NMR Studies of Polyethylene: From Chemical Characterization Towards the Organization of Semi Crystalline Polymers

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Outline

Chain Branching

^{13}C NMR Branch Quantification

^{13}C NMR Optimisation

- Hardware Setup
- Method

Applications

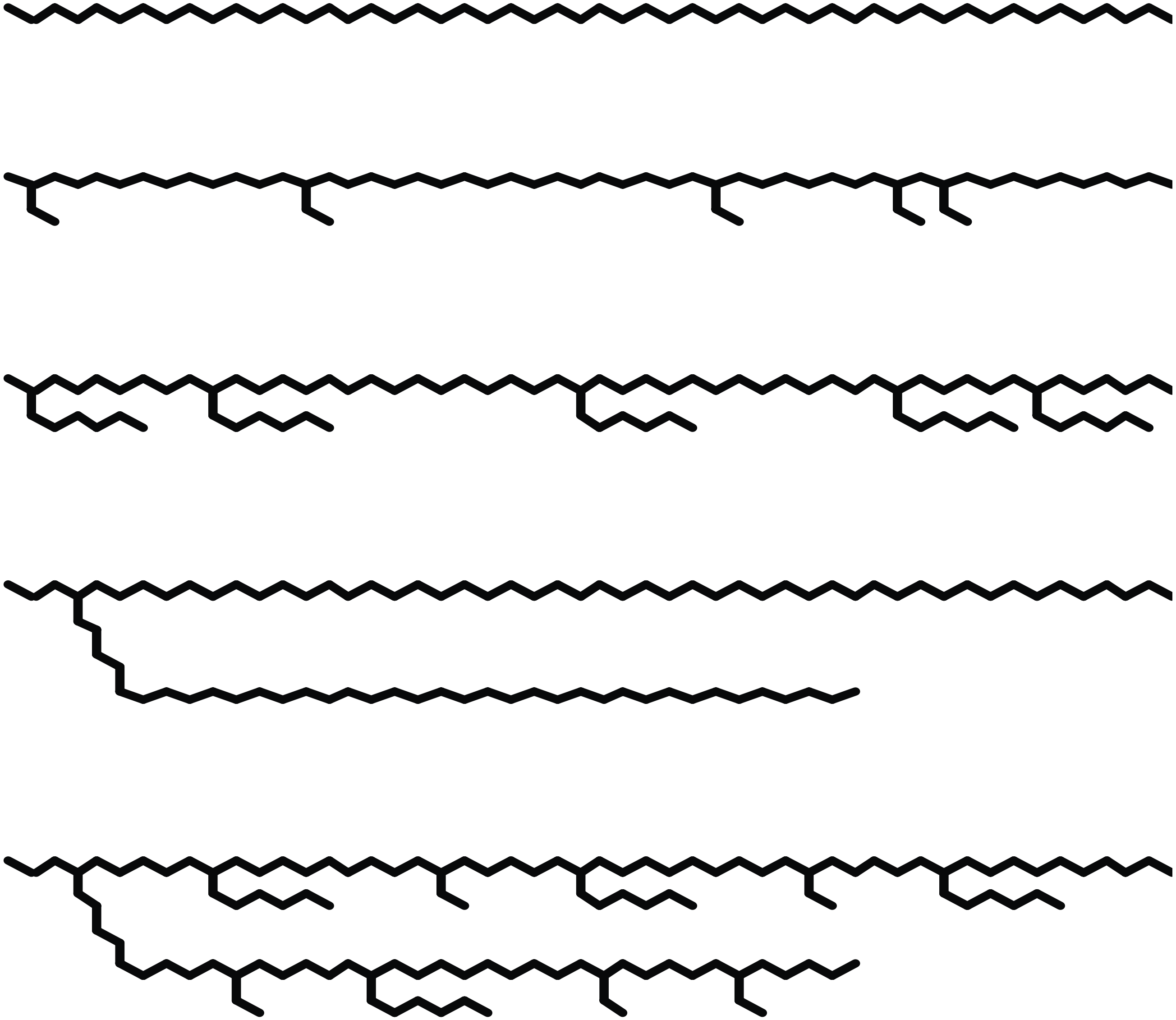
Chain Dynamics & Morphology

Anisotropic NMR Interactions

NMR and Chain Translation

Applications

Types of Branching



SCB

< 30 C

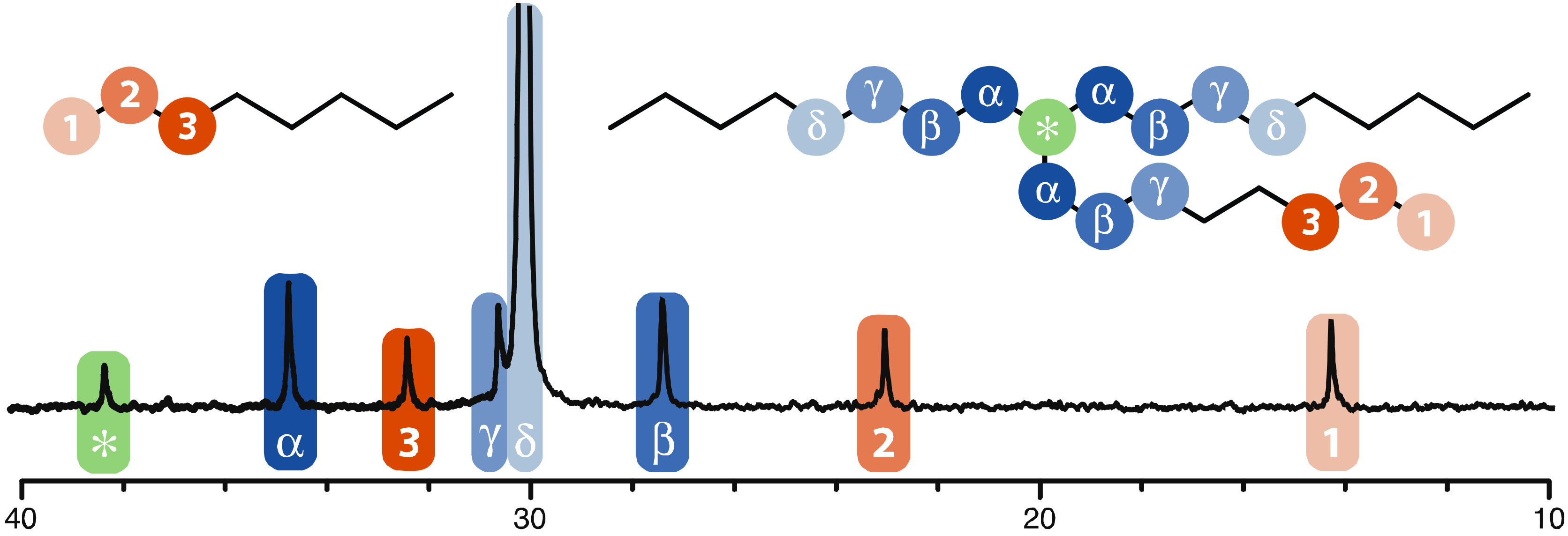
LCB

> 270 C

M_e

NMR Branch Quantification

Solution-State NMR



Direct quantification via ratio of integrals:

- branch content ∗:δ or α/3:δ

Disadvantages:

- maximum 20 wt % solubility
- up to 2,000,000 scans for 3–8 per 100,000 CH_2

Optimised NMR Branch Quantification

Strategies for Optimisation

Measurement of bulk polymer:

- more NMR active nuclei per volume
- more signal per unit time
- faster branch quantification

