Current Trends *in* Polymer Photochemistry

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Current Trends in Polymer Photochemistry

Preface

Over the last two decades the photochemistry of polymers has become a field of central importance in polymer science and technology. In June 1982 the first international conference on the subject of Polymer Photochemistry was held at the Hahn–Meitner Institute in Berlin. This was followed a little later in August 1985 by the second conference, at the Royal Institute of Technology in Stockholm. This second auspicious occasion was in honour of one of the Institute's retiring directors, namely Professor Bengt Râonby, who is one of the early founding scientists in this field. It was not, however, until September 1993 that a third conference was held. In this case the venue was the very pleasant resort of Sestri Levante in Italy. On this occasion the organizers of the meeting decided, along with the publishers (Ellis Horwood), to produce a book that would be based on the latest current developments in the field rather than a compilation of conference papers. On this basis, therefore, a large number of research specialists (both contributors and non-contributors at the conference) were asked to provide selected overviews, both specialized and diverse, on their current research topics.

The theme of the book, therefore, embraces a wide spectrum of subjects covering both academic and industrial developments in radiation chemistry, photochemistry and photophysics of polymeric and related materials. The book, although wide ranging, is not comprehensive. Contributions include aspects of the photodegradation and photooxidation of polymer systems and the latest theories on photostabilization with particular emphasis on hindered piperidine light stabilizers. Many polymers, dyes and pigments have important applications in holography, photography, electrophotography and photoconductive polymers. Specialized areas within these topics are covered as well as the luminescence behaviour and the liquid crystalline properties of such materials. Other important areas that are covered include photopolymerization, photoimaging sciences, photoinitiators and photografting and their applications in technologies such as coatings, resists/lithography, electronics, composite membrane systems and printing. It is hoped that this book will bring together many recent developments in the field as well as provide the reader with a valuable insight into current trends and thinking and therefore form a useful basis for the future development of this important subject.

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Applications of luminescence spectroscopy to the study of polymers

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1. INTRODUCTION

The physical and dynamic behaviour of macromolecules is an extremely important area of research in polymer science. Within this sphere of activity, luminescence techniques have become increasingly popular as means of revealing information, at the molecular level, in systems of considerable diversity (cf., for example, [1]–[3]). In this article, we hope to illustrate the scope of the luminescence approach in the characterization of polymer properties through reference, in particular, to recent studies in our laboratories of water-soluble polymers and aqueous dispersions of macromolecular systems.

The term 'luminescence' describes the radiative evolution of energy which may accompany the decay of a population of electronically excited chromophores as it relaxes to that of the thermally equilibrated ground state of the system. Two spectrally and temporally distinct forms of luminescence exist: *fluorescence* and *phosphorescence*. Fluorescence, occurring between states of like multiplicity, is a quantum-mechanically 'allowed' transition and generally occurs at higher energies and upon shorter timescales than the 'lower probability' process of phosphorescence (which occurs between electronic states of differing multiplicity). In addition to its wavelength and temporal characteristics, the luminescence observed from a given population of excited states is dependent upon both the concentration of chromophores, dispersed in the medium under investigation, and their orientations with respect to the incident radiation and its polarization characteristics. It is this combination of parameters which determine the intensity of luminescence emitted by a system, which makes this spectroscopic approach to the study of molecular phenomena so versatile.

As a result of this versatility there are many ways in which luminescence techniques find application in polymer science, as illustrated below. These approaches include studies of spectroscopy, energy transfer and emission anisotropy. In each of these adopted methodologies, valuable information regarding the

physical characteristics of a particular polymer-based system can be gained using a photostationary state approach, wherein the luminescence from the medium is studied under conditions of continuous excitation, in a conventional spectrometer. However, the use of a time-resolved spectroscopic approach adds (literally) another dimension to such investigations.

In this article we attempt to provide an overview (as opposed to a comprehensive review) of the ways in which luminescence techniques can be used to enhance our knowledge of the physical behaviour of polymer systems. In particular, we should like to discuss the applications of photophysical methods to the study of aqueous solutions and dispersions of polymeric systems. Illustrative examples of such applications have been chosen from research programmes currently in progress in our laboratories.

2. LUMINESCENCE ANISOTROPY

In theory, studies of the anisotropy of the emission from a system of chromophores dispersed in a matrix constitute *the* most powerful means of interrogation of its molecular dynamics. The principal problems confronting the investigator concern the retrieval, in a reliable form, of the relaxation data characteristic of the molecular motions of interest. Luminescence anisotropy experiments can be directed either at probes, simply dispersed within the system under investigation, or at labels designed to reflect, in their dynamic behaviour, upon that of their polymeric substrates.

