Phases and Conduction in Ion-Containing Polymers

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Solutions:

Polyelectrolyte solutions
Polyelectrolyte/surfactant mixtures
Polyelectrolyte/protein mixtures
Synovial fluid rheology and osmotic pressure
Polyelectrolyte gels

Melts:

Randomly branched polymers
Miscible polymer blends
Ionomers for actuators, batteries and fuel cells
Glass-forming liquids
Liquid crystal polymers

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Phases of Ion-Containing Polymers

Polyelectolyte: Many ions dissociate from the chain in a high-dielectric medium – dominated by charge repulsion

Ionomer: All counterions are paired with the ions attached to the chain in a low- dielectric medium and ion pairs cluster – dominated by dipolar attraction

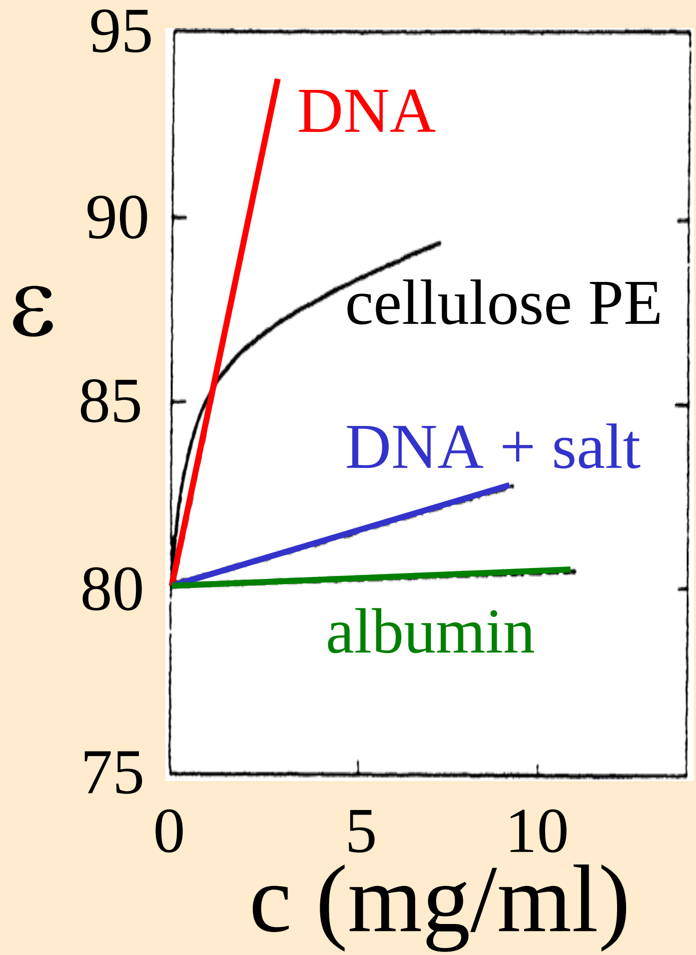
Phases of Ion-Containing Polymers

Polyelectolyte: Many ions dissociate from the chain in a high-dielectric medium – dominated by charge repulsion

Chain of Dipoles Phase: Ions are mostly paired but do not aggregate to form ion domains

Ionomer: All counterions are paired with the ions attached to the chain in a low- dielectric medium and ion pairs cluster – dominated by dipolar attraction

How should the charge on the polyelectrolyte change with concentration?



