KATHOLIEKE UNIVERSITEIT
LEUVEN

Polymers and nano-composites

Michael Wübbenhorst

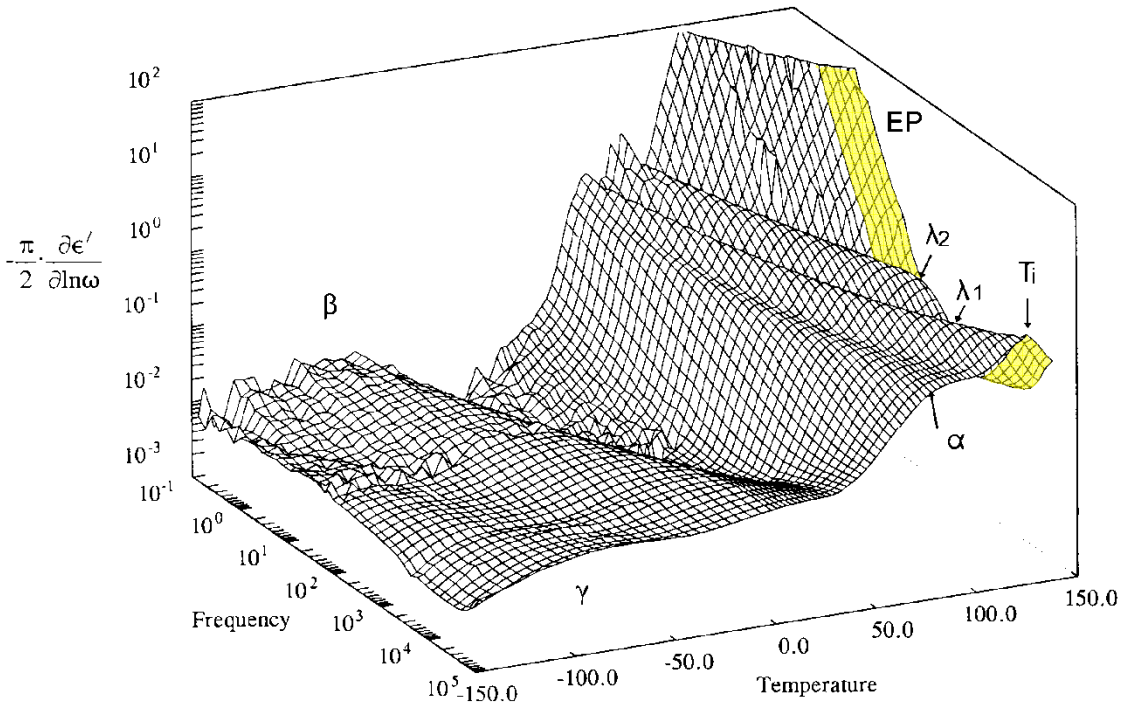
Laboratorium voor Akoestiek en Thermische Fysica, Katholieke Universiteit Leuven
Celestijnenlaan 200D, B-3001 Leuven,
http://fys.kuleuven.be/atf

Tutorial: Novel Applications of Broadband Dielectric Spectroscopy
Rome, 30 August 2009

Introduction

Why DRS to study polymer systems?

1. Polymers show various relaxation phenomena



Introduction - Why DRS to study polymer systems?

2. They are (more or less) insulators

   → Losses due to molecular relaxations >> electrical conduction

3. DRS easily to use and powerful technique (extremely broad dynamic range → **B**roadband **D**ielectric **S**pectroscopy)

4. Many other reasons

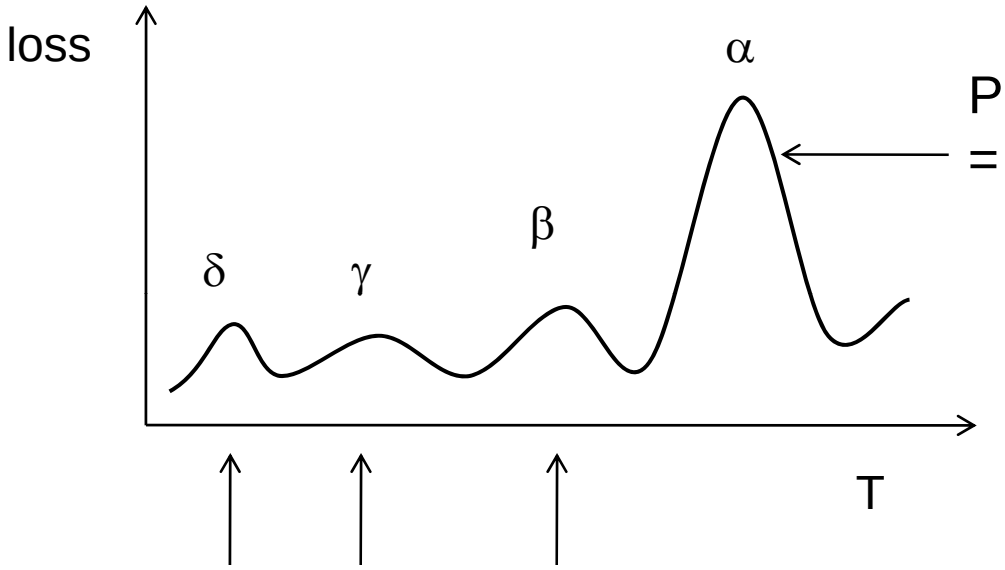
Relaxations in polymer materials

More introduction:

- DRS basic theory (see also previous lectures) [link]
- Various representation of complex dielectric spectra [link]
- **Classification of relaxation processes (classical denotation)**
- Dipoles in polymers (part II of this lecture)

Classification of relaxation processes

Classical denotation



Primary relaxation
= dynamic glass transition

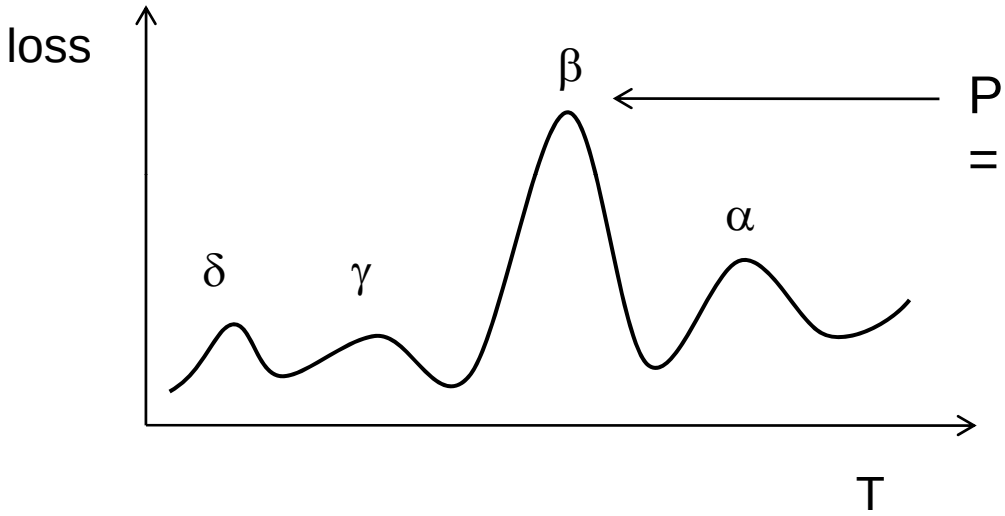
secondary relaxation, usually sub-T_g processes

➔ Widely accepted schema for amorphous polymers

Classification of relaxation processes

Deviations from this “standard” notation

Case 1: some semi-crystalline polymers (PE, PP)



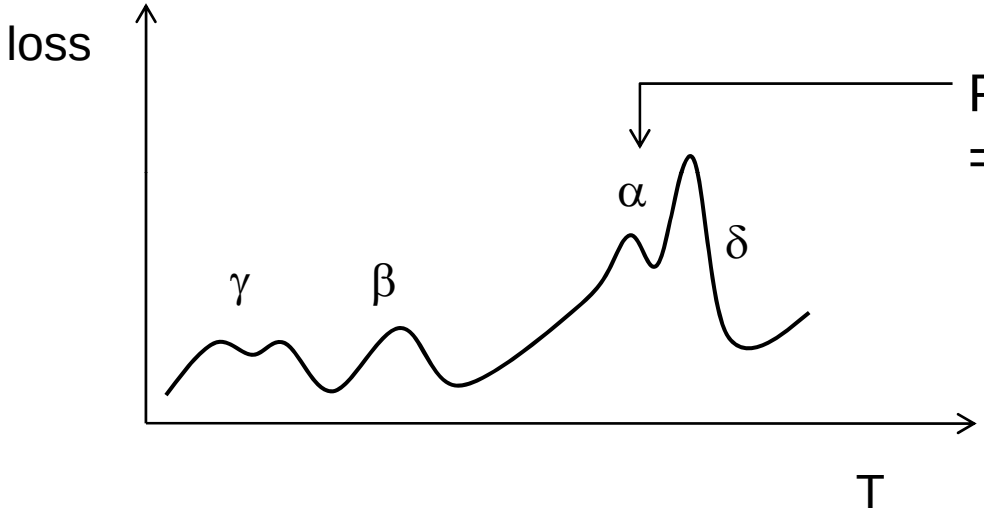
Primary relaxation
= dynamic glass transition

Here, α-relaxation relates to molecular relaxation in crystalline phase (rotator-phase mode)

Classification of relaxation processes

Deviations from this “standard” notation

Case 2: liquid-crystalline polymers



Primary relaxation
= dynamic glass transition

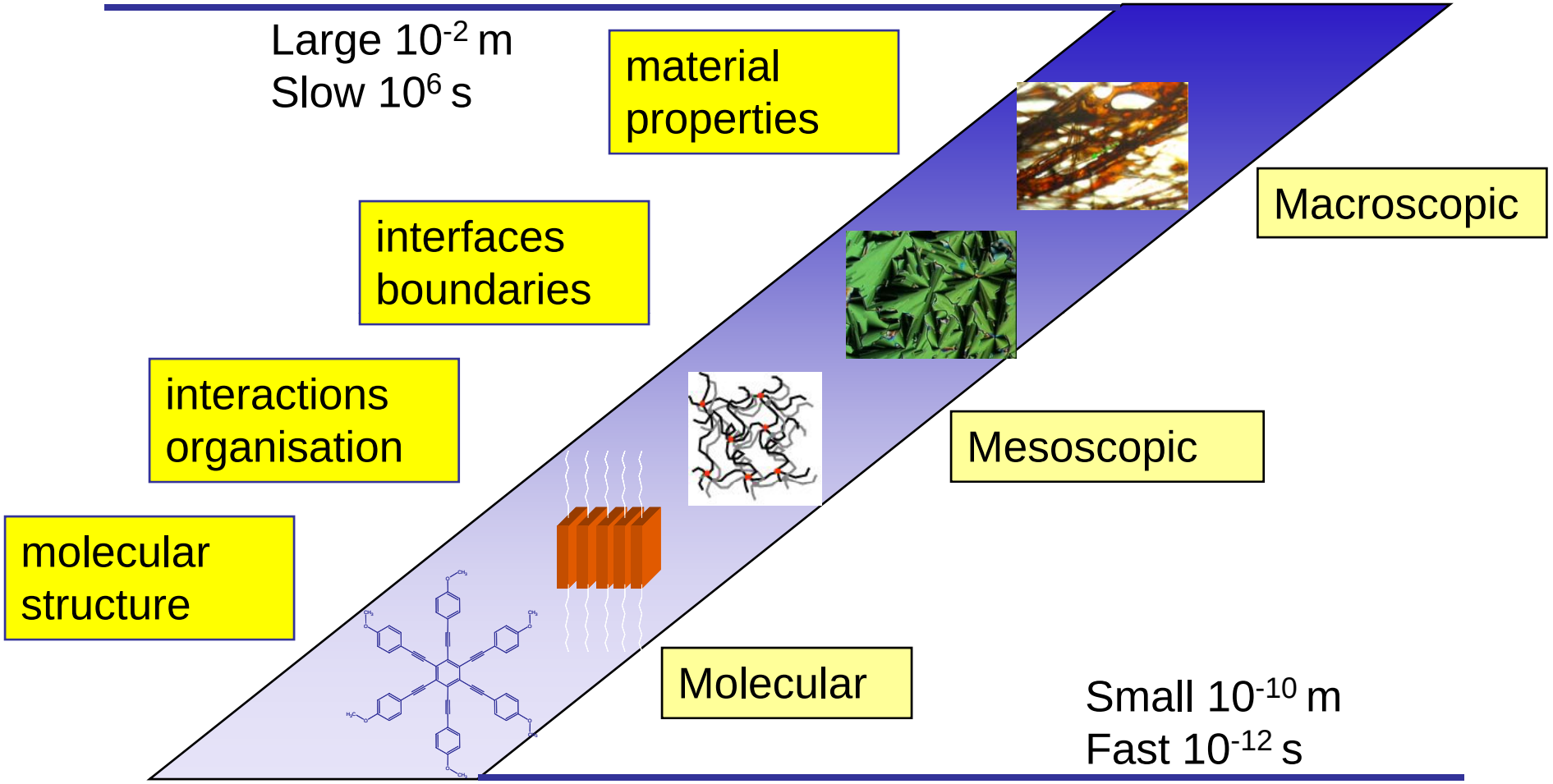
Very confusing denotation, see later…

Outline

- Introduction
- Part 1: Polymer dynamics as “seen” by Dielectric Spectroscopy
  - Length- and time scales of dynamic processes in polymers
  - Relaxation phenomena in various polymer architectures
- Part 2: DRS using dielectric probes
- Part 3: Dielectric relaxations in nano-composites

→ *Separate lecture on Friday*

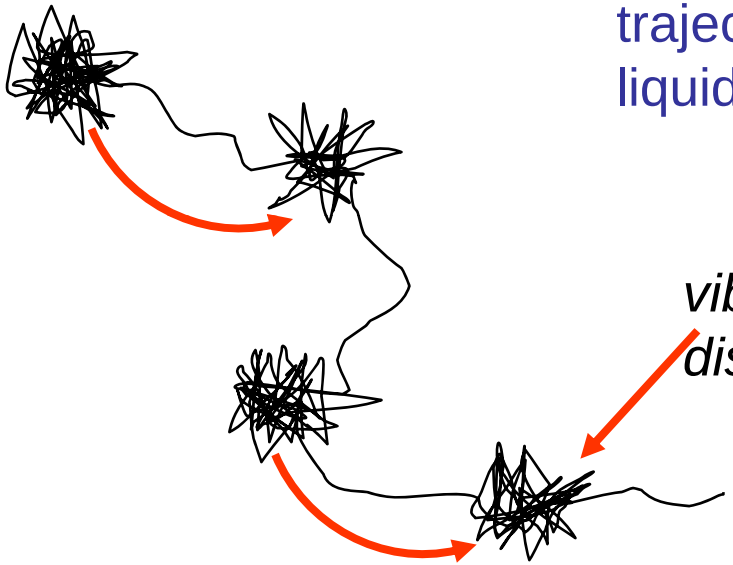
Polymer dynamics: Length- and time scales



KATHOLIEKE UNIVERSITEIT LEUVEN

Polymer dynamics: molecular vibrations

Fast dynamics – molecular vibrations ($t < 10^{-12}s$)



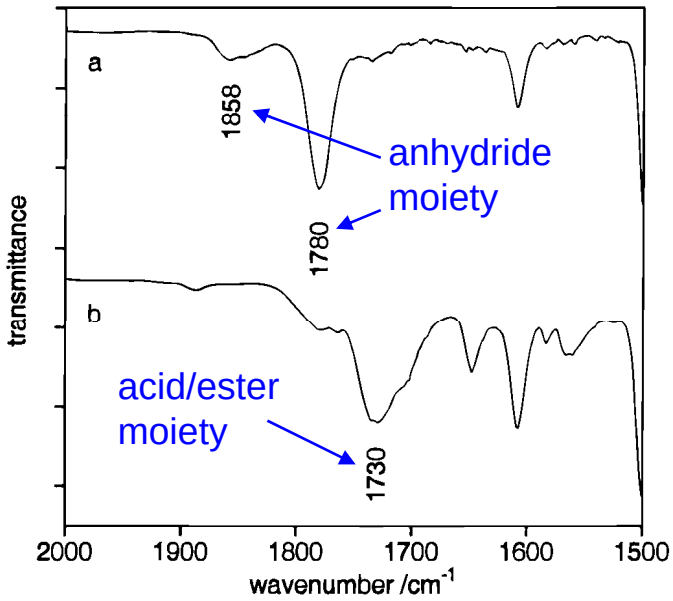
trajectory of a carbon atom in a dense liquid ($T>T_g$)

vibrational displacements around discrete (lattice) positions x

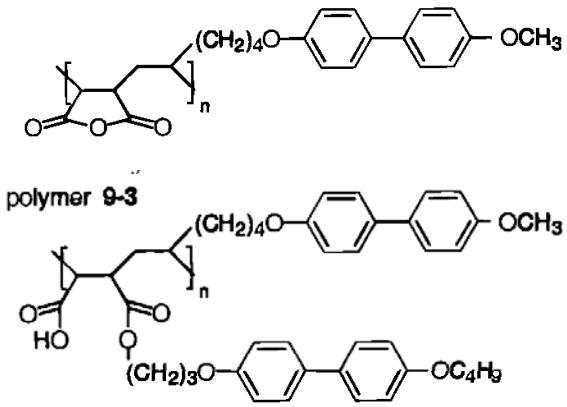
jumps between discrete (lattice) positions → slower than vibrational motions

Polymer dynamics: molecular vibrations

Fast dynamics – molecular vibrations ($t < 10^{-12}s$)



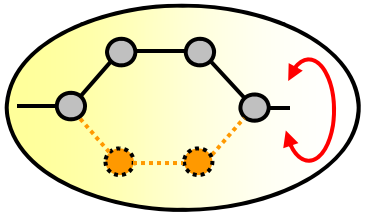
FTIR absorption spectrum of two LC polymers 6 (a) en 9-3 (b).



