Temperature Effects on the Solution Behaviour of Pyrene-Labeled Poly(N-Isopropylacrylamide)

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Abstract

A series of poly(N-isopropylacrylamide) (PNIPAM) polymers end-labeled with pyrene were dissolved in aqueous solution and their light scattering and fluorescence properties were determined as a function of temperature. Light scattering measurements showed a sharp increase in particle size at a temperature below the LCST (measured by % Transmittance). Steady-state and time-resolved measurements showed distinct changes in fluorescence emission as the light scattering intensity increased. Analysis of the fluorescence decays showed a decrease in pyrene mobility above the LCST.

Introduction

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. PNIPAM is known to possess a lower critical solution temperature (LCST) commonly reported as 32 °C.

Pyrene was chosen as a fluorescent label for PNIPAM due to its ability to form an excited dimer (excimer) species which emits at much longer wavelengths than the monomer.

Excimer can form either from the direct excitation of a ground-state dimer or by the diffusional encounter of an excited pyrene monomer with a ground state monomer. The intensity ratio of excimer vs. monomer (IE/IM) is obtained via steady-state fluorescence and informs on the relative amount of excimer formation. The amount of excimer specifically formed by diffusion can be determined from the excimer fluorescence decay, via multi-exponential fits of the time-resolved fluorescence decays.

Effect of Molecular Weight (Mw):

- Increasing the Mw of the polymer chain has a number of effects:
  - It increases the average distance between two pyrenes, thus lowering the rate of excimer formation by diffusion.
  - It reduces the pyrene content of the chain affecting the water solubility, aggregation behaviour and LCST of the chains.

The temperature was varied in order to determine the samples' behaviour below, at, and above the lower critical solution temperature (LCST) of aqueous solutions of PNIPAM. The pyrene labeled PNIPAM samples were dissolved in either water, or an aqueous solution containing a ten-fold excess of unlabelled PNIPAM. The unlabelled PNIPAM was added in an attempt to reduce the effect of the hydrophobic pyrene labels on the aggregation level of the PNIPAM chains below the LCST.

Results and Discussion

LCST Determination by Turbidimetry:

As the Mw increases and/or the pyrene content decreases, the LCST increases. This implies that the pyrene end groups are causing the chain to aggregate, and eventually become insoluble.

Of note, the shortest chain that was soluble in water at room temperature was 12k.

Right-Angle Light Scattering:

Under Dilute conditions, the light scattering intensity of the sample was far more sensitive than turbidimetry. The light scattering transition for the 12k sample was lower than the 26k and 45k samples, this indicates that the Hydrophilic/Hydrophobic balance (H/LB) reaches a critical value in the 12k sample, causing its LCST to lower significantly.

As the solution approaches the LCST the IE/IM ratio increases. The two possible causes of this are an increase in the rate of excimer formation from the added thermal energy, or an increase in aggregation level of the pyrene groups as the coil contracts due to worsening solvent quality.

Once the LCST is reached IE/IM decreases as the aggregated chains cause a decrease in the mobility of pyrene or a decrease in local pyrene concentration as PNIPAM monomers join pyrene in the core of the aggregate.

The results in ethanol show that these changes in fluorescence behaviour are not present when a good solvent for pyrene and the polymer is used.

Conclusions:

Light scattering, steady-state and time-resolved fluorescence were used to determine the aggregation behaviour of pyrene-labelled PNIPAM in aqueous solution below, at and above their LCST. Undergoing an LCST transition causes the IE/IM ratio and the rate of excimer formation to decrease, and if the polymer chains are sufficiently long the pyrene lifetime will also increase. These observations are consistent with a decrease in mobility experienced by the pyrene end groups as the polymers undergo a coil-to-globule transition. Further analysis of the fluorescence decays is expected to describe the aggregation level of the pyrene as PNIPAM proceeds through the coil-to-globule transition.

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