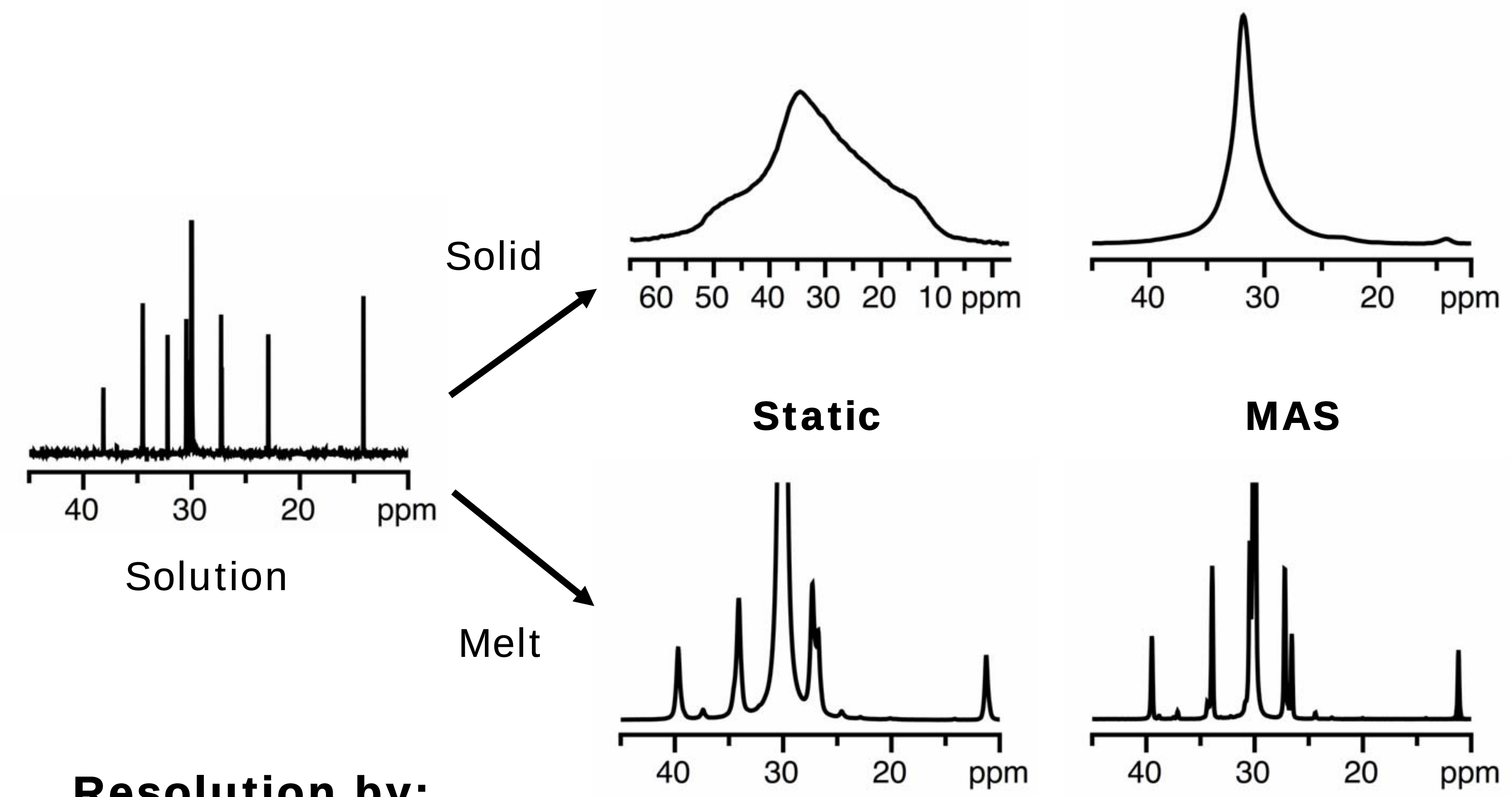
Type of NMR:

- solid-state NMR
- melt-state NMR

Parameters Investigated:

- external magnet field
- coil geometry
- pulse sequence
- recycle delay
- decoupling method

Resolution Enhancement



Solid

Solution

Melt

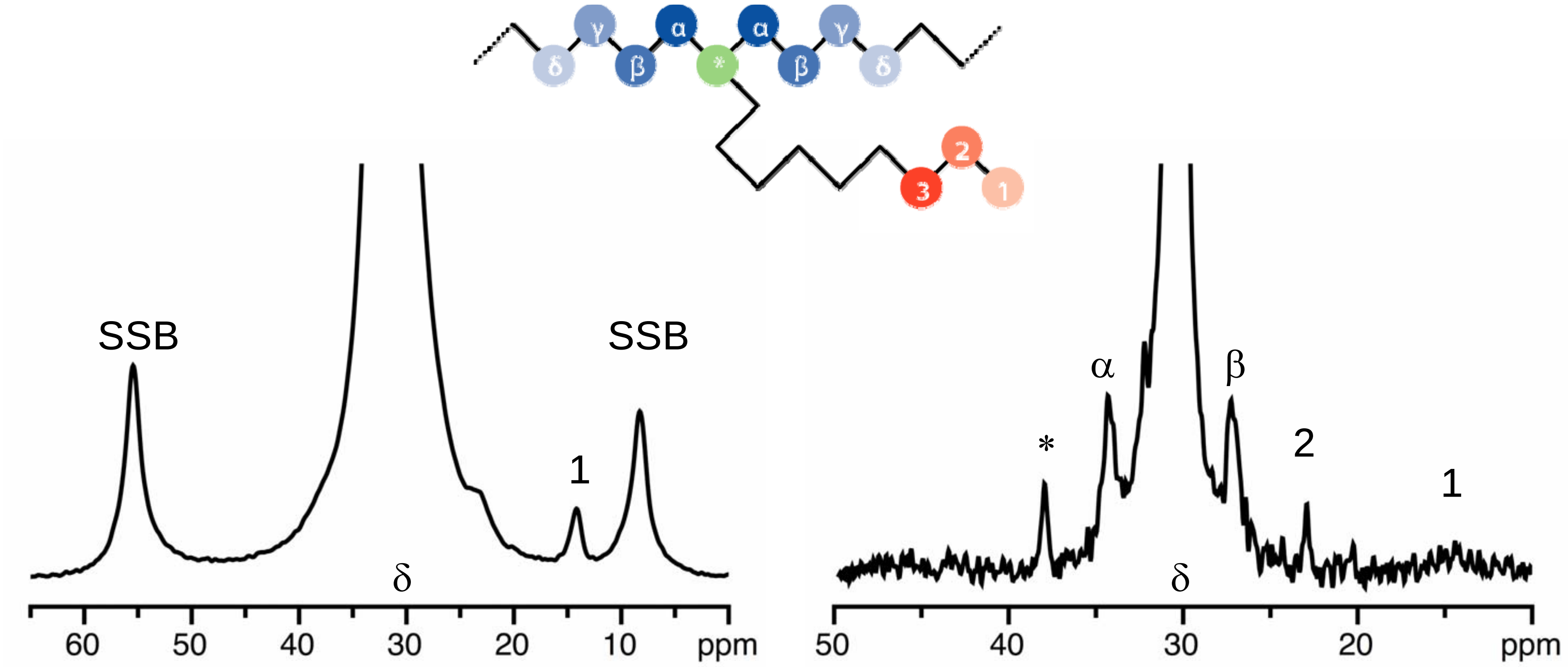
Static

MAS

Resolution by:

- **magic angle spinning (MAS)**
- **high-power heteronuclear dipolar-decoupling**
- **motional averaging of anisotropic interactions**