The principles of the luminescence anisotropy approach to studies of molecular dynamics are illustrated, schematically, in Figure 1.1. In the mode of application

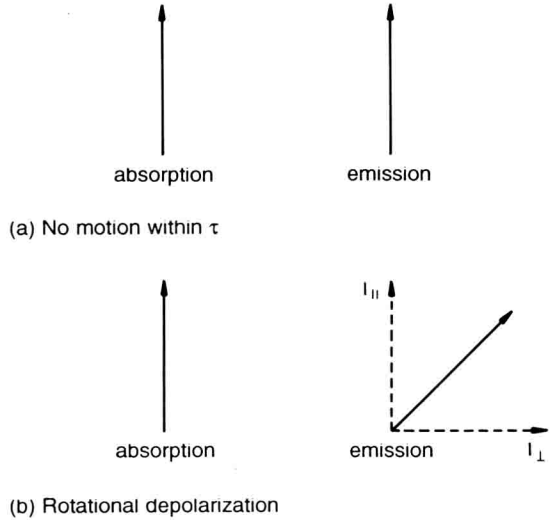

Figure 1.1 Principle of the emission anisotropy technique.

most commonly adopted, vertically polarized radiation is used to photoselect (via preferential absorption) those chromophores whose transition vectors are disposed in a plane parallel to that of the incident excitation. The anisotropy of the radiation emitted by the distribution of excited states created in the photoselection process is dependent upon the degree of molecular reorientation which occurs prior to luminescence: if the rate of rotational relaxation is slow, relative to that of the decay of the distribution of luminescent excited states under investigation, the emitted radiation will be highly anisotropic. If, on the other hand, molecular reorientation is significant within the lifetime of the excited state, the observed luminescence is depolarized to an extent dependent upon the relative rates of the rotational randomization and excited state depopulation processes.

The rotational information encoded in the relative intensities, $I_{\parallel}$ and $I_{\perp}$, of luminescence analyzed in planes parallel and perpendicular to that of the photoselection may be retrieved by use of the anisotropy, r, defined as follows:

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \tag{1.1}$$

In a steady-state experiment, resolution of the reorientational kinetics is achieved in terms of a single average correlation time, τ_r, via equation (1.2):

$$r^{-1} = r_0^{-1} (1 + \tau/\tau_r) \tag{1.2}$$

where τ represents the lifetime of the excited label or probe and r_0 is the 'intrinsic anisotropy', a spectroscopic characteristic of the chromophore.

Upon examination of equation (1.2) it is evident that the excited state lifetime, τ, establishes the timebase of the test. The experiment should be designed such that τ is reasonably closely matched to the τ_r characteristic of the relaxation process to be studied. Furthermore, it is obvious that both τ and r_0 need to be estimated independently if τ_r is to be quantified.

Measurement of τ requires access to time-resolved luminescence instrumentation. In phosphorescence, lifetime measurements can often be made on conventional spectrometers. In fluorescence, access to a lifetime spectrometer is necessary (such as a time-correlated single photon counter; see, e.g., [4]).

Equation (1.2) reveals that r_0 is attained as the value of the *measured* anisotropy when the ratio τ/τ_r is zero. This suggests that r_0 may be estimated, in principle, by either of two equivalent extrapolation procedures:

(1) r_0 may be obtained as the value of r in the limit whereby $\tau_r \rightarrow \infty$. Means of either attaining or extrapolating to this condition and their limitations in applications concerning the dynamic properties of synthetic macromolecules have been discussed elsewhere (see, e.g., [3] and [5]). Suffice it to say that this procedure is particularly inappropriate for the study of the relaxation behaviour of macromolecules in aqueous media.
(2) In the alternative extrapolation procedure [6], r_0 is obtained by extrapolation of anisotropy data to the limit of $\tau = 0$. Variation of the lifetime of the luminescent species is accomplished by addition of varying amounts of a

