DTU, May 2019

Rheological and mechanical properties of polystyrene with hydrogen bonding and ionic bonding

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Outline

PS with sticky chain

- Objective
- Methodology
- Results – PS with hydrogen bonding
- Neutralised acid-functional polymers
- Outlook

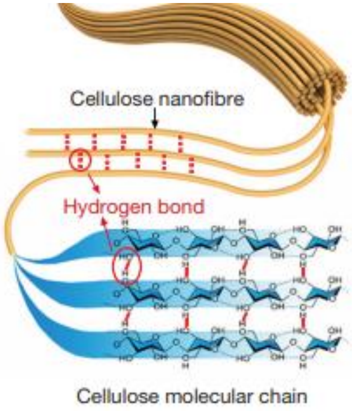
DSM sample

- Sample description
- DSC result
- Experiment feasibility (literature)
- Outlook

Objective

- Current work:

  Rheological and mechanical properties of polystyrene with hydrogen bonding



Flexible polystyrene

Cracks of recovered sample after bending

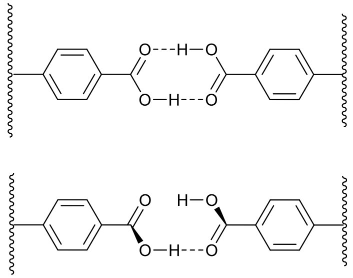
J. Song et al., *Nature*, 2018, vol 554, 224

Methodology

Material:

Three PS based sample

Sample	Mn(g/mol)	Mw(g/mol)	Đ	Tg (ºC)
PS pure	86 k	142 k	1.65	100
PS 5% acid	92 k	122 k	1.33	114
PS 9% acid	94 k	116 k	1.23	122

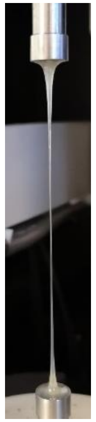


Characterizations:

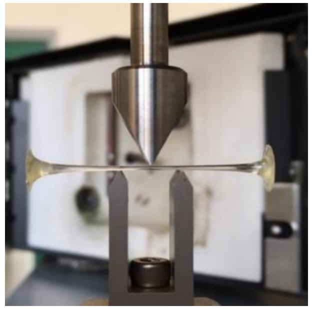
Linear viscoelastic properties

Nonlinear extensional properties

Tensile test

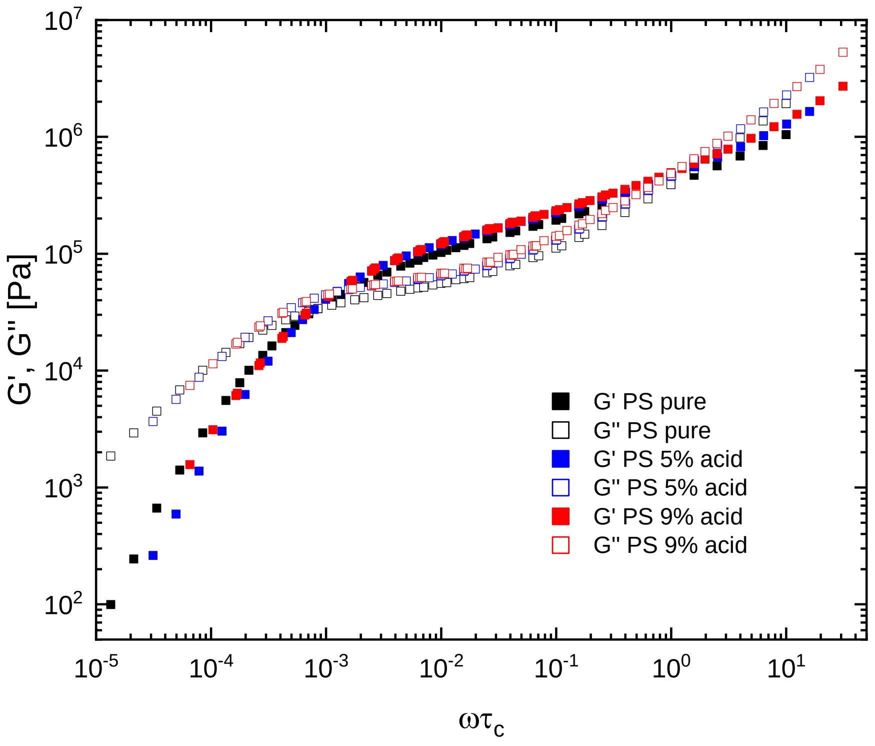


Three-point bending test



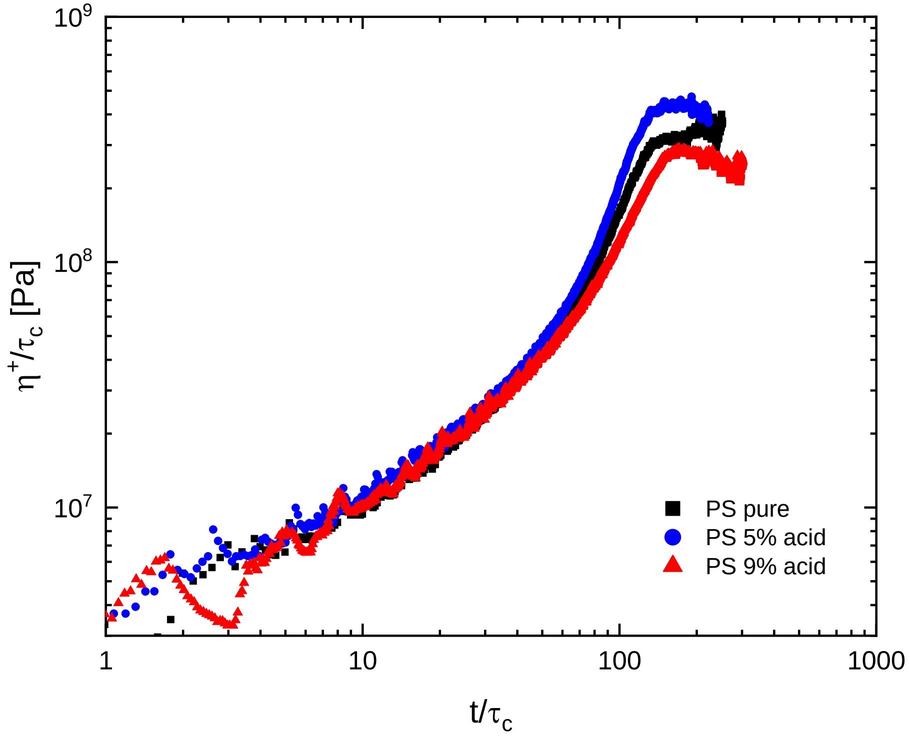
Results

- Small Amplitude Oscillatory Shear (SAOS)



