Cyclic oligomers of poly(ether ketone ketone) and their polymerisation by entropy

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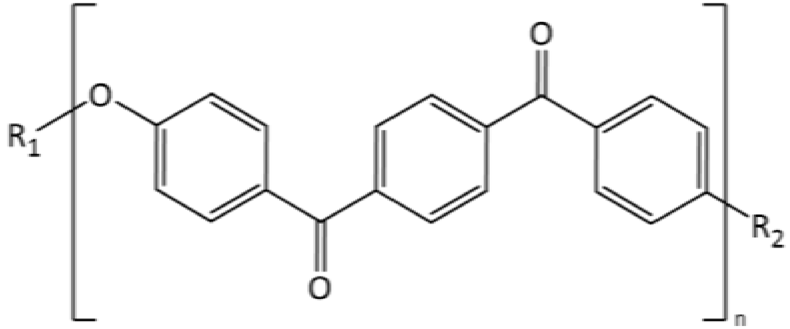
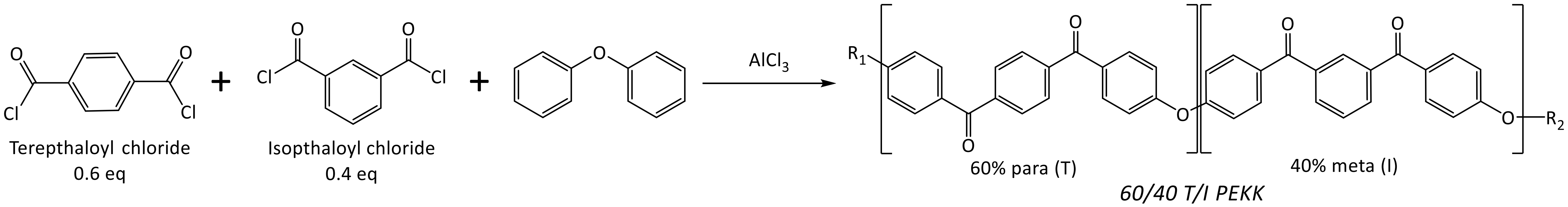
Background

- Composites are seeing increasing use in aerospace for lightweighting, especially low viscosity, unrecyclable epoxy thermosets
- Poly ether ketone ketone (PEKK) is a high-performance thermoplastic
- PEKK boasts high thermal stability, high strength, high chemical and fire resistance, and lighter weights.



PEKK

Commercial PEKK synthesis

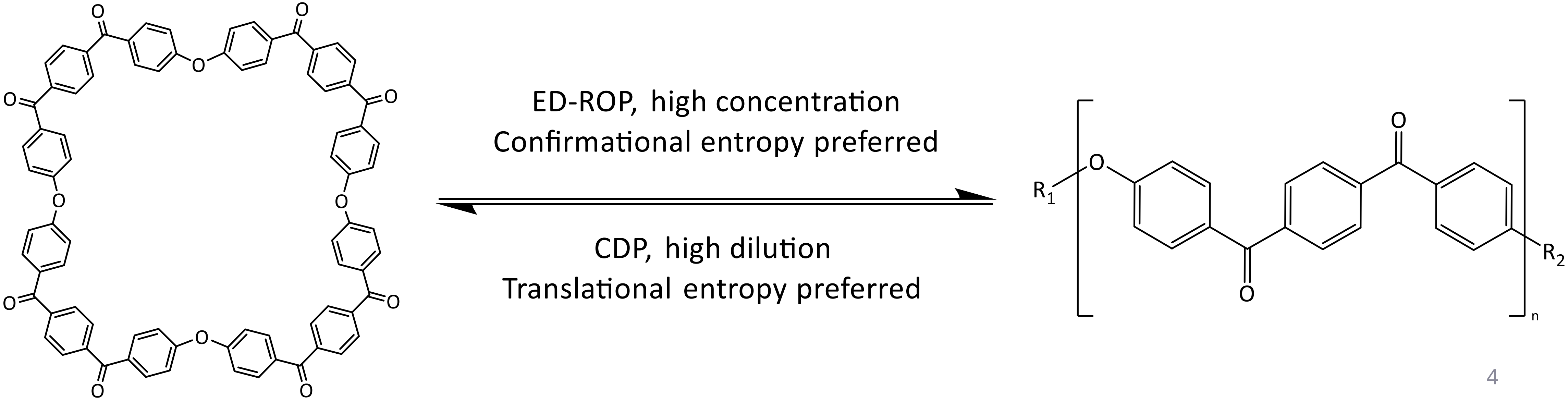


- PEKK currently produced by Friedel-Crafts acylation, usage limited by high-viscosity polymer
- PEKK products defined by their T/I ratio, the ratio of para and meta links in the polymer, allowing for range of applications

Arkema's Kepstan® PEKK product series				
Series	T/I ratio	T_m	T_g	Crystallization speed
6000	60/40	305°C	160°C	Slow
7000	70/30	332°C	162°C	Medium
8000	80/20	358°C	165°C	Fast

Entropy Driven Ring Opening Polymerisation (ED-ROP)

- ED-ROP is the polymerisation of large, strainless ring structures called macrocyclic oligomers (MCOs)
- The reaction is driven by the increase in conformational entropy of the linear polymer
- ED-ROP produces no heat or volatiles, can be performed neat, and MCOs are generally lower viscosity than their polymers.



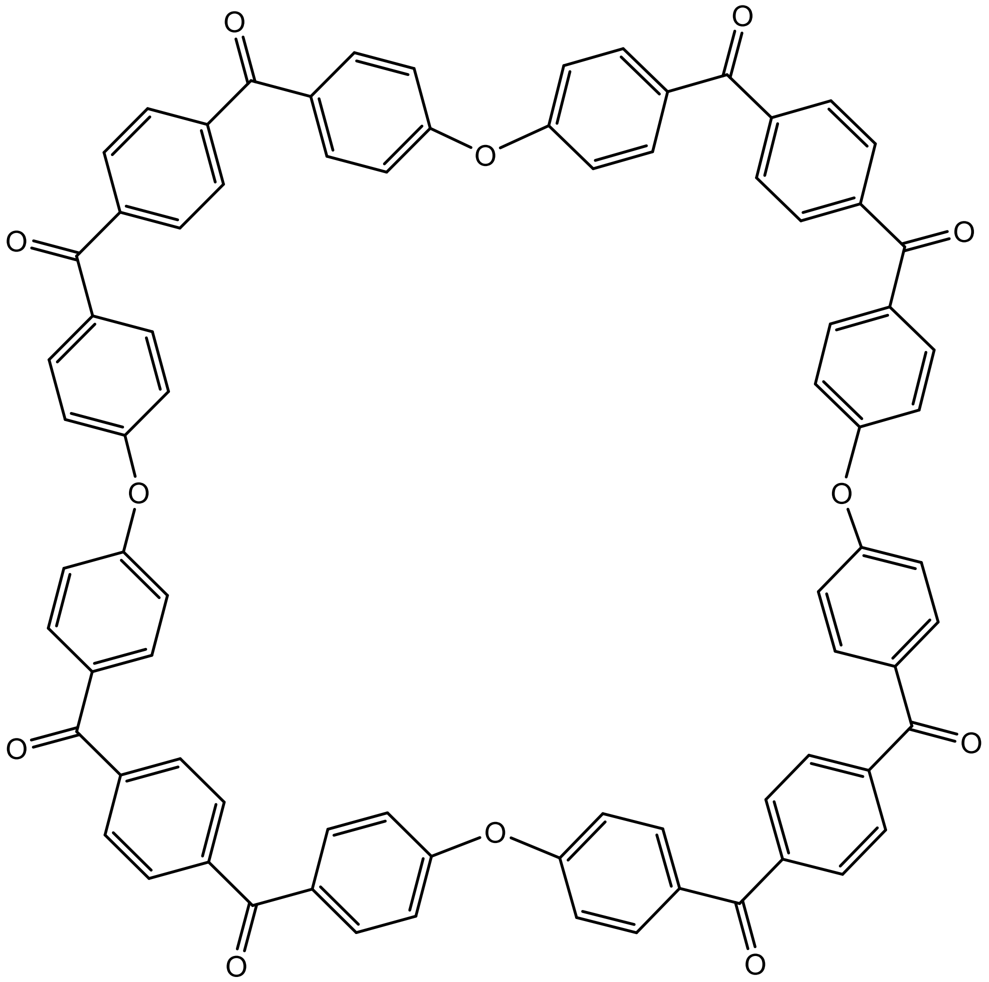
Synthesising MCOs

- Few examples of cyclic PAEKs and their polymerisation, no complete examples of cyclic PEKK nor PEKK polymer from ED-ROP [1], [2]

- Only one example of PAEK/carbon fibre composites by ED-ROP in-situ polymerisation [3]

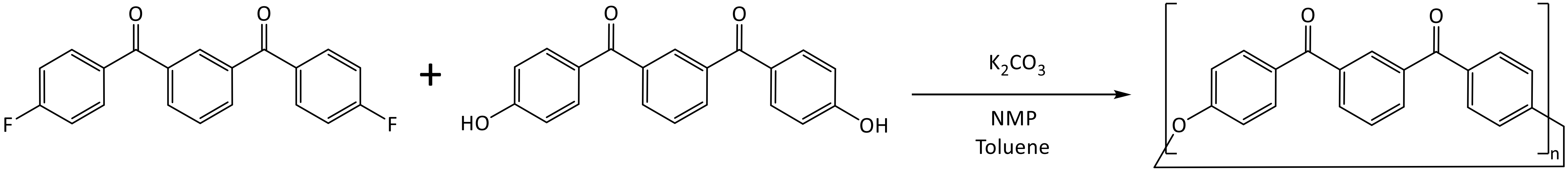
- Nucleophilic substitution in a pseudo-high dilution environment is the common strategy

