Functional Organic and Polymeric Materials

Molecular Functionality—Macroscopic Reality

Edited by

Tim H. Richardson

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West Sussex PO19 1UD, England

National 01243 779777 International (+44) 1243 779777 e-mail (for orders and customer service enquiries): cs-books@wiley.co.uk Visit our Home Page on http://www.wiley.co.uk or http://www.wilev.com

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Other Wiley Editorial Offices

John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158-0012, USA

WILEY-VCH Verlag GmbH, Pappelallee 3, D-69469 Weinheim, Germany

Jacaranda Wiley Ltd, 33 Park Road, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons (Canada) Ltd, 22 Worcester Road, Rexdale, Ontario M9W 1L1, Canada

Library of Congress Cataloging-in-Publication Data

Functional organic and polymeric materials / edited by Tim H. Richardson.

Includes bibliographical references. ISBN 0-471-98724-7 (cloth : alk, paper) 1. Polymers. 2. Organic compounds. 3. Thin films. 4. Monomolecular films. I. Richardson, Tim H.

TA455.P58F85 2000

99-31707 620.1'92-dc21

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0 471 98724 7

Typeset in 10/12 Times by Thomson Press (India) Ltd., New Delhi Printed and bound in Great Britain by Antony Rowe, Chippenham, Wilts This book is printed on acid-free paper responsibly manufactured from sustainable forestry, in which at least two trees are planted for each one used for paper production.

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Functional Organic and Polymeric Materials

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Editor's Acknowledgements

Finding time to write a book chapter is never easy as a research scientist and I am truly grateful for the contributions of the authors. I know that their enthusiasm for their research area, which is carried by their words, remains triumphant even whilst operating in the confused world of third millenium academia. Most of the authors are personal friends as well as research colleagues, so I take this opportunity to thank them for their friendship over the years. The publishers have been very patient with me in the preparation of this book and I thank them for that and for their guidance. My own journey in Molecular Materials has been aided tremendously by my research group at the University of Sheffield and by many colleagues both in the UK and overseas. I am grateful to you all for the friendly working environment you have created. In particular, I would like to thank Gareth Roberts who steered me in the beginning, Fred Combley who kept me on track and Rifat Capan who continues to give me new enthusiasm for this work. Finally I thank my wife and our parents for their support and dedicate this book to my sons, Matthew and Liam, not because of the content, but to show them an example of how people can help each other.

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Molecular Functionality— Macroscopic Reality

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A Formula One racing car mechanic expends a great deal of time and energy tinkering with the innards of the engine and the peripheral components which are housed around it, such as the suspension system. Highly sophisticated machinery is used to modify and test the resulting performance of the vehicle, with large amounts of data being constantly fed back to the team of technicians to provide valuable information that will determine yet further modifications to the car when it next makes a pit stop. In principle, this process not only ensures that the best possible performance is achieved from the car during a particular race, but when elongated over a time period of years, it also provides the opportunity for huge technological advances to be made in combustion-engine-based transport.

This unlikely introduction to a book concerned with *organic materials* highlights several of the key themes that characterize this field. Like much of all materials work, organic materials research is iterative in nature. It involves making adjustments to the material of interest before an evaluation of its properties is made. The resulting characterization data enable researchers to determine which further modifications (composition, purity, shape, polarity, electron density distribution, polymer chain length, etc.) are necessary in order to achieve the sought after performance. Often slight modifications can have dramatic effects on properties, such as in the doping of silicon in order to modify its electronic conductivity, or in the doping of iron to produce steels of different hardness or elasticity. In these two examples, the macroscopic properties of the materials (e.g. electronic conductivity and Young's modulus) are governed most critically by the packing of the many billions of atoms contained within them. In the case of silicon, for example, the band structure

formation brought about by the packing of atoms is a complex process which is only easily predicted with the use of sophisticated computer simulation and modelling software. It is simply not possible to draw a diagram representing a silicon atom and then use it to successfully predict the physical properties of the *material* formed when many such atoms are assembled. The strong interatomic forces that govern atomic packing in crystals are all powerful determinants for their physical properties [1].

Generally speaking, and indeed there are notable exceptions, organic molecules often interact loosely via relatively weak van der Waals forces and dipole—dipole forces. Their properties are more closely described by the specific arrangement of atoms within each molecule rather than how the molecules themselves are packed. This is not to say that molecular packing is unimportant—far from it. This remark simply highlights one of the most important opportunities that we have been given, i.e. that with organic materials we have the opportunity to attempt to predict the macroscopic properties of a material based on the atomic arrangements within a discrete molecule or very small assemblies of molecules. An illustrative example of this is found on inspection of the molecule in Figure 1, i.e. *p*-nitroaniline (*p*NA)

This molecule has been studied by several researchers interested in secondorder nonlinear optical effects (see Chapter 11) [2]. The benzene ring acts as a rich source of electrons which are delocalized, that is they are not confined to oscillate around individual atomic nuclei but rather they can be polarized as an electron cloud which extends over the entire region of the benzene ring. The nitro- and amino-groups are examples of chemical groups that are capable of withdrawing or donating electron density into such a ring structure, thus producing this polarized electron distribution. The resulting polar molecule can be polarized further by the application of an electric field. However, the ease of charge flow is asymmetric—the electron density can flow more easily in the direction towards the nitro-group than it can in the opposite direction. Hence the resulting polarization of the molecule is asymmetric. Fourier analysis shows that an alternating electric field, driven at a frequency ω , imposed on our discrete molecule, will result in the broadcast of electric field components at new frequencies in additions to ω . The second-harmonic frequency, 2ω , is particular useful for extending the range of available laser wavelengths towards the ultraviolet [3]. More importantly, the required molecular asymmetry (which