LVE data with normalized frequency at 150°C

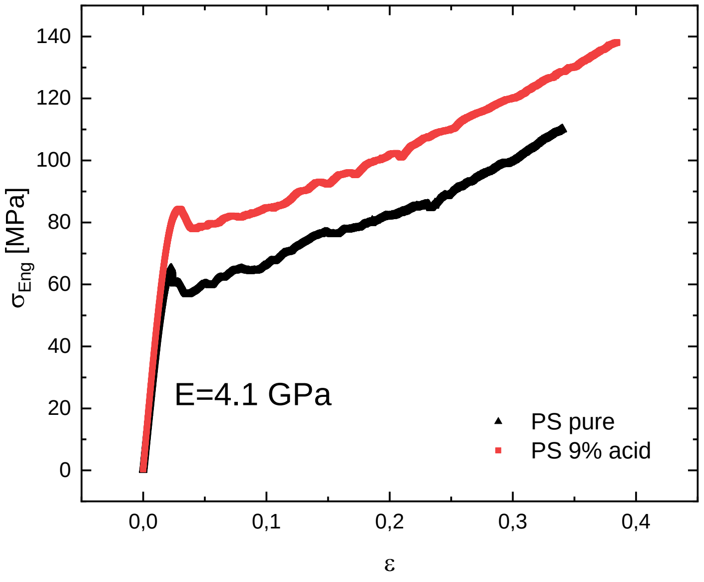
- Filament stretching at constant rate



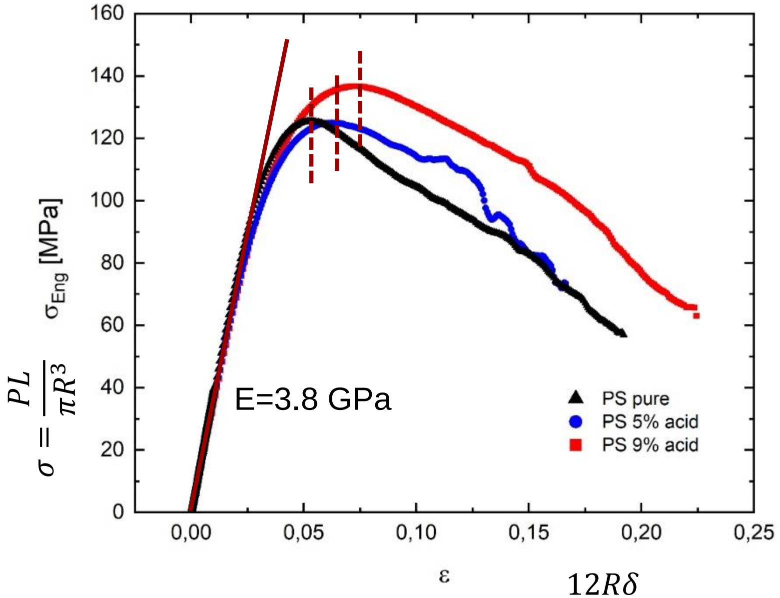
Comparison of normalized extensional stress growth coefficient for three samples

Results

- Tensile test
- Three-point bending test

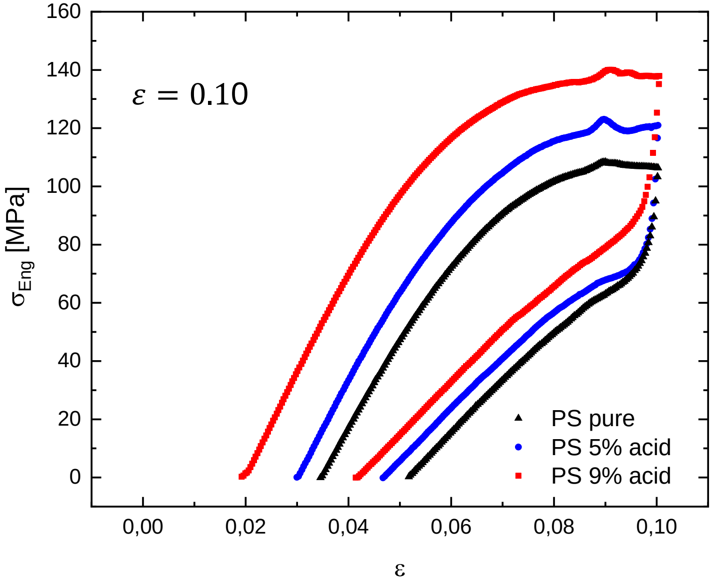


Engineering stress as a function of strain in tensile tests at room temperature, with a strain rate 0.001 s^{-1}



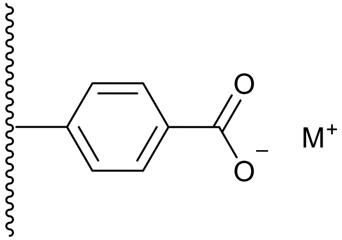
$$\epsilon = \frac{12R\delta}{L^2}$$

3-point bending test on different samples at room temperature: Sample is stretched to ε=3.5 at melt state followed by fast quenching to RT.



Step strain measurements for samples with different acid group contents

Neutralised acid-functional polymers



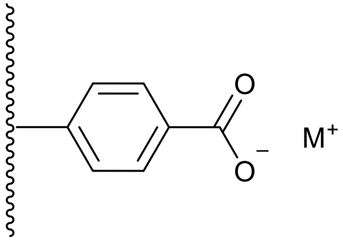
'M' = Na^+, Zn^{2+}, $(CH_3CH_2)_3NH^+$

T_g (°C)	H	Na^+	Zn^{2+}	$(CH_3CH_2)_3NH^+$
PS 5% acid	114	96	89	92
PS 9% acid	124	113	92	107

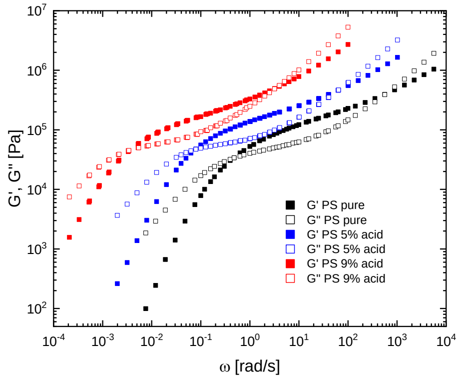
- Hard (small) ions (Na^+) leads to brittle films – strong localised binds
- Soft (larger) ions ($(CH_3CH_2)_3NH^+$) – more fluid-like behaviour

