DoDyNet online meeting, September 2020

Rheological and Mechanical Properties of Diamine Neutralized Entangled Poly(styrene-co-4-vinylbenzoic acid) Ionomers

ESR 6: Wendi Wang

Jeppe Madsen
Anne Ladegaard Skov
Ole Hassager
Qian Huang

Outline

- **Rheological properties** of neutralized ionomers: towards designing ionomers with good flowability, stretchability and extensibility

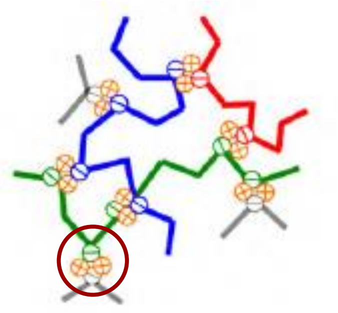
- Background and objective
- Materials
- Linear rheology
- Non linear extensional rheology
- Summary and conclusion

- **Mechanical properties** of neutralized ionomers

- Background and objective
- Materials
- Sample preparation
- Mechanical tests
- Outlook

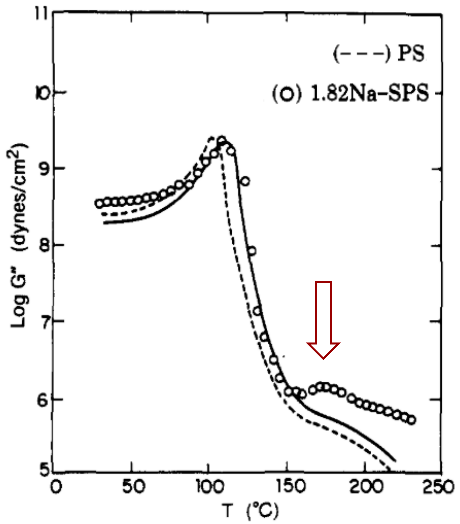
Ionomers

- What is ionomer?



Soft Matter 2018, 14, 2961

- Feature

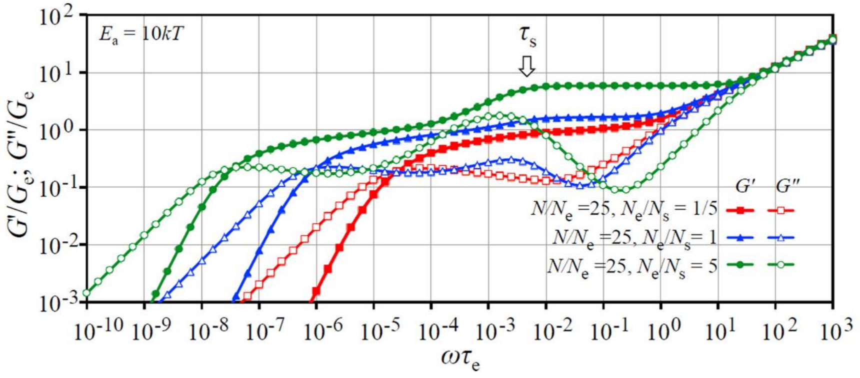


Macromolecules 1991, 24, 1071

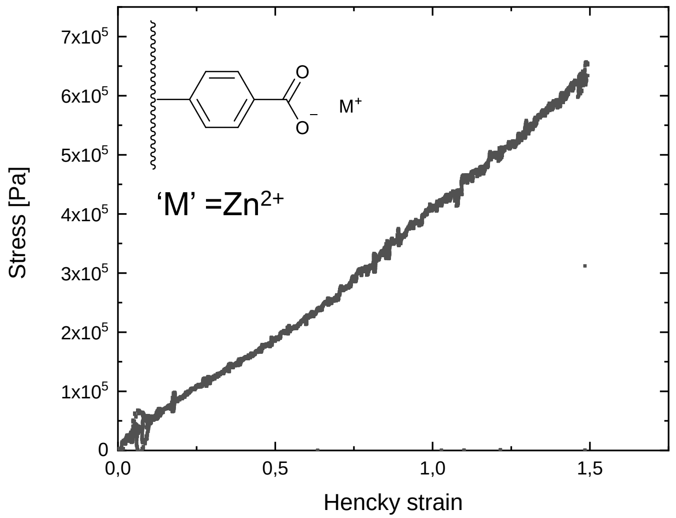
- Consequence

Long relaxation time

Difficult to process



JOR 2016, 60, 1031



170°C, 0.004 s^{-1}

Objective and strategy

Design **entangled** ionomers with good:

