

# 35

# NMR

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# **Ab Initio Calculations of Conformational Effects on $^{13}\text{C}$ NMR Spectra of Amorphous Polymers**

By R. Born and H. W. Spiess

Volume Editor: J. Seelig



Springer

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ISBN-13: 978-3-642-64490-0      e-ISBN-13: 978-3-642-60644-1  
DOI:10.1007/13:978-3-642-60644-1

ISSN 0179-5989

Springer-Verlag Berlin Heidelberg New York

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© Springer-Verlag Berlin Heidelberg 1997  
Softcover reprint of the hardcover 1st edition 1997  
Library of Congress Catalog Card Number 93-9522

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Typeset with  $\LaTeX$ : Danny Lewis Book Production, Berlin  
Cover: Medio GmbH, Berlin  
SPIN: 10551778      66/3020 - 5 4 3 2 1 0 - Printed on acid-free paper

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## Preface

In NMR, it is well-known that the chemical shift conveys structural information, e.g. a carbonyl carbon will have a resonance frequency appreciably different from a methyl carbon, etc. The relation between structure and chemical shift is mostly established by empirical rules on the basis of prior experience. It is only quite recently that the advent of both comparatively cheap computing power and novel quantum chemistry approaches have provided feasible routes to *calculate* the chemical shift at the ab initio level for molecules of reasonable size. This raises the question whether application of these novel theoretical concepts offers a means of obtaining new structural information for the complex chain molecules one deals with in polymer science.

Solid state  $^{13}\text{C}$ -NMR spectra of glassy amorphous polymers display broad, partially structured resonance regions that reflect the underlying disorder of the polymer chains. The chemical shift responds to the variation of the geometry of the chain, and the broad resonance regions can be explained by an inhomogeneous superposition of various chain geometries (and thus chemical shifts). In this review, we present a novel approach to combine polymer chain statistical models, quantum chemistry and solid state NMR to provide quantitative information about the local chain geometry in amorphous polymers. The statistical model yields the relative occurrence of the various geometries, and quantum chemistry (together with a force field geometry optimization) establishes the link between geometry and chemical shift. Finally, the simulated spectra are compared with experimental  $^{13}\text{C}$  CP/MAS spectra. The scheme is applied to various polymer systems of different structural classes.

The computing power of comparatively cheap work stations is still increasing rapidly, and the algorithms of quantum chemistry are becoming more efficient as well. Using these mechanisms, the limitations imposed by the availability of computing resources are gradually relaxed, and more sophisticated calculations are becoming possible. This naturally applies to the calculations presented here. Even in the short period of two years between the actual calculations and the publication of this review some computer time limitations are already less severe. Thus, easier and more accurate calcula-

tions for the 'simple' cases considered here and meaningful simulations for more complicated structures will in the future facilitate the application of these concepts to more problems in polymer science.

The authors want to thank Dr. A. Heuer for continuous discussions on the structure of polymer glasses and for carefully reading the draft. Special thanks are to Prof. Dr. W. Kutzelnigg, Dr. M. Schindler and Dr. U. Fleischer for providing the IGLO program and for helpful discussions. Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB 262) is gratefully acknowledged.

Main, February 1997

R. Born  
H.W. Spiess

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## Table of Contents

<b>Ab Initio Calculations of Conformational Effects on <math>^{13}\text{C}</math> NMR Spectra of Amorphous Polymers</b>	
R. Born, H. W. Spiess .....	1
<b>Author Index Volumes 21–35 .....</b>	<b>127</b>

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# Ab Initio Calculations of Conformational Effects on $^{13}\text{C}$ NMR Spectra of Amorphous Polymers