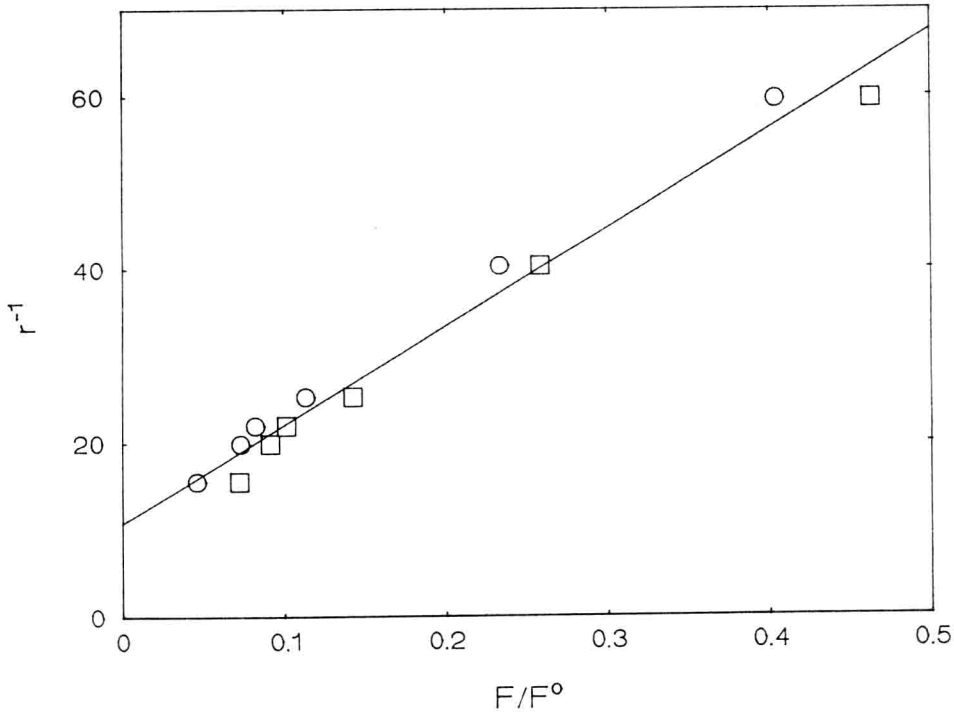

Figure 1.2 'Perrin plot' for acenaphthylene (ACE)-labelled PDMAC (10^{-2} wt%) in methanol at 298 K. F = fluorescence intensity (○) or lifetime (□]; F^o = fluorescence parameter in absence of quencher (CCl_4).

dynamic quencher [3, 5–7]. Figure 1.2 illustrates such an approach in a steady-state study of the relaxation behaviour of poly(dimethylacrylamide) [8] in dilute (10^{-2} wt%) methanolic solution. In this case, copolymerized (0.5 mol%) acenaphthylene acted as the fluorescent label and carbon tetrachloride as dynamic quencher, yielding a correlation time τ_r of about 1.7 ns, which is in reasonable agreement with that (1.3 ns) obtained using the more sophisticated approach of the time-resolved anisotropy experiment [8].

Solubilization and spectroscopic studies indicate that poly(dimethylacrylamide) exists as a relatively open, 'water-saturated' coil in aqueous solution [8, 9]. In such circumstances, water-soluble quenchers *can* often be employed in steady-state anisotropy studies of aqueous polymer solutions. However, in many cases, particularly those involving polyelectrolytes, the very conformational behaviour that we wish to study produces problems [7]: in these instances, the only recourse is to use time-resolved anisotropy measurements (TRAMS).

In a TRAMS experiment, the orthogonal components of luminescence intensity, $I_{\parallel}$ and $I_{\perp}$ (cf. Figure 1.1), are analyzed as functions of time. Typical data are shown in Figure 1.3. These decay data can be transformed, using equation (1.1), into a

