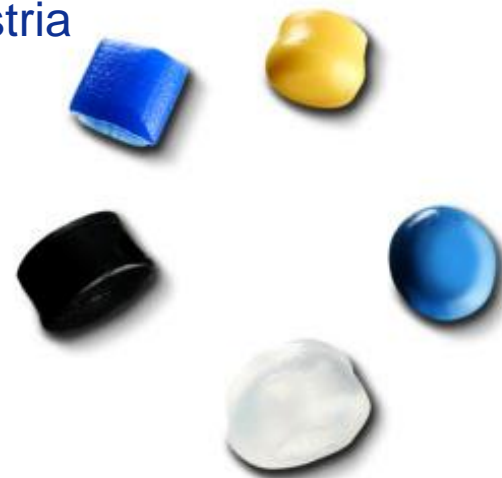


An Introduction to Solid-State NMR of Polymers

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Solid-State NMR Summer School
Linz, Austria
26.9.2015



BOREALIS

SHAPING *the* FUTURE with PLASTICS

Borealis: who we are

- Leading provider of innovative, value creating plastics solutions
- Developing a Base Chemicals business
- More than 40 years of experience
- Unique Borstar® technology to develop polyolefin solutions that are tailored to customers' needs
- 5,400 employees in around 20 countries
- Customers in more than 120 countries
- Ownership 64% IPIC / 36% OMV
- Joint venture in Middle East and Asia: Borouge (Abu Dhabi)



Borealis: where we are



Borealis locations

Production Plants: Austria, Belgium, Brazil, Finland, Germany, Italy, Sweden, United States

Innovation Centres: Austria, Finland, Sweden

Customer Service Centres: Austria, Belgium, Finland, Germany, Italy, Singapore, Sweden, Turkey, United States

Head Office: Austria

Borouge locations

Production Plant: Ruwais (UAE)

Customer Service Centres: Abu Dhabi (UAE), China, India, Singapore

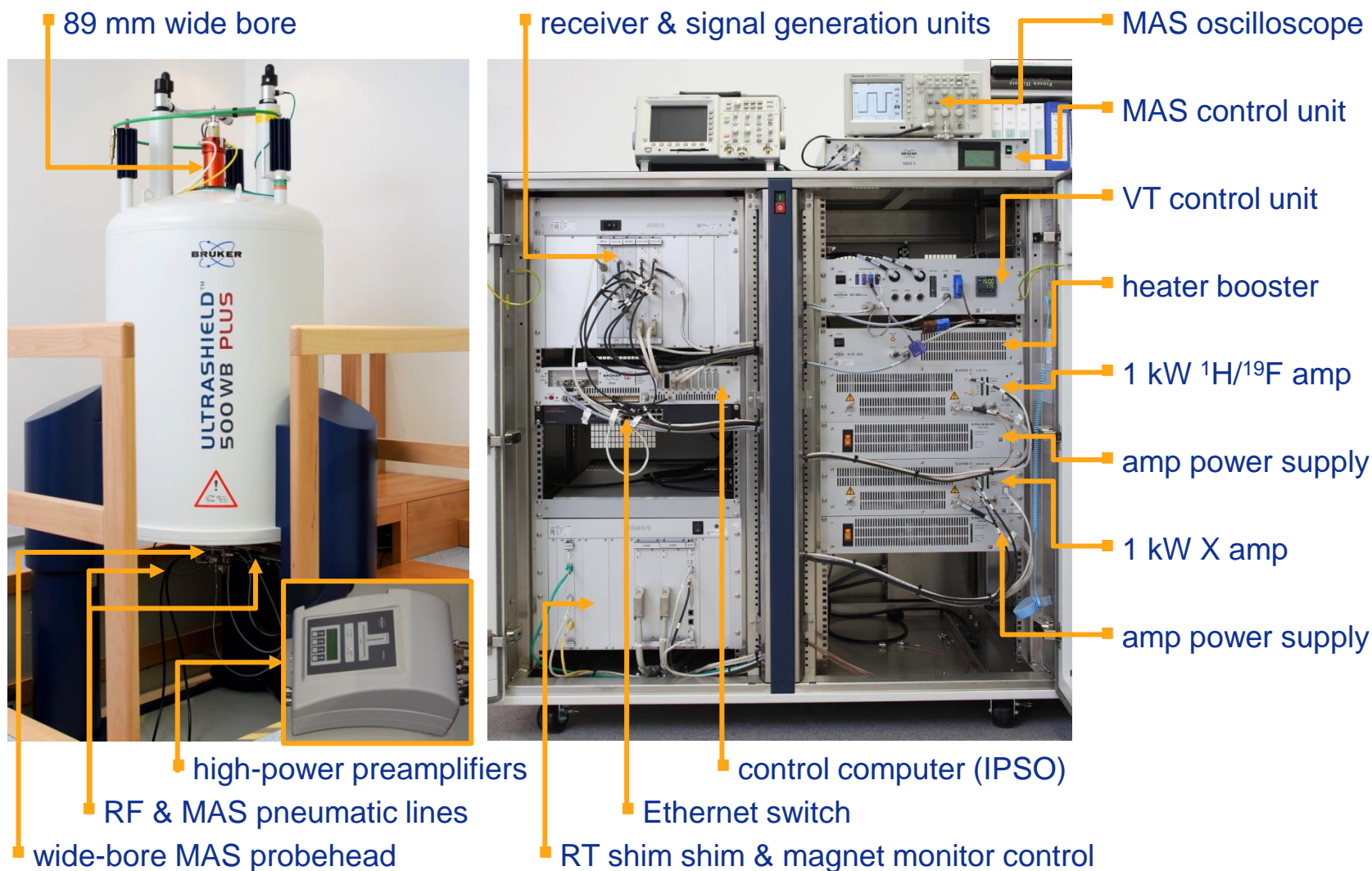
Sales Offices: Abu Dhabi (UAE), Australia, China, Lebanon, New Zealand, Saudi Arabia

Head Offices: Abu Dhabi (UAE), Singapore



- NMR Spectroscopy laboratory at Borealis Polyolefins Linz
 - 400 MHz narrow-bore solution-state NMR spectrometer
 - 500 MHz wide-bore solid-state NMR spectrometer

Bruker AVIII 500 with 11.7 T WB magnet



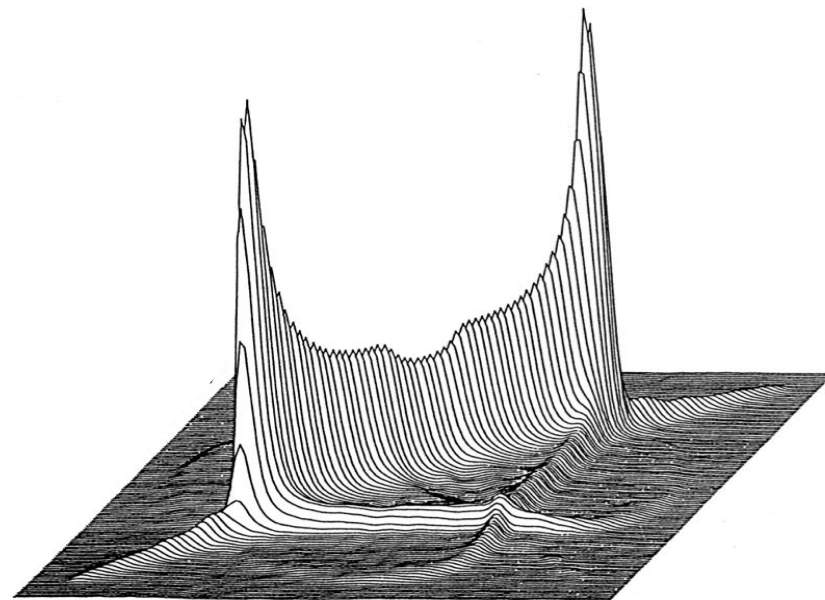
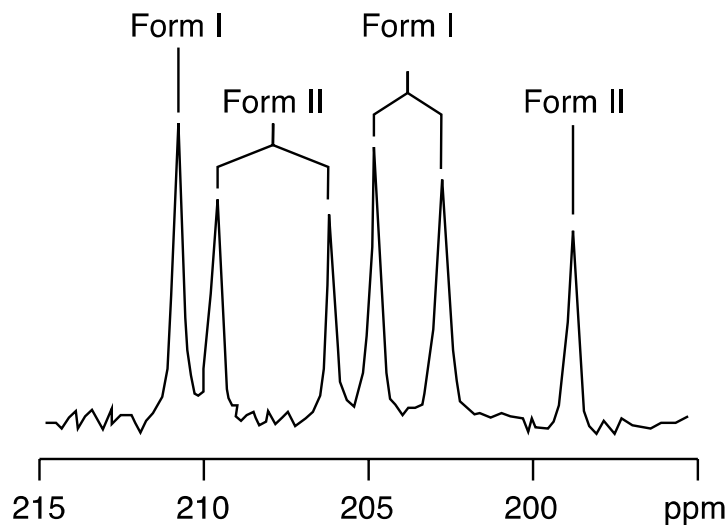
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Solid-State NMR of Polymers