- High temperatures, dipolar aprotic solvent and water removal required

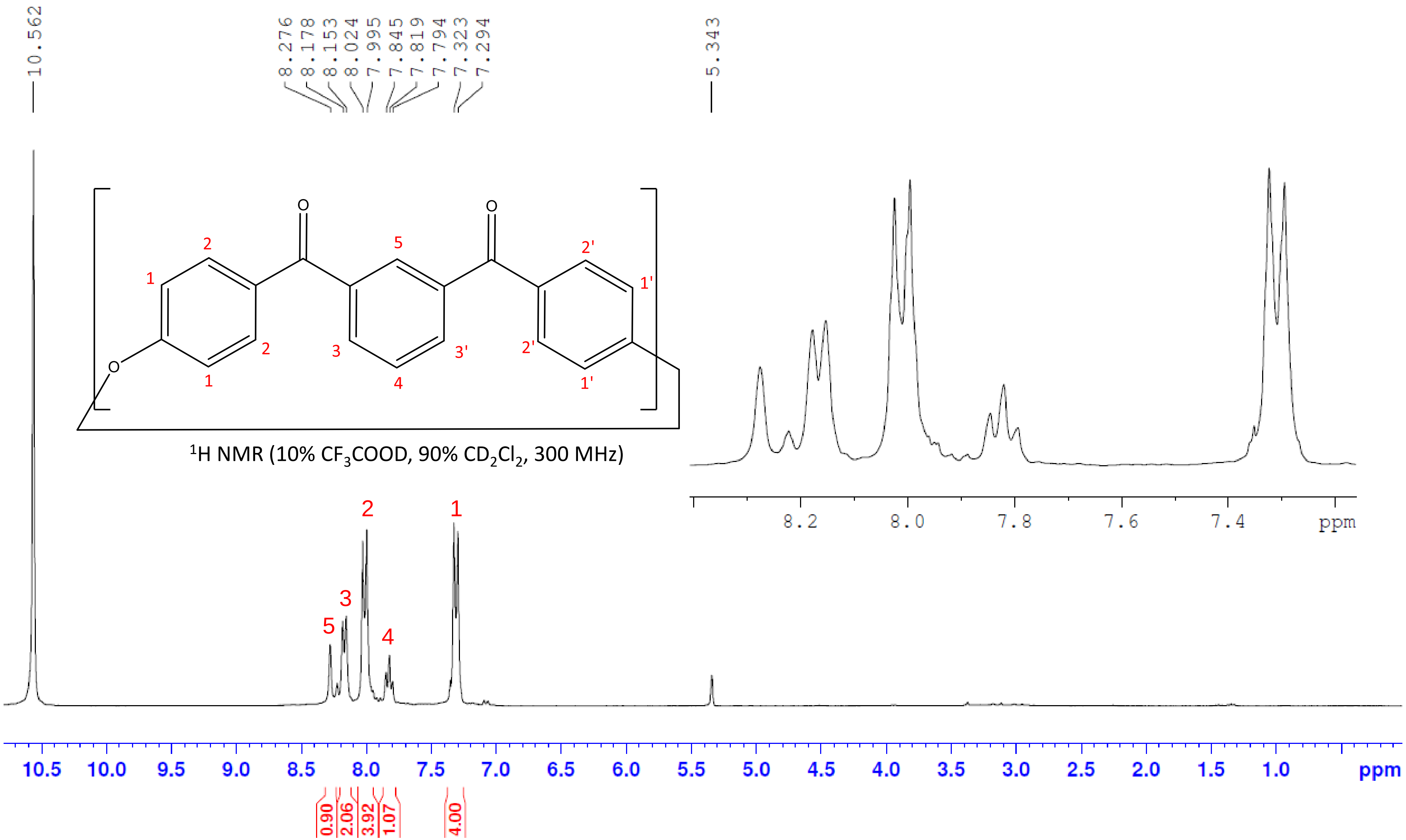


[1]: Hodge, P., Entropically Driven Ring-Opening Polymerization of Strainless Organic Macrocycles. Chemical Reviews, 2014. 114(4): p. 2278-2312
[2]: Ben-Haida, A., et al., Cyclic oligomers of poly(ether ketone) (PEK): synthesis, extraction from polymer, fractionation, and characterisation of the cyclic trimer, tetramer and pentamer. Journal of Materials Chemistry, 2000. 10(9): p. 2011-2016.
[3]: Misasi, J.M., et al., Polyaryletherketone (PAEK) thermoplastic composites via in-situ ring opening polymerisation. Composites Science and Technology, 2021. 201: p. 108534.

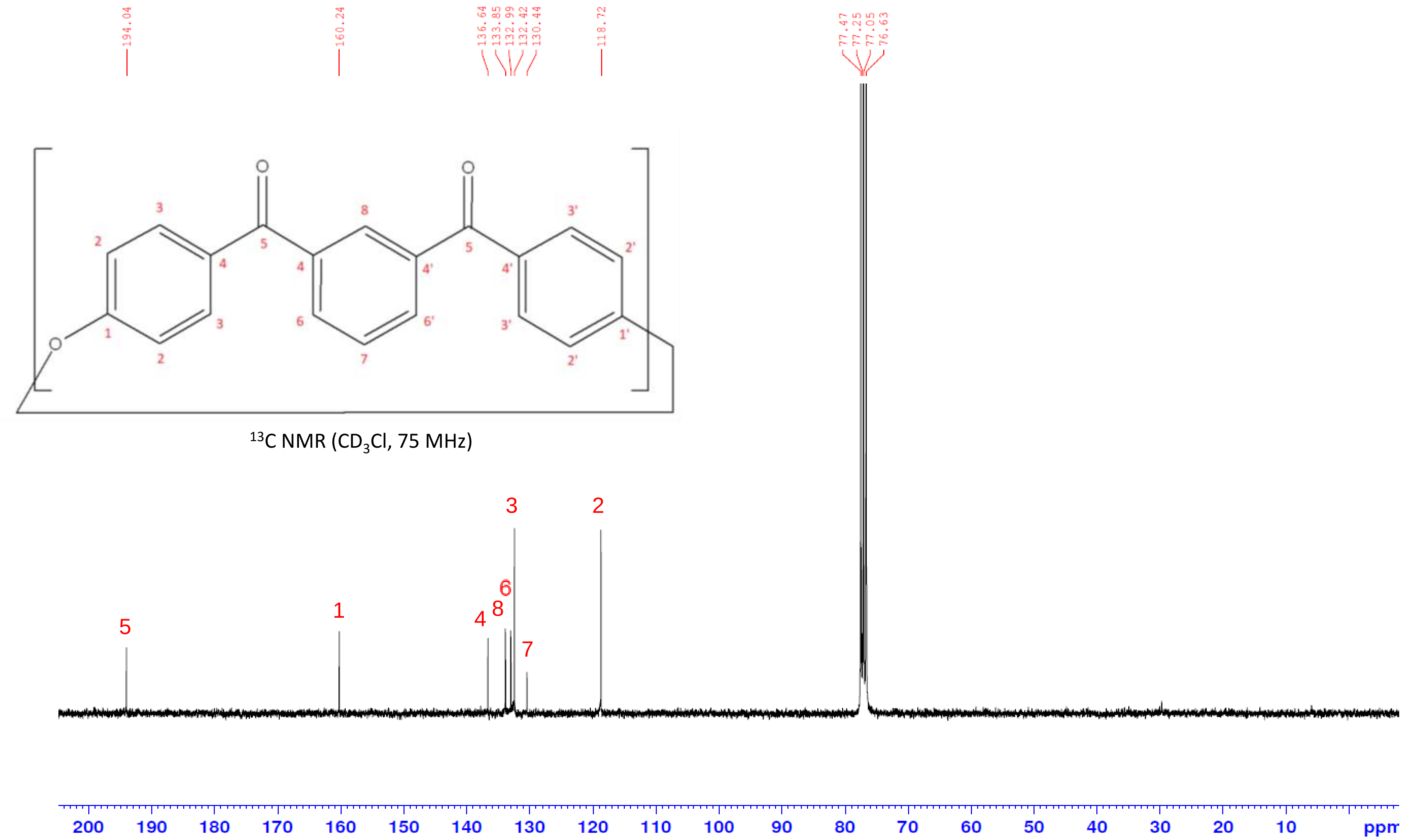
m-PEKK MCO synthesis



m-PEKK MCO characterisation: NMR

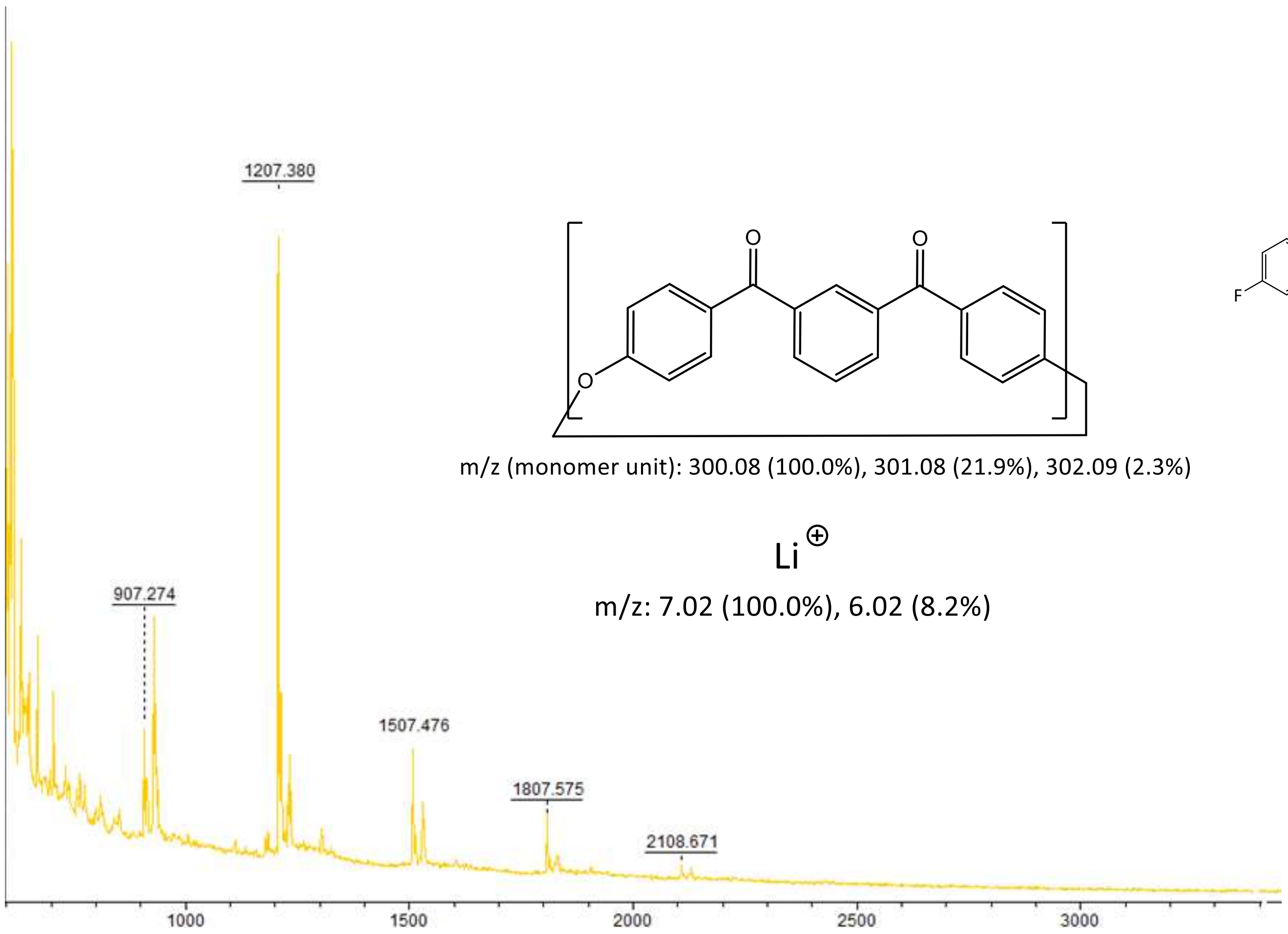


m-PEKK MCO characterisation: NMR



^{13}C NMR (CD_3Cl, 75 MHz)

