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

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Recently, Nakashima and co-workers[1] developed a spectrofluorometric probe method to examine partitioning of pyrene, 4-(1-pyrenyl)butanoic acid, 1-pyrenemethyl hexyl ether, 4-(1-pyrenyl)butanol, and 1-pyrenemethanol between the polystyrene (PS) and poly(vinylpyridine) (PVP) chains in the PS–PVP diblock copolymer. The method assumed that the measured fluorescence emission intensity ratio for vibronic bands one and three, I_1/I_3, was

$$(I_1/I_3)_{BCP} = Y_{PVP}(I_1/I_3)_{PVP} + (1 - Y_{PVP})(I_1/I_3)_{PS} \quad (1)$$

a weighted average of the fluorophore's intensity ratios in the "pure" microphases, where Y_{PVP} is the mole fraction of the probe in PVP. Through suitable mathematical manipulations, the authors claimed that it was possible to determine the fraction of fluorophore in each microphase and the corresponding partition coefficient from the measured fluorescence intensity ratios.

Unfortunately, eq 1 is not consistent with standard spectroscopic principles, as fluorescence emission intensity ratios are by no means additive. To prove this, we will consider a very simple case involving a spectrofluorometric probe molecule dissolved in two different microphases as depicted in the simulated partitioning scheme in Figure 1. Each fluorophore contributes to the observed fluorescence signal, F_{obs}, at each emission wavelength scanned

$$F_{obs} = K'_{fluoro\ A}(P_0 - P_{fluoro\ A}) + K'_{fluoro\ B}(P_0 - P_{fluoro\ B}) \quad (2)$$

where P_0 refers to the intensity of the incoming monochromatic excitation radiation and $P_0 - P_{fluoro\ i}$ is the amount of radiation absorbed by solvated fluorophore type i. Proportionality constants, $K'_{fluoro\ A}$ and $K'_{fluoro\ B}$, depend upon the various optical component placements within the instrument, detector response/efficiency, and quantum yield of the given solvated fluorophore.

Using the Beer–Lambert law to relate the intensity of unabsorbed excitation radiation to the fluorophore concentration, followed by suitable mathematical manipulation, one obtains the following expression

$$F_{obs} = 2.303K'_{fluoro\ A}P_0 b\epsilon_{fluoro\ A}Y_A[fluoro] +$$
$$2.303K'_{fluoro\ B}P_0 b\epsilon_{fluoro\ B}(1 - Y_A)[fluoro] \quad (3)$$

for the measured emission intensity. Here, $\epsilon_{fluoro\ i}$ refers to the fluorophore's molar extinction coefficient in microphase i, [fluoro] is the total stoichiometric fluorophore
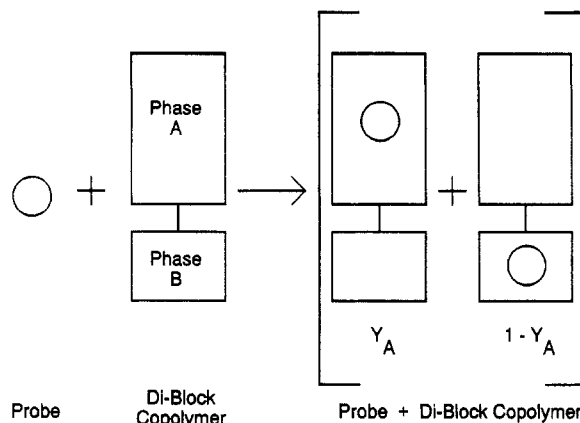
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Figure 1. Schematic representation depicting preferential partitioning of a probe molecule between two different microphases. The solvational sphere around every probe molecule is assumed to be solvated by only one type of polymer chain, which provides the microphase region.

molar concentration, and Y_A and $1 - Y_A$ represent the mole number fraction of each type of solvated fluorophore, i.e., Y_A = [fluoro A]/[fluoro] and $1 - Y_A$ = [fluoro B]/[fluoro]. Inherent in the above treatment is the underlying assumption that neither microphase (or polymer chain) forms a nonfluorescent association complex with the fluorophore. If such complexation does occur, then eq 3 describes only the fraction of the solute molecules that actually fluoresce.

Examination of eq 3 reveals that the observed polycyclic aromatic hydrocarbon (PAH) emission spectrum is a weighted mole fraction average of the fluorophore's spectra in each of the two pure microphases, provided that the molar concentration of fluorophore remains constant for each series of measurements. Emission intensities are additive at each wavelength. In the case of a PAH solvent polarity probe such as pyrene, the calculated I_1/I_3 emission intensity ratio is

$$I_1/I_3 \approx [Y_A I_{1,phase\ A} + (1 - Y_A)I_{1,phase\ B}]/[Y_A I_{3,phase\ A} + (1 - Y_A)I_{3,phase\ B}] \quad (4)$$

Here, we have assumed that both the one and three band emission wavelengths are medium independent, which is not strictly true; hence, the approximately equal to sign is used. Rigorous appplictions require that intensity measurements be made at two fixed emission wavelengths. Readers should note that the correct mathematical description for how emission intensity ratios vary with microphase composition is not a simple weighted fraction average of ratios in the pure microphases, as assumed in eq 1, except under the very special set of circumstances that $I_{3,phase\ A} = I_{3,phase\ B}$. To our knowledge, there is no experimental evidence to justify this particular assumption in the case of the five solutes that Nakashima and co-workers[1] considered.

References and Notes

(1) Nakashima, K.; Winnik, M. A.; Dai, K. H.; Kramer, E. J.; Washiyama, J. *Macromolecules* **1992**, *25*, 6866.