing-in concentration [Q] of quencher one can obtain [M] and, thus, the number N_c of repeat units per microdomain from

$$N = (C - C_f)/[M] \quad (3)$$

where C is the concentration of polymer expressed in mole of repeat unit (monomole/liter) and C_f is the concentration of repeat units not involved in the formation of microdomains. In essence, C_f is the equivalent of the critical micellization concentration of surfactant solutions. It will be seen below that the determination of C_f raises problems.

The assumptions underlying eq 1 have been discussed.[17] In particular, it is assumed that the micelles or microdomains are monodisperse. When such is not the case, eq 1 is not valid because the intramicellar quenching rate constant k_Q decreases as the micelle size increases.[22-25] The system is then characterized by a distribution of k_Q values having a width related to that of the micelle size distribution function. Any fitting of eq 1 to the decay curves of polydisperse systems will result in systematic deviations, as shown in a recent study of aqueous solutions of cetyltrimethylammonium chloride in the presence of sodium salicylate,[26] where the micelles are very elongated and polydisperse. The theory for the fluorescence decay in polydisperse systems has been worked out.[27,28]

Equation 1 also assumes that probe and quencher do not migrate from micelle to micelle on the fluorescence time scale. When migration takes place, the expressions of A_2, A_3, and A_4 become more complex and depend on the mechanism of migration. In particular, A_2 is then a linear function of [Q] with $A_2 > k$.[17-21,29] This last result is used as a criterion to evidence migration. Migration is considered to take place when the difference between the values of A_2 and k measured in separate experiments in the absence and presence of quencher, respectively, is found to be larger than about 1.5 times the experimental error on either quantity (±2%, in most instances). The experimental data (k, A_2, A_3, and A_4) can still be used to obtain N_c and k_Q and also the pseudo-first-order rate constant for migration, k_m (see below). It is essential in systems where the results suggested the occurrence of migration to determine the decay curve over six to seven probe lifetimes.[25b,30,31] Indeed systems

of small monodisperse micelles with migration can be easily confused with systems of polydisperse micelles with no migration. However, the decay behavior at very long times permits a distinction between the two types of systems. Previous studies of polysoap solutions neglected this fact.[12,13]

In TRFQ studies of surfactant systems and of polysoaps the choice of a probe/quencher couple appropriate to the system investigated is extremely important. The probe must have a very long lifetime (small k) and the quenching must be efficient (large k_Q). Moreover both probe and quencher must reside as long as possible in the micelles or microodomains in order that migration through the bulk phase be negligible.[30,31] In this manner any observed migration can be safely attributed to the system investigated, and its study will give information on the dynamics of this system.[17] These criteria have led us to select pyrene as probe and the dodecylpyridinium ion (DPy^+) as quencher. Indeed even though the pyrene lifetime is shorter than the lifetime of the ruthenium(II) tris(bipyridyl) ion used by Hsu and Strauss[12] (370 ns instead of 630 ns), it is likely to be specifically solubilized in microdomains whereas the ruthenium derivative can bind to polysoap carboxylate groups of microdomains as well as to segments connecting microdomains. Also the lifetime of pyrene is longer than that of the positively charged (1-pyrenylbutyl)trimethylammonium ion used by Chu and Thomas[13a] (225 ns). Preliminary experiments on PS10 solutions performed with Cu^{2+} and methylviologen ion as quenchers led us to reject these quenchers which showed evidence of migration. Notice that Chu and Thomas[13a] also used DPy^+ as quencher.

The decay curves were determined by using the same single photon counting setup as in previous studies.[11] Equation 1 was fitted to the decay curves by using a nonlinear weighed least-squares procedure.

Results

1. Decay Behavior of the Pyrene Fluorescence in Polysoap Solutions in the Presence of DPy^+. In studies by other workers[12,13] the reported decay curves stretched over about 1200 ns and the number of counts at time $t = 0$, $I(0)$, was relatively low ($\ln I(0) \simeq 6$). Under such conditions, the decay curves obeyed eq 1 with $A_2 = k$ (no migration) in the Chu and Thomas[13] report on poly(dipotassium maleate-*co*-octadecene). On the contrary, Hsu and Strauss[12] observed that $A_2 > k$ (migration) with acidic solutions of PS6. Likewise, in our previous study of polysoaps,[11] the decay curves determined under conditions similar to those in the above studies, yielded $A_2 > k$ for the fully neutralized PS16. However, in the last two studies,[11,12] the process(es) responsible for this migration was not discussed.

The experimental conditions under which the decay measurements reported below have been performed were such as to give more accurate results than those in the above studies. Thus the decay curves stretched at least over 2000 ns with $\ln I(0)$ up to 11–12. The count number in the last channel was never below 100–300. Figure 1 shows examples of decay curves for the PS10 of DP = 1000. Equation 1 has been fitted to the decay data with four adjustable parameters, $I(0)$, A_2, A_3, and A_4 (Figure 1A), or with three adjustable parameters, $I(0)$, A_3, and A_4, and fixing $A_2 = k$, determined in a separate experiment in the absence of quencher (Figure 1B). In the long time range the four-parameter calculated curve shows a positive deviation with respect to the experimental data, whereas the three-parameter calculated curve shows a negative deviation (see the insets A and B which represent the distribution of residuals and the correlation function of residuals, respectively). Nevertheless, the values of the parameter that characterize the goodness of the fit indicated that the four-parameter fit was of better quality than the three-parameter fit. It is important to note that the distribution function of residuals and the