SHAPING the FUTURE with PLASTICS

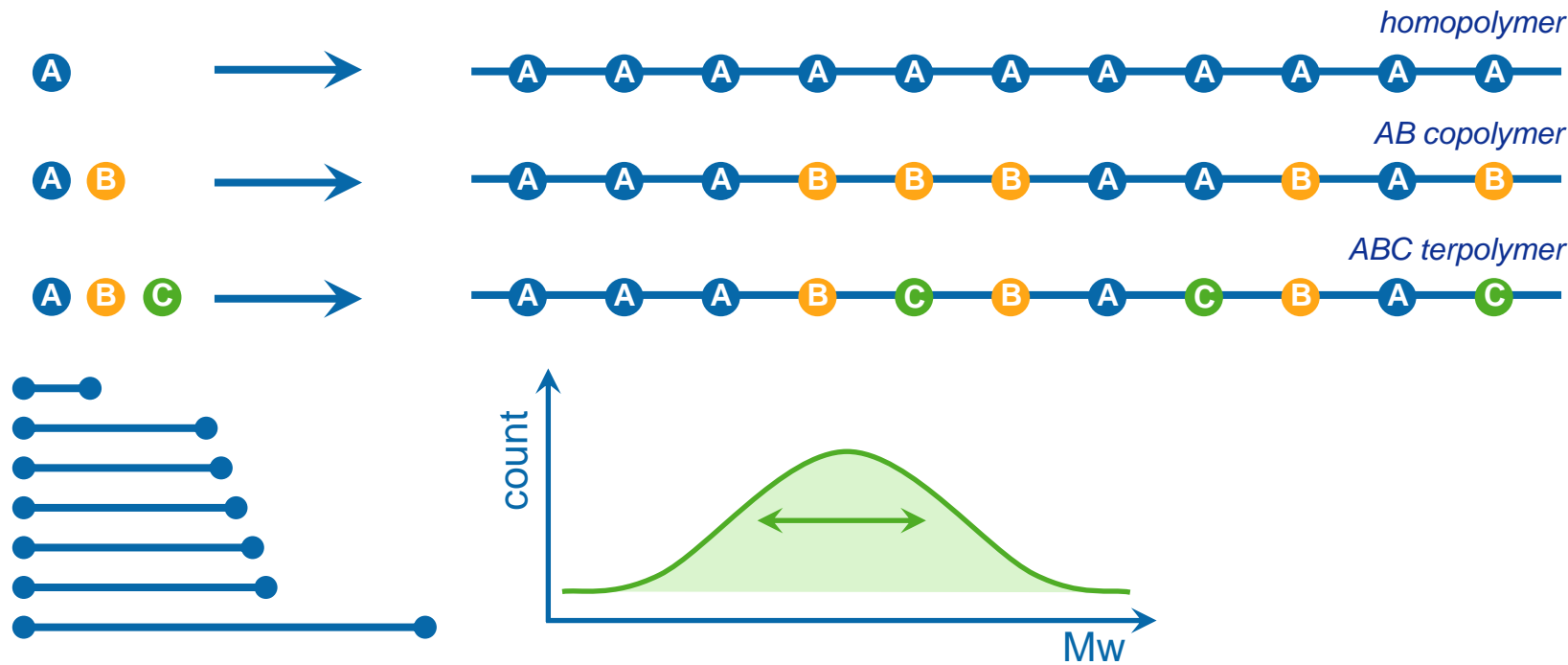
installation date: August 2007



Solid-State NMR Summer School

AN INTRODUCTION TO SOLID-STATE NMR OF POLYMERS

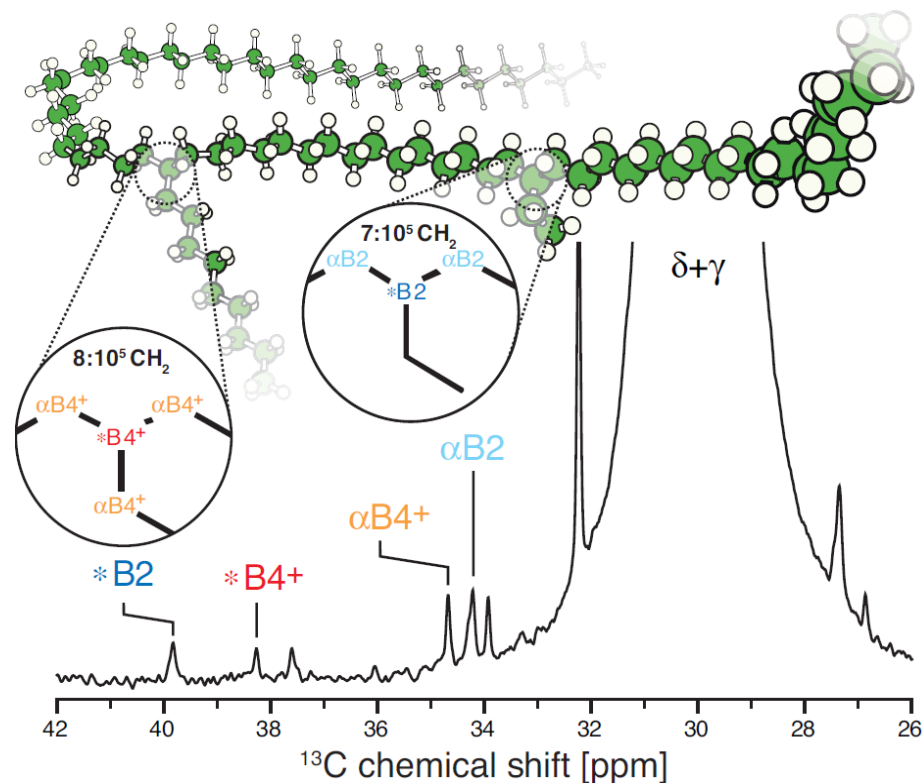
Polymers



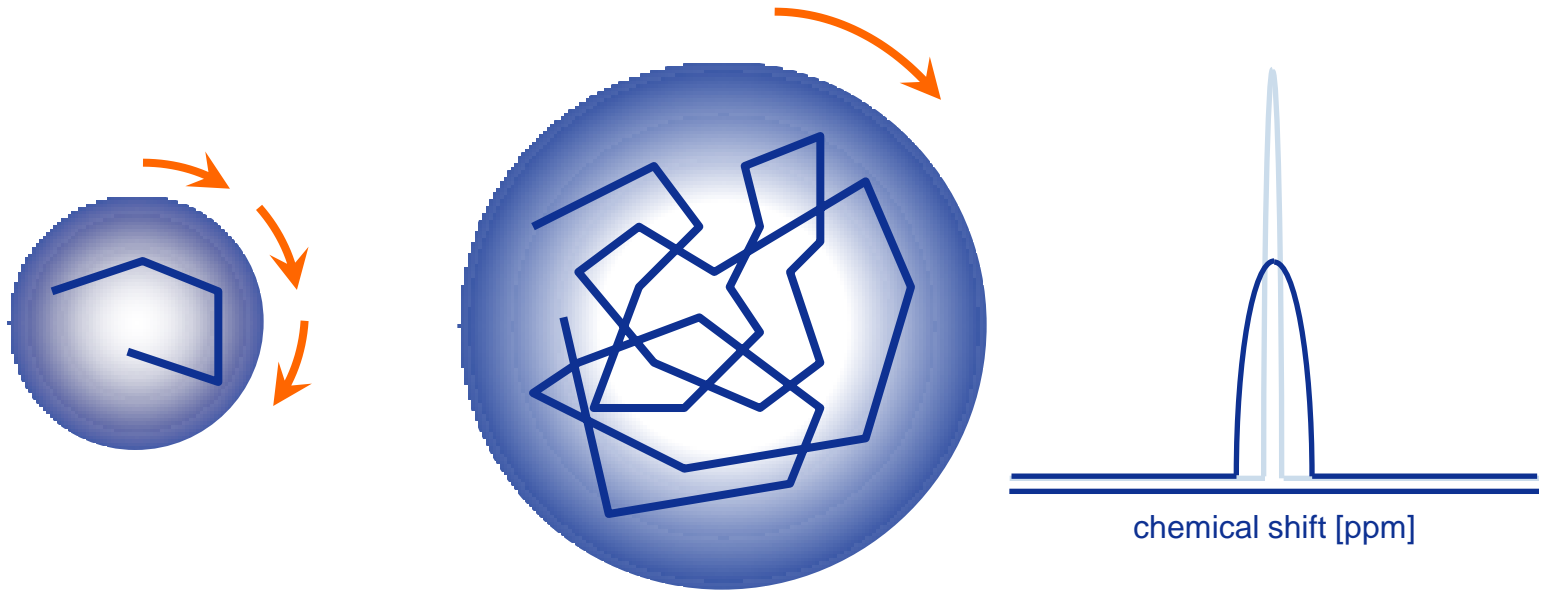
- Always a distribution of chain lengths (molecular weights)
- Characteristic features
 - Degree of polymerisation, molecular weight (M_n or M_w), molecular weight distribution (MWD), tacticity, comonomer content, end-groups

What does spectroscopy tell us?

- spectroscopy provides **direct** evidence about the chemical structure of a material
 - what atomic nuclei are present
 - what chemical environments the atomic nuclei are in
 - how the atomic nuclei are bonded
 - how many of a chemical species are there
- This allows:
 - identification of unknown materials
 - quantification of chemical structure
 - structure-property relationships



Polymer NMR & relaxation



- Polymers have relatively long rotational correlation time in solution
- Influences relaxation & line-widths (longer T_1 and shorter T_2)

Polymer solid-state NMR in general

- Polymers are distributed systems c.f. small molecules or crystalline molecules or macromolecules: Inherent chemical shift distribution
 - doesn't matter how fast you spin, of how strong you decouple you are always limited by this
- Polymers can be quite sensitive to thermal history:
 - how do you pack a rotor without heating the sample?
 - does the sample preparation change the solid state structure?
- Not very easy nor economic to make labelled systems:
 - poly peptides don't count!
 - ^{13}C -PE or ^{13}C PP difficult and expensive to make
- Semicrystalline polymers can have wide variation in T_1 PE 0.5 – 20s
 - very long experiment if you need to be quantitative

Polyethylene (PE)



- Cheap to produce as monomer is byproduct of petrochemical industry
 - Physical and mechanical properties related to chemical structure
 - Through research and development increase properties to expand applications
- Chemical structure not as simple as it first looks!
 - difficult to characterise (low solubility)

Chain branching in polyethylene



short chain branching

copolymer / process

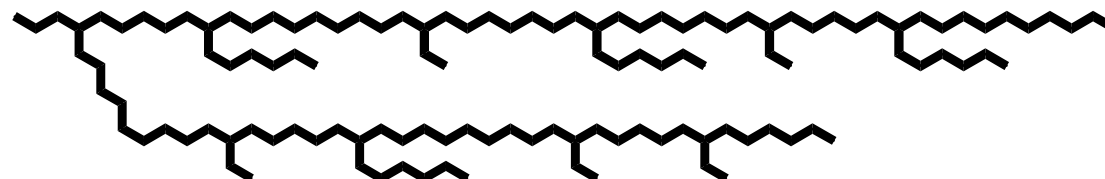
branch length < 30 C



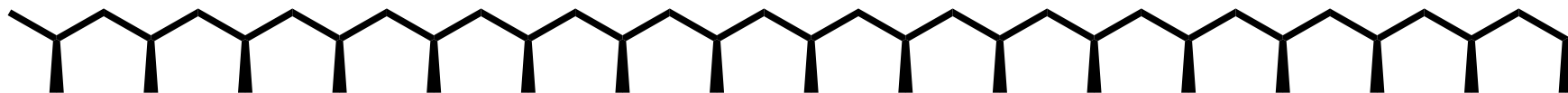
long chain branching

process / post modification

branch length > $M_e \approx 270$ C

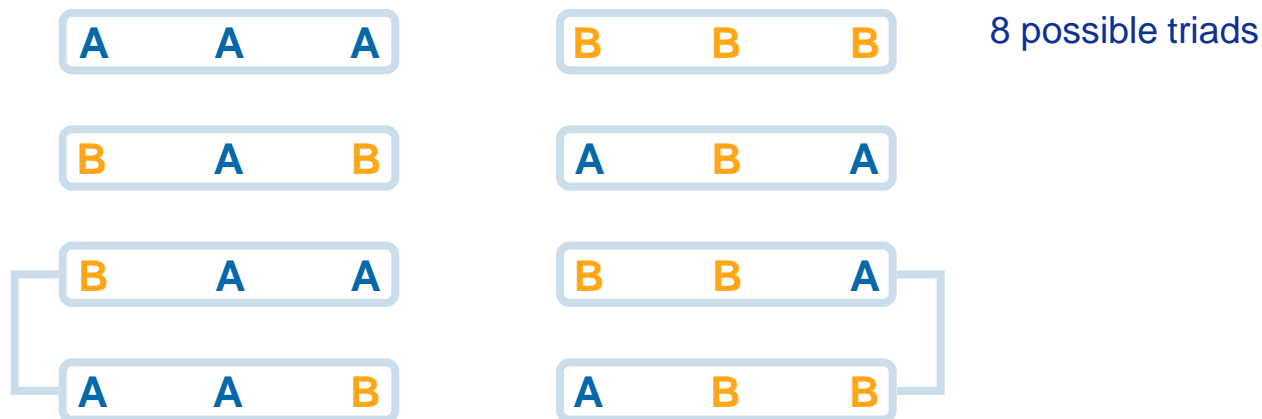
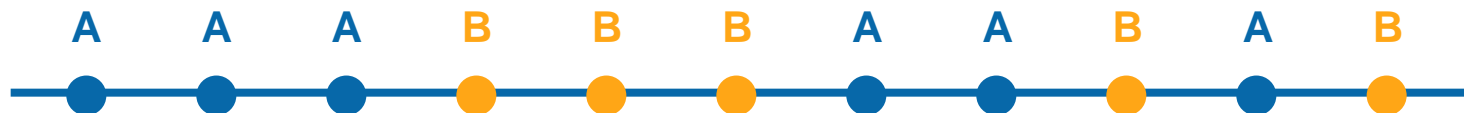


Polypropylene (PP)



- Cheap to produce as monomer is byproduct of petrochemical industry
 - More expensive than polyethylene
 - Physical and mechanical properties related to chemical structure
 - Through research and development increase properties to expand applications
- Complex chemical structure
 - different stereo-chemistry along polymer chain (stereo defects)
 - difficult regio-chemistry along polymer chain (regio defects)
 - multiple types of end-groups
 - difficult to characterise (low solubility)

