Structural Studies of Macromolecules
by
Spectroscopic Methods

Edited by

K. J. Ivin

Structural Studies of Macromolecules
by
Spectroscopic Methods

Edited by

K. J. Ivin

Professor of Physical Chemistry,
Department of Chemistry,
The Queen's University of Belfast

A Wiley–Interscience Publication

JOHN WILEY & SONS
London · New York · Sydney · Toronto

Preface

This volume is based largely on the contributions to a meeting held at Cranfield Institute of Technology, near Bedford, England in July 1974 under the auspices of the Macromolecular Group of the Chemical Society of London. The object of the meeting, and also that of this volume, was to bring together information about the application of some of the more recently developed spectroscopic methods to the study of macromolecules.

The contributions divide into five groups, dealing with neutron scattering (1-4), far infrared and Raman spectroscopy (5-8), electron spectroscopy (9), nuclear magnetic resonance spectroscopy (10-13) and electron spin resonance spectroscopy (14-16).

These techniques allow a wide variety of information to be obtained on polymers, not only about their detailed chemical structure (9-15) but also about their conformations (7), distance between ends (1), rate of collision between ends (16), vibration frequencies (3-8), segmental motions (2, 14, 15), crystallinity (7), lamellar thickness (6), and surface composition (9).

Much of physical science may be imagined on a three-coordinate system in which the axes are labelled 'Method', 'Substance' and 'Molecular property'. In this volume are described perhaps a dozen spectroscopic methods applied to nearly a hundred macromolecular substances in order to obtain about a dozen types of molecular property. It is hoped that the coordinate points thereby established on this universal frame may help to provide the reader with a guide into unknown regions.

K. J. IVIN

Contributing Authors

ALLEN, G. Department of Chemistry, University of Manchester, England.

ANDO, D. J. Department of Physics, Queen Mary College, London, England.

BATCHELDER, D. N. Department of Physics, Queen Mary College, London, England.

BLOOR, D. Department of Physics, Queen Mary College, London, England.

BOVEY, F. A. Bell Laboratories, Murray Hill, New Jersey, U.S.A.

BULLOCK, A. T. Department of Chemistry, University of Aberdeen, Scotland.

CAMERON, G. G. Department of Chemistry, University of Aberdeen, Scotland.

CLARK, D. T. Department of Chemistry, University of Durham, England.

CUDBY, M. E. A. I.C.I. Ltd., Plastics Division, Welwyn Garden City, England.

CUNLIFFE, A. V. E.R.D.E., Waltham Abbey, Essex, England.

EBDON, J. R. Department of Chemistry, University of Lancaster, England.

FULLER, P. E. E.R.D.E., Waltham Abbey, Essex, England.

HENDRA, P. J. Department of Chemistry, University of Southampton, England.

HIGGINS, JULIA S. Institut Laue-Langevin, Grenoble Cedex, France.

LINDBERG, J. J. Department of Wood & Polymer Chemistry, University of Helsinki, Finland.

PETHRICK, R. A. Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow, Scotland.

PRESTON, F. H. Department of Physics, Queen Mary College, London, England.

SCHAEFER, J. Monsanto Company, St. Louis, Missouri, U.S.A.

SHIMADA, K. Department of Chemistry, SUNY College of Environmental Science and Forestry, Syracuse, N.Y., U.S.A.

SHIMANOUCHI, T. Department of Chemistry, University of Tokyo, Japan.

