Fluorescence Experiment 1: Arrhenius Behaviour

Overview

In this experiment you will measure the fluorescence decay of a luminescently labelled polymer sample in solution as a function of temperature using a time correlated single photon counter. You will confirm whether the emission follows an Arrhenius type dependence and derive the activation energy for the thermal deactivation of fluorescence.

Version 1.0

Introduction

The rate of many chemical reactions and certain physical processes increase exponentially with temperature and can be described by the Arrhenius equation[1]

$$k_R = A\, exp^{-Ea/RT} \qquad (1)$$

where k_R is the rate constant[1], E_a, the activation energy for the process[1], R the gas constant and T the absolute temperature in degrees kelvin. A is known as the pre-exponential factor[1] (or frequency factor) and is a measure of the frequency of collisions between reactant molecules while E_a represents the minimum energy required for the reaction to proceed. Equation 1 shows that the rate constant (and therefore reaction rate) of many chemical reactions/physical processes increase exponentially with temperature.

Taking the natural logarithm of equation 1 allows an alternative means of representing the Arrhenius equation

$$\ln k_R = \ln A - \frac{Ea}{RT} \qquad (2)$$

The linear form of the expression (equation 2) allows E_a to be determined since a plot of ln k_R *vs* 1/T in degrees kelvin should be linear with the slope = -Ea / R

The name polymer is derived from the words poly and momomer meaning literally many monomer units: essentially a series of identical monomer units are linked together to form a long polymer chain as shown in Scheme 1.

$$M\text{-}M\text{-}M\text{-}M\text{-}M\text{-}M \longrightarrow (M)_n$$

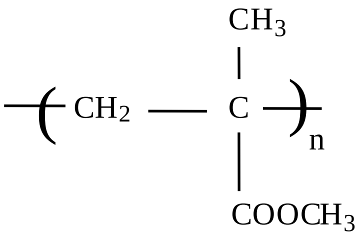
Scheme 1: A polymer chain showing a large number of identical monomer units

Fluorescent molecules (known as labels) can be incorporated in trace amounts into the polymer during synthesis. The fluorescence properties of the label can then be used to monitor the behaviour of the polymer sample in solution, for example.

The fluorescence properties of certain labelled polymer samples in solution will also show an Arrhenius type dependence: the quantum yield[2] and fluorescence lifetime[2] (τ_F) decrease as the temperature increases. Since $k_R = 1/\tau_F$ then consequently, by measuring, τ_F, by single photon counting[3], for example, as a function of temperature, it is possible to determine E_a for the thermal deactivation of fluorescence of the labelled polymer sample.

Aims

Poly(methyl methacrylate), PMMA, is one of the most studied polymers in science. (The structure of PMMA is shown in Figure 1.)



$$-\!\left(CH_2 - \overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{\overset{|}{\underset{|}{C}}}} \right)_n\!-$$

Figure 1: Structure of PMMA

You are provided with two fluorescently labelled PMMA samples: one containing acenapthylene (ACE-PMMA) the other anthrylmethyl methacrylate (AMMA-PMMA). The structures of ACE and AMMA are shown in Figure 2.

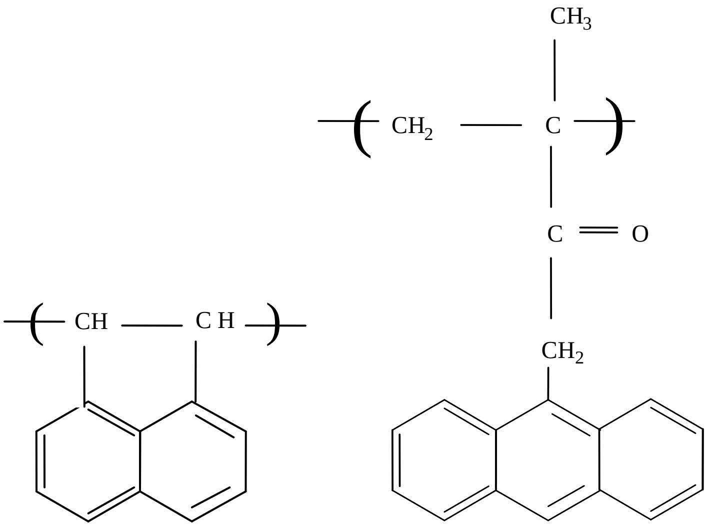


Figure 2: Structures of ACE (on the left) and AMMA (on the right)

You will make up a dilute solution of ACE-PMMA in toluene. The absorbance[4] and fluorescence[2] emission spectra should be recorded. You will determine τ_F of ACE-PMMA in toluene using the single photon counter at 20 °C.

You will then measure τ_F of ACE-PMMA in toluene at nine other temperatures between 20 °C and 60 °C. Finally, you will manipulate the data in order to produce an Arrhenius plot for the thermal dependence of the excited state lifetime of ACE-PMMA in toluene: do the rate constants derived from fluorescence lifetime[2] data for ACE-PMMA in toluene as a function of temperature display Arrhenius[1] behaviour? You will subsequently repeat these experiments for AMMA-PMMA in toluene. Do the two labels provide equivalent information?

Experimental Procedure:

Part (a) ACE-PMMA in toluene

Prepare a *ca.* 0.1 wt% solution of ACE-PMMA in toluene as defined by equation 3.

$$\text{Wt\%} = \text{weight of solute/total weight of solution} \times 100\,\% \qquad (3)$$