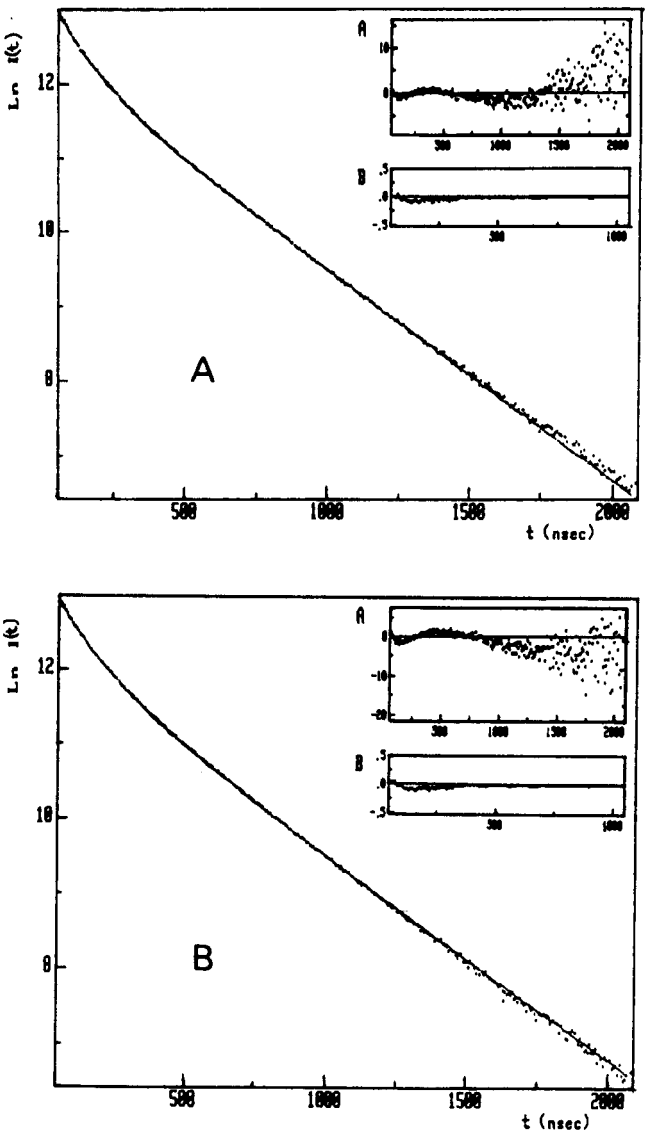

Figure 1. Examples of fitting eq 1 to decay data for a fully neutralized 4.87×10^{-2} monomol/L solution of PS10, DP 1000 with [pyrene] = 2×10^{-6} M, and [DPy^+] = 5×10^{-4} M at 25 °C. (A) four-parameter fit; (B) three-parameter fit with $A_2 = k = 2.70 \times 10^6$ s^{-1}. The line going through the data obeys eq 1. Inset A: distribution of residuals. Inset B: correlation function of residuals.

correlation function of residuals have the same shape as that for polydisperse micellar systems,[26] although the deviations from horizontal are less pronounced. A similar shape was found for all polysoap solutions investigated, suggesting some size polydispersity of the microdomains. Since these deviations were not large, the effect of polydispersity was not considered in the analysis of the decay data for both PS10 and PS16.

Moreover, in the case of PS10 the difference between k and A_2 from the four-parameter fit was generally small, only slightly above the experimental error. This small difference may very well arise from the effect of the small polydispersity discussed above, and it may be that decay curves determined over 3000 ns, had this been possible, rather than 2000 ns would yield $A_2 \simeq k$. This led us to assume that migration, if any, present in PS10 systems was too slow to affect the decay data. The decay curves were therefore analyzed with the three-parameter fit, setting A_2 equal to k, determined from a separate experiment.

In the case of PS16 solutions the three-parameter fits with $A_2 = k$ were generally of much lower quality than

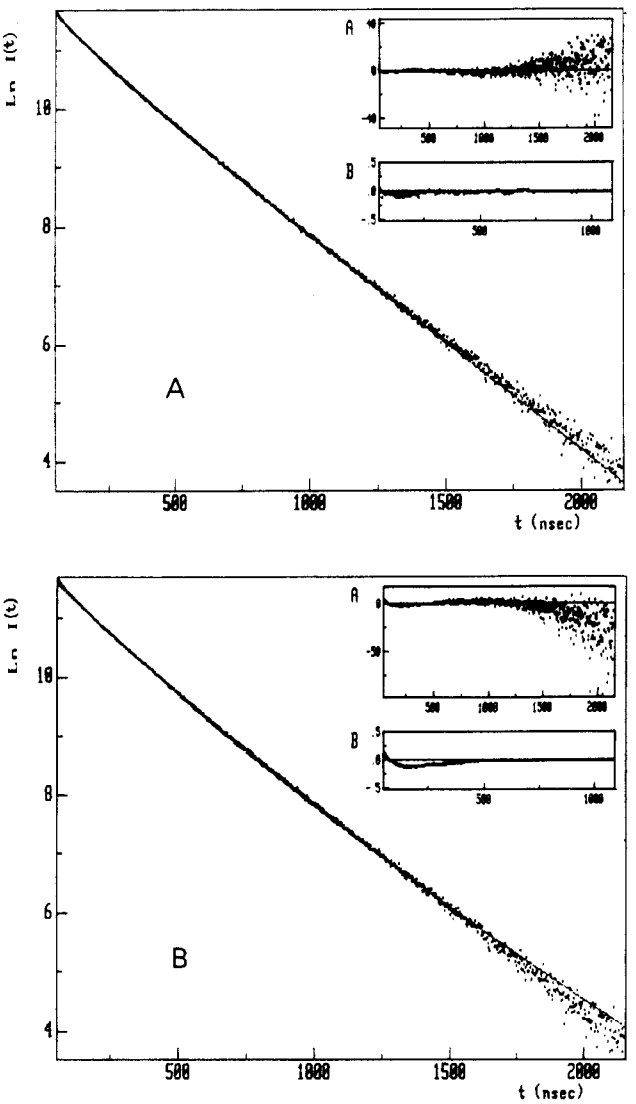

Figure 2. Examples of fitting of eq 1 to decay data for a fully neutralized 10^{-2} monomol/L solution of PS16, DP 140 with [pyrene] = 2.3×10^{-6} M, and [DPy^+] = 1.76×10^{-4} M, at 25 °C: (A) four-parameter fit; (B) three-parameter fit with $A_2 = k = 2.46 \times 10^6$ s^{-1}. The line going through the data obeys eq 1. Insets A and B: same as in Figure 1.

the four-parameter fits (see Figure 2) and could not be used. Also the four-parameter fits were not of very good quality and, as for PS10, showed evidence of some polydispersity (shape of the distribution of residuals and correlation of residuals, insets A and B). Nevertheless, the four-parameter fits led to A_2 values much larger than k, indicating probe and/or quencher migration. However, pyrene and DPy^+ had been selected in this work because their residence times in model anionic micelles are long with respect to the pyrene fluorescence lifetime.[32-34] Since the same is likely to be true in polysoap microdomains, the migration observed in PS16 solutions must take place through some process involving the polysoap. This migration appears to be negligible for PS10.