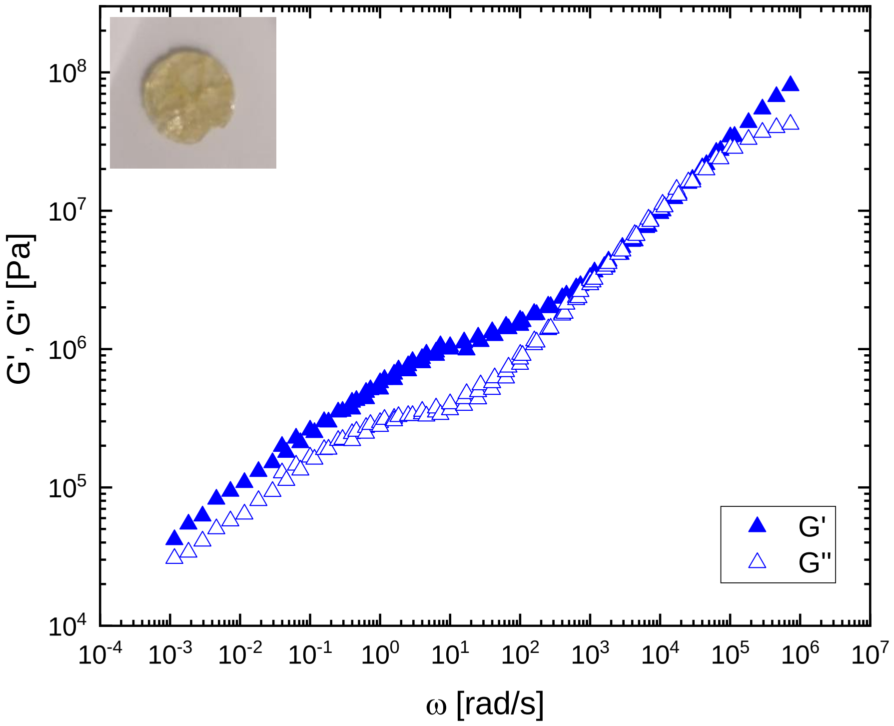
Protocol (poly(ethylene methacrylic acid)): *Macromolecules* 1996, 29, 598-604

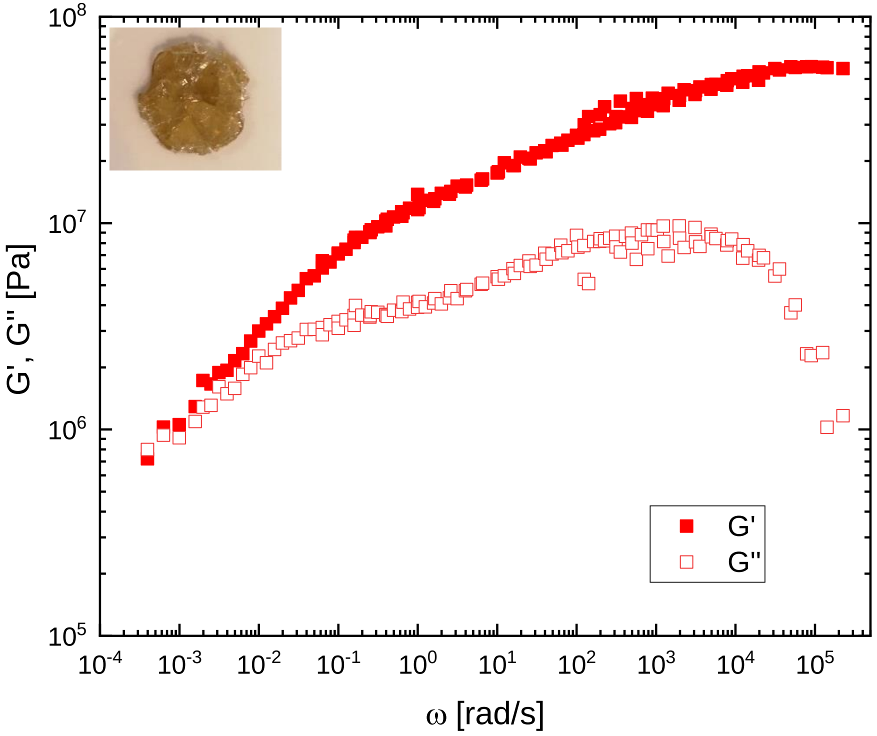
LVE – neutralised with Zn^{2+}



'M' $=Zn^{2+}$



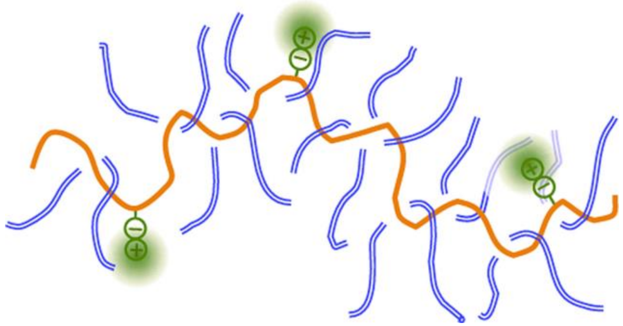




Neutralised from PS 5% acid, LVE built up at 150ºC

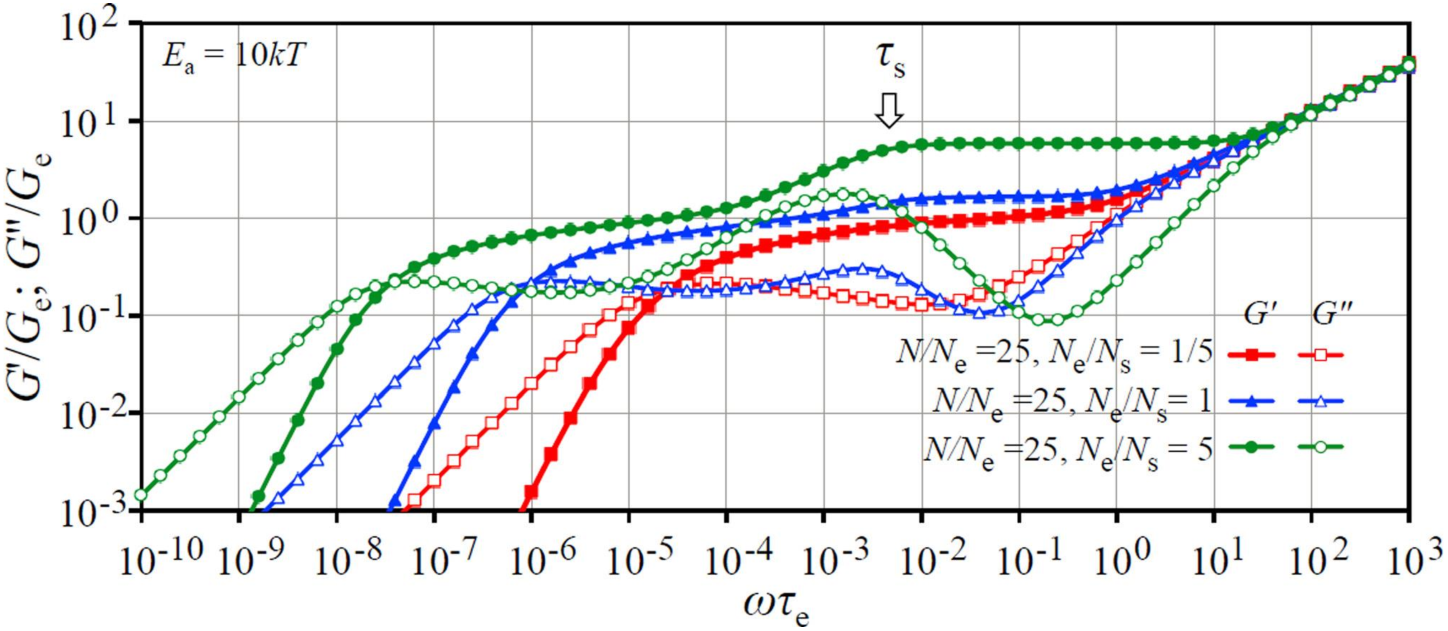
Neutralised from PS 9% acid, LVE built up at 150ºC