1. Flowability (avoid ionic clusters)

    - ion concentration

    - counter ion species

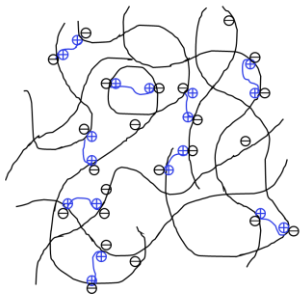
2. Stretchability

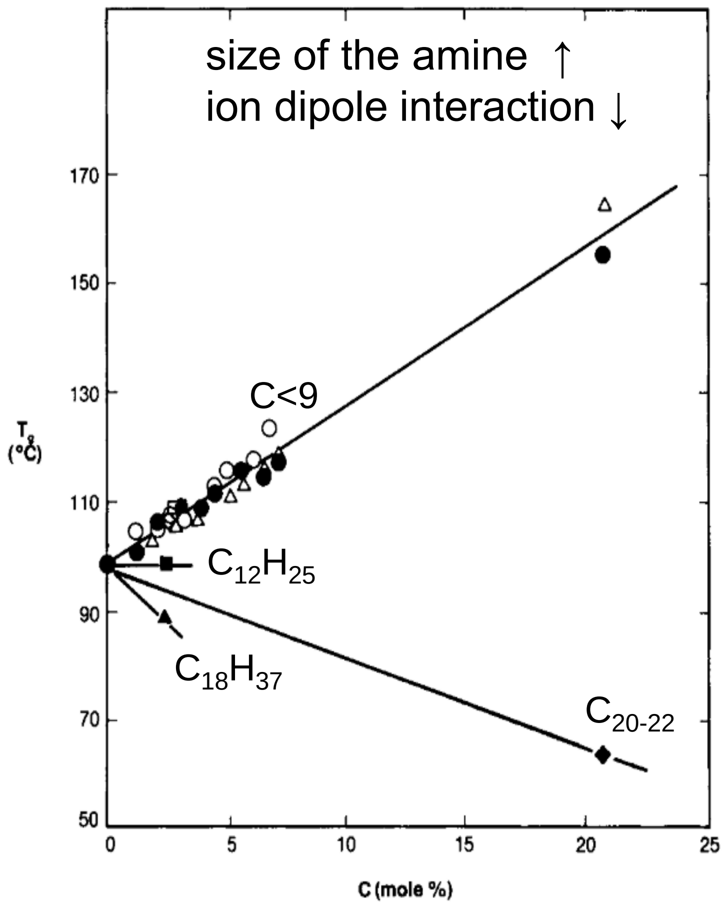
    - higher strain hardening

3. Extensibility

    - double dynamics network of

ionic interaction and entanglements





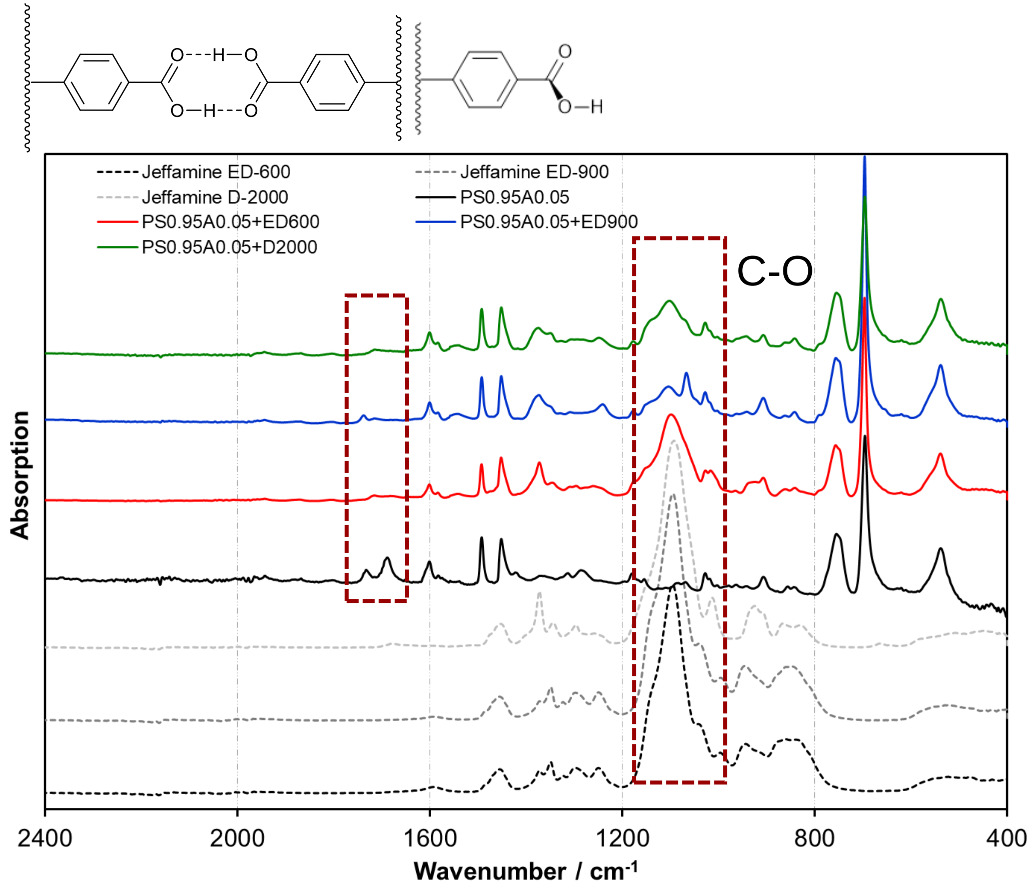
J. Appl. Polym. Sci 1984, 29, 2719

T_g vs. sulfonate concentration for alkyl ammonium salts of the form NRH_3^+

Materials

- Poly(styrene-co-4-vinylbenzoic acid) (PS-co-PVBA, 5 mol%, ~40 acid groups/chain), Z=6.4
- Diamines

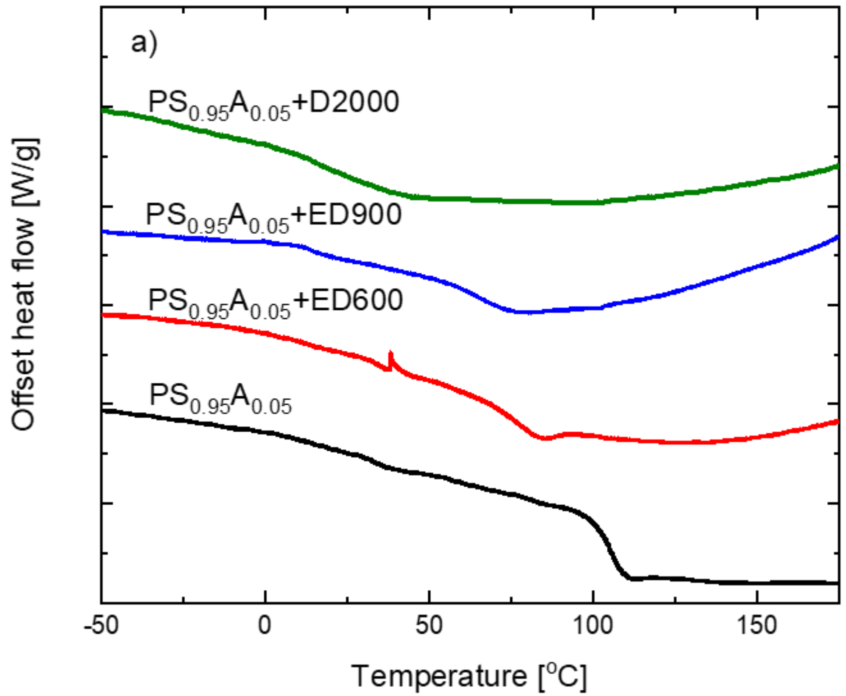
Material	M_w [g/mol]	M_w/M_n
$PS_{0.95}A_{0.05}$	85400	1.22
Jeffamine ED600	656	1.08
Jeffamine ED900	940	1.22
Jeffamine D2000	2144	1.18

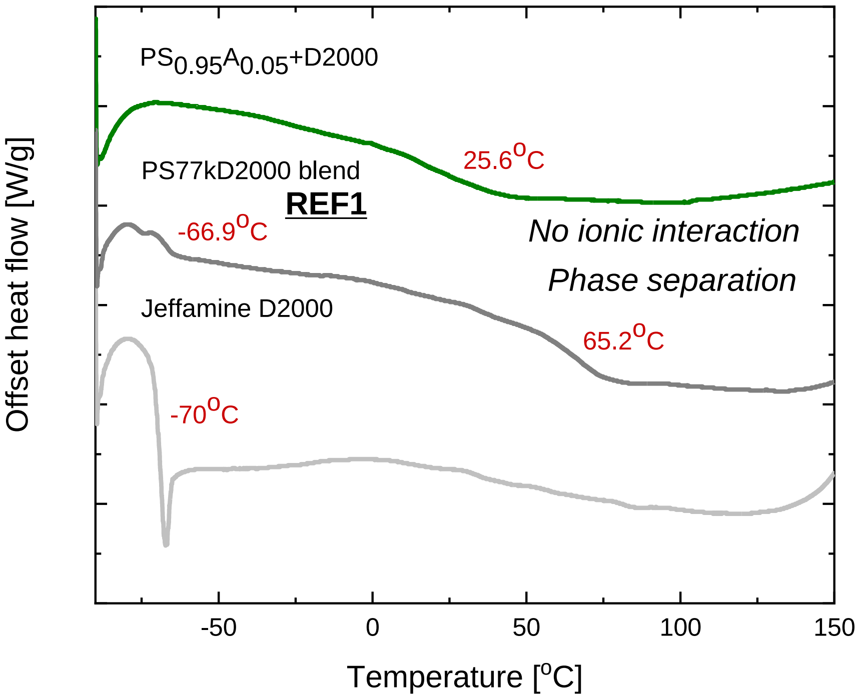


Materials

Material	T_g [ºC]
$PS_{0.95}A_{0.05}$	105
$PS_{0.95}A_{0.05}$+ED600	76
$PS_{0.95}A_{0.05}$+ED900	66
$PS_{0.95}A_{0.05}$+D2000	25

- DSC results

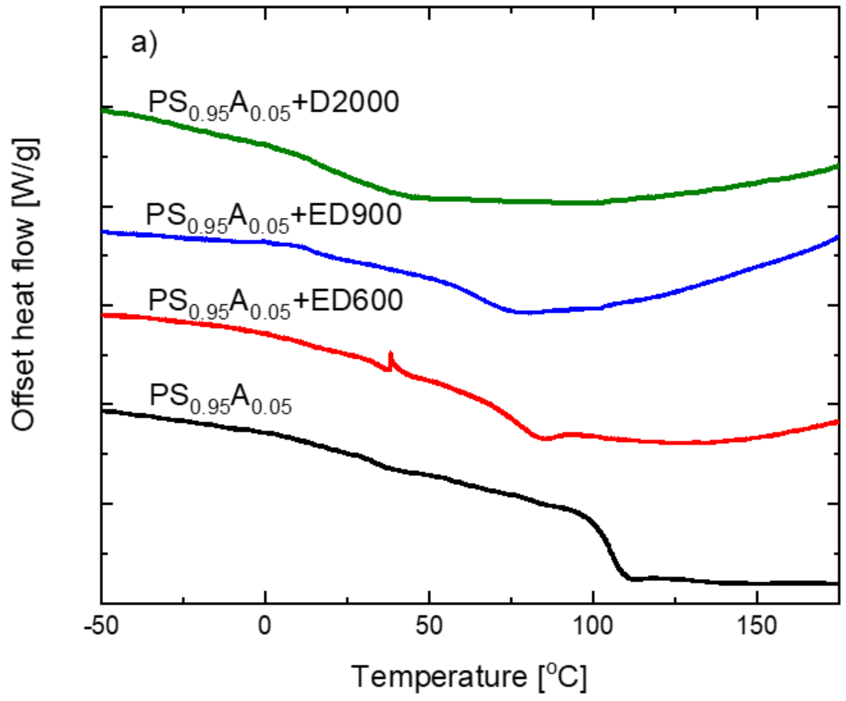


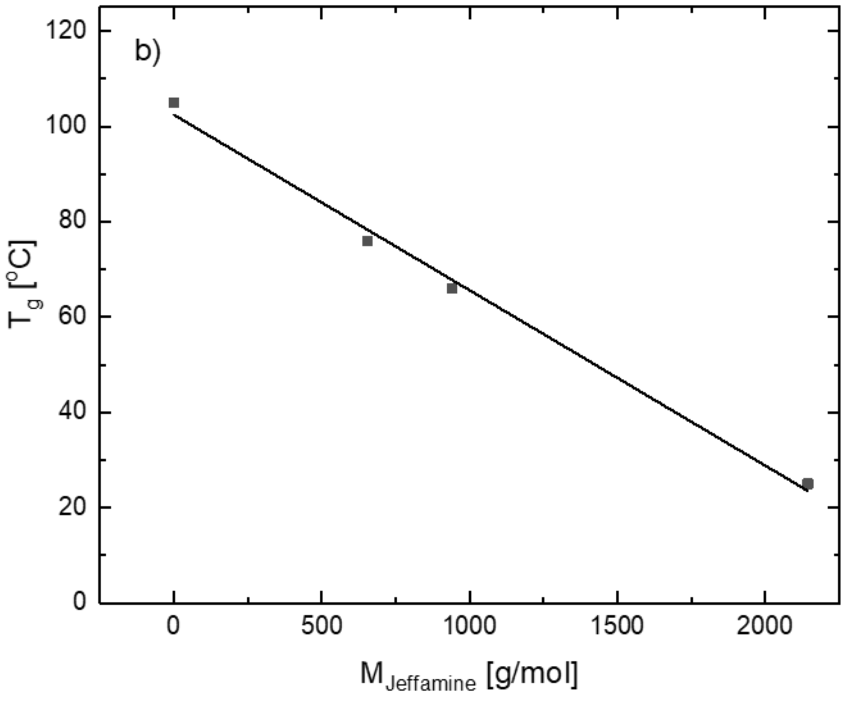


Materials

- DSC results

Material	T_g [ºC]
$PS_{0.95}A_{0.05}$	105
$PS_{0.95}A_{0.05}$+ED600	76
$PS_{0.95}A_{0.05}$+ED900	66
$PS_{0.95}A_{0.05}$+D2000	25



