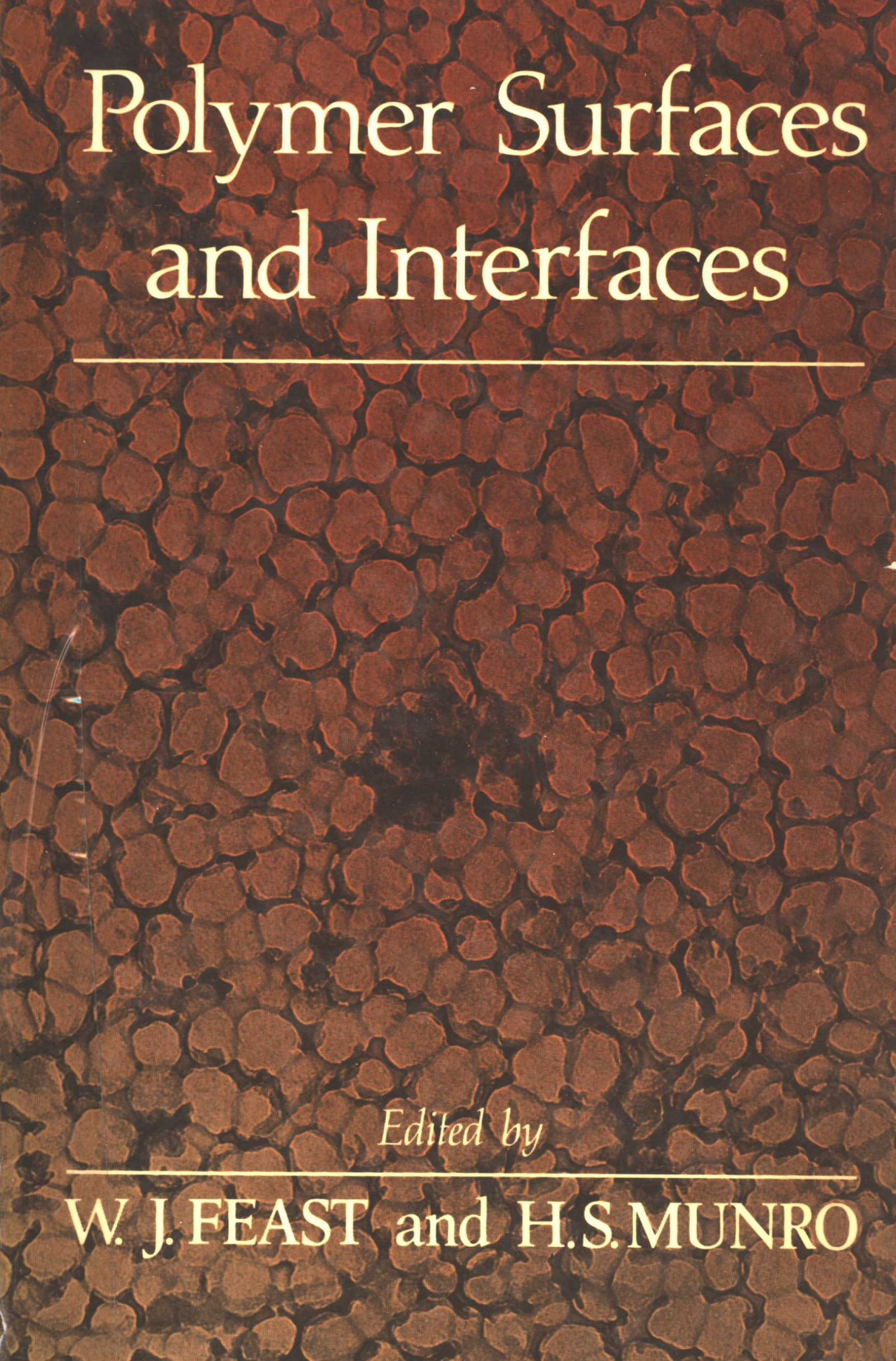
Polymer Surfaces and Interfaces



Edited by

W. J. FEAST and H. S. MUNRO

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JOHN WILEY & SONS

Chichester · New York · Brisbane · Toronto · Singapore

Library of Congress Cataloging-in-Publication Data:

Polymer surfaces and interfaces.