This important difference between PS10 and PS16 is further discussed below.

2. Effect of the Neutralization Degree α of the Polysoap. This study has been performed on the PS10 sample of DP $\simeq$ 1000, at a concentration of 4.87×10^{-2} monomol/L and at 25 °C, keeping the pyrene and DPy^+ concentrations constant and equal to 2×10^{-6} and 4.87×10^{-4} M, respectively. The neutralization was performed by addition of aliquots of a concentrated solution of NaOH. The neutralization degree α represents

Table I
Effect of the Neutralization Degree of PS10 ($C_{PS} = 4.87 \times 10^{-2}$ monomol/L) on the N_c and k_Q Values Characterizing the Microdomains at 25 °C

	$10^2\alpha$				
0	10	30	50	75	100
N_c	90 ± 30	98 ± 20	104 ± 15	101 ± 15	102 ± 15
$10^{-6}k_Q$, s^{-1}	0.79	1.0	1.84	3.54	4.10
$N_{c,corr}$	79 ± 25	65 ± 15	52 ± 8	30 ± 4	15 ± 3

the percentage of neutralized carboxylic groups. The N_c values were first calculated on the assumption that all decyl chains contributed to the formation of microdomains, i.e., $C_f = 0$ in eq 3. These values are listed in Table I together with those of the rate constant for intradomain quenching, k_Q. The error on N_c is large, particularly at low α, where the decay curves are almost linear. It is seen that the N_c values so obtained depend little on α. This is unexpected in view of the large increase of electrostatic repulsions between head groups with α. Also the k_Q values, which are obtained directly from the fitting of eq 1 to the decay curves, increase significantly with α. Recall that k_Q always increases when the aggregate size decreases.[22-25] This result led us to question the assumption $C_f = 0$ made in calculating N_c. More likely, as α increases, the number of chains involved in microdomain formation decreases and C_f increases, becoming comparable to C.

The determination of C_f is, however, difficult. We know of no method which directly measures C_f. In the present work, we have used an approximate method based on the solubilizing capacity of the polysoap solution for a water-insoluble compound, pyrene. This method assumes that at $\alpha = 0$ all polysoap alkyl chains belong the microdomains and that the solubility S_α of pyrene at a neutralization degree α, expressed in moles of pyrene per monomoles of PS10, is proportional to the number of alkyl chains involved in microdomain formation. The N_c values of Table I must therefore be corrected by the factor S_α/S_0, S_0 being the pyrene solubility at $\alpha = 0$.

The solubility of pyrene in aqueous PS10 solutions was determined as follows. PS10 solutions of known concentration were saturated with pyrene, shaken for 24 h, allowed to equilibrate and centrifuged to eliminate pyrene microcrystals. The pyrene concentration was then obtained spectrophotometrically by using the value $\epsilon_{307} = 11\,900$ mol^{-1} cm^{-1} for the absorption coefficient of pyrene in PS10 solution, measured as part of this work.

Figure 3 shows the plot of the pyrene solubility in mole/liter as a function of the PS10 concentration. The plots are linear and go through the origin for the three α values investigated. The slope of these lines yielded the values of S_α, plotted as a function of α in Figure 4. The values of N_c, corrected for the free chains, $N_{c,corr}$, are listed in Table I. The correction is very large, particularly at high α. Nevertheless the values of $N_{c,corr}$ now decrease almost linearly upon increasing α, as can be seen in Figure 5 which also represents the changes of k_Q with α. Moreover, the product $N_{c,corr} \times k_Q$ now varies much less with α than the product $N_c \times k_Q$, as to be expected for small aggregates.[25a]

Notice that similar values of $N_{c,corr}$ have been obtained through pyrene fluorescence decay measurements, in the absence of quencher but at a pyrene concentration such that [P]/[M] $\simeq$ 1, i.e., pyrene excimers formed in the PS10 microdomains. However the values of the rate constant for excimer formation, k_E, were well below those for pyrene quenching by DPy^+, as in other studies.[35,36] These low values of k_E made the decay curves analysis

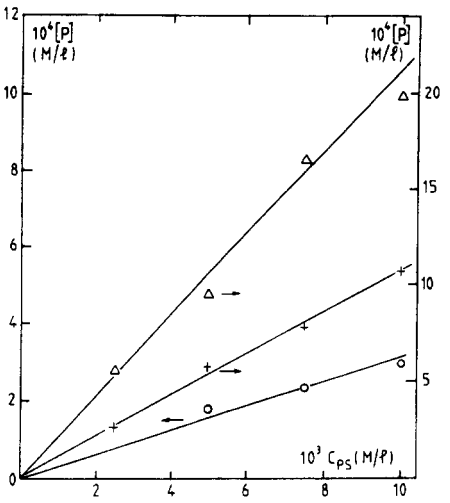

Figure 3. Pyrene solubility in PS10 solutions of increasing concentration at neutralization degrees: α = 0 (△); α = 0.50 (+); and α = 1.0 (○) at 25 °C.

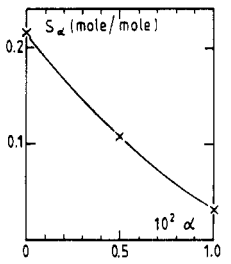

Figure 4. Variation of the pyrene solubility expressed in moles of pyrene per monomoles of PS10 with the degree of neutralization of PS10.