Polymer NMR & comonomer sequences



- Each triad has characteristic chemical shift
- Quantification of comonomer distribution provides insight into structure

m m m m

$m \quad m \quad m \quad r$

m m r m

m *r* *m* *m*

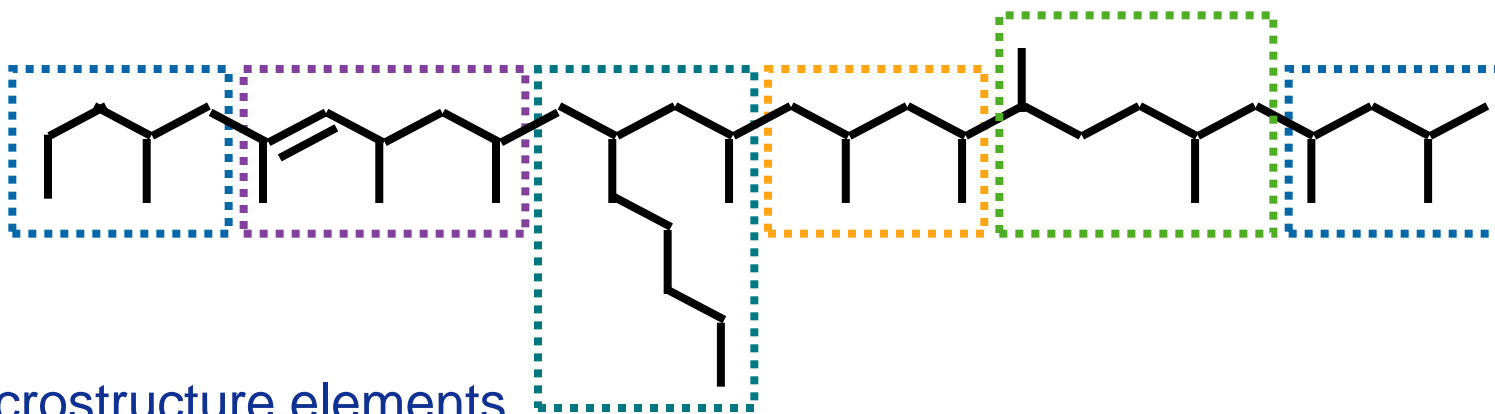
r m m r

m m r r

m *r* *r* *m*

- SHAPING *the* FUTURE *with* PLASTICS

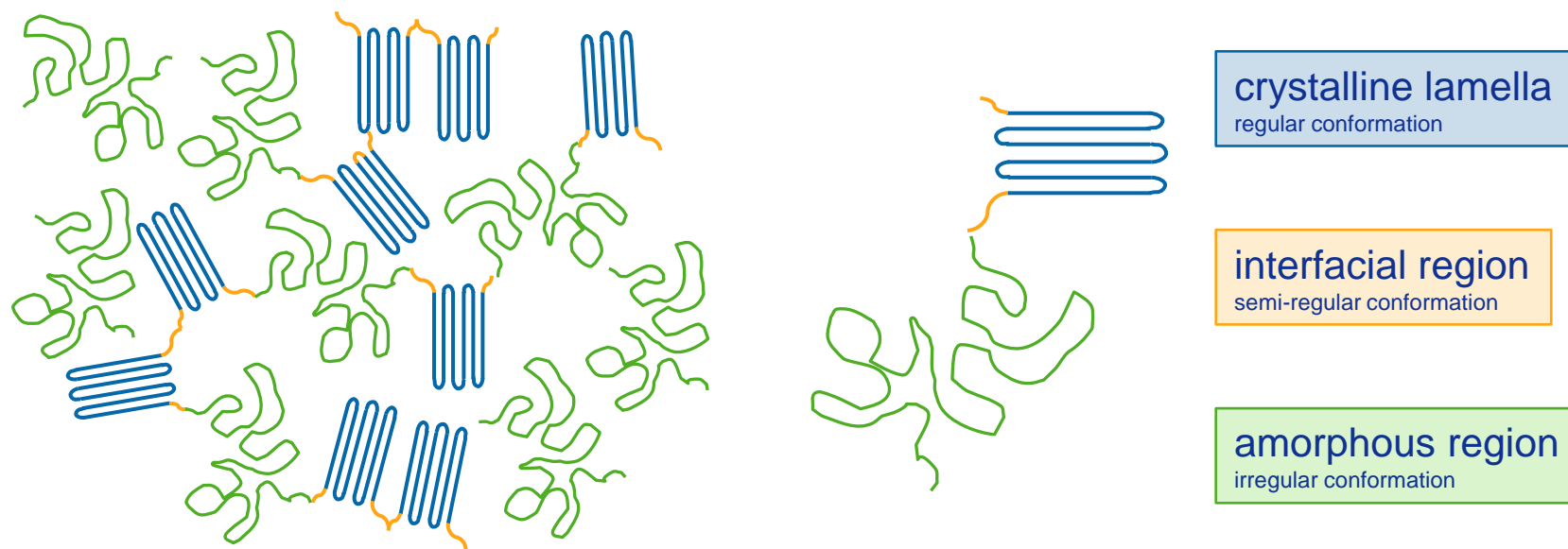
Polypropylene microstructure



microstructure elements

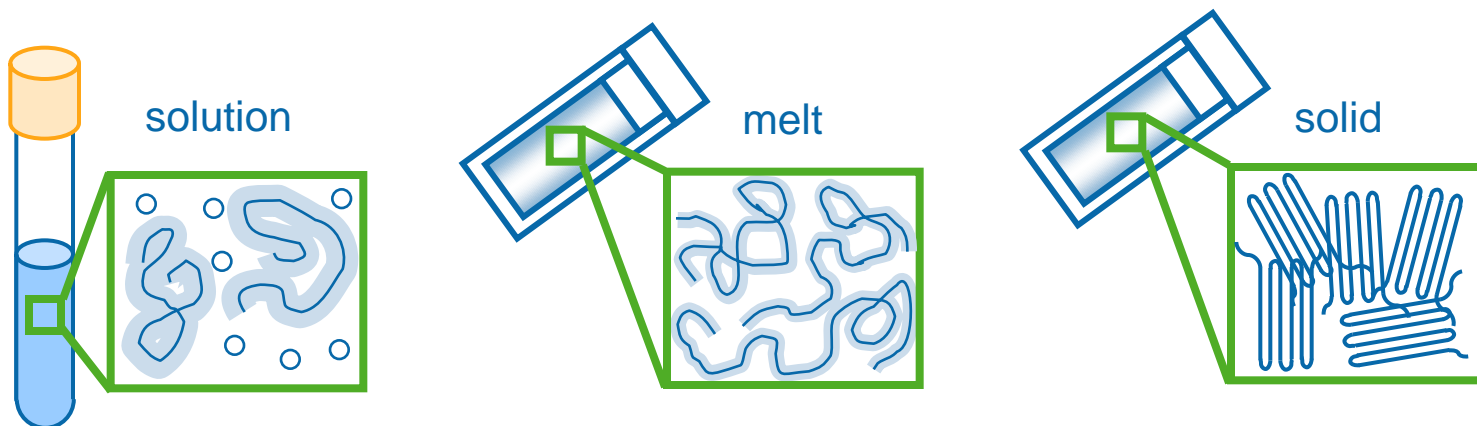
- stereo structure
 - regio structure
 - comonomer content/distribution
 - unsaturation
 - end-groups
-
- all can be **directly** observed by NMR spectroscopy
 - most can be directly **quantified** by NMR spectroscopy

Semi-crystalline polymers: PE & PP



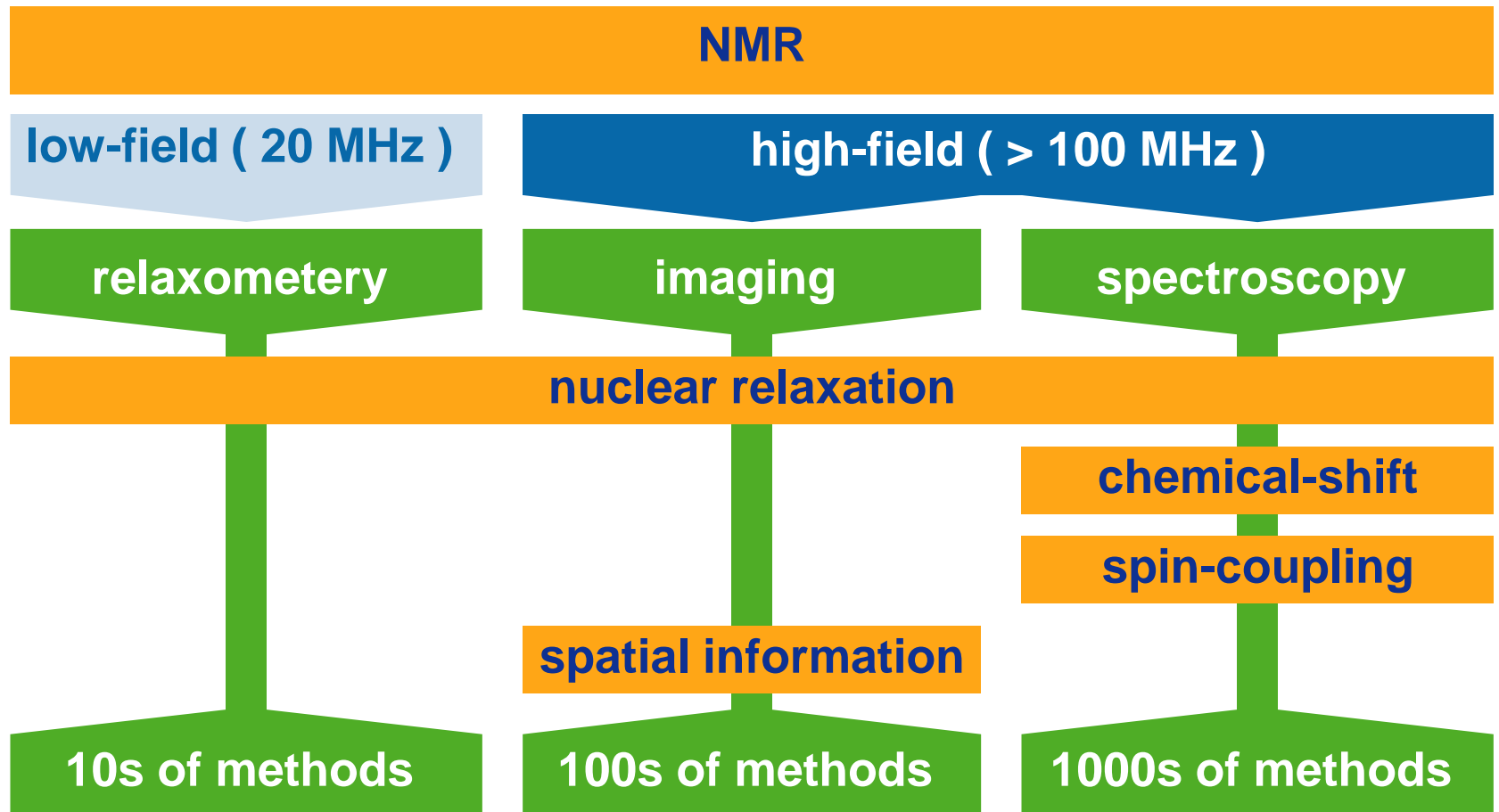
- Some segments of polymer chain crystallise into ordered regions
 - rigid regular structures with limited molecular motion, ordered
- Other segments remain disordered leading to amorphous regions
 - less regular structures with higher degrees of molecular motion, disordered
- At boundaries between crystalline and amorphous regions
 - semi-rigid structures with restricted molecular motions, semi-ordered

Implementation of NMR spectroscopy



- Comonomer type
 - Comonomer content
 - Microstructure analysis
 - Limited resolution
 - Morphology studies
- Melt-state NMR (non standard)
 - High sensitivity for polyolefines but less resolution than solution-state NMR
 - Solid-state NMR (complex)
 - Low resolution but access to insoluble materials or materials as used

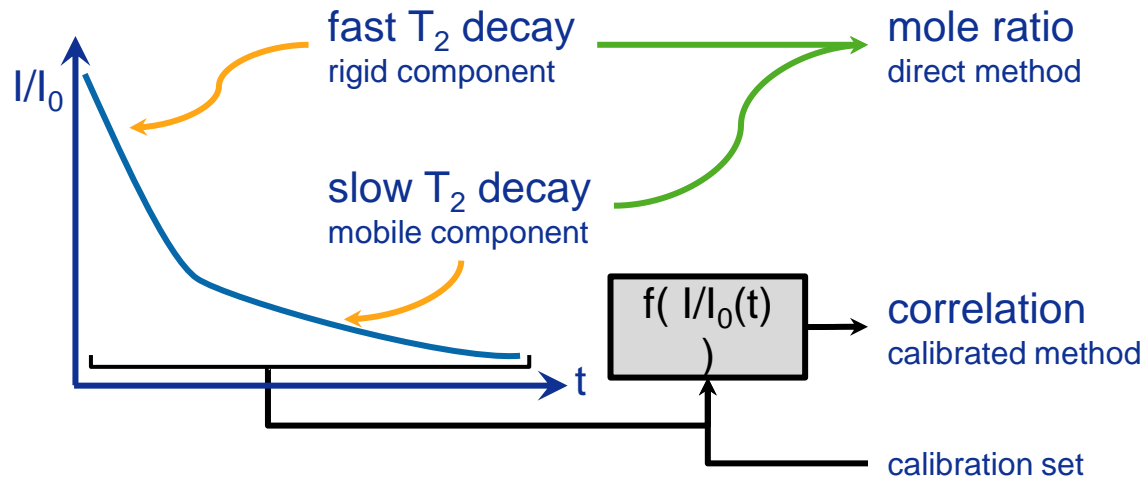
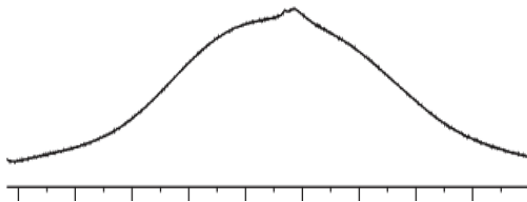
Types of NMR Implementation