Includes index.
1. Polymers and polymerization—Surfaces.
2. Surface chemistry. I. Feast, W. J. II. Munro, H. S.
QD381.9.S97P65 1987 547.7'045453 86-15692

ISBN 0 471 91214 X

British Library Cataloguing in Publication Data:

Polymer surfaces and interfaces.

1. Polymers and polymerization—Surfaces
I. Feast, W. J. II. Munro, H. S.
547.7'045453 QD381

ISBN 0-471-91214-X

Printed and bound in Great Britain

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Preface

Several years ago a symposium was organized in Durham which gave rise to the book *Polymer Surfaces* edited by D. T. Clark and W. J. Feast (Wiley, 1978). The success of both the symposium and the book, together with the prompting of colleagues, persuaded us that the time was ripe for another foray into the area. Consequently a symposium was organized in Durham during April 1985 under the title Polymer Surfaces and Interfaces and this book arises from that meeting. The symposium was held under the auspices of the Pure and Applied Macromolecular Chemistry Group of the Royal Society of Chemistry and the Society of Chemical Industry. Durham University again acted as hosts for the meeting, and financial sponsorship was provided by Imperial Chemical Industries plc; British Petroleum plc; The University Bookshop (SPCK); The University; Polymer Laboratories Ltd, and the Department of the Army, US Army Research, Development and Standardization Group (UK).

The enormous practical importance of polymer surfaces and interfaces is self evident. A good understanding of the science involved can be crucial with respect to the efficient utilization of processes in which surfaces and interfaces are generated or modified, or in which they interact with other environmental components. These meetings in Durham have been organized on the assumption that scientists from very diverse backgrounds, but with a common interest in polymer surfaces and interfaces, have something to learn from each other. In view of the very great variety of situations in which polymer surfaces and interfaces are important it is impossible to discuss all aspects of the subject within the confines of a symposium or the covers of one volume and so we have not attempted to achieve comprehensive cover. Instead we have tried to select some of the topics which we, and the many colleagues who advised us during the planning of the meeting, thought were interesting in one way or another and which served to illustrate the diversity of the topic. The diversity of topics actually covered will be obvious from a quick scan of the chapter titles. The participants at the symposium were drawn from similarly diverse backgrounds (see below) and speakers/authors were asked to bear in mind that they were preparing their contribution for a scientifically sophisticated but largely non-specialist audience. The audience at the symposium had an advantage over the reader in that they were able to question speakers and seek clarification of specific points in the formal and informal discussions which took place at the time. Nevertheless,

we believe that the authors of the chapters which follow have been successful in their efforts to make their speciality accessible to the non-specialist, and we hope that the diversity of topics, approaches and content contained in the eleven chapters which constitute this volume will reward the reader's attention and application.

One of the more rewarding and interesting phenomena which resulted from the meeting was the generation of a number of cross-disciplinary research collaborations. We hope that this volume may act as a stimulant for the generation of further research programmes which cross the traditional subject boundaries.

The symposium attracted participants from fifteen countries and those from industry outnumbered those from academia and governmental establishments by three to two. The book contains most of the invited lectures presented at the meeting but, for a variety of reasons, a few authors did not prepare a chapter for this book; for example, the greater part of Dr Harry Gibson's interesting presentation, 'A Chemist's View of Triboelectric Charging of Polymer Surfaces' had been the basis of a relatively recent review (*Polymer,* **25**(3), 1984), and two other speakers were simply unable to produce a manuscript within the publication time scale. We thank the authors for their efforts to meet the objectives of this volume, any obscurities which remain are our responsibility.

W. J. Feast and H. S. Munro

Durham, 1986

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Luminescence Techniques Applied to Polymer Interfaces

Mitchell A. Winnik

INTRODUCTION

Fluorescence and phosphorescence spectroscopy provide a broad spectrum of tools for studying morphology and dynamics,[1,2] and these have obvious applications in the study of polymer interfaces and interphases. As is so often the case with new techniques, these tools were first developed for applications in biological science. The pioneering efforts were carried out by Weber[3] and his coworkers at Illinois, dating back to the early 1950s, and by Stryer[4] and his group originally at Yale and later at Stanford University. A sure sign of the perceived importance of a technique is its use by research groups whose interests lie outside the area of developing new applications for that technique. This situation may be found in the fields of protein chemistry, immunology and biomembranes, where fluorescence measurements are common.[1,2] In polymer science these tools are still employed primarily by groups specializing in luminescence spectroscopy.