Solid-State MAS NMR

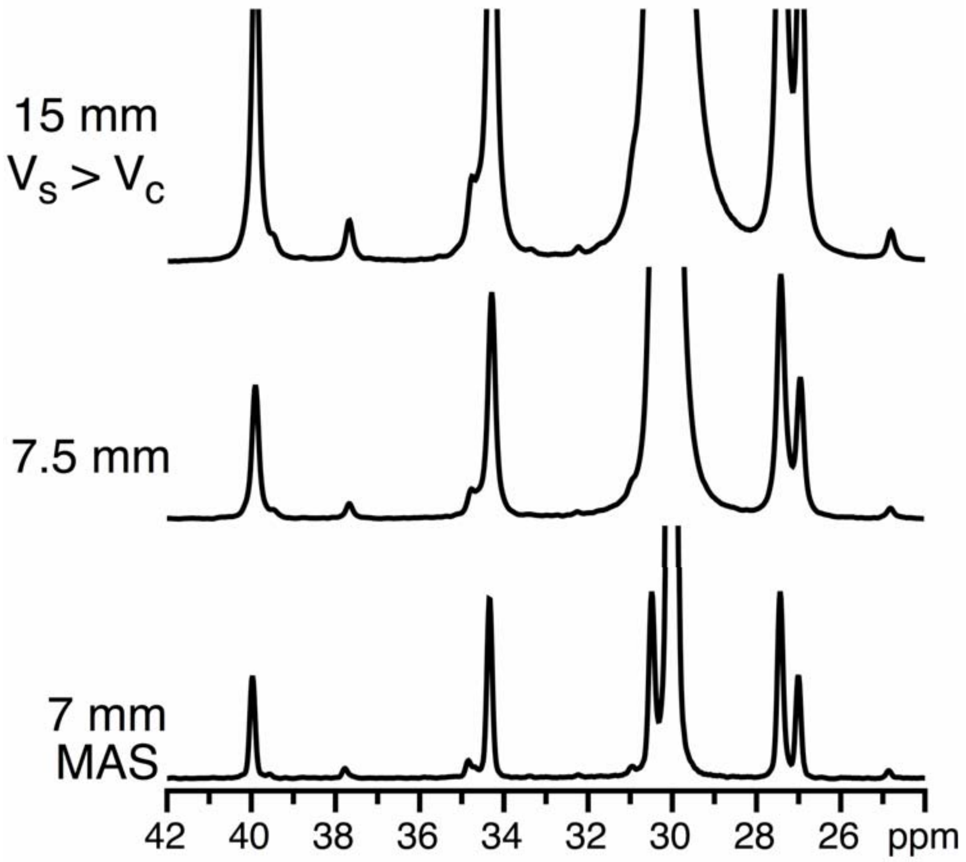


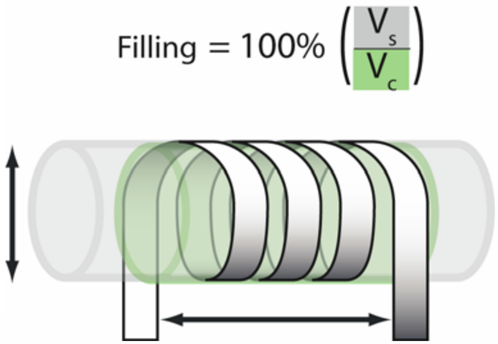
500 MHz / 7 mm
3 kHz MAS

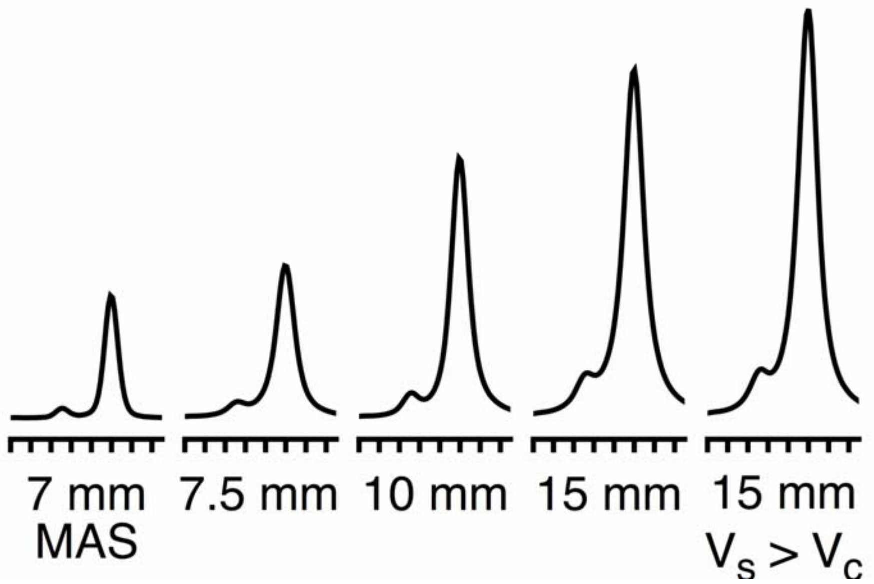
700 MHz / 2.5 mm
30 kHz fast MAS

semi-quantitative at low temperature (-15°C)

Melt-State Static NMR



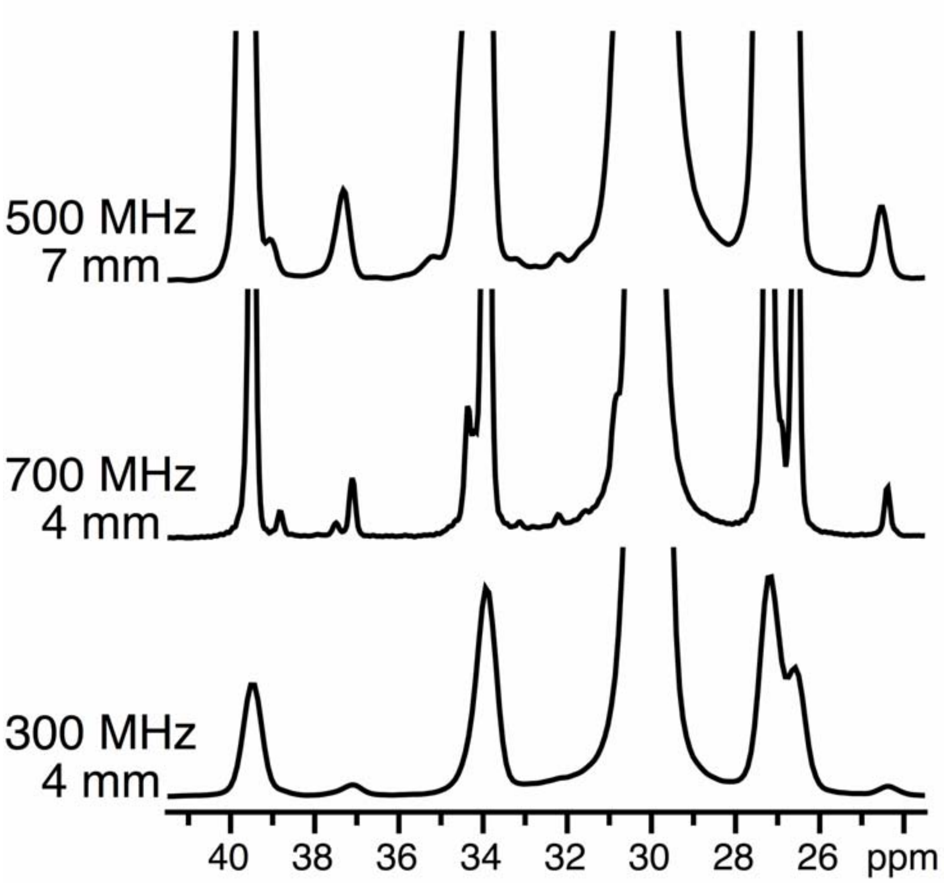




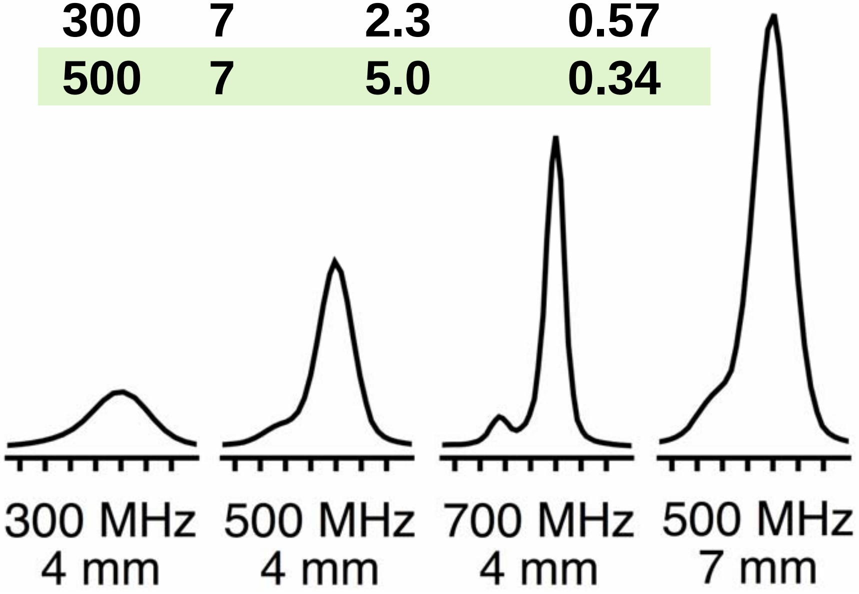
Highest sensitivity but with reduced resolution

- large detection coils at 300 MHz
- high degree of detection coil filling

Melt-State MAS NMR



B_0 MHz	ϕ mm	relative Sensitivity	FWHH_δ ppm
300	4	1.0	0.49
500	4	1.8	0.34
700	4	2.0	0.17
300	7	2.3	0.57
500	7	5.0	0.34