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A new approach for the simulation of inhomogeneously broadened solid state NMR spectra is presented. The geometry dependence of the chemical shift is investigated and used to analyze the local molecular organization of amorphous glassy polymers by comparison of simulated lineshapes with experimental spectra. The method combines statistical conformational models, force-field optimization and the advanced quantum chemical ab initio IGLO scheme for the calculation of chemical shifts. An introduction to these topics is given together with a detailed derivation of our approach. The novel scheme is used to assess the validity of statistical models of polymer conformations and to discriminate between competing theories. Moreover, the molecular orbital contributions to the chemical shift, the configurational splitting in solution, and the role of the anisotropy of the chemical shift as a source of structural information are addressed. Methodical aspects, including preconditions and limitations, are covered in a separate chapter. To check the range of applicability, the method is applied to various polymer systems of different structural classes (poly(ethylene), poly(propylene), poly(isobutylene), poly(butadiene), poly(isoprene), poly(vinyl chloride), poly(methyl methacrylate)).

## Contents

Abbreviations and Symbols . . . . .	3
1 Introduction . . . . .	5
2 Notions and Concepts in Chain Molecules and Quantum Chemistry	12
2.1 Constitution, Configuration and Conformation in Amorphous Polymers . . . . .	12
2.1.1 Experimental Aspects . . . . .	16
2.2 Statistical Mechanics of Chain Molecules . . . . .	17
2.3 Empirical Force Fields . . . . .	21
2.4 Ab Initio Quantum Chemical Calculation of the Chemical Shift by the IGLO Method . . . . .	23
2.4.1 The Gauge Dependence of the Chemical Shift . . . . .	23
2.4.2 Basis Sets . . . . .	27
2.4.3 Comparison of Experiment and Theory . . . . .	29
2.5 Geometry Effects in NMR Spectra – the $\gamma$ -gauche Effect . . . . .	29

<b>3</b>	<b>Method of ab initio Simulation of Solid State NMR Spectra – The Example of Atactic Poly(propylene) . . . . .</b>	<b>33</b>
3.1	Atactic Poly(propylene) . . . . .	33
3.2	Statistical Model . . . . .	33
3.3	Simulation of the Spectra . . . . .	37
3.3.1	Identification of Important Conformations . . . . .	37
3.3.2	Geometry Optimization and Quantum Chemistry . . . . .	38
3.3.3	Simulated Spectrum as a Combination of Statistical Model and ab initio Quantum Chemistry . . . . .	40
3.3.4	Symmetry . . . . .	42
3.3.5	Summary of the Approach . . . . .	43
3.4	Simulated Solid State Spectrum – Comparison with Experiment .	44
3.5	Correlation of Chemical Shift and Geometry – the $\gamma$ - <i>gauche</i> Effect Revisited . . . . .	46
3.6	Molecular Orbital Contributions to the Chemical Shift . . . . .	53
3.7	Configurational Splitting in Solution . . . . .	55
3.8	The Anisotropy of the Chemical Shift as a Source of Structural Information . . . . .	57
<b>4</b>	<b>Some Remarks on the Method . . . . .</b>	<b>61</b>
4.1	Intra- and Intermolecular Contributions to the Chemical Shift . .	61
4.2	Influence of the Endgroups . . . . .	63
4.3	Influence of the Atomic Basis and the Empirical Force Field . . . .	65
4.4	The Role of the Conformational Statistics . . . . .	68
4.5	Limiting Factors and Computer Time Considerations . . . . .	69
4.6	Simulation of Other Amorphous Systems . . . . .	70
<b>5</b>	<b>Application to Other Polymers . . . . .</b>	<b>72</b>
5.1	Poly(ethylene) . . . . .	72
5.2	Poly(isobutylene) . . . . .	80
5.2.1	Simulation and Comparison with Experiment . . . . .	80
5.2.2	Geometry Effects . . . . .	85
5.2.3	Effects of the Atomic Basis, Endgroups, and Empirical Force Field	91
5.3	Poly(butadiene) and Poly(isoprene) . . . . .	94
5.4	Poly(vinyl chloride) . . . . .	97
5.5	Poly(methyl methacrylate) . . . . .	101
5.5.1	Calculations and Simulated Spectra . . . . .	101
5.5.2	Geometry Effects, Role of Atomic Basis, and Configurational Splitting	107
<b>6</b>	<b>Conclusion . . . . .</b>	<b>117</b>
	<b>References . . . . .</b>	<b>113</b>
	<b>Author Index Volumes 21–35 . . . . .</b>	<b>123</b>