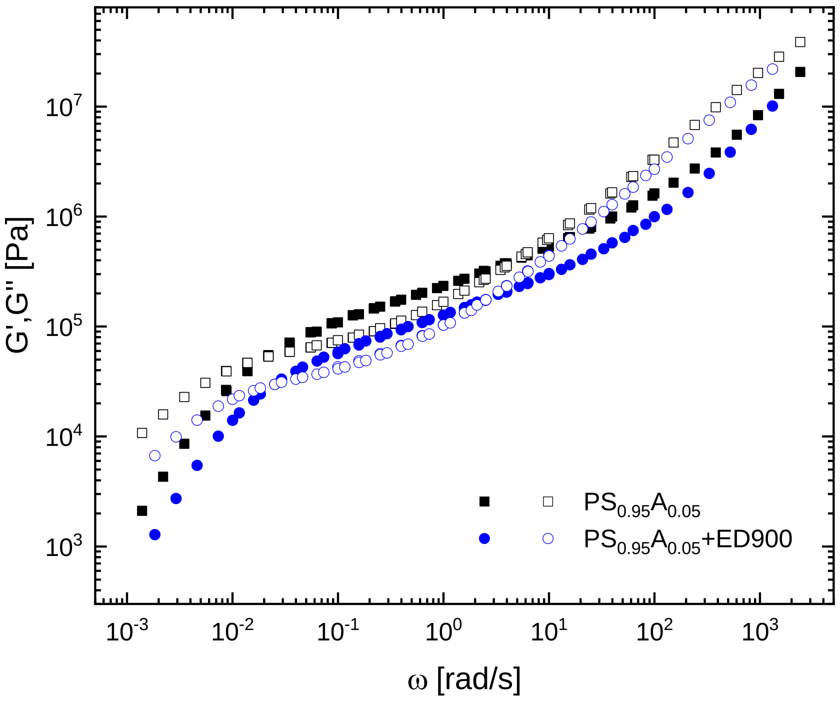


Linear rheology

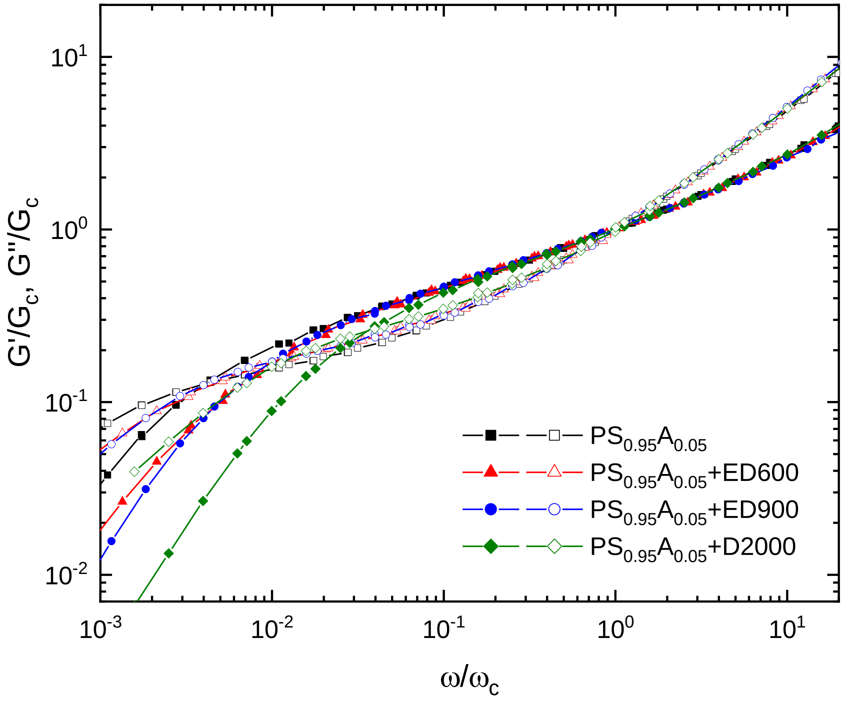
- SAOS measurements

High frequency, same Rouse relaxation

Low frequency, diamine length ↑, terminal relaxation time↓



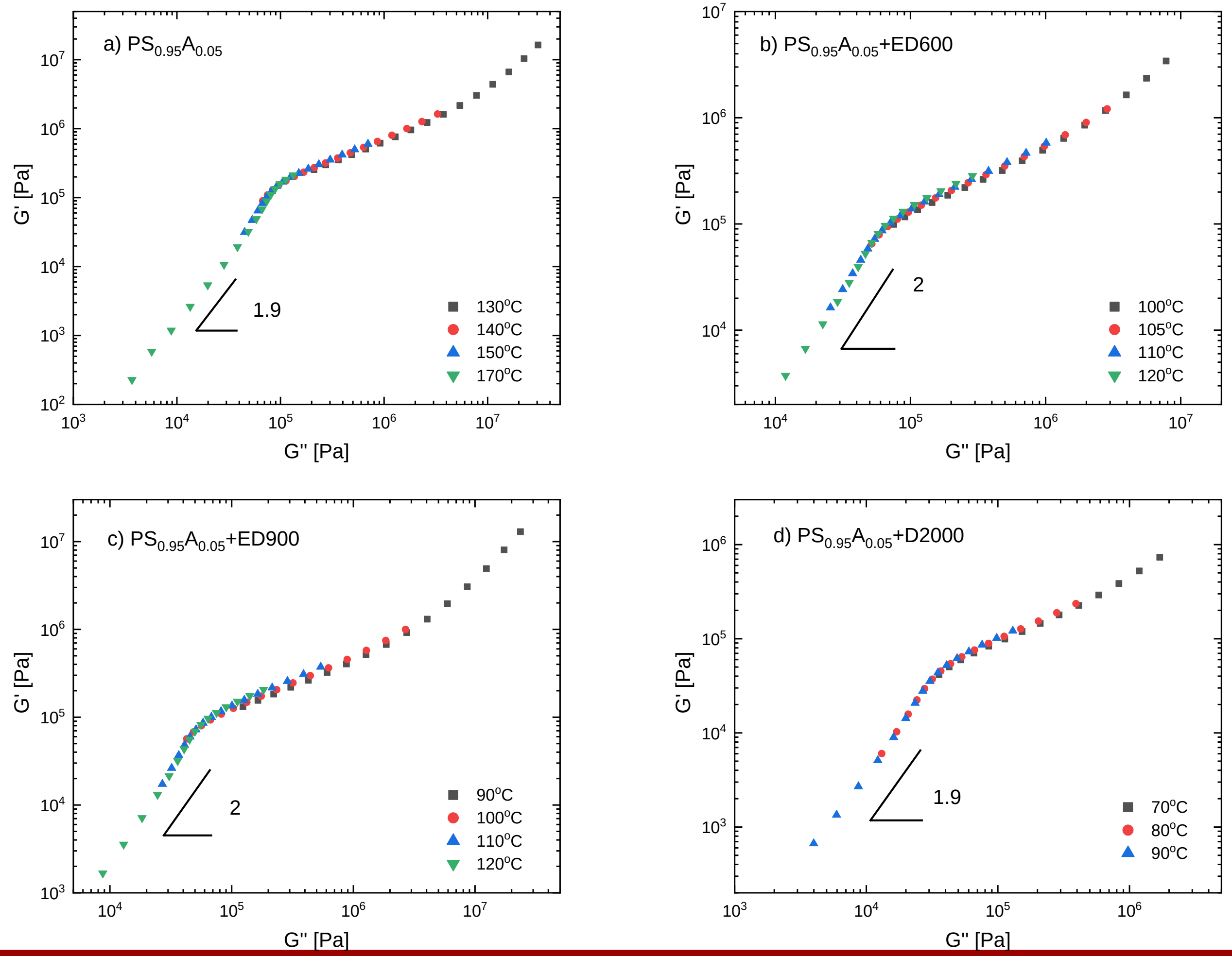
LVE temperature from top to bottom: 140, 100ºC (same $T-T_g$)