LVE – PS ionomer



average number of segments per ionic group N_s

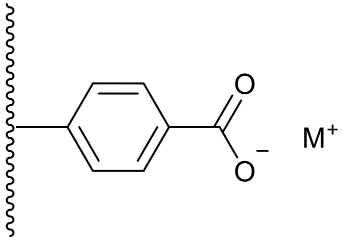
number of segments per entanglement N_e



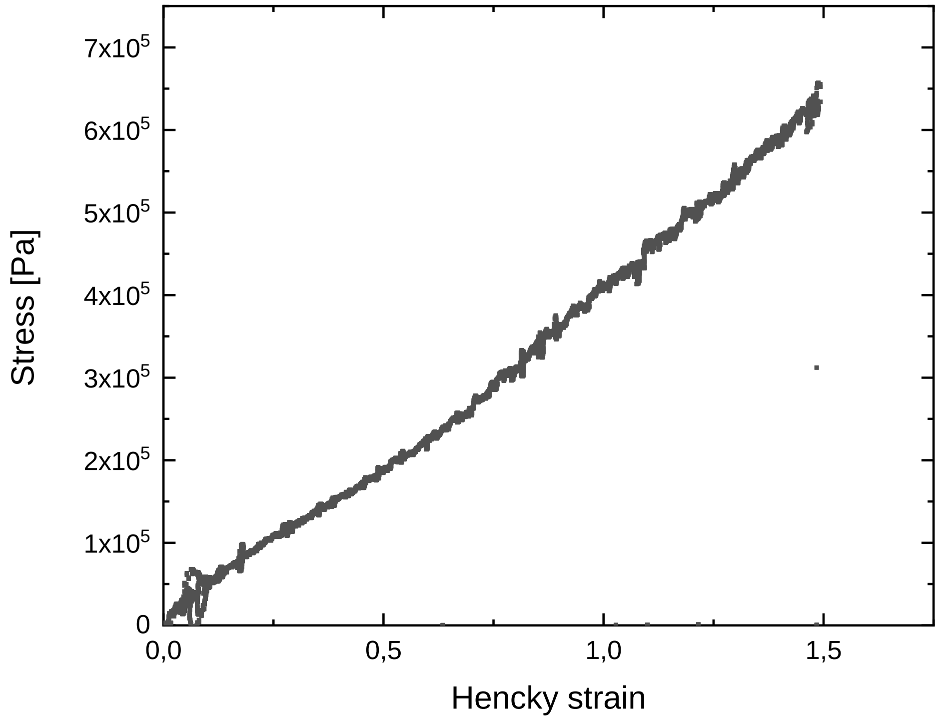
Sticky double reptation predictions for storage (filled symbols) and loss (unfilled symbols) moduli of three ionomers

Q.Chen, et al, *J. Rheol.* 60(6), 1031-1040

Extensional rheology – neutralised with Zn^{2+}

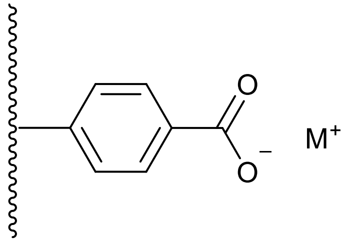


‘M’ =Zn^{2+}

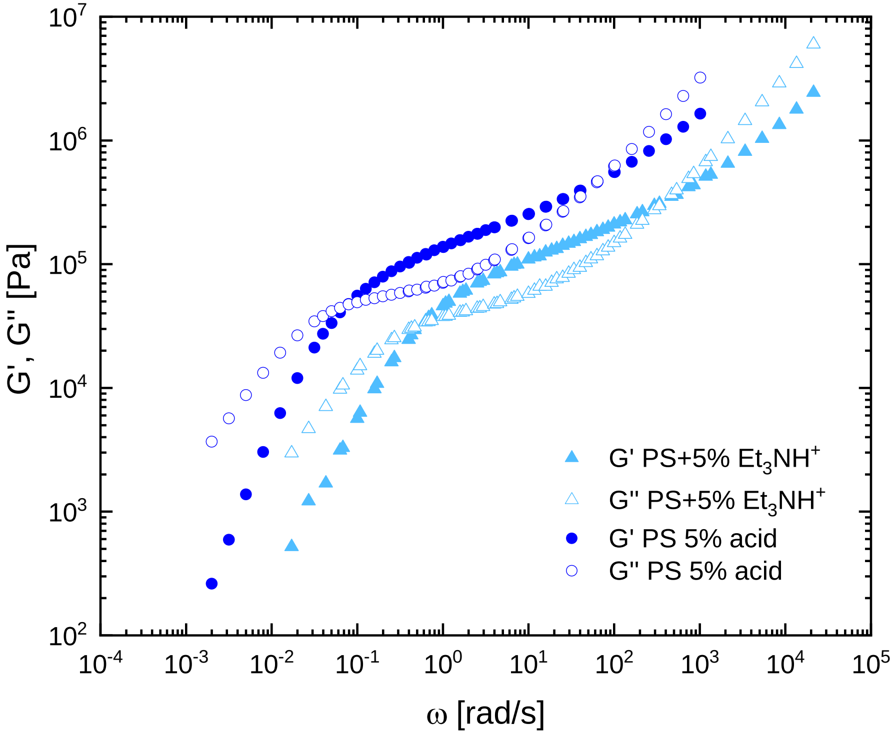


True stress as function of hencky strain for sample neutralised from PS 5% acid at 170^{o}C, 0.004 s^{-1}