Figure 1 p-Nitroaniline: an example of a second-order nonlinear optical material

is not the only criterion which must be satisfied in order to obtain useful optical second-harmonic generation) can be easily understood by using simple chemical drawings. In other words, this is an example of a macroscopic property which, provided other symmetry considerations are overcome, can be predicted by consideration of the behaviour of the discrete individual molecules. This is just one example of many that have evolved over the last three decades throughout which the growth in organic materials research has continued to increase significantly. The principal aim of this present book is to provide many other examples of organic systems whose design begins with the consideration of the properties of their discrete molecules.

Although it is true to say that the predictability of the macroscopic properties of organic systems is usually greater than with inorganic materials, the exact behaviour obviously depends somewhat upon how individual molecules are assembled together in the material. A number of techniques exist which allow researchers, in effect, to cheat nature. If we take a solution of an organic material in a test tube and allow the solvent to evaporate slowly, we might expect to form small crystallites of solute in which the molecules are arranged in a completely 'natural' packing arrangement. This packing arrangement will depend on several parameters, including molecular shape, and dipole and charge distribution, among others. However, the molecular packing can often be modified considerably via the use of deposition techniques which effectively introduce new forces to be experienced by the molecules. The self-assembly technique is the simplest of these processes, involving the provision of additional 'binding sites' on a substrate, on to which solute molecules can attach in preference to their natural packing sites [4]. The Langmuir-Blodgett deposition method also provides a way in which the orientation of molecules can be modified by using a highly polar liquid, usually water [5]. These techniques and others are overviewed in Chapter 2 of this book, which intends to provide a survey of the available methods and to guide researchers in selecting the most suitable technique for their particular application. Those particularly wishing to focus on either self-assembly or Langmuir-Blodgett techniques will find other, more specialist chapters elsewhere in this book.

If we were asked how organic materials had made the strongest impact on our lives, we could give several different answers depending on the context of the question. From a medical point of view, we would probably describe the startling advances made in pharmaceuticals which have increased average life expectancy in the developed world to well beyond the age of seventy. Wearing our 'engineering hats', we would argue that engineering plastics have revolutionized virtually all everyday objects that we encounter, from sky-scrapers to CD players. Focusing on electronics, we would almost certainly describe the liquid crystal devices which can be found in almost all objects containing an electronic display. Chapter 3 and 4 in this book are devoted to describing how a range of useful macroscopic properties can be achieved by

following a relatively small number of design rules. The story of the unravelling of these design criteria is told for both low-molar-mass and polymeric liquid crystal materials.

Chapters 5, 6, and 7 describe what have become known as 'layer-by-layer' techniques in which single monolayer sheets of organic molecules are deposited (either by chemisorption or physisorption) on to solid substrates. Chapter 5 describes the self-assembly from solution process in which highly organized and ordered functional molecular assemblies can be built up with on specialized equipment, while Chapter 6 details the physics of floating monolayers at an airwater interface. This is followed in Chapter 7 by an account of how such floating monolayers can be transferred on to solid supports to form useful functional materials, covering a wide range of applied physics fields. By the end of Chapter 7, it is hoped that the reader will begin to understand the major attraction of organic materials as a research field and has now sensed the fascination held by many wishing to exploit academically and commercially the concept of molecular functionality—macroscopic reality.

The second part of the book focuses on a detailed description of some of the most interesting electrical and optical properties of organic materials. The emphasis remains tightly focused on the processes of conduction through molecular materials, including conjugated polymers (Chapter 8) and polyetherbased polymers (Chapter 9). These chapters are followed by accounts of second- and third-order non-linear optics (Chapters 10 and 11, respectively). The data storage industry has been dominated for the last thirty years by magnetic storage systems. More recently, optical storage has risen to prominence in the form of either ablative or photochromic approaches. The latter technique is reviewed (Chapter 12) in order to show how the optical properties of coloured organic materials can be made use of at the macroscopic level for memory applications. Nowhere more than in the field of light-emitting devices have organic materials made themselves the centre of attention. The last eight years in particular has seen an enormous growth area in light-emitting plastics, with the UK boasting a world lead in the area of luminescent polymers [6]. Chapter 11 describes the evolution of a wide range of low-molar-mass and polymeric organic materials and shows how macroscopic materials properties now match or surpass those of their inorganic counterparts.

There are many other topics which could have been included in a book of this nature, namely organic magnets, piezoelectric polymers, organic adhesives, gas and chemical sensors, biosensors, structural assessment techniques such as X-ray and neutron reflectometry, scanning tunnelling microscopies and molecular and biocomputing to name just a few. Restrictions on space, however, have unfortunately closed this book on such topics for now.

It is hoped that, in reading this book, those who are considering organic materials research will be strongly encouraged to pursue this field. It is an area that is characterized by a strong interdisciplinary and multidisciplinary culture,