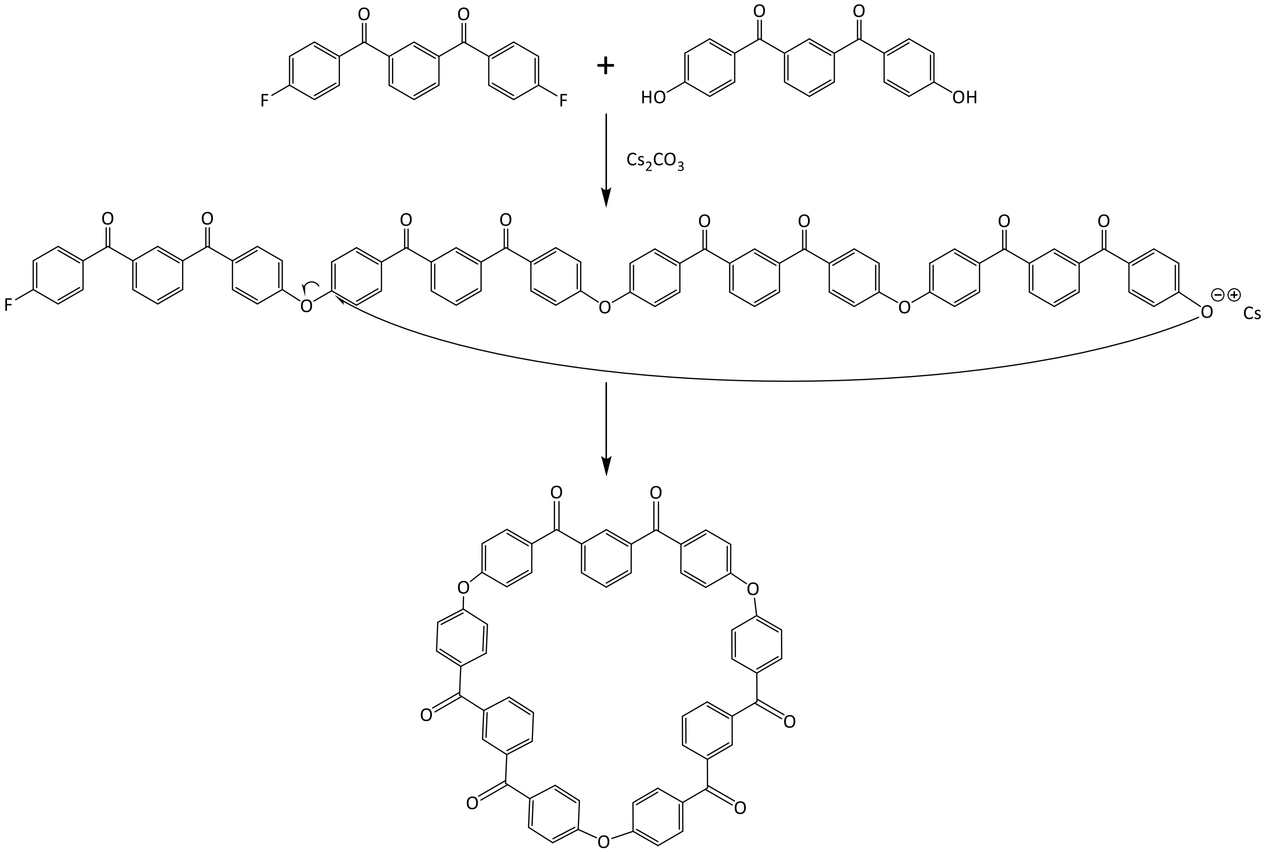
m-PEKK MCO characterisation: MALDI



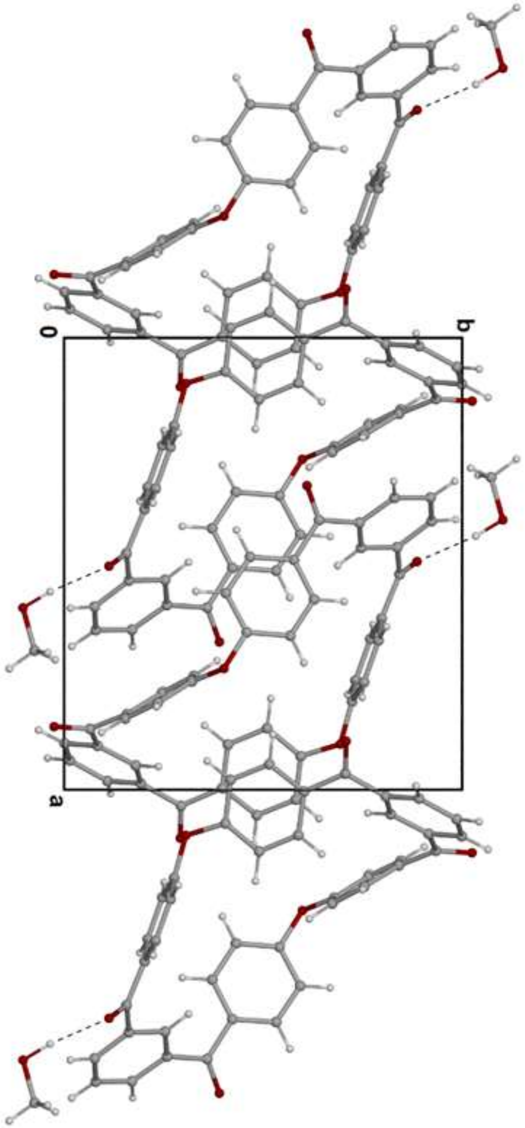
m/z (monomer unit): 300.08 (100.0%), 301.08 (21.9%), 302.09 (2.3%)

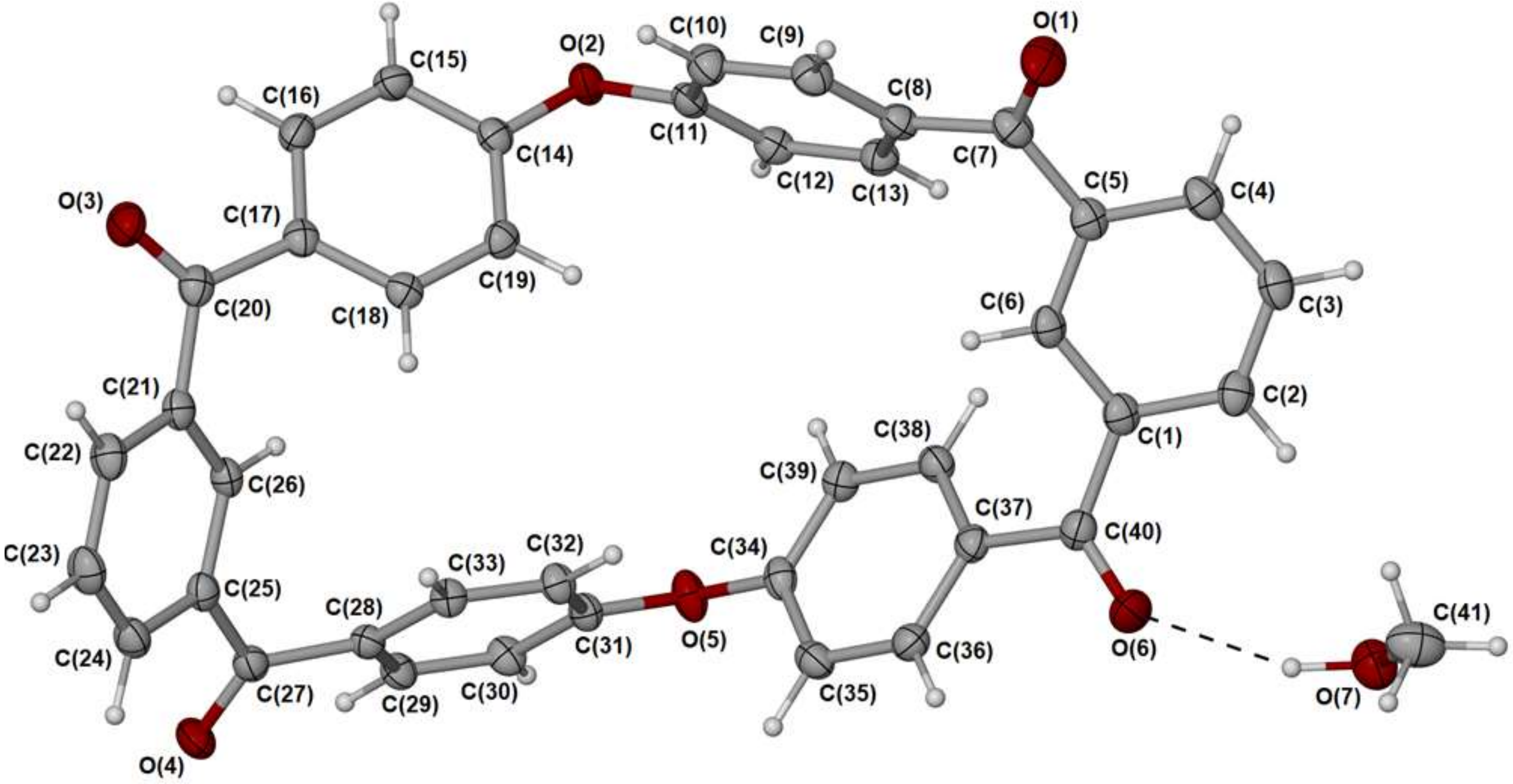
$Li^{\oplus}$

m/z: 7.02 (100.0%), 6.02 (8.2%)