Polymer dynamics: relaxation processes

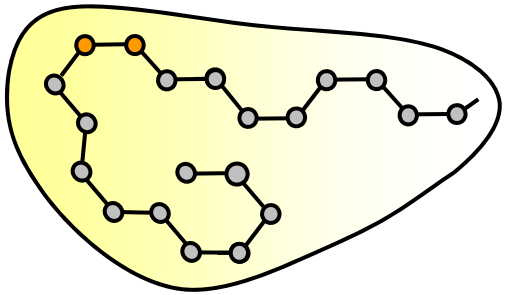
Relation between polymer dynamics and dielectric relaxations

local motions, e.g.
simple bond rotations



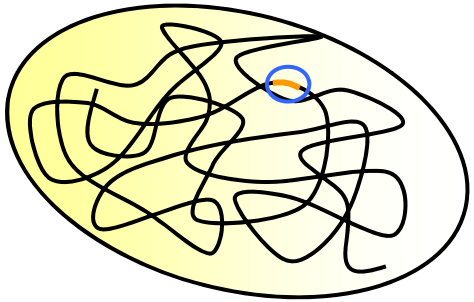
< 1 nm

segmental motions
(dynamic glass transition)



$2 < \xi < 10$ nm

chain relaxation
(Rouse, Reptation)

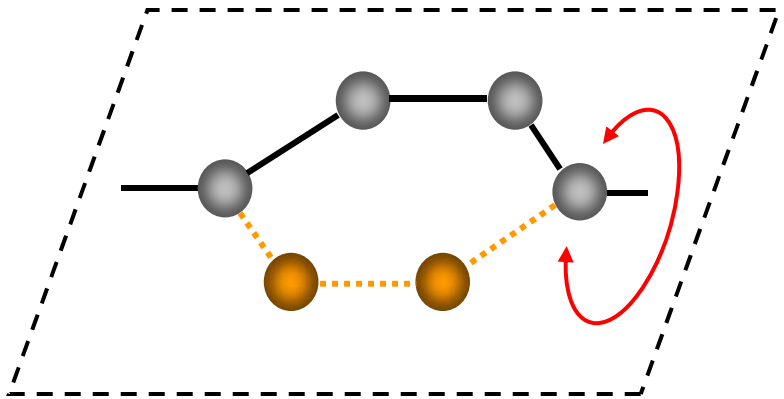


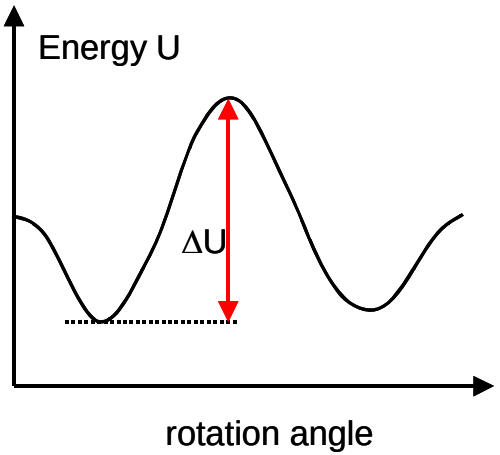
$10 < \xi < 200$ nm

increasing relaxation time, characteristic length scale

1. Local Relaxation Processes

Local processes ($\tau > 10^{-12}$s)

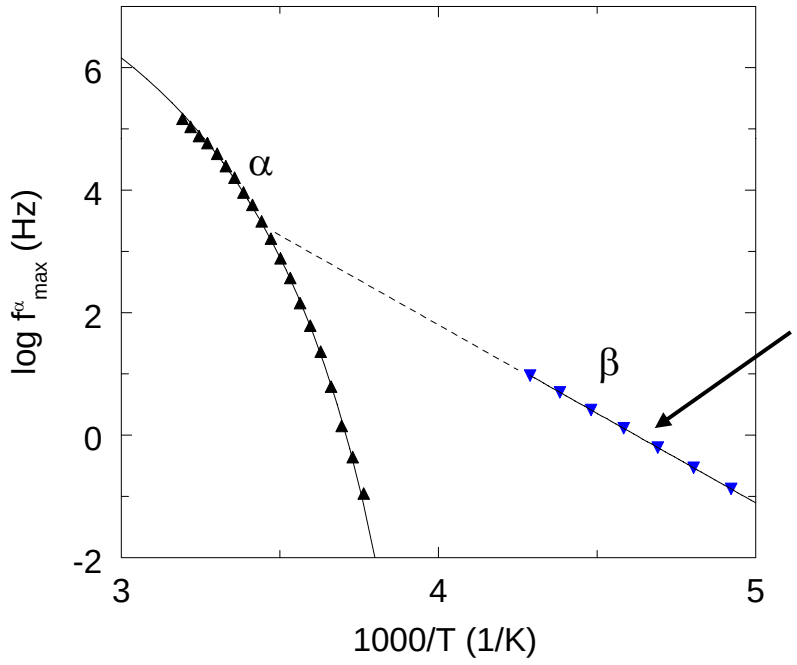




- discrete rotations of bonds resulting in **local conformational changes**
- possible in liquid, amorphous solid and crystalline state

1. Local Relaxation Processes

Temperature dependence of relaxation time: Arrheniuslaw
→ thermal activation of τ



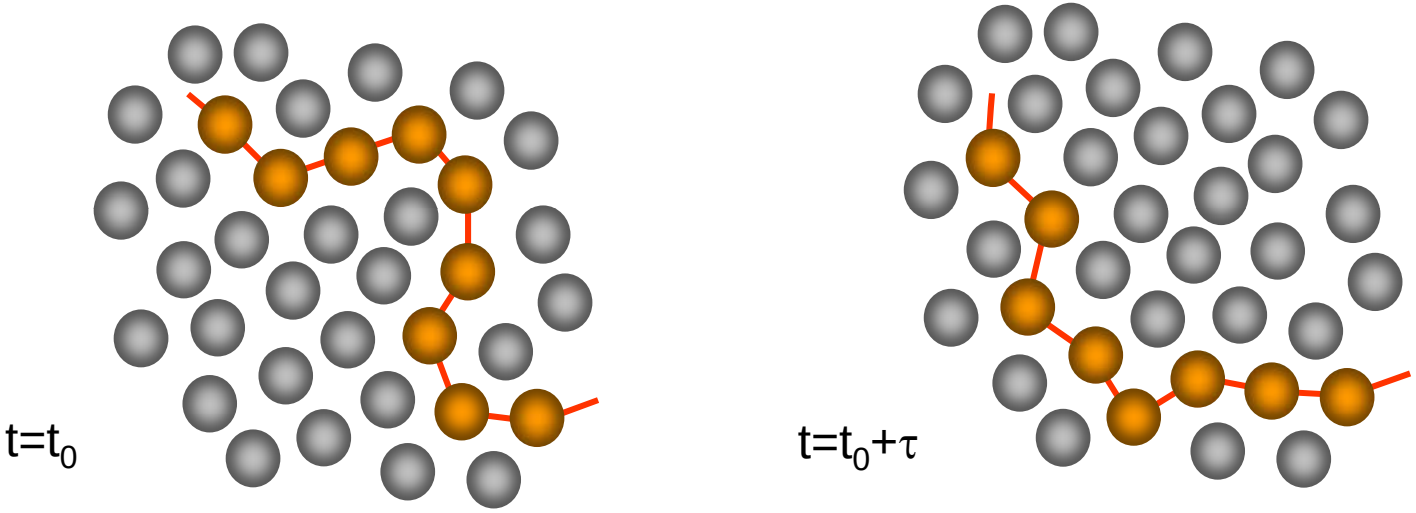
$$\tau(T) = \tau_\infty \exp\left(-\frac{E_a}{kT}\right)$$

β-process

T-dependence $\tau(T)$ of α and β-process in a poly(ether ester)
[Mertens et al. 1999, pol. 1a]

2. Segmental dynamics – dynamic glass transition

Medium slow – fast dynamics : glass transition (10^{-4} s < τ < 10^{-10}s)

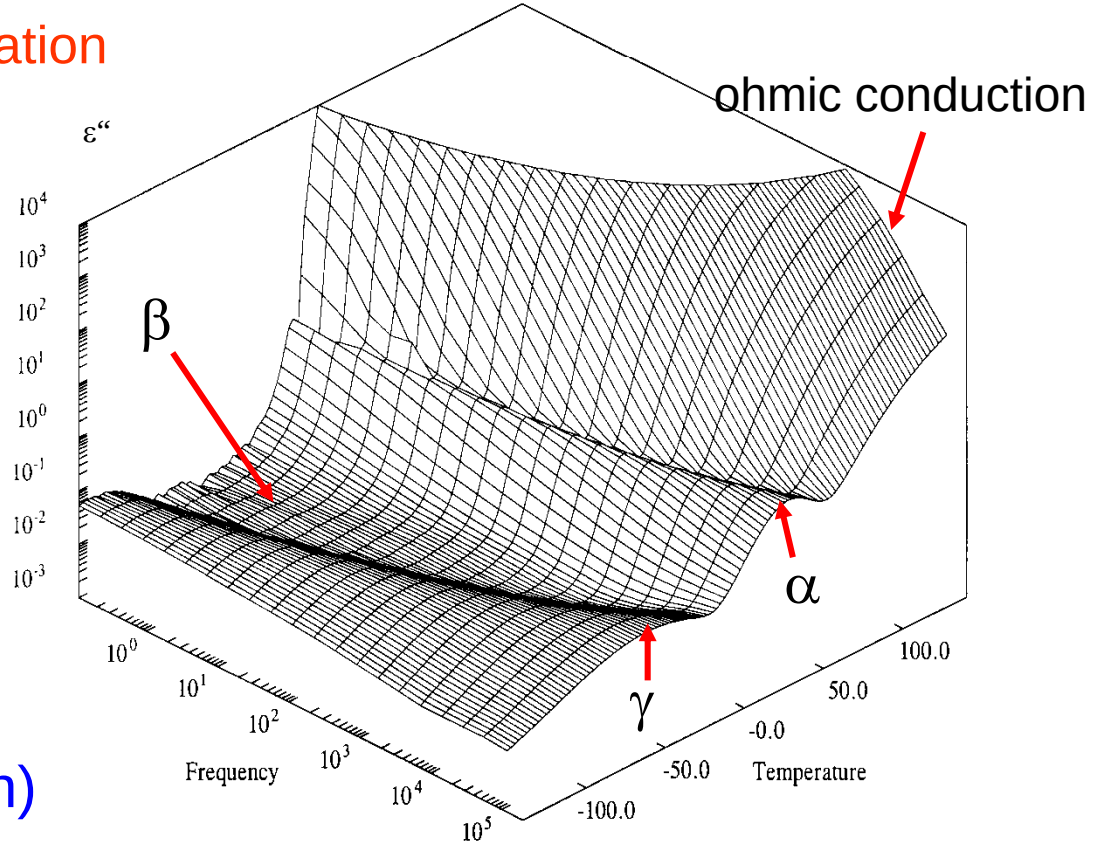


cooperative motions of a few monomer units (polymer segments) at $T>T_g$

2. Segmental dynamics – dynamic glass transition

typical f-T-dependence of an amorphous polymer

α-process = main-relaxation



segmental relaxations
(dynamic glass transition)

2. Segmental dynamics – dynamic glass transition

Curved τ(T) vs. 1/T dependence: Vogel-Fulcher-Tammann law (VFT)

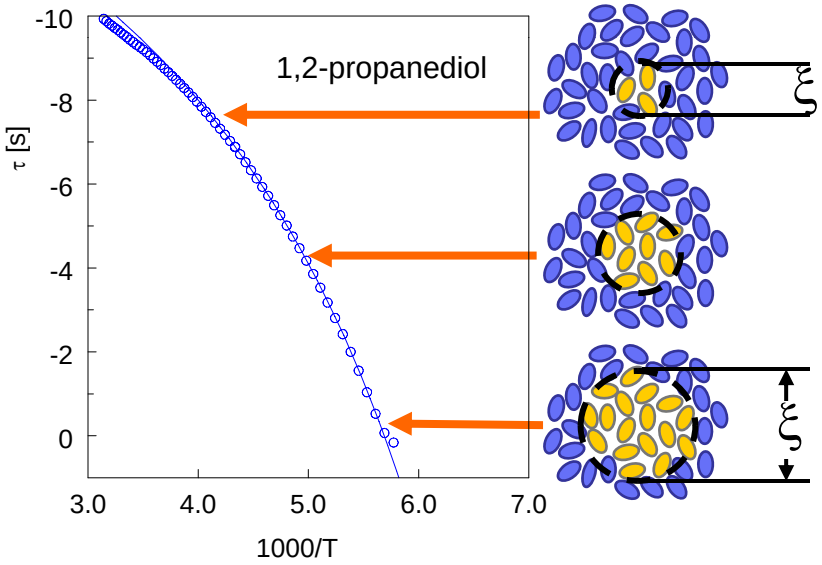
$$\tau(T) = \tau_\infty \exp\left(-\frac{E_V}{k(T - T_V)}\right)$$

- typical for dynamics of supercooled liquids (glass-forming materials) : α-relaxation
- glass transition temperature T_g usually T_V + 50K

WLF ←→ VFT equation

Rationalization of VFT law:

Temperature dependent length scale ξ=ξ(T) of cooperatively rearranging regions (CRR) (Adam and Gibbs, 1965)



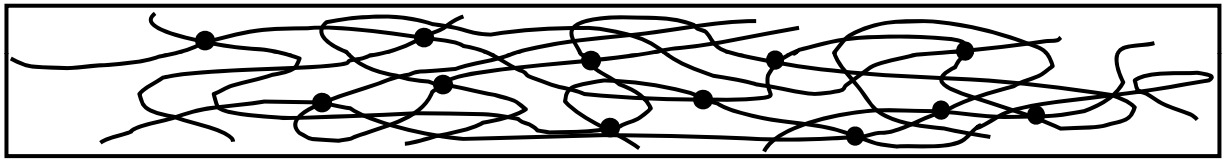
KATHOLIEKE UNIVERSITEIT LEUVEN

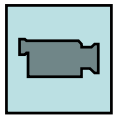
3. Whole chain dynamics

Slow dynamics involving reconfiguration of whole chains → viscosity

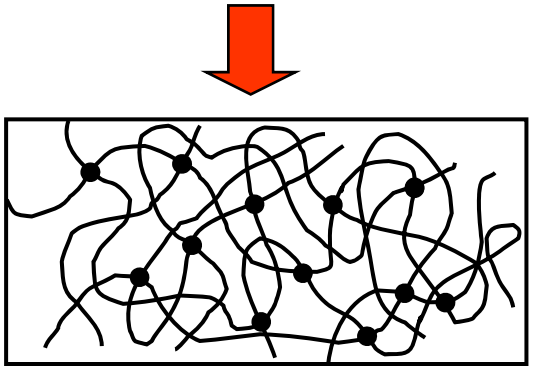
For very long chains (M_w > 20000g/mol) high morelaxation of an entanglement network

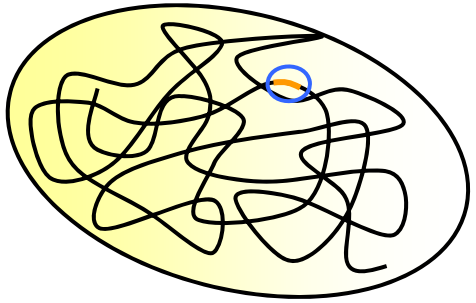
PMMA film, 10x stretched just above T_g





heating again to $T > T_g$: retraction of the film to original size

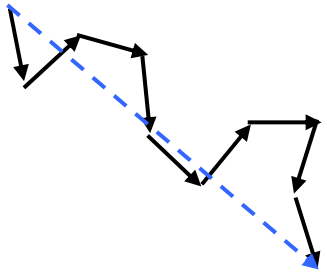


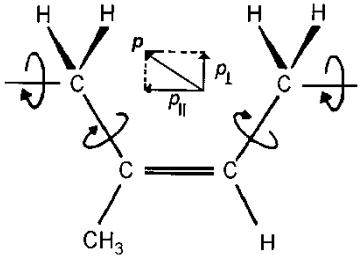


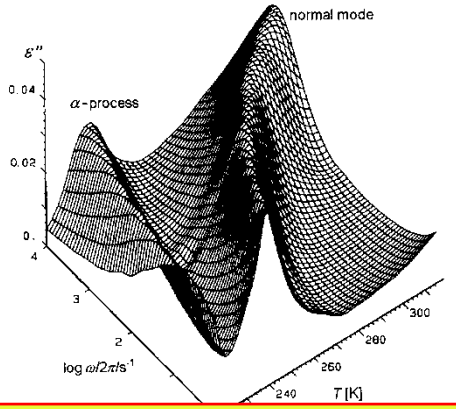
$10 < \xi < 200$ nm

3. Whole chain dynamics – Normal relaxation

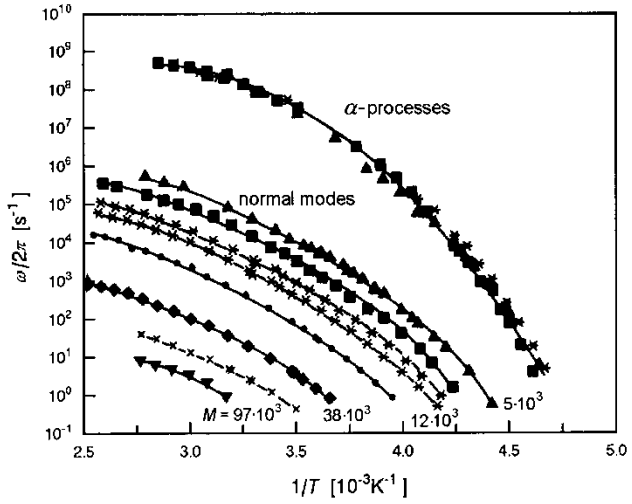
Normal relaxations, e.g. cis-polyisoprene







End-to-end vector fluctuations cause dielectric normal relaxation
→ chain relaxation → self-diffusion of whole polymer chain



τ_{nm} depends on molecular mass *M*

$$\tau \propto M^{\nu} \qquad \nu = 3.7 \text{ for } M > 10^4 \qquad \nu = 2 \text{ for } M < 10^4$$

KATHOLIEKE UNIVERSITEIT LEUVEN

Relaxation phenomena in various polymer architectures

Numerous polymer architectures known, e.g.:

- Linear chain polymers (Polyolefines, PS, PC, PMMA…)
- Side-group polymers
- (hyper)branched polymers, polymer networks
- Copolymers, e.g. random and block-CP's

Classification based on functionality:

- Liquid-crystalline polymers
- Polyelectrolytes, Polymer electrolytes
- Ferro-, piezo-, pyroelectric and NLO-active polymers
- Polyamphiphilics….