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## Abbreviations and Symbols

### Important Symbols

$g_K(\sigma)$	simulated line shape for nucleus K
$G^j$	optimized geometry belonging to $k^j$
$k^j$	configurational/conformational sequence
$P_{config}$	configurational statistics
$P_{conform}^{RIS}$	conformational statistics
$s_b$	Gaussian broadening function
$T$	temperature
$T_g$	glass transition temperature
$x_i$	configuration of a diad in a pseudoasymmetric polymer, either $m$ or $r$
$\gamma_X$	$\gamma$ - <i>gauche</i> constant
$\delta$	chemical shift (experimental scale), measured from TMS
$\delta_{aniso}$	anisotropy of the chemical shift tensor
$\Delta\delta_X$	relative chemical shift
$\eta$	asymmetry of the chemical shift tensor
$\vartheta_i$	main chain dihedral angle
$\sigma$	chemical shift (theoretical scale), with respect to the bare nucleus
$\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$	principal values of the chemical shift tensor
$\chi_i$	orientation of the COOCH <sub>3</sub> sidechain in PMMA

### Abbreviations

AO	Atomic Orbital
aPP	atactic poly(propylene)
CHF	Coupled Hartree-Fock
CVFF	Consistent Valence Force Field
CP/MAS	Cross Polarization / Magic Angle Spinning
DSC	Differential Scanning Calorimetry
DZ	atomic basis of <i>double zeta</i> quality
GIAO	Gauge Including Atomic Orbitals
IGLO	Individual Gauges for Localized Molecular Orbitals

iPMMA	isotactic poly(methyl methacrylate)
iPP	isotactic poly(propylene)
LMO	Localized Molecular Orbital
LORG	Local Gauge/Local Origin
MC	Monte Carlo
MC-SCF	Multi-Configurational Self-Consistent Field
MD	Molecular Dynamics
MO	Molecular Orbital
MP	Møller-Plesset
PBD	1,4-poly(butadiene)
PE	poly(ethylene)
PIB	poly(isobutylene)
PIP	1,4-poly(isoprene)
PMMA	poly(methyl methacrylate)
PP	poly(propylene)
PVC	poly(vinyl chloride)
RIS	Rotational Isomeric State
SCF	Self-Consistent Field
sPMMA	syndiotactic poly(methyl methacrylate)
sPP	syndiotactic poly(propylene)
TMS	tetra methyl silane

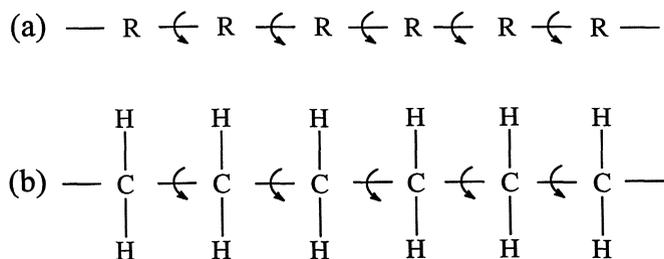
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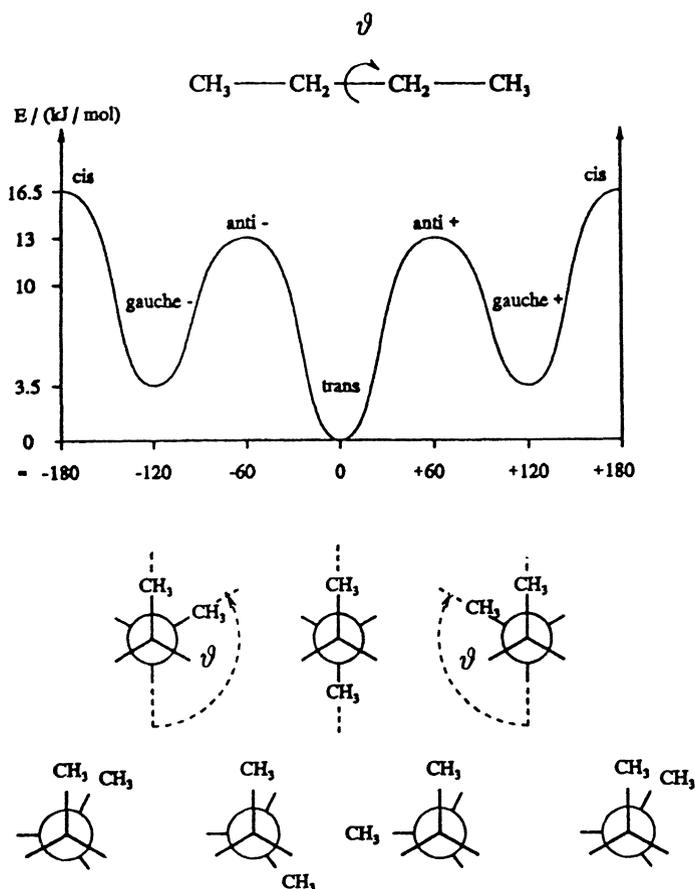
## Introduction