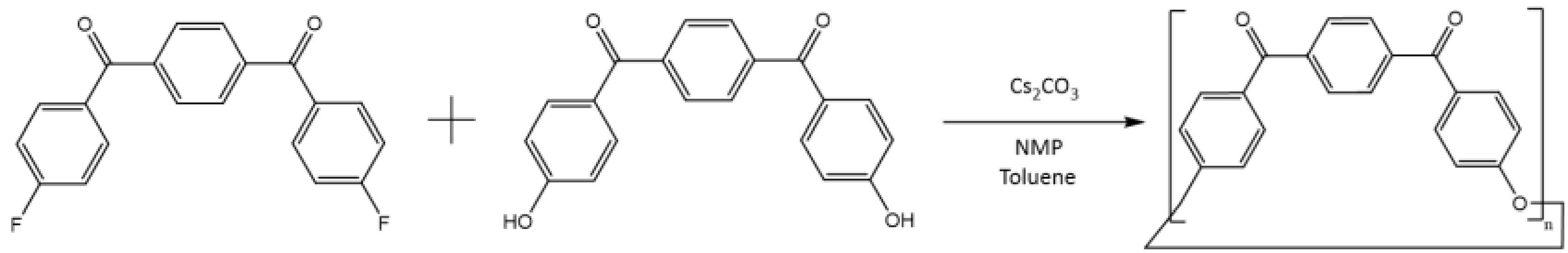


X-ray crystallography of m-PEKK dimer

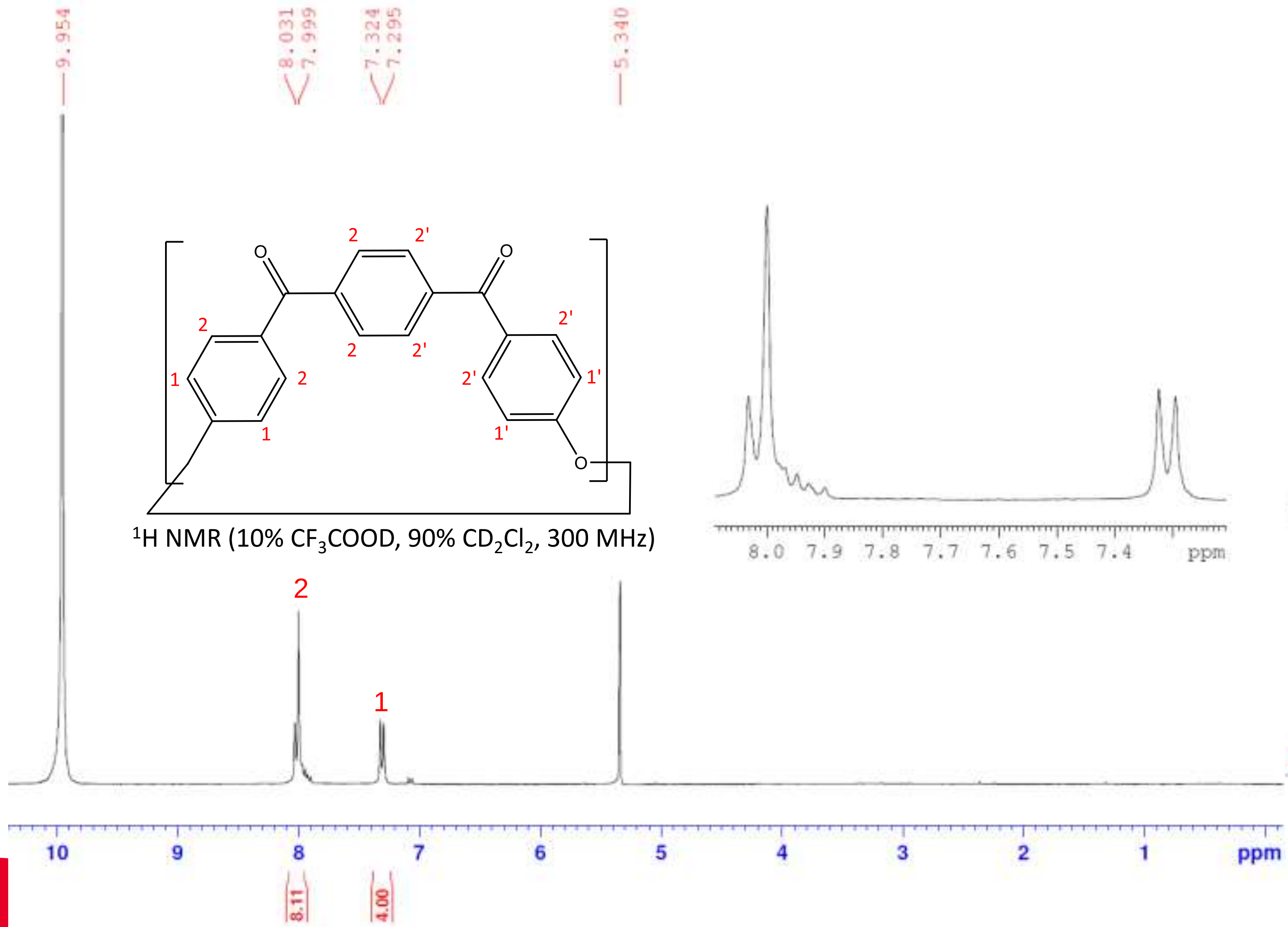




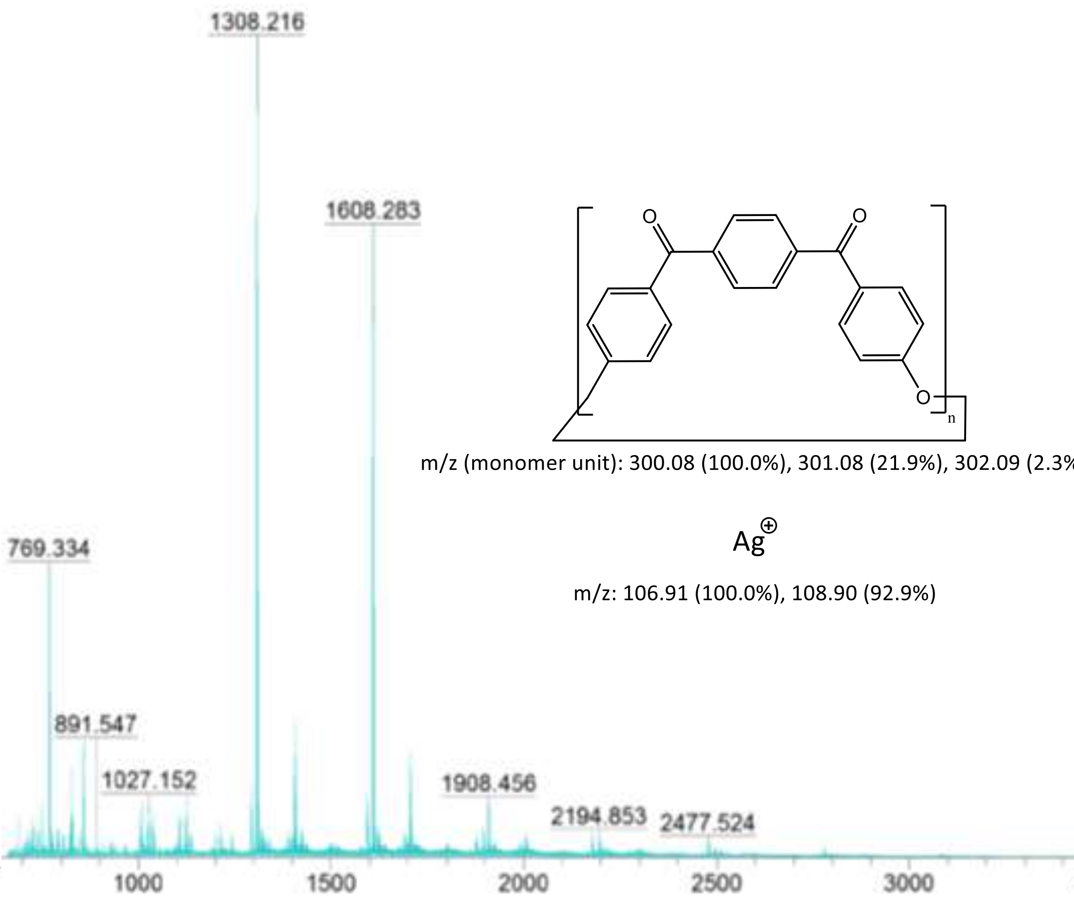
p-PEKK MCO



O
O
F
F
+
O
O
HO
OH
Cs_2CO_3
NMP
Toluene
O
O
O
n

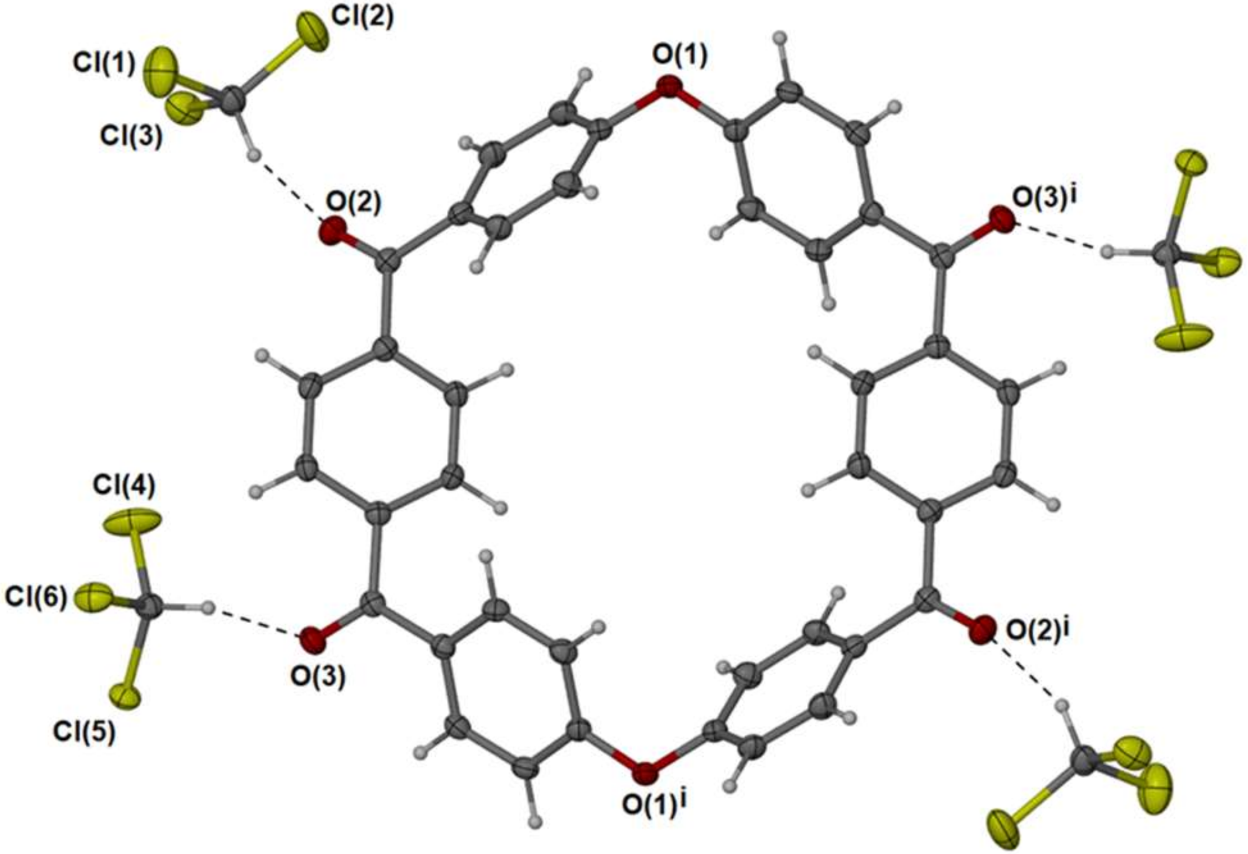


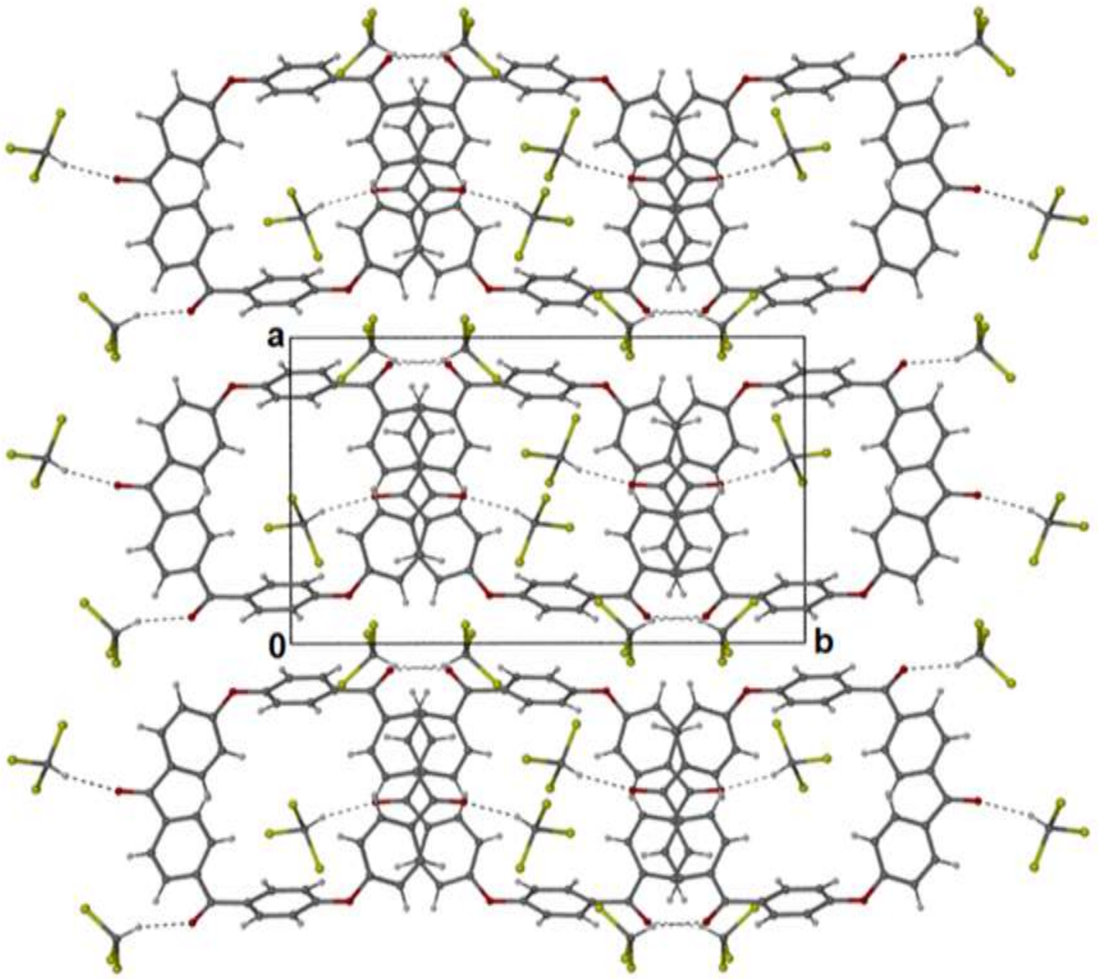
9.954
8.031
7.999
7.324
7.295
5.340
2
2'
O
O
2
2'
2
2'
1
2
2'
1'
1
1'