Time-domain NMR / NMR relaxometry

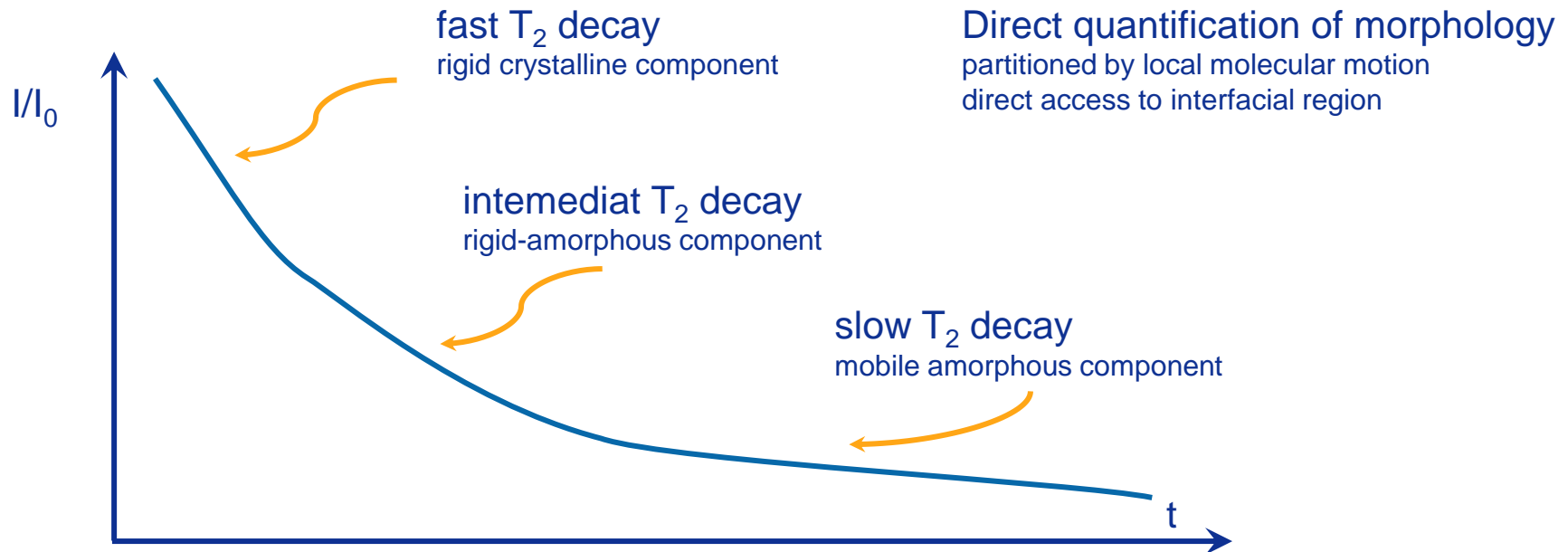


no spectroscopic information $I(\nu)$



- Static solid-state NMR experiments undertaken using B_0 low-fields
 - typical $B_0 = 0.5 \text{ T}$ & 20 MHz and only address ^1H or ^{19}F (^{31}P)
 - fully coupled with no-line narrowing applied, no spectral resolution (wideline)
 - only measure bulk relaxation of solids T_1 , T_2
 - parameterised fitting of time domain signal to mobility (multi exponential fit)
 - chemometric fitting of whole time-domain signal to properties (comonomer content, xylene sol.)

NMR relaxometry of PE



- Low field solid-state ^1H NMR of PE shows three main decay processes
 - rapid decay: rigid crystalline structure
 - intermediate decay: rigid-amorphous interfacial structure
 - slow decay: mobile amorphous structures

Some application of Time-domain NMR

Chemical Industry

- Free & bound moisture content in powders
- Moisture content in solids/liquids/catalysts/detergents
- Activity of catalysts
- Loading efficiency of catalysts
- Molecular diffusion rates in solids/liquids
- Coating weight of solid particles
- viscosity of liquids
- component analysis of solids/liquids
- Hydrogen/fluorine content of solids/liquids
- Particle sizes of pigments
- Adsorption selectivity of zeolites

Cosmetics industry

- Moisture & oil content in powders & pigments
- Droplet size distributions in emulsions
- Oil content of liquids

Polymer Industry

- Density of polyethylene
- Xylene soluble of polypropylene
- Finish content of synthetic fibres
- Moisture content of synthetic fibres
- Plasticizer content of polymers
- Solid & mobile content of polymers
- Extent of polymerization of polymers
- Hydrogen content of polymers
- Fluorine content of polymers
- Extent of cure & cross-linking in polymers/resins
- Viscosity, molecular weight during polymerisation
- Filler content of polymer composites
- Rubber content of polymer blends
- Copolymer ratios of polymer blends
- Polymer mixing & compatibility of polymer blends

- All based on the same idea:
 - Components can be distinguished by their different T_2 s
 - Property correlates to local molecular mobility which is expressed in the NMR signal

More applications of Time-domain NMR!

Food Industry

- Solid fat content in fat containing products
- Moisture content in margarine
- Component analysis of milk
- Moisture & fat content of milk powder
- Moisture & fat content of food products in general
- Oil composition of oils
- Moisture content of rice
- Moisture & oil content of flour
- Moisture & oil content of emulsions
- Droplet size distributions of emulsions
- Moisture & solid distributions of gels
- Freezing process research of solids
- Moisture content of starches
- Extent of cooking/hydrolysis of cooked foods

Agricultural Industry

- Moisture & oil content in solids/seeds/feed
- component analysis in fertiliser
- organic content in soil

Petroleum industry

- Hydrogen content of petroleum distillates
- Hydrogen content of coal
- Oil content & mobility distribution of waxes
- Oil content of rocks/oil sands/shales
- Porosity, pore size distribution of rocks
- Viscosity of oil and petroleum products
- Free vs bound components

Pharmaceutical industry

- Moisture & oil content of capsules/tablets
- Coating weight of capsules/tablets
- Component analysis
- Fluorine & hydrogen content

Research

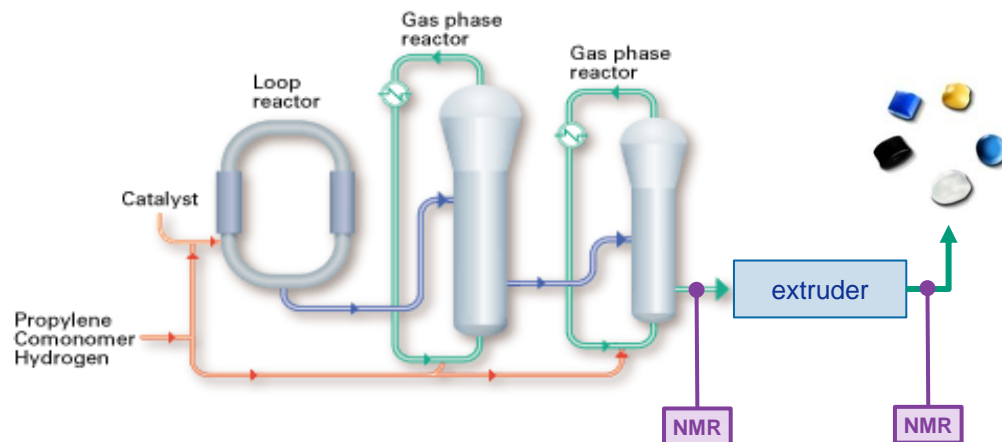
- relaxation measurements
- diffusion measurements
- imaging
- particle size distribution
- spin-diffusion

■ All based on the same idea:

- Components can be distinguished by their different T_2 s
- Property correlates to local molecular mobility which is expressed in the NMR signal

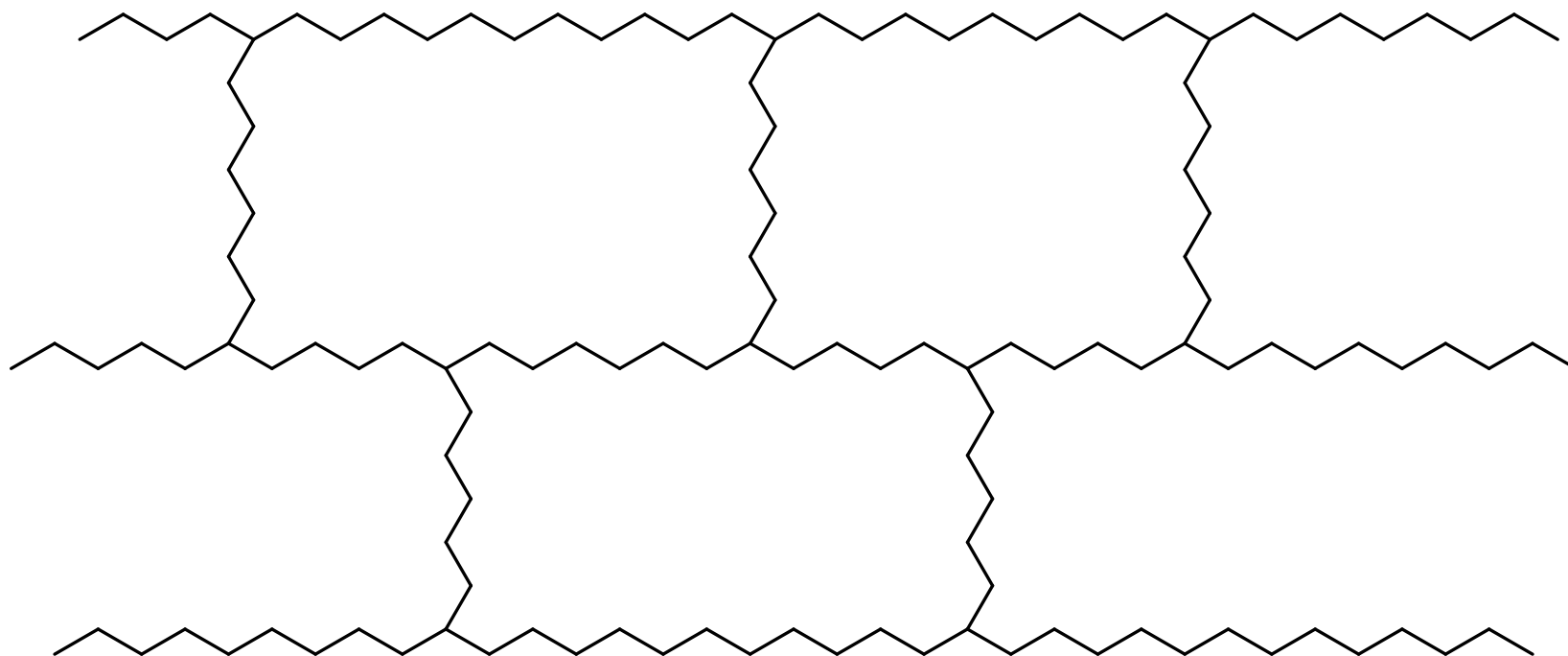
<http://www.pctnmr.com/Applications.htm>