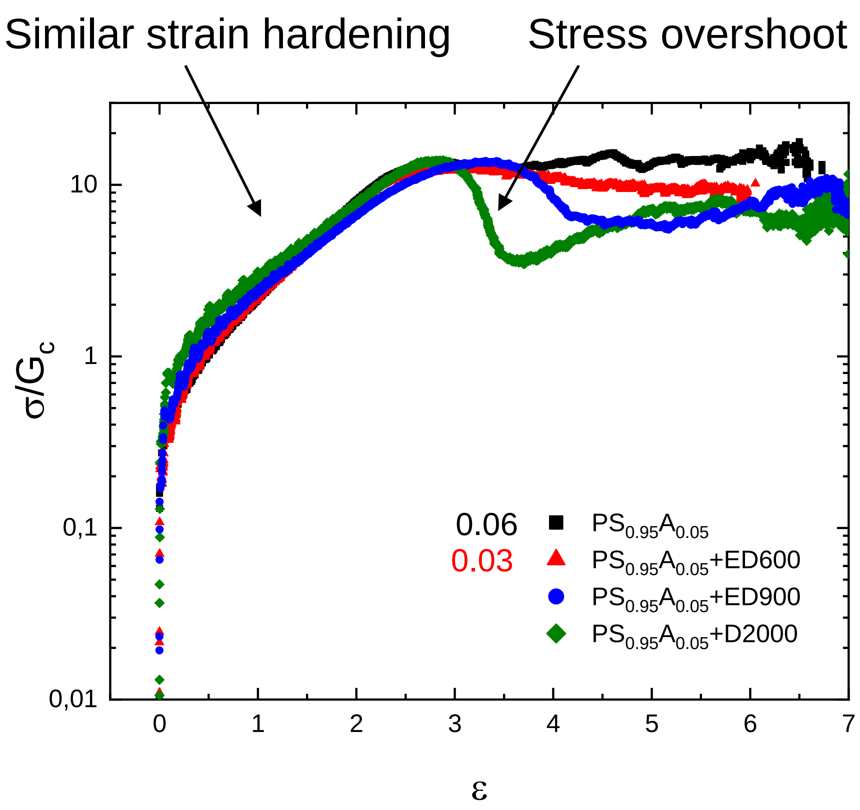
LVE data after normalization with ω_c and G_c

Linear rheology

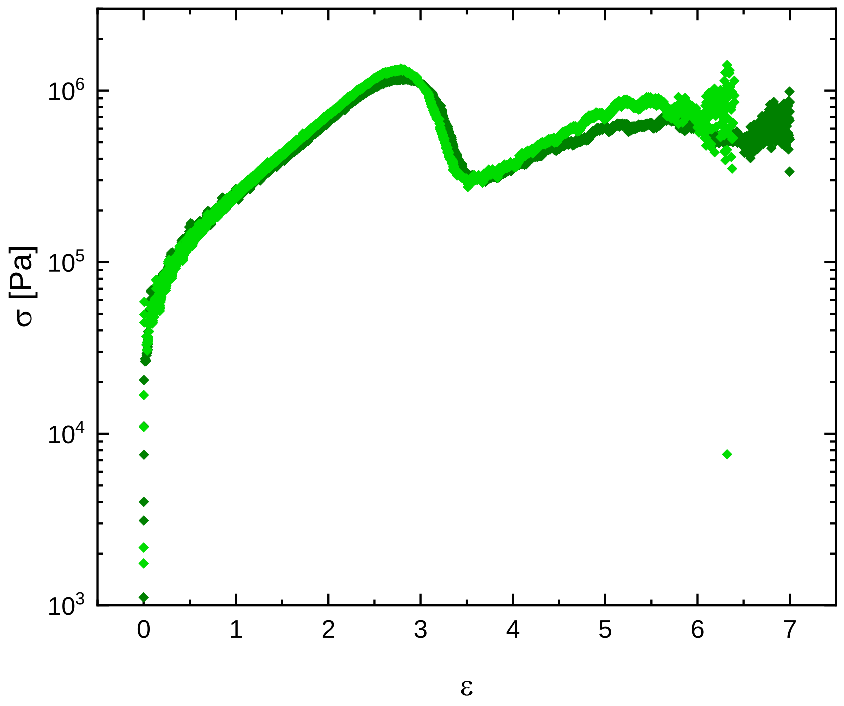
- Han's plot: a blend is truly homogenous if plot logG' vs logG" has a slope of 2 in the terminal region



Non linear extensional rheology



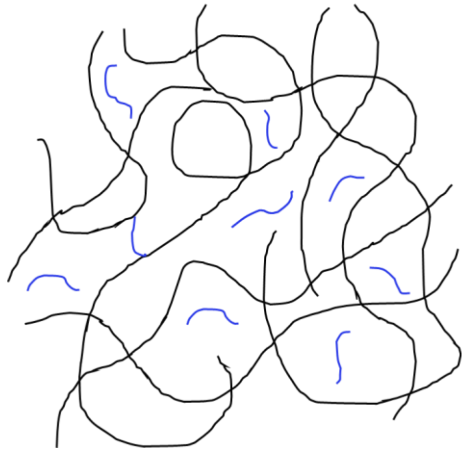
Focus on sample $PS_{0.95}A_{0.05}$+D2000

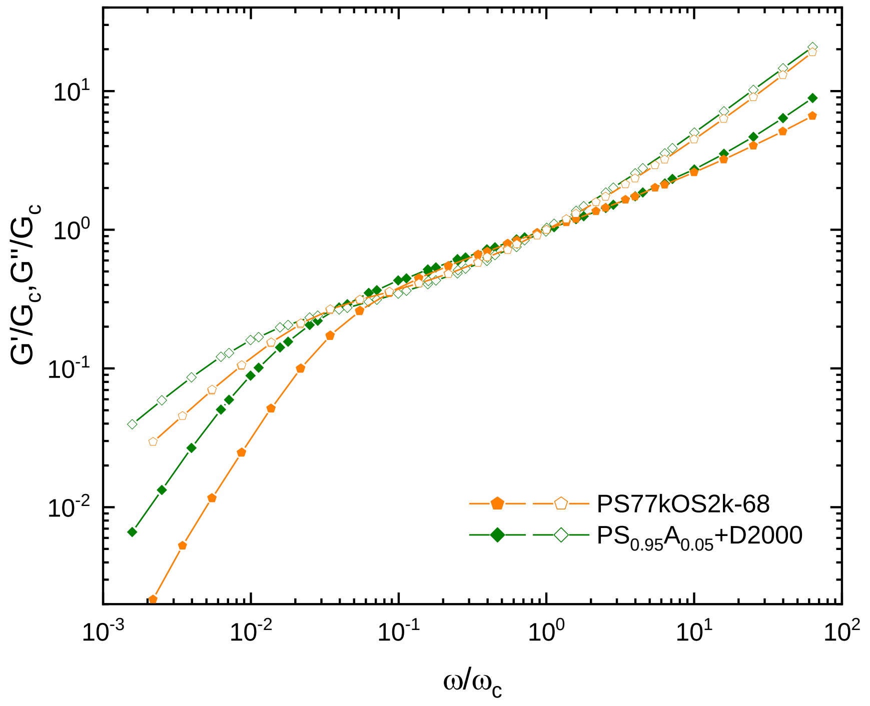


Role of ionic interaction (stickers) at equilibrium

- Diluting extent at equilibrium?

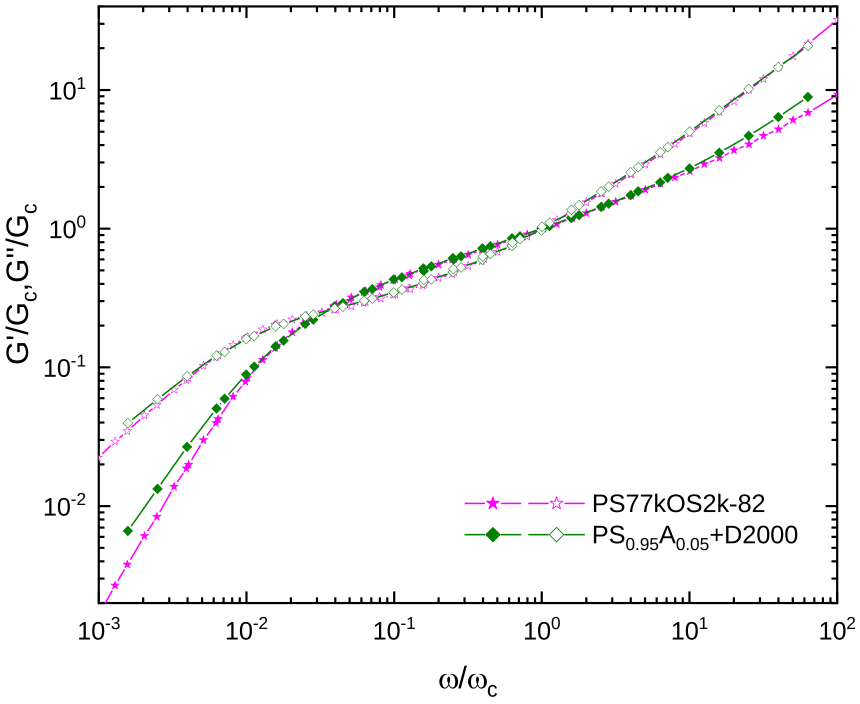
- **<u>REF2</u>**: PS77k/OS2k, **same** weight fraction of long chain as in the ionomer (68%)

