Are Giant Micelles Living Polymers?

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We report the first self-diffusion measurements of elongated micelles in the semidilute regime performed with fringe-pattern photobleaching-recovery techniques. These measurements give evidence for the power-law dependence of the self-diffusion coefficient D_s versus concentration, but polymer models are not adequate. Suggestion is made that such micellar systems behave like "living polymers."

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Static and dynamic properties of polymer solutions (in dilute and semidilute regimes) are now well known.[1-3] In contrast, dynamic properties of "living polymers" are still poorly understood. These are solutions of linear macromolecules which can break and recombine. There have been only recently some theoretical attempts to describe their rheological properties.[4] Examples of living polymer systems are end-functionalized polymers, cylindrical microemulsions,[5] or, as in our case, elongated micelles. Micelles are aggregates of amphiphilic molecules in water[6]; the aggregation of these molecules is spontaneous above a well-defined concentration called the critical micellar concentration. The shapes of these aggregates may be different (spheres, rods, disks, wormlike micelles) depending upon various parameters such as the nature of the amphiphilic molecules, their concentration, the presence and the nature of added salt, the temperature, etc. In the case of wormlike micelles, it has been suggested that there could be some analogy between these systems and polymer solutions.[7] This analogy has been put on firm experimental basis by Candau, Hirsch, and Zana.[8,9] Obviously, in the case of such systems, one must be aware of the transient character of the micellar aggregates; the aim of this paper is then to show the effects of this transient character on self-diffusion mechanisms by comparison with reptation theories used to describe these mechanisms in polymer solutions.

Theoretical background.— In this section, we recall the classical results on polymer models, micellar systems, and the new living polymers concept. In the framework of reptation theory, the self-diffusion coefficient D_s of polymer chains obeys the following scaling law[1]:

$$D_s \propto N^{-2} c^{-1.75}, \tag{1}$$

where N is the number of monomers per chain and c is the monomer concentration. For experimental work on self-diffusion in polymers, see Leger, Hervet, and Rondelez.[10] The main difference between polymers and micelles is that in the latter case, the chain length is not a constant, but is concentration dependent. The classical model of Tanford[11] gives a polydisperse distribution centered on a mean value N_0, which increases with concentration as

$$N_0 \propto c^{0.5}$$

This growth model is based on the assumption of ideal solutions (i.e., no interactions between micelles). Improvement of this model consists of taking into account at least excluded-volume interactions, which leads Gelbart *et al.*[12] to the following law:

$$N_o \propto c.$$

Combination of these laws with the scaling law (1) leads to

$$D_s \propto c^{-2.75} \tag{2}$$

or

$$D_s \propto c^{-3.75}. \tag{3}$$

Furthermore, in the case of elongated micelles one must take into account the transient character of the aggregates. Indeed, such a character may be critical as has been observed in the case of self-diffusion in percolating microemulsions.[13] A theoretical approach has recently been proposed by Cates,[4] who considers a kinetic model of chain breakage and recombination. He obtained with this model the distribution of the chain lengths (which is the same as that given by the above-mentioned thermodynamic model, i.e., $N_0 \propto c^{0.5}$). To describe the dynamic properties of the chains, he introduced two characteristic times: the classical reptation time τ_R of a chain of mean length N_0, and the mean time τ_B for a chain of length N_0 to break into pieces. If $\tau_R < \tau_B$, the dominant stress-relaxation mechanism is simply reptation. If $\tau_R > \tau_B$, stress relaxation should be characterized by a new intermediate time scale $(\tau_R \tau_B)^{1/2}$ associated with a process whereby the chain breaks at a point close enough to a given segment of tube for reptative relaxation of that segment to occur before the new chain end is lost by recombination. This model gives the dependence of the self-diffusion coefficient

$$D_s \propto N_0^{-2/3} c^{-5/4}$$

which gives, with the assumption of the above-mentioned

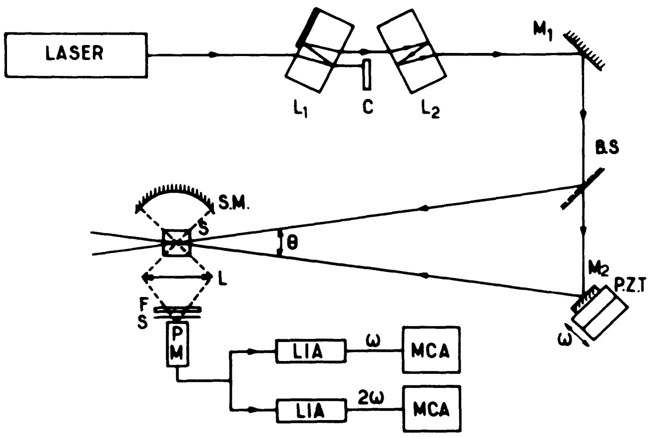

FIG. 1. Experimental setup for FRAP experiments. L_1 and L_2, parallel glass plates producing perfectly superimposed beams of unequal intensity; C, chopper; M_1 and M_2, mirrors; B.S., beam splitter; S, sample; S.M., spherical mirror; L, collecting lens; F, filter; S, shutter; LIA, lock-in amplifier; MCA multichannel analyzer.

distribution,

$$D_s \propto c^{-1.58}. \tag{4}$$

Experimental details.— We have studied the same system as the authors of Refs. 8 and 9, using cetyl trimethyl ammonium bromide (CTAB) as amphiphile, with added KBr. We will only recall the following results.

