Temperature Response of Aqueous Solutions of a Series of Pyrene End-Labeled Poly(N-isopropylacrylamide)s Probed by Fluorescence

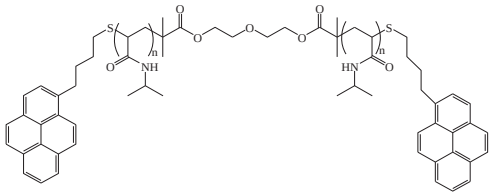
Michael A. Fowler,[1] Jean Duhamel,[1] Xing Ping Qiu,[2] Françoise Winnik[2]

[1]*Department of Chemistry, University of Waterloo, ON, CANADA N2L 3G1*

[2]*Faculty of Pharmacy and Department of Chemistry, Université de Montréal, CP 6128 Succursale Centre Ville, Montréal QC H3C 3J7, Canada*

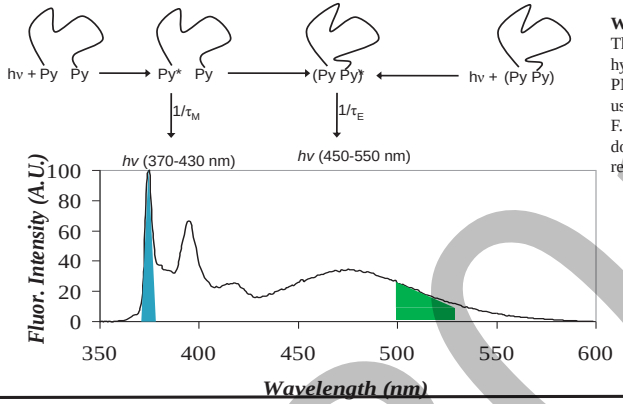
Background

In this study, a series of poly(N-isopropylacrylamide) (PNIPAM) polymers end-labeled with pyrene were dissolved in aqueous solution and their fluorescence properties were determined as a function of temperature.



Sample Mw:
14k
25k
45k

PNIPAM was chosen since it possesses a lower critical solution temperature (LCST) commonly reported as 32 ºC. Pyrene was chosen since it is strongly hydrophobic, fluorescent and able to form an excited dimer called an excimer.



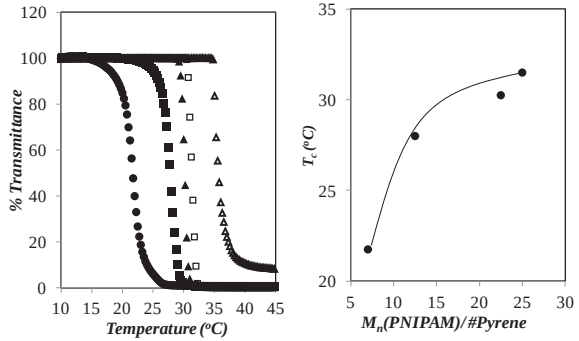
Winnik et al. Model:
The behaviour of hydrophobically end-labelled PNIPAM has been described using a model developed by F. M. Winnik et al., broken down into 3 thermodynamic regimes.

Regime I
- Temperatures below T_c.
- Chains form micelles with a shell of hydrated PNIPAM, a hydrophobic core composed of pyrene labels, and a middle region composed of dehydrated PNIPAM
- As T increases, PNIPAM in the shell dehydrates and the micelles decrease in size

Regime II
- Temperatures between T_c and T_m.
- At T_c, the PNIPAM micelles aggregate to form particles called mesoglobules.
- As T increases, PNIPAM further dehydrates as the mesoglobules grow in size.
- Eventually, the core-shell structures within the mesoglobules are disrupted and the hydrophobes disperse throughout a continuous phase of dehydrated PNIPAM.

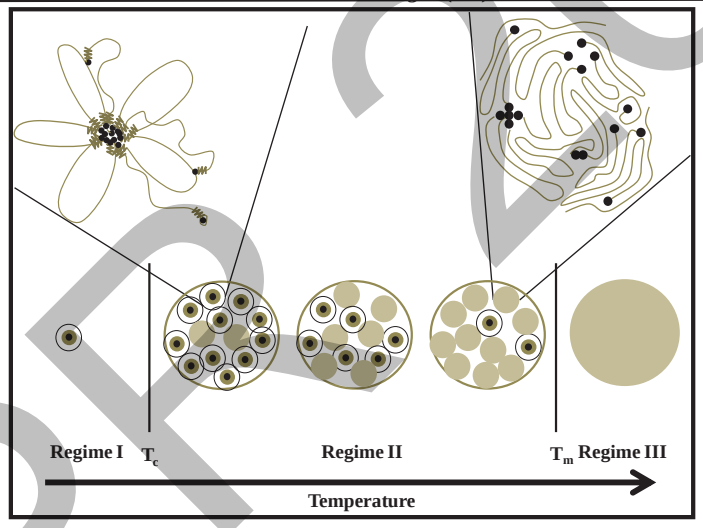
Regime III
- Temperatures above T_m.
- The PNIPAM chains have finished dehydrating.
- The mesoglobules are stable in both size and composition