LVE – neutralised with $(CH_3CH_2)_3NH^+$

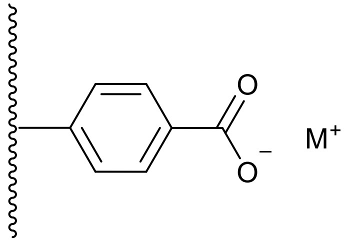


'M' = $(CH_3CH_2)_3NH^+$

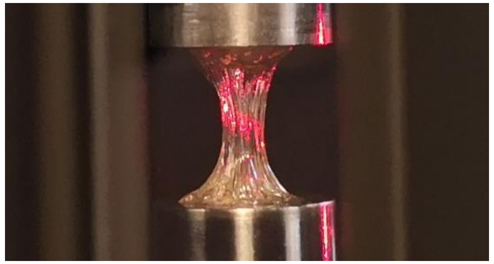


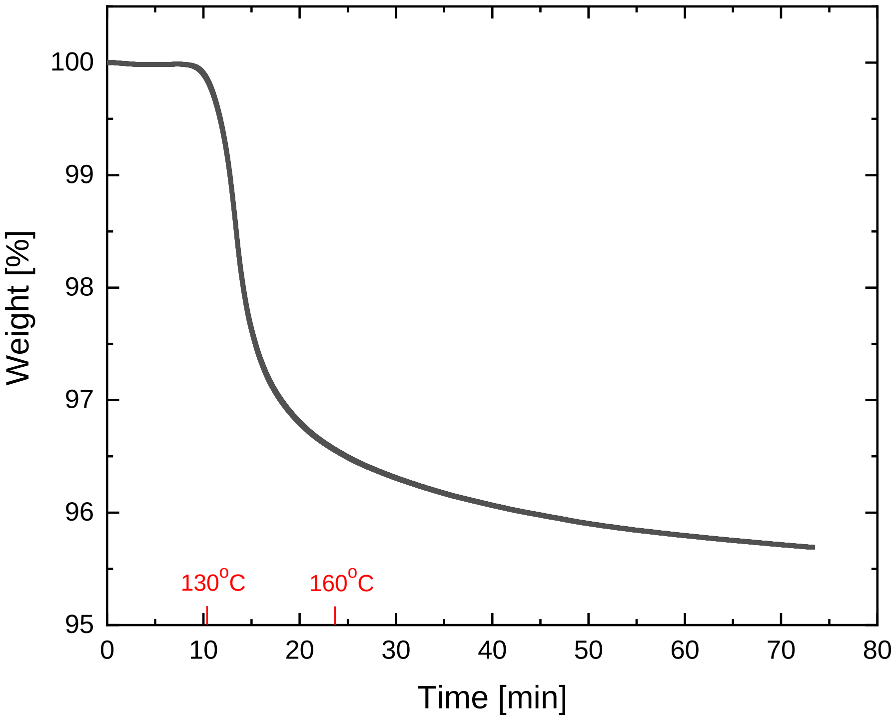
LVE data comparison of PS with 5% acid and neutralized with $(CH_3CH_2)_3NH^+$ at 150^oC

Sample problem – neutralised with $(CH_3CH_2)_3NH^+$



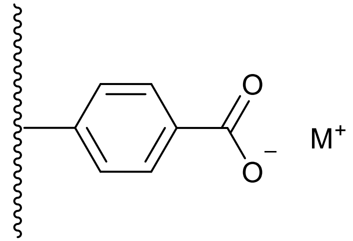
'M' = $(CH_3CH_2)_3NH^+$





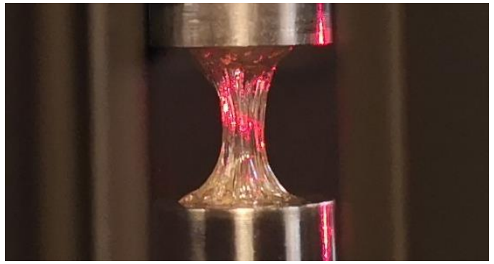
TGA measurement: Ramp 10.00 °C/min to 160.00 °C; Isothermal 60.00 min

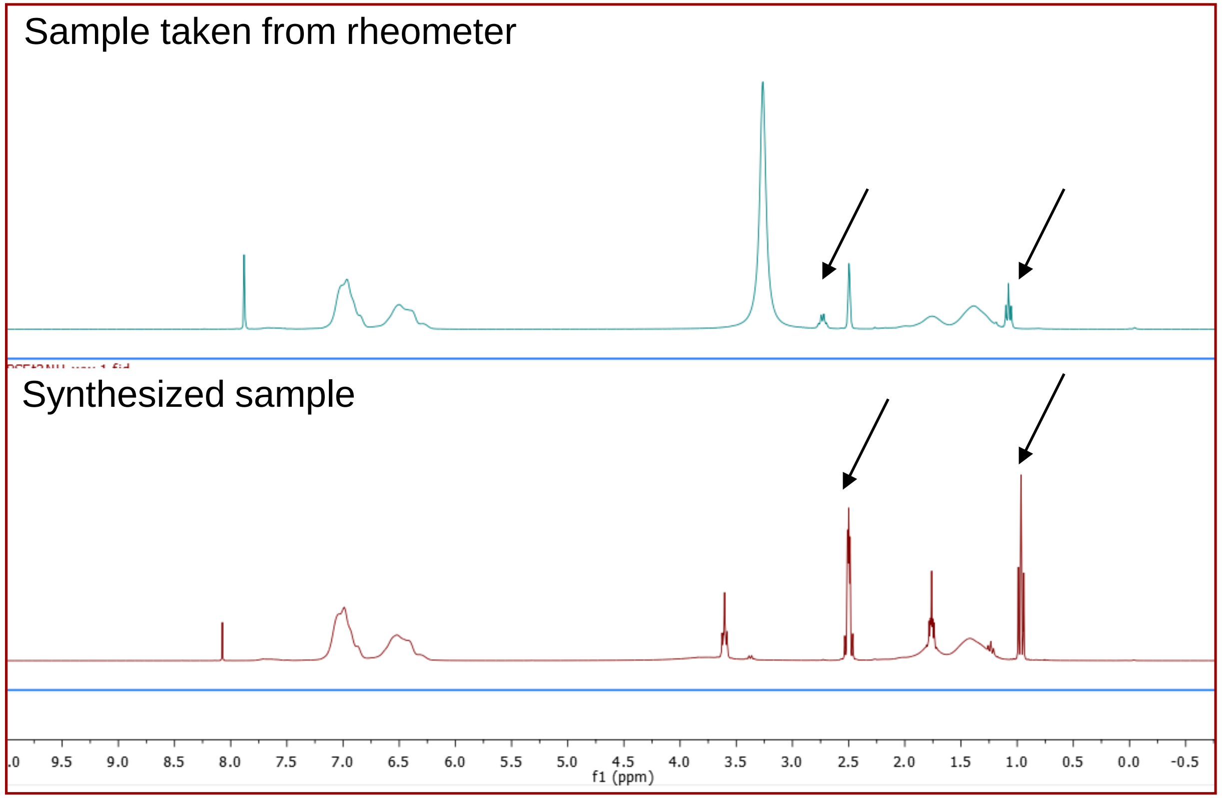
Sample problem – neutralised with $(CH_3CH_2)_3NH^+$