Aqueous solutions of CTAB form elongated micelles, even at low concentration, and these micelles grow with increasing concentration until they overlap at high enough concentration. One might wonder whether the chains are still linear at such concentrations: We can then consider the next phase occurring at higher concentration (i.e., $\simeq 3$ mol·l^{-1}) which is a rectangular phase,[14] constituted of alignments of long linear aggregates. This strongly supports the idea that the chains are linear at the highest concentration studied here.

In $0.1M$ KBr, the scattered intensity and cooperative diffusion coefficient clearly have a polymerlike behavior (in a good solvent).

We made our study with CTAB solutions in $0.05M$, $0.1M$, and $0.25M$ KBr at 30 °C and $0.05M$ and $0.25M$ at 35 °C using the technique of fluorescence recovery after fringe-pattern photobleaching (FRAP), which allows us to measure the self-diffusion coefficient D_s of micelles labeled with fluorescent probes; these probes have the same structure as the amphiphilic molecules: a polar head, here the fluorescein group, and an aliphatic tail. When strongly illuminated these probes irreversibly lose their fluorescent properties (photobleaching). In the illuminated volume the fluorescence intensity is measured afterwards by use of a low-intensity light beam: The signal increases as new probes enter the studied volume and D_s can be deduced from the recovery time. This method was improved by use of a fringe pattern and by modulation of the fluorescence signal. The self-diffusion coefficient is then

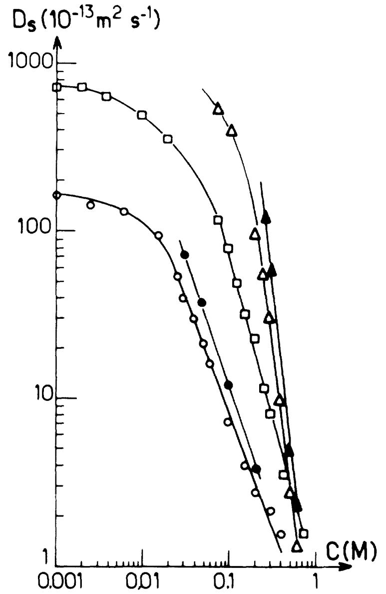

FIG. 2. Plot of D_s vs c in log-log form. We clearly see that a change in temperature does not change the slope, but salinity (interaction) is critical. Values of the slope are as follows: open circles ($0.25M$, 30 °C), -1.4 ± 0.1; filled circles ($0.25M$, 35 °C), -1.57 ± 0.07; squares ($0.1M$, 30 °C), -2 ± 0.07, open triangle ($0.05M$, 30 °C), -4.4 ± 0.1, filled triangles ($0.05M$, 35 °C), -4.6 ± 0.1. The sizes of the geometric figures giving the experimental points are representative of the error bars on our data, which are, in fact, small in this sort of experiment. We clearly see then a linear regime in log-log scale, as often in polymer studies.

$$D_s = 1/\tau q^2, \tag{5}$$

where τ is the recovery time and $q = 2\pi/i$ is the fringes' wave vector. Experiments were made at least at three different i values to verify this relation.[5] The experimental setup is shown in Fig. 1. For further details see Axelrod *et al.*,[15] Lanni and Ware,[16] and Davoust, Devaux, and Leger.[17] For monodisperse polymer chains the recovery curves are expected to be single exponentials.

Obviously in our case one has to be aware of possible migration of the probe from one micelle to another. We performed our experiments in dilute and semidilute regions with two different probes: hexadecanoylaminofluorescein and octadecanoylaminofluorescein. The second one has a longer aliphatic chain: This increases its residence time in the micelle by at least 1 order of magnitude.[18,19] At low concentration we found with both probes the same zero-concentration diffusion coefficient D_0 as the authors of Refs. 8 and 9, and, in the whole concentration range studied, no difference was observed between the two probes. So we conclude that, even if the probe migrates from one micelle to another, it has no measurable effect on the value of D_s.

Results.—Our experimental data are gathered in Fig. 2 where we have plotted on a log-log scale the values of D_s versus concentration. From these curves one may immediately conclude that we observe two regimes (as already proposed by the authors of Refs. 8 and 9): a dilute regime and a semidilute one in which D_s exhibits a power-law dependence on concentration. It should be noted that the recovery curves are different in the two regimes: slightly nonexponential in the dilute regime and perfectly exponential in the semidilute one (see Fig. 3). We must note that the effect of the temperature on the slope is not significant, while the effect of salt concentration on the slope is large: It goes from -4.4 at $0.05M$ KBr to -1.4 at $0.25M$ KBr.