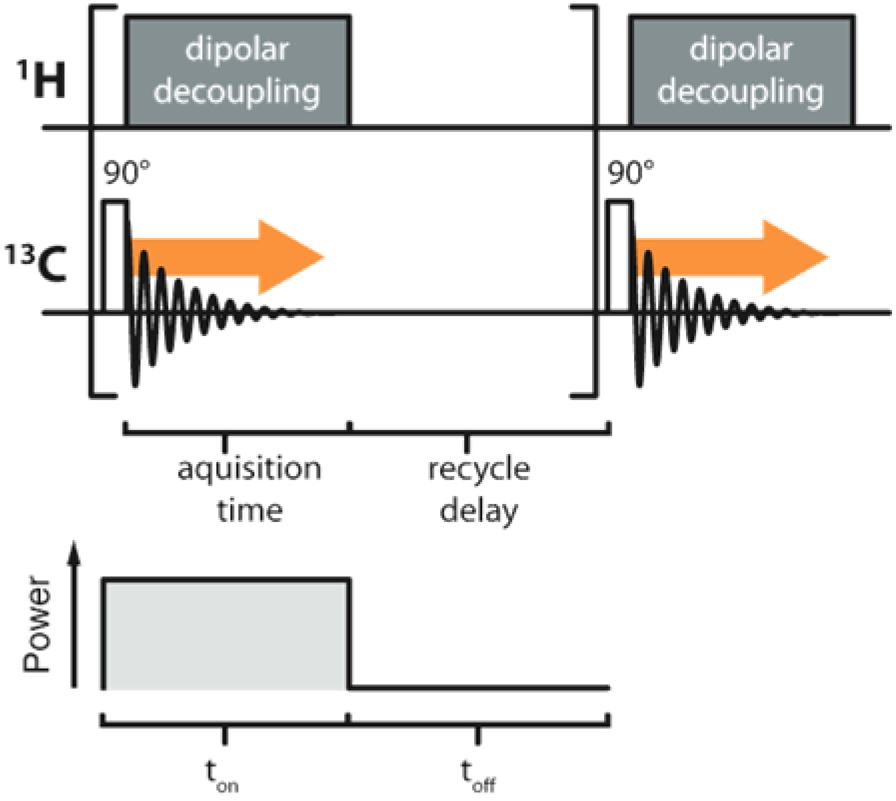


Compromise between sensitivity and resolution

– ^{13}C-^{1}H optimised 7 mm MAS probehead at 500 MHz

Direct Polarisation

Single Pulse Excitation (SPE)



Hardware Limits

Maximum Pulse Length

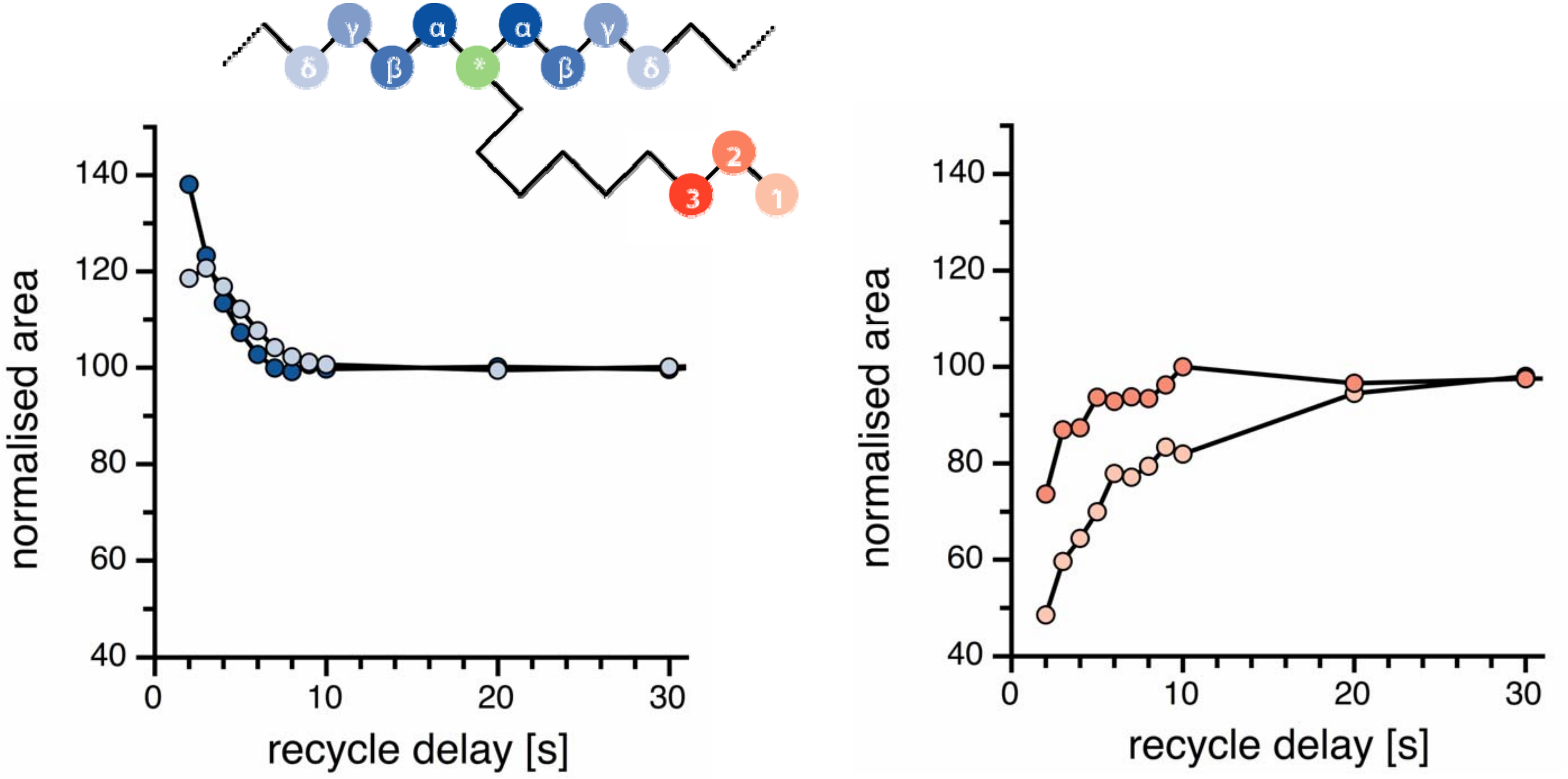
$$t_{on} < 200\ \text{ms}$$

Maximum Duty-Cycle

$$D_{\%} = 100\% \left(\frac{t_{on}}{t_{on} + t_{off}}\right) < 2\%$$

Quantitative but limited by T_1^C

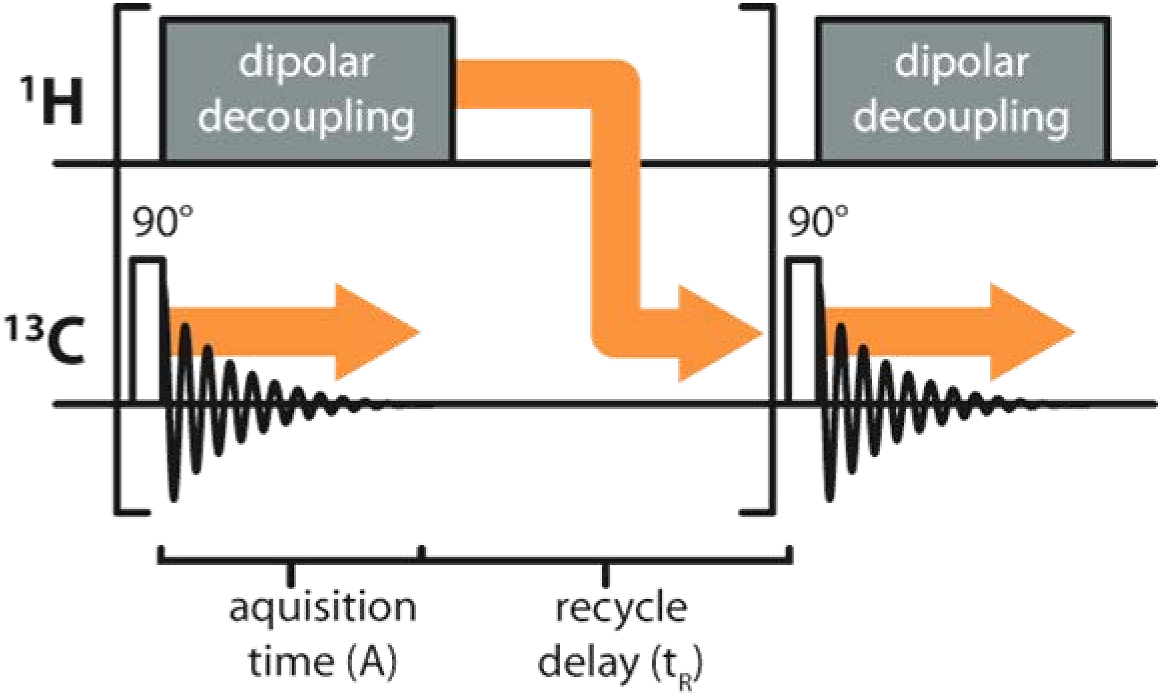
Short Recycle Delays I



Short recycle delays

- saturation effects on branch carbons 1,2 and 3
- enhancement of backbone signals $*$, α, β and δ

