

On the location of the free ends of the insoluble block in micelles formed by diblock copolymers

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Summary

Nonradiative singlet energy transfer has been used to monitor the formation of micelles by diblock copolymers of poly(styrene) and poly(oxyethylene). The acceptor is placed at the junction between the two blocks in sample A1. The donor is placed either at the junction point between the blocks (D1) or free end of the block of poly(styrene) (D2). The experiment finds similar efficiencies of nonradiative singlet energy transfer in micelles formed by D1 and A1, and micelles formed by D2 and A1. This result implies that the free ends of the insoluble blocks do not seek out the center of mass of the micelle, but instead have a distribution throughout the micelle that is similar to the distribution of the junction points. Therefore the result confirms a crucial prediction from a recent simulation of the internal structure of the micelle formed by diblock copolymers in a selective solvent.

Introduction

It is well known that diblock copolymers can form micelles in dilute solution in a medium that is a good solvent for one block, and a poor solvent for the other block. The simplest model for this micelle postulates a close-packed, spherical core composed of the insoluble blocks, with the junction points between the two blocks located on the surface of this sphere, and the soluble blocks extending into the solvent as a corona.

Recently methods have been developed for simulating the micelles formed by diblock copolymers (1). A projection in two dimensions of a snapshot of the simulation of a micelle formed by twenty diblock copolymers is depicted in Figure 1. Each diblock copolymer contains 10 units of A and ten units of B. The Figure depicts the overall shape of the micelle, but it does not distinguish between the two types of blocks. The simulations do not find a sharp interface between the insoluble core and the soluble corona (2), and in this respect they are not in harmony with the simplest core-shell model. The simulations also find that there is surprisingly little difference between the distribution functions for the free ends of the insoluble block and the junctions between the two blocks.

Here we describe the result of an experiment that provides a test for the validity of this prediction from the simulations. The test makes use of diblock copolymers that have been labelled with a probe attached either at the junction points or at the free ends of the insoluble blocks. A spectroscopic experiment that is sensitive to the distribution of these probes in the micelle cannot distinguish one of the labelled

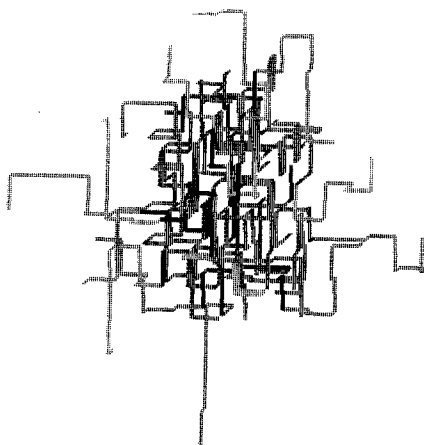


Figure 1. Projection in two dimensions of a snapshot of a micelle formed by twenty diblock copolymers, each of which contains 10 units of A and 10 units of B. The different types of units are not distinguished from one another in the snapshot.

samples from the other, which implies that the distribution of the labels in the micelle is similar in both cases, as predicted by the simulations.

Materials

The experiments were performed with three samples of diblock copolymers of poly(styrene) and poly(oxyethylene). One sample is labelled with pyrene at the junction point. The other two samples are labelled with naphthalene. The naphthalene is present at the junction point in the second sample, and at the free end of the poly(styrene) block in the final sample. The number average molecular weights of each block, the location of the label, and the fraction of the chains bearing labels are listed in Table 1, along with the abbreviation that will be used for each sample. The method used for the preparation of the labelled diblock copolymers has been presented elsewhere (3,4).

TABLE 1
Characterization of the Diblock Copolymers

| Sample | M_n PS | M_n POE | Label | Position | % Labelled |
|--------|----------|-----------|-------------|----------|------------|
| A1 | 5000 | 3800 | Pyrene | Junction | 90 |
| D1 | 5000 | 4900 | Naphthalene | Junction | 95 |
| D2 | 6000 | 4100 | Naphthalene | Free end | 90 |