Time-domain NMR & Borealis



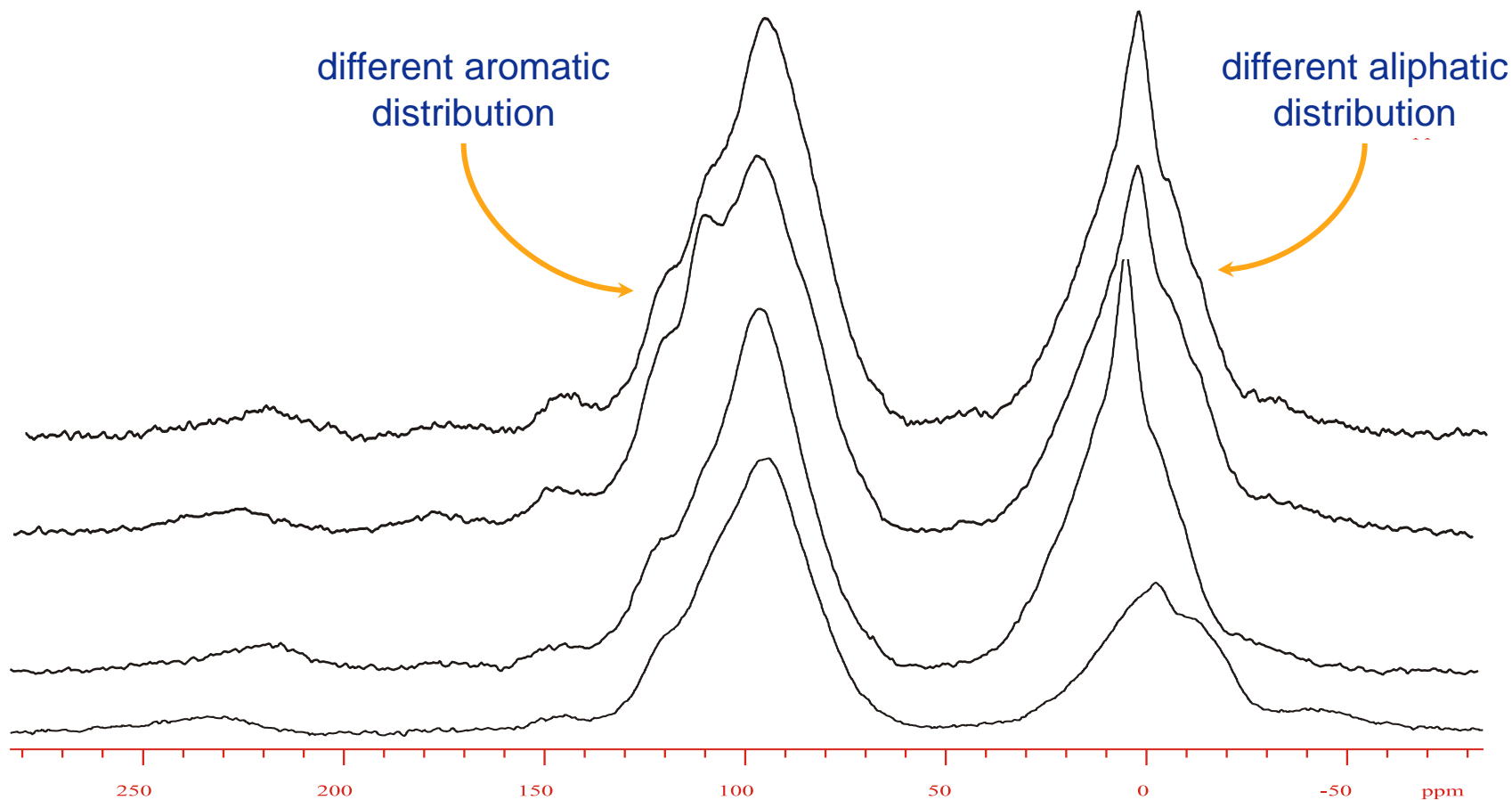
- Time-domain NMR used to monitor/control continuous polymerisation process in plant
 - Online process control via XS, C2, IV...

Cross linked systems



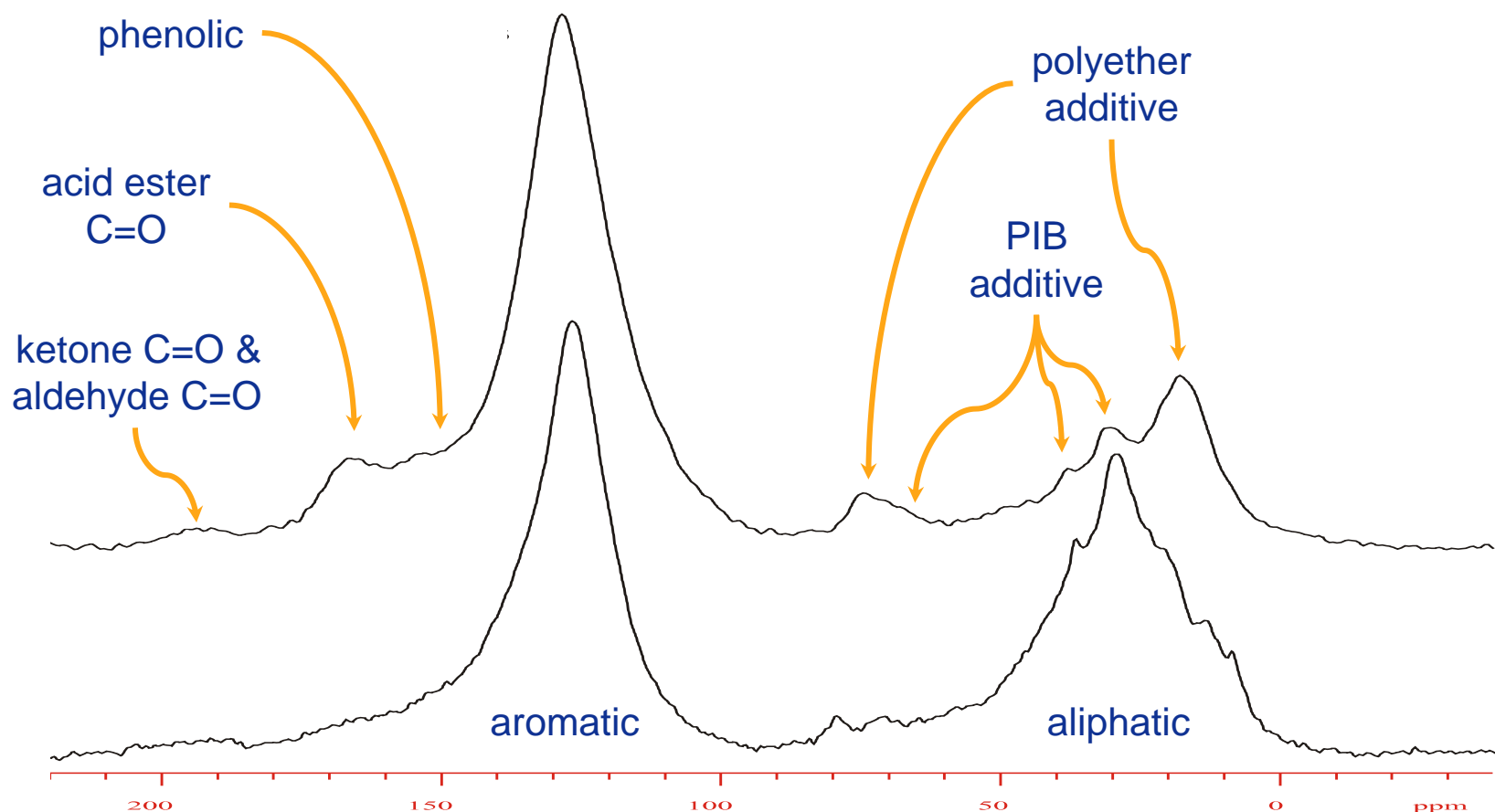
- Do not dissolve, maybe they swell in small molecule solvents
 - standard solution-state NMR limited, HR-MAS on swollen state
 - possibly strong residual coupling

^{13}C CPMAS of coal



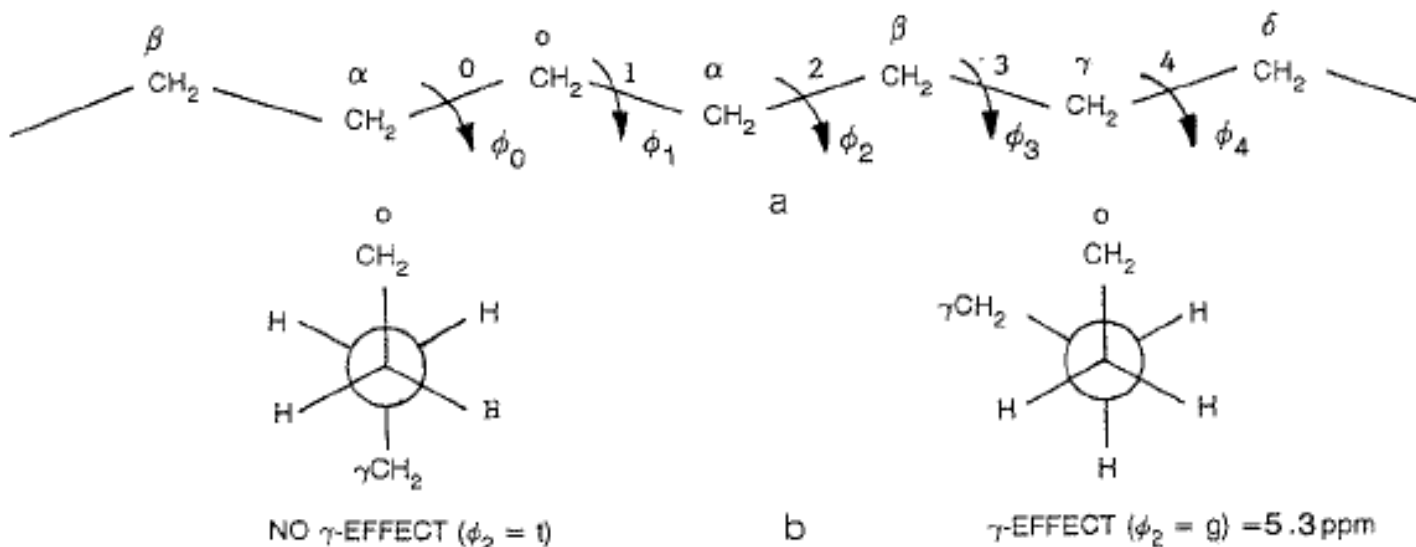
- Complex black bio-solid difficult to analyse by other techniques

^{13}C CPMAS of combustion deposits



- Complex black bio-solid difficult to analyse by other techniques

Conformation & CSA

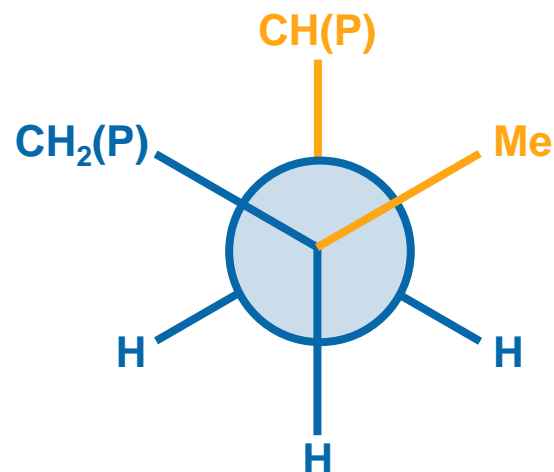


- The C-C backbone bonds in vinyl polymers usually adopt the three staggered rotational states: trans (*t*), gauche+ (*g*+) and gauche – (*g*-)
 - In the gauche (*g* \pm) conformation the observed and γ carbon are close
 - The magnetic environment (CSA) of the observed nuclei changes depending on the local backbone conformation.