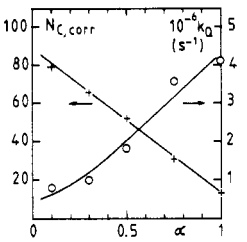

Figure 5. Variation of $N_{c,corr}$ and k_Q with the neutralization degree of PS10 at 25 °C and C_{PS} = 4.87 × 10^{-2} monomol/L.

relatively inaccurate. This is the main reason for which quenching through excimer formation was not further used in the present work.

A last remark must be made concerning the values of k_Q listed in Table I. These values are 5 to 10 times smaller than those obtained in micelles of anionic surfactants. Thus, for instance, as part of this work the values of k_Q were found to be 5.0 × 10^7 and 3.0 × 10^7 s^{-1} in potassium dodecanoate and disodium tetradecylmalonate micelles at 25 °C. (The last compound includes two carboxylate groups and is chemically close to the repeat unit of polysoaps.) A similar observation was made by Chu and Thomas,[13a] who interpreted this result as indicating a larger rigidity or microviscosity of the microdomains with respect to usual anionic micelles, likely because of geometric constraints arising from covalent bonding between monomers.

3. Effect of the Polysoap Concentration, C_{PS}, and of the Ionic Strength. This study has been also performed on the fully neutralized PS10 sample of DP ≃ 1000, in the range between 5.4 × 10^{-3} and 5.4 × 10^{-2} monomol/liter at 25 °C, keeping the ratio C_{PS}/[DPy^+] around 115. The $N_{c,corr}$ values have been obtained by multiplying the N_c values calculated by using eq 3 by the ratio $S_{1.0}/S_0$ from Figure 3. In doing so we have assumed $S_{1.0}/S_0$ to be independent of concentration. This is borne out by the linear plots in Figure 3. The $N_{c,corr}$ values listed in Table II show no dependence on C_{PS}, within the experimental error. A similar result has been reported for PS6.[12] This result suggests that microdomain formation mainly involves alkyl chains from a single polysoap molecule. This conclusion is similar to that of Hsu and Strauss.[12]

Table II
Effect of the Concentration of PS10 (α = 1) in Monomole/Liter on the $N_{c,corr}$ and k_Q Values Characterizing the Microdomains at 25 °C

C_{PS}, monomol/L	5.4 × 10^{-2}	2.7 × 10^{-2}	1.35 × 10^{-2}	5.4 × 10^{-3}
$N_{c,corr}$	13.5 ± 3	14 ± 3	14 ± 3	14.5 ± 3
$10^{-6}k_Q$, s^{-1}	5.7 ± 1	5.6 ± 1	5.8 ± 1	5.5 ± 1

We have also found, still on fully neutralized PS10, that $N_{c,corr}$ is independent of the ionic strength, in the NaCl concentration range where the polysoap did not precipitate out (up to 8 × 10^{-2} M NaCl for C_{PS} = 5 × 10^{-2} M), within the experimental error. In this respect the microdomains in polysoap solutions do not behave like micelles of usual ionic surfactants, the size of which increases with ionic strength.[37,38] The difference may be due to a combination of factors such as the absence of free monomers in the bulk phase, the effect of counterion condensation which renders the repulsions between head groups much less sensitive to the presence of external salt,[39] and the existence of covalent bonds between polysoap repeat units.

4. Effect of the Polymerization Degree, DP, and of the Alkyl Chain Length of the Polysoaps. The experiments have been performed at 25 °C, on the fully neutralized samples of PS10 (DP 100 and 1000) at a concentration of 5 × 10^{-2} monomol/L and of PS16 (DP140 and 4000) at a concentration of 10^{-2} monomol/L.

The values of $N_{c,corr}$ for PS10 were found to be 16 ± 4 and 13 ± 3 for the DP 100 and 1000. The same correction factor $S_{1.0}/S_0$ has been applied to the N_c data for the samples of DP 100 and 1000.

The method used to correct the N_c values for PS10 cannot be extended to PS16 because this polysoap is insoluble at α < 0.75. However in view of the much larger hydrophobicity of the hexadecyl chain with respect to the decyl chain, we have assumed that all hexadecyl chains are involved in microdomains, i.e., C_f = 0 in eq 3. This assumption results in upper-bound values of N_c, and the error it involves is difficult to evaluate. Nevertheless, it is worth noting that if C_f decreased upon increasing chain length somewhat similarly to the cmc of ionic surfactants, that is by a factor of 2 per additional CH_2 group,[38] the value of C_f/C_{PS} for PS16 would be 30 times smaller than for PS10 and the above assumption would be quite valid. Even if C_f only decreased by a factor of 6 in going from PS10 to PS16 the error made in neglecting C_f in eq 3 would amount to about +15%, i.e., close to the errors inherent to the method itself. In the next paragraph results which suggest that segments of PS16 molecules are not involved in microdomains will be presented. Another difficulty arises in the calculation of N_c from the decay parameters A_2, A_3, A_4, and k characterizing PS16 solutions. Indeed, as noted above the fit of eq 1 to the decay data yielded $A_2 > k$ indicating probe and quencher migration. In this case the expressions of A_2, A_3, and A_4 are more complex. In particular they include a pseudo-first-order rate constant k_m which characterizes the migration of probe and quencher. Nevertheless, if one assumes that only small amounts of probe and quencher are out of the micelles or microdomains, one can still obtain [M]

and k_Q as well as k_m, from the values of A_2, A_3, A_4, and k, using the equations[40,41]

$$[M] = \frac{[Q]}{A_3}\left(\frac{A_3A_4}{A_3A_4 + A_2 - k}\right)^2$$
$$k_Q = A_3A_4^2/(A_3A_4 + A_2 - k) \quad (4)$$
$$k_m = A_4 - k_Q$$

Using eqs 3 and 4, on the assumption that $C_f \simeq 0$, the N_c values were calculated to be 60 ± 9 and 50 ± 7, for the PS16 of DP 140 and 4000.

Thus for both PS10 and PS16 the effect of the DP is small. In that respect our results differ from those from small angle neutron scattering.[14] In agreement with Hsu and Strauss[12] our results indicate that a polysoap molecule can give rise to a number of microdomains which increases with its DP.