Szw...., M. *Department of Chemistry, SUNY College of Environmental Science and Forestry, Syracuse, N.Y., U.S.A.*

T. .... *Department of Wood and Polymer Chemistry, University of Helsinki, Finland.*

WHITE, J. W. *St. John's College, Oxford, England.*

WILLIS, H. A. *I.C.I. Ltd., Plastics Division, Welwyn Garden City, England.*

WRIGHT, C. J. *A.E.R.E. Harwell, Didcot, Berkshire, England.*

Contents

3. Torsion Vibrations in Polymers

C. J. WRIGHT

4. Studies of Phonons in Polymer Crystals

J. W. WHITE

5. A New Aspect of Vibration Spectroscopy of High Polymers

T. SHIMANOUCHI

10. High-Resolution Carbon-13 Studies of Polymer Structure

F. A. BOVEY

11. The Analysis of ^{13}C n.m.r. Relaxation Experiments on Polymers

J. SCHAEFER

12. ^{13}C n.m.r. Studies of α-Methylstyrene-Alkane Copolymers

A. V. CUNLIFFE, P. E. FULLER and R. A. PETHRICK

13. The Characterization of Diene Polymers by High Resolution Proton Magnetic Resonance

J. R. EBDON

14. Spin Labels and Probes in Dynamic and Structural Studies of Synthetic and Modified Polymers

P. TÖRMÄLÄ and J. J. LINDBERG

15. E.s.r. Studies of Spin-Labelled Synthetic Polymers

A. T. BULLOCK *and* G. G. CAMERON

16. E.s.r. Studies of Dynamic Flexibility of Molecular Chains

K. SHIMADA *and* M. SZWARC

1

A Review of Neutron Scattering with Special Reference to the Measurement of the Unperturbed Dimensions in Macromolecules

G. Allen

University of Manchester

1.1. INTRODUCTION

A few years ago a group of British chemists and physicists presented a case for the construction of a High Flux Beam Reactor (HFBR) to be devoted to neutron scattering studies of the properties of matter. The case included a programme of work concerned with the structure and dynamics of polymeric materials. In the event the Science Research Council (U.K.) obtained[1] a one-third share in the Franco-German HFBR, at that time under construction at Grenoble. The first four contributions to this volume are presented by workers who pioneered the use of the low-flux facilities at Harwell for studies of polymeric materials and who are now using the new facilities at Grenoble. Our aim is to present an overall view of the status of neutron scattering work on polymers. In this first contribution the general principles of neutron scattering from molecular systems are cursorily reviewed and then the results are presented of measurements of the radii of gyration of macromolecules by small-angle neutron scattering.

1.2 NEUTRON SCATTERING[2]

The neutron has a mass of 1 a.u., it is uncharged and has a spin $I = \frac{1}{2}$. The wavelength distribution of thermal neutrons produced from reactors has a Maxwellian peak at $1 \cdot 8 \, \text{Å}$. In most neutron scattering experiments longer wavelength neutrons are used and so cold neutron sources have been developed to enhance the flux at $5–10 \, \text{Å}$. Liquid hydrogen refrigeration is usually used to cool the neutrons and the flux at $5 \, \text{Å}$ is enhanced by an order of magnitude relative to the corresponding flux of thermal neutrons.

At a wavelength of 5 Å, neutrons have velocities of ~ 1000 m s^{-1} and kinetic energy of 300 J mol^{-1} ($\equiv 23$ cm$^{-1} \equiv 4$ meV). For a given wavelength the kinetic energy of a neutron beam is very much lower than the photon energy of electromagnetic radiation. Furthermore much larger momentum transfers can be studied because of the large mass of the particle. Neutron scattering is distinguished by the fact that it is the only scattering phenomenon for which the energy and momentum transfers are simultaneously of the required orders of magnitude for the study of molecular systems—and hence polymers.

1.2.1 Energy and momentum transfer

When a neutron of incident wavelength λ_0 and velocity v_0 is scattered through an angle θ in an inelastic process (Figure 1.1) which changes the scattered
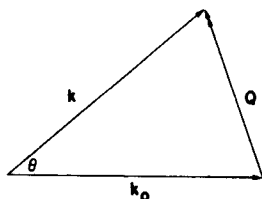
Figure 1.1 Momentum transfer in a neutron scattering event. k_0 is the initial wave vector, k the scattering wave vector and Q the momentum transfer

wavelength to λ and the velocity to v, then the energy transfer is:

$$\Delta E = \tfrac{1}{2}m(v^2 - v_0^2) = \frac{\hbar^2}{2m}(k^2 - k_0^2)$$

where m is the mass of the neutron and $k_0 \doteq 2\pi/\lambda_0$ and $k = 2\pi/\lambda$ are the wave vectors.