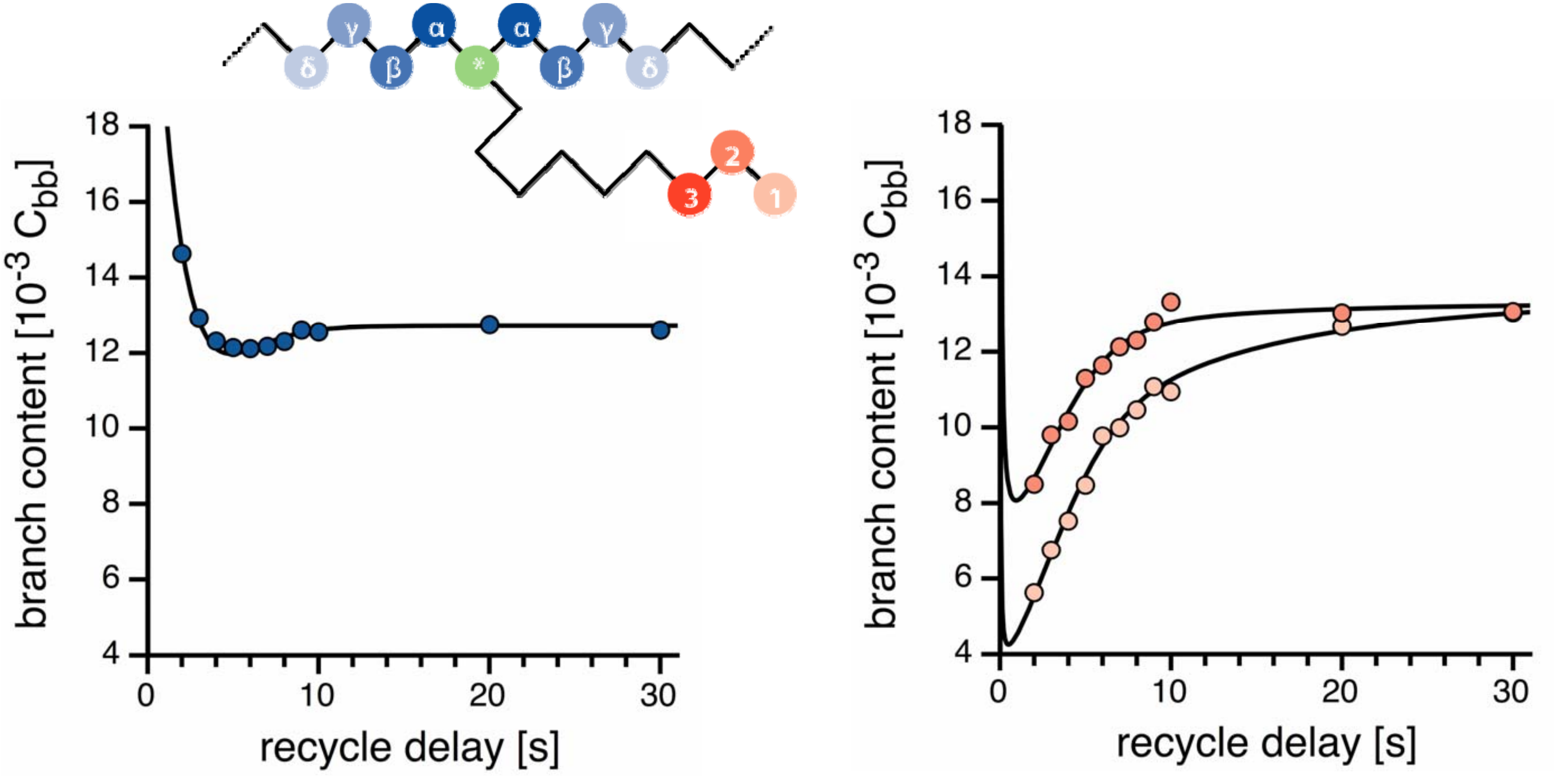
Short Recycle Delays II



Transient NOE

- residual proton polarisation from decoupling
- enhancement dependent on nuclear relaxation times

Short Recycle Delays III

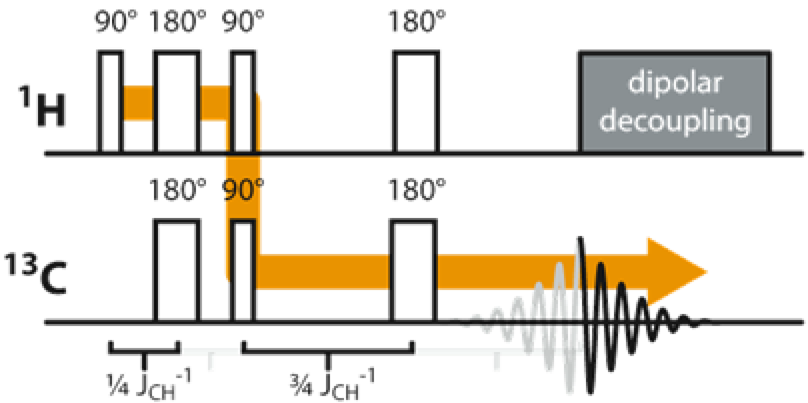


Short recycle delay

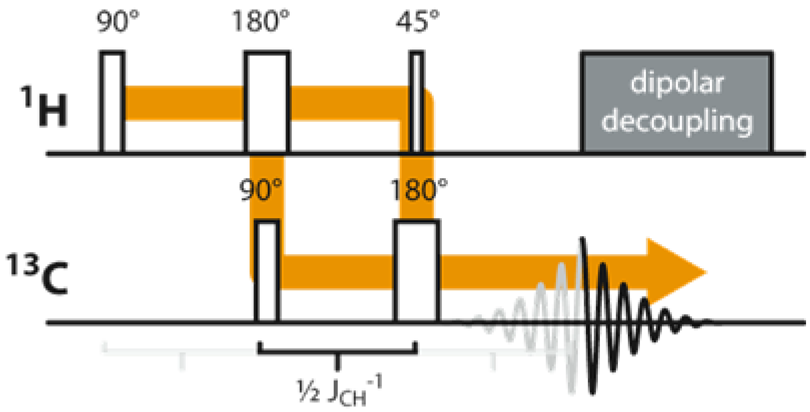
- backbone carbons better suited for quantification