The way chain molecules are organized either in bulk or in solution has attracted a lot of experimental [1, 2, 3] and theoretical [4, 5, 6] interest. In this work we focus on a detailed investigation of the *local* structure of a polymer glass by a combination of solid state NMR and *ab initio* theory.

A typical (homo)polymer chain consists of many repetitions of the same monomeric unit (Fig. 1). In many cases, the bonds along the main chain will be  $\sigma$ -bonds, which introduces a considerable degree of flexibility [4, 5, 6]. The dihedral angles belonging to these bonds are not restricted to a single value, but several positions are energetically achievable, as can be seen in the simple case of butane (Fig. 2). This degree of freedom is called *conformation*. As a consequence, the pattern of molecular organization of chain molecules in bulk is much more complicated than that of simple, low molecular weight compounds. As a first possibility, the polymer melt may crystallize; in this case a single chain forms (at least for parts of its length) a helix with a regular sequence of dihedral angles. The helices themselves are in turn packed in a regular way (Fig. 3.a). These polymer crystals can be analyzed by the customary scattering methods (X-ray, neutron scattering). In principle, the positions of the nuclei, the dihedral angles and the relative positions of the helices, even the nature of the crys-



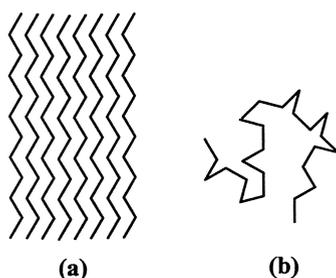
**Fig. 1.** A typical homopolymer consists of many repetitions of the same monomeric unit, which are connected by  $\sigma$ -bonds introducing a considerable degree of flexibility (a). Poly(ethylene) is shown as an example (b)



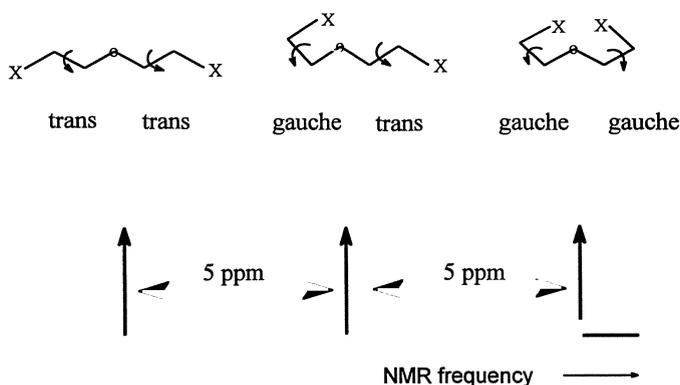
**Fig. 2.** The molecular energy of butane as a function of the dihedral angle  $\vartheta$  is depicted (top). The energies of the *trans* and *gauche* states are quite low; they are separated by states of comparably high energy (*cis*, *anti*) which are only poorly populated themselves but still allow for rapid transitions among the low energy states. In the Newman projections (bottom), the various states are depicted (cf. Fig. 10)

talline defects [7] can be inferred from a scattering experiment, though, in practice, the open structure of polymer crystals imposes some limitations.

