Luminescence Study of Polymer Chain Dynamics Using Long–Lived Ruthenium Complexes

Cristina Quinn, Jean Duhamel

ABSTRACT

Luminescence is a common technique used to characterize polymer dynamics in solution. Use of the Blob Model to analyze the luminescence data obtained with several pyrene labeled polymers has provided information on the dynamics of these polymer chains. The hydrophobicity of pyrene restricts its use in aqueous solutions because of pyrene aggregation. A water soluble dye used in place of pyrene would overcome this problem. In this study, the water–soluble dye ruthenium (II) bisbipyridine 5–amino–1,10–phenanthroline hexafluorophosphate will be synthesized, characterized, and used as a luminescent label on poly(N,N–dimethylacrylamide). Since the Blob Model has previously been applied to study the chain dynamics of pyrene labeled poly(N,N–dimethylacrylamide), comparison of the Blob Model results obtained for the same polymer but labeled with a different dye will further demonstrate the generality of the Blob Model. Furthermore, the two positive charges on the Ruthenium complex are expected to enhance the solubility of this dye in water which will enable luminescence studies of water–soluble polymers.

INTRODUCTION

There are few techniques available to study the folding dynamics of polymer chains. One method consists in labeling the ends of a monodisperse chain with a dye and its quencher and measuring the rate of encounter between the two ends using luminescence. However, this method essentially treats the bulk of the chain as being invisible.
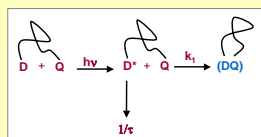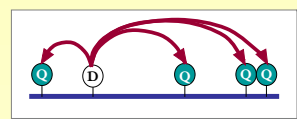

Figure 1: Illustration of Birks Scheme

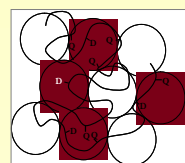Figure 2: Schematic representation of possible encounters for a randomly labelled polymer.

This problem is overcome by randomly labeling a polymer with a dye and quencher. However, since the rate of encounter depends strongly on the length of chain spanning the dye and its quencher,[1] this introduces an infinite number of rate constants and therefore obtaining quantitative information about the system becomes difficult. The Blob Model is able to mathematically deal with the random labeling of a polymer chain by arbitrarily dividing the polymer coil into blobs where a blob is the volume of the polymer coil which is probed by the excited dye during its lifetime.[2]

k_{diff} = rate constant for diffusional encounter between a dye and a quencher

N_{blob} = number of monomer units per blob

Figure 3: Schematic representation of the Blob Model approach.

PURPOSE

The goals of this project are:

1) To establish a set of luminescent dye and quencher which can be used to study water–soluble polymers.
2) To demonstrate the generality of the Blob Model concept by using a second dye/quencher system to investigate the dynamics of poly(N,N–dimethylacrylamide) which has previously been studied using pyrene and the Blob Model.

The water soluble luminescent dye selected for this project is ruthenium bisbipyridine 5–aminophenanthroline hexafluorophosphate 1 (Ru–bpy). The positive charges on the ruthenium atom will help solubilize the molecule in water while the primary amine group on the phenanthroline ligand will allow for the attachment of the dye onto a polymer backbone. Ru–bpy is synthesized by coupling 5–amino–1,10–phenanthroline to cis–bis(bipyridyl) ruthenium (II) dichloride as shown in Scheme 1.
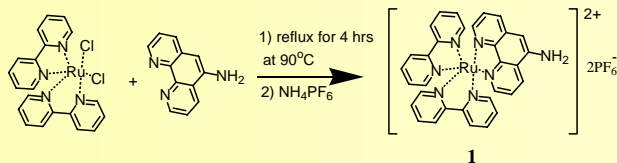
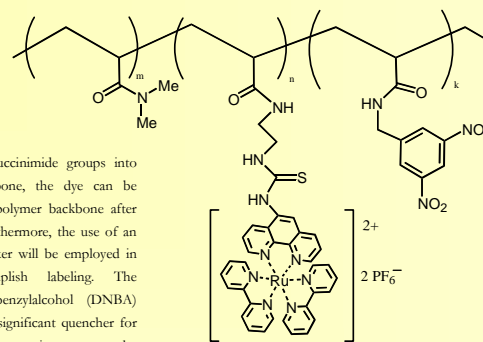Scheme 1: Synthesis of ruthenium (II) bisbipyridine 5–amino–1,10–phenanthroline hexafluorophosphate 1 (Ru–bpy).[3]

By incorporating succinimide groups into the polymer backbone, the dye can be attached onto the polymer backbone after polymerization. Furthermore, the use of an ethylenediamine linker will be employed in order to accomplish labeling. The compound dinitrobenzylalcohol (DNBA) was found to be a significant quencher for Ru–bpy. In order to incorporate the quencher into the polymer, it will be converted from an alcohol to an amine. The amine group is expected to react with the succinimide groups on the polymer. The final structure of the polymer is illustrated in Figure 4.

