

# **ANNUAL REPORTS ON NMR SPECTROSCOPY**

**Volume 34**

- **Multidimensional NMR methods for elucidating structure and dynamics of polymers**
- **Structure and dynamics of polymer gel systems viewed using NMR spectroscopy**
- **NMR studies of cross-linked polymers**
- **The conformational connection between the microstructures of polymers and their NMR spectra**
- **A review of high resolution NMR studies of vulcanized elastomers**
- **Structural analysis of oriented polymers by solid state NMR**



**ACADEMIC PRESS**

ANNUAL REPORTS ON  
**NMR SPECTROSCOPY**

Edited by

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**VOLUME 34**



**ACADEMIC PRESS**

San Diego • London • Boston  
New York • Sydney • Tokyo • Toronto

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Academic Press, Inc.  
525 B Street, Suite 1900, San Diego, California 92101-4495, USA  
<http://www.apnet.com>

Academic Press Limited  
24-28 Oval Road, London NW1 7DX, UK  
<http://www.hbuk.co.uk/ap/>

ISBN 0-12-505334-7

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

Typeset by Keyset Composition, Colchester, Essex  
Printed in Great Britain by Hartnolls Ltd, Bodmin, Cornwall

97 98 99 00 01 02 EB 9 8 7 6 5 4 3 2 1

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## Preface

It is a very great pleasure for me to welcome my longstanding co-worker and friend, Professor I. Ando of the Tokyo Institute of Technology, as co-editor of this volume of *Annual Reports on NMR Spectroscopy*, which represents the third in the series of special issues. The theme of this volume is applications of NMR in polymer science. The lambent insight into the structure and dynamics of molecules afforded by NMR techniques is well established. Volume 34 of *Annual Reports on NMR Spectroscopy* consists of six chapters covering a wide range of polymer topics, each one demonstrating the unique ability of NMR to provide information of both general and special interests.

Multidimensional NMR methods for elucidating structure and dynamics of polymers are covered by Professor H. W. Spiess; structure and dynamics of polymer gel systems are reported on by Professor I. Ando together with Drs H. Yasunaga, M. Kobayashi, S. Matsukawa and H. Kurosu; NMR studies of crosslinked polymers are reviewed by Dr A. K. Whittaker; Professor A. E. Tonelli deals with the conformational connection between the microstructures of polymers and their NMR spectra; a review of high-resolution NMR studies of vulcanized elastomers is provided by Dr M. Mori and Professor J. L. Koenig; the volume is completed with an account of the structural analysis of oriented polymers by solid-state NMR from Professor T. Asakura, Dr M. Demura and Dr N. Nishikawa.

My thanks go to all of these contributors, and to my co-editor and the production staff at Academic Press (London), for their very generous cooperation in the genesis of this volume.

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October 1996

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# Multidimensional NMR Methods for Elucidating Structure and Dynamics of Polymers

H. W. SPIESS

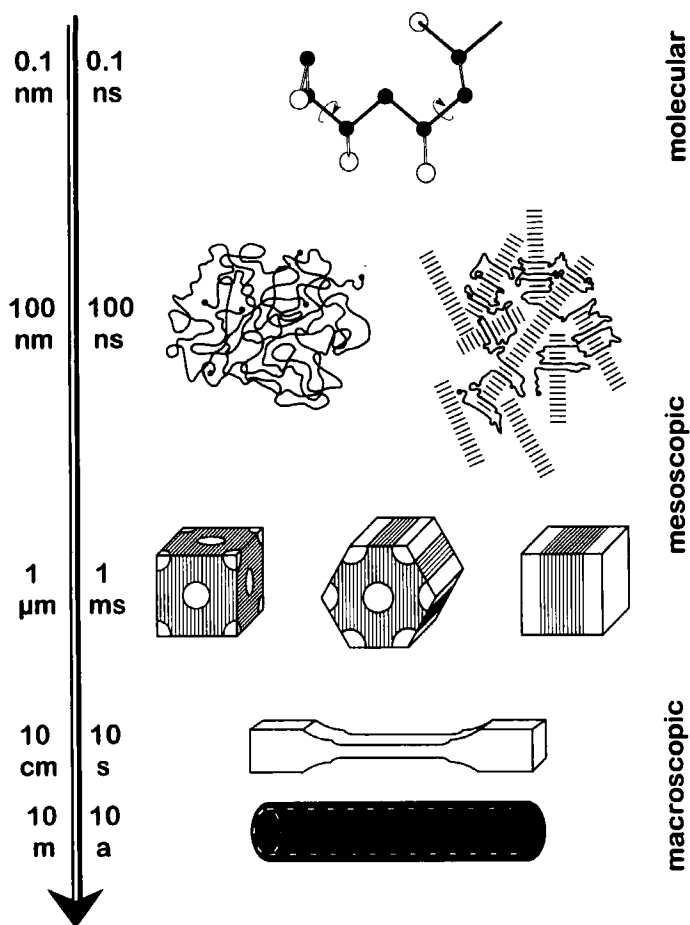
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*This report describes new developments in multidimensional solid-state NMR, which is evolving as an indispensable tool for polymer characterization. After a short introduction, the unique information available by solid-state NMR is demonstrated by specific examples of structural studies of chain conformation, advanced aspects of chain dynamics, phase separation and interfacial effects, as well as non-linear plastic deformation in polymers. Emphasis is placed on the new development of high-resolution multiple-quantum NMR spectroscopy of abundant nuclei in solids with first experimental examples on the location of hydrogen positions in organic solids and chain order in polymer melts and elastomers.*