O
^1H NMR (10% CF_3COOD, 90% CD_2Cl_2, 300 MHz)
8.0 7.9 7.8 7.7 7.6 7.5 7.4 ppm
2
1
10 9 8 7 6 5 4 3 2 1 ppm
8.11
4.00



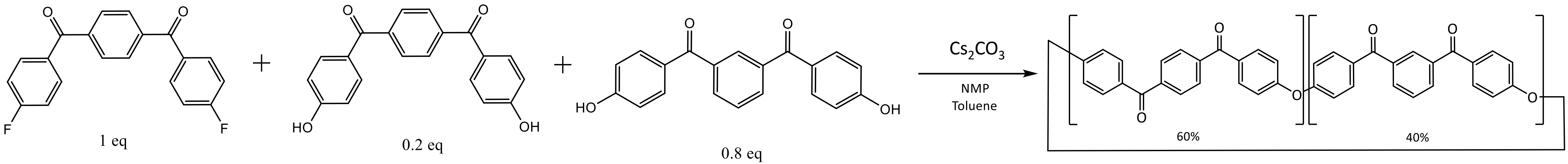
1308.216
1608.283
769.334
891.547
1027.152
1908.456
2194.853
2477.524
1000 1500 2000 2500 3000
O
O
O
n
m/z (monomer unit): 300.08 (100.0%), 301.08 (21.9%), 302.09 (2.3%
$Ag^{\oplus}$
m/z: 106.91 (100.0%), 108.90 (92.9%)