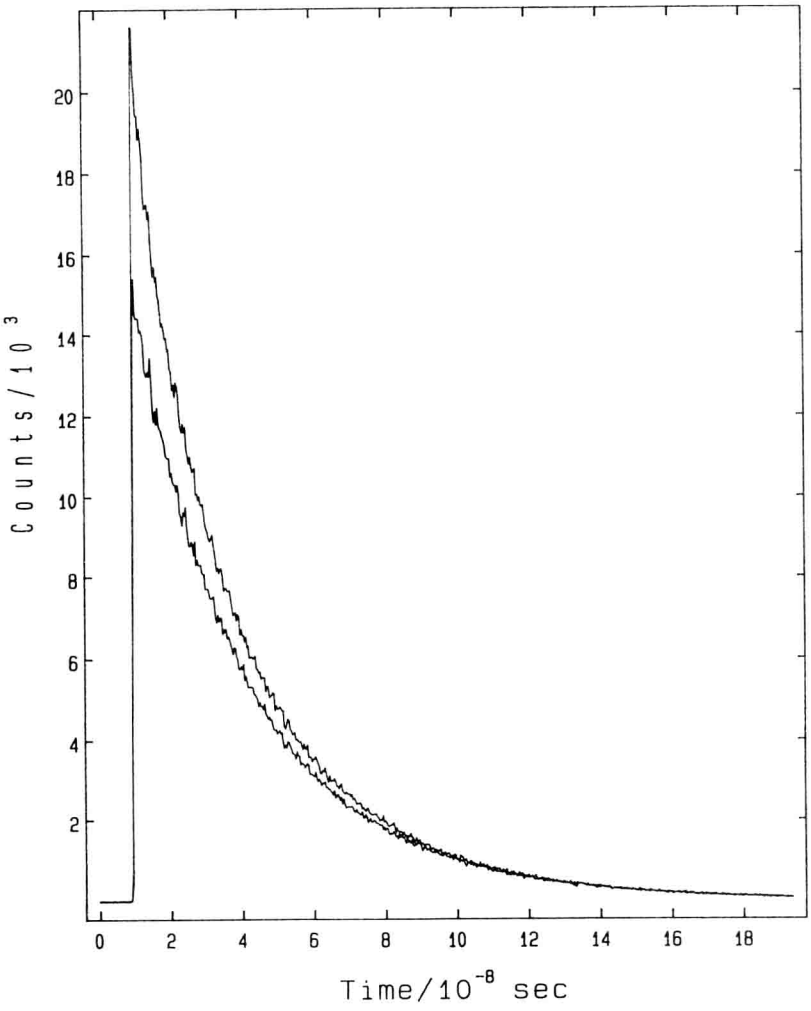

Figure 1.3 Parallel and perpendicular components of fluorescence intensity of PMAA/ ACE following excitation using vertically polarized synchrotron radiation.

time-dependent anisotropy function, $R(t)$. $R(t)$, constructed in this fashion, not only contains the reorientational information sought from the experiment but also reflects the distortions induced in the emission intensity functions $I_{\parallel}(t)$ and $I_{\perp}(t)$ by the finite nature of the excitation pulse. This presents little problem in the study of relaxation phenomena which occur on timescales which are long compared to that of the excitation pulse width and associated instrument response (and which are studied using luminescent groups of comparable excited state lifetimes). However, when both the luminescence lifetime and the reorientational correlation time are of magnitudes comparable to those of the instrumental response function, problems in

data retrieval can result since $R(t)$ is not amenable to direct forms of reconvolution analysis. Analytical procedures for the recovery of segmental relaxation data from TRAMS experiments upon polymers labelled with fluorescent species have recently been discussed (see, e.g., [5, 10, 11]).

Given a means of data analysis appropriate to the particular time-resolved experiment and the relaxation characteristics of the system under investigation, the true anisotropy, $r(t)$ (i.e. a function containing solely reorientational information), is modelled by a mathematical function appropriate to the 'expected' relaxation behaviour *and* the quality of the data. For example, for an isotropic rotor, located in a single, fluid environment, the anisotropy would decay according to a simple first-order kinetic law:

$$r(t) = r_0 \exp(-t/\tau_r) \tag{1.3}$$

Such a function adequately describes, for example, the anisotropy behaviour of poly(methacrylic acid), PMAA, in dilute solution, at high pH (where the polymer is present in its fully-neutralized, polysalt form) [12]. As the pH of the solution is reduced, however, a single exponential decay becomes an increasingly inadequate descriptor of the observed anisotropy behaviour [12].

Polyacids exhibit conformational changes in coil dimension which are 'driven' by their degree of neutralization, and thence the pH of the medium. At high pH, the polysalt exists as a relatively open coil, minimizing the Coulombic repulsions between the negatively charged (carboxylate, for example) chain substituents. At pH values low enough for the fully acidified form of the polyelectrolyte to exist, the polymer coil contracts under the influence of hydrophobic effects. This pH-dependent conformational change is particularly marked in the case of PMAA and produces two major effects upon the fluorescence anisotropy of a labelled polymer:

(1) The increasing diversity of environments experienced by the polymer segments (and thence the fluorescent label) results in a greater complexity of the anisotropy decay (as noted above).
(2) The segmental motion of the polymer becomes increasingly impeded as the macromolecular coil becomes more compact. This effect is illustrated in Figure 1.4 where the correlation time, τ_r, characteristic of segmental motion of the PMAA varies between about 50 ns at low pH to less than 10 ns at high pH [12, 13].

Poly(acrylic acid), PAA, on the other hand, lacking the enhancement of intramolecular hydrophobic interactions induced by the backbone methyl groups of PMAA, exhibits a much less dramatic conformational transition. This, in turn, is reflected in a relatively small change in the segmental motion of PAA as the pH of the solution is varied (cf. Figure 1.4).

The pH dependences of the τ_r data for PMAA and the MAA- and AA-based copolymers show (cf. Figure 1.4), to varying extents, a maximum in the pH region below that of the conformational transition. A plausible explanation for this effect,