J-Mediated Methods I

Refocused Decoupled INEPT



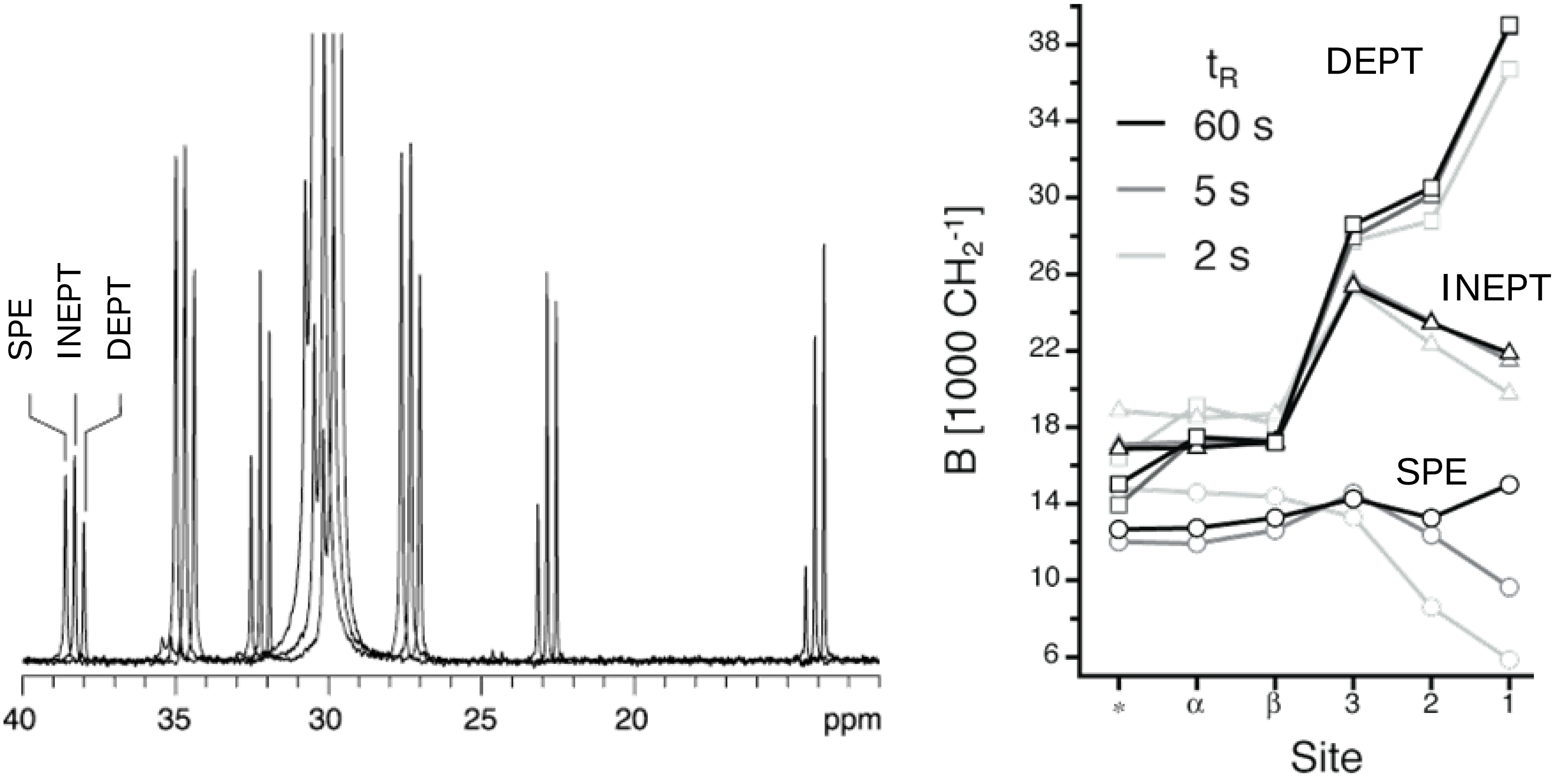
Decoupled DEPT-45°



J-Mediated polarisation transfer

- limited by T_1^H not T_1^C
- access to attached proton tests

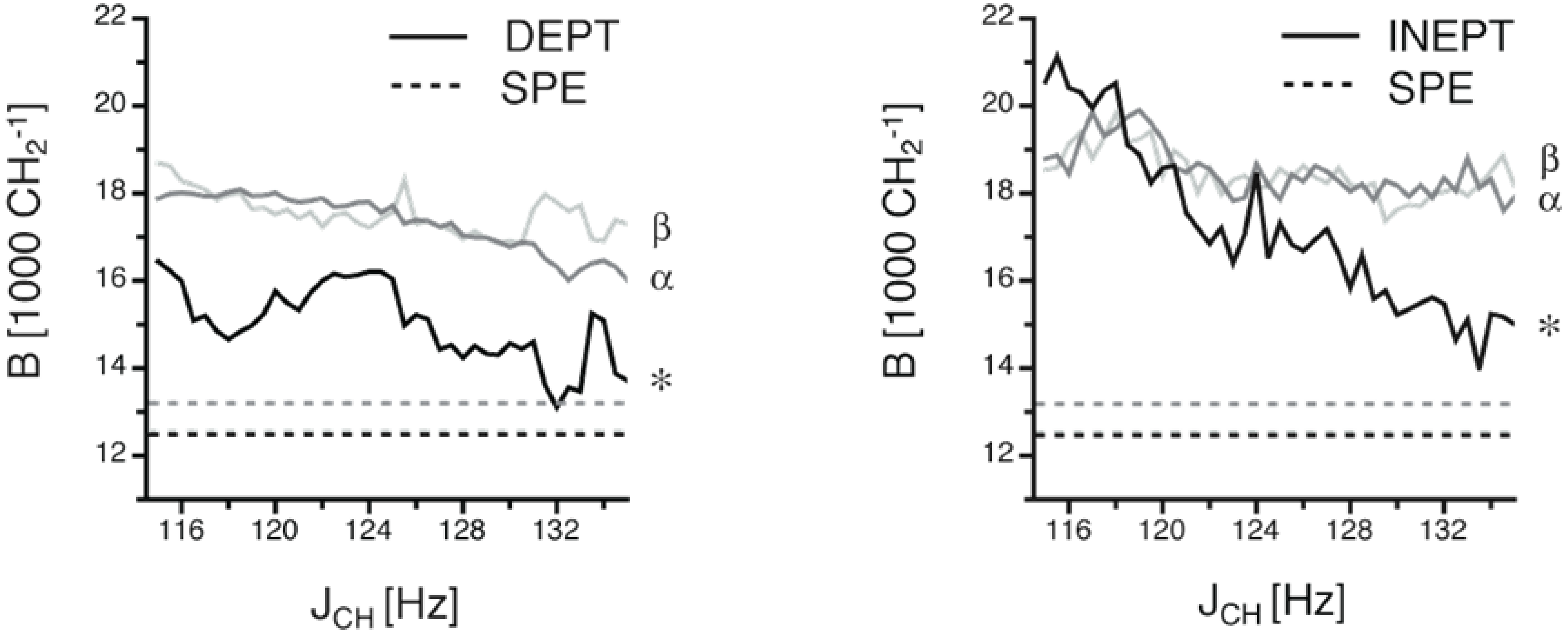
J-Mediated Methods II



Both INEPT and DEPT

- overestimate branch content
- show less effect of recycle delay on branch content
- show potential for branch quantification (∗, α, β)