‘M’ = $(CH_3CH_2)_3NH^+$

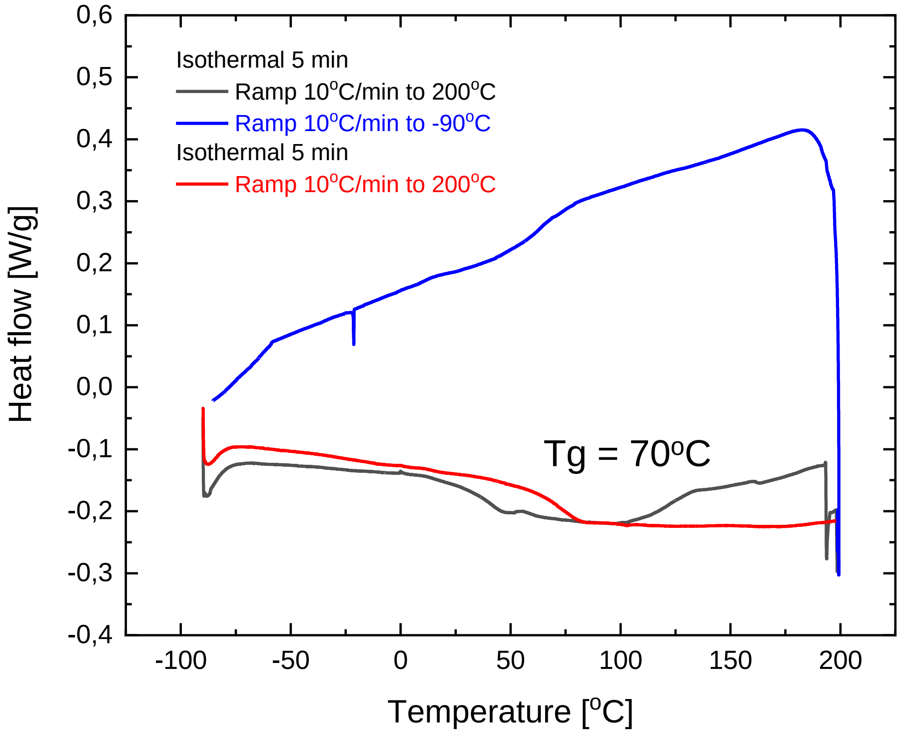
$PVBA^- \ Et_3NH^+$ <-> PVBA-H + Et_3N



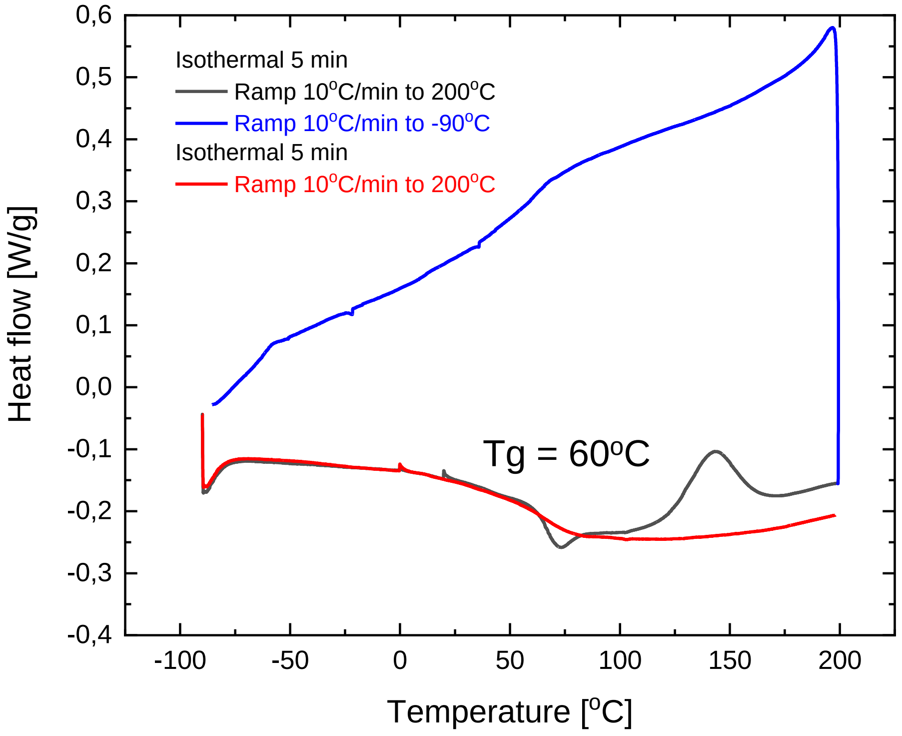


Outlook

- PS with Jeffamine for neutralization (lower Tg, more friendly processing temperature)



Neurtralised with PS 5% acid



Neurtralised with PS 9% acid

Outline

PS sticky chain

- Objective
- Methodology
- Results – PS with hydrogen bonding
- Neutralised acid-functional polymers
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DSM sample

- Sample description
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DSM sample

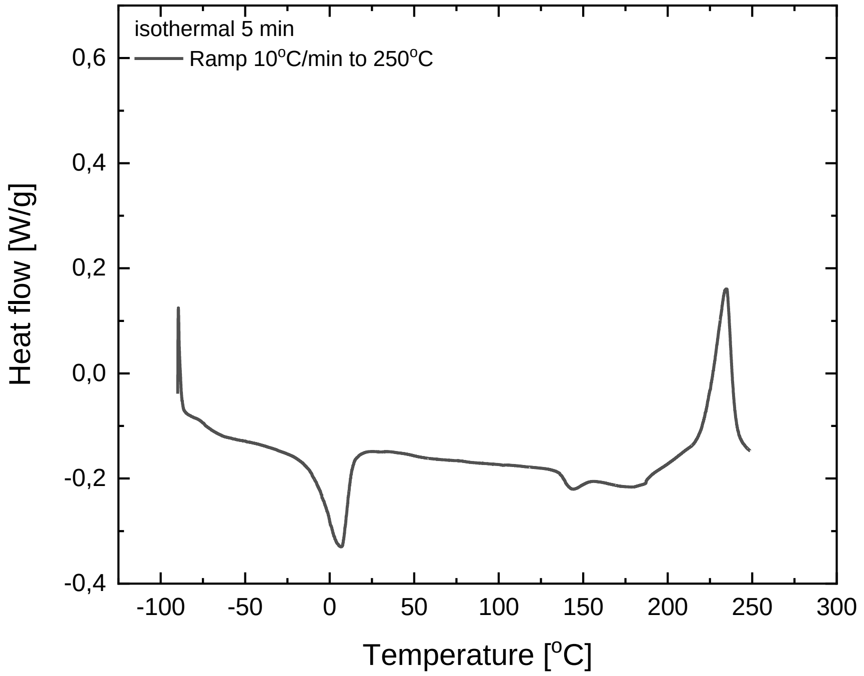
	Soft segment Mn	Wt% PTMO	HB	avg PBT segment Ln	Polymer Mn (kg/mol)
70_PTMO2k_51	PTMO2k	70	PBT	4.3	51
70_PTMO2k_33	PTMO2k	70	PBT	4.3	33

Flow induced crystallization (between Tc and Tm)
Or
Align polymer chains above Tm