X-ray crystallography of p-PEKK dimer

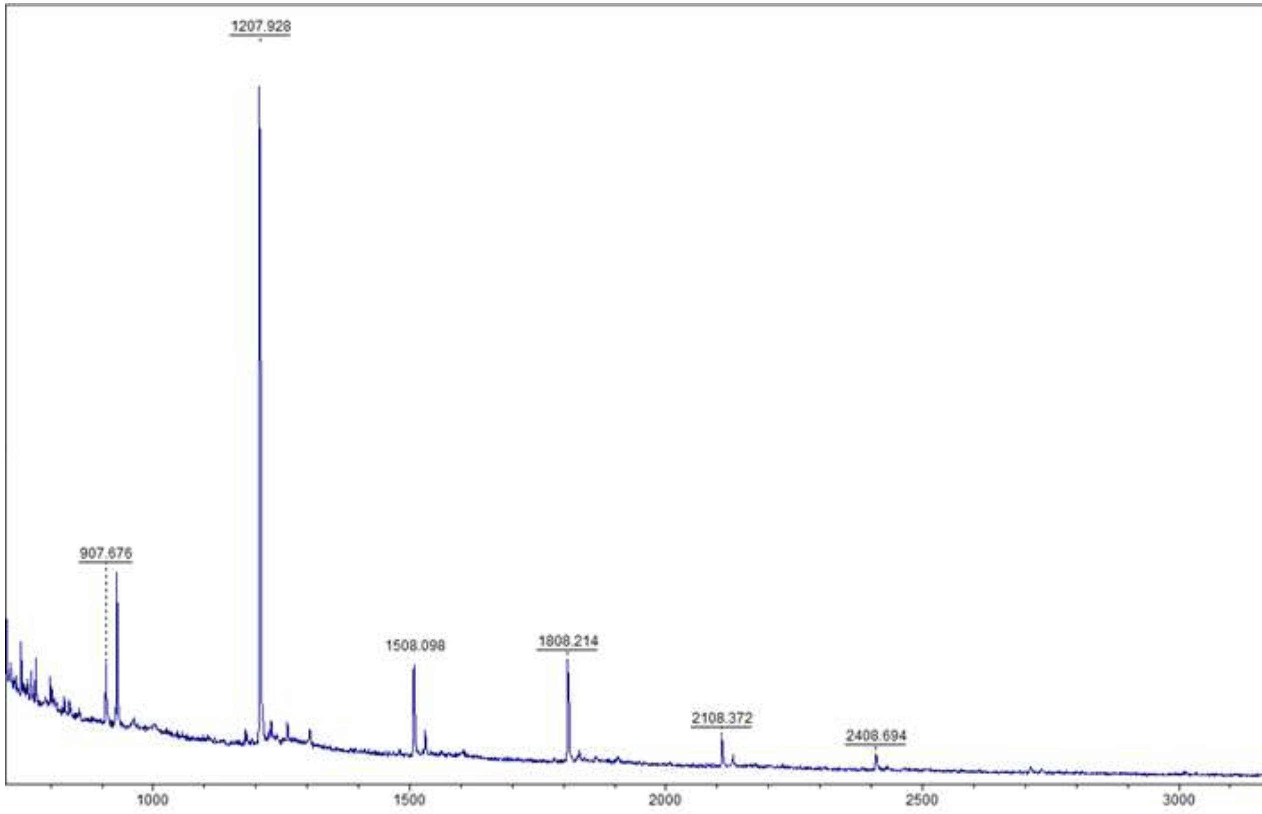




Synthesis of MCOs with T/I blends

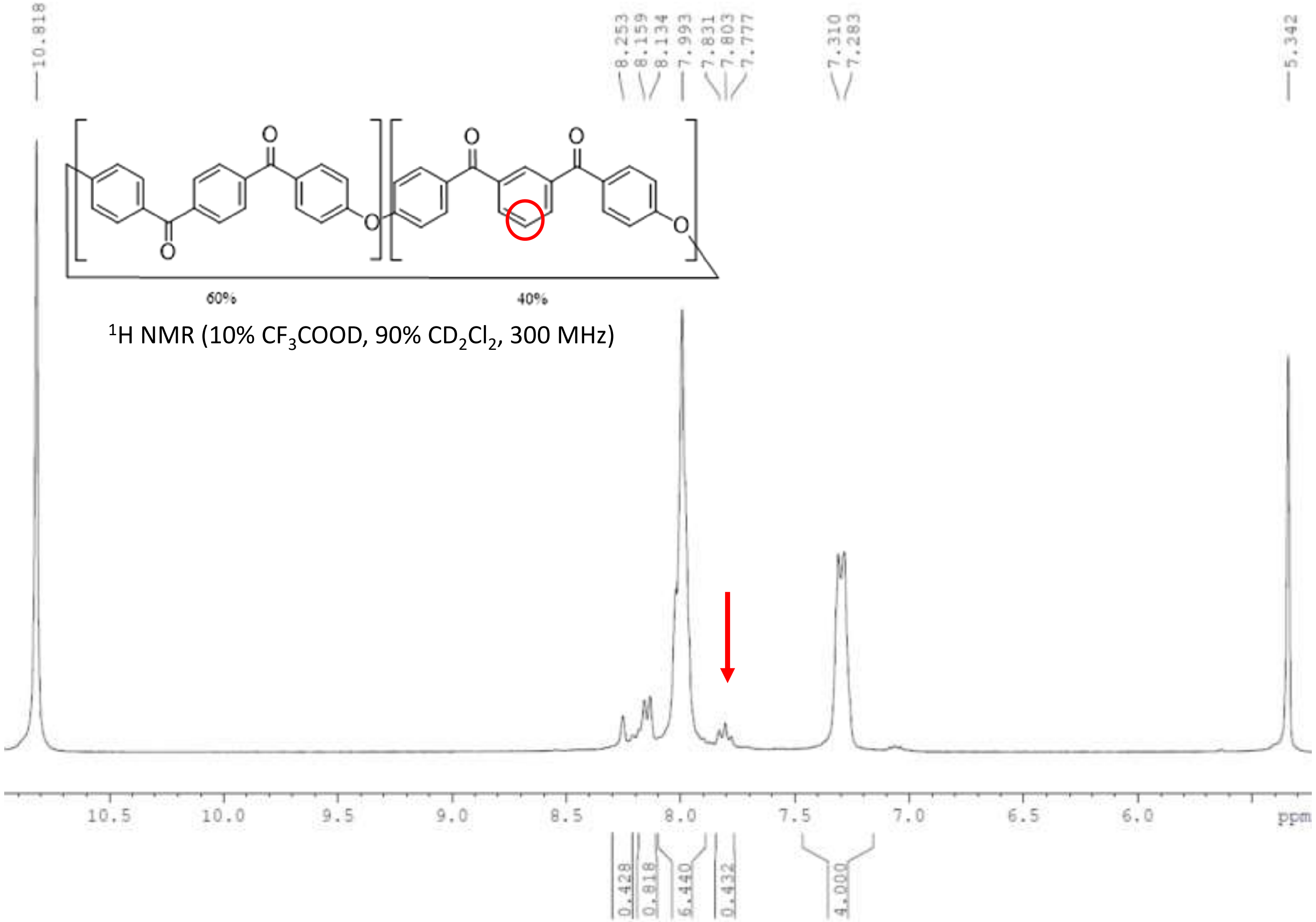


[1] [2]



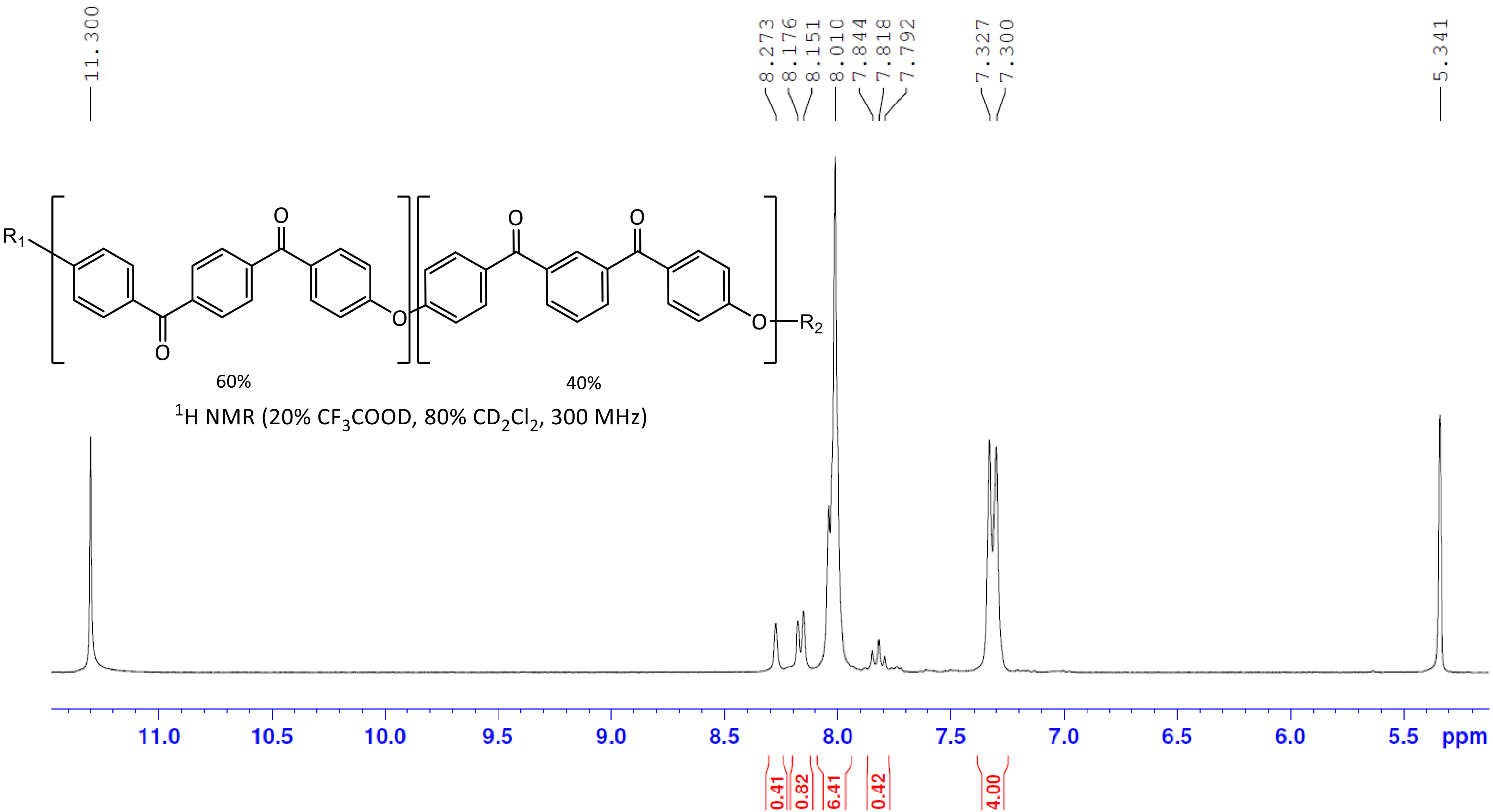
T/I blend	1,4-phenylenebis((4-fluorophenyl)methanone) [1]	1,3-phenylenebis((4-fluorophenyl)methanone) [2]
60/40	0.25 mmol	1 mmol
70/30	0.50 mmol	0.75 mmol
80/20	0.75 mmol	0.50 mmol

Determining T/I from NMR



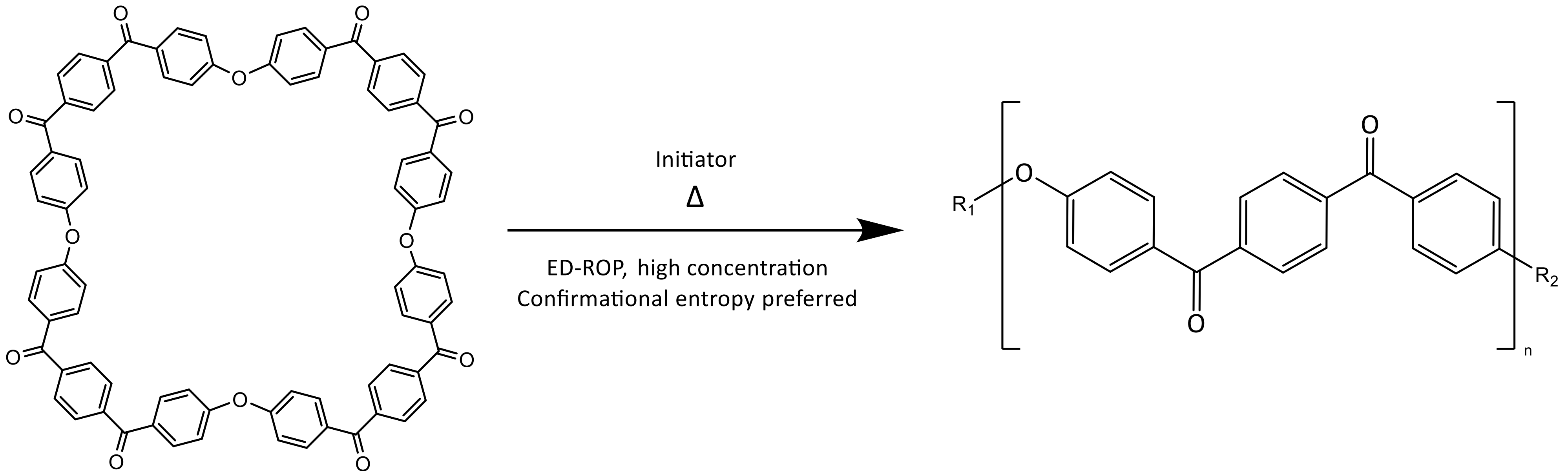
Desired T/I ratio of MCO	NMR determination of T/I ratio
60/40	57/43
70/30	67/33
80/20	85/15