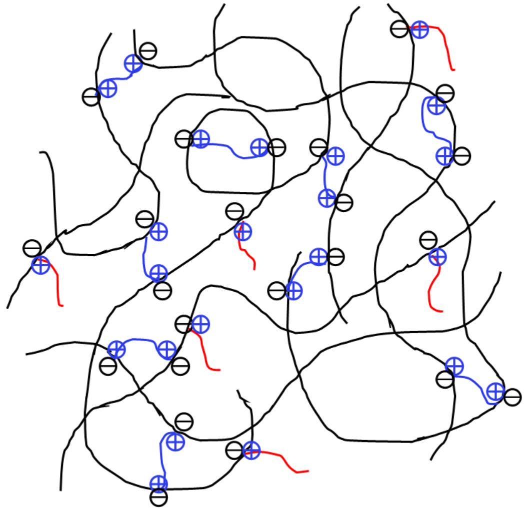




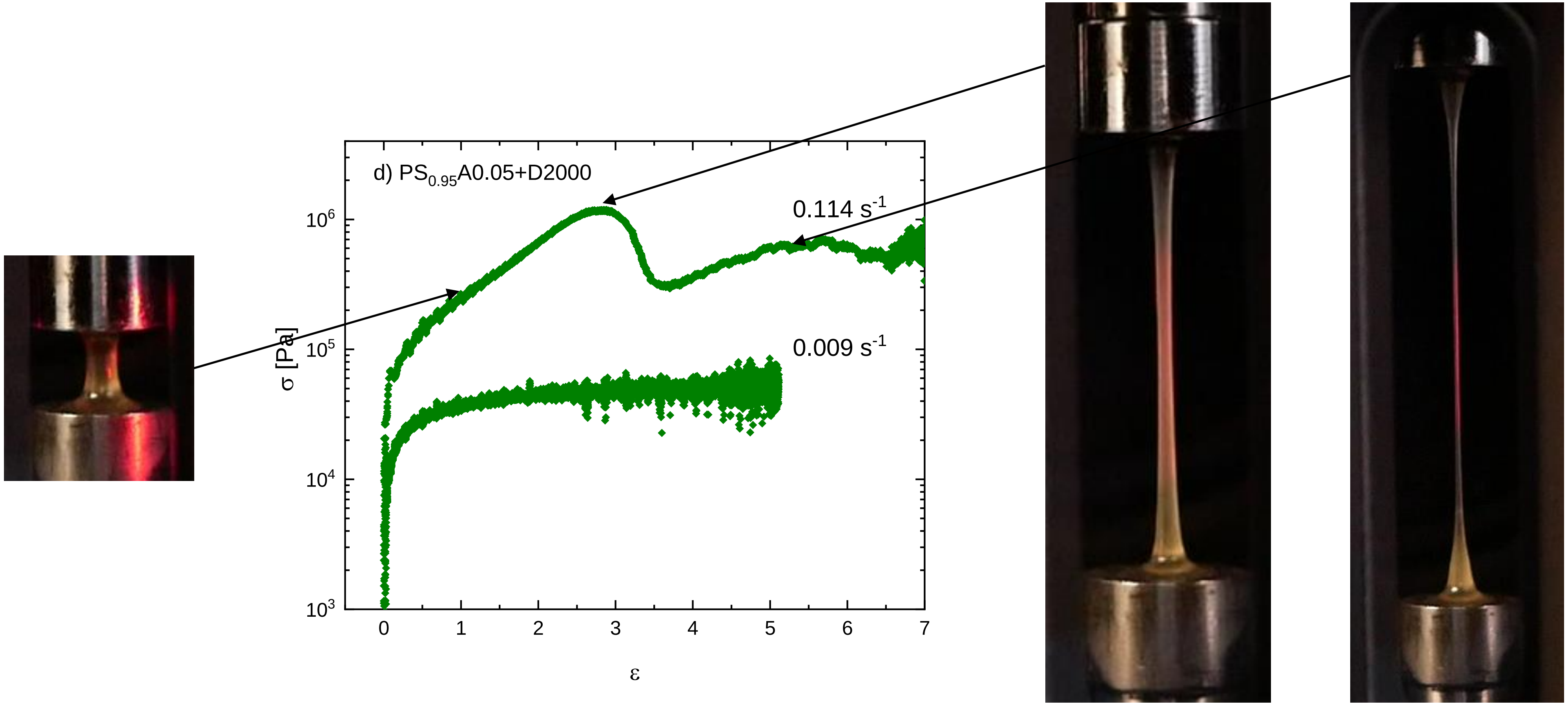
Role of ionic interaction (stickers) at equilibrium

- Diluting extent at equilibrium?
- **REF3**: PS77k/OS2k, **higher** weight fraction of long chain than in the ionomer (82%)