Relaxation Processes in specific polymers

Linear polymers, flexible:

- poly(ethylene) - PE
- poly(dimethylsiloxane) – PDMS
- poly(ethylene oxide)
- Bisphenol-A PC

Linear polymers, (semi) stiff:

- aromatic polyesters (PET, PEN)
- Vectra

Side-group polymers

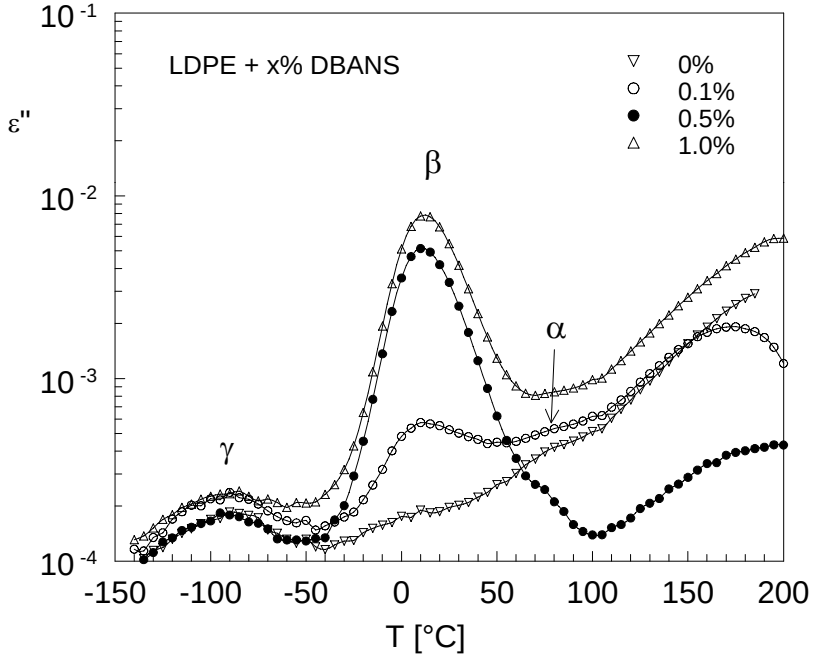
- polystyrene – PS
- poly(methyl methacrylate) – PMMA
- polysiloxane, functionalized
- aliphatic polycarbonates

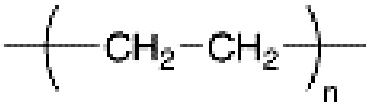
These architecture might result in

- Amorphous polymers
- Semi-crystalline polymers
- Liquid crystalline polymers

Linear, flexible polymers

Low density polyethylene (LDPE)





T_g: ~ -35°C

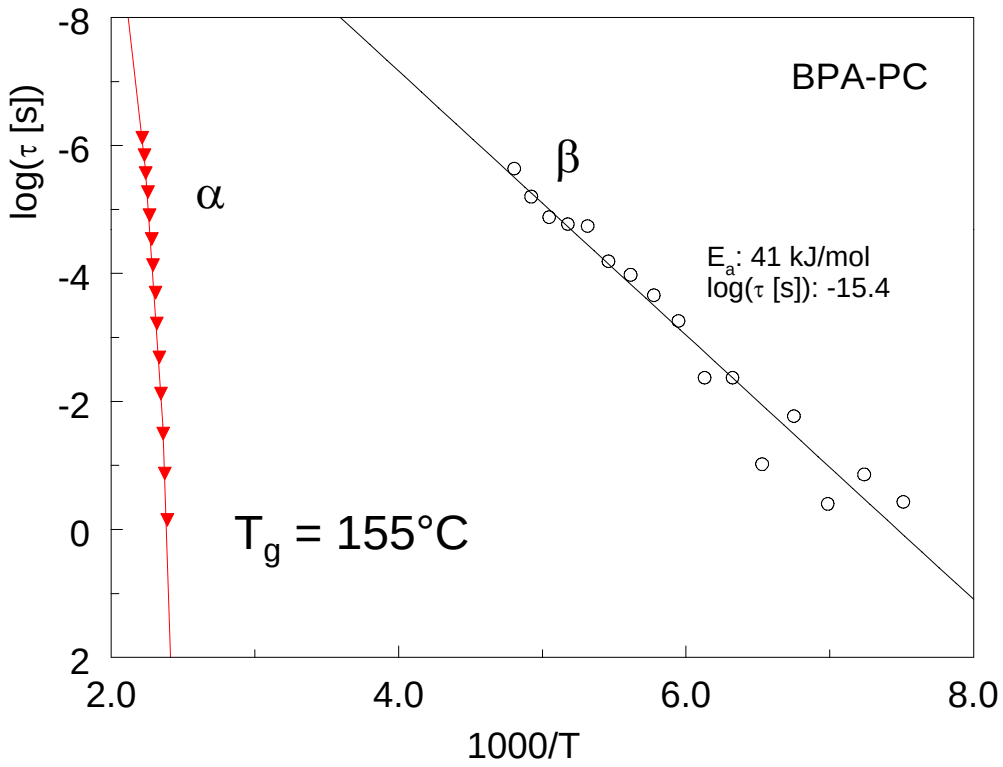
no intrinsic dipole moment
→ only weak dielectric relaxations due to

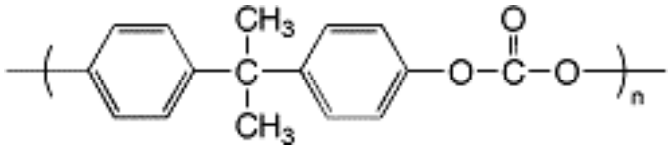
- partial oxidation (C=O)
- dielectric probes

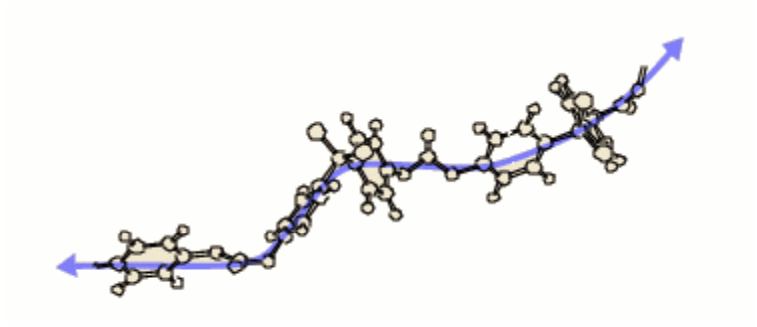
Linear, flexible polymers

Amorphous, linear flexible polymers

Bisphenol A Polycarbonate



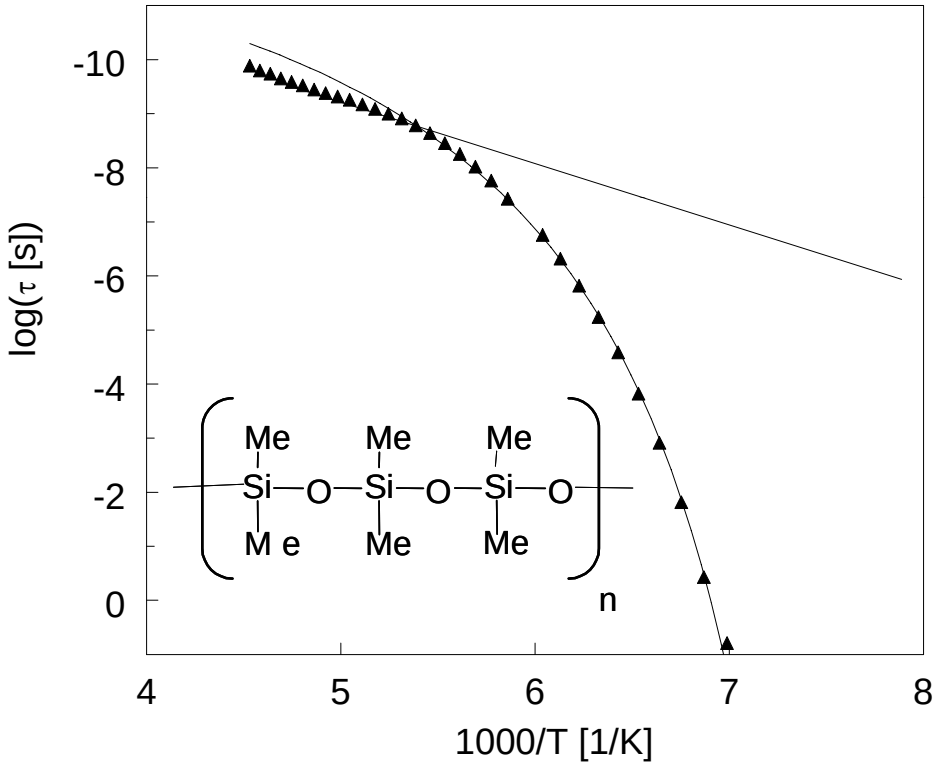




β-relaxation involves several backbone bonds

Amorphous, linear flexible polymers

PDMS

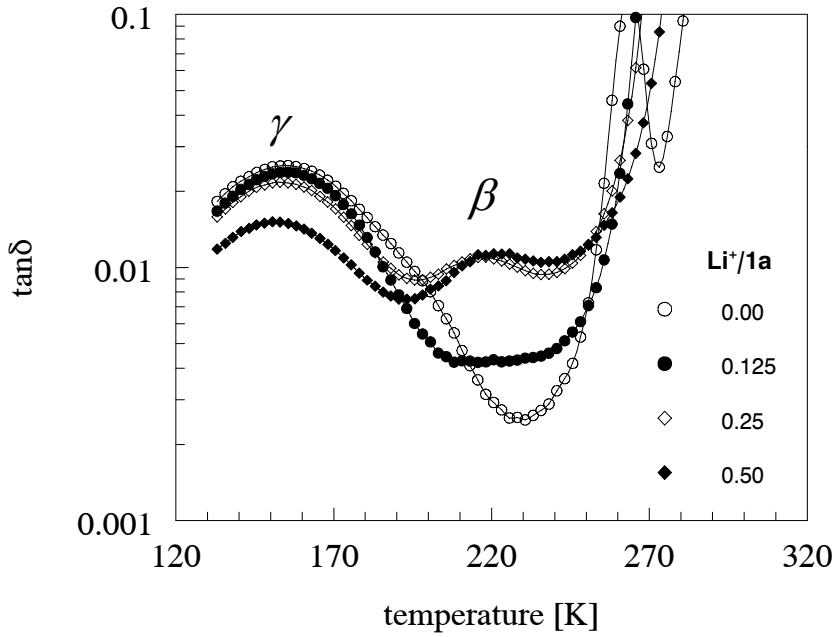


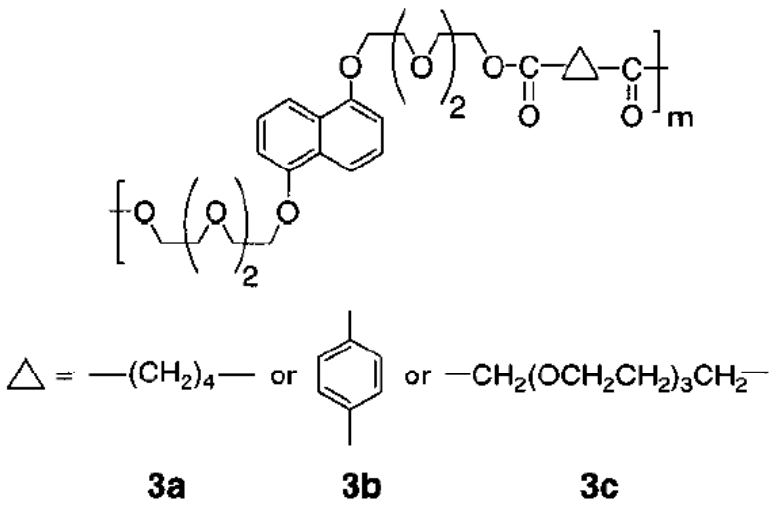
No explicite dielectric β-process found

T_g = - 130°C

Amorphous, linear flexible polymers

Poly(ether esters)