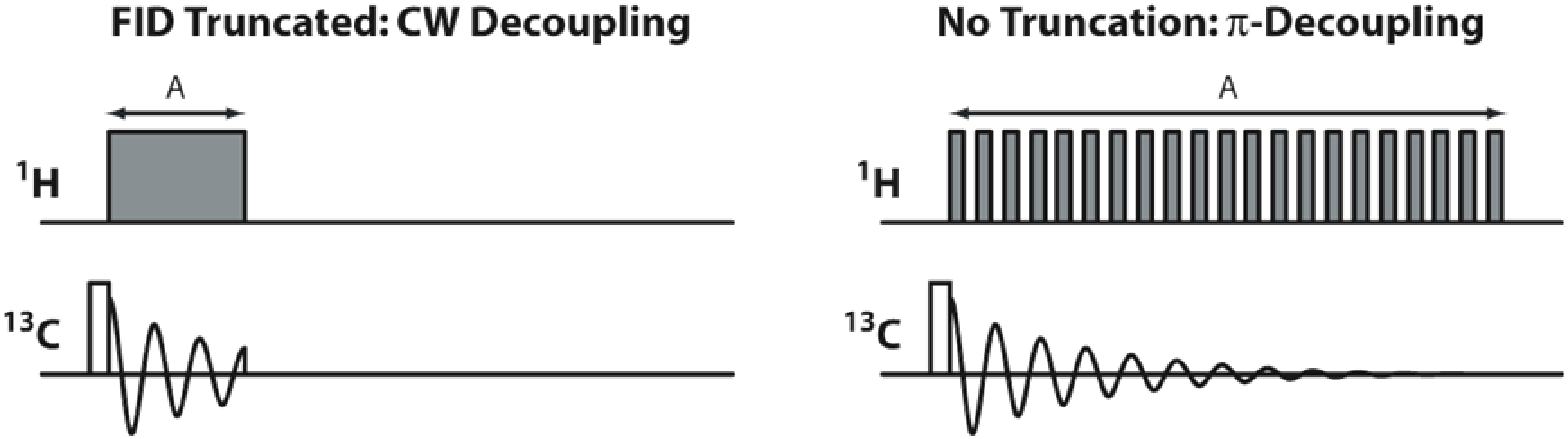
J-Mediated Methods III



Not fully quantitative

- branch content dependent on J_{CH}

Decoupling Method I

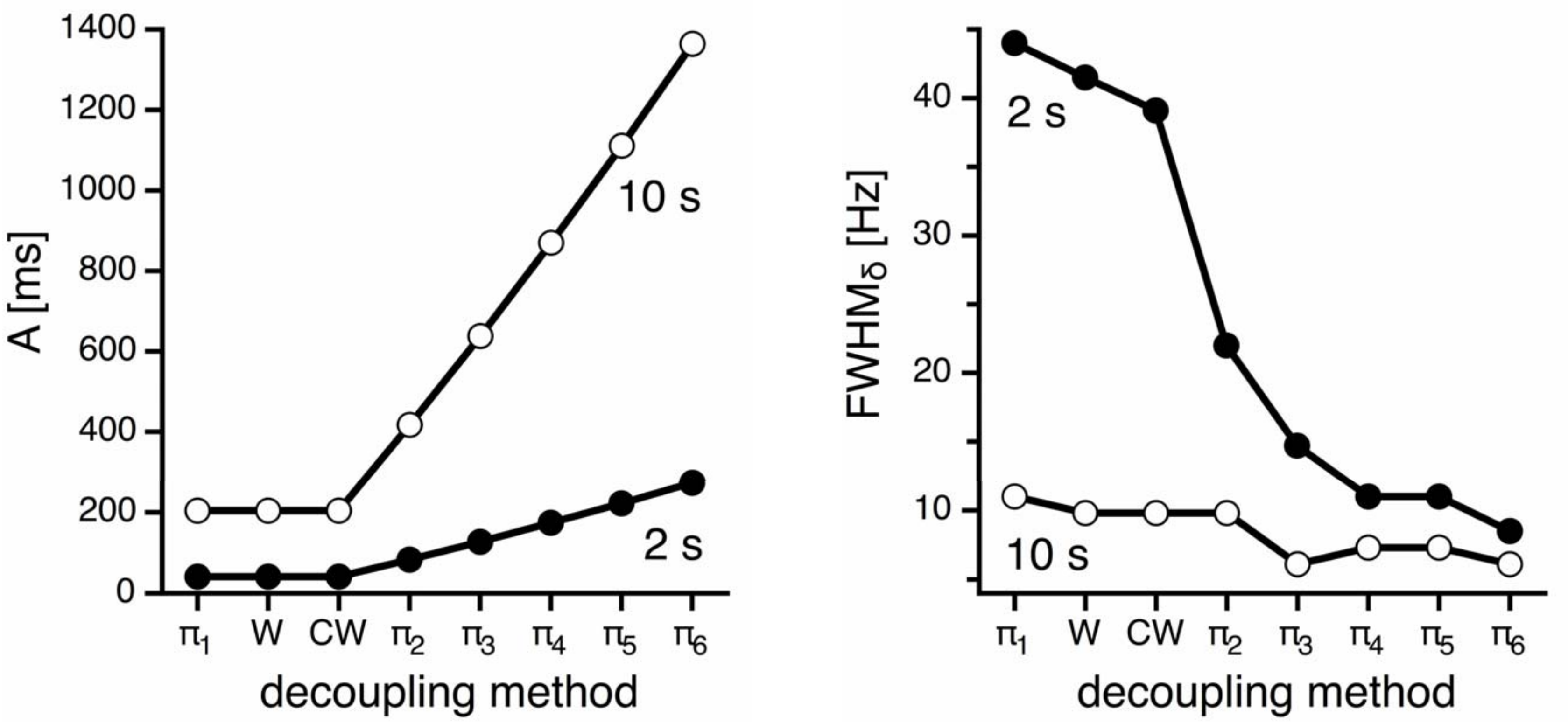


t_R = 2 s: A_{Max} = 41 ms A_{Max} = 272 ms

Advantages

- longer acquisition possible
- less artificial line-broadening / more T_2-based line-widths