Results

The experiment relies on the fact that naphthalene and pyrene constitute a donor-acceptor pair for nonradiative singlet energy transfer (Förster transfer) (5). A donor (naphthalene) in an excited singlet state can nonradiatively transfer its excitation to the acceptor (pyrene) with an efficiency, E , that depends on the distance, R , between the two probes according to the simple expression

$$E = \frac{R_0^6}{R_0^6 + R^6} \quad (1)$$

The Förster radius, denoted by R_0 , has the value 29 Å for this donor-acceptor pair. The efficiency falls off very rapidly as R rises above R_0 . In a dilute solution of A1 plus D1, or A1 plus D2, the labels will usually be separated by a distance much greater than R_0 if the medium is a good solvent for both blocks. The efficiency of Förster transfer will be low. If the medium is a good solvent for poly(oxyethylene) and a poor solvent for poly(styrene), the system will form micelles in which the blocks of poly(styrene) are located, on average, closer to the center of mass than are the blocks of poly(oxyethylene). In the system comprised of a mixture of A1 and D1, the value of E will be determined by the distance distribution in the micelle when both the donor and the acceptor are located at the junctions between the blocks. On the other hand, if the system is comprised of a mixture of A1 and D2, the efficiency of Förster transfer is determined by the distance distribution in the micelle when the donors are at the free ends of the insoluble block, and the acceptors are at the junctions.

The result of the experiment is reported in Figure 2. Here the ratio of the intensities of the fluorescence from the acceptor and donor, I_A/I_D , is used as a measure of the efficiency of Förster transfer. It is depicted as a function of the volume percent of methanol in the mixture of methanol and dichloroethane. The measurement was performed with an SLM 8000C fluorometer equipped with a double monochromator in the path for excitation. Excitation is at 270 nm, slit widths for excitation and emission are 8 nm, and I_A and I_D are monitored at 395 and 330 nm, respectively. The concentration of the copolymer is constant at 0.05 mg/ml, and the concentration of the labels is approximately 5×10^{-6} M for naphthalene and 2.5×10^{-6} M for pyrene.

The value of I_A/I_D changes by an order of magnitude as the solvent composition is varied using mixtures of dichloroethane and methanol. The smallest values of I_A/I_D are seen in media that are solvents for both blocks. As the medium becomes very rich in methanol, the values of I_A/I_D rise strongly. It is in this region that the system forms micelles, because the medium is no longer a good solvent for poly(styrene). The experiment shows that the manner in which the rise occurs in solvents rich in methanol is independent of whether the naphthalene label is placed at the junction point in the diblock copolymer, or at the free end of the insoluble block of poly(styrene).

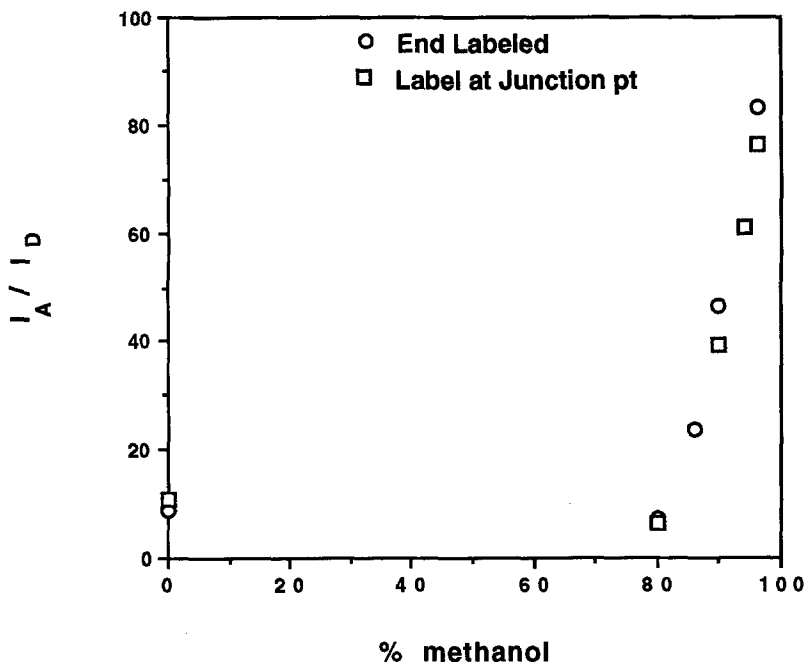


Figure 2. Values of I_A/I_D measured for mixtures of A1 and D1 (squares), or mixtures of A1 and D2 (circles), as a function of the volume % of methanol in mixtures of methanol and dichloroethane. The concentrations are: copolymer, 0.05 mg ml^{-1} ; naphthalene, $5 \times 10^{-6} \text{ M}$; pyrene, $2.5 \times 10^{-6} \text{ M}$.