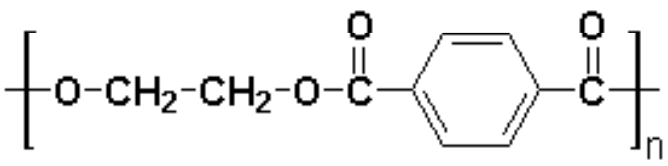


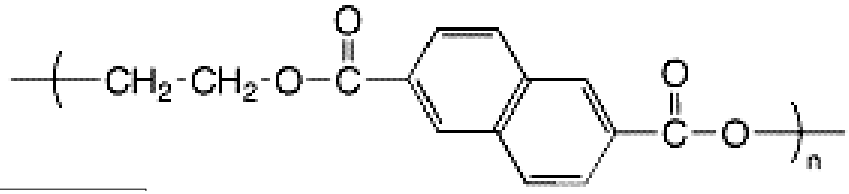


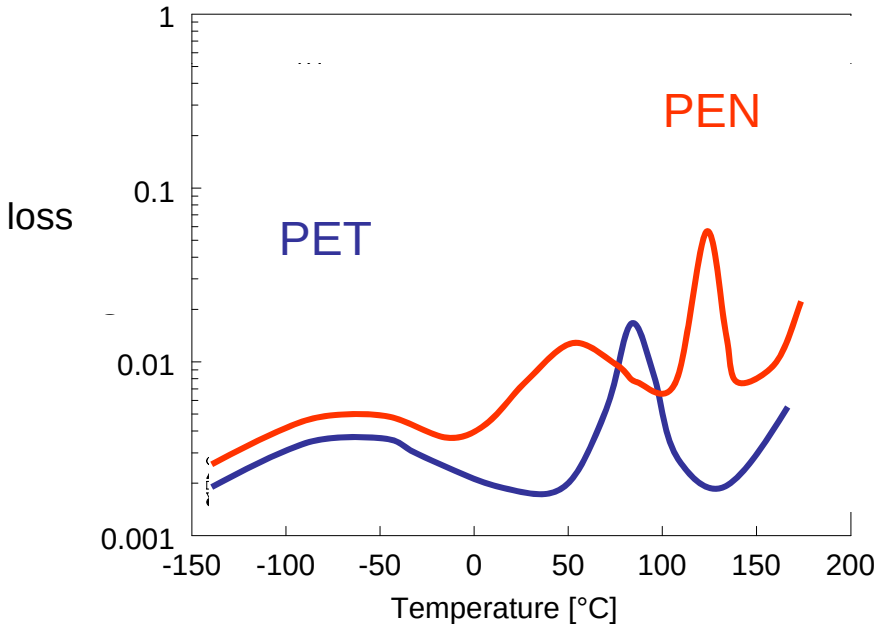
γ-process: twist motion of ether groups

Linear, semi-stiff polymers

Aromatic polyesters, PET and PEN - semicrystalline



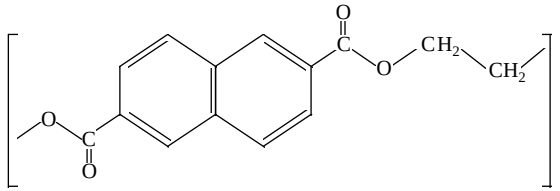


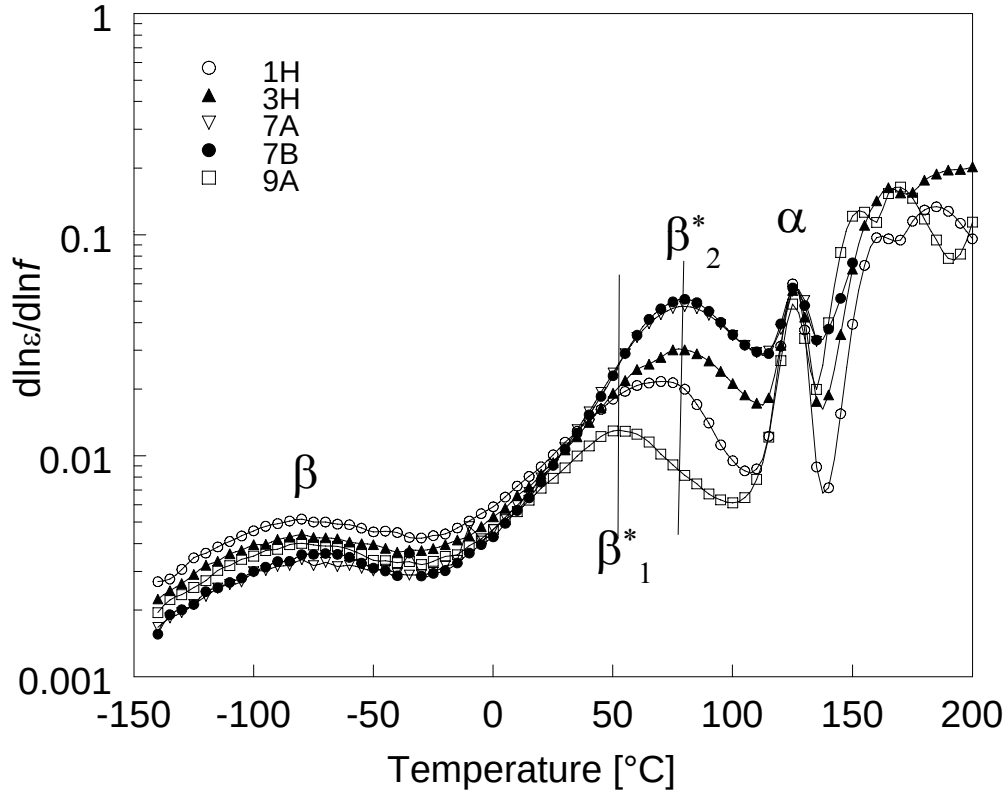


PEN:
additional process
between α and β-relaxation

Linear, semi-stiff polymers

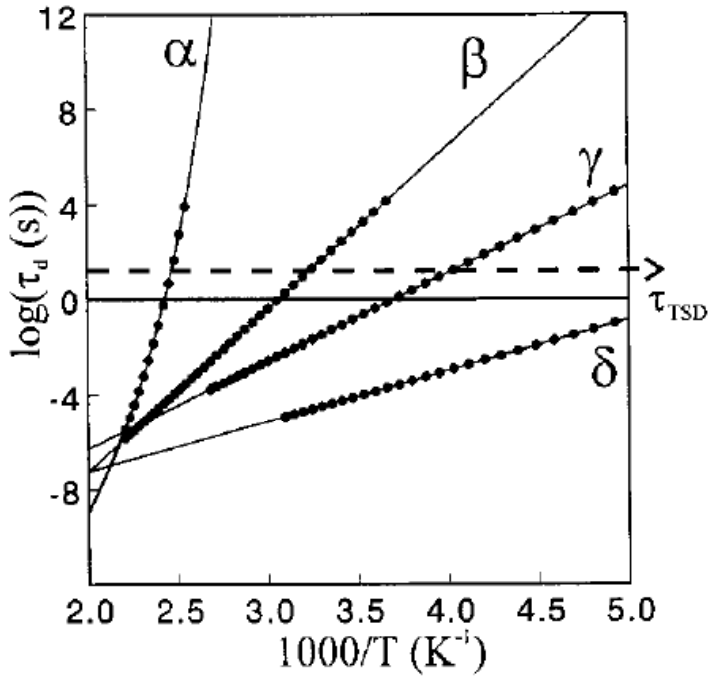
Aromatic polyesters, PET and PEN





Linear, semi-stiff polymers

Aromatic polyesters (3) – Vectra B950

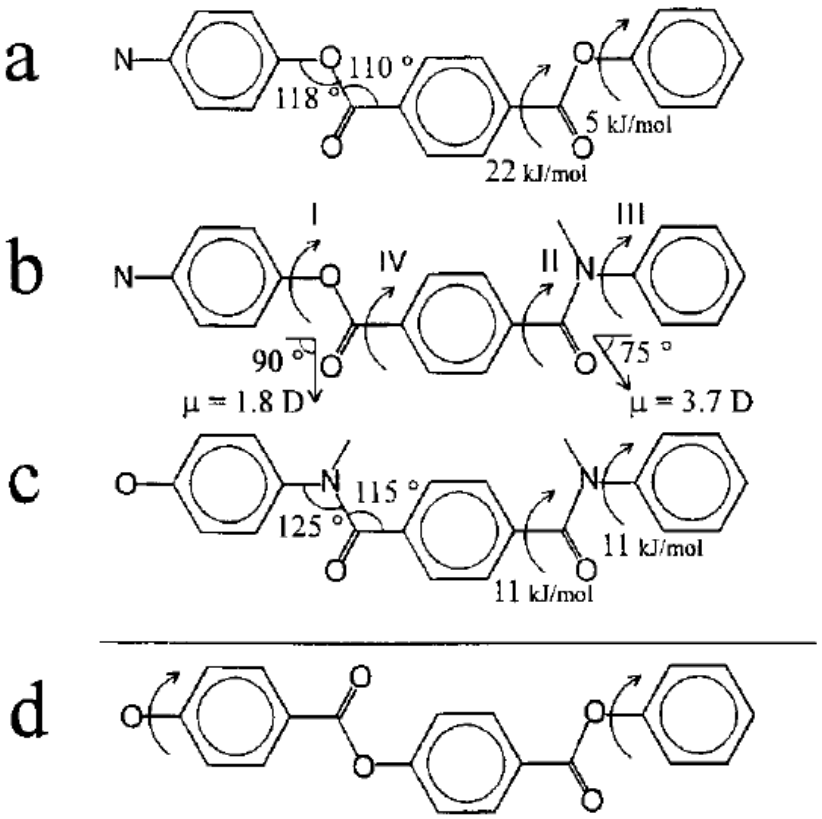


	E_a [kJ/mol]	$\log(\tau_0)$
δ	**41**	**-11.5**
γ	**71**	**-13.7**
β	131	-21.0

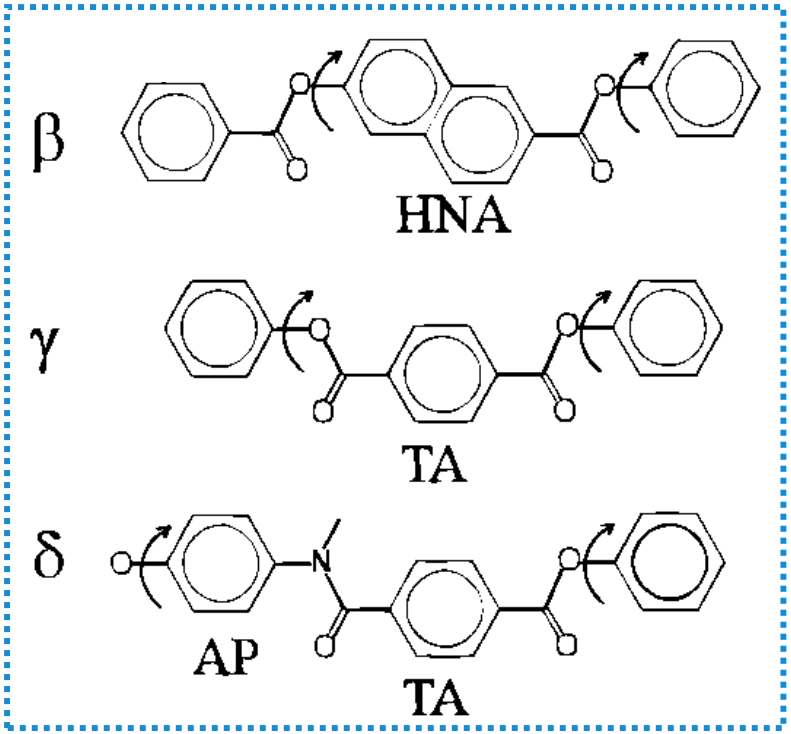
3 Arrhenius processes,
but only 2 of them are local relaxations