Bjerrum length $l_B = e^2/\varepsilon kT$

Add polyions $\Rightarrow$ ε increases

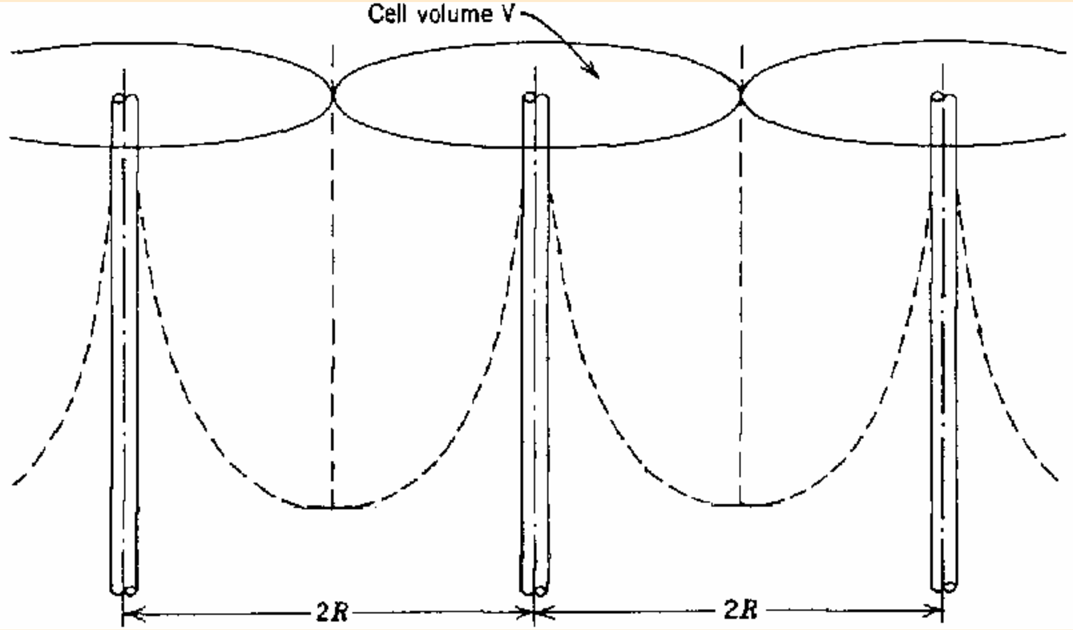
$\Rightarrow$ l_B decreases

$\Rightarrow$ counterion release

The fraction of monomers with an effective charge f should increase with concentration.

F. Oosawa, *Polyelectrolytes*, Marcel Dekker (1970).

Counterion Distribution in the Katchalsky Cell Model

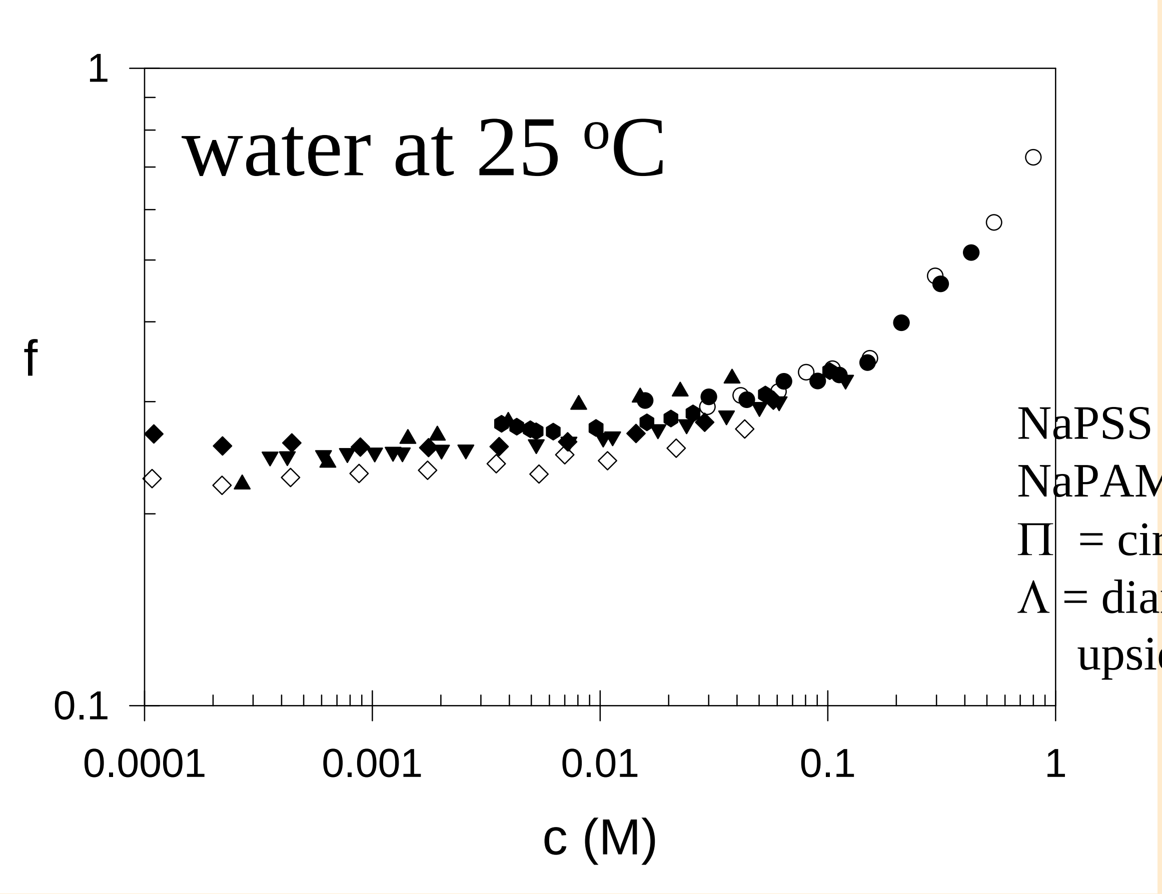


The two-state model assumes that all non-condensed counterions are equivalent and completely free.