From Figure 1.1, the momentum transfer is:

$$\hbar Q = \hbar(k - k_0)$$

For an inelastic process

$$Q = 2\left[\left(k_0^2 + \frac{m\,\Delta E}{\hbar^2}\right) - k_0\left(k_0^2 + \frac{2m\,\Delta E}{\hbar^2}\right)^{\frac{1}{2}}\cos\theta\right]^{\frac{1}{2}}$$

and for an elastic process, or a quasi-elastic process for which $\Delta E \sim 0$

$$Q = \frac{4\pi \sin(\theta/2)}{\lambda_0}$$

Elastic ($\Delta E = 0$), quasi-elastic ($\Delta E \sim 0$) and inelastic ($\Delta E \neq 0$) scattering events are observed in neutron experiments and these events are studied as a

function of momentum transfer $\mathbf{Q}$. We shall see shortly that each type of scattering process has a specific application in the study of polymeric materials.

1.2.2 Scattering cross-sections; coherent and incoherent

In one popular type of neutron scattering spectrometer, the time-of-flight instrument, energy transfer is measured by the difference in velocity of the incident neutrons and of the neutrons scattered in a fixed direction. The momentum transfer is defined by the incident wavelength λ_0 and the angle of scatter θ for elastic and quasi-elastic events; for inelastic events ΔE is required in addition in order to measure $\mathbf{Q}$.

Being uncharged, neutrons are scattered by the *nuclei* in the sample under investigation. Consequently the optical selection rules which govern the scattering and absorption of electromagnetic radiation do not apply. In principle *all* possible energy and momentum transfers are observable in neutron scattering experiments.

The scattering cross-section σ (or alternatively the scattering length b, since $\sigma = 4\pi\langle b^2\rangle$) is different for each kind of nucleus—i.e. for each isotope, and is independent of energy for the low-energy neutrons usually used. For example $\sigma^{1H} \neq \sigma^{2H} \neq \sigma^{12C}$ etc. However, because the neutron has a spin of $\frac{1}{2}$, the scattering cross-section also depends on the total spin angular momentum of the neutron and the scattering nucleus. For a nucleus with spin I the net spin can take on values $I + \frac{1}{2}, I - \frac{1}{2}$. Thus if we consider an array of nuclei containing only one isotopic species of spin I, provided the nuclear spins are uncorrelated, two scattering components are generated:

(i) Spin-coherent scattering, with associated interference effects; its intensity is proportional to the square of the mean scattering length averaged over the array of nuclei, i.e.

$$\sigma_{coh} = 4\pi\langle b\rangle^2$$

(ii) Spin-incoherent scattering, displaying no interference effects; its intensity is proportional to the mean square of the deviation from the average over the array,

$$\sigma_{incoh} = 4\pi[\langle b^2\rangle - \langle b\rangle^2]$$

Table 1.1 Nuclear scattering cross-sections (in barns) for low-energy neutrons

	I	σ_{coh}	σ_{incoh}
^{1}H	$\frac{1}{2}$	1·8	79·7
^{2}H	1	5·6	2·0
^{12}C	0	5·6	—
^{14}N	1	11·6	0·3
^{16}O	0	4·2	—
^{28}Si	0	2·0	—

A special case arises for nuclei for which $I = 0$, since only the coherent component is generated for these isotopes. Table 1.1 lists the coherent and incoherent scattering cross-sections for the nuclei most commonly occurring in synthetic and natural polymers; note the wide range of values for both components.