## 1. INTRODUCTION

The study of structure and dynamics of polymers by NMR can be viewed as part of a more general endeavour of materials science, aimed at establishing structure-property relationships in order to improve known and



**Fig. 1.** Length- and timescales of polymer materials showing (from top to bottom) a conformational unit, random coils of amorphous and lamellae of semicrystalline polymers, phase separated structures, a testing bar for mechanical measurements and part of a tube as final product.

design new materials. Polymer behaviour depends on both the molecular structure and the organization of the macromolecules in the solid state.<sup>1</sup> Therefore, it involves enormous length- and timescales as indicated in Fig. 1. Most polymers are amorphous, where the chains form random coils on mesoscopic scales. Stereoregular macromolecules can partially crystallize to form ordered lamellar structures separated by non-crystalline regions. Multicomponent polymer systems are phase separated in most cases to form micellar, cylindrical or lamellar structures, depending on the fraction of the

**Table 1.** Methods of polymer characterization.

Method	Type
Microscopy	Light, electron, scanning tunnel, force
Spectroscopy	NMR, EPR, IR/Raman, UV/VIS
Scattering	Light, X-ray, neutron
Relaxation	Dielectric, mechanical
Simulation	Computer

different components. On a macroscopic level the mechanical behaviour is typically probed by a tensile bar and the final product might be a large-scale tube.

Therefore, polymer characterization must cover these wide length- and timescales. This calls for powerful analytical tools and, in fact, all variants of microscopy, spectroscopy, scattering, relaxation and computer simulation techniques as collected in Table 1 are used in this area. In view of the fact that these methods are generally far advanced and well established in polymer physics the question may arise: do we need yet another tool, such as solid-state NMR? The answer will be yes only if NMR compares favourably with the other techniques and yields important information which cannot be obtained in an easier way. Indeed, NMR spectroscopy offers several advantages, such as:

- unique selectivity;
- exceptionally high versatility;
- high potential for further developments.

These are demonstrated here through recent examples from our laboratory covering a wide range of length- and timescales, probing the local chain conformation, advanced aspects of chain dynamics, phase separation in multicomponent systems, and immobilization due to non-linear mechanical deformation.

## 2. SOLID-STATE NMR

Before describing specific examples we briefly review the techniques used in these applications. Most of them involve concepts of two-dimensional spectroscopy.<sup>2</sup> A full treatment is available in our extended monograph on multidimensional solid-state NMR and polymers.<sup>3</sup>

NMR clearly outranks the other techniques of polymer characterization as far as *selectivity* is concerned. First of all, NMR is highly site-selective, since the precession (Larmor) frequency is vastly different for the nuclei of

different elements or even for different isotopes of the same element. Furthermore, internal couplings of the nuclei to their surroundings render NMR sensitive to the details of the chemical structure. The enormous signal contrast due to the differences of natural abundance for the different isotopes provides a route of further increasing selectivity by isotopic labelling. The build-up of magnetization, which can subsequently be utilized in the NMR experiment, requires exchange of energy between the nuclear spins and their surroundings (spin–lattice relaxation, time constant  $T_1$ ). This process strongly depends on the molecular dynamics. Likewise, the free induction decay (FID) (transverse relaxation, time constant  $T_2$ ) depends on the strength and the fluctuations of the couplings the nuclear spins experience. Thus “relaxation filters” can be applied to record selectively NMR spectra of mobile or rigid parts of a heterogeneous polymer material. Last, but not least, after recording multidimensional data sets, repeated Fourier transformation (FT) yields multidimensional NMR spectra. They offer fundamental advantages over conventional (one-dimensional, 1D) spectra, such as increase of spectral resolution and routes to new information, unavailable from 1D NMR even in the limit of highest resolution.