Linear, semi-stiff polymers

Analysis of bond rotation contributions



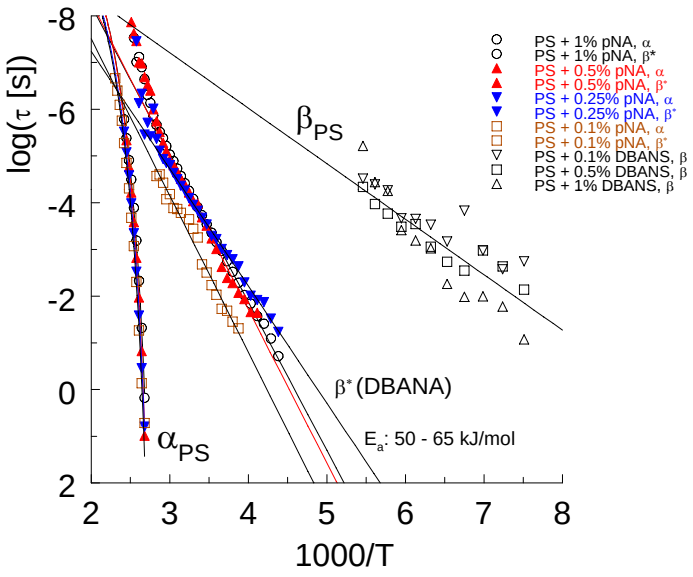
Vectra B950

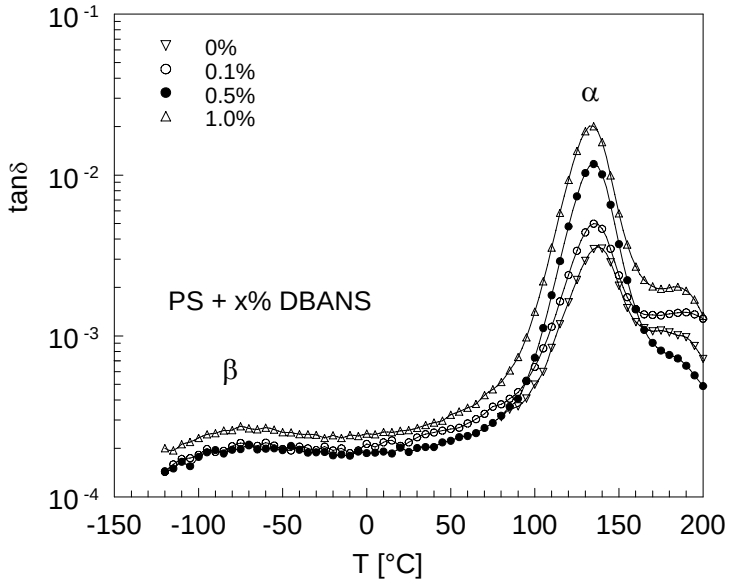


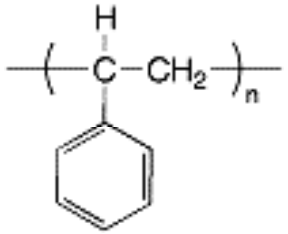
→ various crankshaft motions

Amorphous, linear side-group polymers

Atactic Polystyrene



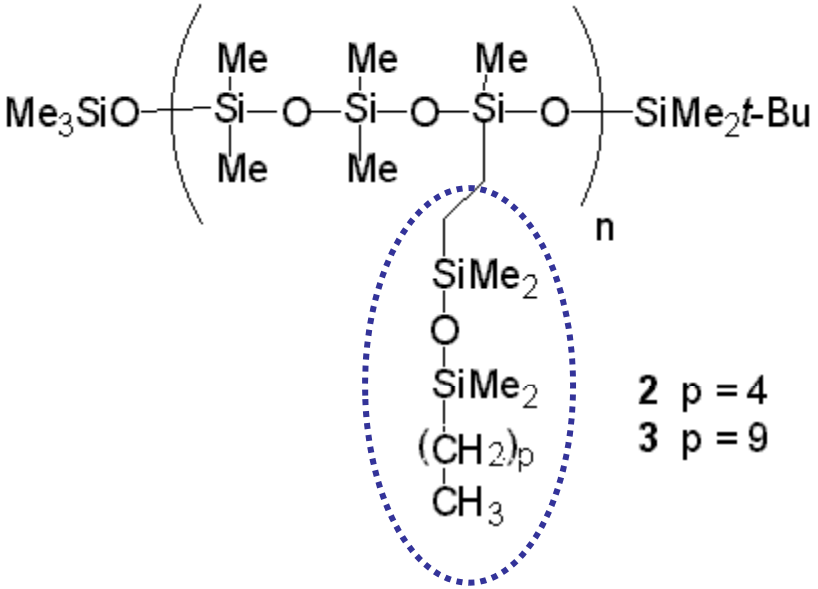


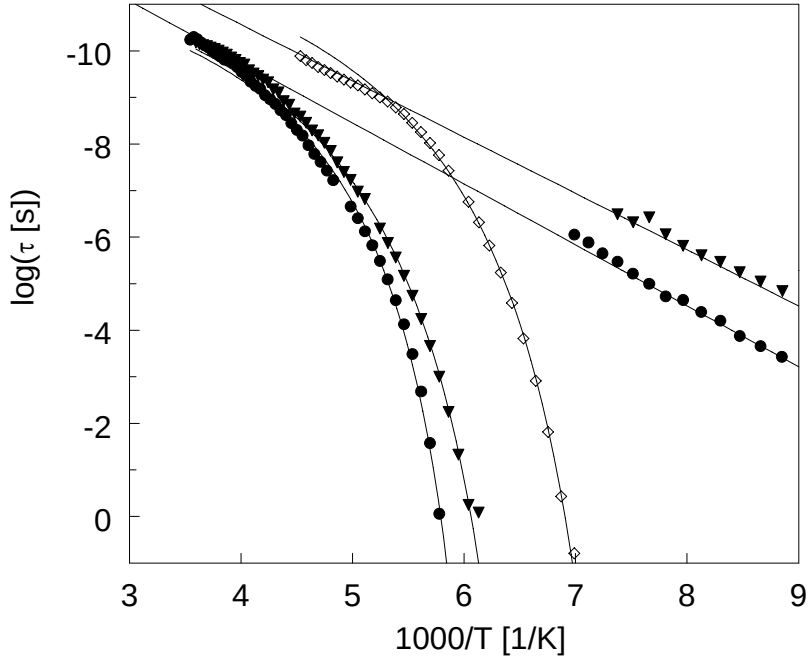


β-process: E_a ~ 25 kJ/mol
crankshaft mechanism

Amorphous, linear side-group polymers

Side-group polysiloxane

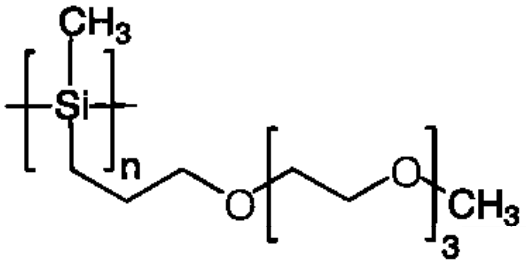


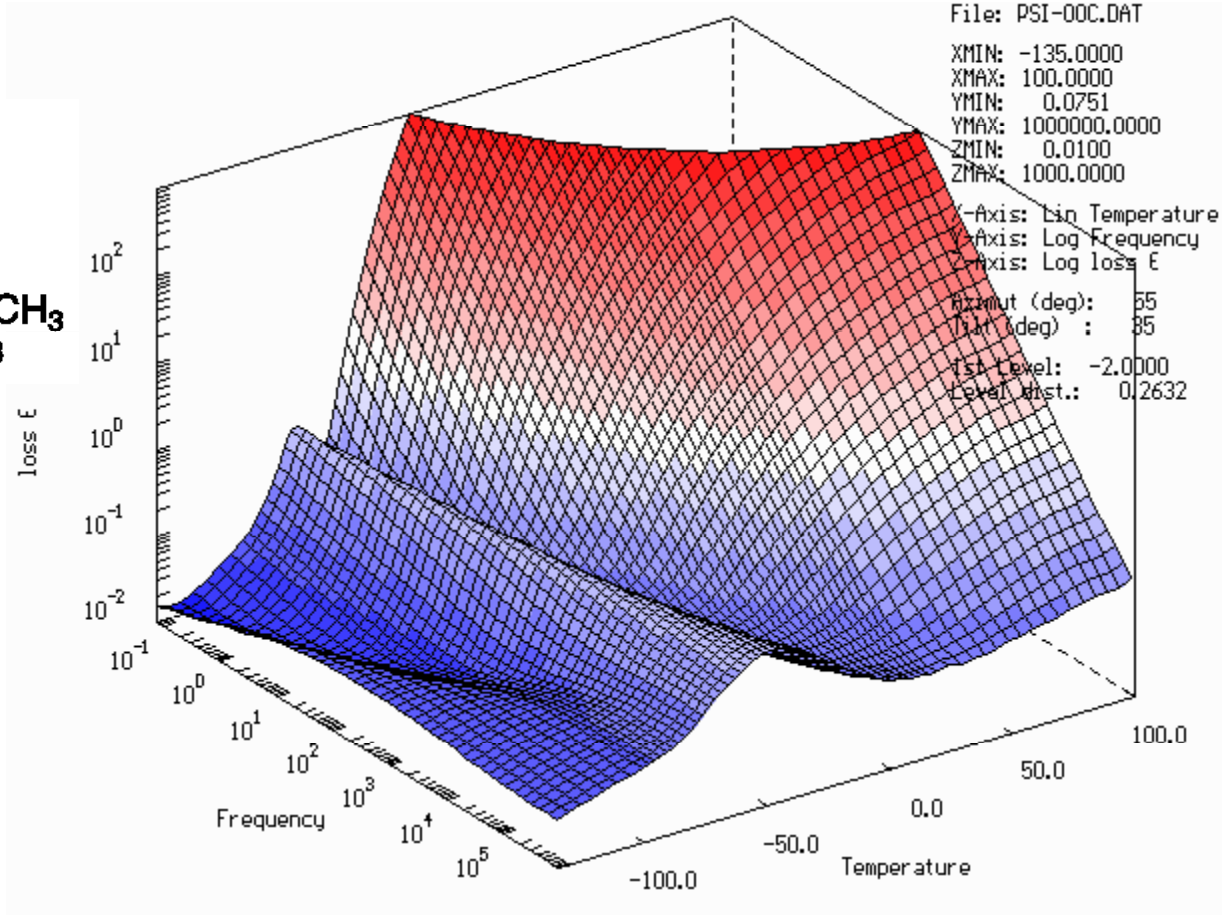


β-process: E_a ~ 20 kJ/mol

Amorphous, linear side-group polymers

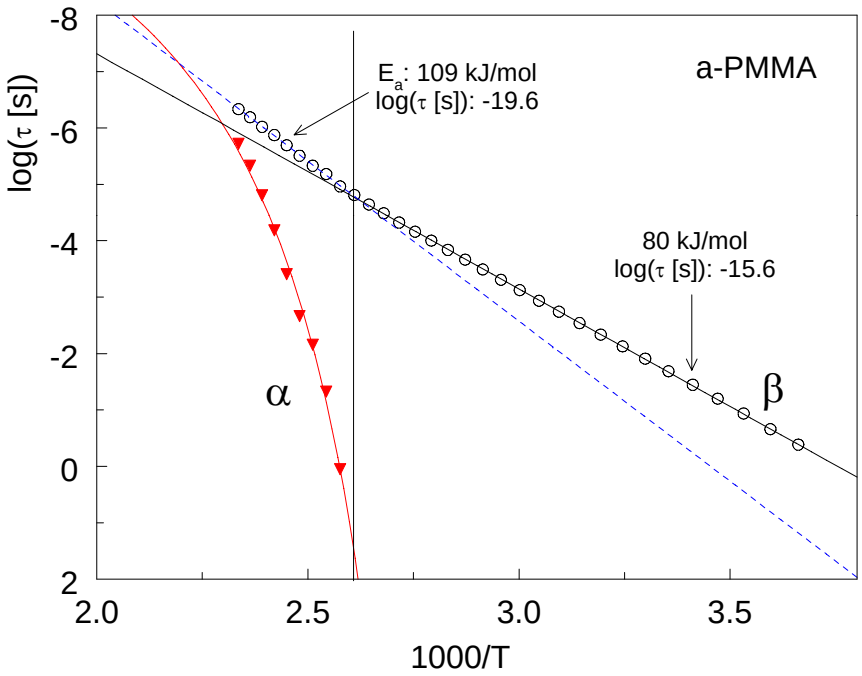
Polysilane

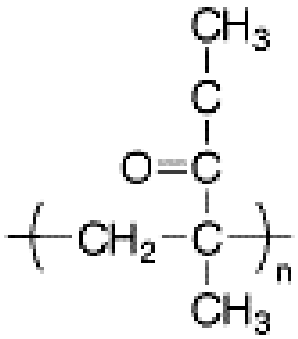




Amorphous, linear side-group polymers

Poly(methyl methacrylate), PMMA



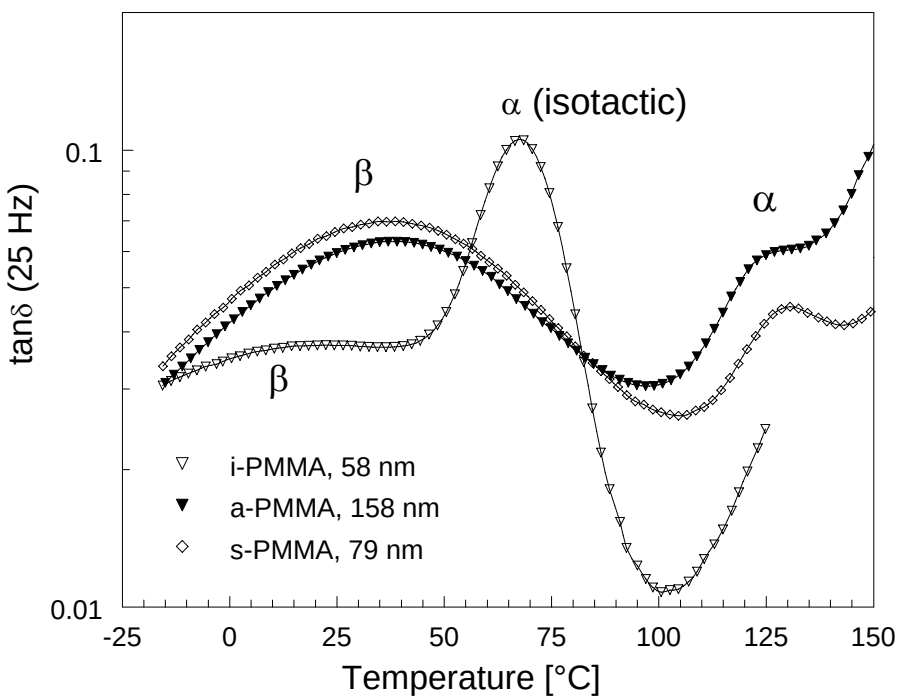


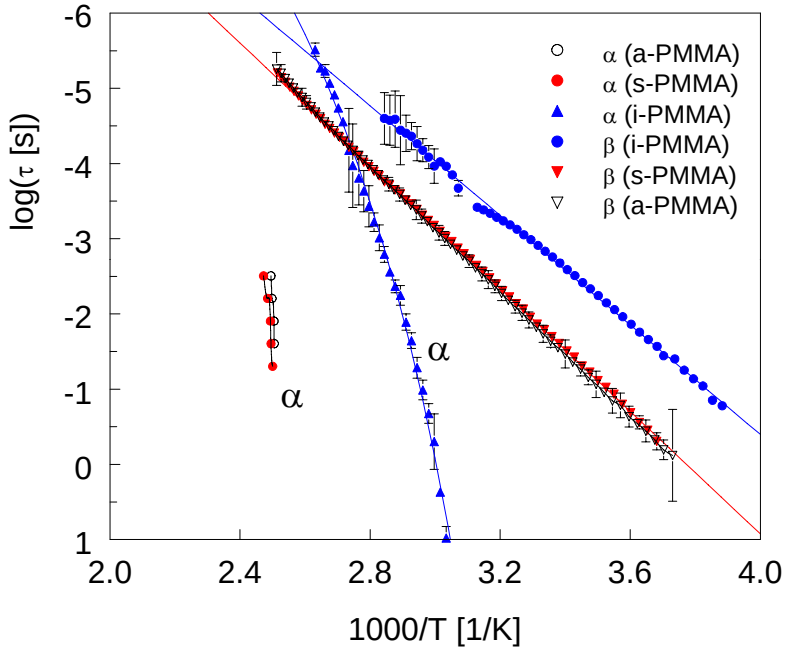
dielectric β-process

	E_a [kJ/mol]	$\log(\tau_0)$
β	80	-15.6

Amorphous, linear side-group polymers

Poly(methyl methacrylate), PMMA

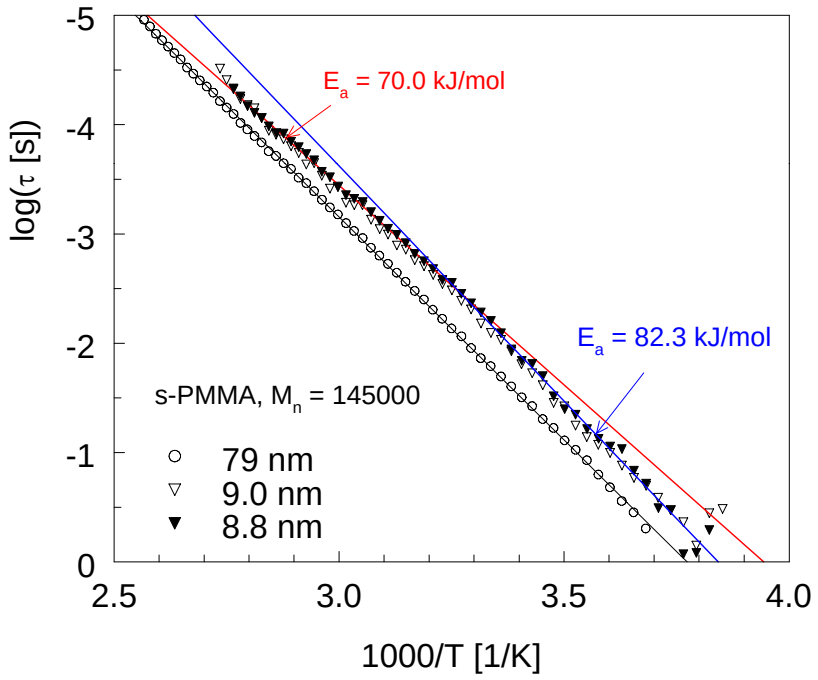


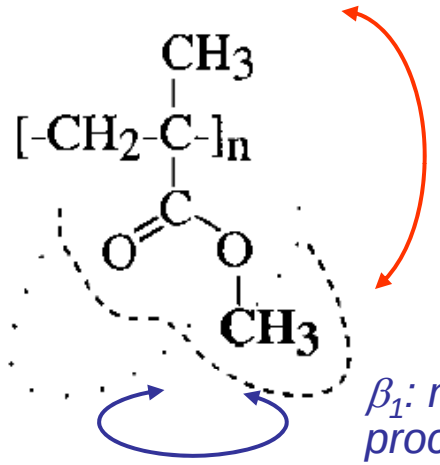


large influence of stereoregularity: i-PMMA: E_a ~ 70kJ/mol

Amorphous, linear side-group polymers

Molecular mechanism of dielectric β-process





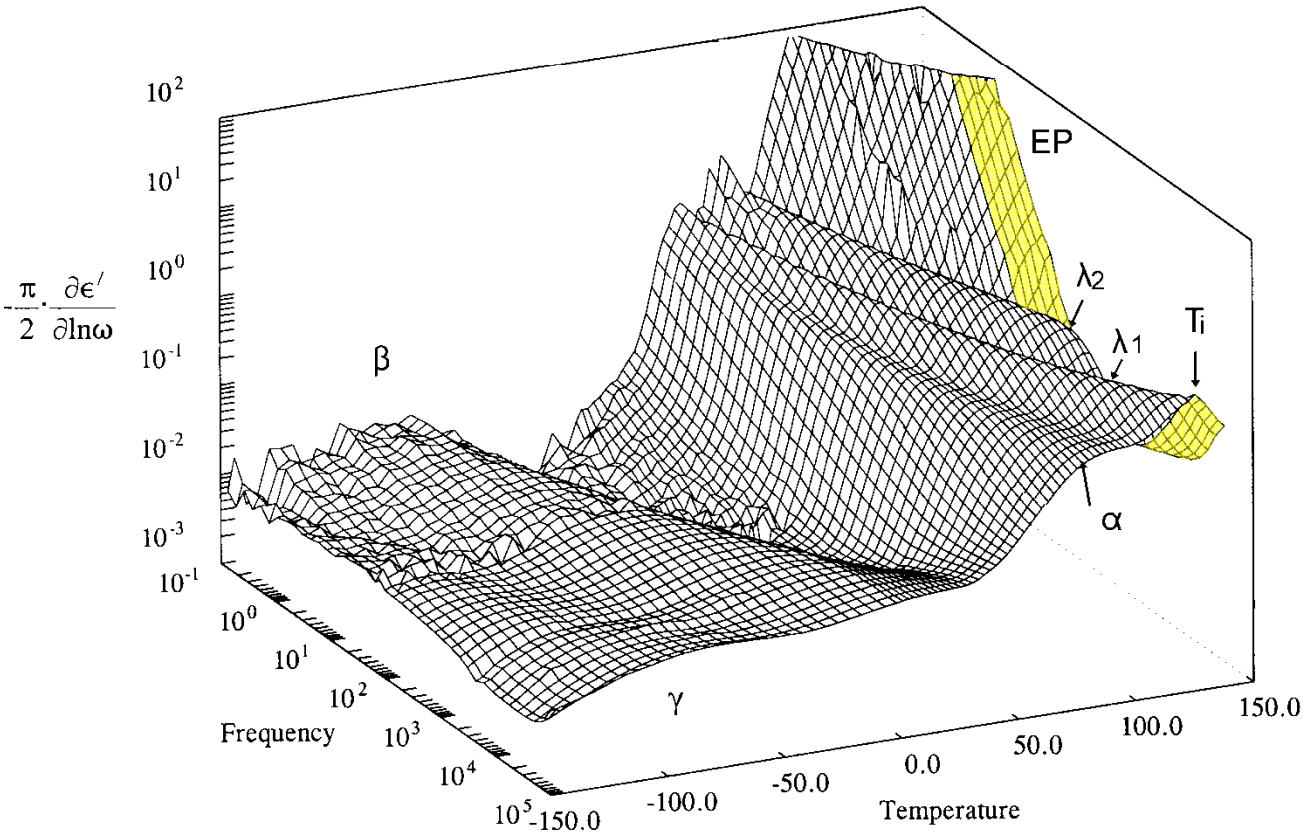
β_2: cooperative process involving the backbone

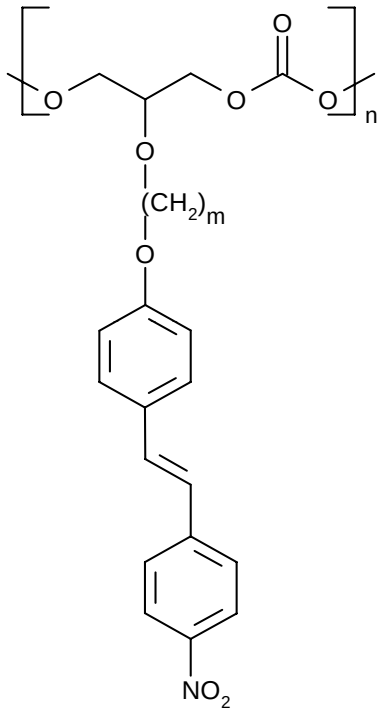
β_1: noncooperative process

2 main components contribute to dielectric β-process in PMMA

Liquid crystalline polymers

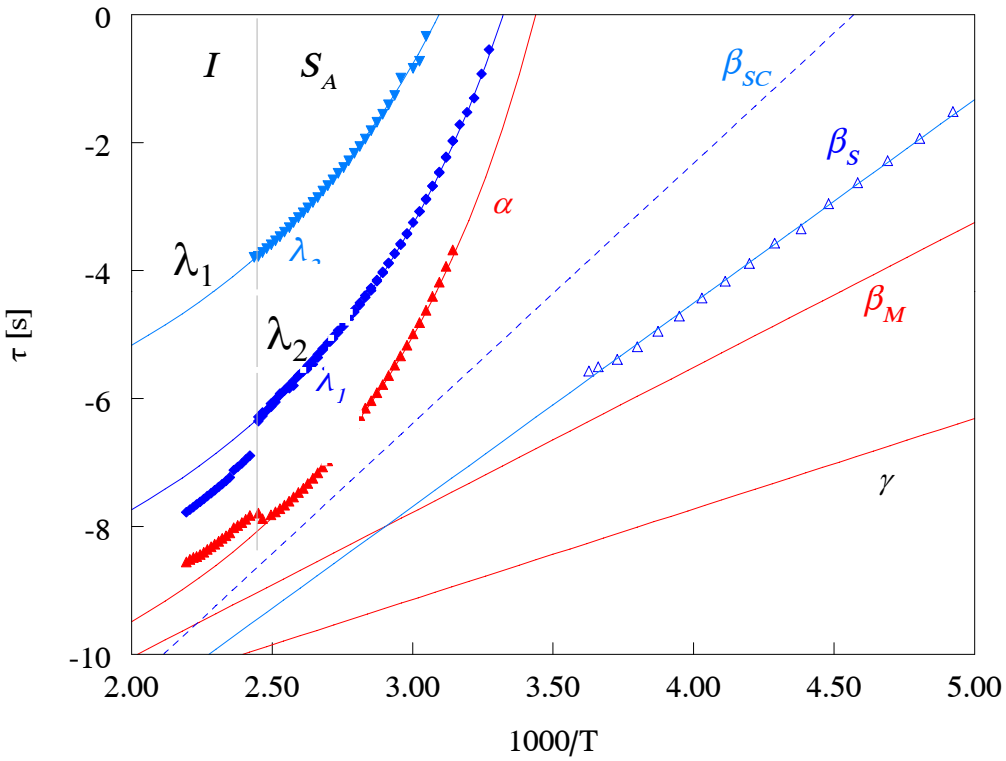
Liquid crystalline polycarbonates

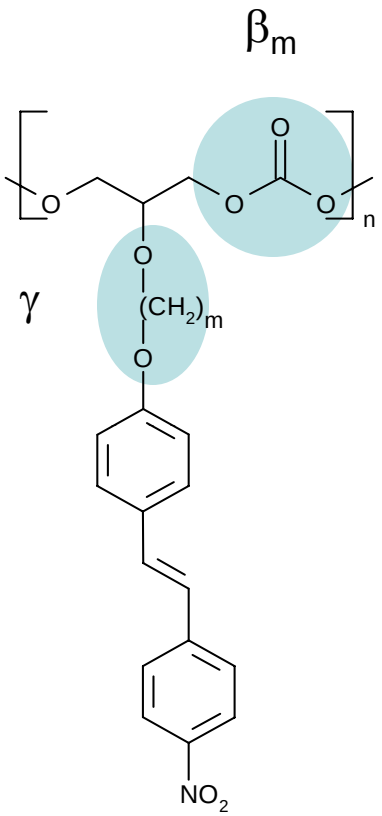




Liquid crystalline polymers

Liquid crystalline polycarbonates (2)

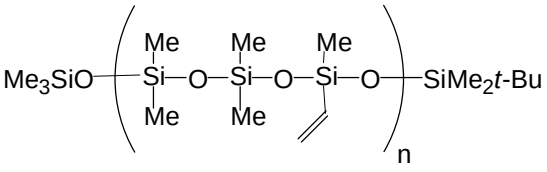




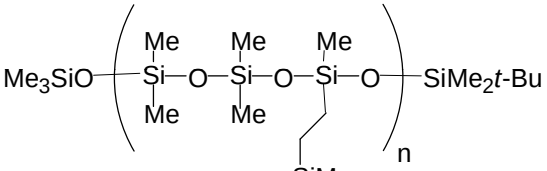
3 VFT-type relaxations (related to segmental dynamics) !

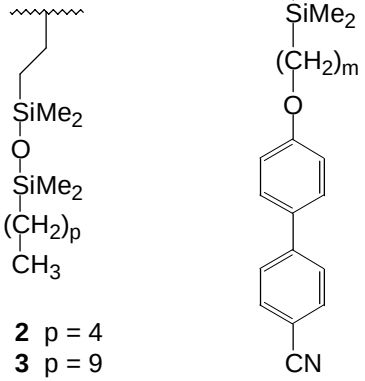
Symbols λ_1 and λ_2 introduced for clarity

Liquid crystalline polymers - Polysiloxanes

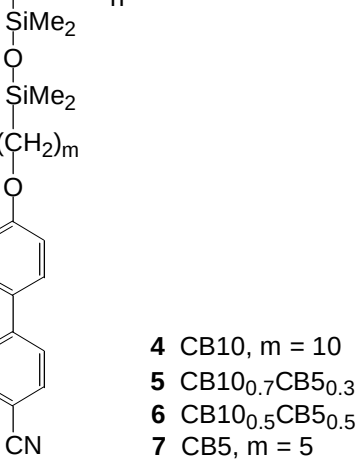


1

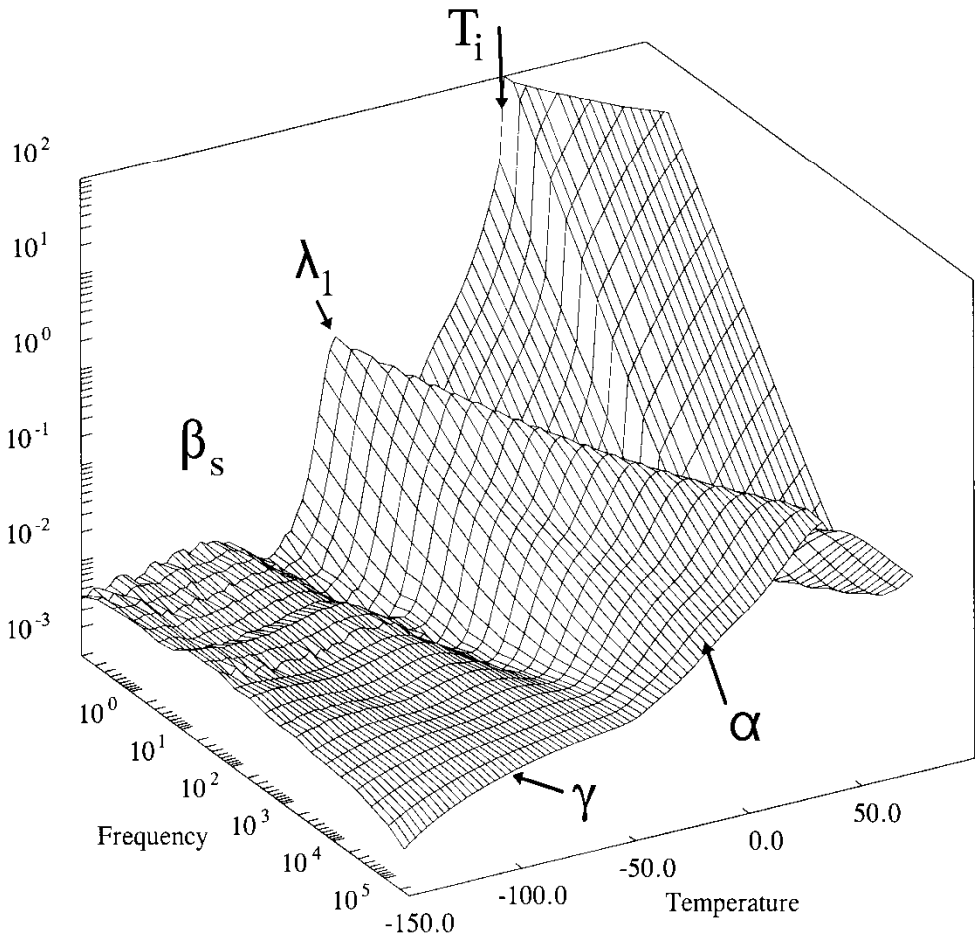




2 p = 4
3 p = 9



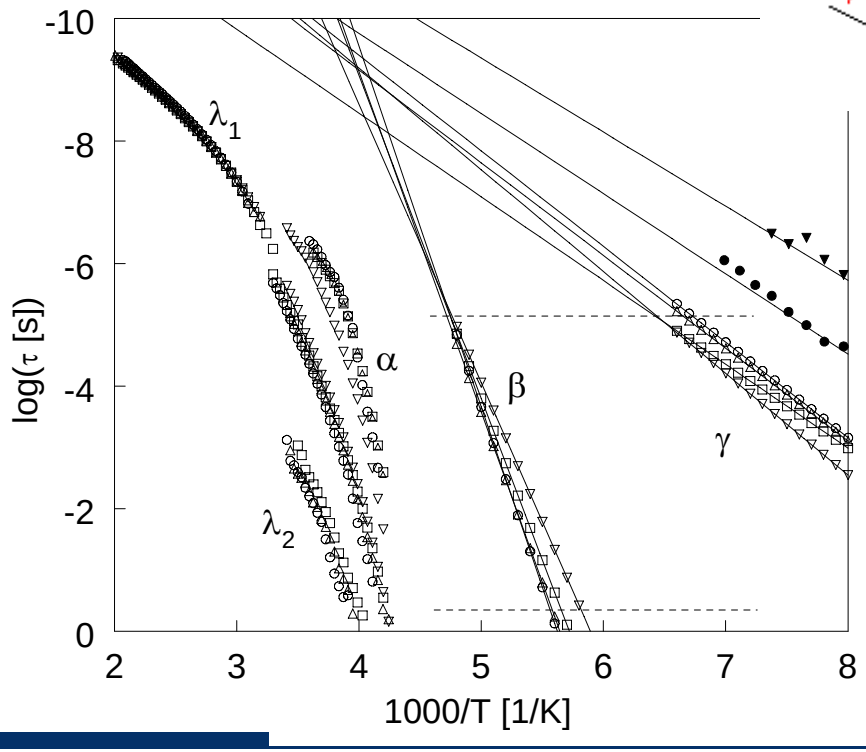
4 CB10, m = 10
5 $CB10_{0.7}CB5_{0.3}$
6 $CB10_{0.5}CB5_{0.5}$
7 CB5, m = 5