A second possibility of solid state molecular organization is the amorphous phase. Here the dihedral angles along the chain do not have a regular sequence of fixed values but are subject to a statistical probability distribution; the average chain forms a random Gaussian coil like in the melt or in the solution (Fig. 3b). In the amorphous case, the scattering methods provide mainly *global* parameters on a longer length scale like the radius of gyration

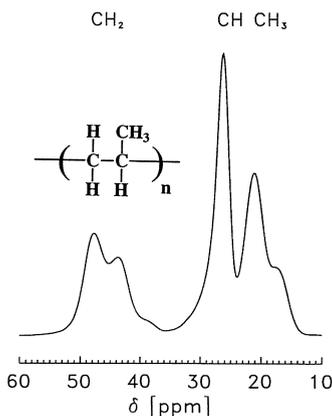


**Fig. 3.** In bulk, polymer chains either form helices (with a regular sequence of dihedral angles along the chain) that are packed in a regular polymer crystal (a) or they are in a disordered amorphous state where the average chain can be described as a random Gaussian coil (b)



**Fig. 4.** The chemical shift is sensitive to the conformation ( $\gamma$ -gauche effect) of the molecule. In the extended *trans* conformation, the central carbon atom (denoted by  $\circ$ ) experiences a chemical shift that is reduced by  $\approx 5$  ppm for every  $\gamma$ -neighbor being in *gauche* position. This simple qualitative understanding will have to be modified in the light of the *ab initio* calculations

(approximately the size of the random coil) and the characteristic ratio. The *local* geometry and its statistical distribution are more difficult to obtain. To investigate this topic, nuclear magnetic resonance (NMR) should be suitable because the chemical shift is susceptible not only to the chemical structure of the molecule (constitution, configuration), but also to the geometric pattern, i.e. the conformation [8]. Historically, the most important geometry dependence has long been known under the name of  $\gamma$ -gauche effect: The chemical shift of a  $^{13}\text{C}$  nucleus is influenced by the geometrical position of its heavy atom  $\gamma$ -neighbors and thus by the value of the corresponding dihedral angle (Fig. 4). If a nucleus experiences a  $\gamma$ -neighbor in a *gauche* position, its chemical shift mostly changes by about 5 ppm with respect to the *trans*

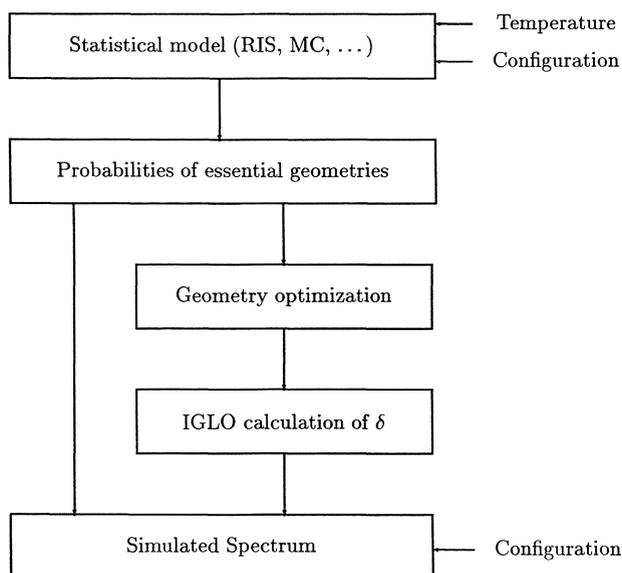


**Fig. 5.** Experimental spectrum of atactic poly(propylene) recorded at  $T = 260$  K, below the calorimetric glass transition temperature. The various resonances are considerably broadened and partly structured

