

Förster Resonance Energy Transfer across interpolymer complexes of poly(acrylic acid) and poly(acrylamide)



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ABSTRACT

Interpolymer complexes of homopolymer macromolecules are often described as 'laddered' or 'ribbon' type structures. The proposition of the existence of these ladder structures seems to us not reasonable and here we examine this hypothesis. To address this we have used polymers enabled for Förster Energy Transfer (FRET). Chromophores bound to a macromolecular backbone can transfer energy across short distances via FRET. The close binding of poly(acrylamide) and poly(acrylic acid) interpolymer complex formation at low pH forms a structure compact enough for significant energy transfer to occur between different chains containing naphthalene and anthracene labels. In the context of the proposition that ladder polymers can form it was surprising that the distance between labels on the same polymer backbone was equivalent regardless of whether the polymer was complexed or not. The data indicated that the bicomponent structure may be more compact than previously supposed: i.e. the complexes are not ladders composed of extended chains. This evidence suggests formation not of ordered 'ladder' systems but colloidal 'co-globules'.

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1. Introduction

Many aspects of biological systems are determined by interactions of macromolecules that give rise to protein conformational changes [1,2]. It is well known that cooperative interactions in aqueous media of certain synthetic macromolecules can lead to interpolymer complexation [3–7]. This is an important phenomenon in a number of areas of emerging materials science [1]. The complexation is driven either by van der Waals forces to form stereocomplexes [8], polyelectrolyte bindings between polyacids [9], coordination complexes [10] or hydrogen bonding [11,12]. All of

these have been investigated over recent years and careful polymer design can lead to new composite materials [8,13] and new applications as sensors [14,15] or delivery vehicles [11,16]. There are a variety of methods for detecting interpolymer complexes (IPC) including viscometry, conductivity measurements, NMR spectroscopy and fluorescence [9,17–19]. Pyrene, which forms excimers as the local pyrene concentration increases, has also been added as a probe to study segmental motion of partially hydrolysed poly(-acrylamide) (i.e. PAA-co-PAM) [19]. Using these techniques it was proposed that a decrease in excimer formation in the complex indicated the formation of rigid conformations in the complex and extended conformations. However, the same authors also suggested that measurements of intrinsic viscosity showed that complexes had "compact polymer structures" [19,20] and Bain and Liu also showed that the complex formation between PAA and poly(-dimethyl acrylamide) gave reductions in intrinsic viscosities as the coils contracted [21].

Other fluorescence techniques can also be used to convey information about the solubility, conformation and structure of dissolved macromolecules [15,22–25] and we were interested to further probe the nature of chains in these potentially technologically important interpolymer complexes. Both Naphthalene and

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Anthracene are fluorescent units that are useful in studies of large polymeric systems [26–29]. Probing of macromolecules via fluorescence can be used in a variety of ways. These include: the dissolution of a soluble dye into a polymer solution [30]; chemical attachment of a probe directly into the polymer backbone [31] or as a grafted subunit [32]. Acenaphthylene (ACE) is derivative of naphthalene, that when copolymerized into a soluble polymer backbone is linked by two bonds. On the other hand 9-anthryl methyl methacrylate (AMMA) is copolymerized to attach an anthracene unit pendant to the main chain backbone (Fig. 1) by an ester linkage. It has been shown that both units report differing information about polymer solution behaviour [33].

Förster Resonance Energy Transfer (FRET) uses electronic non-radiative exchanges between ‘donor’ and ‘acceptor’ labels to predict molecular scale distances. Multiple studies have shown that transfer efficiency begins to decrease sharply at separations in excess of 30 Å [34] although in fully optimized systems transfer is still possible up to 120 Å [35]. FRET enabled polymers have been considered for some years as potential biosensors (i.e. for oligonucleotides, proteins, inhibitors, enzymes, metal ions) but it is interesting to note that most of these systems use conjugated polymers [36–44]. Whilst conjugated polymers offer excellent light harvesting possibilities they exhibit limited solubility and thus these polymers are only suited to certain applications. Alternatively, in non-conjugated polymers, with pendant chromophores located along the polymer chain [45], or chain ends [1], FRET occurs intramolecularly. For this reason this technique has been used to study the conformation of stimulus responsive polymers [15,23,24,46], the formation of supramolecular assemblies [47] or to measure the diffusion across surfaces [25,48], as the dimensions of the polymer change in response to external stimuli [49]. To achieve this two fluorescent chromophores (ACE and AMMA) have been attached to a single polymer backbone. The communication between these species is dependent on their proximity, on the 1–10 nm length scale [28,29]. In FRET measurements one of the chromophores is excited (considered the donor excited state) but then the energy is transmitted non-radiatively to the acceptor chromophore, which then emits via radiative decay. This process can be summarised via the resonant energy transfer process; $D^*+A \rightarrow D+A^*$. As the donor and the acceptor must be in close proximity the effect is reduced by the increased separation of chromophores as the chain volume is increased (Fig. 2). Polymers containing a single chromophore do not undergo FRET processes but other factors can affect their decay, therefore these need to be studied to give suitable reference states.