A commercial comparison



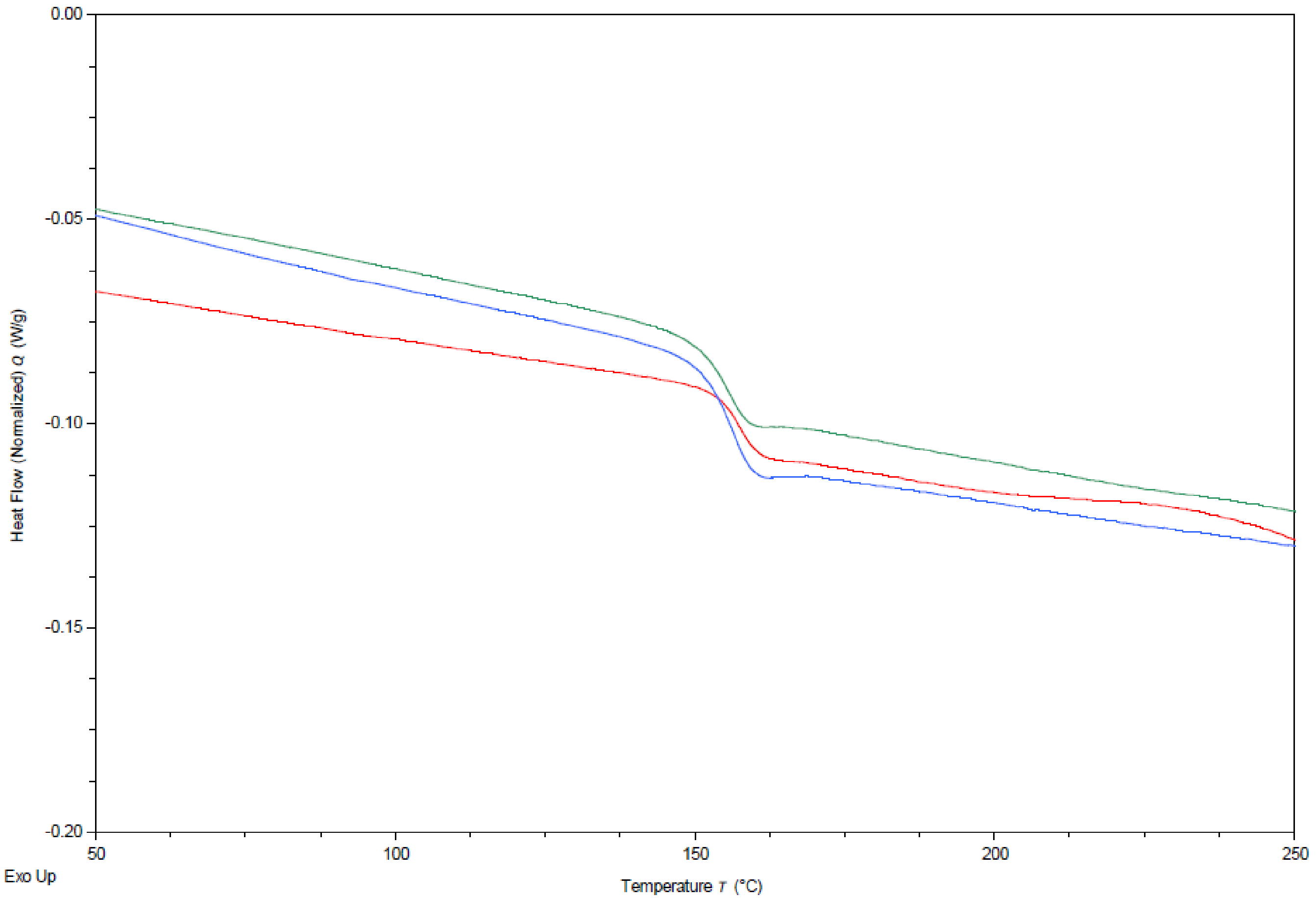
PEKK MCO polymerisation conditions

- No literature concerning PEKK MCOs, but some for the PAEK family
- Alkali and phenolate salts shown in literature to be good initiators, in particular CsF [4]
- Reaction occurs at ~150ºC in solvent, but higher temps required to melt MCOs/chains so they can participate
- Oxygen and moisture sensitive
- Potential interference from dimer, likely due to higher melting point



[4]: Teasley, M.F., D.Q. Wu, and R.L. Harlow, Synthesis, Characterization, and Ring-Opening Polymerization of the Cyclic Oligomers of Poly(Oxy-1,3-phenylenecarbonyl-1,4-phenylene). Macromolecules, 1998. 31(7): p. 2064-2074.

DSC – comparison

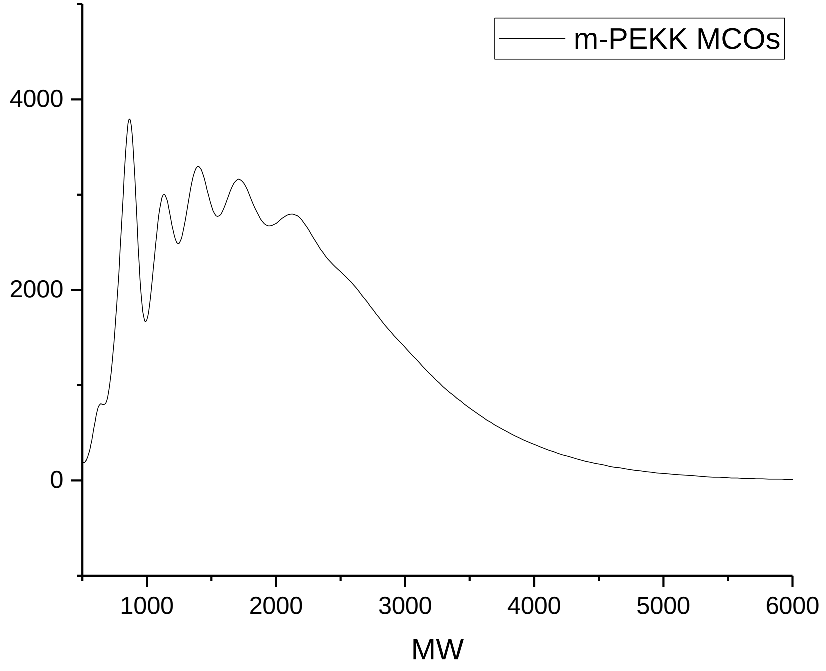


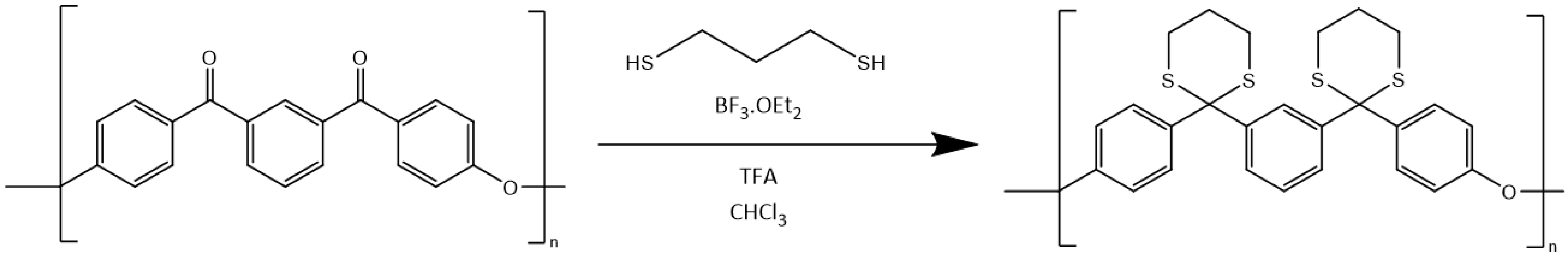
Commercial 60/40 T/I PEKK - blue
Polymerised 60/40 T/I MCOs - red
Polymerised m-PEKK MCOs - green

MCO Sample	T_g
m-PEKK	151°C
p-PEKK	172°C
60/40 PEKK	156°C
70/30 PEKK	154°C
80/20 PEKK	162°C

GPC and Derivatisation

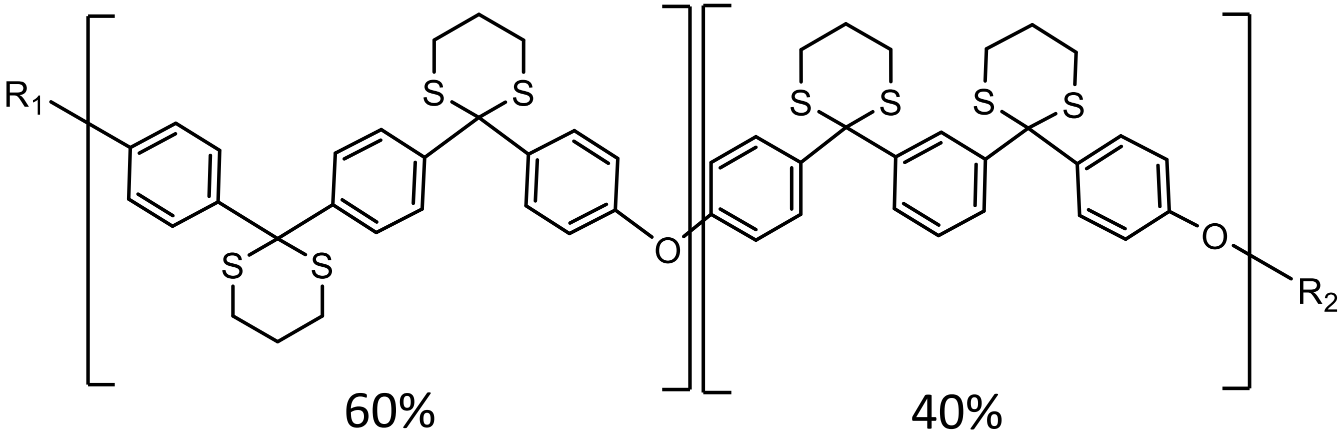
- MCOs are (somewhat) soluble in chloroform
- PEKK only soluble in exotic solvent systems
- Thioketal derivatisation strategy pursued to assess degree of polymerisation [5]

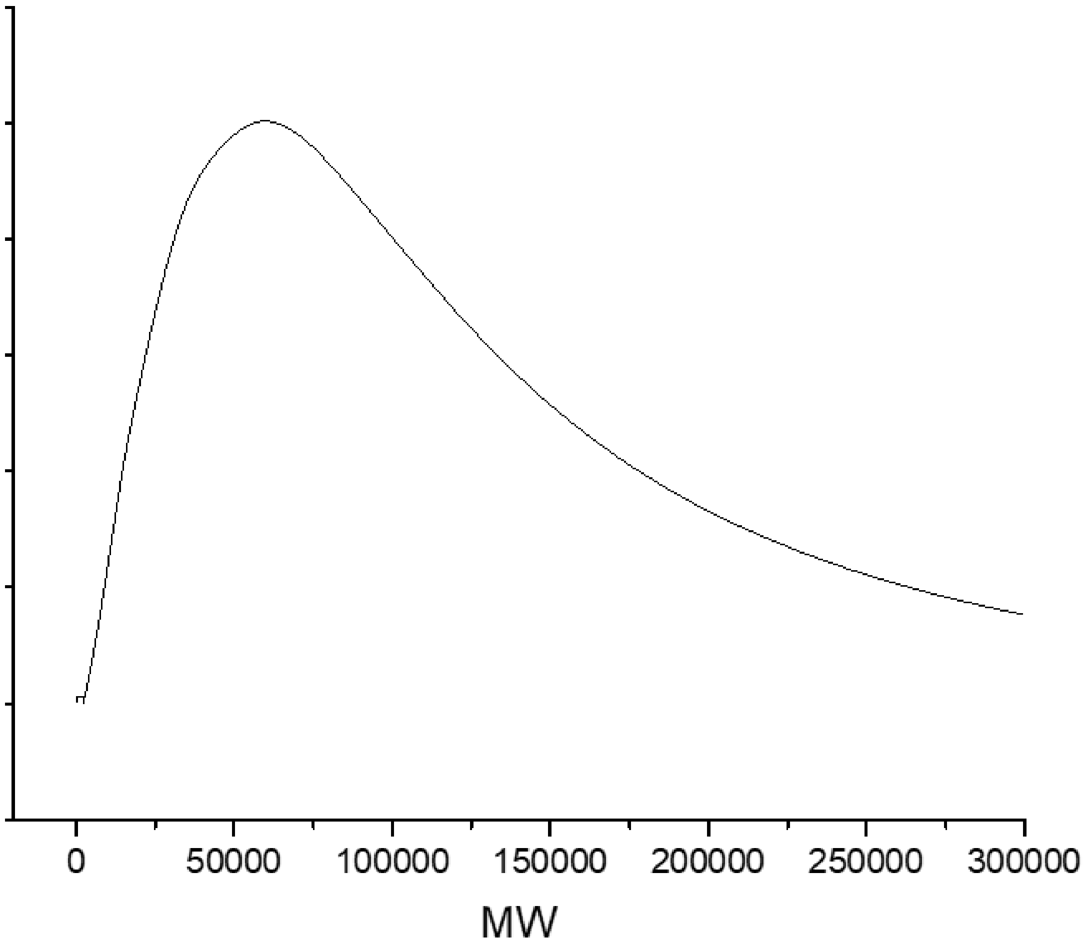




[5]: Colquhoun, H.M., et al., Reversible, Nondegradative Conversion of Crystalline Aromatic Poly(ether ketone)s into Organo-Soluble Poly(ether dithioketal)s. Macromolecules, 2009. 42(6): p. 1955-1963.