A. Katchalsky, *Pure Appl. Chem.* **26**, 327 (1971)

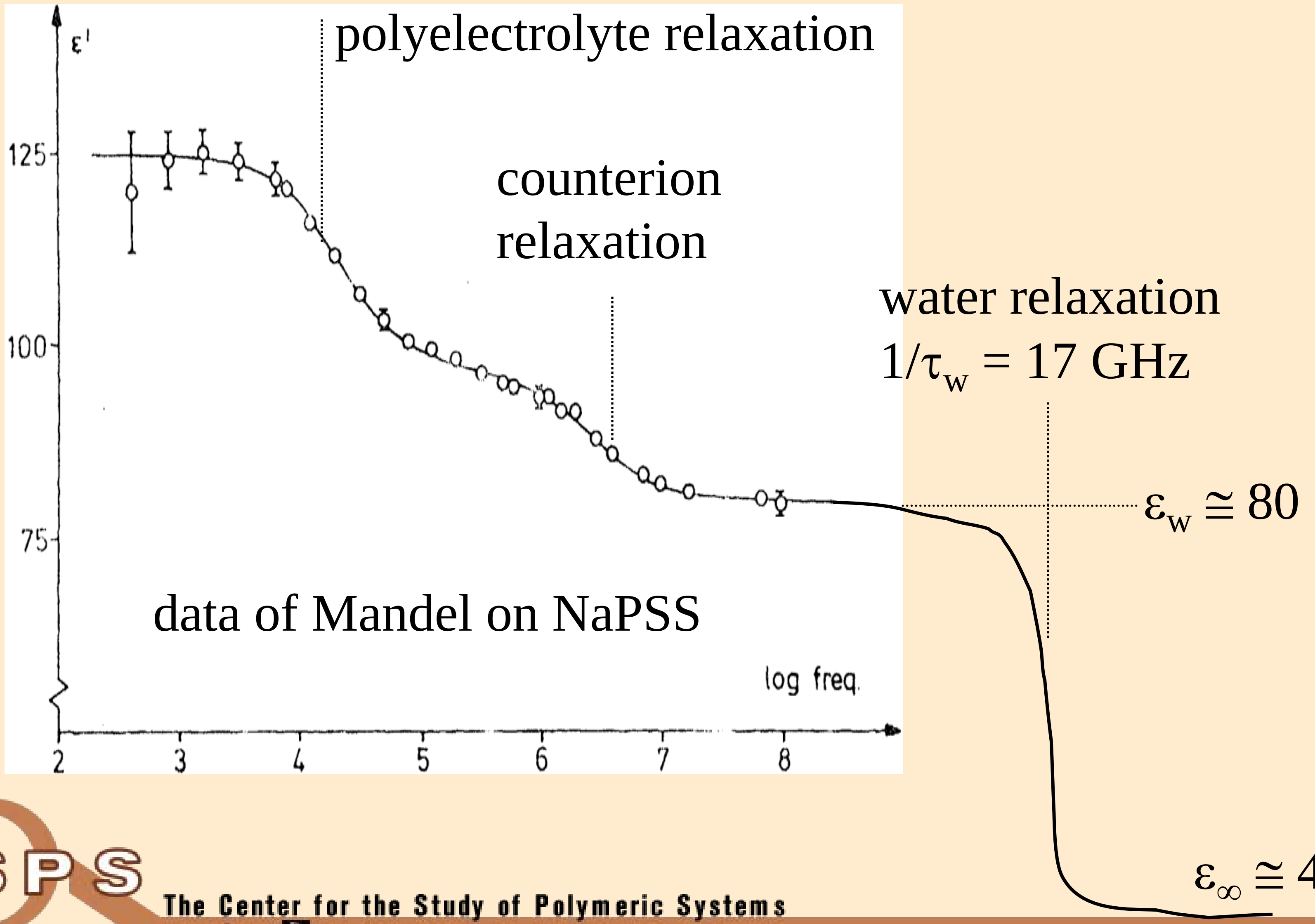
Concentration Dependence of the Fraction of Monomers Bearing an Effective Charge

de Gennes assumes $f \sim c^0$



NaPSS = filled
NaPAMS = open
Π = circles, triangles
Λ = diamonds, hexagons, upside down triangles