## 2.1. One-dimensional NMR

NMR spectra are site-selective, because the magnetic fields that the nuclei experience are slightly different from the external field  $\mathbf{B}_0$  due to the magnetic shielding by the surrounding electrons. The *chemical shift* spans about 10 ppm for  $^1\text{H}$  and 200 ppm for  $^{13}\text{C}$  in different functional groups. In solids, several anisotropic couplings of nuclear spins with their surroundings exist<sup>2,3</sup> which can be used to provide angular dependent information. In particular, the magnetic *dipole–dipole coupling* of nuclei among themselves leads to broad NMR lines covering approximately 50 kHz for  $^1\text{H}$ – $^1\text{H}$  homonuclear coupling and approximately 25 kHz for  $^1\text{H}$ – $^{13}\text{C}$  heteronuclear coupling. The *anisotropy* of the *chemical shift* results in powder patterns, which for  $^{13}\text{C}$  cover approximately 15 kHz at a field strength of 7 T. In addition to these magnetic interactions, nuclei with spin  $I > 1/2$  can also have electric quadrupole moments and are subject to *quadrupole coupling* to the electric field gradient at the nuclear site. For  $^2\text{H}$  ( $I = 1$ ) in C– $^2\text{H}$  bonds this leads to spectral splittings of approximately 250 kHz. Since C–H bonds are common in polymers,  $^2\text{H}$  labelling is particularly useful.

The angular dependence of the NMR frequency in high magnetic fields is alike for all couplings and is given by

$$\omega = \omega_L + \frac{1}{2}\Delta(3 \cos^2 \vartheta - 1 - \eta \sin^2 \vartheta \cos 2 \varphi) \quad (1)$$

Here  $\omega_L$  is the Larmor frequency including isotropic chemical shifts and  $\Delta$

