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Abstract

The behaviour of polymeric chains at the molecular level has momentous implication in phenomena such as proteins folding, electron-transfer processes or in the rheology of viscosity modifiers. It is therefore not surprising that significant research has been deployed to characterize the chain dynamics of polymers. One important approach is fluorescence dynamic quenching (FDQ) which measures the rate of encounter of a chromophore and a quencher attached to a polymer. The complexity of the mathematical analysis of the fluorescence decays for randomly labeled polymers has been successfully handled with the development of the fluorescence blob model (FBM).¹ Ruthenium-labeled polymers are also particularly interesting as they stand as promising candidate for light-harvesting and hydrogen production.²

From this viewpoint, statistical copolymers of styrene and 4-aminostyrene have been synthesized and covalently attached to Ru(II) complexes. The 4-aminostyrene units present can be directly used as a quencher and inhibited to a desired level by acetylation. UV-visible analysis was used to determine the ruthenium and quencher contents, and luminescence spectroscopy allowed us to investigate the photophysical properties of the polymers. Analysis using the FBM was also undertaken.

Fluorescence Blob Model (FBM)

The fluorescence blob model (FBM) was devised to enable the study of complex fluorescence decays and to extract information regarding the dynamics of polymer chains.³ Building on the theoretical work developed for micellar systems, the FBM divides a polymer coil into sub-volumes or *blobs*, defined as the volume probed by an excited chromophore during its lifetime.



The time-dependent concentration profile of the chromophore is given by the following equations:

$$f(t) = f_{diff} \exp\left[-\left(A_2 + \frac{1}{\tau_M}\right)t - A_3(1 - \exp(-A_4 t))\right] + f_{free} \exp\left(-\frac{t}{\tau_M}\right)$$

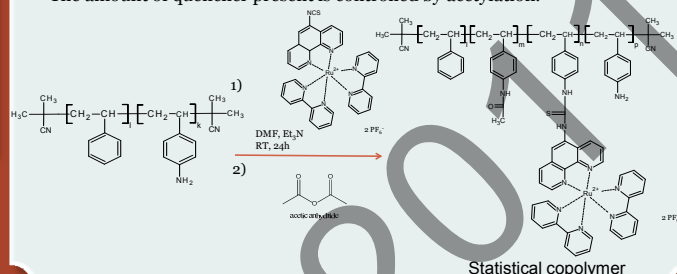
$$A_2 = \langle n \rangle \frac{k_{blob} k_e [blob]}{k_{blob} + k_e [blob]} \quad A_3 = \langle n \rangle \frac{k_{blob}^2}{(k_{blob} + k_e [blob])^2} \quad A_4 = k_{blob} + k_e [blob]$$

From the choice of a particular quencher and its lifetime, one can selectively probe short or long range interactions. The following parameters obtained from the analysis of luminescence decays provide information regarding the dynamics of the polymeric chains:

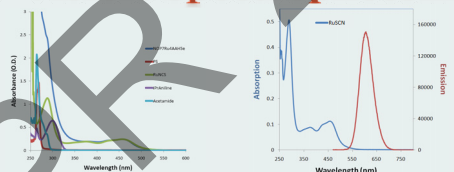
- k_{blob} : Rate constant of diffusional encounter between a chromophore and a quencher
- k_e : Rate of exchange of a quencher between blobs
- $[blob]$: Local concentration of blobs within the polymer coil
- $\langle n \rangle$: Average number of quencher per blob

Synthesis

- Synthesis of a statistical copolymer of styrene and 4-aminostyrene by radical polymerization using AIBN as an initiator.
- The amino groups are reacted with the chromophore and used as quencher.
- The amount of quencher present is controlled by acetylation.



UV-Visible Spectrophotometry



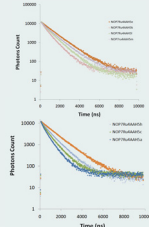
- Ruthenium and quencher contents are determined by UV-Vis spectrophotometry using Beer-Lambert law: $A = \epsilon lc$

(A is the absorbance, ϵ the molar extinction coefficient, l the path length, and c the concentration.)