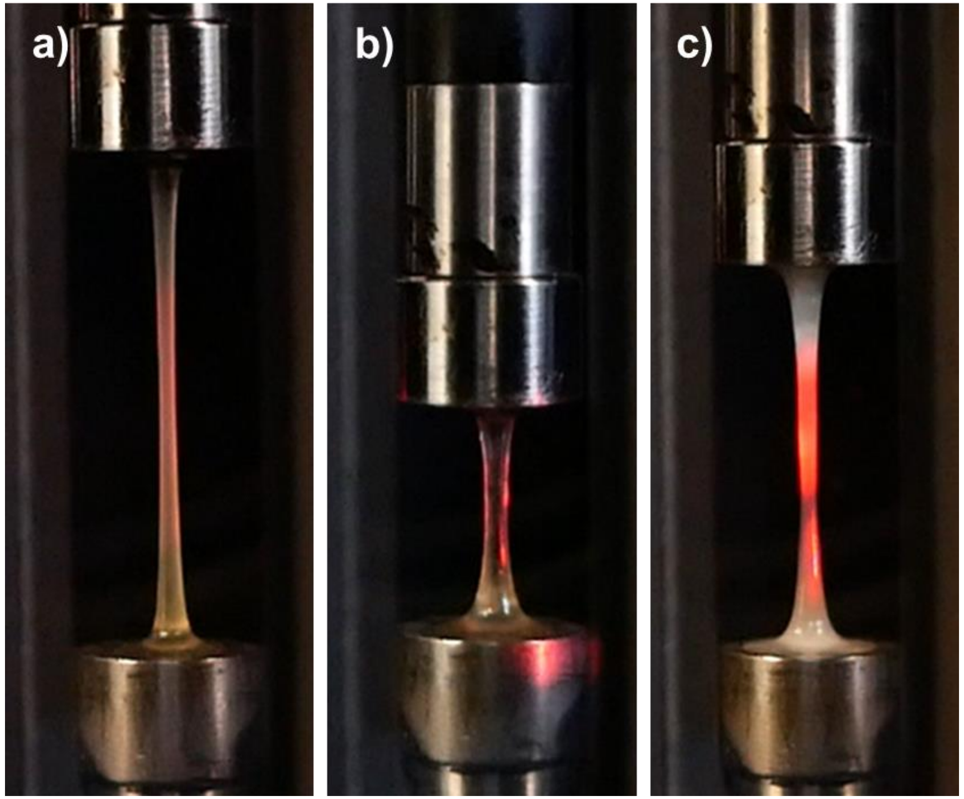




Role of ionic interaction (stickers) in start-up flow

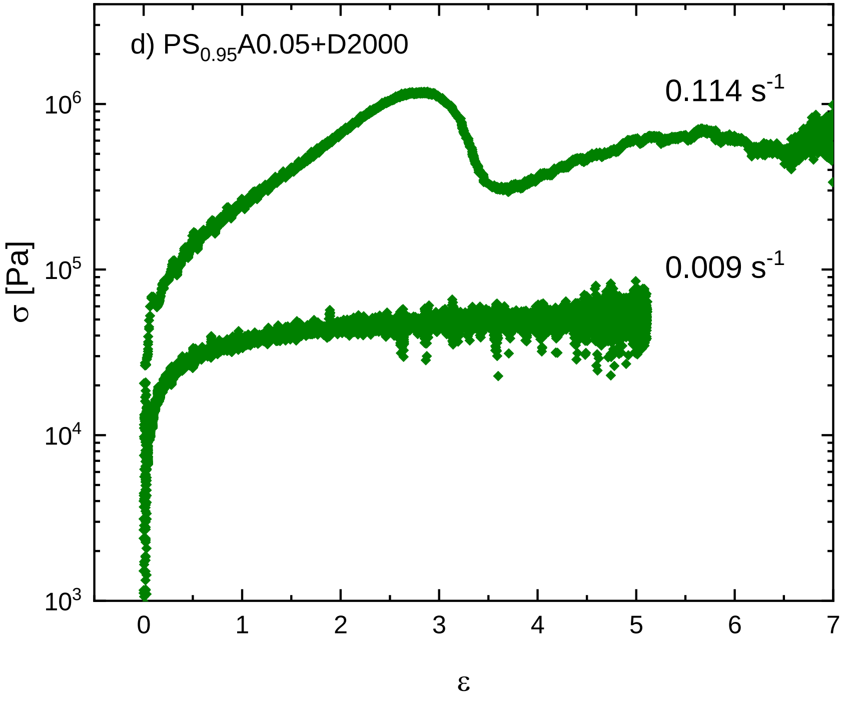


Role of ionic interaction (stickers) in start-up flow

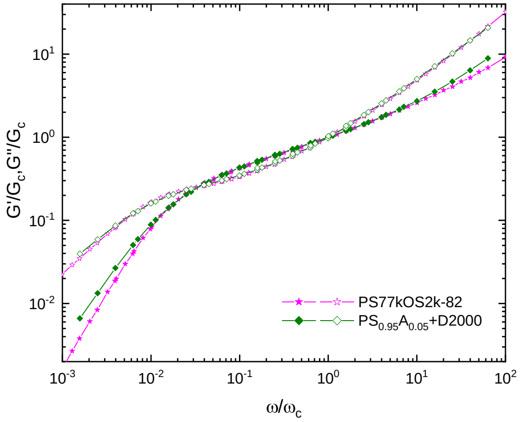


0.114 s^{-1} 0.009 s^{-1} REF1 (PS77kD2000)

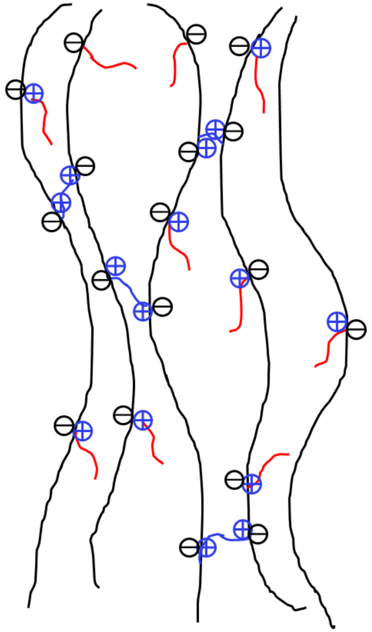
$PS_{0.95}A_{0.05}$+D2000

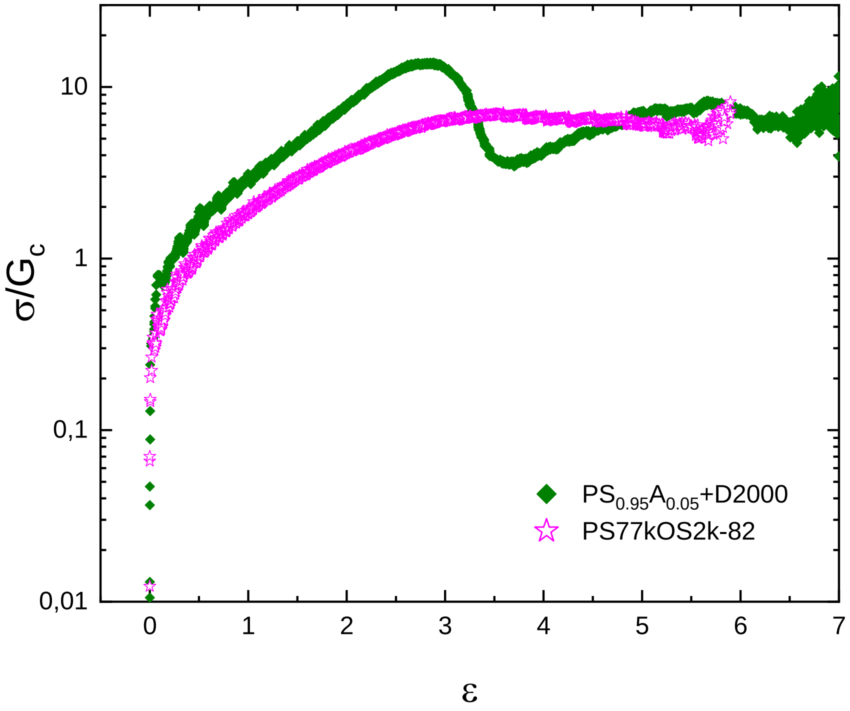


Role of ionic stickers at large strain



- Sticker re-association





Sample PS77kOS2k-82 and $PS_{0.95}A_{0.05}$+D2000 are stretched at same W_i.

Summary and conclusion

- A series of PS based ionomers are prepared by neutralizing poly(styrene-co-4-vinylbenzoic acid) with diamines.

- The resulting ionomers showed lower T_g compared to the parent polymer.

- **Flowability**: Ionic cluster formation was prevented by using a low fraction of ion concentration and ammonium as counter ion.

- **Stretchability**: The introduction of stickers of different lengths provides the possibility to tune stretchability of the materials.

- **Extensibility**: The sticker reorganization together with entanglement enable an excellent extensibility of ionomers.

Outline

- **Rheological properties** of neutralized ionomers: towards designing ionomers with good flowability, stretchability and extensibility

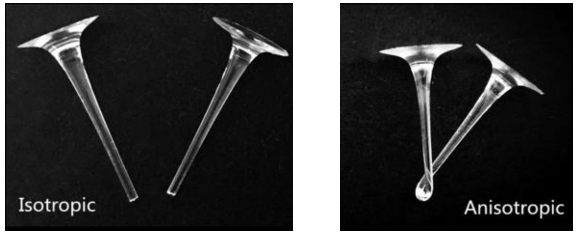
- Background and objective
- Materials
- Linear rheology
- Non linear extensional rheology
- Summary and conclusion

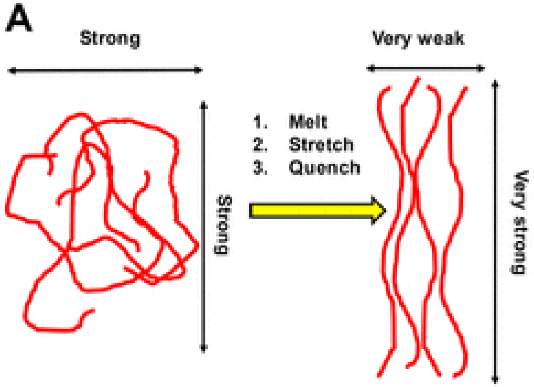
- **Mechanical properties** of neutralized ionomers

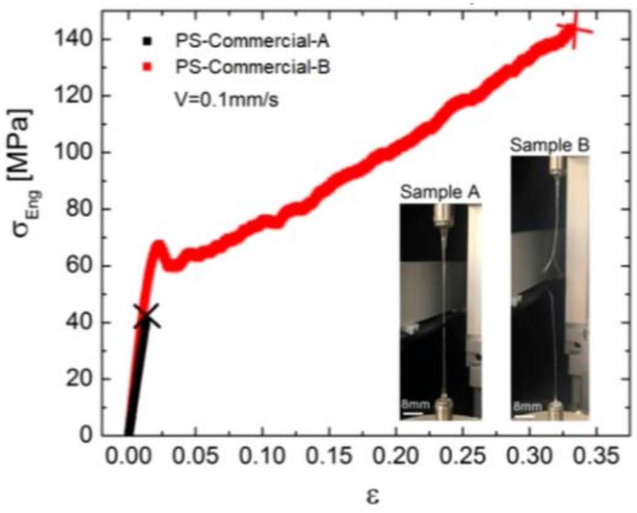
- Background and objective
- Materials
- Sample preparation
- Mechanical tests
- Outlook