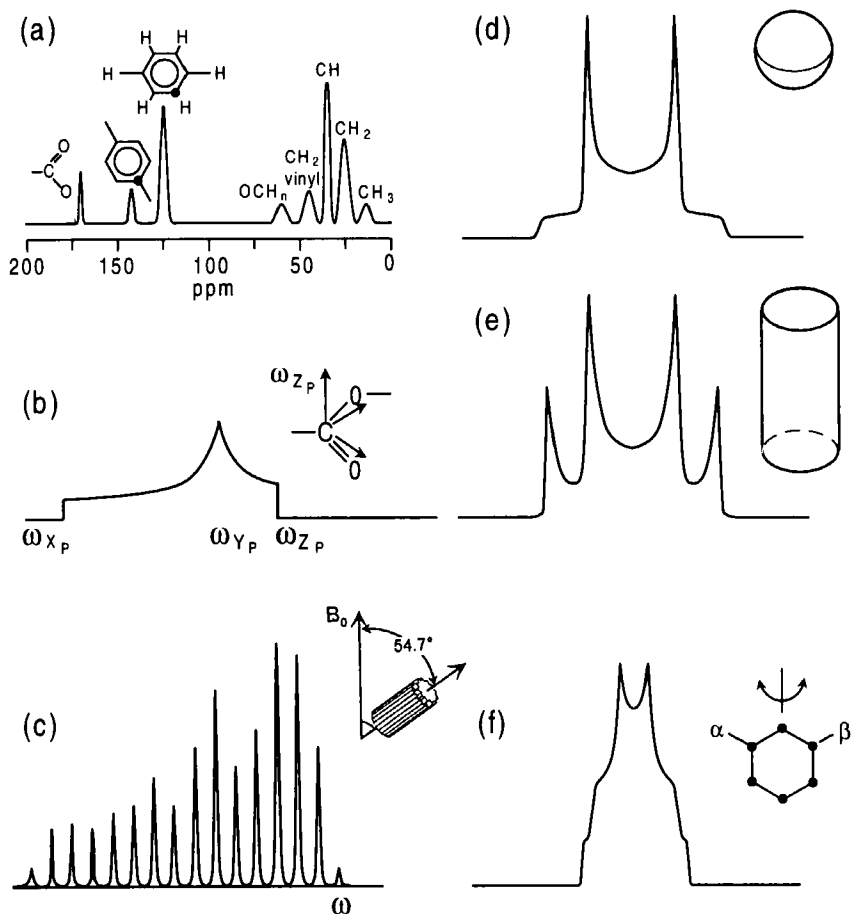
describes the strength of the anisotropic coupling, i.e. anisotropic chemical shift or  $^{13}\text{C}$ - $^1\text{H}$  dipole-dipole coupling for  $^{13}\text{C}$  and quadrupole coupling for  $^2\text{H}$ . The asymmetry parameter  $\eta$  describes the deviation of the anisotropic coupling from axial symmetry ( $0 \leq \eta \leq 1$ ). The angles  $\vartheta$ ,  $\varphi$  are the polar angles of the magnetic field  $\mathbf{B}_0$  in the principal axes system of the coupling tensor. This in turn is often related in a simple way to the molecular geometry: the unique axis ( $z$ ) is along a  $^{13}\text{C}$ - $^1\text{H}$  bond (dipole-dipole coupling), or a  $\text{C}$ - $^2\text{H}$  bond (quadrupole coupling) or perpendicular to an  $sp^2$  plane as for  $^{13}\text{C}$  chemical shift tensors in aromatic rings etc. If one of the above-mentioned couplings dominates, either because of its strength, or because the others have been suppressed by decoupling, the NMR spectra are particularly simple. Depending on the total spin involved, signals described by equation (1) and their mirror images with respect to  $\omega_L$  may be superimposed and in powder samples, spectra for all orientations are added to yield the powder line shape (e.g., the Pake pattern for  $^2\text{H}$  with spin  $I = 1$ ). Thus, advanced solid-state NMR techniques make use of the fact that the orientation of molecules is directly reflected in the *position* of the respective line in a suitably recorded NMR spectrum.

These anisotropic interactions are averaged out in liquids due to the rapid isotropic rotational motions of the molecules, and only the isotropic chemical shift remains. This yields much better resolved spectra. In solids a similar averaging effect can be achieved by mechanically rotating the sample at the “magic” angle of  $\theta_M$  relative to  $\mathbf{B}_0$ , for which the angular function ( $3 \cos^2 \theta_M - 1$ ) vanishes. Such magic angle spinning (MAS) yields liquid-like spectra if the spinning frequency  $\omega_R$  is significantly larger than the width of the anisotropic powder pattern ( $\omega_R \gg \Delta$ ). In the slow spinning regime,  $\omega_R < \Delta$ , the centre band at the isotropic chemical shift is flanked by sidebands at multiples of  $\omega_R$ , thus retaining information about the anisotropic coupling.

A few examples of 1D NMR spectra exemplifying the information they provide about structure and dynamics of polymers are collected in Fig. 2, displaying single  $^{13}\text{C}$ -lines at the isotropic chemical shifts (Fig. 2(a)), a chemical shift powder pattern for  $^{13}\text{C}$  in a carbonyl group and its relation to the molecular geometry (Fig. 2(b)), a  $^{13}\text{C}$  MAS sideband pattern (Fig. 2(c)), and  $^2\text{H}$  NMR line shapes for an isotropic powder (Pake pattern, Fig. 2(d)), a uniaxially drawn fibre (Fig. 2(e)), and a phenyl ring with motional averaging due to flipping about the axis shown (Fig. 2(f)).