The gamma effect

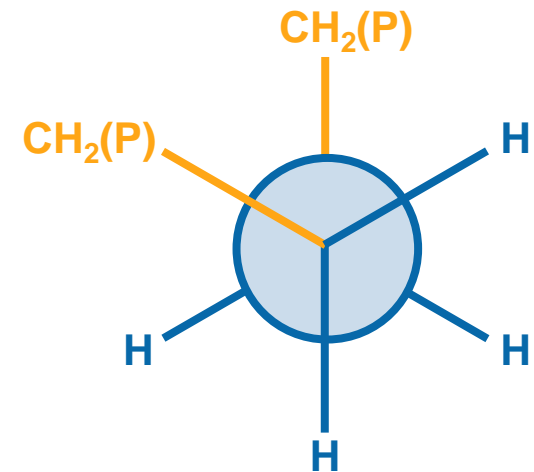
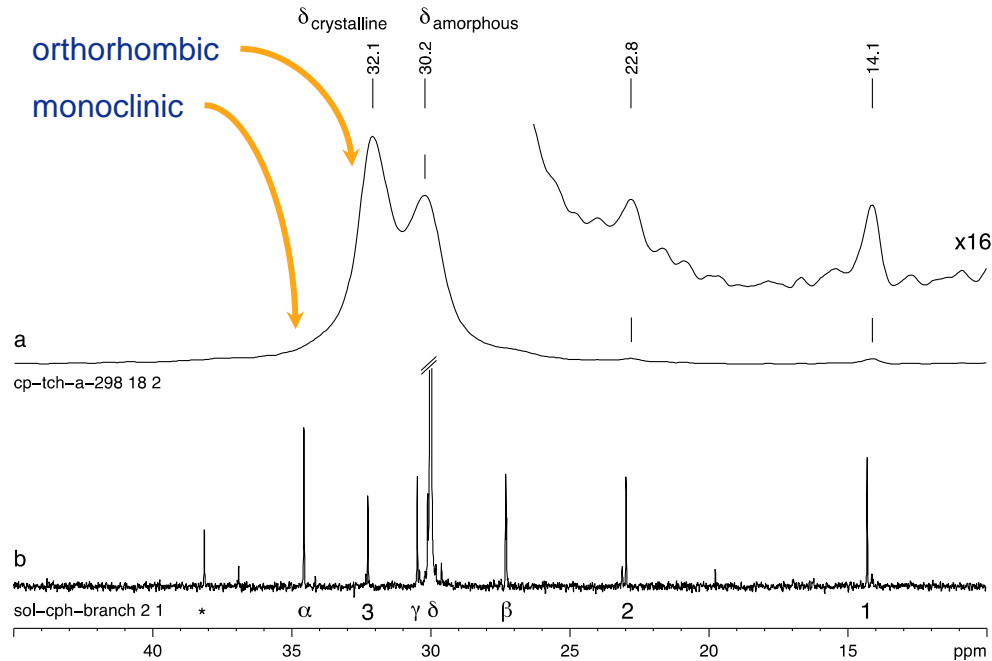
- Why does the chemical shift change with stereo configuration?
 - Empirical correlation between structure and relative chemical shift:

α effect (ppm)		β effect (ppm)		γ effect (ppm)	
$\text{CH}_3\text{-H}$	± 0.0	$\text{CH}_3\text{-CH}_2\text{-H}$	± 0.0	$\text{CH}_3\text{-CH}_2\text{-CH}_3$	± 0.0
$\text{CH}_3\text{-CH}_3$	+8.0	$\text{CH}_3\text{-CH}_2\text{-CH}_3$	+9.7	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$	-2.4
$\text{CH}_2\text{-(CH}_3)_2$	+10.2	$\text{CH}_3\text{-CH-(CH}_3)_2$	+8.7	$\text{CH}_3\text{-CH}_2\text{-CH-(CH}_3)_2$	-1.9



- Gamma effect is small but depends both on structure and conformation
 - Maximum influence seen for gamma-gauche structure/conformation
 - Likelihood of finding gamma-gauche groups depends on relative stereo chemistry (average chain conformation in solution)

Solid-state NMR of polyethylene (PE)

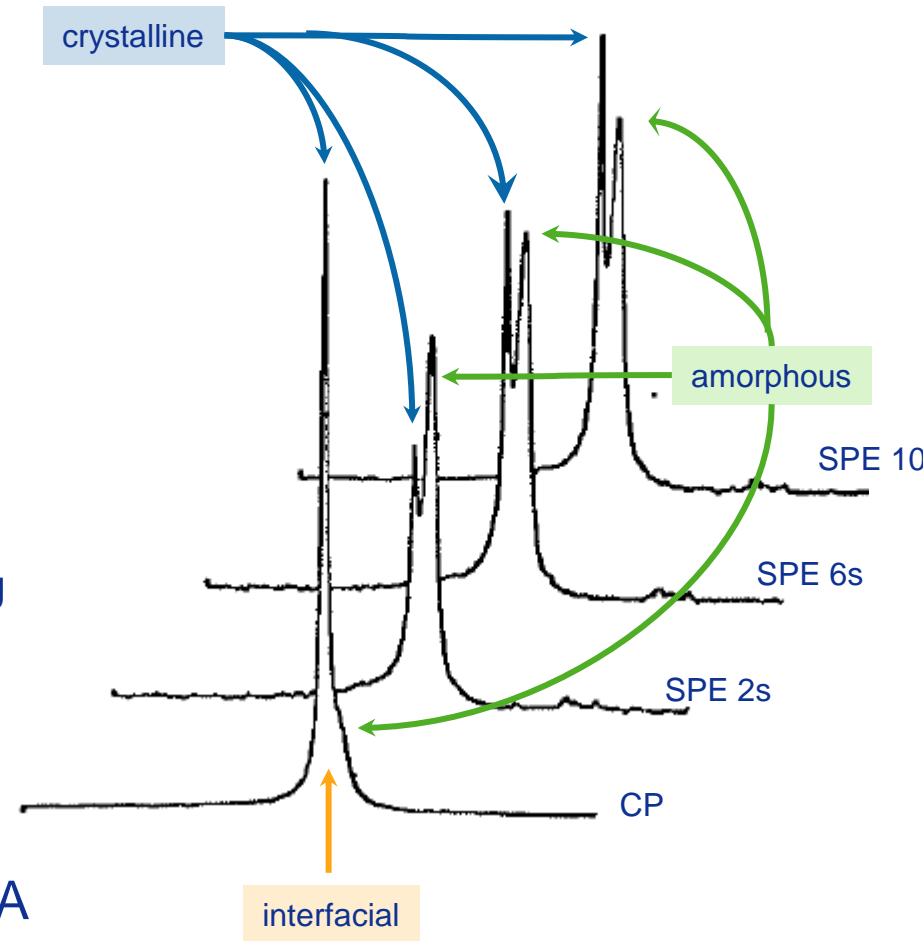


$$\delta_g = \delta_t - 1.9 \text{ ppm}$$

- Polyethylene is semi crystalline comprising all-trans crystalline lamellae joined by amorphous regions with conformational disorder
- In the solid-state ^{13}C NMR spectrum reports on the morphology
 - broad peak at 30 ppm disordered amorphous regions (lower δ due to more γ -gauche)
 - narrow peak at 32 ppm ordered rigid crystalline regions (polymorph at 35 ppm)

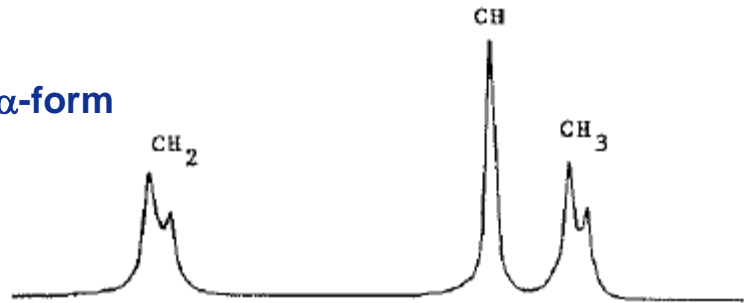
Solid-state NMR of polyethylene (PE)

- Spectra can be edited based on the degree of heteronuclear dipolar coupling
- ^1H - $^{13}\text{C}\{^1\text{H}\}$ CP MAS
Vs $^{13}\text{C}\{^1\text{H}\}$ SPE MAS
 - crystalline = rigid therefore stronger coupling CP +
 - amorphous = mobile = weaker coupling
 - What is quantitative?
- More complex experiments filter based on specific coupling or CSA

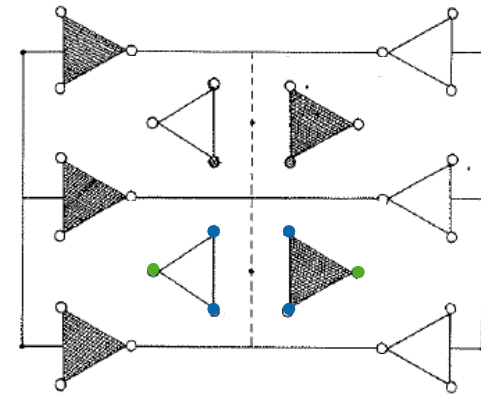
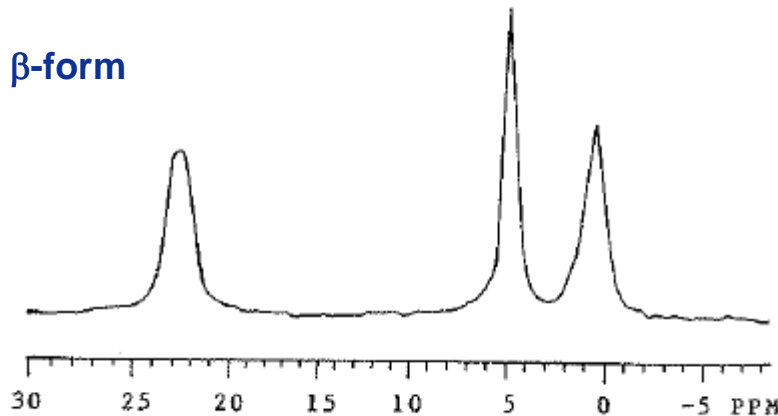


Solid-state NMR of polypropylene (PP)

iPP α -form



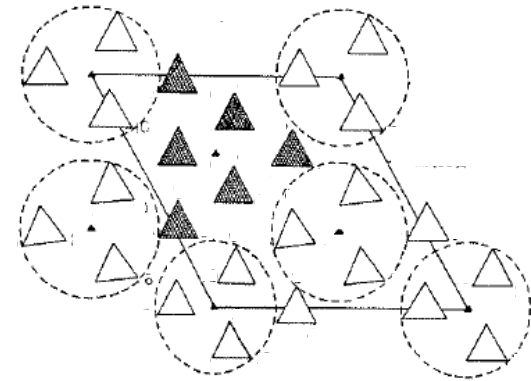
iPP β -form



handedness of
3,1 helix in iPP


right-hand

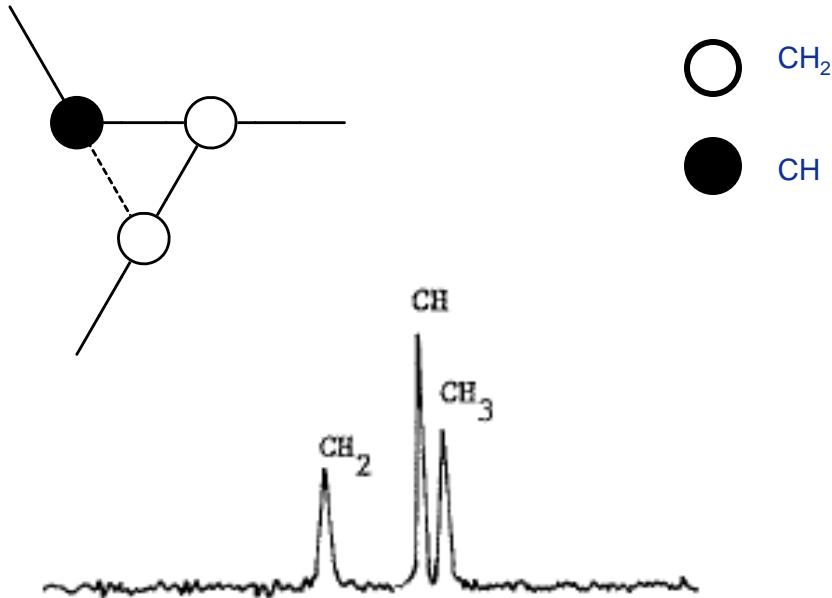

left-hand



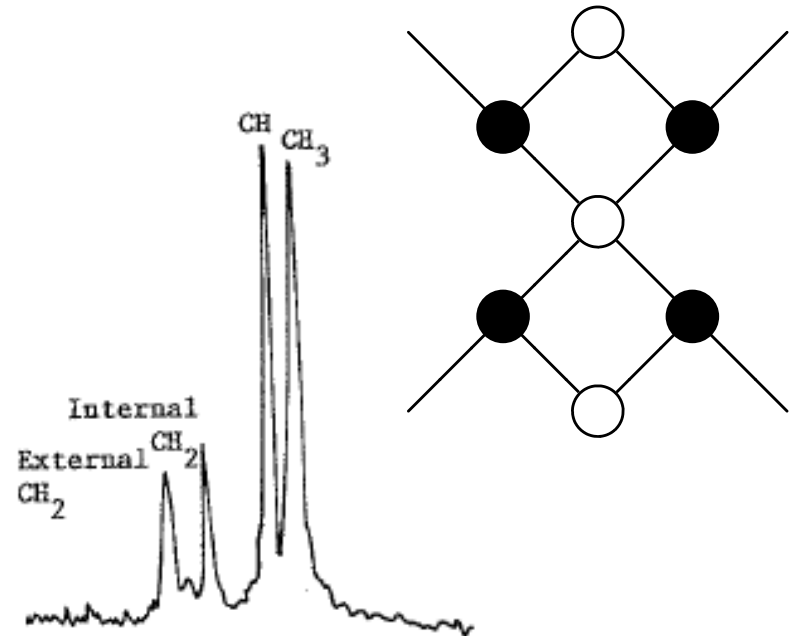
- Polyethylene is also semi crystalline with multiple polymorphs (α , β , γ)
 - all crystalline phases exist as 3,1 helix but with different packing the unit cell

