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Reply to Comments Concerning "Fluorescent Probe Studies on the Microstructure of Polystyrene–Poly(vinylpyridine) Diblock Copolymer Film"

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Acree et al.[8] criticize our use of intensity ratios instead of absolute peak intensities in estimating the partition coefficient of pyrene derivatives between two phases of a block copolymer system. Their comments provide an opportunity to examine in more detail practical and technical aspects of using pyrene fluorescence and the I_1/I_3 ratio to study phase-separated systems. To clarify the discussion, we consider the problem by differentiating it into two cases: (a) the system is a phase-separated solid film and (b) the system is a fluid solution.

In case a, the "preferential solvation model" by Acree and co-workers is essentially the same as our "two phase model". As they point out, eq 1 (in their paper) is a special case of eq 9. Equation 1 is justified under the assumption that $I_{3,\mathrm{solvent\ A}} = I_{3,\mathrm{solvent\ B}}$. Therefore, the validity of eq 1 depends on whether this assumption is correct. Acree and co-workers state that the assumption is too particular to be acceptable. In the specific case of pyrene and 1-alkylpyrene derivatives, however, this assumption is reasonable. Band 3 is a b_{1g} vibronic band of a forbidden $S_1(B_{3u}^-) \rightarrow S_0(A_g^-)$ electronic transition, and this band acquires its allowed character through a b_{1g} vibrational perturbation. As a consequence, the intensity of this band is not significantly affected by environment. In contrast to band 3, band 1 is the origin band with a completely forbidden character, so that its intensity is strongly affected by environmental perturbation, especially perturbation by polar media. This is the theoretical basis for the I_1/I_3 ratio to be a polarity parameter for microenvironments. The fact that I_3 is essentially independent of the pyrene environment is supported by many sets of experiments.[1–3]

Although eq 9 is more general than eq 1, the treatment by Acree et al. will meet severe difficulties in practice when applied to film samples because one has to measure the absolute intensities of bands 1 and 3, keeping the conditions constant for all samples. This is relatively easy in the case of transparent fluid solutions but is very difficult for film samples. The optical path length b (i.e., film thickness) will vary from sample to sample, and the effective intensity of the excitation light, P_0 will also fluctuate, depending upon the local surface conditions of the films.

On the other hand, one can avoid such difficulties in intensity ratio measurements because they do not require the measurement of absolute peak intensities. We now examine the specific assumptions necessary to obtain correct values of the partition coefficient for pyrene through measurements of the I_1/I_3 intensity ratios in film samples. The proportionality constant K' in eq 4 of Acree et al. can be expressed as a product of an instrumental response function $S(\lambda_j)$ and the fluorescence quantum yield $\phi(\lambda_j)$ of a band at wavelength λ_j. Here we define $\phi(\lambda_j)$ as $N_f(\lambda_j)/N_{\mathrm{abs}}$, where $N_f(\lambda_j)$ is the number of photons emitted as fluorescence at λ_j; N_{abs} is the number of photons absorbed by the fluorophore. Note that $\phi(\lambda_j)$ is different from the usual fluorescence quantum yield which is defined as $\sum N_f(\lambda_j)/N_{\mathrm{abs}}$. Now eq 8 of Acree et al. is written as:

$$F_{\mathrm{obs}}(\lambda_j) = \phi_{\mathrm{Py,A}}(\lambda_j)\, S(\lambda_j)\, P_0 b \epsilon_{\mathrm{Py,A}} Y_{\mathrm{A}}[Py] + \phi_{\mathrm{Py,B}}(\lambda_j)\, S(\lambda_j)\, P_0 \mathrm{B} \epsilon_{\mathrm{Py,B}}(1-Y_{\mathrm{A}})[Py] \quad (1)$$

where the constant 2.303 is omitted and the notations "fluoro" and "Fluoro" are replaced by "Py", for simplicity. Note that the dependence of the quantities on λ_j is explicitly shown in eq 1. It is obvious that $I_1 = F_{\mathrm{obs}}(\lambda_1)$ and $I_3 = F_{\mathrm{obs}}(\lambda_3)$. In fluorescence measurements we usually excite pyrene by $S_2 \leftarrow S_0$ or $S_3 \leftarrow S_0$ allowed transitions, so that ϵ_{Py} is not significantly affected by environment (i.e., $\epsilon_{\mathrm{Py,A}} \simeq \epsilon_{\mathrm{Py,B}}$). Therefore, the assumption that I_3 is constant irrespective of surroundings leads to the condition that $\phi_{\mathrm{Py,A}}(\lambda_3) = \phi_{\mathrm{Py,B}}(\lambda_3)$.