Because micelles and synthetic lipid bilayer systems are considered to be models for biological membranes they have received considerable attention in the scientific literature over the past ten years. Measurements based upon fluorescence and phosphorescence spectroscopy have been among the most powerful tools for examining these systems.[5] As in the case of biological membranes, these studies involved treating the system with a fluorescent dye, either bound passively to a specific environment in the system or covalently linked to a membrane component. Several different kinds of luminescence measurements are possible with these tagged systems. Each of these various luminescence measurements provide different information about the system, offering high-resolution information about structure, local molecular order, interfacial characteristics and transport phenomena. Of course, the most powerful information comes from applying a variety of techniques to each system.

Luminescence techniques form an ideal complement to other high-resolution techniques such as nmr and electron microscopy as well as light-, X-ray- and neutron-scattering measurements.

While the study of synthetic polymers by fluorescence and phosphorescence spectroscopy can be traced back many years, the early studies were devoted to the spectroscopy of polymers such as polystyrene[6a] polyvinylcarbazole[6b] and polyvinylnaphthalene,[6c] which contain a fluorescent group in the repeat unit. Use of these methods to address more general questions in polymer science is more recent. Some of the early experiments of this type were reported by Frank[7] at Stanford, by Monnerie[8] in Paris, by Morawetz[9] in Brooklyn and by ourselves in Toronto.[10] Also very important for making scientists in the polymer area aware of these techniques were review articles by Morawetz,[11a] Nishijima[11b] and Phillips and coworkers.[11c]

TERMINOLOGY

Every field develops its own language for classifying situations or systems which are frequently encountered. We will find it useful to distinguish experiments in which a fluorescent dye is dissolved passively into a system from experiments in which the dye is covalently attached to a particular component. The term 'probe' refers to the former situation, whereas the covalently bound species is referred to as a fluorescent or phosphorescent 'label'. The author likes the term luminescent 'sensor' as a general word to encompass the entire spectrum of experiments. Others have also used the term 'reporter group'.

In the protein field one distinguishes between 'intrinsic' and 'extrinsic' labels. The former, such as tryptophan, are natural constituents of the system. Extrinisic probes and labels have no natural function in the system but are introduced in such tiny amounts that one hopes, or tries to establish, that they do not perturb the environment they are supposed to investigate. One might refer to these types of experiments as molecular spy techniques. The objective is to introduce a foreign element into a strange environment, hopefully unobtrusively, to gather and report specific kinds of information.

Spectroscopy and photophysics also have a language of their own. Readers are referred to standard texts for more detailed explanations. We can distinguish fluorescence from phosphorescence. Fluorescence describes prompt emission, typically with nanosecond duration, which in our applications originates from singlet-excited states of dyes. Phosphorescence describes much slower emission, typically from excited triplet states, with decay times on the order of microseconds to seconds. When the decay profile is exponential in form, the excited-state lifetime τ is defined as the $1/e$ time for excited state decay. Experiments are sometimes designed so that the time profile of the excited state decay is used to obtain information, particularly about dynamics. Under these circumstances one can think of the chromophore as a 'molecular chronometer'.

Anthracene, for example, has a fluorescence lifetime ($^1\tau$) of 5 ns in non-polar solvents; pyrene has $^1\tau \approx 500$ ns; and aromatic ketones have phosphorescence lifetimes $^3\tau$ on the order of hundreds of microseconds.

Several bimolecular processes between excited dyes (F^*) and ground state species need to be defined. 'Quenching' is the general word. This refers to any interaction which decreases the emission intensity of F^* and hastens the excited state decay rate. It is a phenomenological word and conveys no information about process or mechanism. Among the many quenching mechanisms energy transfer is particularly useful. It refers to the process

$$F^* + Q \rightarrow F + Q^*$$

in which singlet or triplet energy from F^* is transferred to Q, producing electronically excited Q^*. Energy transfer by the dipole-coupling (Förster) mechanism[12] can occur over substantial distances, up to F^*/Q separations of 100 Å. Energy transfer by the exchange (Dexter) mechanism[12, 13] requires molecular proximity, and occurs with characteristic distances of 5–15 Å.