position. Thus, NMR as a local method is sensitive to the variation of the local geometry (conformation). Consequently, a thorough NMR investigation might yield structural information about the local molecular organization of the amorphous phase of polymers. In the glass, the conformational disorder is frozen on the NMR time scale and the NMR resonances are inhomogeneously broadened (Fig. 5). This reflects the presence of multiple geometries in the amorphous polymer glass. The broad, smooth character of the experimental resonances suggests that a phenomenological explanation by a few combinations of well-defined *trans*- and *gauche* states (with correspondingly sharp subresonances) is too simplistic. Instead, a continuum of geometries exists that requires a detailed investigation.

In this review, we will mainly concentrate on simulations of  $^{13}\text{C}$  spectra in the amorphous glassy state by a novel approach, combining established microscopic statistical models and quantum chemical *ab initio* calculations of the chemical shift. The statistical model is used to identify the important geometries which – in a second step – are generated by an empirical forcefield and fed into an *ab initio* calculation of the chemical shift by the Individual Gauges for Localized Molecular Orbitals (IGLO) method. Finally, the probabilities for the geometries (inferred from the statistical model) and the corresponding chemical shifts (calculated by IGLO) are combined to yield a simulated line shape (Fig. 6).

The present paper is organized as follows. In Sect. 2, a few relevant notions in polymer science (Sect. 2.1) will be introduced and discussed. Next, a short survey of the essential tools of the approach will be given, including the statistics of chain molecules (Sect. 2.2), empirical force fields (Sect. 2.3),



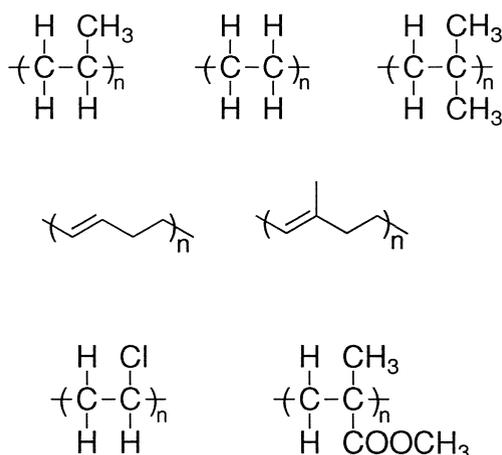
**Fig. 6.** Schematic outline of the ab initio method for the simulation of  $^{13}\text{C}$  solid state NMR spectra. Important building blocks are the statistical conformational model, the technique of geometry optimization and the quantum chemical IGLO method for the computation of the chemical shifts

and the quantum chemical IGLO method for the calculation of the chemical shifts (Sect. 2.4). Finally, the geometry effects in NMR shifts are reviewed briefly (Sect. 2.5).

In the central part (Sect. 3), the simulation technique will be explained in detail and illustrated by the example of atactic poly(propylene) (Sects. 3.1–3.3). Special sections are devoted to the simulation of the solid state spectrum (Sect. 3.4), the correlation of chemical shift and geometry (Sect. 3.5), a molecular orbital (MO) analysis (Sect. 3.6), the configurational splitting in solution (Sect. 3.7) and the role of the anisotropy of the chemical shift as a source of structural information (Sect. 3.8).

In Sect. 4, some methodical aspects will be investigated, addressing the relative size of *intra*- and *intermolecular* contributions to the chemical shift (Sect. 4.1), the influence of the endgroups on the results (Sect. 4.2), the significance of the atomic basis and the empirical forcefield (Sect. 4.3), as well as some more general remarks on the preconditions of spectral simulation in disordered systems (Sect. 4.4–4.6).