The N_c values are much larger for PS16 than for PS10, even though the difference may not be as large as it is suggested by the above N_c values. This trend is the same as that reported for usual ionic surfactant micelles.[42,43]

As part of this work we have determined at 25 °C the micelle aggregation number of two soaps at a concentration of 0.1 M: potassium dodecanoate, N = 51, and disodium tetradecylmalonate, N = 46, using the TRFQ method with the pyrene–DPy^+ couple. The N value relative to the disodium tetradecylmalonate is smaller than that for potassium dodecanoate even though the former has a longer alkyl chain. This result clearly shows that the presence of two charged carboxylate groups in the malonate soap brings about a large decrease of aggregation number with respect to a soap having only one carboxylate group. As pointed out above the malonate soap is somewhat chemically close to the repeat unit of polysoaps. At this point, it is interesting to note that the N value of the malonate soap is somewhat smaller than the upper bound value found for PS16. Taking into account the difference of alkyl chain length between the malonate soap and PS16 and the error on the N_c value for the latter, the aggregation behavior of the two surfactants do not differ much. The same conclusion appears to hold for PS10. Indeed the decyl malonate is expected to have an aggregation number of $46 \times (10/14)^2 \simeq 23$ as compared to 15 ± 3 for PS10.

It thus appears that the number of alkyl chains involved in a polysoap microdomain differs only little from the aggregation number of a micelle of a surfactant having a chemical structure close to that of the polysoap repeat unit.

5. Effect of Temperature. This study has been performed on the fully neutralized solutions of PS10, DP 100, and of PS16, DP 140 and 4000.

The results for the PS10 solutions obtained from a fit of eq 1 to the decay curves with three adjustable parameters, taking $A_2 = k$, and with four adjustable parameters are given in Table III. The N_c values from eq 3 have been corrected by the $S_{1.0}/S_0$ value from Figure 3, obtained at 25 °C. Indeed pyrene solubility measurements performed with the available equipment proved highly inaccurate when the temperature differed too much from the ambient temperature. It is however unlikely that the results would be much affected by the possible change of $S_{1.0}/S_0$ with temperature. Indeed the solubility may change much with T, but this is less likely for a solubility ratio.

It is seen that in the range 13.4–45 °C, $k^{-1} \simeq A_2^{-1}$ and $N_{c,corr}$ depends only little on T. The $N_{c,corr}$ value at 13.4 °C differs a little from that at higher T, but it is also the value most affected by experimental errors because of the low value of the k_Q/k ratio at this temperature.

Table III
Effect of Temperature on the Values of k^{-1}, k_Q, and $N_{c,corr}$ for PS10 in Solution[a]

T, °C	k^{-1} (A_2^{-1}), ns	$10^{-6}k_Q$, s^{-1}	$N_{c,corr}$[b]
13.4	384 (367)	2.8 (3.5)	12 (11)
25	371 (364)	3.8 (4.8)	14.5 (13.5)
45	333 (327)	6.2 (6.6)	14 (13.5)
60	322 (290)	4.4 (8.1)	14 (13.0)

[a] C_{PS} = 5.4 × 10^{-2} monomol/L; [pyrene] = 1.88 × 10^{-5} M; [DPy^+] = 4.21 × 10^{-4} M; the values in parentheses have been obtained with a four-parameter ($I(0)$, A_2, A_3, and A_4) fit of eq 1 to the data. [b] Error = ±3.

Table IV
Decay Parameters and Values of N_c, k_Q, and k_m for PS16 Solutions at 25 and 41 °C[a]

T, °C	k^{-1}, ns	A_2^{-1}, ns	A_3	$10^{-6}A_4$, s^{-1}	N_c	$10^{-6}k_Q$, s^{-1}	$10^{-6}k_m$, s^{-1}
25 *b*	406	275	0.433	4.84	60 ± 10	3.1	1.7
c	395	285	0.486	4.69	50 ± 10	3.3	1.4
41 *b*	368	199	0.925	3.82	140 ± 20	2.3	1.5
c	368	207	1.03	3.86	120 ± 20	2.5	1.3

[a] C_{PS} = 10^{-2} monomol/L; [pyrene] = 2.3 × 10^{-6} M. [b] DP = 140; [DPy^+] = 1.76 × 10^{-4} M. [c] DP = 4000; [DPy^+] = 2.2 × 10^{-4} M.

At 60 °C, the three-parameter fit was of poor quality, the difference between k and A_2, as obtained from a four-parameter fit, was well above the experimental error and the value of k_Q from the three-parameter fit was lower than at 45 °C, contrary to what is usually observed. All these facts indicate the probable occurrence of migration. Indeed, k_Q obtained from the values of A_2, A_3, and A_4 using a four-parameter fit and eq 4 is larger than that at 45 °C, as expected. Nevertheless the overall change of $N_{c,corr}$ between 13.4 and 60 °C remains very small.

For the PS16 solutions the measurements were performed only at 25 and 41 °C. As pointed out above the results reveal migration even at room temperature. The difference between A_2 and k increased with temperature. The decay curves were thus analyzed by using a four-parameter fit of eq 1. The results listed in Table IV demand the following remarks:

(i) N_c increases much with T. This variation is opposite to that reported for aqueous micelles of all ionic surfactants investigated thus far.[41,44,45] At the present time we can give no explanation to this result. Notice that this change of N_c does not seem to arise from the approach of a phase separation boundary. Indeed the polysoap solution did not phase-separate or even become turbid at temperature up to 90 °C. On the other hand the intradomain quenching rate constant k_Q decreases upon increasing T, whereas an increase is usually observed.[41,44,45] This peculiar behavior of k_Q confirms the increase of microdomain size with T, as for nonionic surfactants at temperatures close to the cloud temperature, where the effect of size increase dominates the variation of k_Q.[35]

(ii) The migration rate constant, k_m, is large and appears to depend little on temperature. For PS10, k_m has been evaluated at 60 °C from the values of the decay parameters listed in Table III and found to be 3 × 10^5 s^{-1}, i.e. much smaller than for PS16.

(iii) The polymerization degree of PS16 has practically no effect on the values of N_c, k_Q, and k_m.