Figure 4: Proposed structure for labeled polymer

RESULTS

Thus far, the dye Ru–bpy has been synthesized according to the method described by Ellis et al. with an 87% yield.[3] The structure of the dye was confirmed by both ^{1}H NMR and ESI–TOF–MS
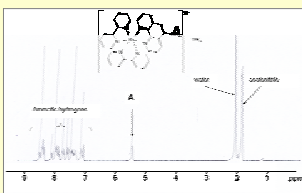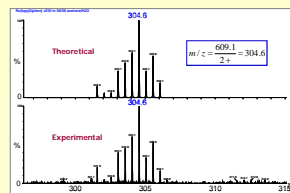

Figure 5: ^{1}H NMR spectra of Ru–bpy.

Figure 6: Electrospray ionization – time of flight – mass spectrometry spectra of Ru–bpy.

The literature reports that the extinction coefficient for Ru–bpy in 0.1 M Na$_2$CO$_3$ solution of pH 9.6 is equal to 13 800 M^{-1}cm^{-1} at 454 nm.[4] As Figure 7 indicates, the experimental results obtained in this study are in agreement with the reported value.
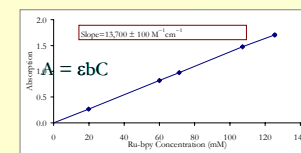

$A = \varepsilon bC$

Figure 7: Plot of absorption versus dye concentration to determine the extinction co–efficient of Ru–bpy in a 0.1 M Na$_2$CO$_3$ solution of pH=9.6 at 454 nm.

The strongest quencher for Ru–bpy was found to be DNBA. A Stern–Volmer plot (Figure 8) was obtained for this system and a quenching constant of 2.7×10^9 M^{-1}s^{-1} was obtained. Since the theoretical maximum value is 1.0×10^{10} M^{-1}s^{-1}, DNBA is considered to be an acceptable quencher. The extinction coefficient of DNBA in a 0.1 M Na$_2$CO$_3$ solution at pH 9.6 was found to be 15 300 M^{-1}cm^{-1} at 246 nm. DNBA absorbs strongly at 246 nm with no overlapping absorption with the dye in the 454 nm region. Therefore, the dye and quencher content of the polymer will be determined by its UV–visible absorption.
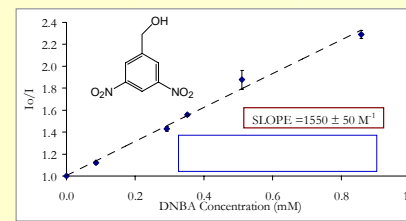

Figure 8: Stern–Volmer plot to determine quenching effects of DNBA on Ru–bpy where [Ru–bpy]=0.5mM.

FUTURE WORK

Having successfully synthesized and characterized a water–soluble dye, the fist goal of the project has been fulfilled. The next step will be to synthesize the proposed labeled polymer and to carry out the Blob Model analysis. Since the lifetime of Ru–bpy is much longer than the lifetime of pyrene, Ru–bpy will be quenched such that its lifetime approaches that of pyrene. If the Blob Model holds true, then it is expected that N_{blob} will vary with lifetime according to the trend which was previously observed for the PDMAA system labelled with pyrene (Figure 8).
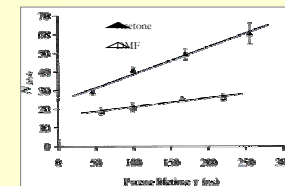

Figure 8: Plot of the linear relationship between N_{blob} and lifetime.[5]

ACKNOWLEDGEMENTS

REFERENCES

1. Winnik, M. A. *Acc. Chem. Res.* **1985**, *18*, 73–79.
2. Mathew, A. K.; Siu, H.; Duhamel, J. *Macromolecules*, **1999**, *32*, 7100–7108.
3. Ryan, E.; O'Kennedy, R.; Feeney, M.M.; Kelly, J.M.; Vos, J.G. *Bioconjugate Chem.* **1992**, *3*, 285–290.
4. Ellis, C.D.; Margerum, L.D.; Murray, R.W.; Meyer, T.J. *Inorg. Chem.* **1983**, *22*, 1283–1291
5. Kanagalingam, S.; Spartalis, J.; Cao, T.M.; Duhamel, J. *Macromolecules* **2002**, *35*, 8571–8577.