Improvement of mechanical properties of glassy PS

- Highly anisotropic glassy PS are flexible

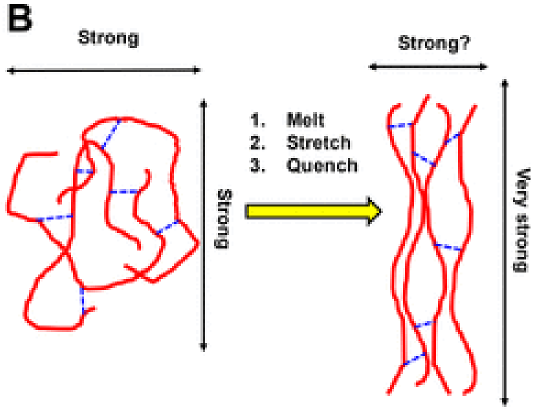


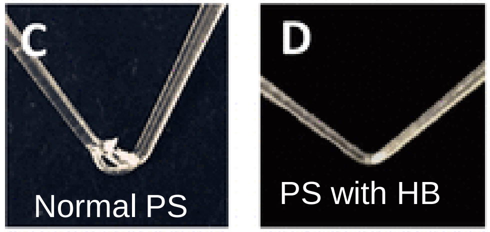


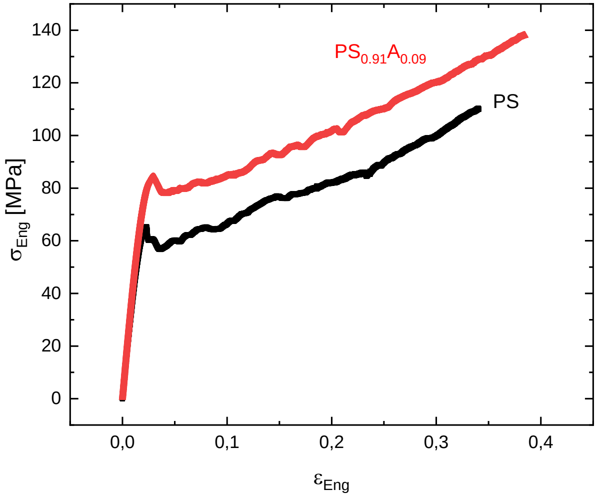


ACS Macro Lett. 2018, 7, 1126

- Enhance fiber strength ⊥ to the stretching direction

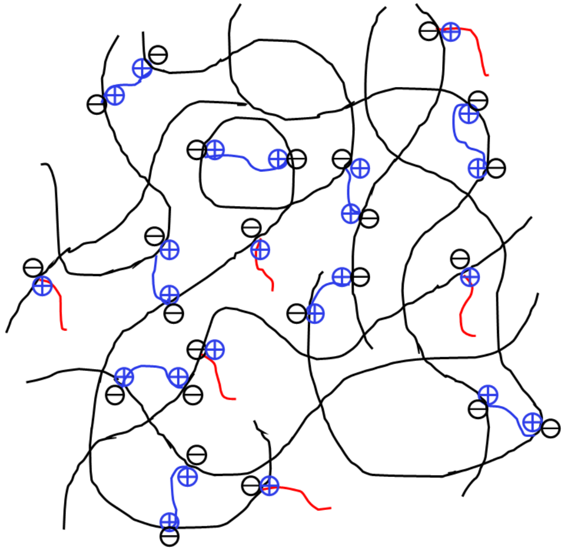






Macromolecules 2019, 52, 9261

Polystyrene used at low temperature?

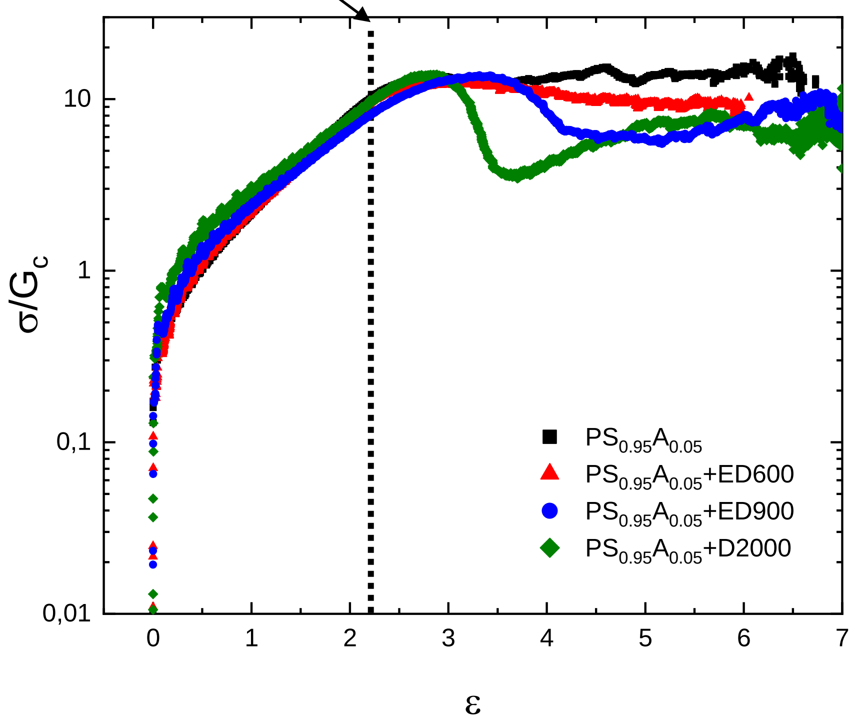


Material	T_g [ºC]	T_{test} [ºC]
PS0.95A0.05	105	25
PS0.95A0.05+ED600	76	-4
PS0.95A0.05+ED900	66	-14
PS0.95A0.05+D2000	25	-55

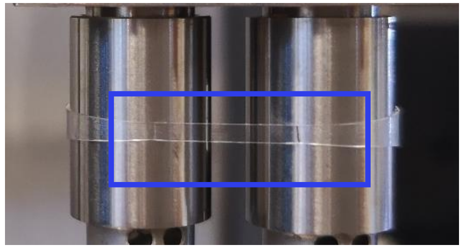
Theoretically, flexibility can be achieved at low temperature!

Sample preparation

Quench at Hencky strain 2.2 and test mechanical properties

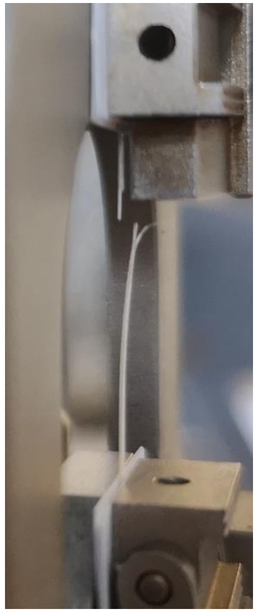


Normalized stress with strain for all four samples



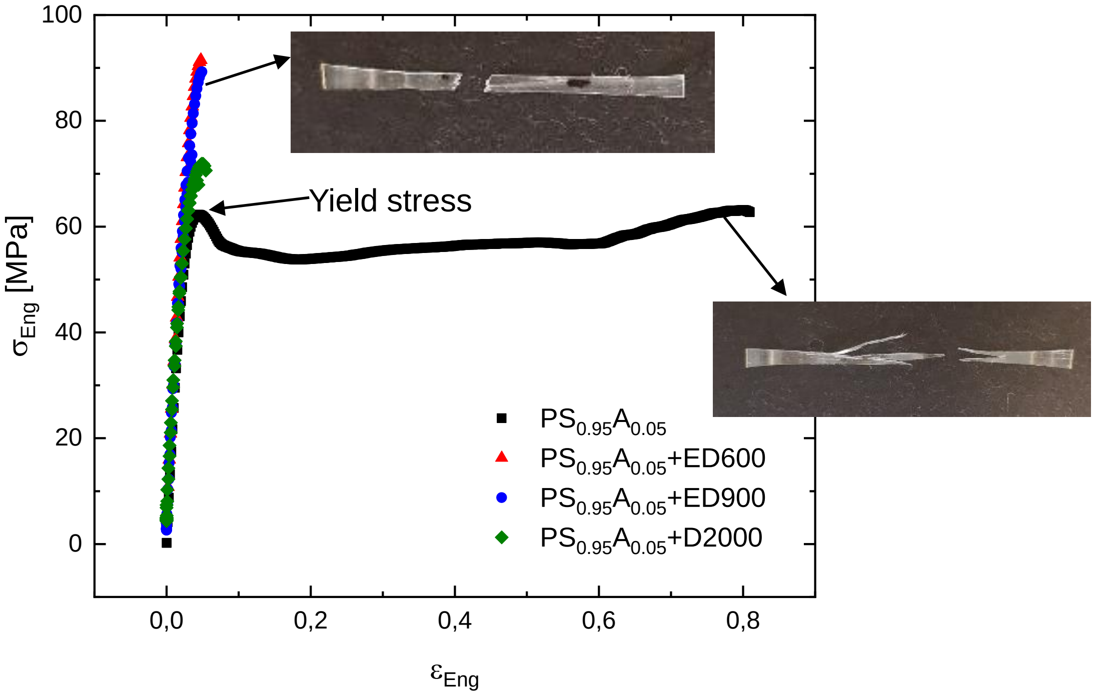
- Prestretch sample
- Wait for relaxation
- Sample was stretched to Hencky strain 2.2, quench while motor is blocked.

