

*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

Copyright © 1976, by John Wiley & Sons, Ltd.

All rights reserved.

No part of this book may be reproduced by any means, nor transmitted, nor translated into a machine language without the written permission of the publisher

*Library of Congress Cataloging in Publication Data:*

Main entry under title

Structural studies of macromolecules by spectroscopic methods.

'A Wiley-Interscience publication.'

Includes bibliographical references

1. Macromolecules—Analysis 2. Spectrum analysis.

I. Ivin, Kenneth John. [DNLM 1. Macromolecular systems—  
Congresses. 2. Spectrum analysis—Congresses  
QD380 S927 1974]

QD381.S8 1976 547.7 75-19355

ISBN 0 471 43120 6

Set-on Monophoto Filmsetter and printed in Great Britain  
by J. W. Arrowsmith Ltd, Bristol

## *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.*

SZWARCZ, M.

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

TEKONEN, E.

*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*

## **1. A Review of Neutron Scattering with Special Reference to the Measurement of the Unperturbed Dimensions in Macromolecules**

**G. ALLEN**

1.1	Introduction	1
1.2	Neutron Scattering	1
1.2.1	Energy and momentum transfer	2
1.2.2	Scattering cross-sections; coherent and incoherent	3
1.2.3	Selection rules and molecular spectroscopy	4
1.3	Basic Neutron Scattering Experiments in Polymers	4
1.4	Measurements of Molecular Dimensions in Bulk by Small-Angle Neutron Coherent Scattering	5
1.4.1	Apparatus and experimental technique	7
1.4.2	Results of small-angle neutron scattering measurements	9
1.4.2.1	Poly(methyl methacrylate).	9
1.4.2.2	Polystyrene	9
1.4.2.3	Polyethylene	10
1.4.2.4	Rubber elasticity	10
1.5	References	11

## **2. Diffusional Motion of Rubbers**

**J. S. HIGGINS**

2.1	Introduction	13
2.1.1	Correlation functions for polymeric systems	14
2.2	Experimental	15
2.2.1	Measurement	15
2.2.2	Analysis	16
2.3	Bulk Polymers	17
2.3.1	Polydimethylsiloxane	17
2.3.2	Other polymer systems	19
2.3.3	Temperature dependence	20
2.4	Polymers in Solution	21
2.4.1	Small molecules in CS <sub>2</sub>	22
2.4.2	Poly(ethylene oxide) in solution	23

2.5	Higher Resolution Studies of Bulk Polymers	23
2.5.1	The functional form of $S(Q, \omega)$	23
2.5.2	High resolution experiments	23
2.5.3	The broadening function and its half-width variation	25
2.6	Outlook	26
2.7	References	28

### 3. Torsion Vibrations in Polymers

C. J. WRIGHT

3.1	Introduction	29
3.2	Experimental	30
3.3	Results	30
3.3.1	Poly(propylene oxide) and polypropylene: torsion frequencies and energy barriers	30
3.3.2	Poly(methyl methacrylate) and poly( $\alpha$ -methylstyrene): effect of microstructure	34
3.3.3	Polystyrene: torsion frequency of the phenyl group	37
3.4	Relationship to Mechanical and Dielectric Loss Data	38
3.5	Conclusion	39
3.6	References	39

### 4. Studies of Phonons in Polymer Crystals

J. W. WHITE

4.1	Introduction	41
4.2	Polymer Vibrations and Forces	42
4.3	Techniques of Neutron Scattering Spectroscopy	44
4.4	Phonons in Polycrystalline Polytetrafluoroethylene	46
4.5	Polyethylene	49
4.6	Polyoxymethylene	51
4.7	Neutron Diffraction from Collagen	56
4.8	References	58

### 5. A New Aspect of Vibration Spectroscopy of High Polymers

T. SHIMANOCHI

5.1	Introduction	59
5.2	n-Paraffin Molecules	59
5.3	Longitudinal Acoustical Modes of n-Paraffin Molecules	63
5.4	Low-Frequency Raman Bands of Crystalline n-Paraffins	66
5.5	Polypeptide Chains and Protein Molecules	68
5.6	Local and Non-Local Vibrations of Polypeptide Chains	69
5.7	Overall Vibrations of Polypeptide Chains and Protein Molecules	70
5.8	References	72



## **6. The Measurement of Lamellar Thickness by Raman Methods**

**P. J. HENDRA**

6.1 Methods for the Investigation of Lamellae in Polymers . . . . .	73
6.2 Experimental Methods. . . . .	75
6.3 Applications of the Raman Technique . . . . .	77
6.4 Conclusion. . . . .	80
6.5 References . . . . .	80

