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Notes

Blob Model Analysis of the pH-Induced Fluorescence Quenching of Two Anthracene-Labeled Poly(2-vinylpyridine)s

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In a previous paper in this issue, Clements and Webber used fluorescence to investigate the behavior of two monodisperse poly(2-vinylpyridine)s (PVP) which are labeled with anthracene at either one end of the chain (BA-e-PVP) or the middle of the chain (A-m-PVP).[1] Addition of 0.1 M HCl to the PVP solutions leads to the protonation of the pyridine rings and ionization of the polymers. Both anthracene-labeled PVPs are soluble for degrees of protonation (α) larger than 0.20. α is defined as the ratio $[PH^+]/([P] + [PH^+])$, where [P] and $[PH^+]$ represent the concentration of unprotonated and protonated pyridine units, respectively. Upon addition of HCl to the PVP solutions, the authors report for α values larger than 0.23 that the protonated pyridines quench efficiently the excited anthracene via an electron-transfer mechanism.[1] A Bernoullian statistical model was applied to fit the trends obtained for the fluorescence quenching of anthracene. Satisfactory fits were obtained when the authors assumed that the pyridines next to the anthracene were preferentially protonated. For A-m-PVP, preferential protonation of the pyridines next to the anthracene was found to occur very efficiently for α values between 0.23 and 0.43, but less so for α values between 0.43 and 0.60.

Interestingly, additional information about the polymeric system studied by Webber and Clements can be gained by using the fact that “the quenching is the result of electron-transfer from the excited anthracene to neighboring pyridinium units”.[1] It is often the case that the occurrence of quenching over a short distance grants the use of a simple static-quenching approach of the type used for surfactant micelles.[2] As for the traditional Perrin model based on the concept of the sphere of action, a volume centered on the chromophore is defined within which quenching can occur with a probability of 1.0.[3] The model assumes that only those chromophores located inside spheres of action devoid of quenchers will fluoresce.[2,3] Because the concept of the sphere of action was initially derived to study homogeneous systems, it needs to be adapted to polymeric systems where the photophysical process occurs intramolecularly inside a polymer coil. By analogy with the work carried out by theoreticians studying polymeric systems,[4] the sphere of action can be referred to as a blob in the case of polymers.[5−9] The polymer chain is divided into blobs into which the quenchers will distribute themselves randomly according to a Poisson distribution. In the case of BA-e-PVP and A-m-PVP, the quenchers are the protonated pyridines which are assumed to distribute themselves randomly among the blobs. There are now a few examples where blob models have been used successfully to analyze the fluorescence data obtained with several other polymeric systems.[5−9] The main difference existing between the blob model used for polymeric systems[5−9] and the Turro−Yekta (TY) model used for surfactant micelles[2] lies in the definition of the sphere of action used in each system. In the TY model, the sphere of action is defined by the physical boundary of the surfactant micelle; i.e., the radius of the sphere of action equals the radius of the surfactant micelle. In the blob model, the sphere of action is defined by the photophysical properties of the chromophore and its quencher; i.e., the radius of the sphere of action is related to the distance over which quenching occurs.

A blob model representation of the anthracene-labeled PVPs is depicted in Scheme 1. It is assumed that quenching can occur between anthracene and several protonated pyridine units yielding blobs made up of 10 pyridine units for A-m-PVP and 5 pyridine units for BA-e-PVP. The actual number of pyridine units per blob will be determined by the analysis.

Following the work by Turro and Yekta carried out with surfactant micelles[2] and applying it to polymeric systems, fluorescence is emitted by those blobs which contain one dye with no quencher. The probability of having no quencher inside a blob equals $\exp(-\langle n\rangle)$ where $\langle n\rangle$ is the average number of quenchers per blob. It can be shown that the ratio I/I_o equals $\exp(-\langle n\rangle)$,[2] where I and I_o represent the fluorescence intensities of the solution in the presence and absence of quencher, respectively. The implication to BA-e-PVP and A-m-PVP are that only those blobs which contain the anthracene with no protonated pyridine unit will fluoresce and that the ratio $I(\alpha)/I_o$ equals $\exp(-\langle n\rangle)$, where $I(\alpha)$ is the fluorescence intensity of the PVP solutions obtained with a given α value and $\langle n\rangle$ is the average number of protonated pyridines per blob. Because a minimum level of protonation ($\alpha_{min} > 0.20$) must be reached to ensure the solubilization of BA-e-PVP and A-m-PVP, fluorescence measurements were acquired for protonation levels larger than α_{min}. Consequently, only the ratio $R(\alpha) = I(\alpha_{min})/I(\alpha)$ is obtained experimentally.[1]

The average number of protonated pyridines per blob equals $[PH^+]$/[blob] where [blob] is the blob concentration. The blob concentration is obtained by dividing the total pyridine concentration ($[P]_T$) by N_{blob}, where N_{blob} is the number of pyridine units inside a blob. The degree of protonation of the polymer, α, equals $[PH^+]/[P]_T$. Consequently, one finds eq 1

$$\ln\left(\frac{I_o}{I(\alpha)}\right) = \langle n\rangle = \alpha N_{blob} \qquad (1)$$