Luminescence Decays

The photophysical properties of the polymers were determined using time-correlated single-photon counting method. The luminescence decays were fitted with a sum of 2 exponential functions:

$$i(t) = \sum_{j=1}^{n_{exp}} a_j e^{-t/\tau_j}$$



	No Quencher	NOP7Ru4AAH5m (2.6%)	NOP7Ru4AAHSI (3.4%)	NOP7Ru4AAHSK (4.4%)
τ_1 ns (a _j)	1338 (0.5)	1078 (0.8)	958 (0.7)	816 (0.6)
τ_2 ns (a _j)	912 (0.5)	424 (0.2)	393 (0.3)	345 (0.4)
τ_{av} ns	1106	941	786	632
χ^2	1.01	1.14	1.10	1.16

	No Quencher	NOP7Ru4AAH5h (3.6%)	NOP7Ru4AAH5C (5.0%)	NOP7Ru4AAH5a (6.0%)
τ_1 ns (a _j)	1338 (0.5)	954 (0.7)	809 (0.6)	696 (0.5)
τ_2 ns (a _j)	912 (0.5)	436 (0.3)	363 (0.4)	290 (0.5)
τ_{av} ns	1106	774	616	493
χ^2	1.01	1.16	1.58	1.39

Blob Model Analysis

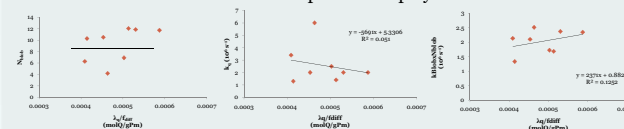
Analysis of the luminescence decays from the 1st series with the FBM allows the determination the following parameters, and N_{blob} :

Exp.	χ^2	Exch ($10^3 s^{-1}$)	f_{diff}	k_q ($10^7 s^{-1}$)	$\langle n \rangle$	$k_e \langle n \rangle$ ($10^7 s^{-1}$)	τ_4 (ms)
4.4%	1.68	16	0.89	2.0	0.70	1.3	1118
3.4%	1.04	17	0.77	3.4	0.38	1.3	1118
2.6%	1.20	13	0.51	6.0	0.29	1.7	1118

$$N_{blob} = \frac{\langle n \rangle}{\left(\frac{\lambda_Q}{\lambda}\right) [M_Q x_Q + M_D x_D + M_{inh} x_{inh} + M(1 - x_Q - x_D - x_{inh})]}$$

- N_{blob} : Number of structural units per blob
- λ_Q : Number of moles of quencher per gram of polymer
- f : Fraction of luminophore quenched
- M_Q, M_D, M_{inh} : Molar masses of the aniline, Ru-containing and acetanilide structural units, respectively

The results obtained for all the samples are displayed below:



This study allows to bridge the gap between the investigations realized with pyrene as a chromophore and with those realized with ruthenium. Comparison with similar pyrene-labeled PS described in the literature⁴ seem to indicate the presence of a more rigid system with a smaller N_{blob} .

	Py-PS ⁴	Ru-PS
N_{blob}	56 (± 3)	9 (± 3)
k_{blob} ($10^7 s^{-1}$)	0.9 (± 0.1)	0.2 (± 1.5)
$k_{blob} \times N_{blob}$ ($10^7 s^{-1}$)	49 (± 4)	2 (± 0.4)

The quenching rate constant (k_q) obtained from a Stern-Volmer analysis, reveals a less efficient quenching of the ruthenium luminophore when compared to pyrenemethanol:

	PyMeOH	RuNCS
k_q ($10^7 M^{-1} s^{-1}$)	140	8.4

Conclusions & Future Work

- Blob model: Applicable to Ru(II)-containing polymers
- This study allows the comparison between ruthenium and pyrene-labeled polymers
- Origin of the differences observed (stiffness of the chains, quenching rate constant, etc.)
- Effect of Pd as a quencher