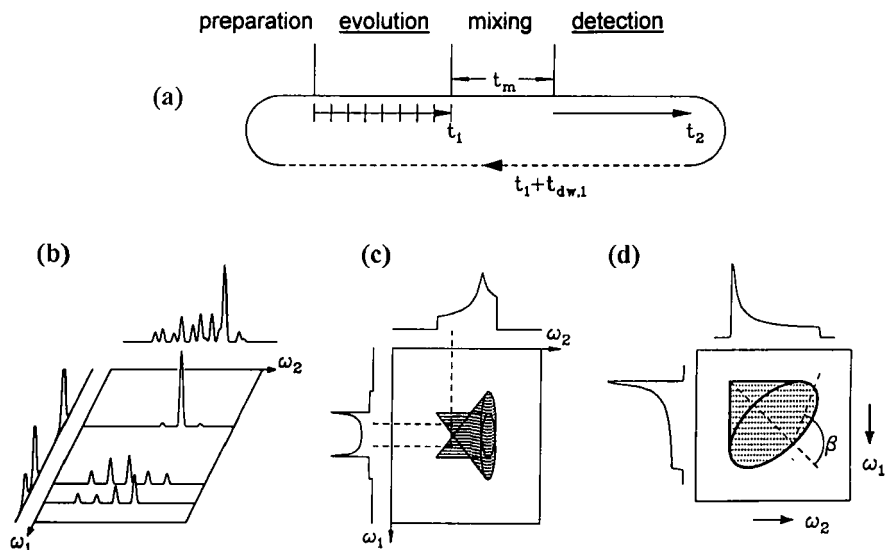
## 2.2. Two-dimensional NMR

A 2D NMR spectrum<sup>2,3</sup> is generated by recording a two-dimensional data set following pulsed irradiation as a function of two time variables, as shown schematically in Fig. 3(a), and subsequent double Fourier transformation.



**Fig. 2.** Examples of solid-state NMR spectra. (a)  $^{13}\text{C}$  CP MAS spectrum displaying isotropic chemical shifts of different functional groups. (b)  $^{13}\text{C}$  powder pattern for a carbonyl group, governed by the chemical shift anisotropy and relation of the principal axes system of the shielding tensor to the molecular framework. (c)  $^{13}\text{C}$  sidebands due to anisotropic chemical shift and slow MAS. (d)  $^2\text{H}$ -NMR line shape for a rigid isotropic powder (Pake pattern). (e)  $^2\text{H}$ -NMR line shape for a uniaxial fibre. (f)  $^2\text{H}$ -NMR line shape for flipping phenyl rings.

The development of the nuclear spin system in the *evolution period* with incremented time  $t_1$  at the beginning of the pulse sequence provides the basis for the first frequency dimension  $\omega_1$ . The NMR signal is detected in the *detection period* with time  $t_2$  at the end of the pulse sequence, providing the basis for the second frequency dimension  $\omega_2$ . In *exchange experiments*, a variable *mixing period* of duration  $t_m$ , during which dynamic processes can take place, is inserted between evolution and detection.



**Fig. 3.** Principles of 2D-NMR spectroscopy. (a) Basic pulse sequence consisting of preparation, evolution, mixing and detection periods. Prior to this, relaxation filters can be applied in the preparation period to distinguish from, e.g. molecular motion. (b) Separation of isotropic and anisotropic chemical shift sideband patterns. (c) Correlation of anisotropic chemical shift and dipolar interaction. (d) 2D exchange spectrum revealing the reorientation of a polymer segment about the angle  $\beta$  through an elliptical exchange ridge.

The most important aspects of 2D NMR are exemplified in Fig. 3(b)–(d). First, 2D NMR is often used to *increase the spectral resolution* of solid-state NMR spectra by *separating* different interactions. As an example, consider 1D sideband patterns. Their analysis is often hampered by a severe loss of spectral resolution due to overlapping sidebands of  $^{13}\text{C}$  with different isotropic chemical shifts. This loss of resolution is circumvented at the expense of a new frequency dimension as demonstrated in Fig. 3(b), where sideband patterns for different sites experiencing different isotropic chemical shifts are separated from each other.

Other 2D NMR techniques aim at obtaining new information by *correlating* different interactions. As a specific example, Fig. 3(c) displays a 2D NMR spectrum correlating a  $^{13}\text{C}$  chemical shift with a  $^{13}\text{C}$ – $^1\text{H}$  dipolar powder pattern. Since the dipole–dipole coupling is well-understood in terms of bond lengths and angles, such spectra provide valuable information about the orientation of the principal axes of the chemical shift tensor in relation to structural units such as  $\text{CH}_2$ -groups etc.