In Sect. 5, it is demonstrated, that the approach systematically developed in Sect. 3 can be successfully applied to polymers of different structural classes (Table 1, Fig. 7). Our investigations include the



**Fig. 7.** Repeat units for the investigated polymers: poly(propylene), poly(ethylene), poly(isobutylene), poly(butadiene), poly(isoprene), poly(vinyl chloride), poly(methyl methacrylate) (from left to right, top to bottom)

**Table 1.** List of investigated polymers. The characteristic features of the system and the statistical model employed are also included. The corresponding model molecules are displayed in the respective sections

polymer	abbrev.	characteristic feature	statistical model
poly(ethylene)	PE	simplest polymer	[27]
atact. poly(propylene)	aPP	polyolefine, one sidegroup	[86]
poly(isobutylene)	PIB	polyolefine, two sidegroups	[26]
1,4-poly(butadiene)	PBD	unsaturated	[21]
1,4-poly(isoprene)	PIP	unsaturated, sidegroup	[22]
poly(vinyl chloride)	PVC	contains hetero atom	[116, 117, 118]
poly(methyl methacrylate)	PMMA	extended sidegroup	[24]

simplest polymer poly(ethylene) (Sect. 5.1), the bisubstituted polyolefine poly(isobutylene) (Sect. 5.2), the unsaturated rubbers 1,4-poly(butadiene) and 1,4-poly(isoprene) (Sect. 5.3), the hetero atom containing polymer poly(vinyl chloride) (Sect. 5.4), and poly(methyl methacrylate), with a more extended sidegroup (Sect. 5.5). In this section, mainly results will be presented, and only a few details of the methods are mentioned throughout the chapter.

To permit an easy and rapid access to special aspects, the chapters and some of the more important subsections are largely self-contained and should be understandable without extensive study of preceding chapters. Whenever

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possible, important arguments are shortly restated in the respective sections with a reference to the site of the more detailed discussion.

Although this paper is mainly a review, several previously unpublished results have been included, especially in Sects. 4 and 5. Shorter accounts covering special aspects have already been published. [9, 10, 11]

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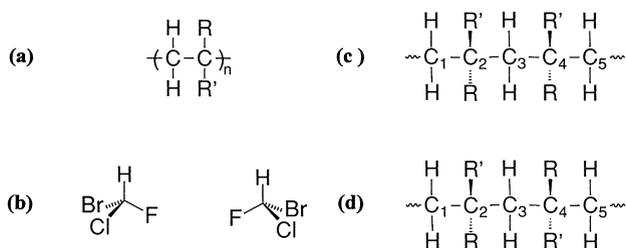
### Notions and Concepts in Chain Molecules and Quantum Chemistry

#### 2.1

##### Constitution, Configuration and Conformation in Amorphous Polymers

We consider a general bisubstituted vinyl polymer (Fig. 8.a) with two different sidegroups. For the characterization of its geometry, the following notions must be recognized. A more detailed account can be found in many textbooks on organic chemistry or polymer science, e.g. [8].

**Constitution** refers to the binding situation, i.e. the sequence of atoms in a molecule. Systems which have the same sum formula, but different structural formulae are called constitutional isomers. The transformation of one constitutional isomer into another requires breaking and forming chemical bonds with activation energies  $> 1$  eV (96.5 kJ/mol). Polymerization defects like head-head-addition (in place of the desired head-tail-addition) introduce constitutional isomers which sometimes have pronounced effects on the material properties. For simplicity however, an ideal, defect-free constitution of the systems inquired will be assumed throughout this review, and constitutional isomerism will not be discussed.



**Fig. 8.** Typical bisubstituted vinyl polymer with two sidegroups R and R'. If R and R' differ, the quaternary carbon is pseudoasymmetric (a). In FClBr-methane (b), the central carbon atom is asymmetric (or chiral), and the molecule and its mirror image can be transformed one into another only by a chemical reaction or the influence of a catalyst. The two molecules are said to differ in **configuration**. In extended vinyl polymer chains, only relative chiralities can be distinguished. In a *meso* diad (c), two consecutive pseudoasymmetric carbon atoms (C<sub>2</sub>, C<sub>4</sub>) have the same configuration, whereas in *syndiotactic* diads (d) the configuration is opposite