## **7. The Study of Crystallinity in Synthetic Polymers by Low-Frequency Vibrational Spectroscopy**

**H. A. WILLIS and M. E. A. CUDBY**

7.1 Introduction . . . . .	81
7.2 The Far Infrared Region ( $400 - 10 \text{ cm}^{-1}$ ) . . . . .	83
7.3 Polyethylene . . . . .	84
7.4 Polypropylene . . . . .	85
7.5 Polytetrafluoroethylene . . . . .	87
7.6 References . . . . .	89

## **8. Resonant Raman Scattering from Diacetylene Polymers**

**D. BLOOR, F. H. PRESTON, D. J. ANDO and D. N. BATCHELDER**

8.1 Introduction . . . . .	91
8.2 Resonant Raman Scattering . . . . .	93
8.3 Vibrational Modes of the Diacetylene Backbone . . . . .	95
8.4 Experimental Techniques . . . . .	98
8.5 Resonant Raman Scattering from Single Crystal Diacetylene Polymers . . . . .	99
8.6 Resonant Raman Scattering from Amorphous Diacetylene Polymers . . . . .	106
8.7 Conclusions . . . . .	108
8.8 References . . . . .	108

## **9. The Application of ESCA to Studies of Structure and Bonding in Polymers**

**D. T. CLARK**

9.1 Introduction . . . . .	111
9.2 Fundamentals of ESCA . . . . .	112
9.2.1 Introduction . . . . .	112
9.2.2 Properties of core orbitals . . . . .	113
9.2.3 The ESCA experiment . . . . .	113
9.2.4 Photoelectric cross-sections . . . . .	116
9.2.5 Energy considerations . . . . .	118
9.2.6 Linewidths . . . . .	121

9.2.7	Simple examples illustrating points discussed in 9.2.1–9.2.6	122
9.2.8	Basic types of information available from ESCA studies	130
9.3	A Preliminary Appraisal of the Application of ESCA to Studies of Structure and Bonding in Polymers	131
9.3.1	Introduction	131
9.3.2	Sample preparation	134
9.3.2.1	From solution	134
9.3.2.2	From pressing or extrusion	134
9.3.2.3	Polymerization in situ	135
9.3.3	Energy referencing	135
9.4	Application to Studies of Homogeneous Materials	138
9.4.1	Homopolymers	138
9.4.2	Theoretical models for a quantitative discussion of results	145
9.4.3	Copolymers	153
9.4.3.1	Copolymer compositions	154
9.4.3.2	Structural details	159
9.5	Application to Surface Studies	164
9.5.1	Surface structure of block copolymers	164
9.5.2	CASING	167
9.5.3	Alkali metal etching of PTFE	169
9.5.4	Oxidation of polymer samples	169
9.5.5	Surface fluorination of polyethylene	173
9.6	References	177

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

F. A. BOVEY

10.1	Introduction	181
10.2	C-13 Chemical Shifts of Paraffinic Hydrocarbons	182
10.3	C-13 Observations of Chain Structure and Branching in Polyethylene and Poly(vinyl chloride)	188
10.4	C-13 Study of Biopolymers	193
10.5	A Final Word	199
10.6	References	199

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

J. SCHAEFER

11.1	Introduction	201
11.2	Relaxation Experiments on Solutions of Polymers and on Solid Polymers above $T_g$	202
11.2.1	Spin-lattice relaxation times	202
11.2.1.1	Polystyrene	203
11.2.1.2	Short-chain alkanes	204
11.2.1.3	Elastomers	206

11.2.2	Nuclear Overhauser Enhancements	208
11.3	Relaxation Experiments on Rigid Solid Polymers below $T_g$	216
11.3.1	Spin-lattice relaxation times and nuclear Overhauser enhancements	216
11.3.2	Cross-polarization	221
11.3.3	Magic-angle spinning	223
11.4	References	225
12.	<b><math>^{13}\text{C}</math> n.m.r. Studies of <math>\alpha</math>-Methylstyrene-Alkane Copolymers</b>	
	A. V. CUNLIFFE, P. E. FULLER and R. A. PETHRICK	
12.1	Introduction	227
12.2	Experimental	230
12.3	$^{13}\text{C}$ n.m.r. Spectra of $\alpha$ -Methylstyrene/Alkane Dimers	231
12.4	$^{13}\text{C}$ n.m.r. Spectra of $\alpha$ -Methylstyrene/Alkane Copolymers	234
12.5	References	239
13.	<b>The Characterization of Diene Polymers by High Resolution Proton Magnetic Resonance</b>	
	J. R. EBDON	
13.1	Introduction	241
13.2	Homopolymers	242
13.2.1	Butadiene	242
13.2.2	Isoprene	244
13.2.3	Chloroprene	245
13.2.4	Other dienes	246
13.3	Copolymers	247
13.3.1	Methyl methacrylate-diene copolymers	247
13.3.2	Acrylonitrile-diene copolymers	252
13.3.3	$\alpha$ -Methylstyrene-butadiene copolymers	252
13.3.4	Other copolymers	253
13.4	References	253
14.	<b>Spin Labels and Probes in Dynamic and Structural Studies of Synthetic and Modified Polymers</b>	
	P. TÖRMÄLÄ and J. J. LINDBERG	
14.1	Introduction	255
14.2	Theoretical Methods	256
14.3	Linear Polymers	259
14.3.1	Spin probe studies	259
14.3.2	Spin labelling studies	263
14.3.3	Application potentialities	265
14.4	Network Polymers	266