Excimers and exciplexes are excited state binary complexes,[14] produced from $F^* + F$ in the case of excimers and $F^* + Q$ for exciplexes. Both $(F/F)^*$ and $(F/Q)^*$ complexes are frequently observed to emit light at significantly lower energy than F^* itself.

SCOPE AND METHODS

Techniques which rely on luminescence detection, as they are applied to macromolecular systems, fall into two quite distinct classes. On the one hand there are the tracer techniques. Here the detailed spectroscopic properties of a dye are less important than its ability to be introduced into a specific site in a complex system. Staining techniques fall into this class. Coupled with optical (fluorescence) microscopy, these techniques have a spatial resolution limit on the order of 0.1 μm.

On the other hand, there are the spectroscopic techniques. Dyes are chosen because of the sensitivity of their spectroscopic properties to specific aspects of their environment. For example, a dye's emission spectrum may be strongly red-shifted in regions of enhanced polarity, or the polarization of its emission might be more pronounced in regions of enhanced viscosity. Bimolecular reactions of the excited state of the dye with other molecules provide added dimensions to these methods, with processes such as fluorescence and phosphorescence quenching, energy transfer and excimer and exciplex formation giving information with spatial resolution—depending upon the detailed spectroscopy—of 5–100 Å.

This chapter will emphasize methods which take advantage of the spectroscopic properties of fluorescent and phosphorescent chromophores.

After a brief outline of some applications of fluorescent tracer techniques we will return to the spectroscopic methods and examine in some detail those that have been particularly useful in the study of polymer interfaces.

Tracer Techniques

The most elegant and powerful tracer experiments involve studies of specific molecules labelled with fluorescent dyes. These techniques can then be used to monitor the dynamics of transport of the labelled molecule in the system. One can observe protein-uptake by cells,[15] protein motion within cells[15b] or lateral (two-dimensional) diffusion of phospholipids or proteins in cell membranes.[16]

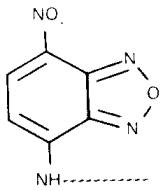
A powerful application of tracer techniques to measure diffusion coefficients of labelled molecules is provided by the FRAPP (fluorescence recovery after pattern photobleaching) experiment.[16] In this technique a thin, flat sample is exposed to intense light for a short period of time. The exposure is made either through a mask or by means of the interference pattern created at the intersection of two coherent laser beams, so that a stripe pattern of light and dark regions is created. In the light regions the photon intensity is so great that a substantial fraction of the dye molecules are destroyed. This photobleaching process probably involves photo-oxidation of the dye.

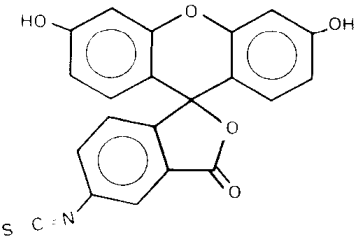
Immediately afterwards the exposure intensity is decreased by many orders of magnitude. This intensity is just adequate for fluorescence of the residual dye to be measured and too weak to cause further photochemistry. One then selects region of the film, encompassing many stripes, and measures the total fluorescence intensity from the region. Since the dyes on the labelled molecules in the dark regions of the pattern were not photobleached, diffusion of these molecules into the bright regions leads to an increase in the total fluorescence from the region. A measurement of the growth kinetics of fluorescence intensity plus knowledge of the distance between the stripes permits the tracer diffusion constant D_t of the labelled molecules to be determined. With stripe separations on the order of 1.0 μm, a measurement on the order of 15 min permits one to determine D_t values as small as 10^{-11} cm^{2}s^{-1}, since l^2, the mean-squared diffusion distance, is related to D_t by

$$l^2 = D_t t$$

Such experiments have been used to measure lateral (two-dimensional) diffusion rates of labelled phospholipids and labelled proteins in lipid bilayer membranes[16c] and to determine translational diffusion coefficients of labelled polymers in polymer melts.[17] In such experiments the concentration of lipid or macromolecule covalently labelled with a fluorescent dye is typically 1 part in 10^3–10^4, and one assumes that these tiny traces of dye do not cause significant perturbations of the system.

(1)





(2)

Two dyes commonly used in these experiments are NBD derivatives ((**1**), 7-nitrobenzo-2-oxa-1,3-diazole) and fluorescein derivatives ((**2**), shown as the isothiocyanate, used to label amino groups).