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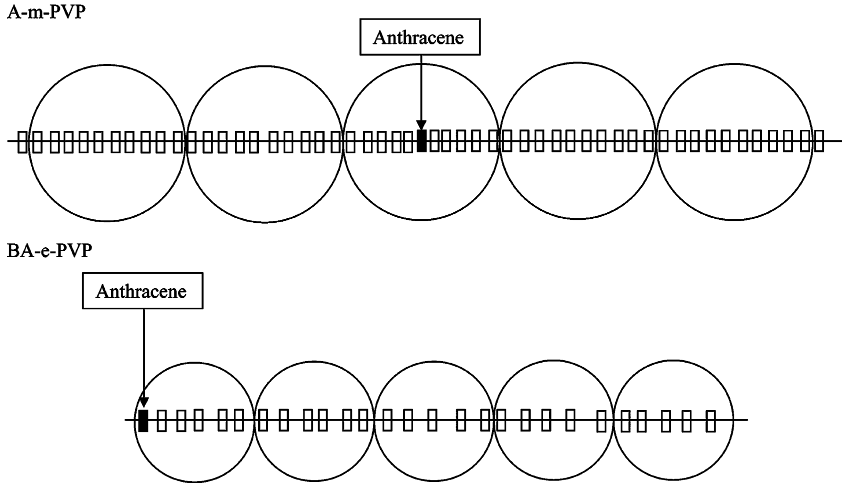
Scheme 1



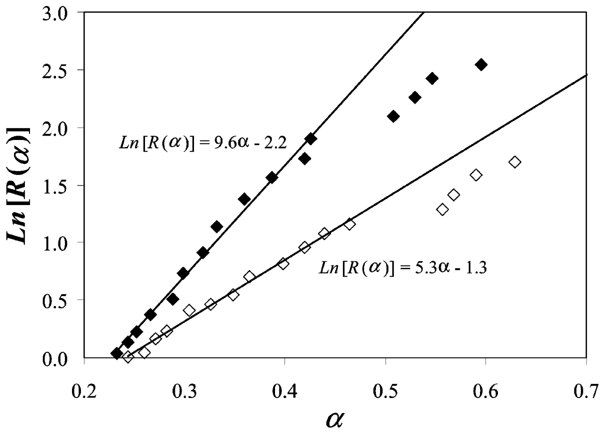


Figure 1. Plot of $\ln[R(\alpha)]$ as a function of α for the polymer A-m-PVP (◆) and BA-e-PVP (◇). Data taken from Clements and Webber.[1] Fit carried out according to eq 2.

which can be rewritten in terms of the ratio $R(\alpha)$ used by Clements and Webber[1]

$$\ln(R(\alpha)) = \alpha N_{\text{blob}} - \ln\left(\frac{I_o}{I(\alpha_{\min})}\right) \qquad (2)$$

where $\ln(I_o/I(\alpha_{\min}))$ is a constant.

Using the data provided by Clements and Webber, a plot of $\ln[R(\alpha)]$ yields nice straight lines between 0.23 ± 0.01 and 0.44 ± 0.02 as shown in Figure 1 for both A-m-PVP and BA-e-PVP, respectively. The fit of the data shown in Figure 1 with eq 2 yields the slopes of the straight lines. The slopes provide the size of the blobs being 5.3 and 9.6 pyridine units for BA-e-PVP and A-m-PVP, respectively. The fact that the N_{blob} value for BA-e-PVP with pyridines located on one side of the anthracene is about half that of A-m-PVP with pyridines located on both sides of the anthracene implies that the excited anthracene is quenched by those protonated pyridines which are within a stretch of five pyridines directly adjacent to the anthracene. In other words, sections of the PVP chain which are located farther away from the anthracene do not loop back to participate in the quenching mechanism. This is certainly a consequence of the electrostatic repulsion which takes place between the protonated segments of the PVP backbone. The excited anthracene of A-m-PVP which is flanked by two PVP chains is being quenched by only those protonated pyridines which are within two stretches of five pyridines directly adjacent to the dye. This result agrees with Clements and Webber's conclusion which states that the excited anthracene is quenched by neighboring pyridinium units.[1]

According to Figure 1, eq 2 fits the data well up to the discontinuity observed by Clements and Webber for α values of 0.46 and 0.43 for BA-e-PVP and A-m-PVP, respectively.[1] This corresponds to $\langle n \rangle$ values of $1.2 + 1.3 = 2.5$ and $1.9 + 2.2 = 4.1$ for BA-e-PVP and A-m-PVP, respectively. In other words, the blobs are about half full. This high level of loading of the blobs requires checking that the blobs of BA-e-PVP and A-m-PVP have a low probability of having more than 5 and 10 protonated pyridines per blob, respectively. This is because a blob cannot contain more protonated pyridines than the number of pyridine units, N_{blob}, it is made of. The probabilities of having more than 5 and 10 protonated pyridines for BA-e-PVP and A-m-PVP can be calculated by using the Poisson probabilities of finding i ($i < 5$ or 10) quenchers per blob, summing them, and subtracting the sum from 1.0. These probabilities equal 0.042 and 0.003 for BA-e-PVP and A-m-PVP, respectively. These values are small which ensures the validity of the blob model analysis in the range of α values between 0.23 ± 0.01 and 0.44 ± 0.02. Problems might arise with the blob model analysis for α values larger than 0.46 especially in the case of BA-e-PVP for which the probability of finding a number of protonated pyridines larger than N_{blob} cannot be neglected anymore.

The discontinuities observed for α values of 0.46 and 0.43 for, respectively, BA-e-PVP and A-m-PVP indicate that quenching is less efficient at higher levels of protonation. It is well-known that electron transfer efficiency is drastically reduced when the distance between the electron-donor (the excited anthracene) and acceptor (the protonated pyridines) increases.[10] It is thus possible that PVP adopts a conformation where the protonated pyridines stretch away from anthracene because of electrostatic repulsion for α values larger than 0.44 ± 0.02. More work is required to demonstrate that this might be happening.

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References and Notes

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