As far as applications to polymers are concerned, 2D *exchange* NMR proves to be particularly valuable.<sup>3</sup> First of all, by varying the mixing time



$t_m$ , slow dynamic processes in the range of milliseconds to seconds can be followed in *real time*. Moreover, 2D exchange NMR spectra yield unique and model-independent information about the *geometry* of rotational motions. In fact, for axially symmetric tensors, ubiquitous in  $^2\text{H}$  NMR of polymers, the 2D exchange spectrum yields elliptical ridge patterns from which the angle about which the segments have rotated can be read off with a ruler (Fig. 3(d)).

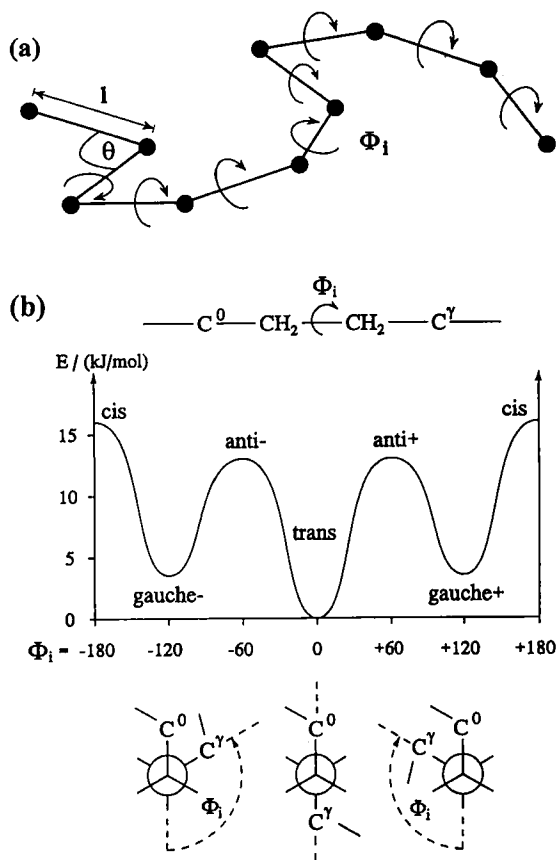
### 3. SPECIFIC EXAMPLES

#### 3.1. Conformational effects on $^{13}\text{C}$ chemical shifts

The packing behaviour of polymers strongly depends on their chain microstructure.<sup>4</sup> A schematic representation of the carbon-backbone of an amorphous polymer is depicted in Fig. 4(a). In order to specify the conformation of a polymer segment one must know the bond length  $l$ , the valence angle  $\theta$  and the rotational states  $\Phi_i$ . The rotational potential  $E(\Phi_i)$  around the central C–C bond in an *n*-butane unit is plotted in Fig. 4(b). The minima for the *gauche* conformers are higher than that of the *trans* by about  $3.5 \text{ kJ mol}^{-1}$ . Since this energy difference is comparable to the thermal energy at ambient temperatures, a large number of conformations is normally present in an amorphous polymer. Therefore experimental techniques are needed which can check the conformational statistics.