Dielectric Spectroscopy of Polyelectrolyte Solutions



Synthesis of Polyester Ionomers

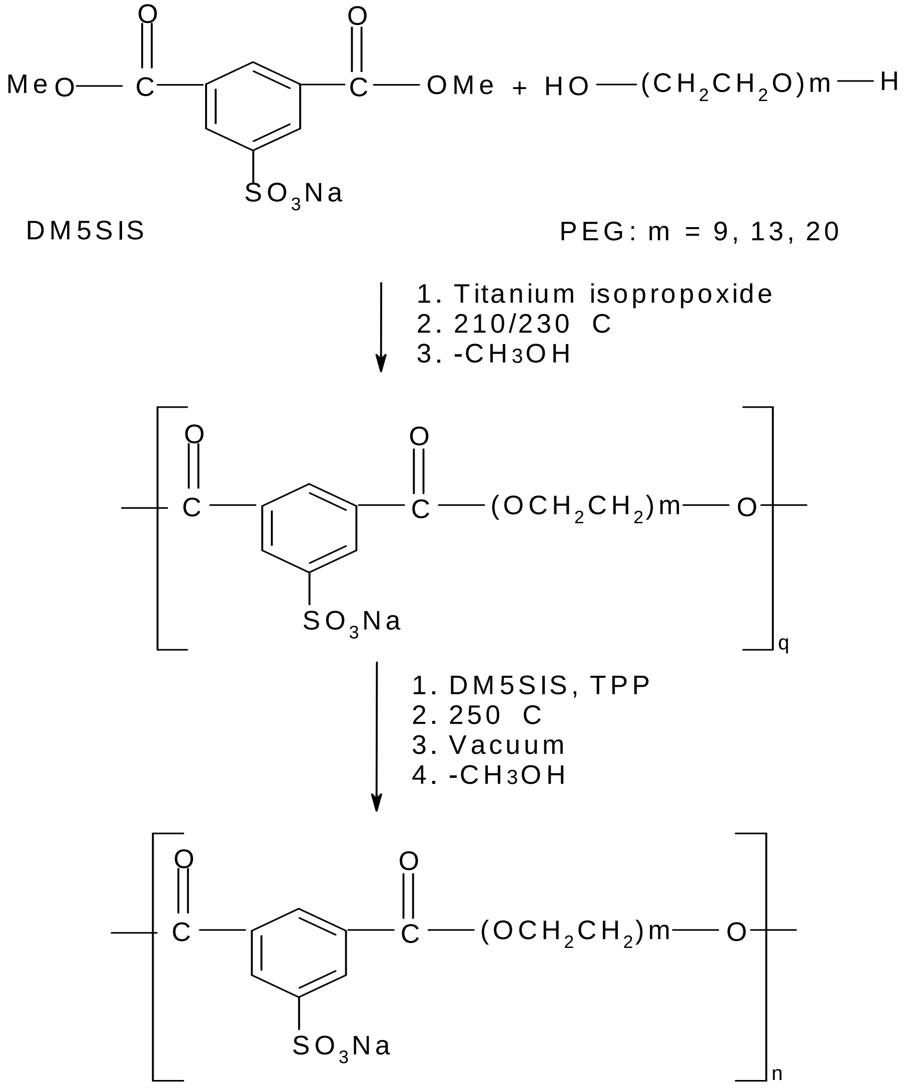
1. Monomers:
   a. poly(ethylene glycol) (PEG)
   b. dimethyl 5-sulfoisophthalate sodium salt (DM5SIS)