LCST Determination by Turbidimetry:

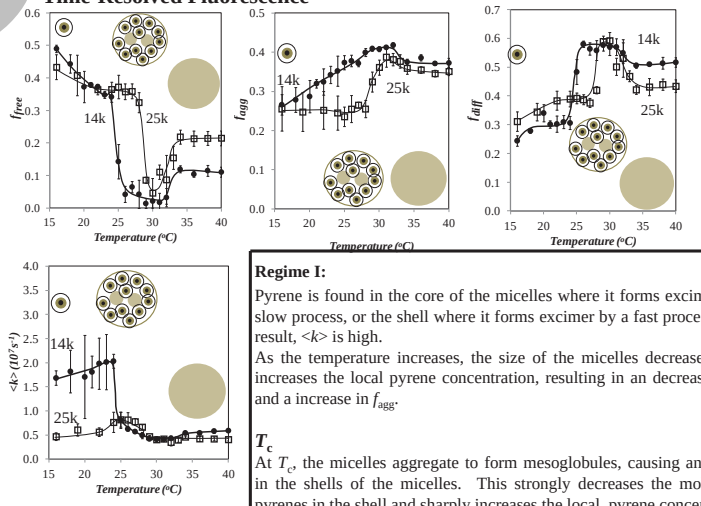


(●) Py_2-PNIPAM(14K), (■) Py_2-PNIPAM(25K), (▲) Py_2-PNIPAM(45K), (□) Py_1-PNIPAM(25K), (Δ) PNIPAM(22K). [Polymer] = 0.5 g/L

As the M_w increases, the pyrene content decreases and the LCST (T_c) increases.



Time-Resolved Fluorescence



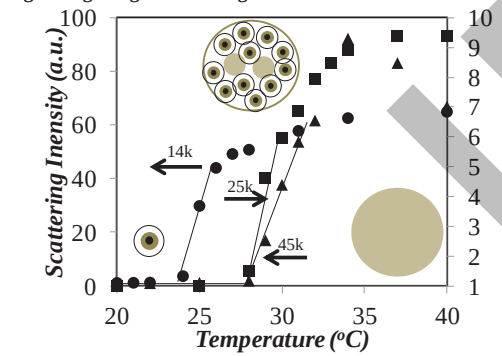
Regime I:
Pyrene is found in the core of the micelles where it forms excimer via a slow process, or the shell where it forms excimer by a fast process. As a result, <*k*> is high.
As the temperature increases, the size of the micelles decreases. This increases the local pyrene concentration, resulting in an decrease in f_{free} and a increase in f_{agg}.

T_c
At T_c, the micelles aggregate to form mesoglobules, causing an overlap in the shells of the micelles. This strongly decreases the mobility of pyrenes in the shell and sharply increases the local pyrene concentration, hence the sharp drop in <*k*> and f_{free}, and the sharp increase in f_{diff}.

Regime II:
<*k*> and the fluorescence fractions remain stable in Regime II until the temperature causes the micelles to disperse. This causes the local pyrene concentration to decrease, reducing f_{agg} and f_{diff} but increasing f_{free}.

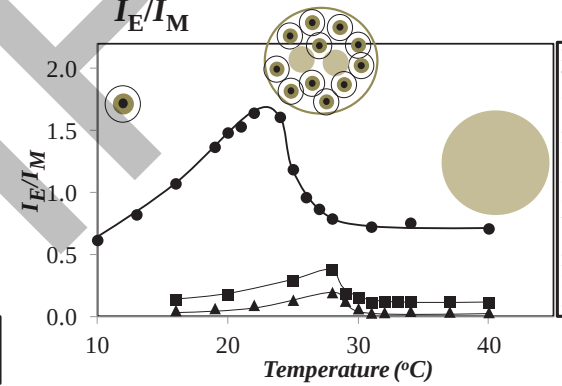
Regime III:
At T_m the solution enters Regime III, where the micelle behaviour stabilizes. This is reflected in the stable values for <*k*> and the fluorescence fractions.

Right-Angle Light Scattering:



(●) Py_2-PNIPAM(14K), (■) Py_2-PNIPAM(25K), (▲) Py_2-PNIPAM(45K)

Under the dilute conditions used for fluorescence, the light scattering intensity of the sample was far more sensitive than turbidimetry and was used to determine T_c.



Regime I:
The I_E/I_M ratio increases due to a decrease in the size of the micelles

Regime II:
I_E/I_M decreases as the micelles aggregate to form mesoglobules, either decreasing the mobility or the concentration of pyrene

Regime III:
I_E/I_M is stable since the micelles are stable

Conclusions:

Light scattering, steady-state and time-resolved fluorescence were used to determine the aggregation behaviour of pyrene-labelled polymers in aqueous solution as the temperature increased. The samples show changes in behaviour that are consistent with what is predicted by the model proposed by F. M. Winnik et al.