Interpretation

The result depicted in Figure 2 suggests that the distribution of the free ends of the insoluble blocks in the micelle is similar to the distribution of the junction points. It is not compatible with a model that would place the junction points at the surface of a dense packed spherical core comprised of the insoluble blocks, with the free ends of the insoluble blocks located near the center of the core.

The simulation of the micelle (1,2) provides an explanation for the results. For each snapshot, we evaluate the squared radius of gyration, s^2 , of the free ends of the insoluble block, and also the squared radius of gyration of the junction points. During the course of the simulation, these squared radii of gyration fluctuate because the micelle is dynamically active. Figure 3 depicts the behavior of both squared radii of gyration over the course of the simulation. The dashed horizontal line is the expectation for the squared radii of gyration of the free ends *if* they are situated as close as possible to the center of mass of the micelle, without having double occupancy of any site on the lattice. The simulation never sees a micelle in which the actual distribution of the free ends is one in which they all seek out the center of mass. Instead the free ends have values of s^2 that fluctuate about much larger

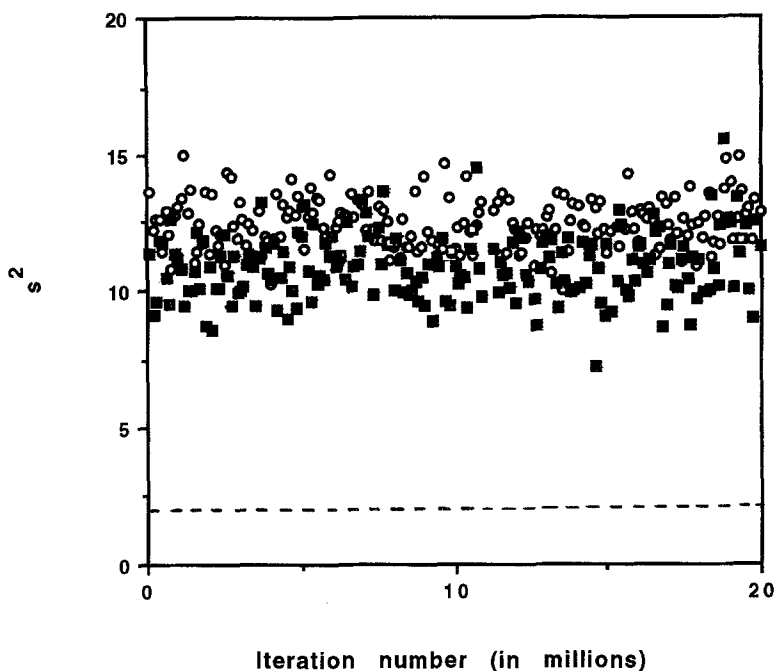


Figure 3. Instantaneous values of the squared radius of gyration of the junctions between the two blocks (open circles) and free ends of the insoluble blocks (filled squares). The dashed horizontal line is the expectation for the square radius of gyration of the free ends if they are located as close as possible to the center of mass.

values, and which overlap with the distribution of s^2 for the junction points. If one averages the values of s^2 over the entire simulation, one finds (2)

$$\langle s^2 \rangle_{free} = 0.89 \langle s^2 \rangle_{junctions} \quad (2)$$

It is worthwhile to inquire whether the slight differences in molecular weights and labelling of D1 and D2 might complicate the interpretation of the experiment. More precisely, might the free ends of the insoluble block truly be distributed near the center of mass, and we misinterpret the experiment because the small differences in the structures and labelling lead to an unexpectedly higher value of E in the case of D2? We note that D2 has a slightly larger block of poly(styrene) than does D1, and it also has a slightly lower degree of labelling. Both of these differences between D1 and D2 should work in the direction of producing a smaller (not larger) value of E in D2 + A1 than in D1 + A1. Therefore the conclusion that the free ends of the insoluble block do not seek out the center of mass is not compromised in the least by the slight differences in the structure and labelling of D1 and D2.

Conclusion

The behavior of the experiment confirms the prediction that the free ends of the insoluble blocks do not seek out the center of mass of the micelle, but instead have a distribution that places them nearly as far from the center of mass as the junction points. In this respect, the internal structure of the core of the micelle formed by diblock copolymers bears a closer resemblance to the model proposed by Dill (6) than the model proposed by Menger (7).

Acknowledgments

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