Tensile tests



DMA Q800 (Copenhagen University)

$\dot{v} = 0.05\ min^{-1}$ T_g-T=80°C



Discussion

- Yield stress may have rate and temperature dependence

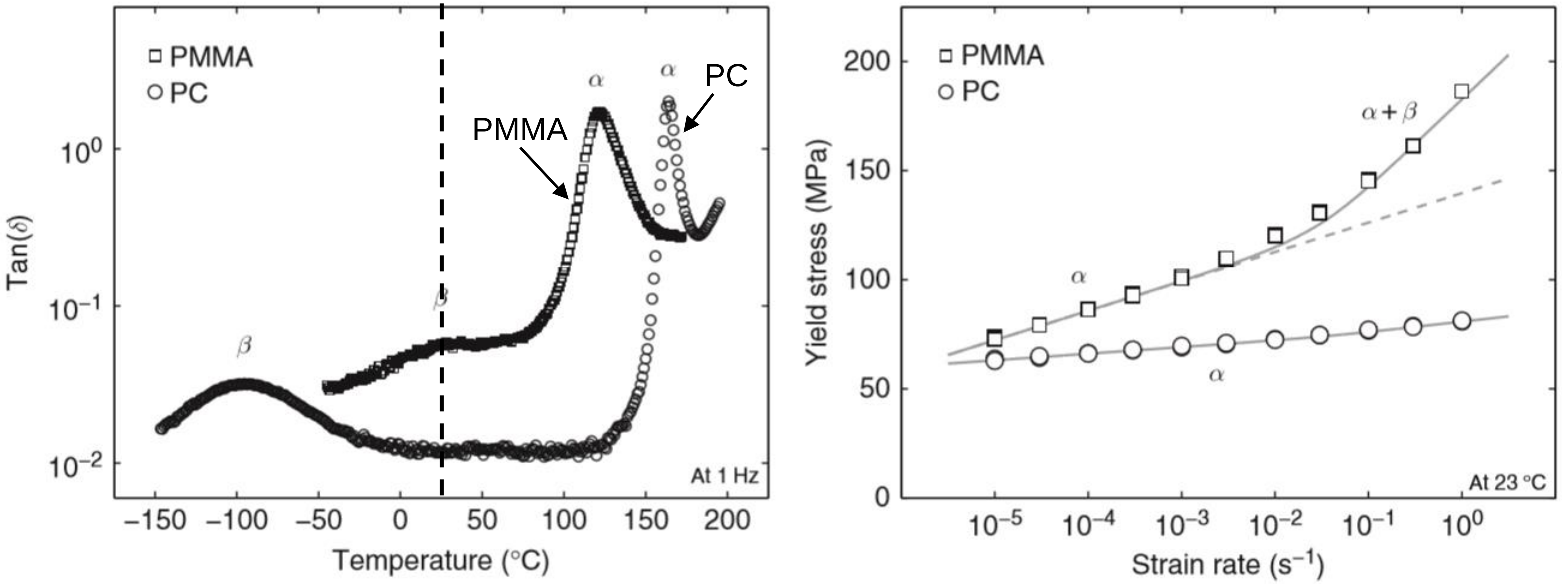
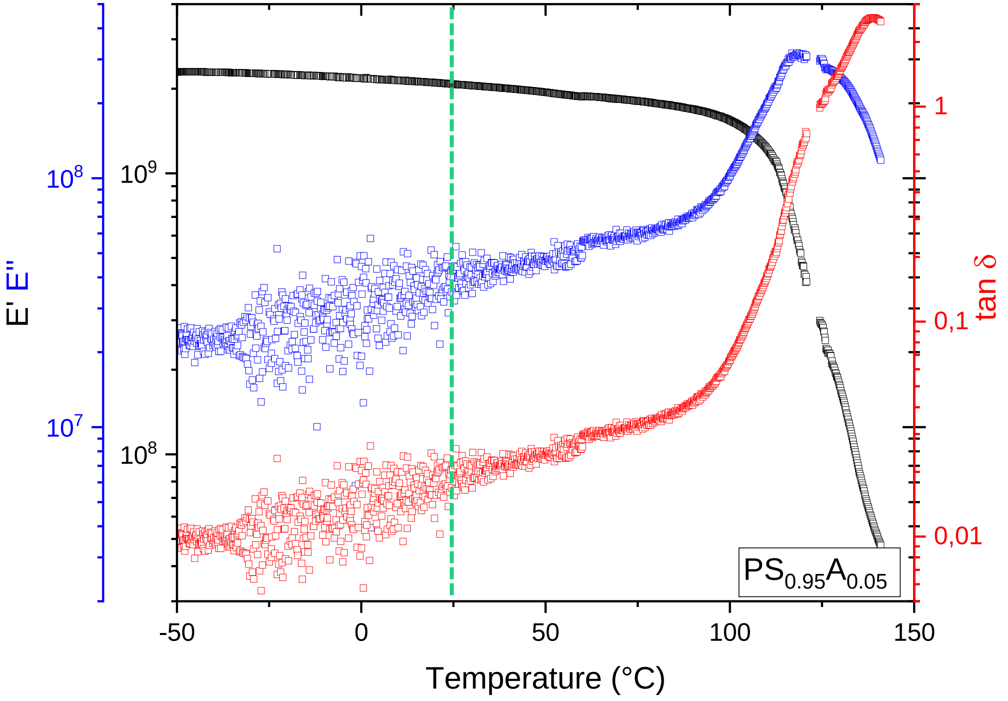


Figure 12 Influence of a secondary relaxation process. Left: Loss angle versus temperature. Right: Compressive yield stress versus strain rate.

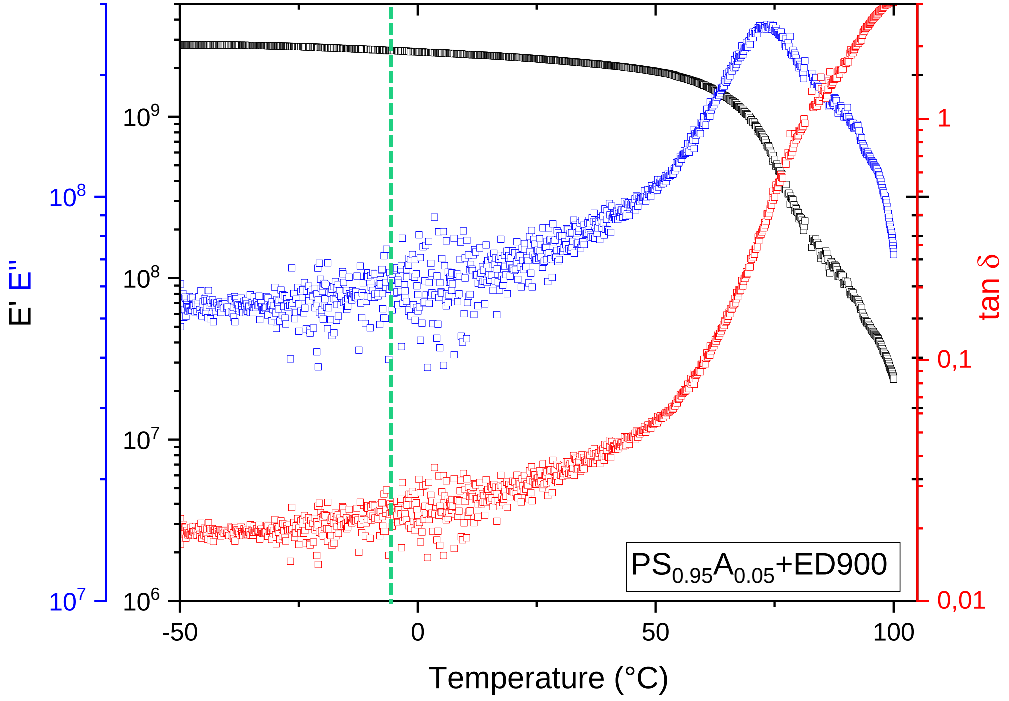
Polymer Science: a Comprehensive Reference, 2012, Volume 2, pp. 723-747

Secondary transition in the materials?

- Temperature sweep tests are performed at 1 Hz with amplitude 20 micron, on film tension clamp
- Corresponding tensile test temperatures are marked in green dash lines.

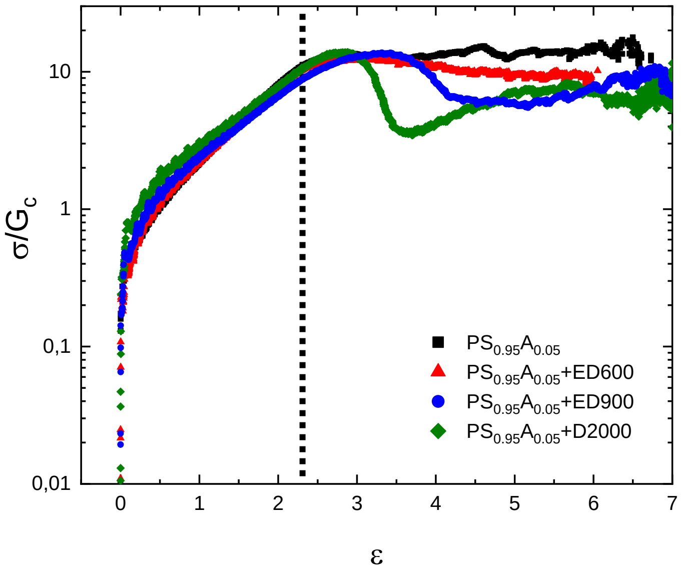


No secondary transition



Outlook

- Qualification of orientation extent



- Compare intrinsic difference of the samples with non-oriented film

DTU