1.2.3 Selection rules and molecular spectroscopy

Finally in this brief review of neutron scattering from molecular systems we must consider the consequences in molecular spectroscopy of the absence of optical selection rules. In infrared spectroscopy only the normal modes for which the element of the dipole moment tensor is finite are active (i.e. $|\partial\mu/\partial q|^2 > 0$) and correspondingly in Raman spectroscopy the element of the polarizability tensor must be finite (i.e. $|\partial\alpha/\partial q|^2 > 0$). Indeed the intensities of the observed bands depend on the magnitude of these elements. If we perform a 'Raman' experiment using neutrons rather than visible light to excite the spectrum (and noting that because $E \equiv 23\,cm^{-1}$ only the anti-Stokes region will be observed) then *all* normal modes will be active, because optical selection rules do not apply for the scattering of neutrons by nuclei. Further, the intensity of each band will be related to the mean-square-displacement of the nuclei in its normal mode. Thus certain torsional intramolecular modes, especially of side groups, in polymer chains will be more intense than stretching and bending modes.

Another consequence of the relaxed selection rules is that in periodic systems such as crystals or polymer chains the dispersion of the modes has to be considered. In optical molecular spectroscopy only the phase difference $\delta = 0$ needs to be considered; in neutron molecular spectroscopy all phase differences are allowed. Thus the computation of the density of vibrational states for a neutron spectrum is in this sense a much more formidable problem than for an infrared or Raman spectrum.

There is, fortunately, an effect peculiar to neutron spectroscopy which greatly aids vibrational assignment. The large difference in cross-section between ^1H and ^2H noted in Table 1.1 means that selective deuteration of, say, a CH_3 group greatly reduces its intensity in the neutron molecular spectrum not only because of the change in cross-section but also because of the reduction in the amplitudes of nuclear displacement in the normal mode.

1.3 BASIC NEUTRON SCATTERING EXPERIMENTS IN POLYMERS

From the point of view of the neutron scattering technique there are six basic types of experiment, which can be classified as elastic, quasi-elastic and inelastic, each category having a spin-coherent and spin-incoherent sub-division. In this section we will simply list the applications to polymer problems which are already being studied or are imminent.

Elastic		
Coherent	Crystallography	Structure of crystalline polymers
	Small-angle scattering	Molecular dimensions (R_g) in bulk polymers
Incoherent	—	—
Quasi-elastic		
Coherent	Doppler broadening of elastic peak as $f(Q)$	Molecular dimensions and molecular dynamics in solutions and rubbers
Incoherent	Dopper broadening of elastic peak as $f(Q)$	Molecular dynamics in solutions and rubbers
Inelastic		
Coherent	Dispersion curves of intra- and intermolecular vibrations	Elastic constants of crystals Intermolecular potential functions
Incoherent	Molecular spectra Lattice vibrations	Molecular vibrations Intramolecular potential functions

In general, deuterated samples must be used for the study of coherent scattering phenomena to reduce the incoherent contribution from protons, and selective deuteration is useful in neutron inelastic incoherent spectroscopy. The list is not exhaustive and the remainder of this contribution will deal only with small-angle neutron scattering. The following three contributions will deal with, respectively, quasi-elastic studies of self diffusion (p. 13), molecular spectroscopy (p. 29), and the study of the dispersion curves of intra- and inter-molecular vibrations in crystalline polymers (p. 41).

1.4 MEASUREMENT OF MOLECULAR DIMENSIONS IN BULK BY SMALL-ANGLE NEUTRON COHERENT SCATTERING

Some 20 years ago Flory[3] put forward the hypothesis that in the amorphous states, rubber and glass, a polymer chain obeys random flight statistics, that is to say that the molecules have unperturbed dimensions as found in θ-solvents at the θ-temperature. Although unperturbed dimensions of polymer chains are readily measured in θ-solvents by Rayleigh light scattering or by small-angle X-ray studies, hitherto no measurements have been possible in the bulk rubber or glass. These techniques are applicable to solutions because of the contrast provided by the difference in refractive index between solute and solvent in light-scattering studies and the difference in electron densities in the case of X-ray scattering.

In the bulk undeuterated polymer there is, of course, no contrast between individual polymer molecules and the matrix. However, if we consider 1% of a perdeuterated polymer dissolved in a matrix of the corresponding protonated