2. Two step polycondensation

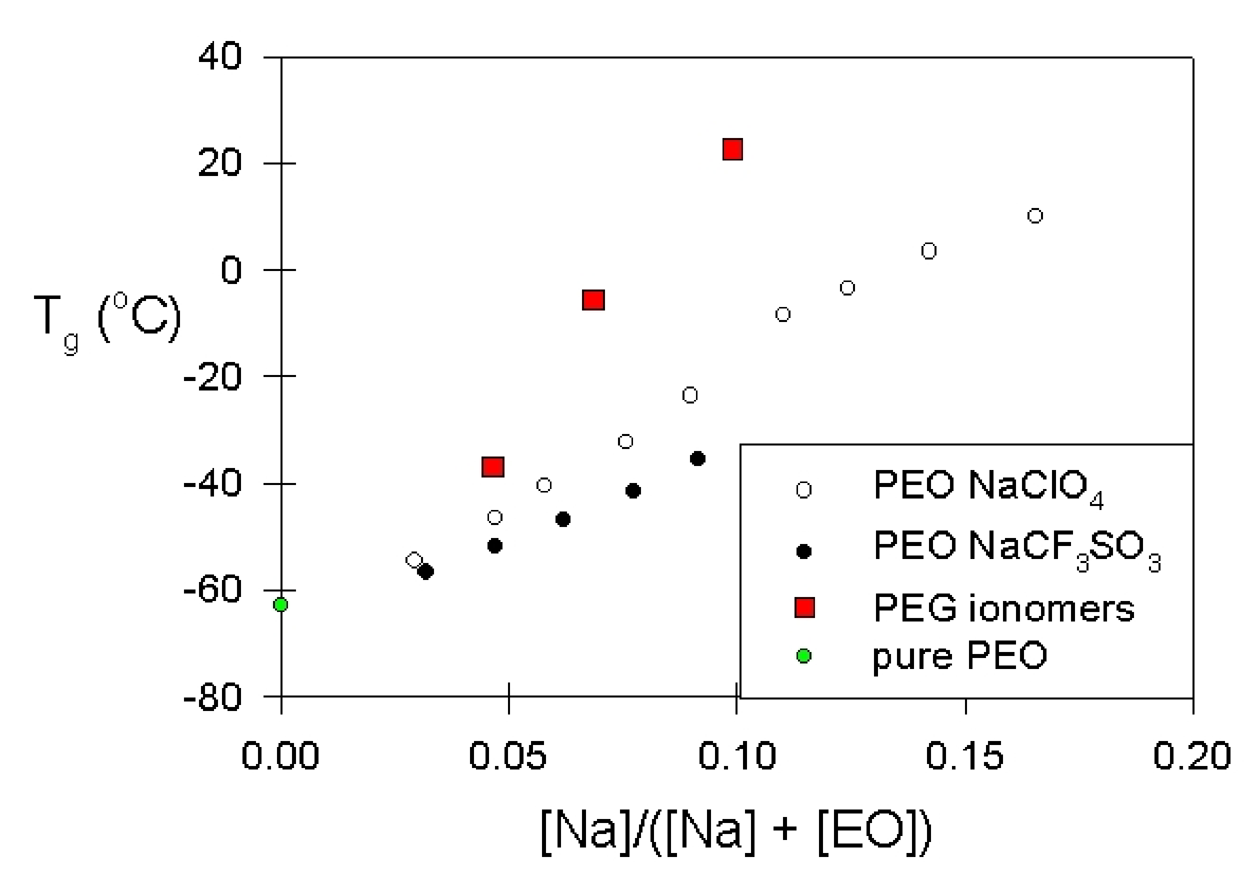
3. End groups: OH and OCH_3

4. Purification by water dialysis

5. Ion-exchange used for the preparation of Li^+ and Cs^+ ionomers

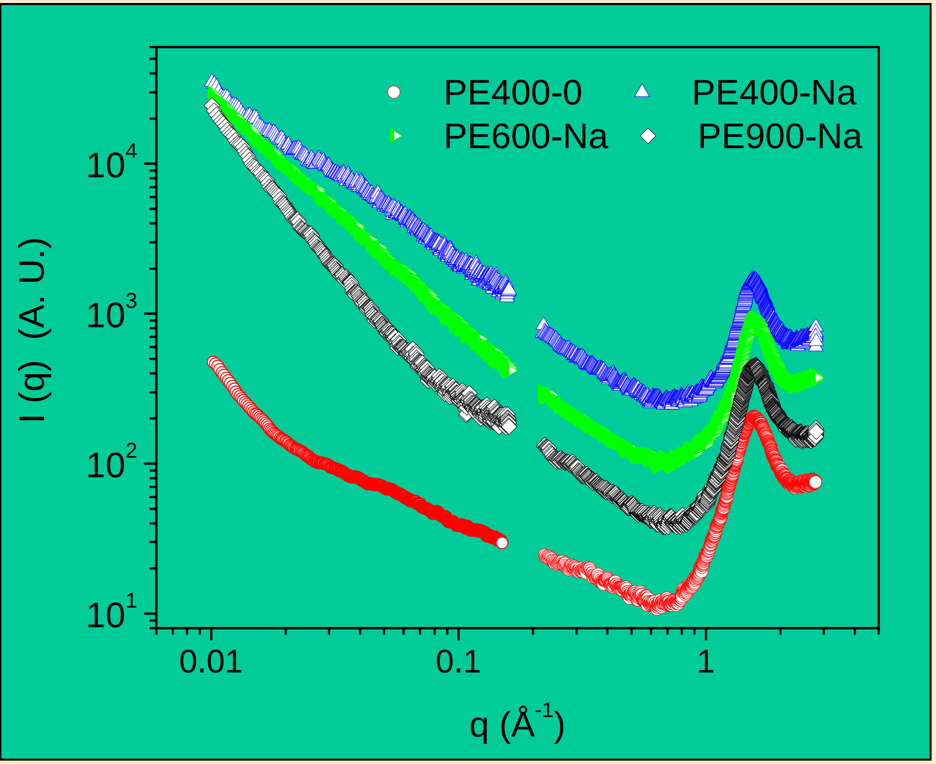


Glass Transition Temperatures



The T_g of PEG-ionomers is much larger than the T_g of the PEO/salt mixtures