Attachment of chromophores onto small conjugating oligomeric

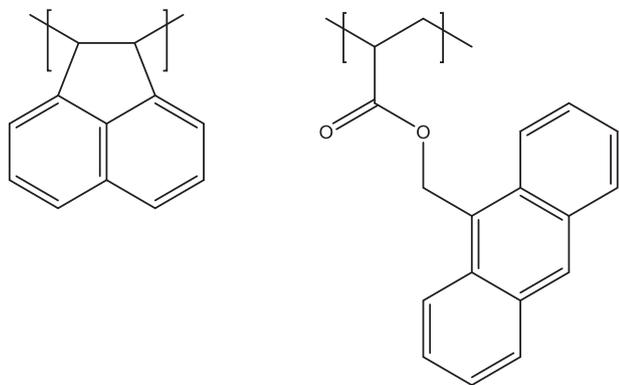


Fig. 1. Structures of direct reporting chromophore acenaphthylene (ACE) and pendant subunit 9-anthryl methyl methacrylate (AMMA) copolymerized along polymer backbone.

systems has been carried out before [16,36,44]. These studies typically used low molecular weight oligomers or polymers with fluorescent chain ends to tag the end of intercalating dyes [44]. Previous studies have shown these systems can be studied using FRET changes across a state change (for example micelle formation [16,50]) but relatively few studies have examined single-molecule conformation reorganisation or dual molecule IPC formation.

Poly (acrylamide) (PAM) is a commonly used synthetic polymer with a range of applications in materials processing [14] and biotechnology [51,52]. It forms strong IPCs with a range of materials, including poly(acrylic acid) (PAA). In the literature this is often modelled as a ‘laddered’ or ‘zipper’ system between two polymer chains. In this work we were interested in the nature of these complexes. In order to do this we employed the two experiments. In the first experiment ACE and AMMA were both copolymerized in small quantities with PAA. This produced a dual labelled polymer in which the FRET process was used to probe the interactions and distances between PAA segments. In the second experiment ACE and AMMA were attached to both polymers separately. This experiment gave information on interaction and complex formation between segments of PAA and PAM. In our previous work and application of this area we have used PAA containing an ACE label to form a highly sensitive anisotropic polarized detection system [15] for detection of ppm level concentrations of interpolymer complexation in fresh water [14].

The generally accepted model describing these systems involves a “zipper” effect in which the two polymer components exist separately then acrylamide and carboxylic acid groups align to form a ladder type structure. However, Deng et al. recently used light scattering techniques to show that the individual chains aggregate also in the one component solutions. They interpreted these results by modifying the “zipper” to propose that the complexes evolve within the aggregates that are present in the single component solutions [53].

In this work we have used FRET to further investigate the IPC formed from PAA and PAM. The data showed that polymers are not extended in the complex form and this supports the hypothesis that the complexes are globular entwined structures that could be derived from the process described by Deng [53].

2. Experimental

2.1. Sample preparation

2.1.1. Materials

All materials were used as supplied and sourced from Sigma-Aldrich unless otherwise stated. Fluorescence label ACE was purified via column chromatography before use.

2.1.2. Synthesis of AMMA

Synthesis of AMMA was performed following a modification of previously published methods [33]. 9-Anthracenemethanol (20 g) and triethylamine (40 ml) were added to tetrahydrofuran (400 ml) and dried under nitrogen at 0 °C. Methacryloyl chloride (28 ml) was added dropwise over a period of 1 h and stirred for 5 h over which time the mixture was allowed to warm to room temperature yielding an orange solution and a solid. Distilled water and then diethyl ether were added to extract the organic product from the mixture. The lower aqueous phase was removed, then the ether extract was filtered and washed with deionized water, 0.5 M HCl solution, saturated NaHCO₃ solution and then dried over anhydrous sodium sulfate (BDH) for 16 h at room temperature. The ether was evaporated using a rotary evaporator at room temperature. The product was recrystallized from spectroscopic grade methanol and purified via column chromatography with silica gel. The

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