Discussion

1. Problems in Evaluating the Number of Repeat Units Involved in the Formation of a Microdomain

in Polysoap Solutions. Two types of problems arose in the determination of N_c values. The first one concerns the value of C_f, that is, the concentration of repeat units not involved in microdomains, in eq 3. We have adopted a method somewhat similar to that used by Hsu and Strauss[12] for obtaining C_f in PS10 solutions, as a function of the neutralization degree. This method was restricted to room temperature, owing to experimental constraints, and did not apply to PS16 since it is insoluble at $\alpha < 0.75$. This method rests on the assumption that the solubility depends on the number of alkyl chains constituting a microdomain but does not depend on the state of ionization of the repeat unit head groups. This last assumption demands to be checked. Unfortunately no other methods were found or were readily accessible to us in the course of this work. In the case of PS16 we have assumed $C_f = 0$, as did Chu and Thomas[13a] in their study of microdomains in poly(dipotassium maleate-*co*-octadecene) solutions. Again, this assumption demands to be checked. The small-angle neutron scattering studies of polysoaps[14] did not discuss the possibility that some segments of polysoap molecules were not involved in microdomains.

The second difficulty concerns the existence of probe and quencher migration between microdomains. We discuss below possible mechanisms for such migration. At this stage we simply note that the present results confirmed our previous report of migration in PS16 solutions.[11] Chu and Thomas[13a] did not detect migration in their study of poly(dipotassium maleate-*co*-octadecene), which is very closely related to PS16. This difference of behavior may well be due to the very low DP, 24, of the polymer used by Chu and Thomas[13a] that may force the polysoap molecule to form a smaller microdomain than in the case of a larger polysoap molecule and also perhaps to the experimental conditions under which the decay curves were determined. Hsu and Strauss[12] detected exchange in PS6 solutions. However they used ruthenium(II) tris(bipyridyl) ion as probe, and, since the measurements were performed in [LiCl] = 0.1 M, one cannot discard a migration of the probe through the bulk. These authors accounted for migration in calculating the N_c values they report.

2. Effect of Various Parameters on the N_c Values. N_c has been found to be independent of concentration, ionic strength, and polymerization degree. These results strongly suggest that microdomains are formed within isolated polysoap molecules and that a polysoap molecule can give rise to a large number of microdomains, connected by polysoap segments made of repeat units having their alkyl chain exposed to water. The length of these segments decreases probably rapidly upon increasing alkyl chain length. From the value of [M] and that of C_f it is possible to evaluate the average number of repeat units in a segment connecting two microdomains in PS10 molecule. For instance, at $\alpha = 1.0$ this number was found to be 85 ± 15, whereas a microdomain involves 15 ± 3 repeat units.

The second important point concerns the T dependence of N_c which remains nearly constant for PS10 but clearly increases for PS16, upon increasing temperature. As pointed out above, this is at variance with the behavior of micelles of ionic surfactants. Such a behavior may arise from the increased conformational lability of the polysoap main chain with temperature, which may facilitates the self-association of the side chains into microdomains, thus giving rise to larger microdomains than at low T.

3. Mechanism of Probe and Quencher Migration between Polysoap Microdomains. Two mechanisms have been proposed to explain migration in aqueous micellar solutions.

The first one involves collisions between micelles with temporary merging of the collided micelles and redistribution of probe and quencher during the time two micelles remain merged.[40,46,47] This process is operative on the fluorescence time scale in solutions of nonionic surfactants[35] and also in water in oil microemulsions,[40,46,47] when in both types of systems the interactions between aggregates are sufficiently attractive. This type of migration has not been observed with aqueous ionic micellar solutions at low ionic strength because the strong electrostatic repulsions existing between charged micelles slow down collisions to a point that migration is "frozen" on the fluorescence time scale. Since microdomains in polysoap solutions are electrically charged, migration through microdomain collision and coalescence should be negligible.

The second type of migration involves the exit of the probe and/or quencher from a micelle, its diffusion in the bulk phase, and subsequent incorporation in another micelle.[18-21] Migration of this type becomes negligible if the probe and quencher have very long residence times in micelles. Recall that the expression of the residence time of a solute in a micelle includes a term $\exp(\Delta G_T/RT)$, where ΔG_T is the free energy of transfer of the solute from the solubilized state to the free state.[48] The larger ΔG_T, the longer the solute residence time. However, in polysoap solutions the microdomains are connected by segments of repeat units with their alkyl chain exposed to water. These segments are hydrophobic. It is then possible that probe and quencher when coming out of a microdomain stick to these segments and diffuse along them to the next microdomains. Clearly the value of ΔG_T for the transfer from the solubilized state to the free state is larger than that for the transfer to a state where the solute is out of the microdomain but in hydrophobic contact with a segment connecting two microdomains. The residence times in this case would be strongly decreased, to the extent that migration along the segments may become detectable on the fluorescence time scale.

This migration along segments connecting microdomains corresponds to a partition of the probe and quencher between microdomains and such segments. This partition permits one to explain the main features of the observed migration. Thus the partition is expected to increase in favor of the segments when the length of the polysoap alkyl chain increases, thereby explaining why little or no migration is observed with PS10, whereas migration is clearly seen with PS16. Also, if the DP is sufficiently large, the partition should depend little on the DP since the fraction of repeat units under the form of microdomains is then not expected to depend on the DP. This would explain the very little dependence of k_m on the DP. However, a change of behavior is expected to occur when the DP becomes very small, smaller than the N_c of the microdomain that the repeat units would tend to form. This may explain the difference between our results and those of Chu and Thomas,[13] who observed no migration in their study of a polymer of very low DP.

It remains that the proposed migration mechanism implies that a small part of the repeat units of PS16 are not in microdomains. This fact was not taken into account in the calculation of N_c as we had no way to evaluate the fraction of free repeat units.