SAXS and WAXD of Ionomers



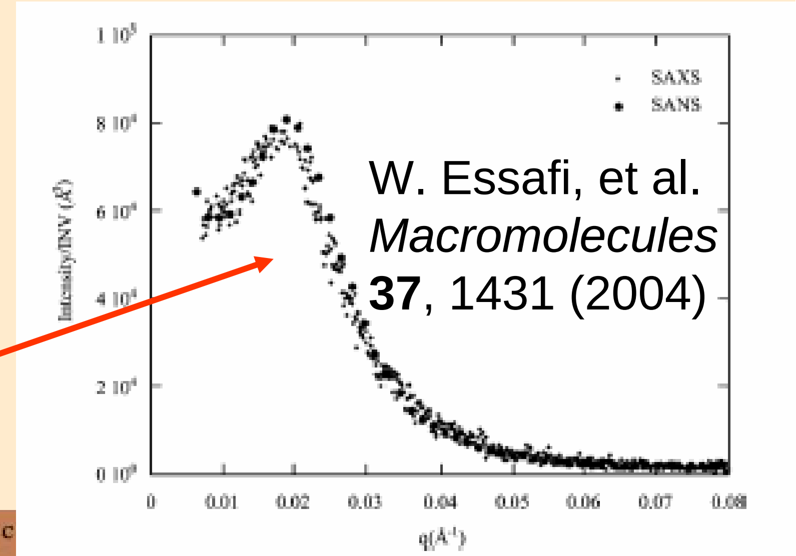
SAXS data: q range 0.01 - 0.16 Å^{-1}

WAXD data: 2θ range from 3 to 40°

The peaks at q = 1.7 Å^{-1} are amorphous halos (also seen in pure PEO)

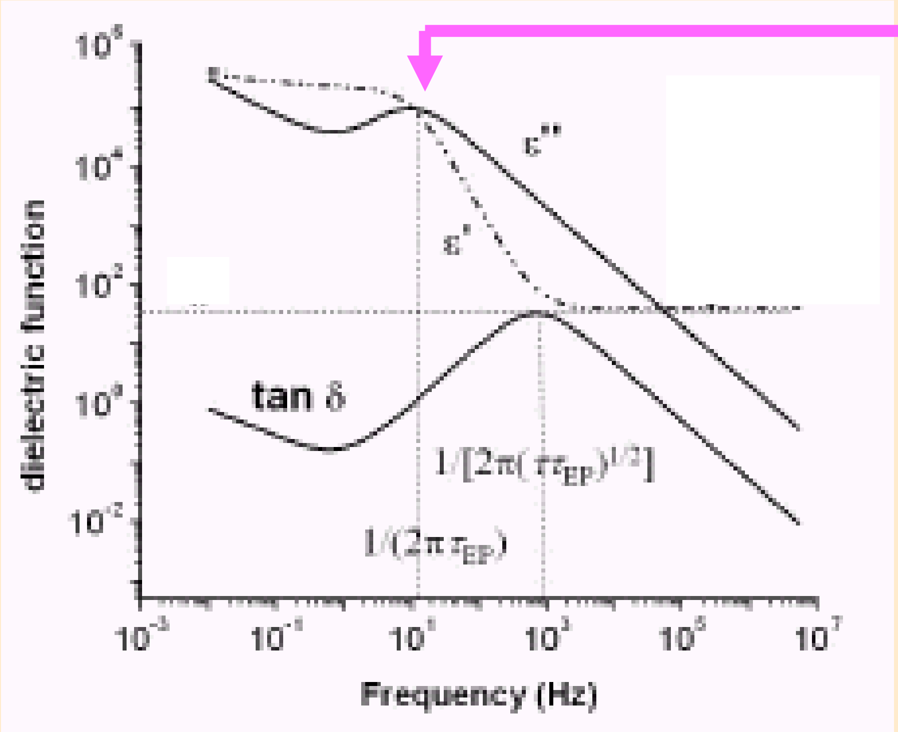
No "ionomer peak" is observed that would suggest clustering.