Discussion.—It is clear that the exponents deduced from our experiments present an important difference with those predicted by the theories: They are strongly salinity dependent. However, we must note that the $0.25M$ exponent agrees with prediction.[5] We may then conclude that the solution at this salinity follows the above-mentioned thermodynamic model, while the discrepancy for the other salinities is harder to interpret: We lack, in fact, both theoretical and experimental data on the salinity dependence of the size distribution, which is probably more complicated than expected.

The living-polymer model is then to be used carefully to fit our data, but we may support it by considering the behavior of fluorescence recovery curves in both dilute and semidilute regimes.

In the dilute regime the micellar solution may be described as a polydisperse solution of amphiphile aggregates as proposed by all thermodynamic models. These aggregates behave as permanent objects and the resulting recovery curve is a superposition of the curves due to each species.

In the semidilute regime, one has also an entangled solution of polydisperse polymeric micelles. But in this case, since one has a single exponential behavior of the recovery curves, one may conclude that chain breakage and recombination occurs at characteristic times much smaller than the diffusion time. Thus the fluorescent probe explores the whole size distribution: Therefore we observe a single process for which the characteristic time is an average of the characteristic times associated with each species.

It still remains to explain the discrepancy between our results and those of Candau, Hirsch, and Zana, who observed a polymerlike behavior; once more, this can be done in the framework of the living polymers concept. Indeed, characteristic times of light-scattering and FRAP experiments, in the semidilute regime, are very different: 10^{-6} to 10^{-3} s for light scattering; 1 to 10^2 s for FRAP. One may then conclude that characteristic times of chain breakage and recombination are intermediate between these experimental times. So polymeric micelles behave as permanent chains for light scattering experiments and as living polymers for FRAP experiments.

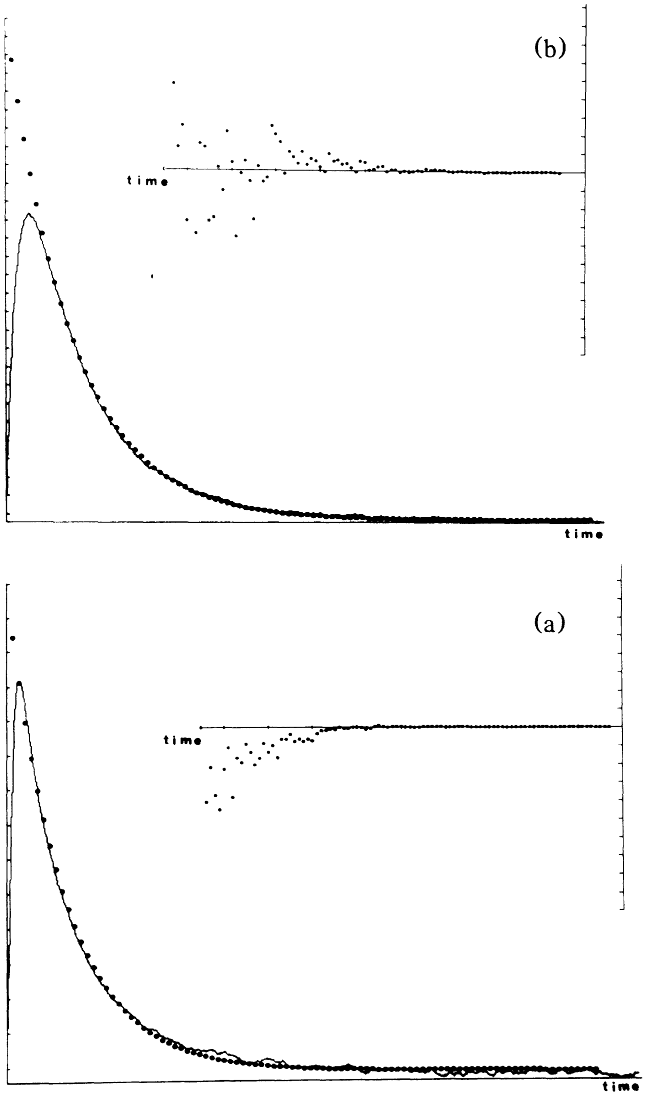

FIG. 3. Left curves: The decrease of the modulated fluorescence intensity (in arbitrary units) vs time. The continuous line is the experimental curve (the increasing section is due to the characteristic time of the lock-in amplifier), and the discontinuous one is the best exponential fit of the experimental one. (a) Dilute sample. (b) Semidilute sample. Right curves (inverted): Plots of residues (difference between experimental and theoretical curves). It is clear that curve (a) is nonexponential while (b) is exponential.

Finally the salt effect probably reflects some changes in the growth law of micellar aggregates, but we still lack some precise information, both experimental and theoretical, about this point.

Conclusion.—Our self-diffusion experiments on elongated micelles do not agree with polymer theories. This is explained by the fact that micelles are not permanent objects, and can break on experimental time scales. The reptation phenomenon is then critically affected and the self-diffusion coefficient is very different from the one expected for polymer solutions, and highly interaction (salinity) dependent.

We have then a system intermediate between classical, permanent polymers, and the new concept of fluctuating objects. We hope that in the near future, theories would allow us to unify these concepts, and it would then be possible to describe a large class of solutions by one unique law.

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