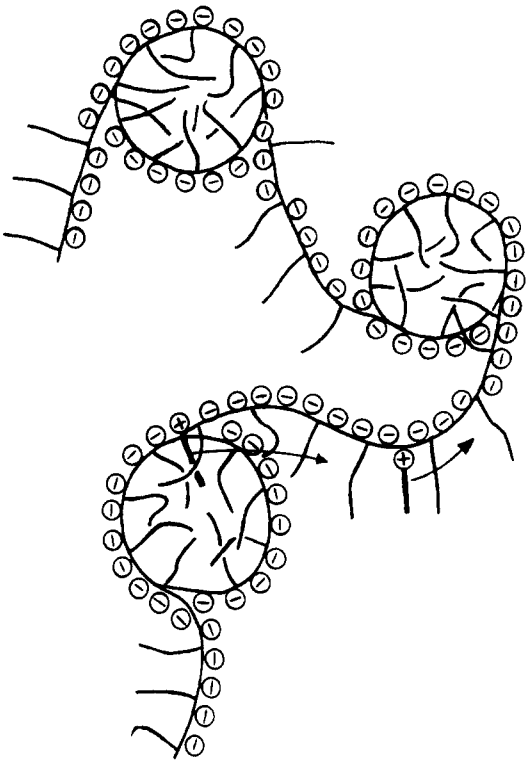

Figure 6. Schematic representation of a part of a polysoap molecule in aqueous solution showing microdomains, segments of free repeat units, and a migrating quencher (—⊕). For the sake of clarity, only cross sections of the microdomains with planar alkyl chains and planar connecting segments have been represented and the counterions have been omitted.

A crude representation of a polysoap molecule with its microdomains connected by segments of free repeat units is given in Figure 6, which also shows how a quencher such as DPy^+ can migrate between microdomains along these segments.

Conclusions

The results reported in this paper provide a first characterization of the microdomains present in aqueous solutions of PS10 and PS16.

The microdomains appear to be somewhat polydisperse. For PS10 the average number of repeat units per microdomain has been found to be independent of the concentration, ionic strength, and polymerization degree, suggesting that microdomain formation involves isolated polysoap molecules. As expected the number of repeat units per microdomain decreases upon increasing neutralization degree of PS10.

The behavior of PS16 is peculiar in two respects. The number of repeat units per microdomain increases with temperature may be as a result of an increased conformational freedom of the polysoap main chain. Also migration of probe and quencher between microdomains takes place on the fluorescence time scale. This migration may involve segments of repeat units connecting one microdomain to another.

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References and Notes

(1) Varoqui, R.; Strauss, U. P. *J. Phys. Chem.* **1968**, *72*, 2507.
(2) Dubin, P.; Strauss, U. P. *J. Phys. Chem.* **1967**, *71*, 2757; **1970**, *74*, 2847; **1973**, *77*, 1427.
(3) See, for instance: Dubin, P. B., Ed. *Microdomains in Polymer Solutions*; Plenum: New York, 1986.
(4) Strauss, U. P. in ref 3, p 1.
(5) Strauss, U. P.; Vesnaver, G. *J. Phys. Chem.* **1975**, *79*, 1558, 2426.
(6) Martin, P.; Strauss, U. P. *Biophys. Chem.* **1980**, *11*, 397.
(7) (a) Crescenzi, V.; Quadrifoglio, F.; Delben, F. *J. Polym. Sci., Part C* **1972**, *39*, 241. (b) *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 357.
(8) Barbieri, B.; Strauss, U. P. *Macromolecules* **1985**, *15*, 1347.
(9) Varoqui, R.; Pefferkorn, E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*, 9 and references therein. See also ref 3, p 225.
(10) Pefferkorn, E.; Schmitt, A.; Varoqui, R. *C.R. Acad. Sci. (Paris)* **1968**, *267*, 349.
(11) Binana-Limbelé, W.; Zana, R. *Macromolecules* **1987**, *20*, 1331.
(12) Hsu, J.-L.; Strauss, U. P. *J. Phys. Chem.* **1987**, *91*, 6238.
(13) (a) Chu, D.-Y.; Thomas, J. K. *Macromolecules* **1987**, *20*, 2133. (b) *J. Phys. Chem.* **1985**, *89*, 4065.
(14) (a) Shih, L.; Sheu, E.; Chen, S. H. *Macromolecules* **1988**, *21*, 1387. (b) Shih, L.; Mauer, D.; Verbrugge, C.; Wu, C.; Chang, S.; Chen, S. H. *Macromolecules* **1988**, *21*, 3235.
(15) Varoqui, R.; Pefferkorn, E. *J. Phys. Chem.* **1975**, *79*, 169.
(16) Strauss, U. P.; Andrechak, J. A. *J. Polym. Sci. Polym. Chem. Ed.* **1985**, *23*, 1063.
(17) Zana, R. In Zana, R.Ed. Surfactant Solutions. New Methods of Investigation; Marcel Dekker Inc.: New York, 1987; Chapter 5, and references therein.
(18) Infelta, P.; Grätzel, M.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 190.
(19) Tachiya, M. *Chem. Phys. Lett.* **1975**, *33*, 289; *J. Chem. Phys.* **1982**, *76*, 340.
(20) Yekta, A.; Aikawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1979**, *63*, 543.
(21) Infelta, P. *Chem. Phys. Lett.* **1979**, *61*, 88.
(22) Gosele, U.; Klein, U. K.; Hauser, M. *Chem. Phys. Lett.* **1979**, *68*, 291.
(23) Tachiya, M. *Chem. Phys. Lett.* **1980**, *69*, 605.
(24) Rothenberger, G.; Grätzel, M. *Chem. Phys. Lett.* **1989**, *154*, 165.
(25) (a) Van der Auweraer, M.; Reekmans, S.; Boens, N.; De Schryver, F. C. *Chem. Phys.* **1987**, *111*, 105. (b) Van der Auweraer, M.; Reekmans, S.; Boens, N.; De Schryver, F. C. *Chem. Phys.* **1989**, *132*, 91.
(26) Makhloufi, R.; Hirsch, E.; Candau, S. J.; Binana-Limbelé, W.; Zana, R. *J. Phys. Chem.* **1989**, *93*, 8095.
(27) Almgren, M.; Löfroth, J.-E. *J. Chem. Phys.* **1982**, *76*, 2734.
(28) Grieser, F.; Warr, G. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1813.
(29) Dederen, J. C.; Van der Auweraer, M.; De Schryver, F. C. *Chem. Phys. Lett.* **1979**, *68*, 45.
(30) Almgren, M.; Alsins, J.; Mukhtar, E.; Van Stam, J. *J. Phys. Chem.* **1988**, *92*, 4479.
(31) Zana, R.; Lang, J. *Colloids Surf.*, in press.
(32) Binana-Limbelé, W.; Zana, R.; Platone, E. *J. Colloid Interface Sci.* **1988**, *124*, 647.
(33) Muto, Y.; Esumi, K.; Meguro, K.; Zana, R. *J. Colloid Interface Sci.* **1987**, *120*, 162.
(34) Zana, R.; Lang, J. Unpublished results on sodium dodecylsulfate micelles.
(35) Binana-Limbelé, W.; Zana, R. *J. Colloid Interface Sci.* **1988**, *121*, 81.
(36) Malliaris, A.; Lang, J.; Zana, R. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 109.
(37) Lianos, P.; Zana, R. *J. Phys. Chem.* **1980**, *84*, 3339.
(38) Mukerjee, P. *Adv. Colloid Interface Sci.* **1967**, *1*, 249.
(39) Manning, G. *Annu. Rev. Phys. Chem.* **1972**, *23*, 117.
(40) Jada, A.; Malliaris, A.; Lang, J. *J. Phys. Chem.* **1988**, *92*, 1946.
(41) Croonen, Y.; Geladé, E.; Van der Zegel, M.; Van der Auweraer, M.; Vandendriessche, H.; De Schryver, F. C. *J. Phys. Chem.* **1983**, *87*, 1426.
(42) Malliaris, A.; Lang, J.; Zana, R. *J. Colloid Interface Sci.* **1986**, *110*, 237.
(43) Grieser, F.; Drummond, C. *J. Phys. Chem.* **1988**, *92*, 5580 (see supplementary material).
(44) Roelants, E.; Geladé, E.; Smid, J.; De Schryver, F. C. *J. Colloid Interface Sci.* **1985**, *107*, 337.
(45) Malliaris, A.; Le Moigne, J.; Sturm, J.; Zana, R. *J. Phys. Chem.* **1985**, *89*, 2709.
(46) Atik, S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3543.