14.5	Conclusions	270
14.6	References	270

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

A. T. BULLOCK and G. G. CAMERON

15.1	Introduction	273
15.2	Preparation and Characterization of Spin-Labelled Polymers	274
15.2.1	Polystyrene	275
15.2.2	End-labelled poly(methyl methacrylate)	283
15.2.3	Polyacrylates labelled on ester groups	284
15.3	Theory and Method of Line-Width Analysis	286
15.4	Results of Dynamic Studies	290
15.4.1	Polystyrene in solution	290
15.4.1.1	The dependence of $\tau_c$ on molecular weight	290
15.4.1.2	Solvent effects	294
15.4.1.3	Concentration effects	297
15.4.2	End-labelled poly(methyl methacrylate)	299
15.4.3	Polyacrylates labelled on ester groups	303
15.4.4	Relaxation in solid polymers	305
15.5	Spin-Labels in Structural Studies	307
15.5.1	Lithiation of polystyrene and styrene-halostyrene copolymers	308
15.5.2	Decomposition products of PMMA anions	310
15.6	References	313

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

K. SHIMADA and M. SZWARC

16.1	Introduction	317
16.2	Experimental Approach and the Method of Calculation	317
16.3	Results and their Significance	321
16.4	Dynamic or Static Model of Intramolecular Exchange?	324
16.5	The Effect of the Viscosity of the Solvent	325
16.6	Concluding Remarks	328
16.7	References	328
16.8	Appendix	329

Subject Index	333
---------------	-----

# *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<sup>1</sup> 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<sup>2</sup>

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 1.8 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 Å. Liquid hydrogen refrigeration is usually used to cool the neutrons and the flux at 5 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  $\sim 1000 \text{ m s}^{-1}$  and kinetic energy of  $300 \text{ J mol}^{-1}$  ( $\equiv 23 \text{ cm}^{-1} \equiv 4 \text{ meV}$ ). 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  $\lambda_0$  and velocity  $v_0$  is scattered through an angle  $\theta$  in an inelastic process (Figure 1.1) which changes the scattered

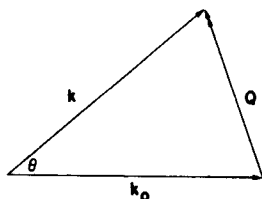


Figure 1.1 Momentum transfer in a neutron scattering event.  $\mathbf{k}_0$  is the initial wave vector,  $\mathbf{k}$  the scattering wave vector and  $\mathbf{Q}$  the momentum transfer

wavelength to  $\lambda$  and the velocity to  $v$ , then the energy transfer is:

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

where  $m$  is the mass of the neutron and  $\mathbf{k}_0 = 2\pi/\lambda_0$  and  $\mathbf{k} = 2\pi/\lambda$  are the wave vectors.

From Figure 1.1, the momentum transfer is:

$$\hbar\mathbf{Q} = \hbar(\mathbf{k} - \mathbf{k}_0)$$

For an inelastic process

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

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  $Q$ . 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  $\lambda_0$  and the angle of scatter  $\theta$  for elastic and quasi-elastic events; for inelastic events  $\Delta E$  is required in addition in order to measure  $Q$ .

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  $\sigma$  (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  $\sigma^1\text{H} \neq \sigma^2\text{H} \neq \sigma^{12}\text{C}$  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

	$I$	$\sigma_{coh}$	$\sigma_{incoh}$
$^1\text{H}$	$\frac{1}{2}$	1.8	79.7
$^2\text{H}$	1	5.6	2.0
$^{12}\text{C}$	0	5.6	—
$^{14}\text{N}$	1	11.6	0.3
$^{16}\text{O}$	0	4.2	—
$^{28}\text{Si}$	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  $E \approx 23 \text{ cm}^{-1}$  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  $^1\text{H}$  and  $^2\text{H}$  noted in Table 1.1 means that selective deuteration of, say, a  $\text{CH}_3$  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 Small-angle scattering	Structure of crystalline polymers 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	Doppler 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 intermolecular 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<sup>3</sup> 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  $\theta$ -solvents at the  $\theta$ -temperature. Although unperturbed dimensions of polymer chains are readily measured in  $\theta$ -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