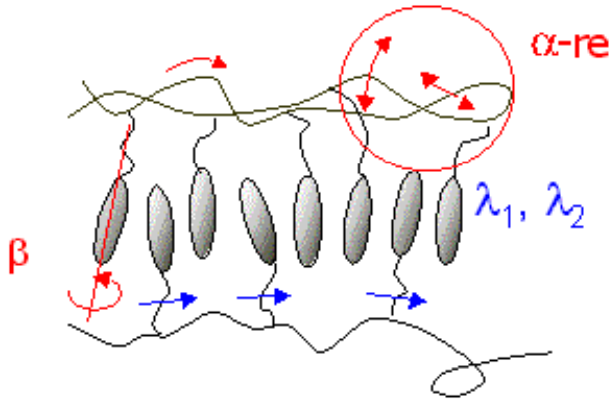


KATHOLIEKE UNIVERSITEIT LEUVEN

Liquid crystalline polymers - Polysiloxanes

Again, 3 VFT-type relaxations observed





rotational and **translational** diffusion of mesogens

Our present interpretation schema

KATHOLIEKE UNIVERSITEIT LEUVEN

Dielectric probes: a powerful tool for the study of glass transition dynamics in apolar polymers in bulk and ultra-thin film geometry

Michael Wübbenhorst

Co-authors:
S. Napolitano, K. Kessairi, S. Capaccioli

Lab. voor Akoestiek en Thermische Fysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven
PolyLab-CNR and Dipartimento di Fisica, Università di Pisa, Largo. B. Pontecorvo 3, Pisa, 56127, Italy

Outline

- Dielectric probes – why do we need them ?
- First applications
- Effect of probe length on dielectric response
- Polystyrene – molecular mass effects
- Dielectric probes in ultrathin polymer films
- Summary & conclusions

Motivation

Dielectric spectroscopy

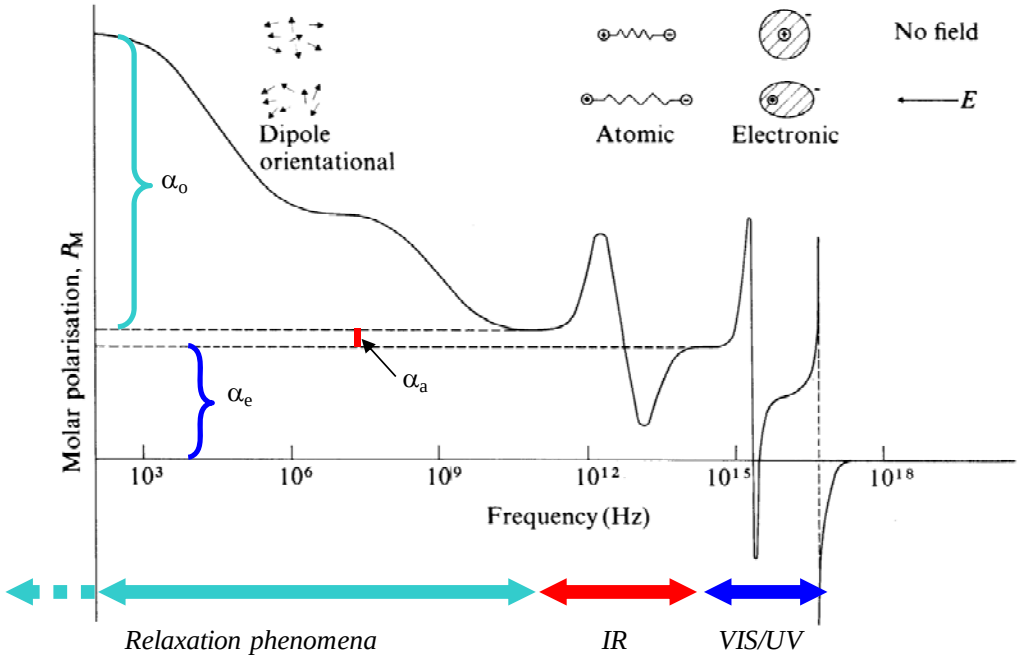
- Versatile tool for study of molecular dynamics in condensed matter
- Exceptionally large frequency range: 10^{-6} – 10^{12} Hz are possible
- Increasing popularity due to availability of “turn-key” instrumentation for more than 15 years

One essential prerequisite

molecular dipoles

⇩

Orientational polarisation



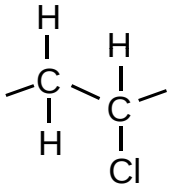
Dipole moments

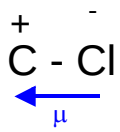
Some dipole moments of simple molecules

Compound	Dipole moment $\times 10^{-30}$ Cm
H_2O	6.1
HF	6.4
HCl	3.6
HBr	2.6
CH_4	0
CCl_4	0
CO_2	0
NH_3	4.9
CH_3Cl	5.3
C_2H_5OH	5.7
$(C_2H_5)_2O$	3.8
C_6H_5Cl	5.7
$C_6H_5NO_2$	14.0

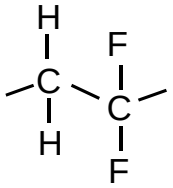
Dipole moments in polymers

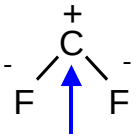
PVC





PVDF





Unfortunately, there are several interesting systems that lack strong polar groups, e.g. PE, PP and PS → introduction of dipoles necessary

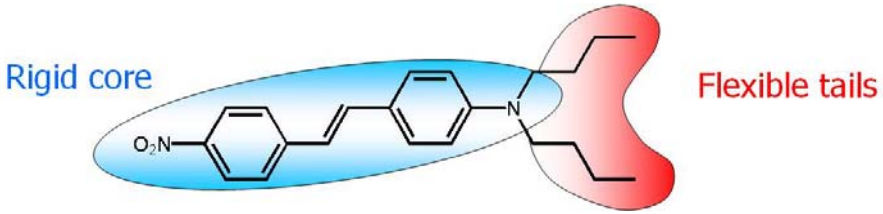
Outline

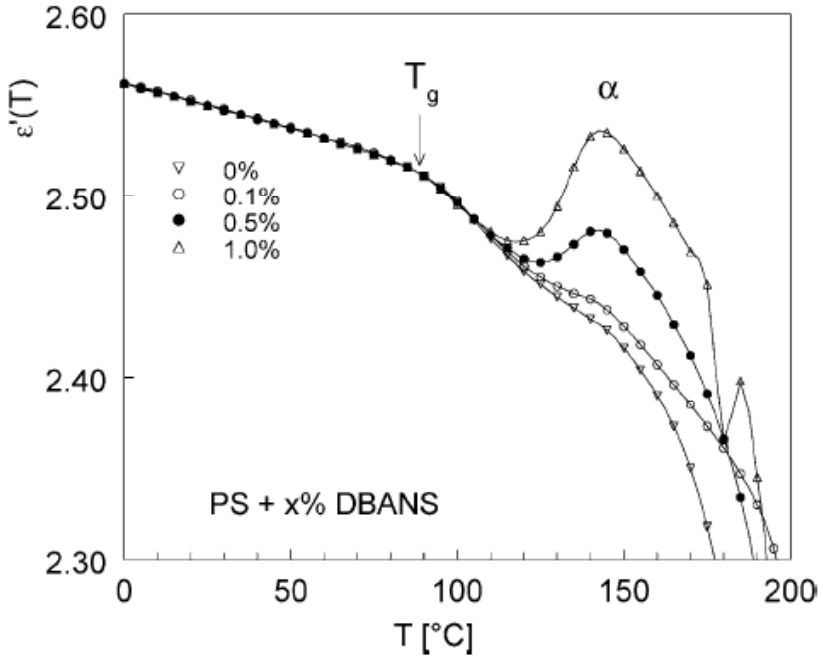
- Dielectric probes – why do we need them ?
- **First applications of dielectric probes**
- Effect of probe length on dielectric response
- Polystyrene – molecular mass effects
- Dielectric probes in ultrathin polymer films
- Summary & conclusions

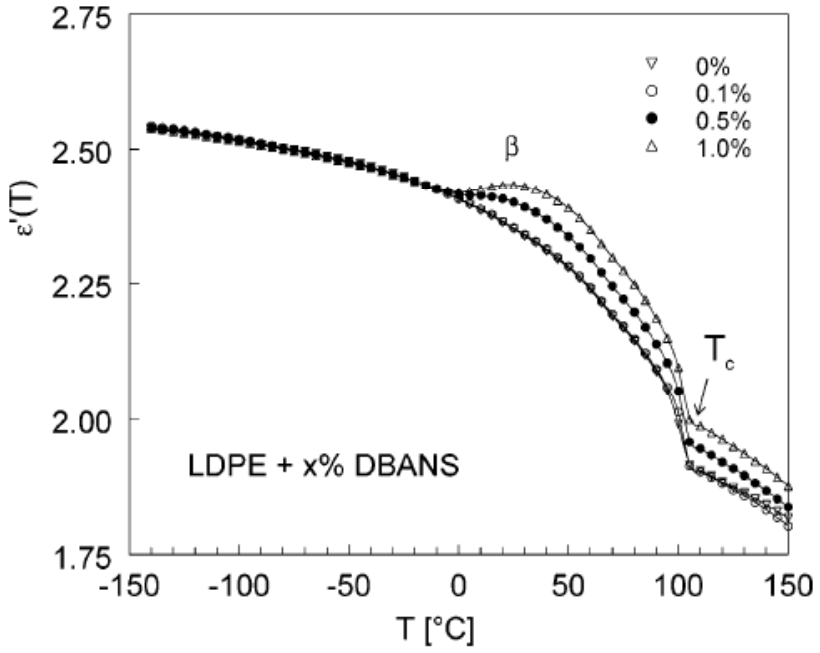
DBANS in apolar polymers

- Synthesis of DBANS (O. van den Berg)
- Both fluorescent and strong dipole moment
- Compatible with aromatic and aliphatic environment

O. van den Berg, W. G. F. Sengers, W. F. Jager, S. J. Picken, and M. Wübbenhorst, *Macromolecules, vol. 37, pp. 2460-2470, 2004.*

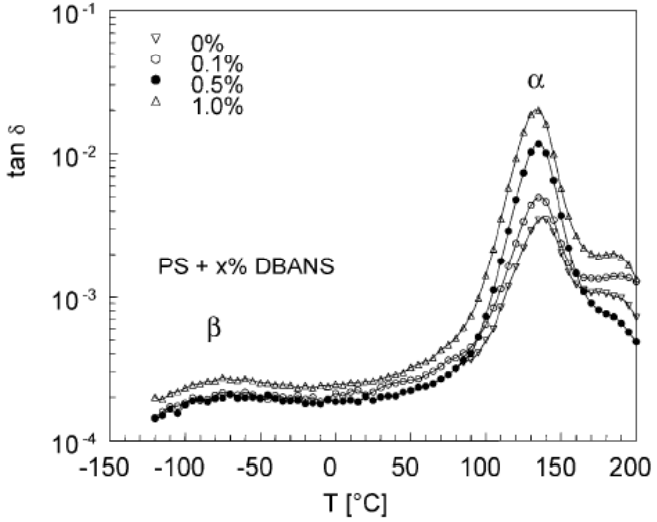




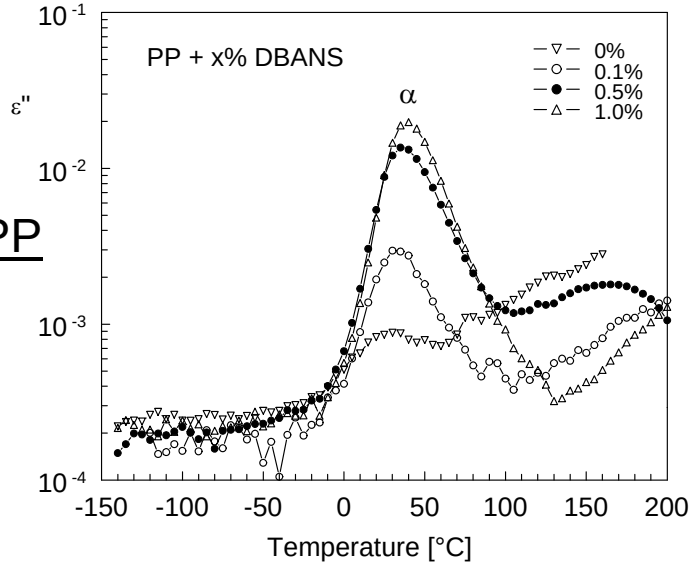


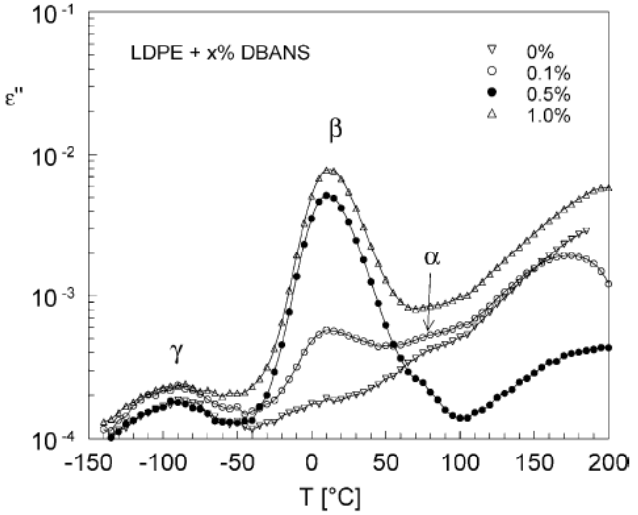
DBANS in apolar polymers

Various polymer/probe combinations:



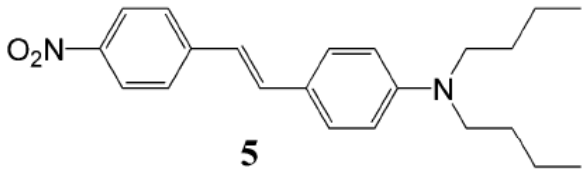
Isotactic PP





PS + DBANS:

- weak intrinsic polarity of pure PS



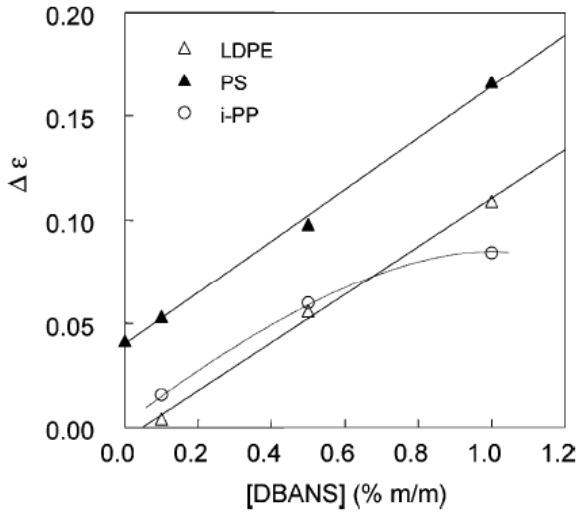
5

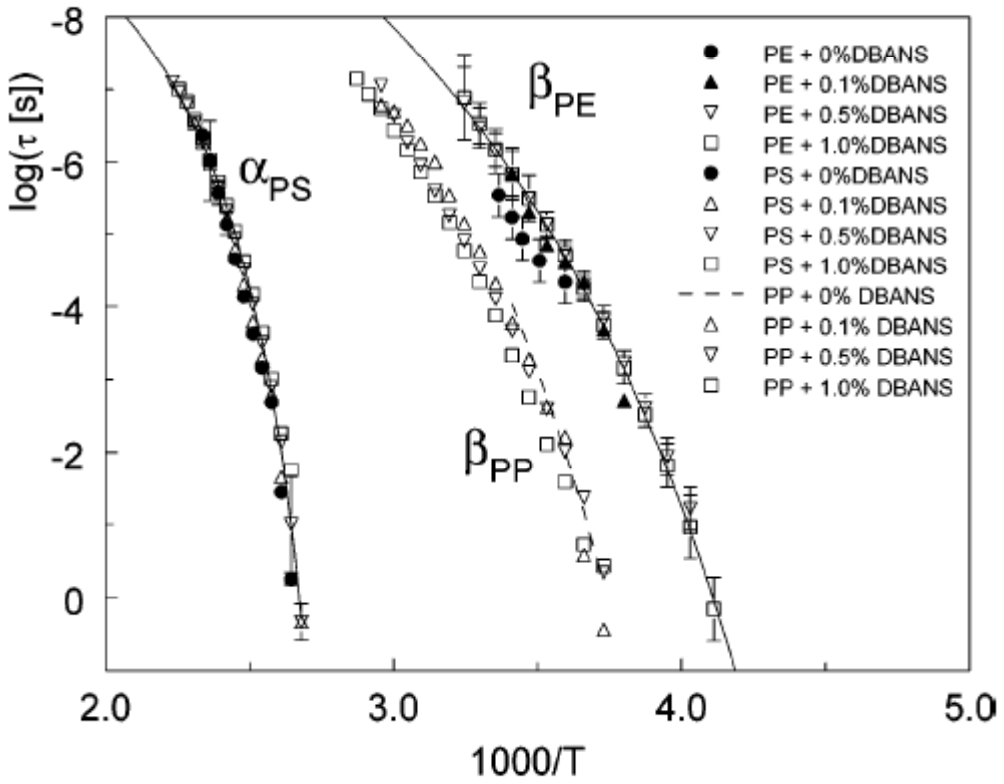
LDPE:

almost no detectable α-process in pure PE!