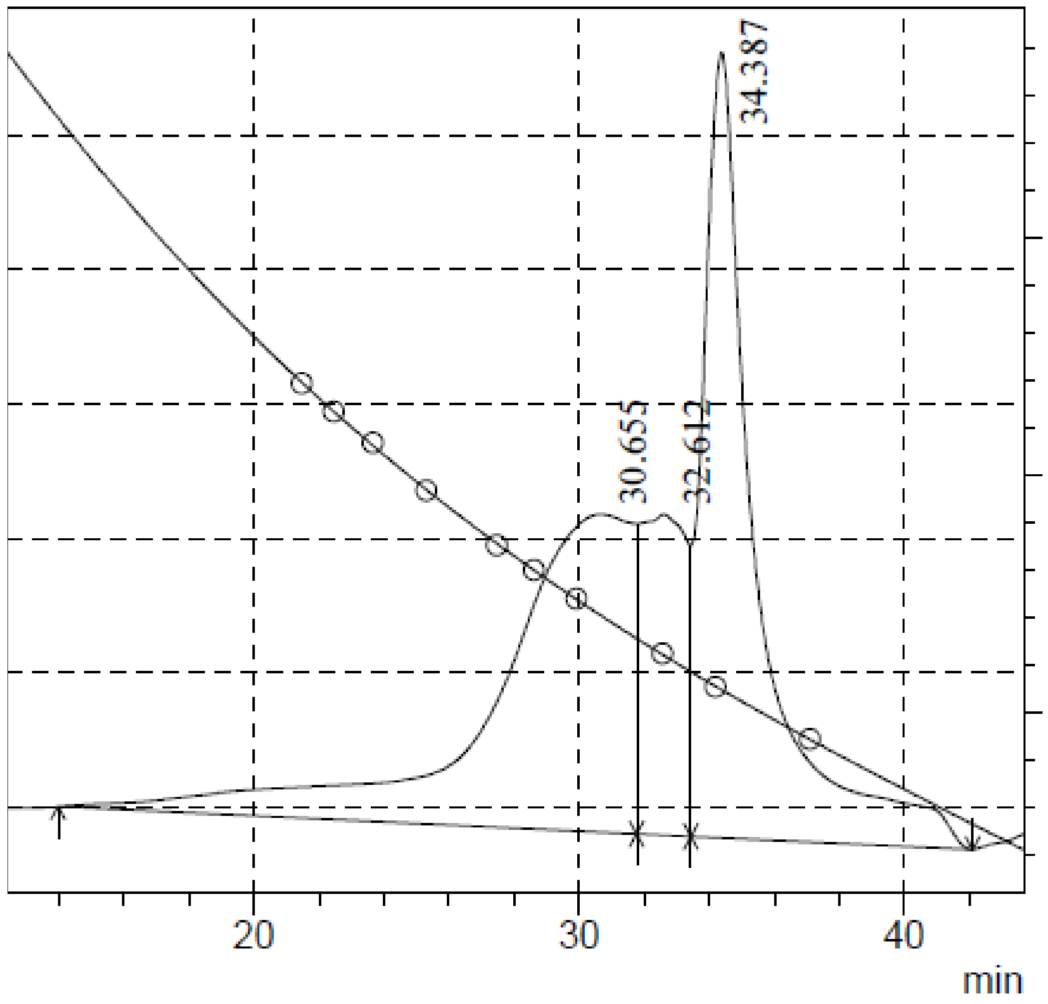
Derivatised commercial PEKK GPC





Initial polymerisation results

- Multiple small-scale polymerisation runs in DSC pans
- Varying temperature, polymerisation catalyst and amount, MCO type and time
- Some evidence of polymerisation, best results around 300-350°C
- No high MW polymers on any run



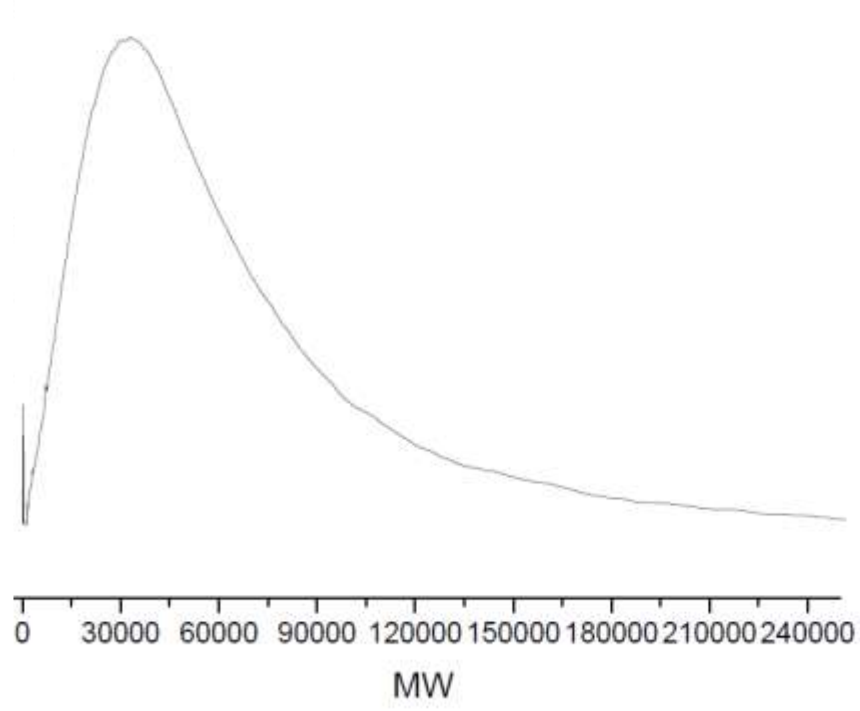
Dimer effect

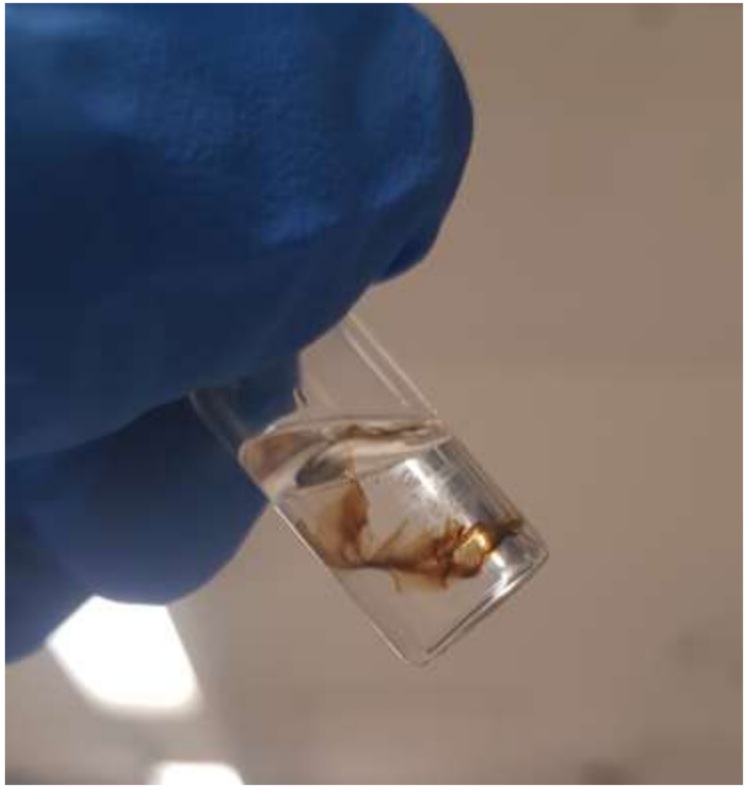
- Appears to impair polymerisation, despite ED-ROP mechanics
- Higher melting point than other MCOs
- Melting point close to degradation point

High vacuum polymerisation

- 0.15g of m-PEKK MCOs (dimer removed)
- Dissolved with 2mol% CsF, sonicated and solvent evaporated
- Dried at 120^{o}C under 10^{-5} mbar vacuum for 20 hours
- Heated to 350^{o}C under 10^{-5} mbar vacuum for 0.5 hours

GPC of high vacuum experiments





Polymer sample	Peak	M_n	M_w	Polydispersity
m-PEKK	20,467 g/mol	21,704 g/mol	38,411 g/mol	1.77
Arkema 6002	37,032 g/mol	18,785 g/mol	45,990 g/mol	2.45

Summary

- Pseudo-high dilution synthesis of MCOs of both m-PEKK and p-PEKK
- Characterisation by NMR, MALDI-ToF and X-ray crystallography
- Adaptation of method to produce PEKK MCOs with varying T/I ratios
- Investigation of polymerisation of MCOs within DSC
- Assessment of degree of polymerisation by GPC of thioketal derivative
- High MW polymer produced under high vacuum conditions
- Continuing work: Polymerisation of MCOs in the presence of carbon fibre

Acknowledgments

A heartfelt thank you to:

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- Dr. Jessirie Dilag
- ATLAS
- The RMIT chemistry and engineering technical staff
- Dr. Craig Forsyth and the Monash X-ray platform
- Mark Hickey and the CSIRO Manufacturing GPC facility

Thank you for your time

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