SPECTROSCOPIC TECHNIQUES

Many molecular sensor methods take advantage of the spectroscopic properties of individual molecules or chromophores. For example, if the lowest singlet-excited state of a dye differs substantially from its ground state in the degree of charge separation both its absorption spectrum and fluorescence spectrum will be very sensitive to solvent polarity. In complex systems, even in optically awkward samples where absorption spectra may be difficult to measure, the fluorescence spectrum of such a dye will convey information about the local polarity of its environment.

An experimental approach which is often more powerful than measuring the properties of a single dye is to examine various types of quenching interactions between an excited dye F^* and a second ground state molecule Q. In these experiments, one chooses F so that it can be excited selectively in the presence of Q. There are many mechanisms possible for F^*/Q interactions.[12] These include energy transfer, both singlet and triplet, to produce electronically excited Q^*; excimer- and exciplex-formation, yielding the species $(FF)^*$ and $(FQ)^*$, which emit light at lower energies than F^*; electron transfer to give ions, or other chemical reactions between F^* and Q; or other processes which lead to quenching of F^* whose mechanisms may not yet have been elucidated. All these processes are useful sensors of dynamics and morphology. If F is localized in one phase of a complex material and Q in the other the interaction of F^* and Q can take place only in the interfacial region.

This section could be written from different points of view. One could, for example, classify sensors according to the phenomena they sense: local polarity, local friction or free volume, local electric field strength or local orientation of the sample. Alternatively, one could classify sensors according to the spectroscopic properties which are sensitive to local environment. In this section we have chosen to review briefly various spectroscopic properties of dyes, indicating how they express sensitivity to their environment. In a subsequent section the application of several sensors to questions about polymer interfaces will be examined in more detail.

Single-chromophore Sensors

Excited-state Dipolarity

All molecules undergo electron redistribution upon electronic excitation. Both absorption and emission spectra show some sensitivity to solvent polarity. The spectra are blue- or red-shifted by polar solvents depending, respectively, upon whether the ground state or excited state is the more polar. A particularly useful class of sensors, typically substituted with donor and acceptor groups, have low-lying charge transfer states.[12] Many dyes fall into this category. Their excited

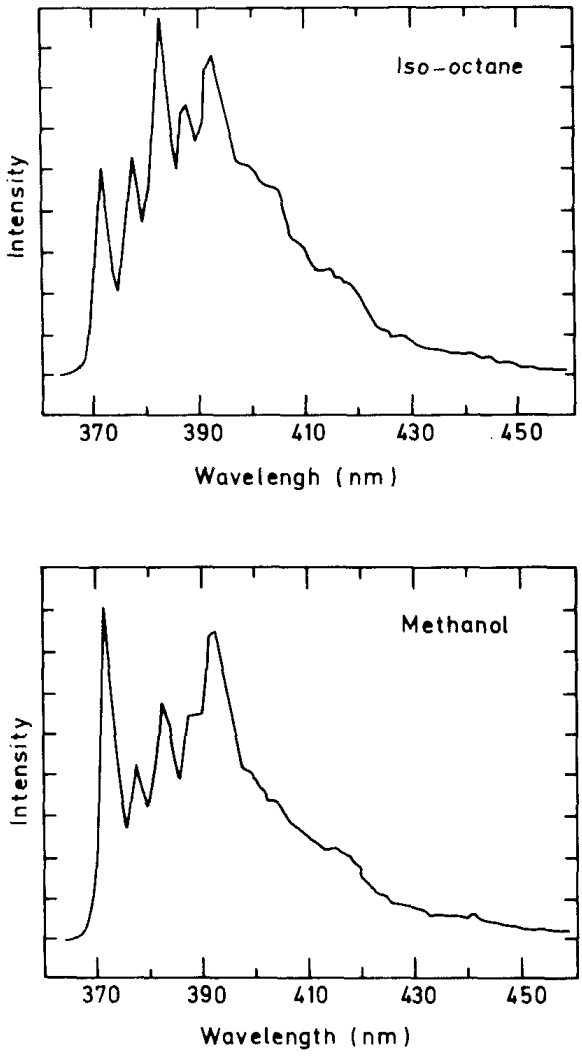


Figure 1. The fluorescence spectrum superscript 22 of pyrene in (a) isooctane and (b) methanol. Note how the (0,0) band at 370 nm has enhanced intensity in the more polar solvent