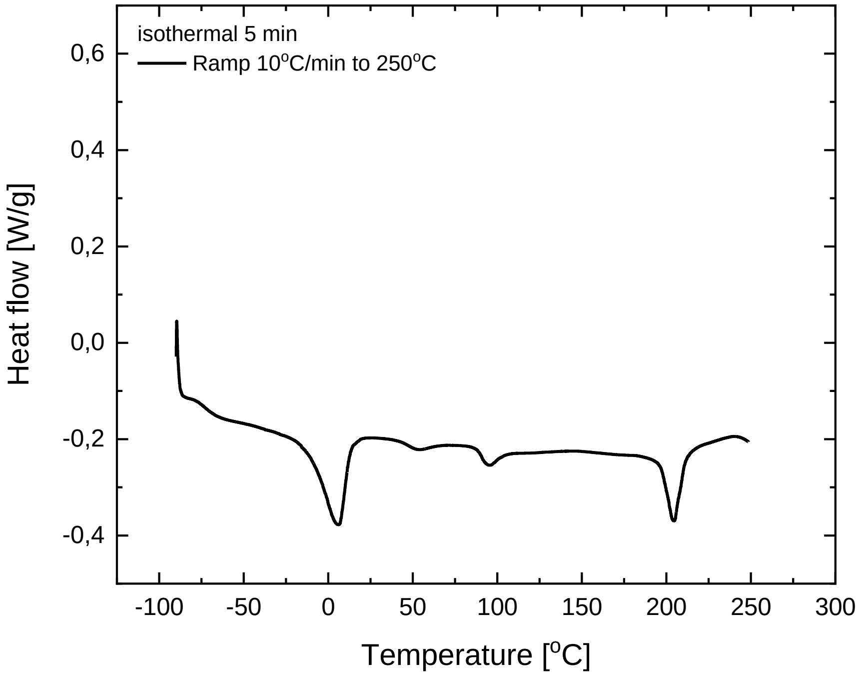
Quench and test mechanical properties

DSC

1. Heat up to 250ºC to eliminate thermal history (black curve)



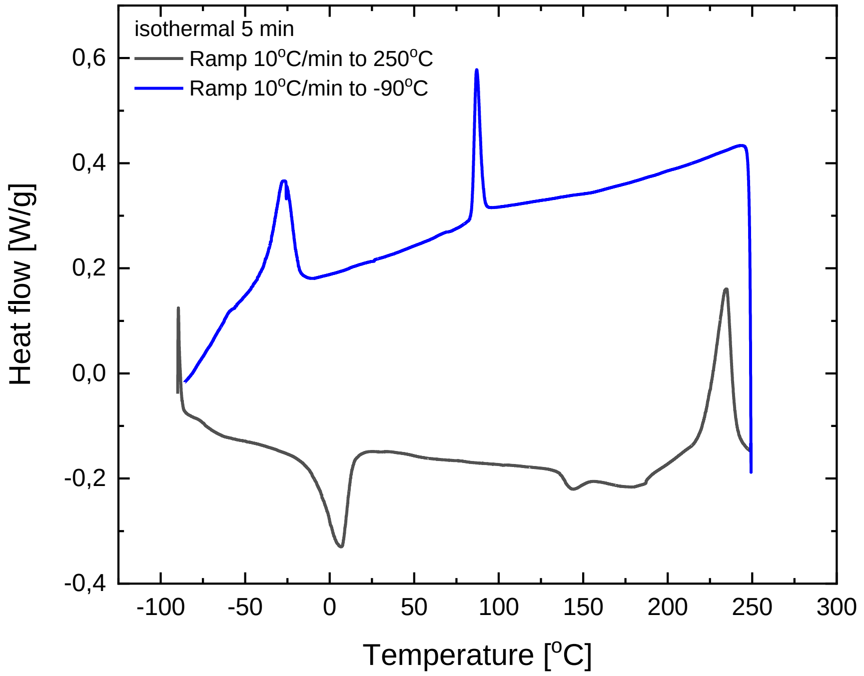
70_PTMO2k_33



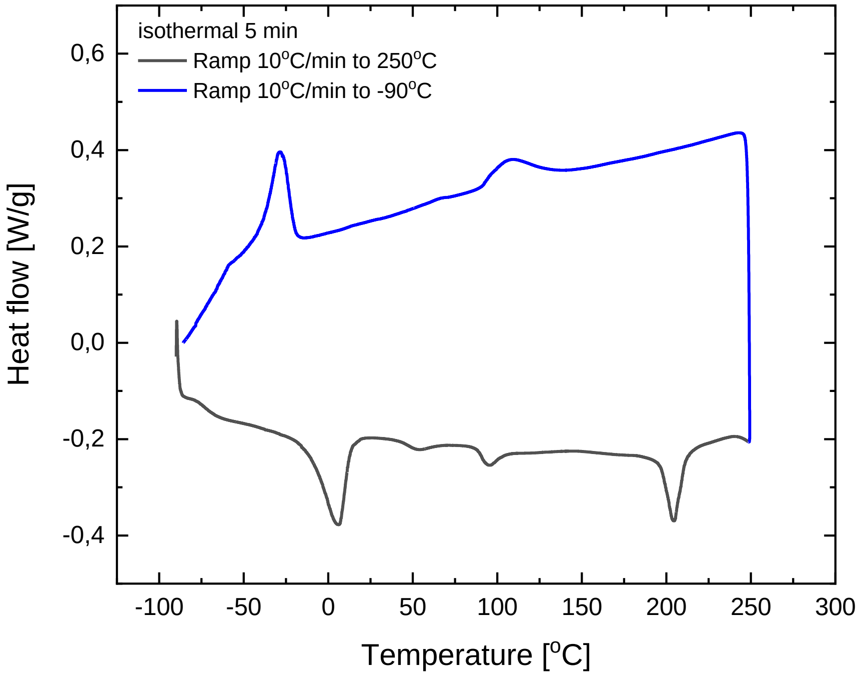
70_PTMO2k_51

DSC

1. Heat up to 250^{o}C to eliminate thermal history (black curve)
2. Cool down to -90^{o}C (blue curve)



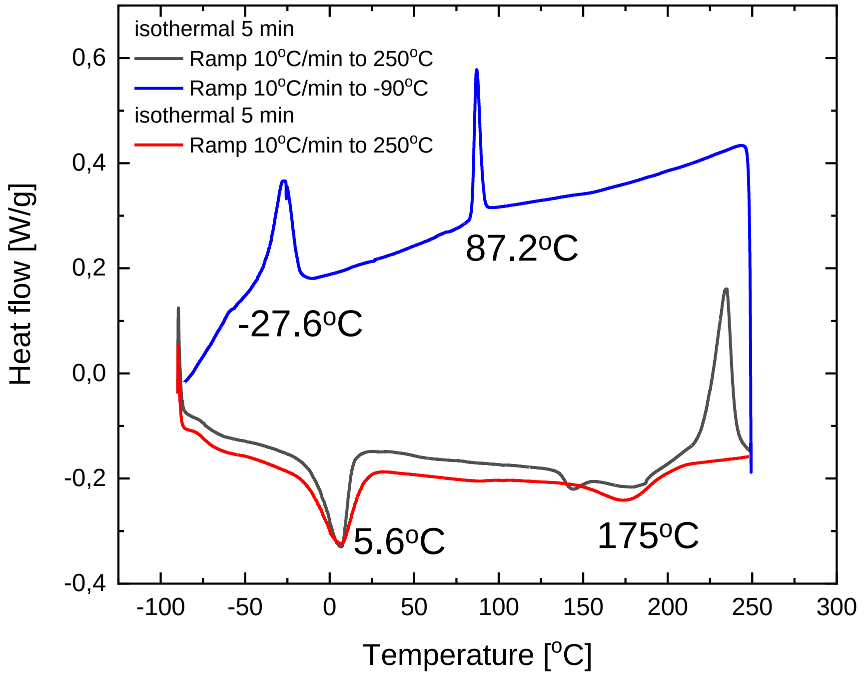
70_PTMO2k_33



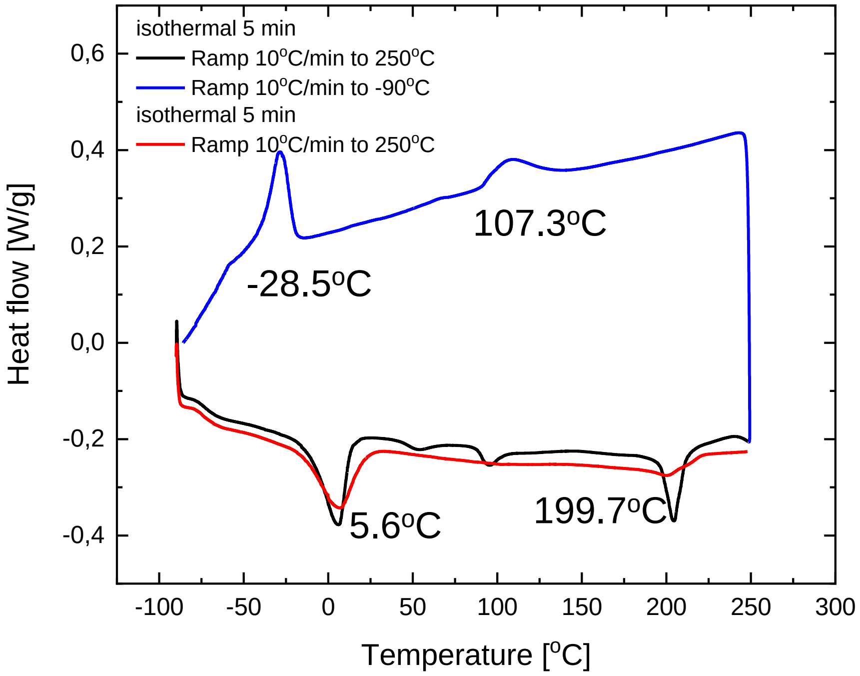
70_PTMO2k_51

DSC

1. Heat up to 250°C to eliminate thermal history (black curve)
2. Cool down to -90°C (blue curve)
3. Heat up to 250°C to melt crystals (red curve)