DBANS in apolar polymers

Proof of linearity between $\Delta\varepsilon$ and c_{probe}



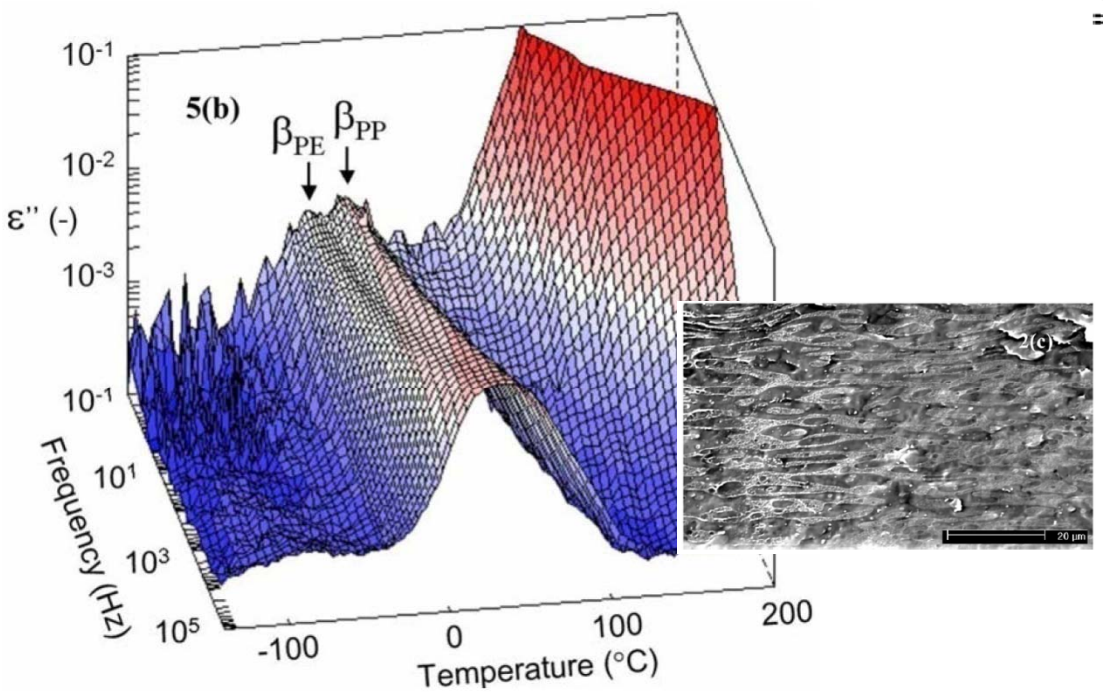


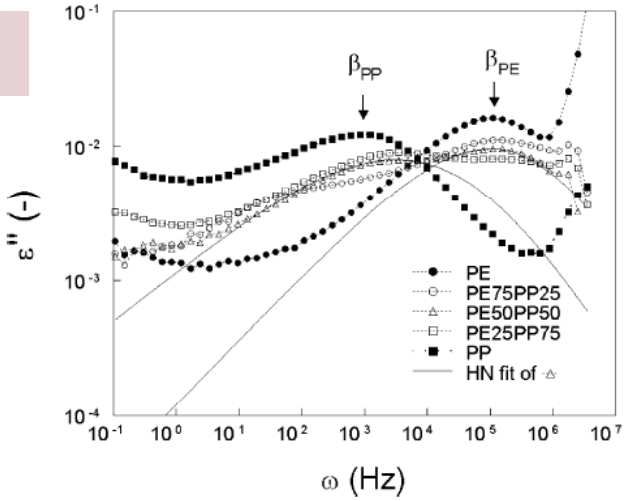
Excellent reproducibility of structural relation time for all systems

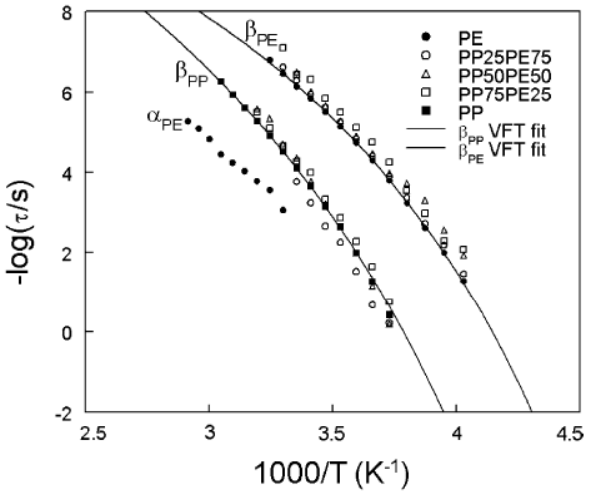
Characterization of immiscible polymer blends

Dielectric probes in more complex systems:

Binary blends of PE and PP







W. G. F. Sengers, O. van den Berg, M. Wübbenhorst, and A. D. Gotsis, "Mapping of relaxation processes in immiscible apolar polymer blends using dielectric spectroscopy," Polymer, vol. 46, pp. 6064-6074, 2005.

First summary

- Addition of dielectric probes amplifies the dielectric relaxation associated with the dynamic glass transition (α-process)
- No effect of DBANS on local (secondary) relaxation processes found

→ Detailed study of cooperative dynamics in complex systems enabled

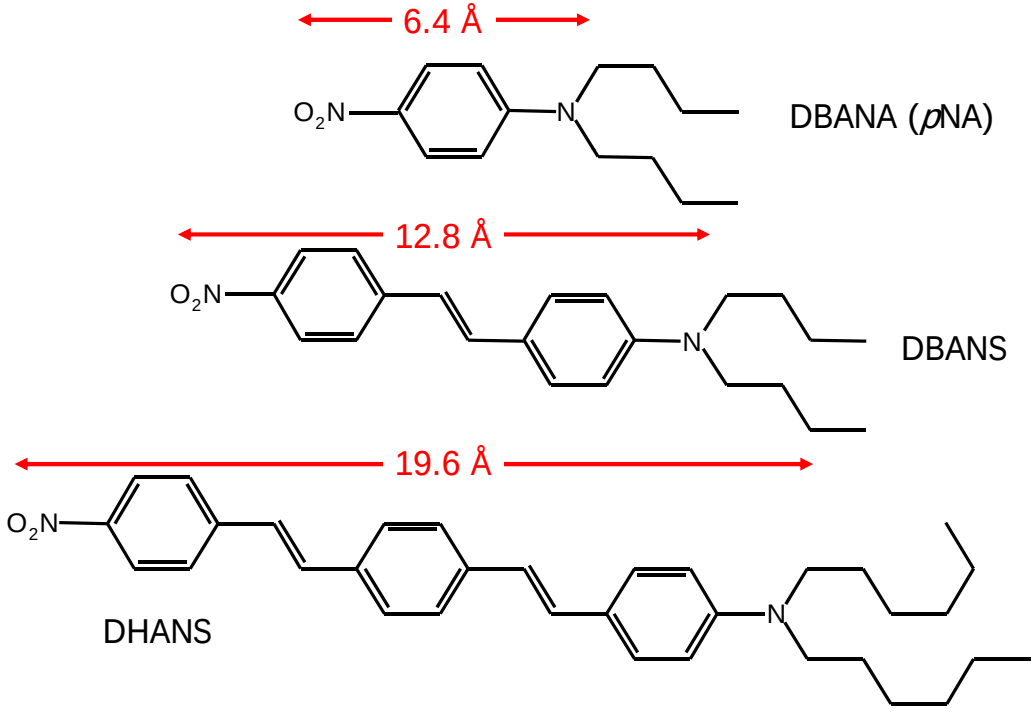
Outline

- Dielectric probes – why do we need them ?
- First applications of dielectric probes
- **Effect of probe length on dielectric response**
- Polystyrene – molecular mass effects
- Dielectric probes in ultrathin polymer films
- Summary & conclusions

Effect of probe length

DBANS appeared to work well for PP, PE and PS

Question: Can we learn anything about the length scale of the α-relaxation by varying the size of the probe?



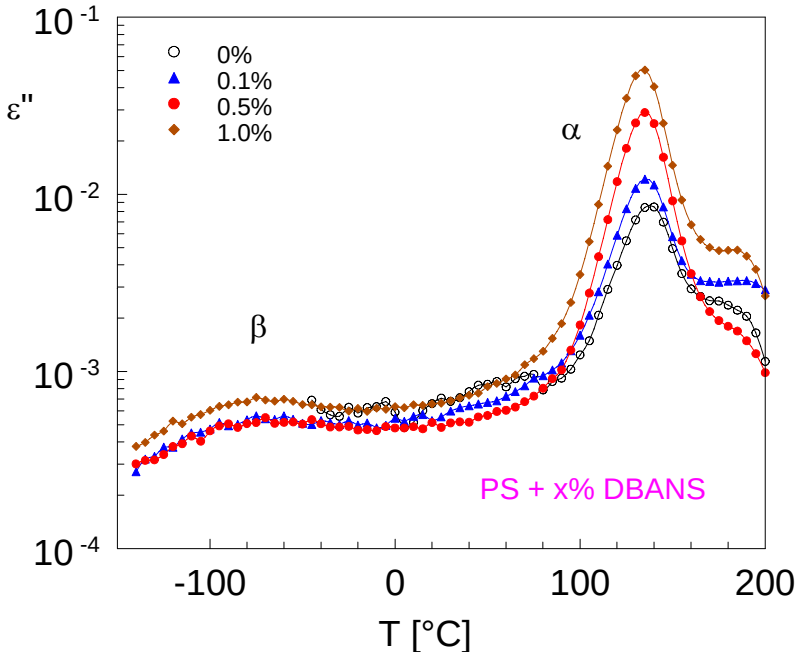
Synthesis of probe molecules with different length of the rigid part by varying the number of aromatic rings (1 – 3).

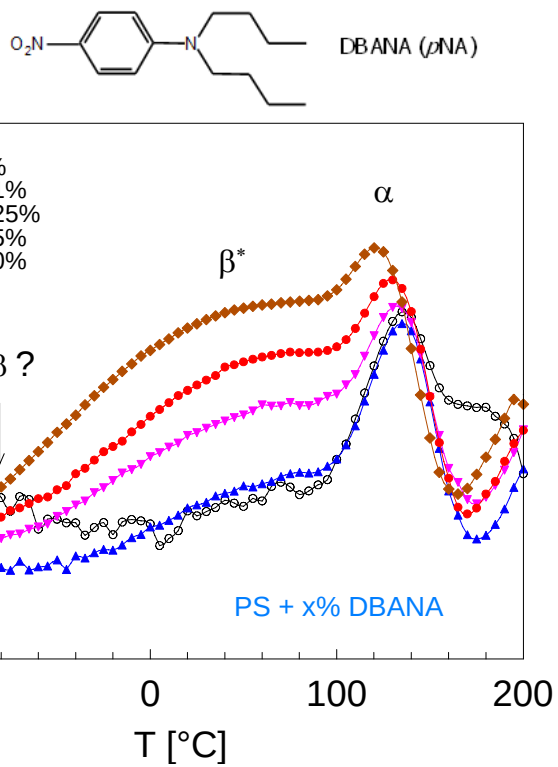
Mixing of probe with PS in solution; Preparation of samples for DRS by film casting.

O. van den Berg, M. Wübbenhorst, S. J. Picken, and W. F. Jager, J. Non-Cryst. Solids, vol. 351, pp. 2694-2702, 2005.

Effect of probe length

Dielectric loss ε"(*T*) at *f* =13 kHz





<u>DBANS and DHANS:</u>

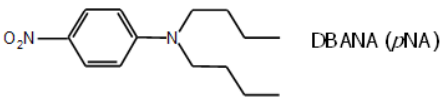
selective amplification of α-proces, no significant effect on β-process

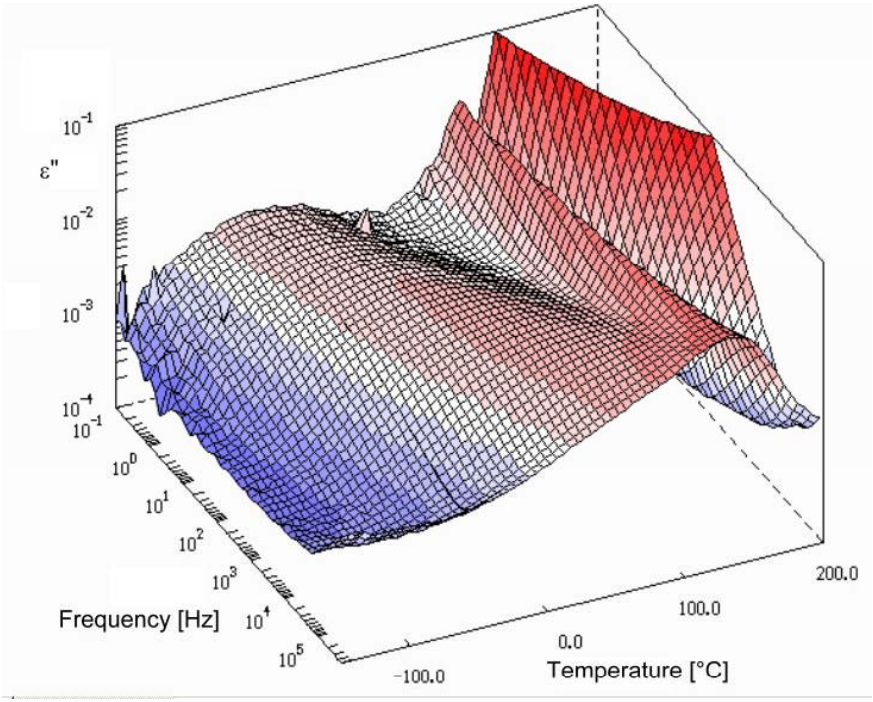
<u>DBANA (short probe):</u>

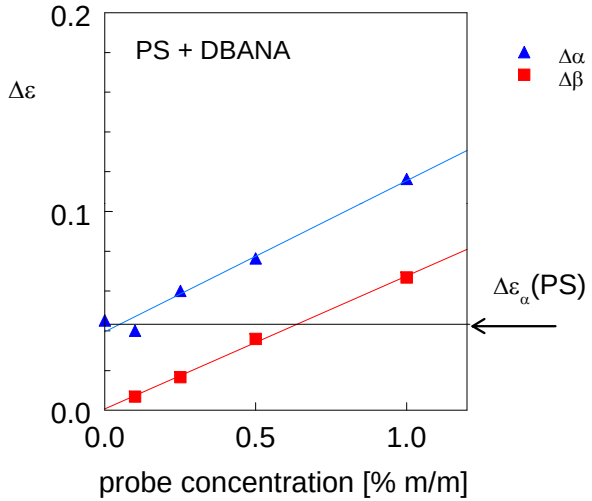
amplification of both α-proces and additional probe relaxation (β*) below T_g

Effect of probe length

Short probe, further analysis



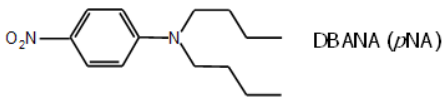


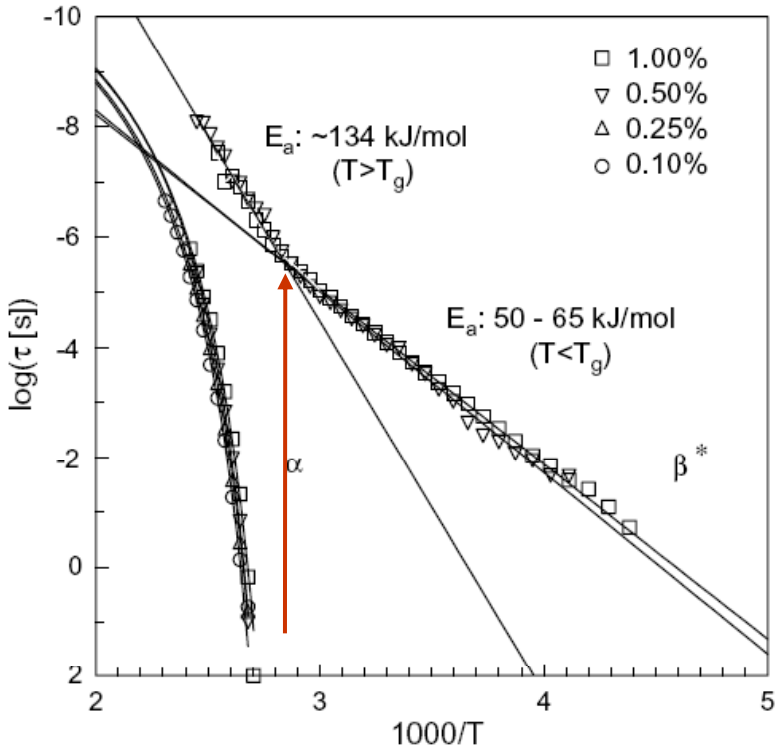


Contribution of probe response $\Delta\varepsilon \propto \langle\mu^2\rangle$ to α and β*-process scales linearly with c_{probe}

Effect of probe length

Short probe, further analysis





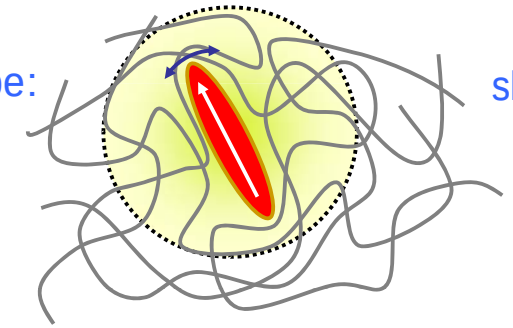
- Arrhenius-type process (β*) with higher activation energy than native β-process of PS
- Kink in $E_a(T)$ close to volumetric T_g