Solid-state NMR of iPP & sPP

isotactic PP (iPP)

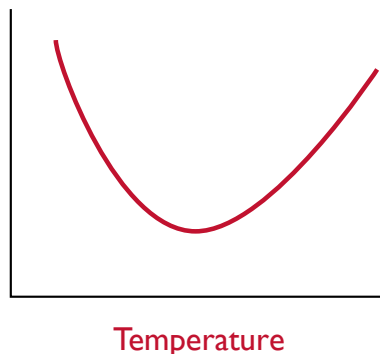


syndiotactic PP (sPP)



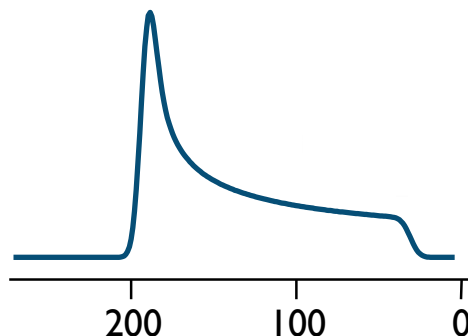
- Polyethylene is also semi crystalline with multiple polymorphs (α , β , γ)
 - all crystalline phases exist as 3,1 helix but with different packing the unit cell

Polymer dynamics by solid-state NMR



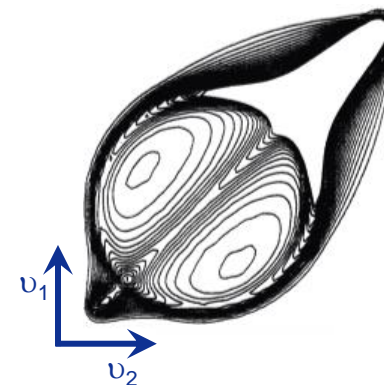
Relaxation

Minima in $T_1(T)$ indicated occurrence of motions in MHz range ($\tau_c < 1 \mu s$)



Lineshape Analysis

observation of motional narrowing in kHz range ($\tau_c < 1 ms$) & geometry information of motion



2D Exchange

Exchange cross peaks indicate very slow motions ($\tau_c > 10 ms$) & detailed geometric information

- Most method only probe time-scale of molecular motion in polymers
 - differential scanning calorimetry, dynamic mechanical and dielectric spectroscopy
- Solid-state NMR provided additional information about:
 - geometry, amplitude and chemical location

^{19}F T_1 & T_2 relaxation in PTFE

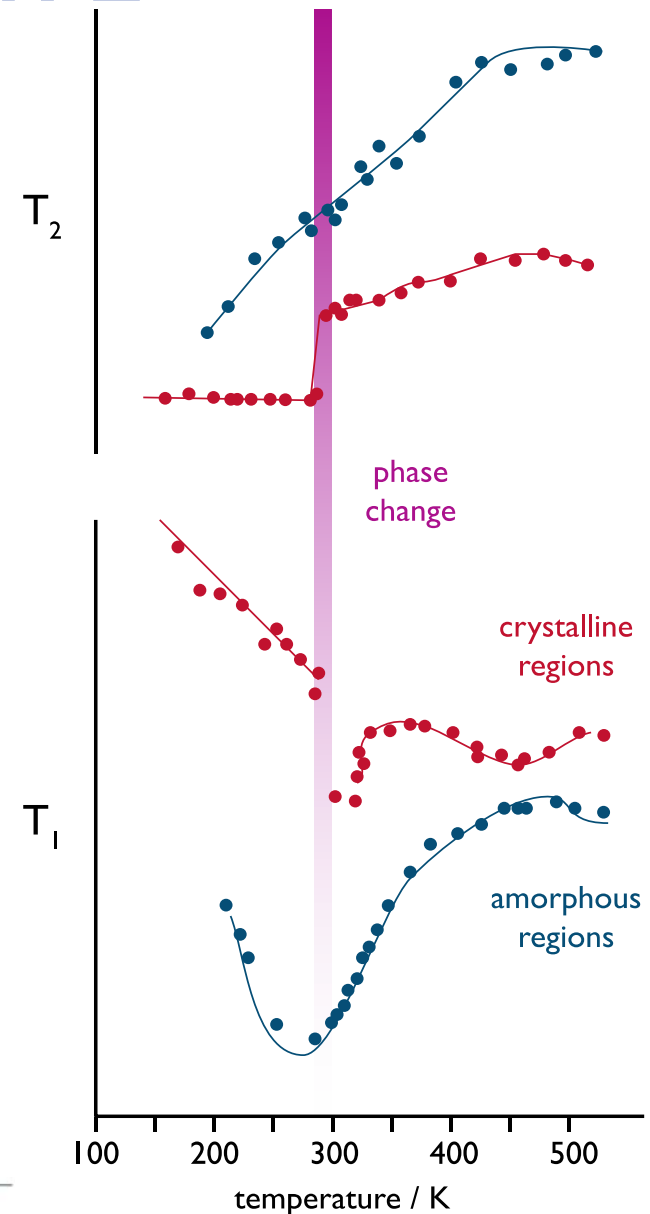
- Poly(tetrafluoroethylene) (PTFE) is an semi-crystalline polymer $T_m = 600 \text{ K}$ & $T_g = 400 \text{ K}$

- In the amorphous regions

- T_1 has a minima at 273 K
 - τ_c^{-1} equal to Larmor frequency (30 MHz): $\tau_c \sim 3 \text{ ns}$
- T_2 increases rapidly from 220 K
 - τ_c^{-1} similar to ^{19}F linewidth to cause narrowing: $\tau_c \sim 20 \text{ ms}$

- In the crystalline regions

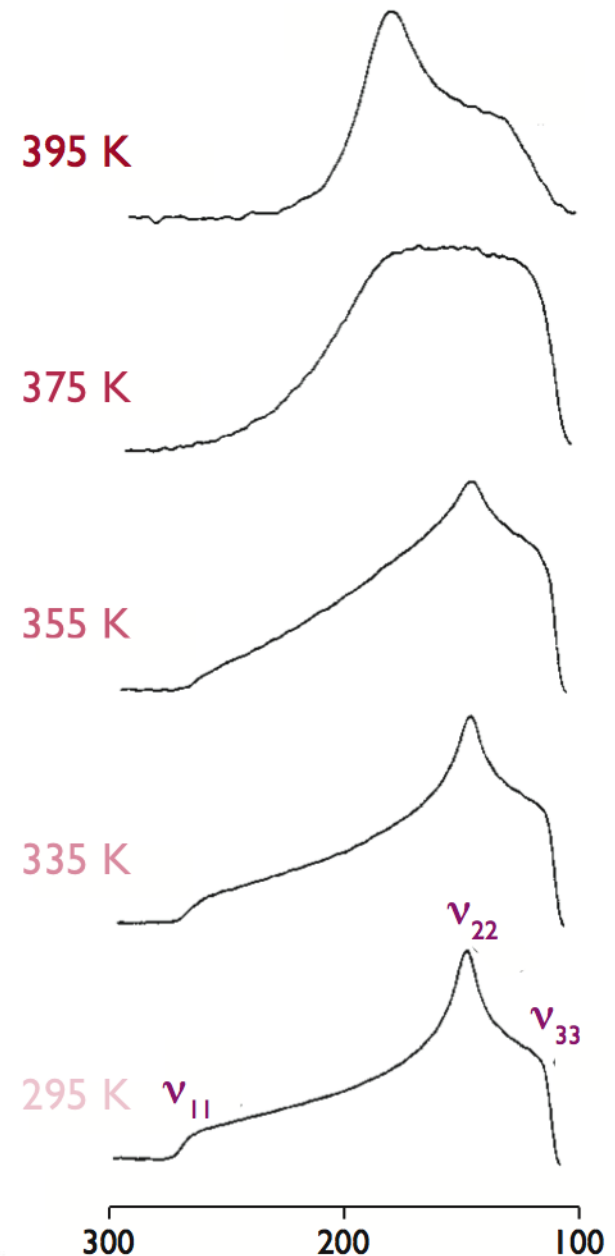
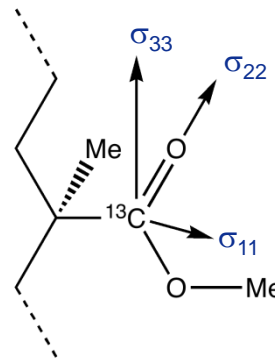
- Both T_1 and T_2 show discontinuity at 292 K
 - indicative of a change in phase transition
- T_1 has minima at 450 K
- T_2 increases rapidly from 340 K



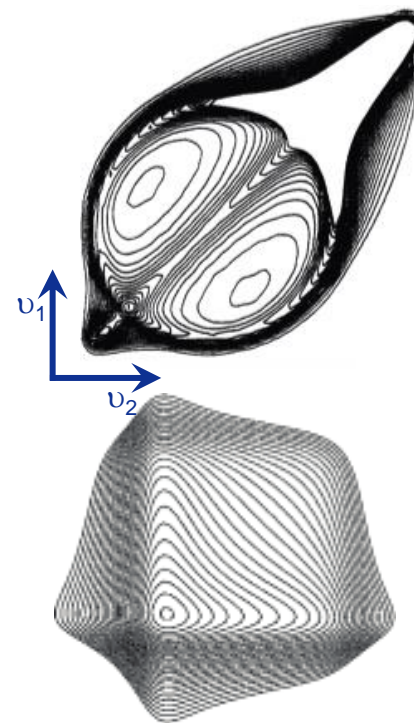
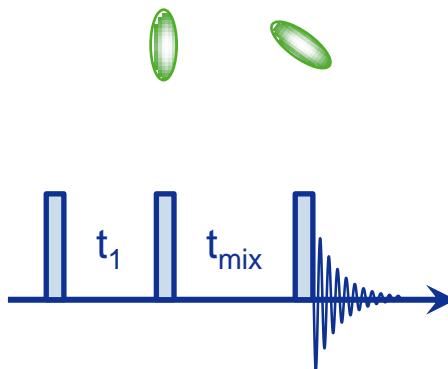
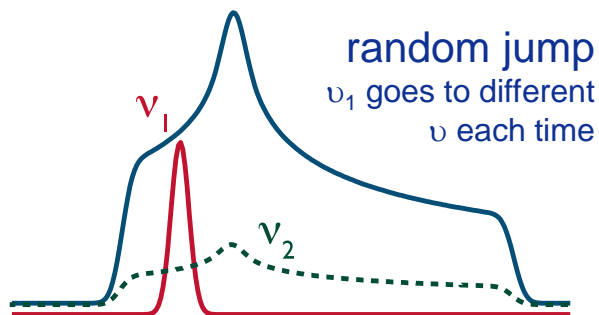
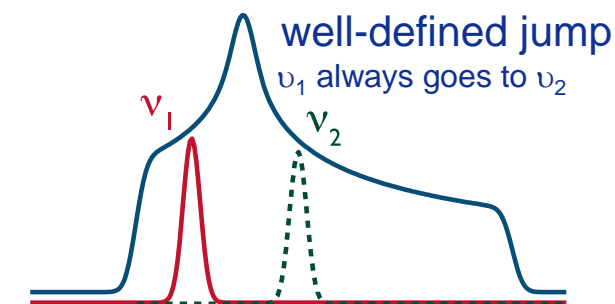
Lineshape & T_g in PMMA