Ionomers usually have clusters of ions with an ionomer peak showing the distance between clusters

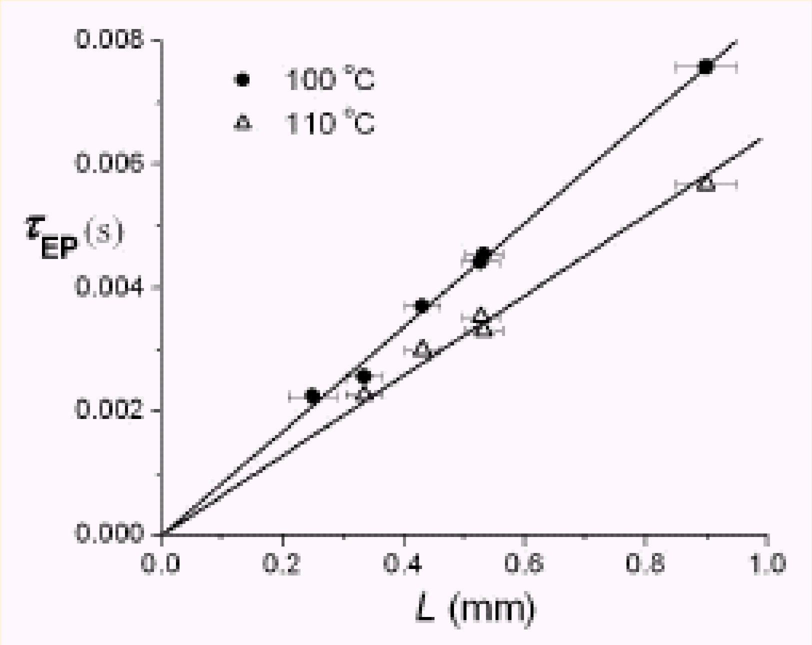


W. Essafi, et al. *Macromolecules* **37**, 1431 (2004)

Extracting Free Ion Concentration and Mobility from EP

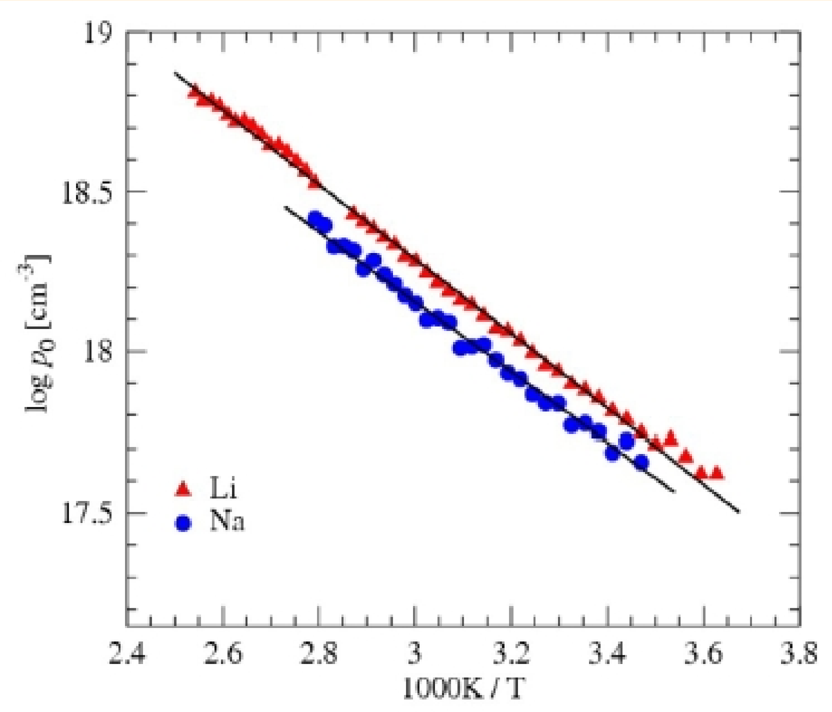


Onset of EP determines the time required for ions to traverse the cell



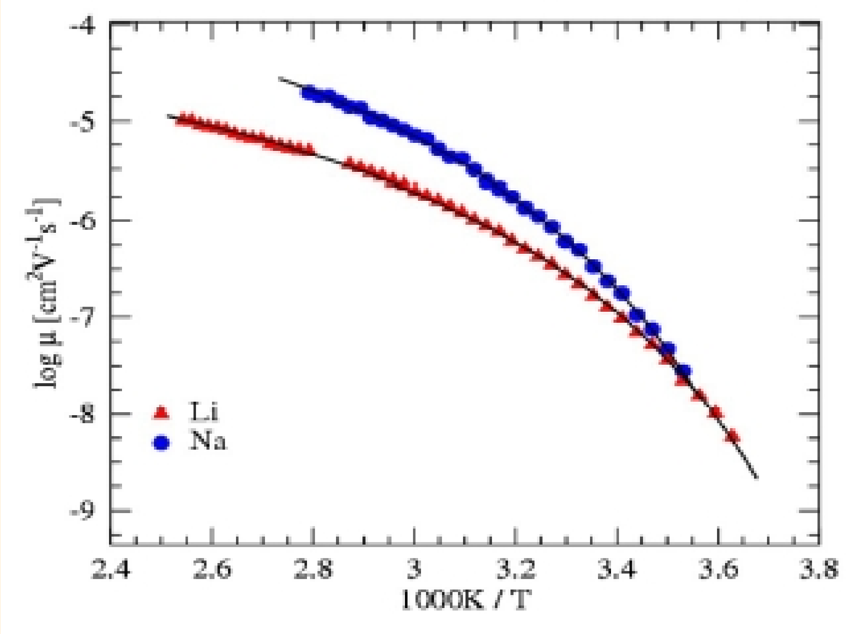
Onset of EP directly measures ion mobility!