- Temperature dependence in τ_{β^*} contains contribution from thermal expansion

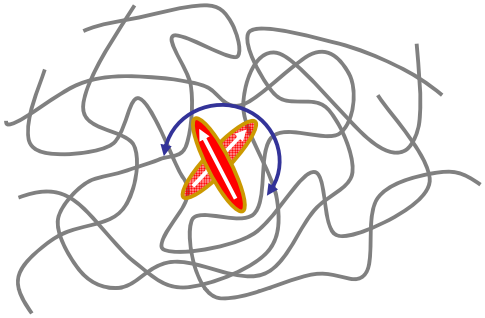
Effect of probe length

Angular fluctuations of the probe molecules: two possible scenario's

large probe:



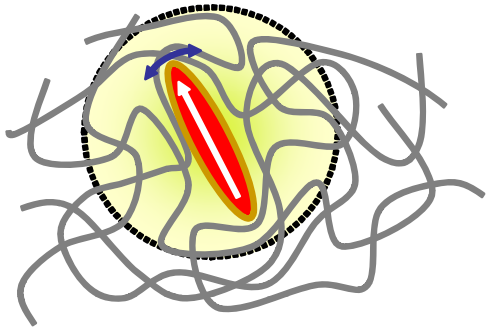
short probe:



	long probe	**short probe**
$T > T_g$	large angular fluctuations in "viscous" matrix → amplification of α-process	large angular fluctuations → contribution to α-process
$T < T_g$	small angular fluctuations → no dielectric response	large angular fluctuations, restricted → β*-process → **free-volume probe**

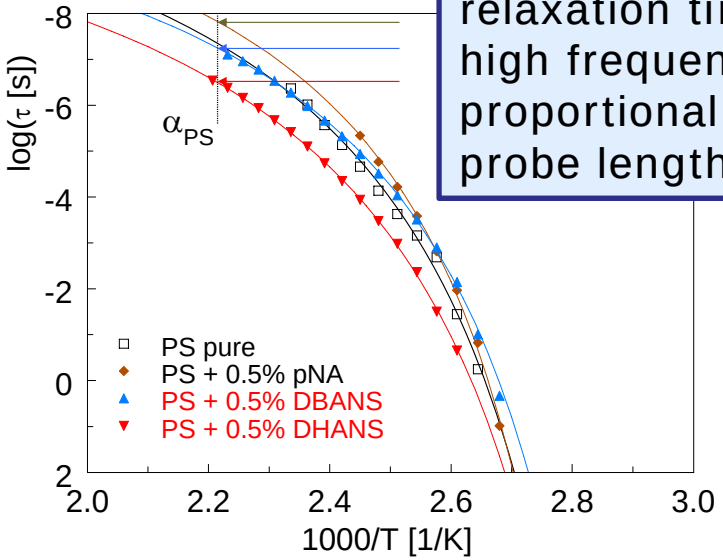
Rotational diffusion

Do DBANS & DHANS behave as true rotational probes?

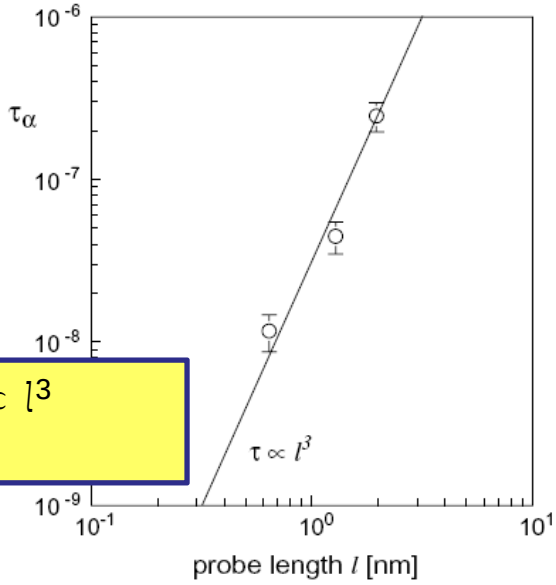


Rotational diffusion time for Brownian rigid rods:

- $\tau \propto l^3$ (l = probe length)
- single-exponential process (“Debye” relaxation)



relaxation time at high frequencies proportional to probe length



Relation $\tau \propto l^3$ holds well

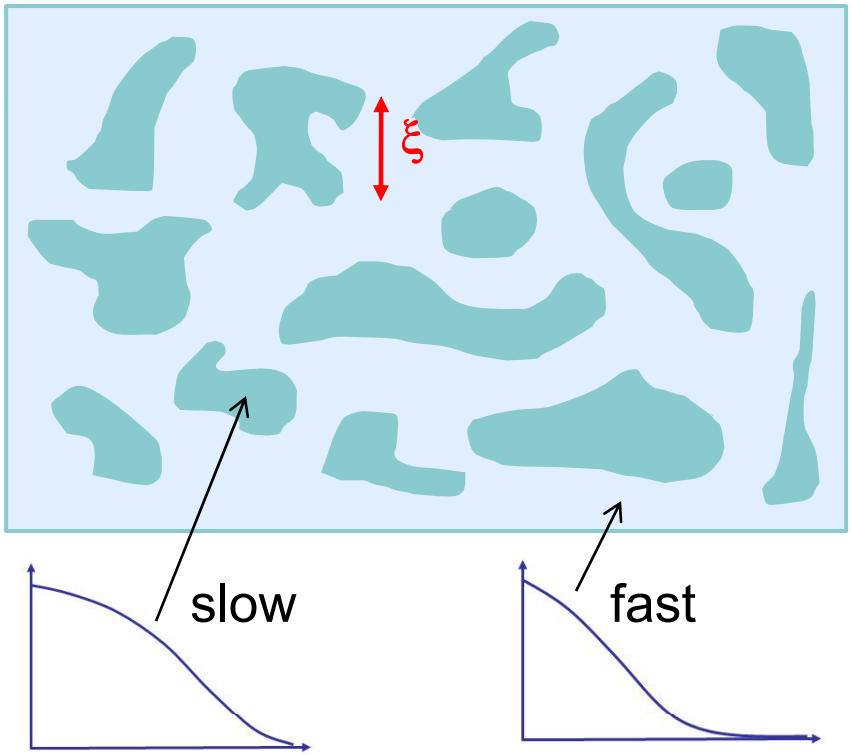
What about the spectral shape of the α-process?

Effect of probe length on spectral shape

From experiment:

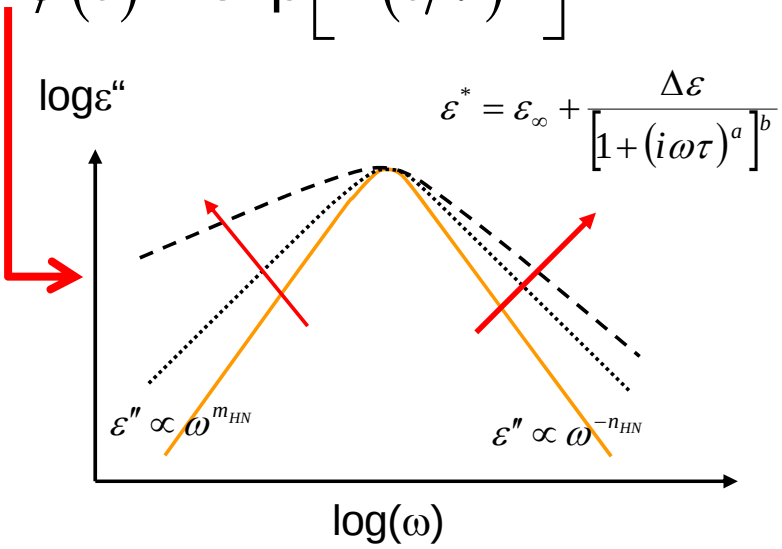
Glass transition dynamics shows usually non-exponential kinetics

Rationalisation by spatially heterogenous dynamics



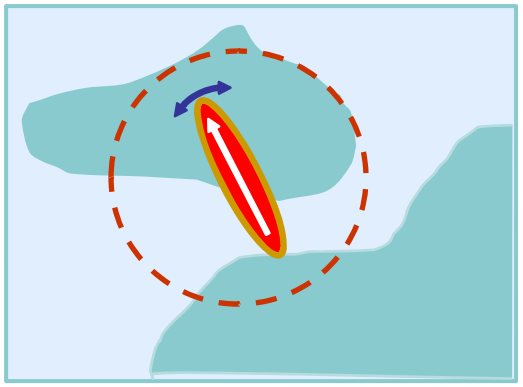
Averaging over different environments yields KWW behaviour.

$$\phi(t) = \exp\left[-(t/\tau)^{\beta}\right]$$



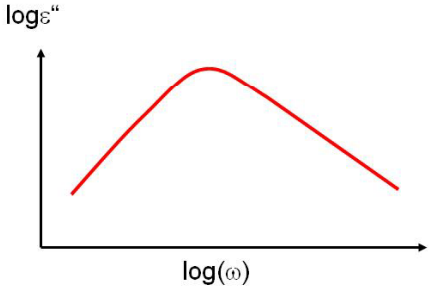
Effect of probe length on spectral shape

Probe rotational diffusion in a heterogeneous scenario

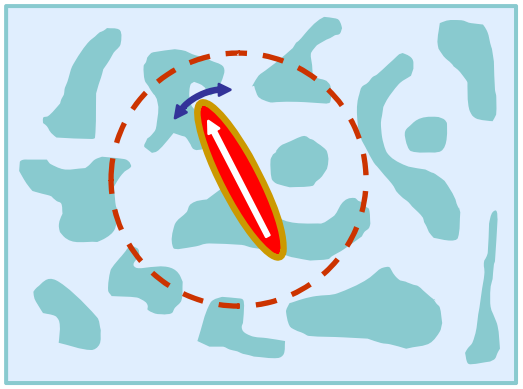


Case 1: probe size ~ ξ

- low temperatures
- small probe molecules

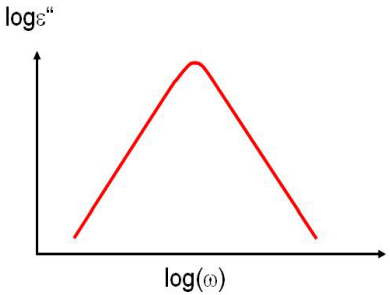


→ Individual probe response reflects heterogeneity



Case 2: probe size >> ξ

- high temperatures
- large probe molecules

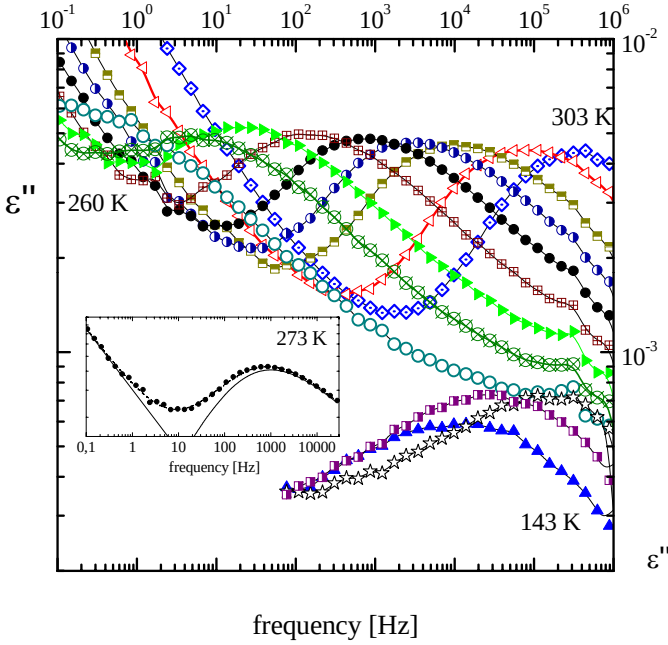


→ Probe averages over spatial heterogeneities
→ Debye relaxation expected

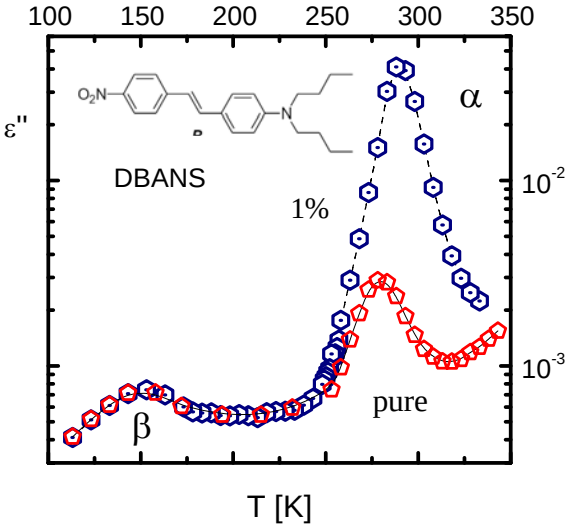
Dynamics of a-PP

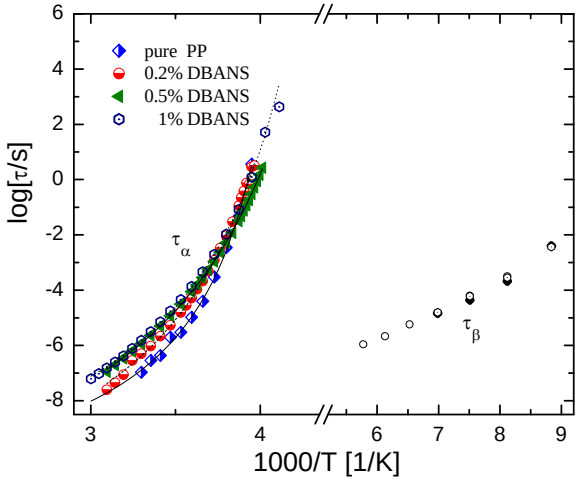
Recent work on atactic (amorphous) PP

K. Kessairi, S. Napolitano, S. Capaccioli, P. A. Rolla, and M. Wübbenhorst, Macromolecules, vol. 40, pp. 1786-1788, 2007.



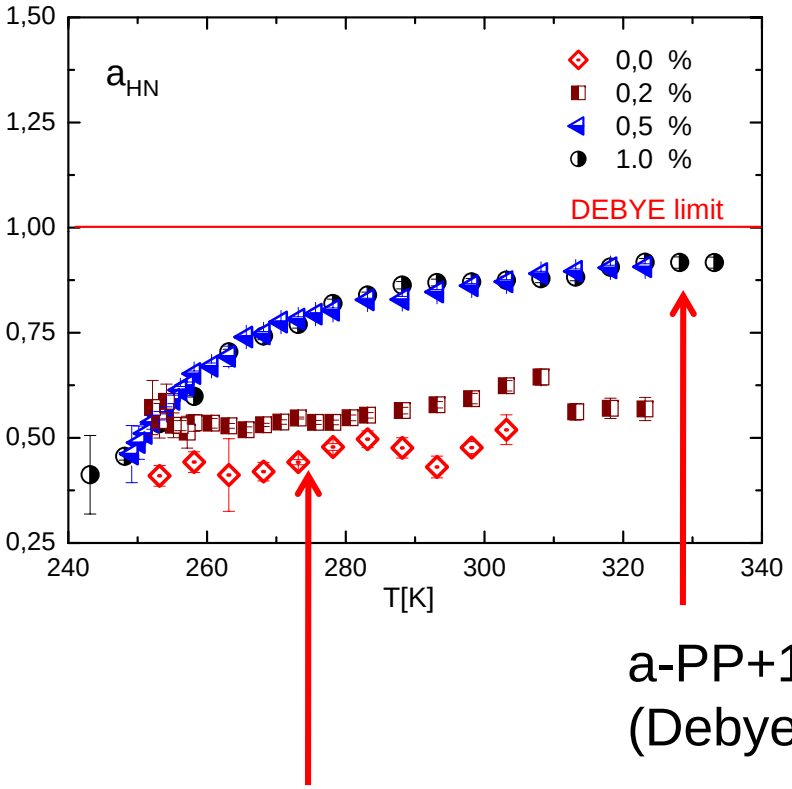
- Tremendous enhancement of dielectric α-process
- Exclusive coupling of DBANS with glass transition dynamics

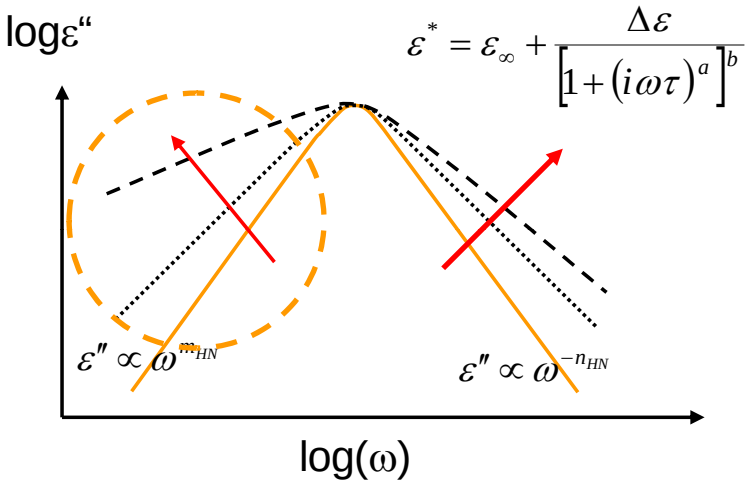




Dynamics of a-PP

Probe concentration and T-dependence of shape parameter a_{HN}





a-PP+1%DBANS: almost single exponential (Debye) process at high temperatures

Pure a-PP: broad α-process (a_{HN} ~ 0.5)

Summary and conclusions

- Rigid-rod type polar molecules with variable length (0.6 nm, 1.3 nm, 2.0 nm) of their stiff core were used as "dielectric probes" in polystyrene, polypropylene and polyethylene

- Dependent on probe length, the dielectric probe response was found to sense specific molecular motions:

  - » shortest probe (0.6nm): **strong mobility in glassy state** of PS → large angular diffusion within free volume holes

  - » medium and large probes: predominant contribution to glass transition dynamics → **amplification of α-relaxation**

Summary and conclusions (2)

- Potential application of the dielectric probe approach for the study of complex materials was demonstrated (M_w-dependence of PS, polymer blends)
- Further potential of dielectric probes lies in the investigation of dynamics in ultrathin polymer films