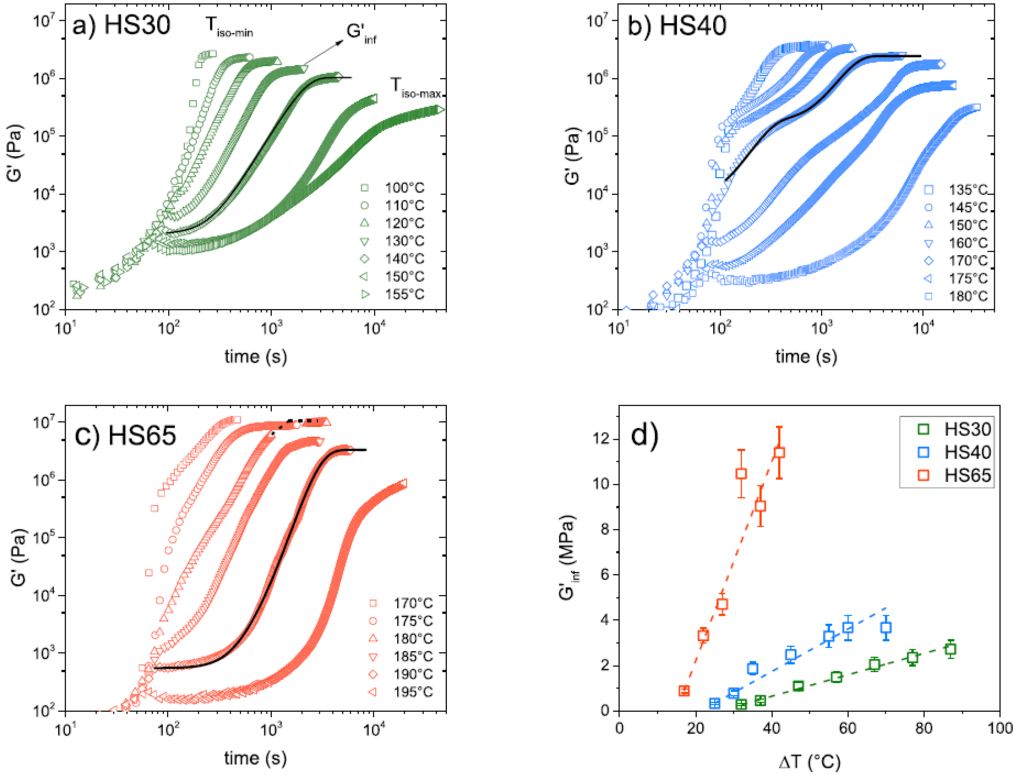
70_PTMO2k_33



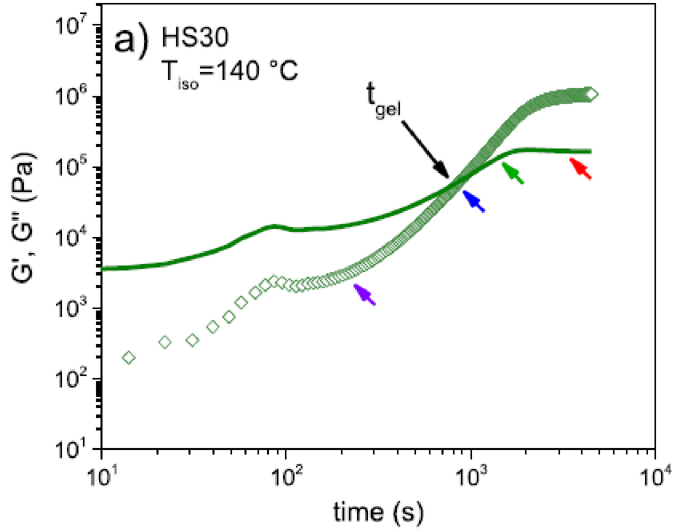
70_PTMO2k_51

TPEs rheology

sample	HS (wt %)	⟨N⟩	M_{HS} (kg mol^{-1})	M_{SS} (kg mol^{-1})	$\bar{M}_n$ (kg mol^{-1})	I_p	$T_m{}^a$ (°C)
HS30	30	7.7	1.0	2.0	25	2	180
HS40	40	6.5	1.5	2.0	25	2	200
HS65	65	7.7	2.1	1.0	25	2	208



Storage modulus as a function of time G′(t)



Gelation time determination

De Almeida et *al. Macromolecules*, 2019, 52

Outlook

- Set up procedure to measure both linear and nonlinear properties of the proposed sample
- Quench sample and test mechanical properties

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