(47) Fletcher, P.; Robinson, B. H. *Ber. Bunsenges. Phys. Chem.* **1981**, 85, 863.
(48) Aniansson, E. A. G. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 981. Aniansson, E. A. G.; Wall, S.; Almgren, M.; Hoffmann, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. *J. Phys. Chem.* **1976**, *80*, 905.

Registry No. PS10, 80508-29-8; PS16, 80508-30-1.

Studies of the Diffusion Process of Camphorquinone in Poly(aryl ether ether ketone) by the Holographic Grating Technique

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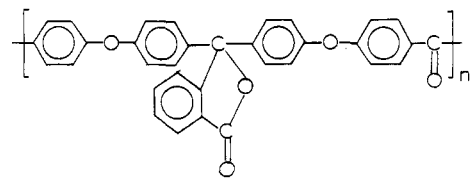
ABSTRACT: The diffusion coefficients of a trace amount of camphorquinone (CQ) and its photoproduct (CQP) in poly(aryl ether ether ketone) (PEEK) are measured as a function of temperature by using the holographic grating relaxation technique. Above T_g the diffusion coefficients are non-Arrhenius, whereas they become Arrhenius below T_g. Comparison of the diffusion data with the dynamic shear modulus data of PEEK shows that diffusion of CQ (or CQP) in PEEK is completely determined by the molecular size (characterized by a parameter ξ) of CQ (or CQP) and by the viscoelastic property of PEEK. However, the ξ parameter is found to be host dependent.

Introduction

Studies of the translational diffusion process of trace amounts of low molecular weight organic dye molecules in molten and glassy polymers are of practical and fundamental interest. Recent work carried out by using the holographic grating relaxation technique[1-3] has shown that in the dye/polymer system the behavior of concentration fluctuations of the dye molecules is dictated by the dynamics of polymer chain motion, provided that the dye concentration is small such that the dye molecule undergoes self-diffusion in the polymer environment and that the lifetime of the excited dye molecule is much longer than the rate of dye diffusion. Under these conditions, the dye molecule serves as a probe of the polymer chain motion, and measurements of the mutual diffusion coefficient in the limit of vanishing dye concentration in the dye/polymer system should provide information about the motion of the polymer chains. When the polymer host is in the rubbery state, the segmental motion of the polymer chain is rapid and the diffusion of the probe can be studied either by using a conventional technique such as a radioactive isotope tracer or by using pulsed field gradient NMR. However, as the dye/polymer system is brought toward the glass transition temperature (T_g) of the polymer, the segmental motion is gradually frozen, and the diffusion process of the probe becomes very slow, thus rendering the conventional techniques ineffective.

The holographic method deals with the detection of the dye diffusion over a distance about the order of one optical wavelength, and consequently it decreases the measurement time by about a factor of 10^8, in comparison with the conventional technique, thereby making the measurement of a very slow diffusion coefficient (as small as 10^{-15} cm^2/s) feasible. This technique is especially useful for polymers with high T_g. In this paper, we apply the holographic grating relaxation technique to measure the diffusion coefficient of a photochromous dye, camphorquinone (CQ), in poly (aryl ether ether ketone) (PEEK).



Poly(ether ether ketone) (PEEK)
Tg = 200°C

Figure 1. Molecular formula of poly(aryl ether ether ketone) (PEEK).

Due to its outstanding thermal and combustion characteristics and its resistance to a wide range of solvents, PEEK has received an increased attention as a high performance thermoplastic.[4,5] In order to gain a better understanding of the properties of this useful material as well as to certify the applicability of the holographic grating technique as a technique for characterizing the high T_g thermoplastic material, we have also measured the temperature dependence of the dynamic shear modulus for comparison.

Experimental Section

Poly(aryl ether ether ketone) (PEEK) (with its repeating unit shown in Figure 1) used in the present study was synthesized

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