In homopolymers of A ($Y_{\mathrm{A}} = 1$) and B ($Y_{\mathrm{A}} = 0$), the I_1/I_3 ratio is expressed as:

$$(I_1/I_3)_{\mathrm{A}} = (I_1)_{\mathrm{A}}/(I_3)_{\mathrm{A}} = F_{\mathrm{obs,A}}(\lambda_1)/F_{\mathrm{obs,A}}(\lambda_3) = [\phi_{\mathrm{Py,A}}(\lambda_1)\, S(\lambda_1)]/[\phi_{\mathrm{Py,A}}(\lambda_3)\, S(\lambda_3)] \quad (2)$$

$$(I_1/I_3)_{\mathrm{B}} = (I_1)_{\mathrm{B}}/(I_3)_{\mathrm{B}} = F_{\mathrm{obs,B}}(\lambda_1)/F_{\mathrm{obs,B}}(\lambda_3) = [\phi_{\mathrm{Py,B}}(\lambda_1)\, S(\lambda_1)]/[\phi_{\mathrm{Py,B}}(\lambda_3)\, S(\lambda_3)] \quad (3)$$

For an A–B block copolymer with separate microdomains of A and B:

$$(I_1)_{\mathrm{AB}} = \phi_{\mathrm{Py,A}}(\lambda_1)\, S(\lambda_1)\, P_0 \mathrm{b} \epsilon_{\mathrm{Py,A}}\, Y_{\mathrm{A}}[Py] + \phi_{\mathrm{Py,B}}(\lambda_1)\, S(\lambda_1)\, P_0 \mathrm{b} \epsilon_{\mathrm{Py,B}}\, (1-Y_{\mathrm{A}})[Py] \quad (4)$$

$$(\mathrm{I}_3)_{\mathrm{AB}} = \phi_{\mathrm{Py,A}}(\lambda_3)\, S(\lambda_3)\, P_0 b \epsilon_{\mathrm{Py,A}}[\mathrm{Py}] = \phi_{\mathrm{Py,B}}(\lambda_3)\, S(\lambda_3)\, P_0 b \epsilon_{\mathrm{Py,B}}[\mathrm{Py}] \quad (5)$$

It should be noted that eq 5 is derived under the assumption that $\phi_{\mathrm{Py,A}}(\lambda_3) = \phi_{\mathrm{Py,B}}(\lambda_3)$ and $\epsilon_{\mathrm{Py,A}} = \epsilon_{\mathrm{Py,B}}$. These are the key assumptions, which are valid for pyrene but which may not be valid for other chromophores. Dividing eq 4 by eq 5 and taking eqs 2 and 3 into account, we obtain

$$\begin{aligned}(I_1/I_3)_{\mathrm{AB}} &= (I_1)_{\mathrm{AB}}/(I_3)_{\mathrm{AB}} \\ &= Y_{\mathrm{A}}[\phi_{\mathrm{Py,A}}(\lambda_1)\, S(\lambda_1)\, /\phi_{\mathrm{Py,A}}(\lambda_3)\, S(\lambda_3)] + (1 - Y_{\mathrm{A}})[\phi_{\mathrm{Py,B}}(\lambda_1)\, S(\lambda_1)/\phi_{\mathrm{Py,B}}(\lambda_3)\, S(\lambda_3)] \\ &= Y_{\mathrm{A}}(I_1/I_3)_{\mathrm{A}} + (1 - Y_{\mathrm{A}})(I_1/I_3)_{\mathrm{B}} \qquad (6)\end{aligned}$$

From the above procedure for deriving eq 6, we understand that one can obtain Y_{A} from the band intensity ratio I_1/I_3 instead of having to measure the absolute intensity of each band. In contrast to absolute intensities I_1 and I_3, the relative intensity I_1/I_3 does not vary even if b and P_0 fluctuate. Therefore, eq 6 is useful especially for systems in which the measurement of absolute intensities is difficult.

In case b, the case of fluid solution, the Acree approach will work well for partition equilibria as, for example, in micellar systems. In terms of preferential solvation, this model is often invalid because it is well known that pyrene interacts specifically with certain polar solvents. For several solvents the formation of a molecular complex with pyrene has been reported.[4–6] Equation 9 of Acree et al. is not applicable to such complex systems. The existence of specific interactions between pyrene and various solvents is the major reason why all attempts have failed to explain the anomalous enhancement of the 0–0 band

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of pyrene in terms of the bulk properties of solvents.

In closing, we note that the major intent of our original publication[7] was to show that pyrene derivatives bearing strong hydrogen-bond donor groups (-OH, -COOH) locate essentially exclusively in the poly(vinylpyridine) phase of PVP-PS block copolymer films. Pyrene itself and simple pyrene derivatives which are not H-bond donors partition between the two phases. The contribution by Acree et al. and this short note help to clarify how one calculates partition coefficients in this particular case.

References and Notes

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