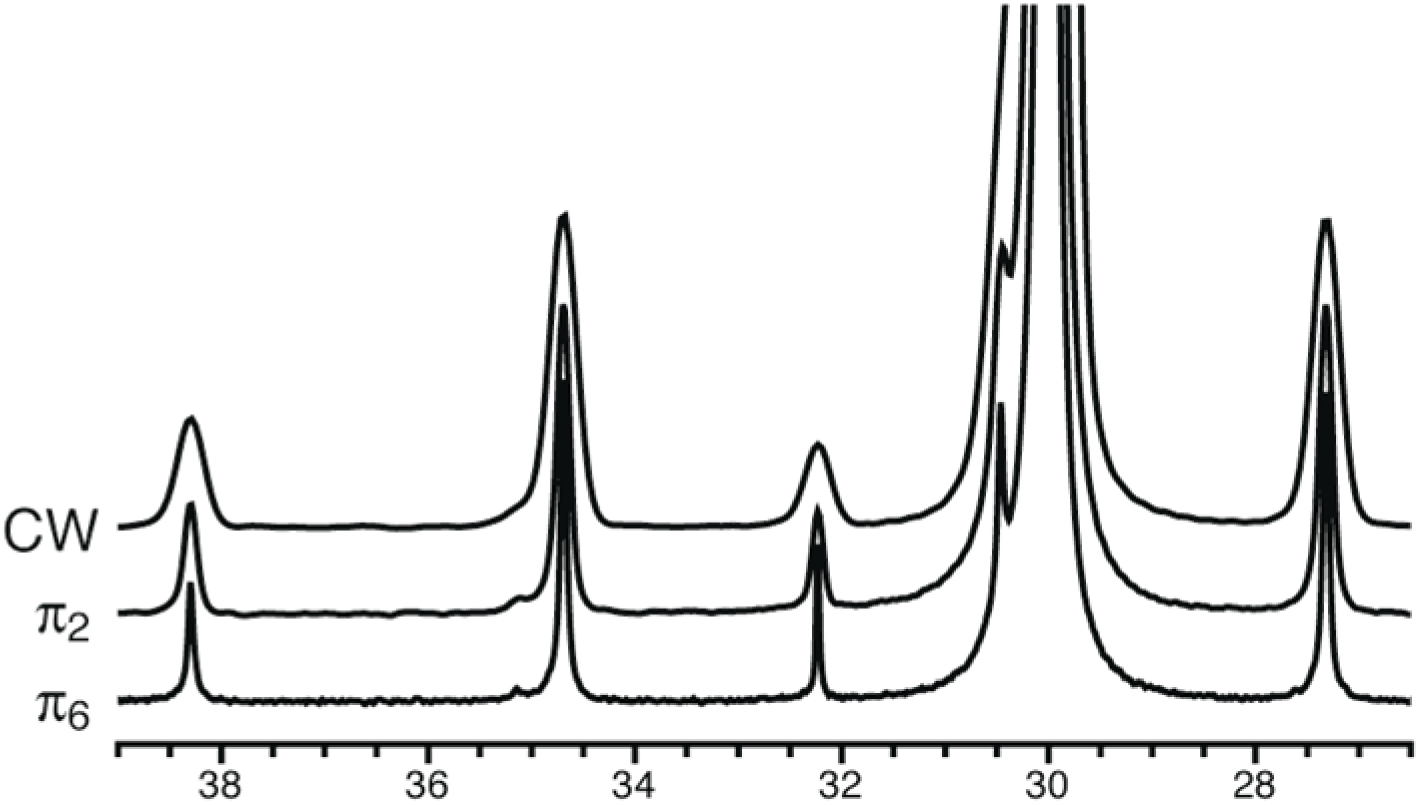
Decoupling Method II



Optimum decoupling method

- π-decoupling at short recycle delay
- extended duty cycle

Decoupling Method III



A

41 ms

83 ms

272 ms

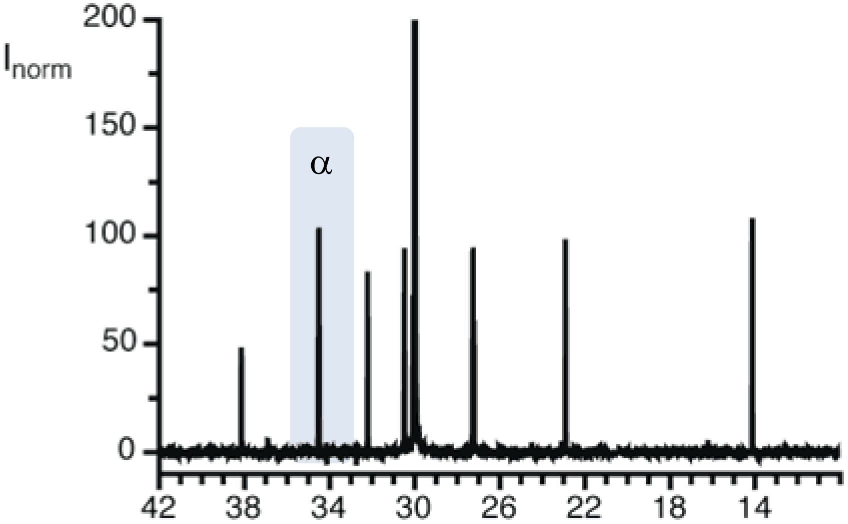
Reduction of FWHH$_\delta$

- 40 Hz to 10 Hz at 2 s

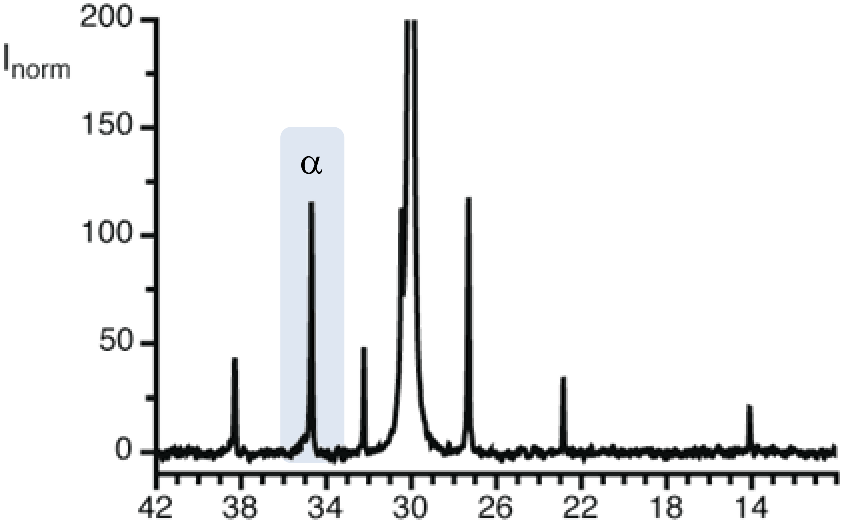
Applications

Comonomer Content

Solution-State PE8-C
12 h / $\text{SNR}_{\alpha} = 52$



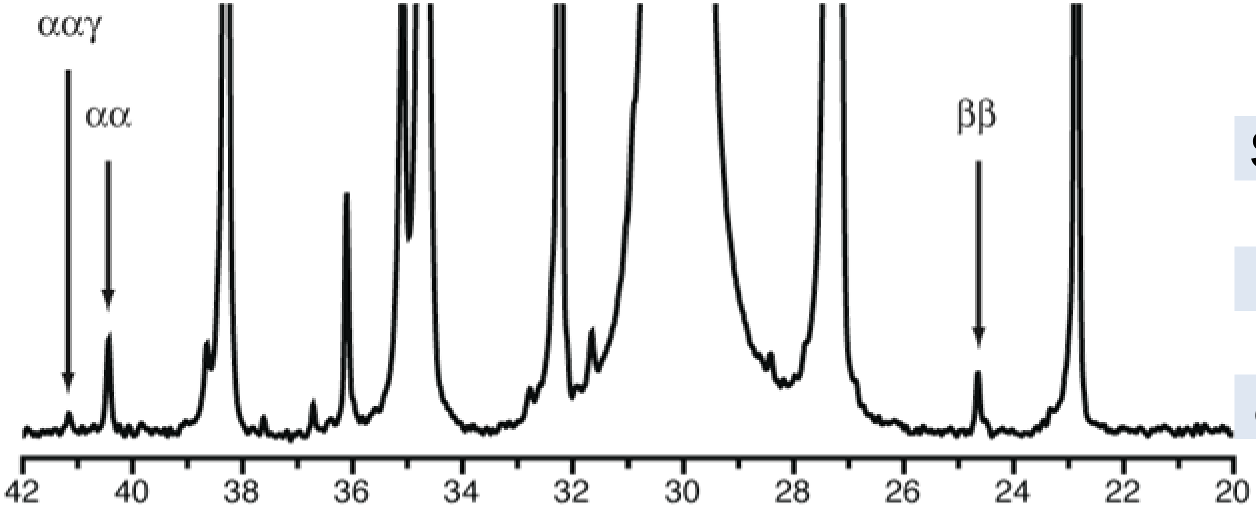
Melt-State PE8-C
70 s / $\text{SNR}_{\alpha} = 58$



Comonomer contents: 2–15 per 1000 CH_2

- Standard solution-state: 12 h per sample
- Optimised melt-state: 70 s – 16 min per sample

Comonomer Distribution

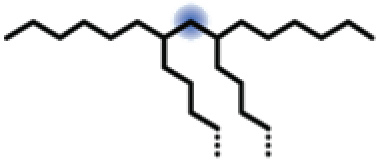


SCB + LCB PE

Site	SNR	B $1000\ CH_2^{-1}$
ββ	12.5	0.54
αα	19.3	0.84
ααγ	3.4	0.06

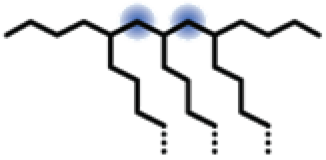
Double

αα



Triple

ααγ



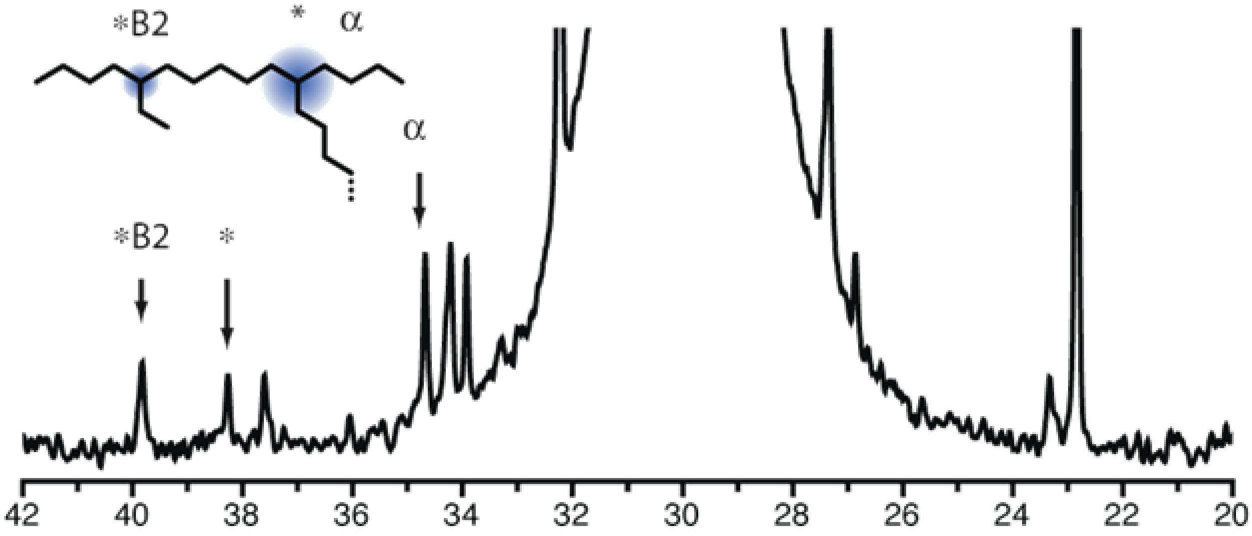
Non-consecutive

ββ

Comonomer incorporation

- quantification of double, triple and non-consecutive

Low Branch Content



Linear PE

Site	SNR	B 1000 CH_2^{-1}
∗B2	4.5	0.07
∗	3.7	0.05
α	9.4	0.08

Access to branch contents of 7–8 per 100,000 CH_2

- Optimised solution-state:
  - 50,000 to 2,000,000 scans (15 & 300 h)
- Optimised melt-state:
  - 21,500 scans (13 h)

Klimke et al., *Macromol. Chem. Phys.* **207**, 382–395 (2006).

Conclusions

Melt-state MAS

-compromise of resolution & sensitivity

-SPE more suitable than J-mediated methods

-highly time efficient due to short recycle delays

π-decoupling

-most aplicable at short recycle delays

-reduced FID truncation with extended duty cycle

-significantly improves resolution

Applicable to wide range of model/industrial polyolefins