- Polymethylmethacrylate (PMMA) is an amorphous polymer with a glass-transition temperature (T_g) of 338 K

- $T = 295 \text{ K} < T_g$
 - σ_{33} aligned parallel to polymer chain and σ_{22} aligned parallel to C=O
- $T = 355 \text{ K} > T_g$
 - lineshape narrows indicating presence of motions with rate $> 10 \text{ kHz}$ (δ_{CSA})
- $T = 395 \text{ K} \gg T_g$
 - anisotropic chain motion leads to motional averaging and axial symmetry of σ

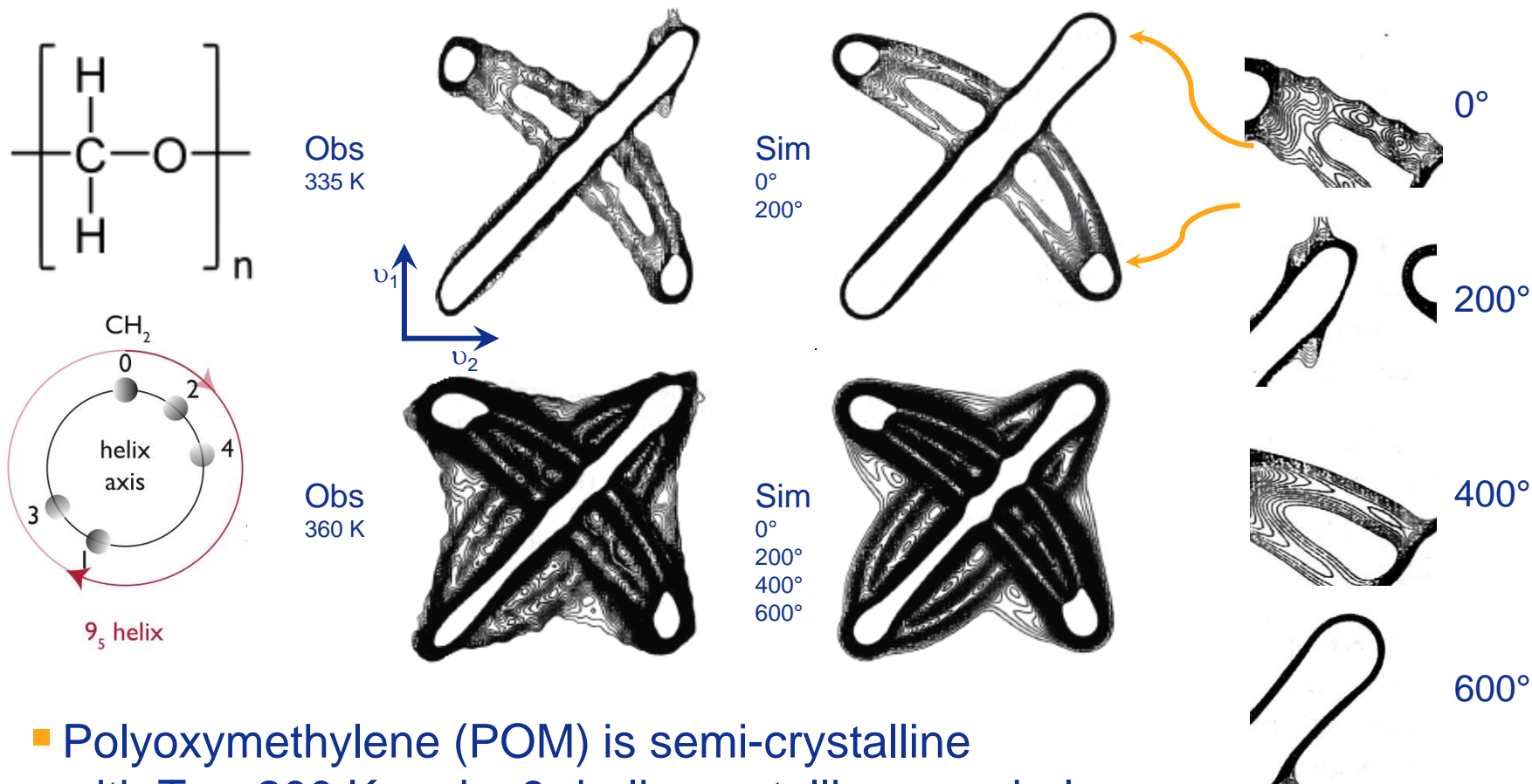


2D exchange spectroscopy



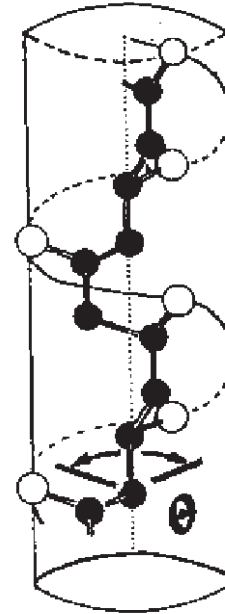
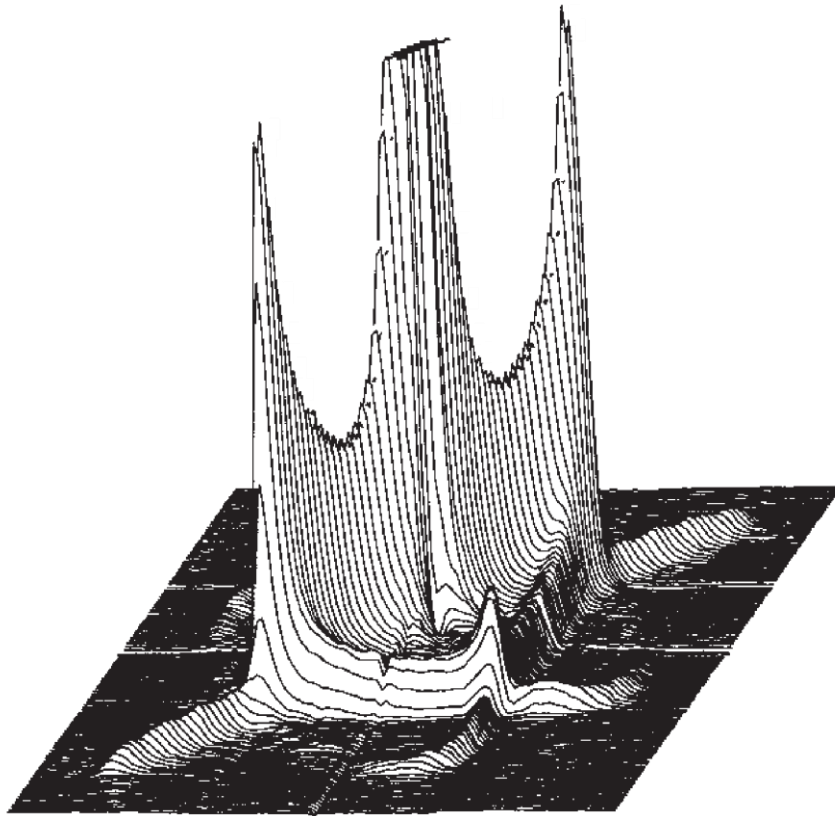
- 2D correlation spectroscopy: magnetisation transferred between spins
- 2D exchange spectroscopy: change of chemical environment of a spin
 - solution-state exchange probes chemical exchange (equilibrium & rearrangement)
 - solid-state exchange probes molecular reorientation

2D exchange spectroscopy of POM



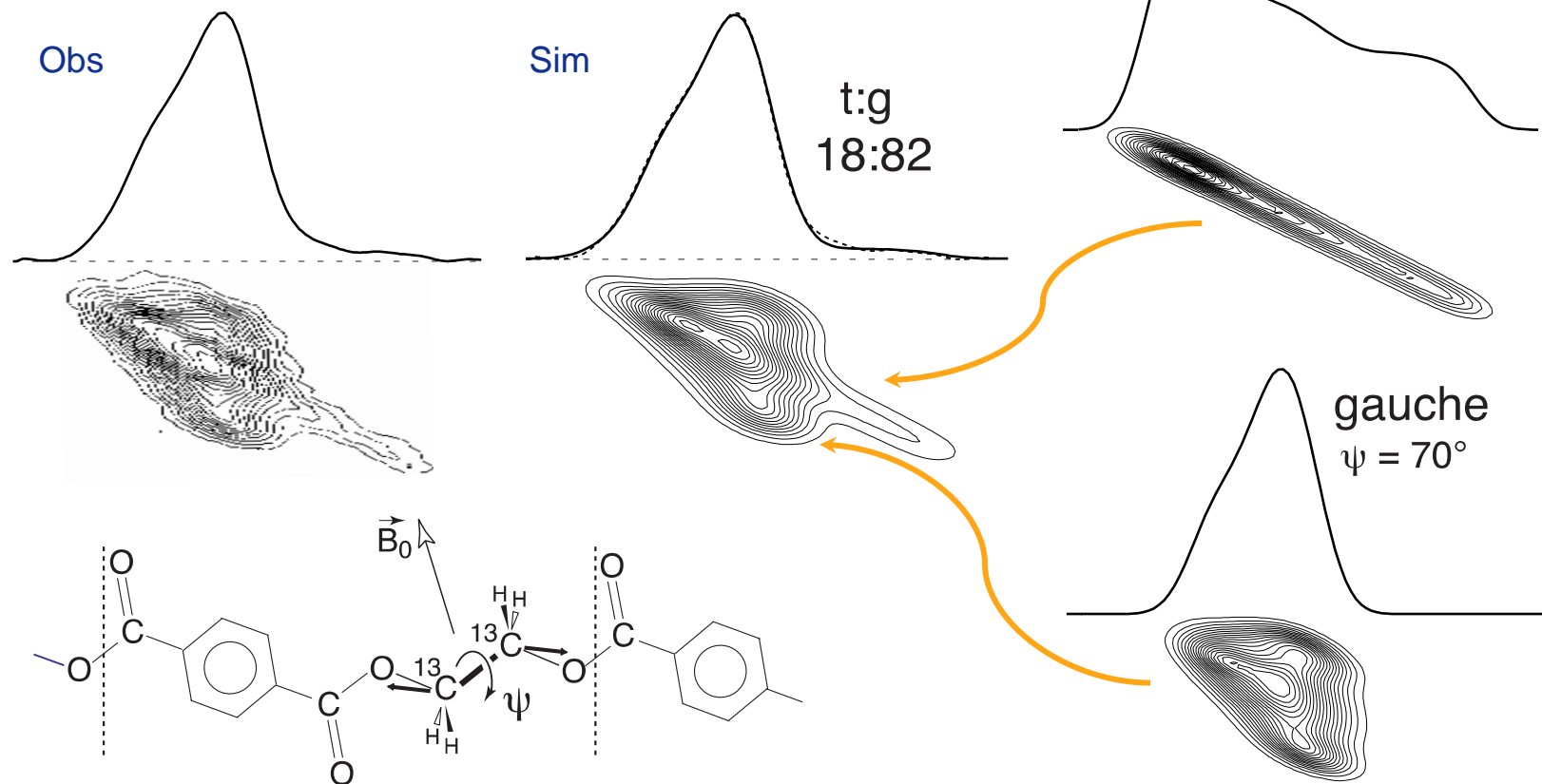
- Polyoxymethylene (POM) is semi-crystalline with $T_g = 200$ K and a 9_5 helix crystalline morphology
 - 9 monomer occupy 5 turns of helix i.e. adjacent CH₂ related by 200° rotation

Static ^2H exchange



- Isotactic polypropylene with methyl group deuterated at $T = 387\text{ K}$
 - Elliptical ridges characteristic of helical chain reorientation

^{13}C - ^{13}C DQ Correlation



- Poly(ethylene terephthalate) (PET) ^{13}C SQ-DQ correlation
 - Torsion angle distribution in an amorphous solid

End of presentation

Matt Parkinson

13.4.2012 – 26.9.2015

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