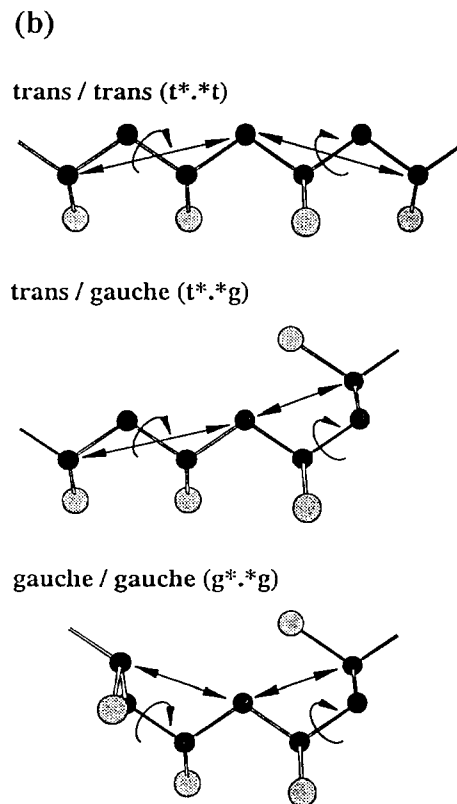
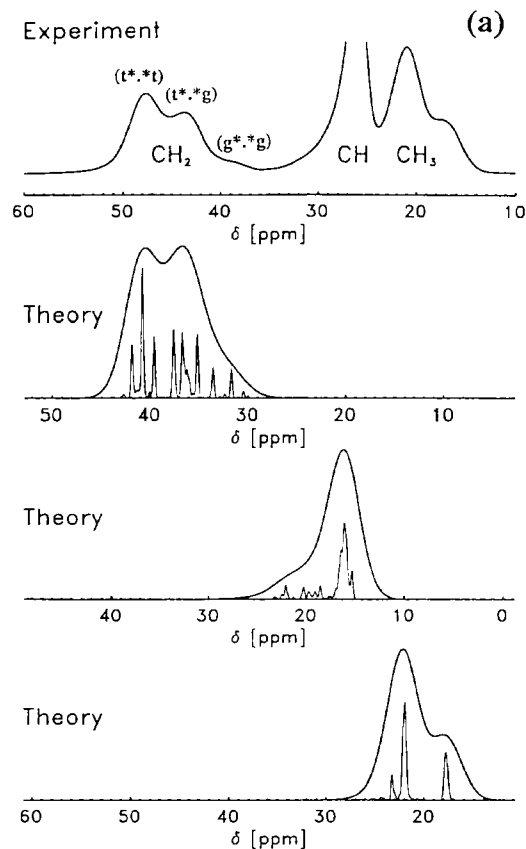
Glassy solid-state amorphous polymers typically display broad  $^{13}\text{C}$  Cross-Polarization Magic Angle Spinning (CP MAS) NMR lines, due to an inhomogenous superposition of contributions from different conformations. These conformational effects on  $^{13}\text{C}$  chemical shifts have traditionally been attributed to the shielding of a reference carbon  $\text{C}^0$  by the  $\gamma$ -substituent  $\text{C}^\gamma$ , (Fig. 4(b)), in a semiempirical fashion (“ $\gamma$ -*gauche* effect”).<sup>4</sup> As a specific example, Fig. 5(a) shows the  $^{13}\text{C}$  CP MAS spectrum of atactic poly(propylene) (aPP) with the assignment of the  $\text{CH}_2$  resonance to specific conformations of a tetrameric unit, displayed in Fig. 5(b).<sup>5</sup> This assignment is readily made by comparison with the chemical shifts in crystalline isotactic and syndiotactic polypropylene. The conformational effects are particularly strong for the  $\text{CH}_2$  group. They should not be confused with the configurational splittings in the NMR spectra of polymers in solution, well-established in determining the chain microstructure.<sup>4</sup>

A complete analysis of such spectra in terms of structural information is now possible, since the conformational effects can be calculated on an *ab initio* level.<sup>6–8</sup> Our approach combines conformational statistics,<sup>9</sup> geometry optimization from molecular mechanics calculations<sup>10</sup> and *ab initio* calculations of the chemical shifts based on individual Gauges for Localized Orbitals



**Fig. 4.** (a) Schematic representation of a carbon-backbone polymer chain in the amorphous state. (b) The potential energy  $E$  for rotation about the central carbon of a butane unit in a polymer chain together with Newman projections illustrating the different interactions between the atom  $C^0$  and its  $\gamma$ -gauche substituent  $C^\gamma$  for the conformations *gauche*- (*g*-), *trans* (*t*) and *gauche*+ (*g*+).

(IGLO).<sup>11</sup> The simulations for the different groups are plotted in Fig. 5(a) below the experimental spectrum. The fine lines display the contributions of the various geometries. The envelopes of the respective patterns are in remarkable agreement with experiment. The absolute heights of the resonance are adjusted arbitrarily, as the different groups have different CP-efficiencies. The absolute positions of the bands for the respective groups are not correctly reproduced by the quantum chemical calculation, since a small atomic basis set was employed in order to save computational time. It has been shown<sup>7</sup> that this does not seriously affect the simulation of conformational effects.



**Fig. 5.** (a) Experimental  $^{13}\text{C}$  CP MAS spectrum of amorphous poly(propylene) (top) and simulations for the various bands.<sup>8</sup> (b) Schematic representation of the conformations of a tetrameric unit in poly(propylene) relevant for the  $\gamma$ -gauche effect of the methylene group  $\text{C}^0\text{H}_2$ . One particular configuration, the *mrr* tetrad, is selected, here. The abbreviation t\*,\*g stands for a conformational unit around a carbon centre denoted by \*,\* with undefined conformations of the neighbouring bonds and t and g conformations of the next neighbouring bonds.