Extracting Free Ion Concentration and Mobility from EP



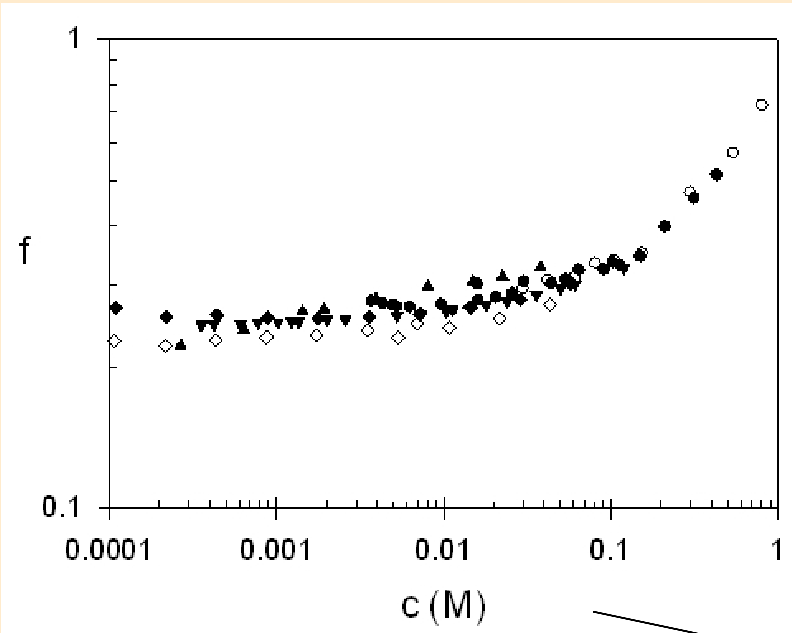
Free ion content is similar for Na^+ and Li^+ ionomers and VERY SMALL 1/10000

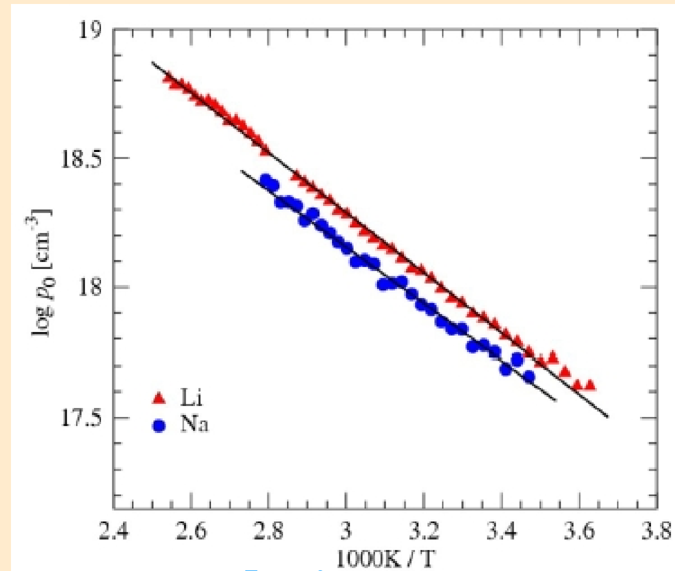
Na^+ ionomer has higher T_g
Mobility has WLF character



Studying single-ion conductors facilitates the separation

Understand What Controls Free Ion Content to Develop New Materials





Piece together: