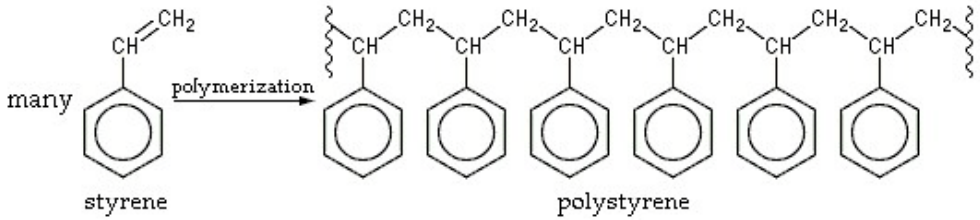
MSE 590 tutorial on PS-b-PMMA copolymers

2011/10/28

Chemical structure and physical properties of PS (Polystyrene)

Chemical structure:

An aromatic polymer made from the monomer styrene $(C_8H_8)_n$



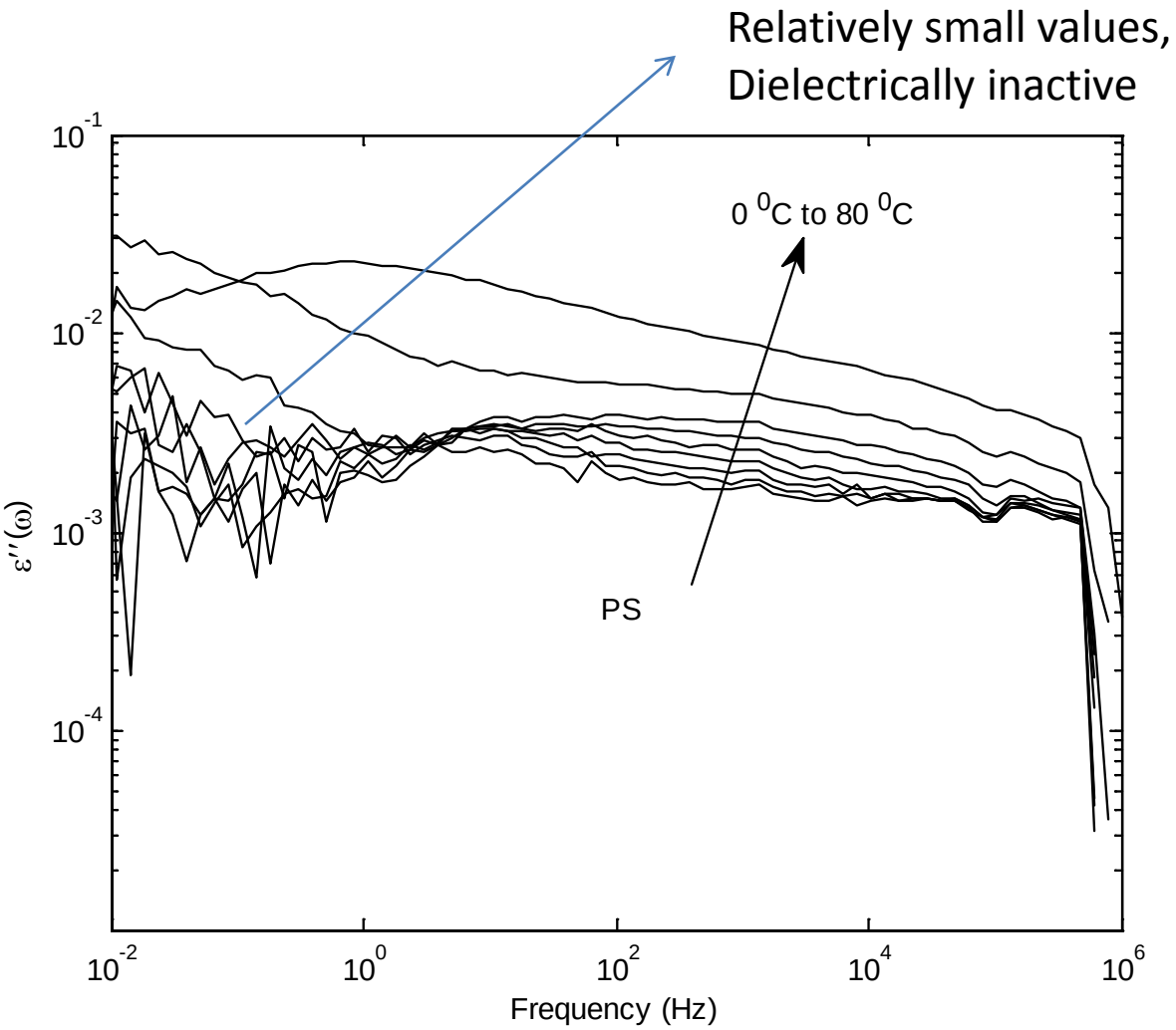
Physical properties:

Glass transition temperature: around 95 °C
Dielectric constant: 2.4–2.7
Density: 1.05 g/cm3
Thermal conductivity: 0.08 W/(m·K)

Application:

Sheet or molded polystyrene, polystyrene foam, copolymers…

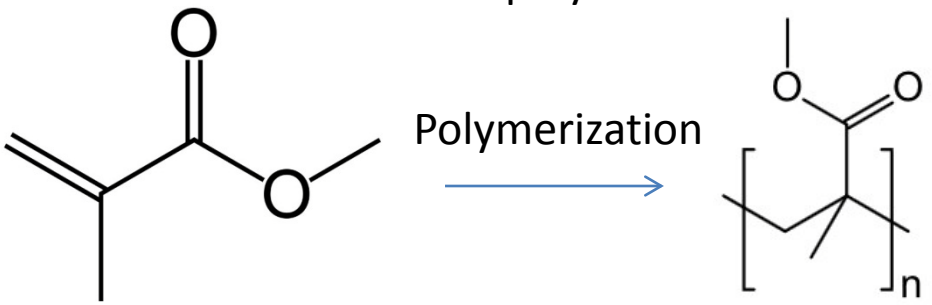
PS loss spectrum



Chemical structure and physical properties of PMMA (Poly(methyl methacrylate)

Chemical structure:

Chemically, it's synthetic polymer of monomer methyl methacrylate $(C_5O_2H_8)_n$



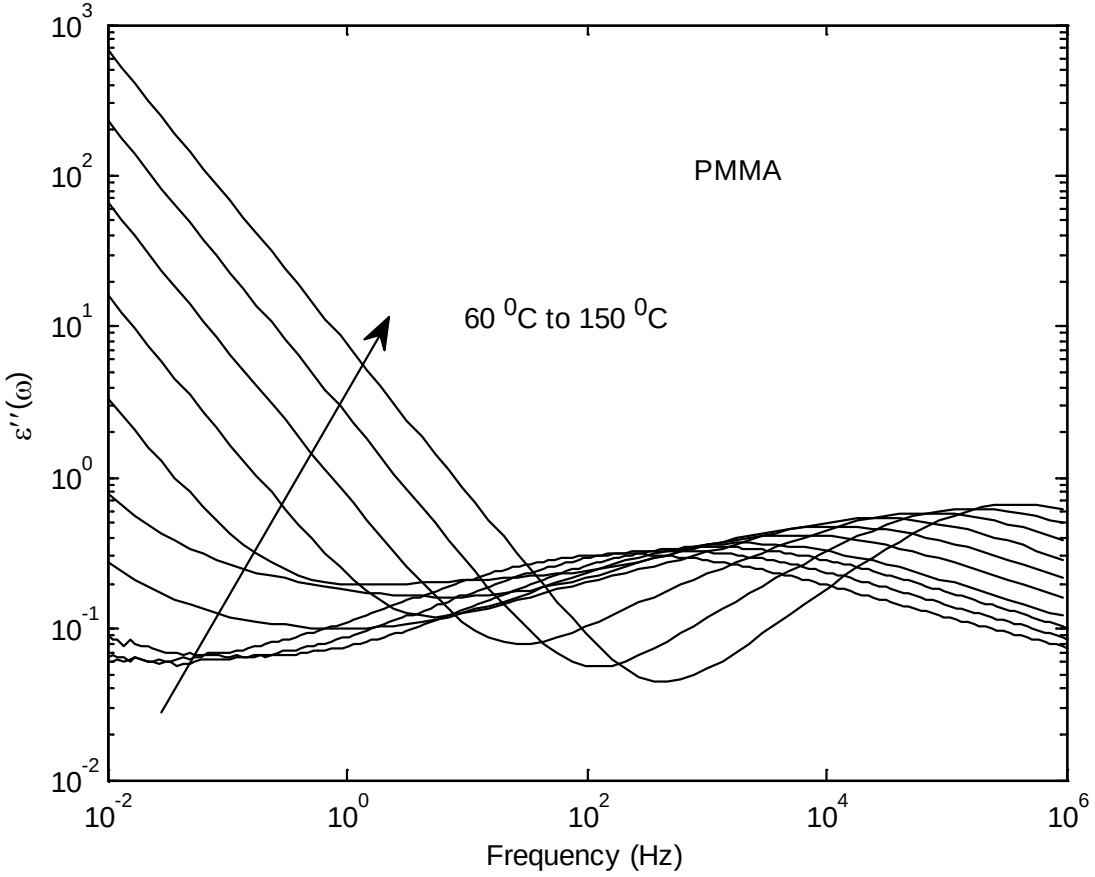
Physical properties:

Glass transition temperature: around 105 °C (atactic)
Refractive index: 1.4914 at 587.6 nm
Density: 1.18 g/cm^3
Melting point: around 160 °C

Application:

Transparent glass substitute (fish tank), Medical technologies and implants, Artistic and aesthetic uses…

PMMA Loss Spectrum



PS-b-PMMA and PS/PMMA samples

Sample preparation

PS-b-PMMA :

1. Heated to 180 °C for 10 minutes and pressed under 1000 lb load.
2. Decreased to room temperature by keeping 300 lb load.

Blends of PS /PMMA:

1. Heated to 180 °C for 30 minutes and pressed under 600 lb load test for 5 minutes.
2. Decreased to room temperature by keeping 600 lb pressure.

After the hot pressing processes, samples were all polished and sputtered by Ag electrodes.

PS-b-PMMA and PS/PMMA samples

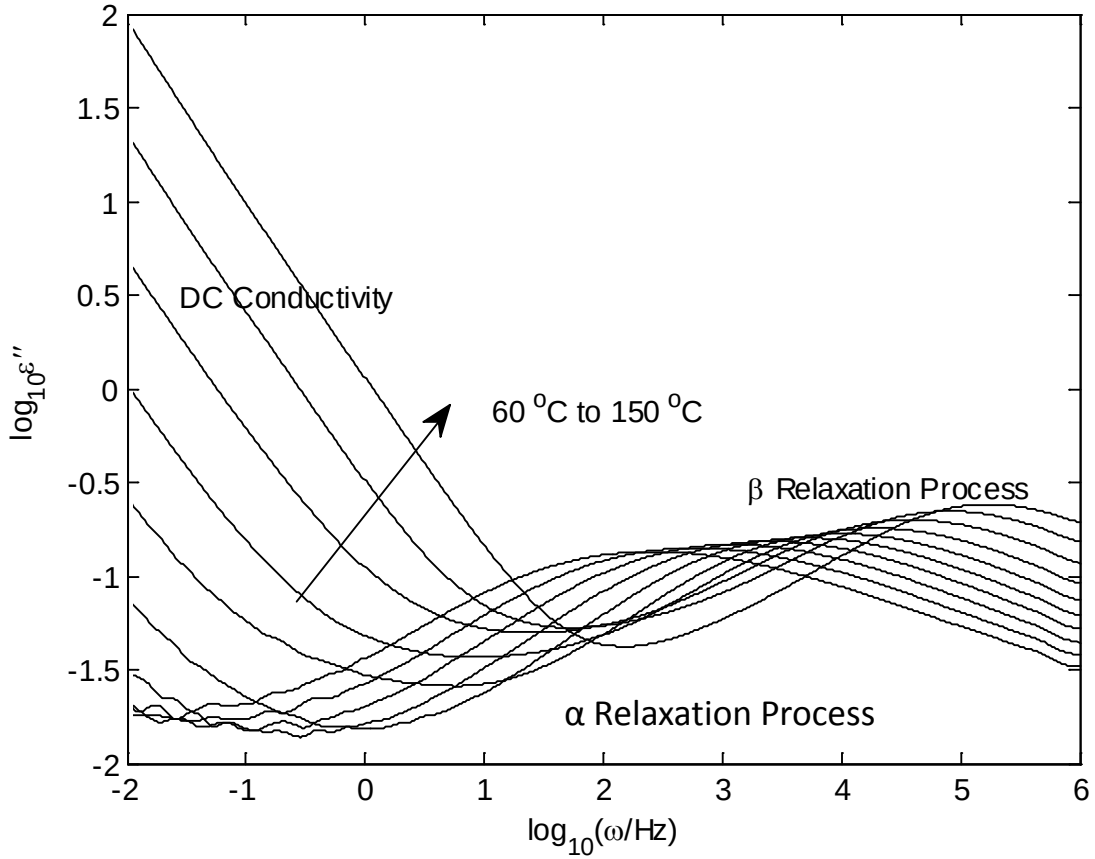
Dielectric measurement

using Broad Band NOVOCONTROL spectroscopy with automatic temperature control from -40 °C to 150 °C and frequency range from 0.01 Hz to 1 MHz.

Table 1. Molecular weight, diameter and thickness of the samples.

Samples	M_w	Diameter (mm)	Thickness (mm)	Volume fraction f_{PS}
PMMA	50 K	19.88±0.01	1.25±0.01	
PS	50 K	19.865±0.005	0.94±0.01	
PS-b-PMMA (Sample 1)	50K-50K	19.88±0.01	0.855±0.005	0.53±0.03
PS-b-PMMA (Sample 2)	50K-50K	19.82±0.01	0.575±0.005	0.53±0.03
PS-b-PMMA	50K-130K	19.82±0.01	0.575±0.005	0.53±0.03
PS/PMMA	50K/50K	19.90±0.01	0.905±0.005	0.53±0.03

2D imaginary permittivity plots of copolymer PS-b-PMMA



Review on the Basic models

Debye formula: $\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau}$.

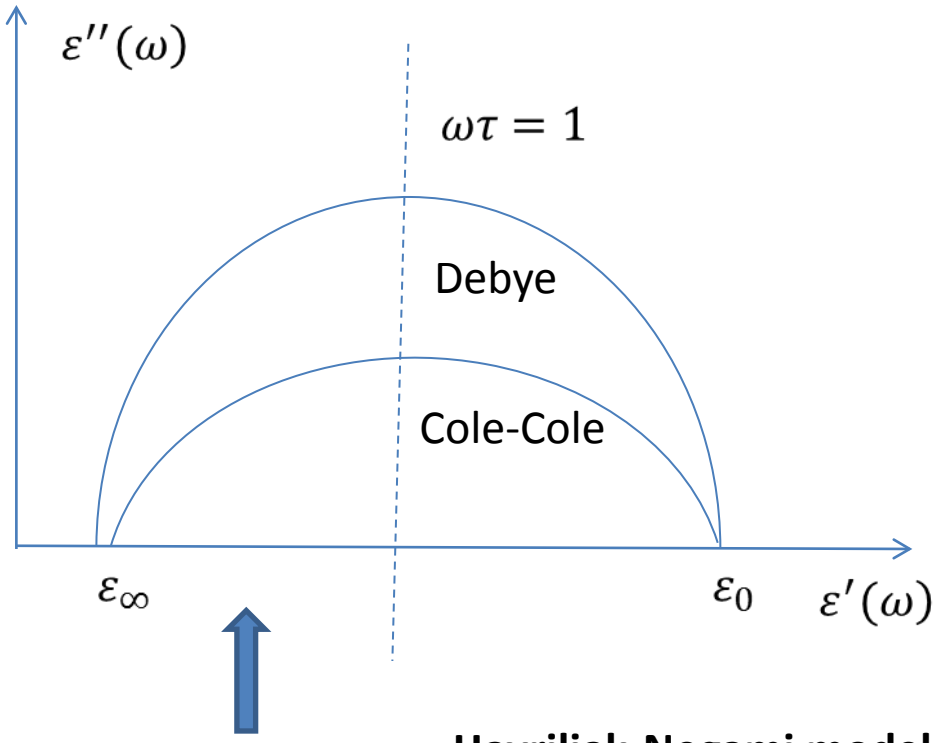
Cole-Cole Model: : $\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = [1 + i(\omega\tau)^{1-\alpha}]^{-1}$

Davidson-Cole Model : $\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = [1 + i(\omega\tau)]^{-\beta}$

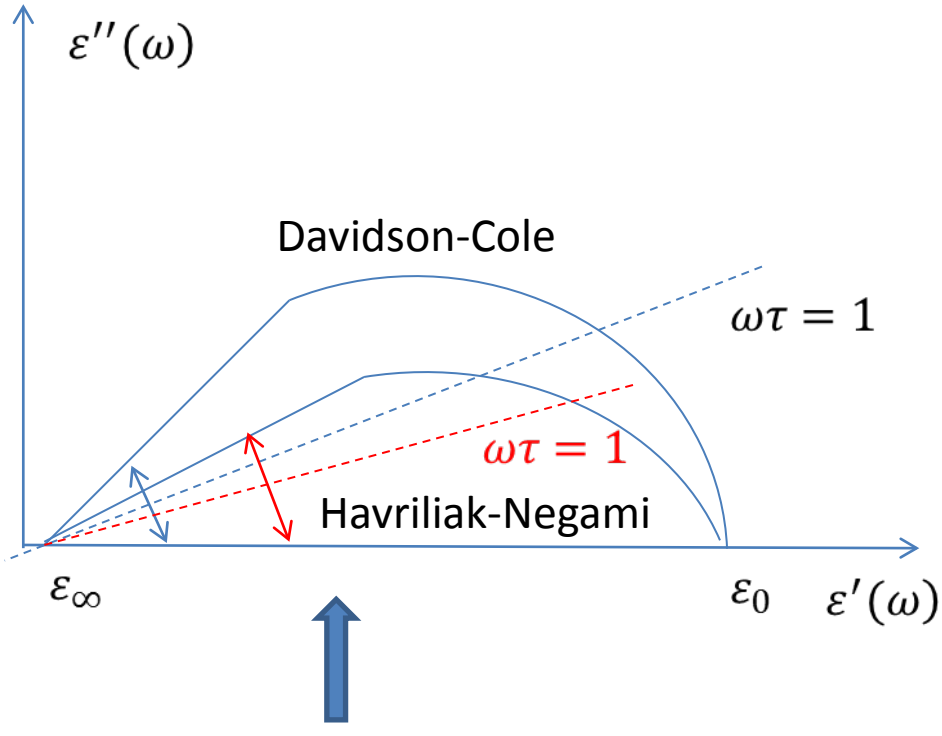
Havriliak-Negami Model:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = [1 + i(\omega\tau)^{1-\alpha}]^{-\beta}$$

Presentation of different Models on Complex Plane of Dielectric Constant



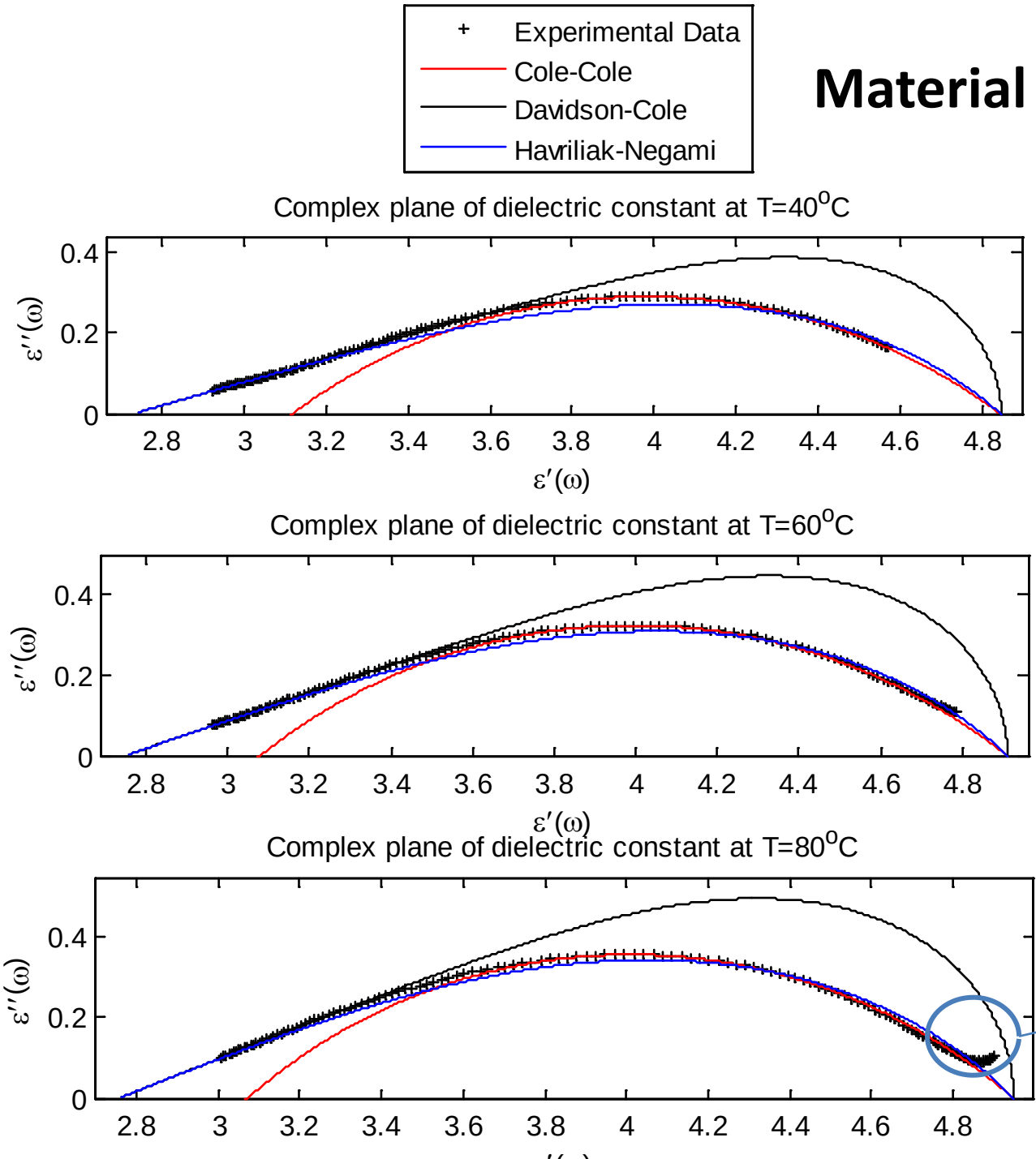
Water



Polymers

Havriliak-Negami model
Is most suitable for PS-b-PMMA

Material of Sample: PMMA



Comparison

1. Cole-Cole describes the circular arc behavior at low frequencies.
2. Davidson-Cole describes the skew line behavior at high frequencies.
3. Havriliak-Negami combines the advantages of the above two models.

Appearance of new relaxation process as T approaches T_g

Physical Mechanisms

frequency of occurrence increases

Conductivity term:

The contribution of free charge carriers

α-relaxation process:

Attributed to long chain segmental motion within the main polymer chain

β-relaxation process:

Primary localized motion of side segments

Fitting Strategy: Least-Squares Fitting of HN parameters

Reference: E. Schlosser & A. Schonhals, 1989.

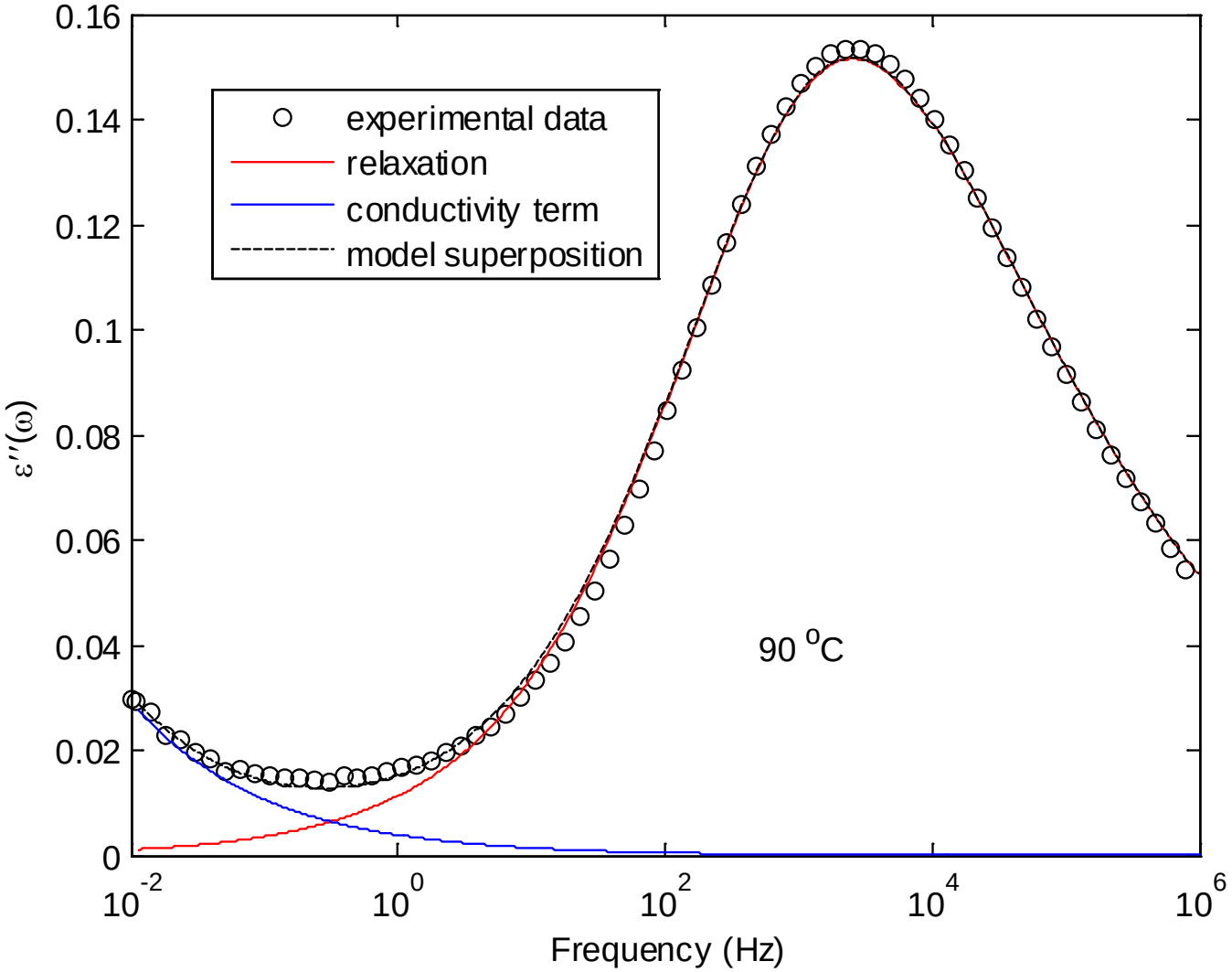
The experimental data can be separated into several intervals by their inflection points; each interval contains a main relaxation process.

HN parameters can be numerically determined by least-squares fits, according to the nonlinear regression:

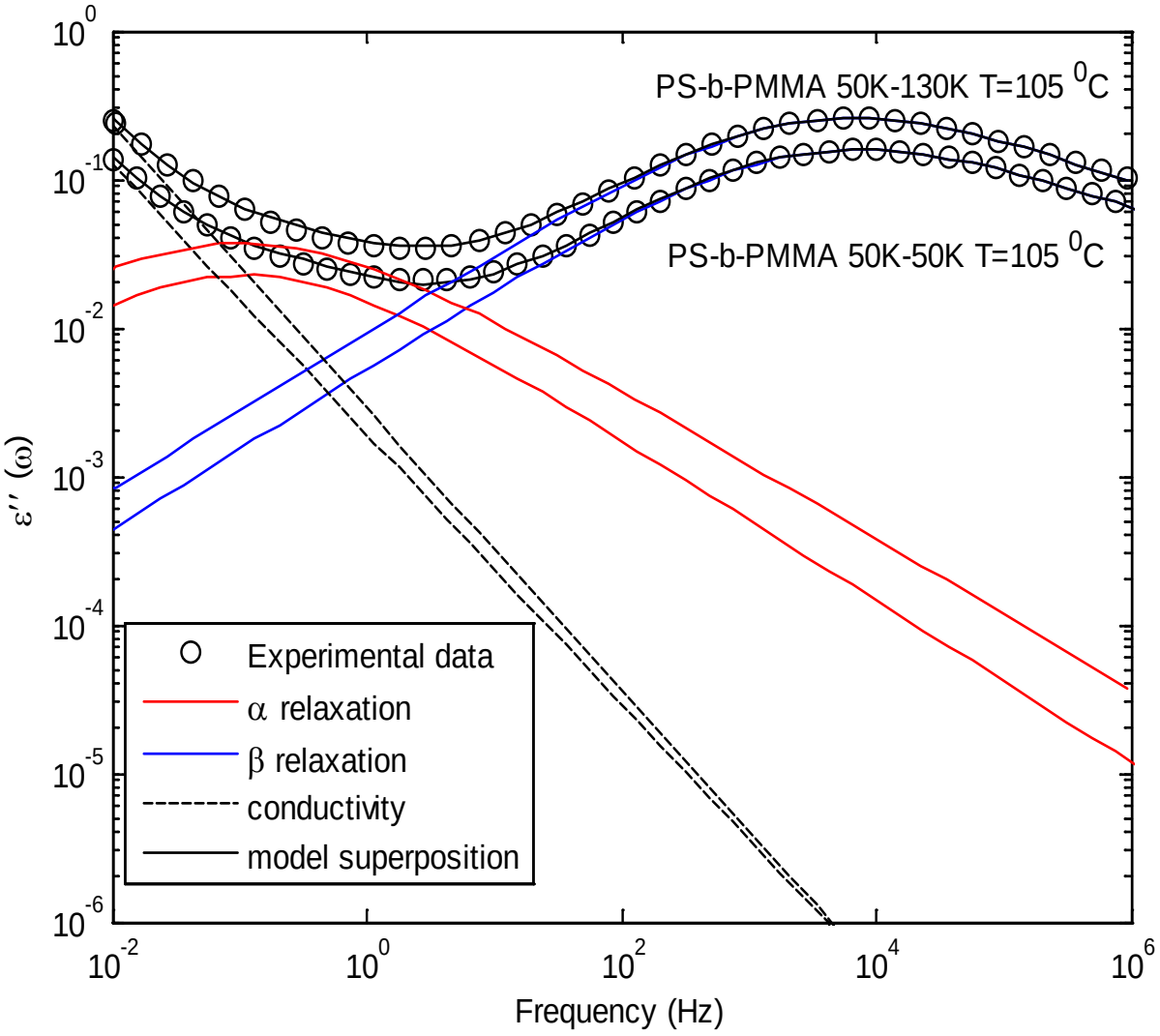
$$\sum_i \left[\varepsilon_i'' - \varepsilon''(\omega_i)\right]^2 + A\omega^{-B} \rightarrow \min$$

- ε_i'' is experimental data, $\varepsilon''(\omega_i)$ is the value given by HN function, $A\omega^{-B}$ is the conductivity term, where 0 < B < 1.

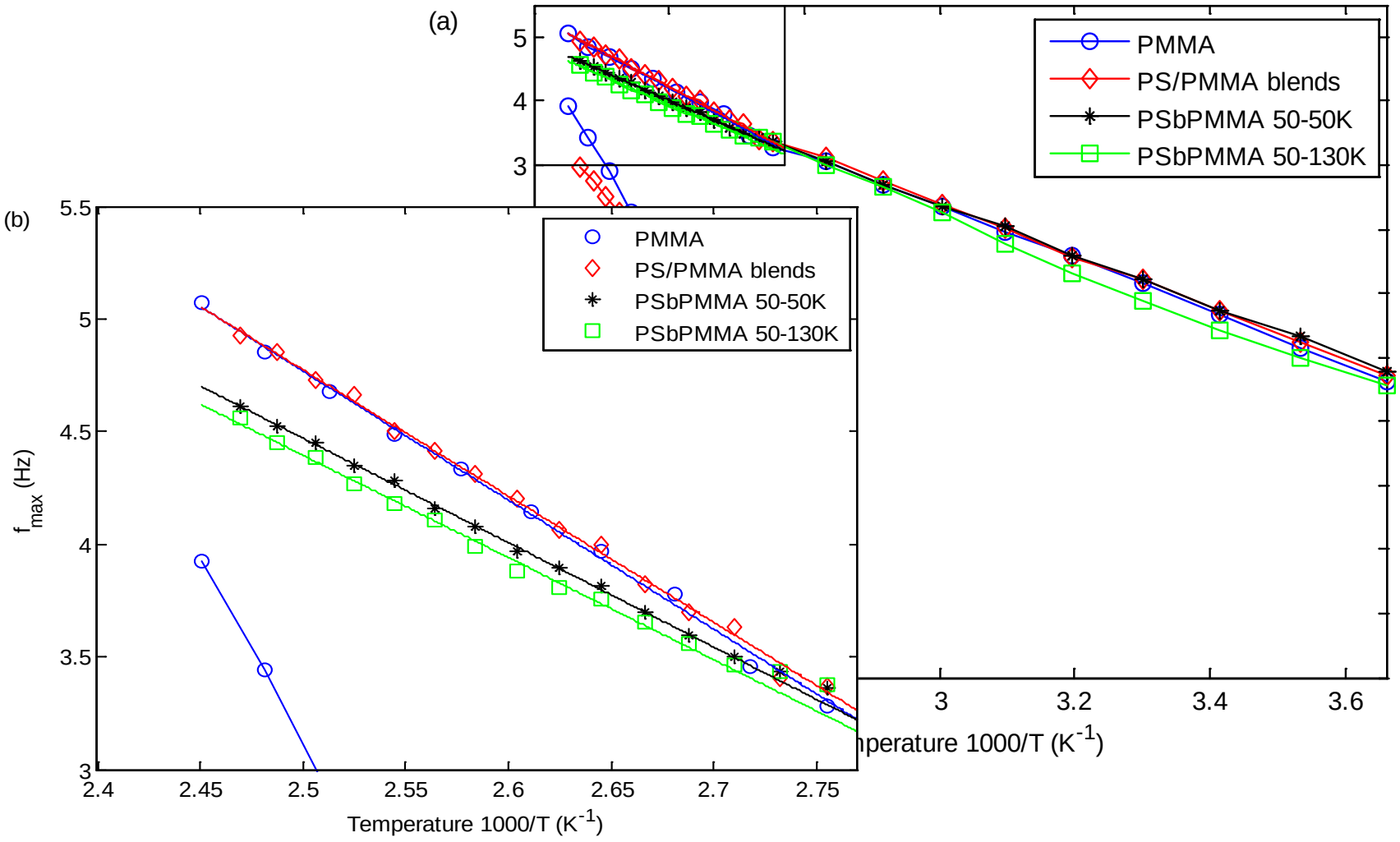
Modeling Example $T < T_g$



Modeling Example T > T_g



Relaxation Map



Temperature-dependence Behavior

Below glass transition temperature, the temperature dependence behavior can be described by Arrhenius equation, which is **β-type** relaxation.
For our acrylic sample, it is:

$$\tau^A = \tau_0^A \exp(\frac{\Delta H}{kT}),$$

Where τ_0^A is the pre-exponential factor, and ΔH is the activation energy.

Above glass transition temperature, the temperature dependence behavior can be described by Vogel-Fulcher equation, which is **α-type** relaxation.
For our acrylic sample, it is:

$$\tau^{V-F} = \tau_0^{V-F} \exp\left(\frac{DT_0}{T - T_0}\right),$$

Where τ_0^{V-F} is the pre-exponential factor and D and T_0 are the fitting parameters.

αβ-type relaxation

For the region around glas
transition temperature, th
temperature dependence
behavior can not be fitted
by both of Arrhenius Eqn. a
Vogel-Fulcher Eqn., it is **αβ**
complicated relaxation.

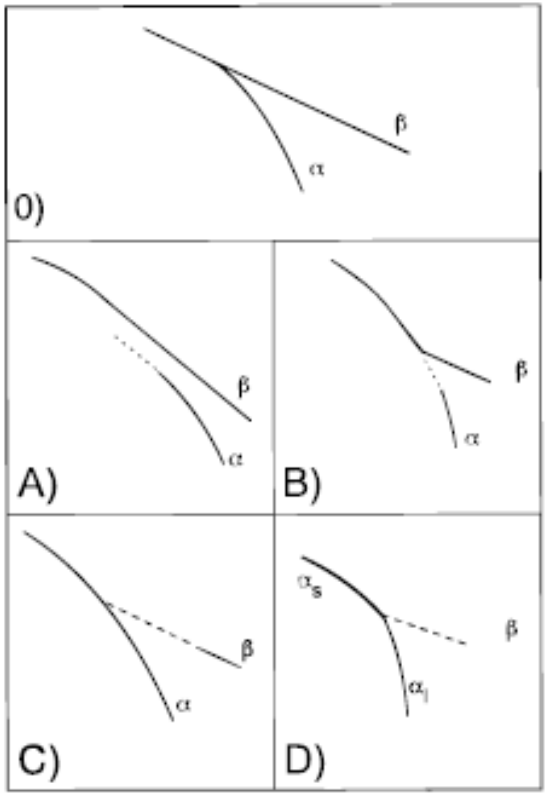


Figure 12. Five general scenarios suggested for the splitting region in the Arrhenius diagram (schematically (—) trace with considerable intensity, (– – –) uncertainty in intensity and trace, (· · ·) intensity tending to zero): (0) conventional, (A) PnBMA type (minimal cooperativity), (B) PEMA type (locally coordinative precursor), (C) PPG type (continuous α transition), and (D) OTP type (crossover between short (α_s) and long (α_l) dynamic glass transition).

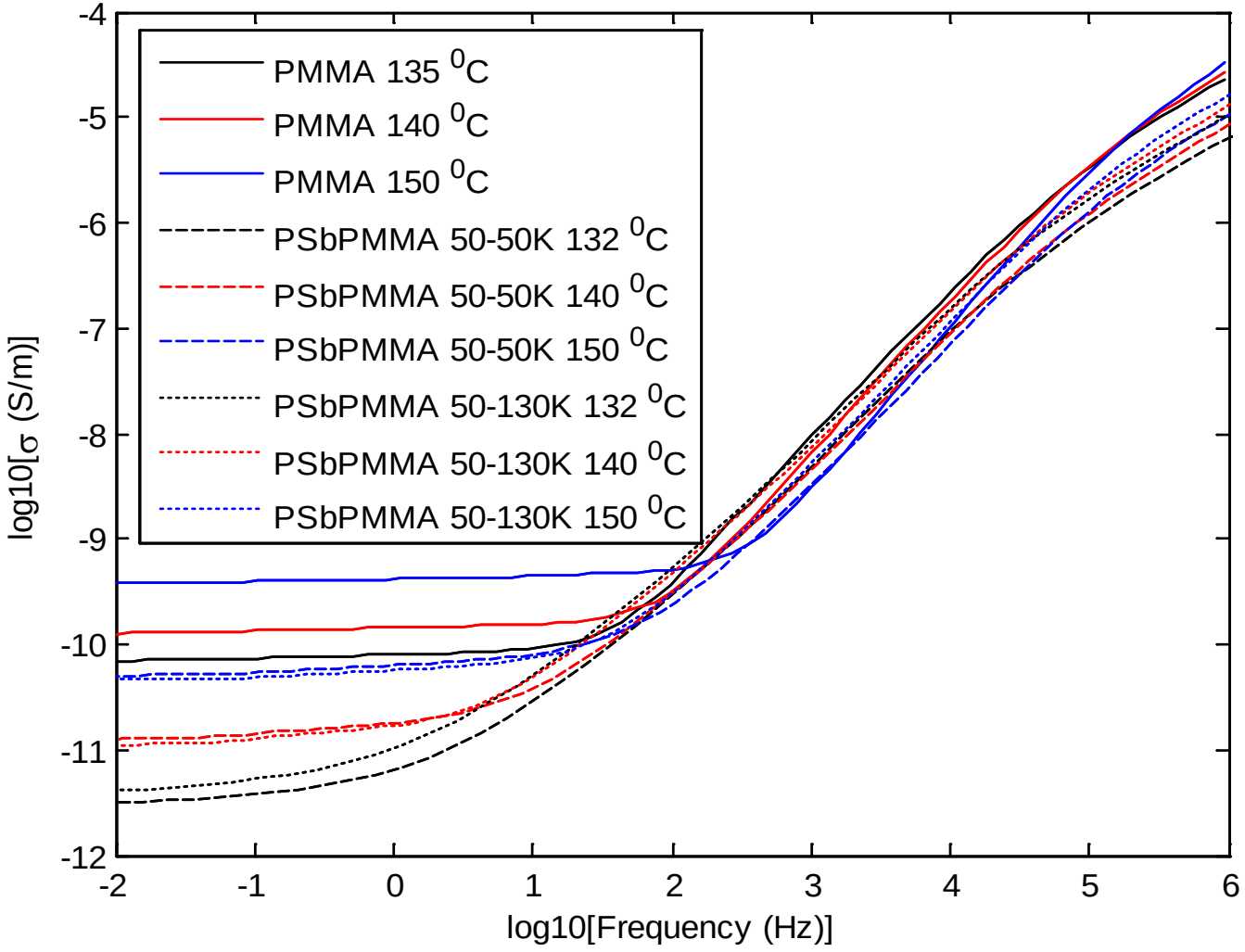
Fitting parameters of α relaxation

α relaxation	f_{max}	D	T_0 (K)	T_g (K)
PMMA	3.97e8	2.50	337	95.4
PS/PMMA blends	1.68e7	1.80	342	96
PSbPMMA 50-50k	4.21e2	0.56	354	96.8
PSbPMMA 50-130k	2.65e2	0.44	358	97.6

Fitting parameters of β relaxation

β relaxation	E_A (KJ, $T > T_g$)	E_A (KJ, $T < T_g$)
PMMA	105.5	78.2
PS/PMMA blends	106.1	77.9
PS-b-PMMA 50-50K	88.6	75.4
PS-b-PMMA 50-130K	88.0	82.0

Conductivity effects



Conductivity effects (Cont'd)

Conductivity is defined as:

$$J_{tot}=\sigma_{tot}E$$

For lossy medium, i. e. polymer materials, in which the conduction current is not negligible in this case, then the total current can be expressed as,

$$J_{tot} = J_c+J_d = \sigma E + j\omega\varepsilon' E = ji\omega\varepsilon_0\varepsilon_r^* E$$

Conductivity can be expressed as:

$$\sigma=i\omega\varepsilon_0\varepsilon''$$

where σ is the conductivity of the medium, ε' is the real part of the permittivity, ε* is the complex permittivity, ε" is the imaginary part of permittivity.

or

$$\sigma(\omega) = \sigma_{DC} + Z\omega^A$$

Conductivity effects (Cont'd)

The values of DC conductivity follow the Vogel-Fulcher-Tamman law,

$$\sigma_{DC} = \sigma_0 \exp\left[-\frac{A}{T - T_0}\right],$$

which indicates transport mechanism of charge carriers of polymers is associated with the motions of polymeric chains. The corresponding fitting parameters of DC conductivity terms are listed in the following table.

DC conductivity	σ_0 (S/m)	A	T_0 (K)
PMMA	5.39e-4	1985	283
PSbPMMA 50-50k	5.15e-6	1075	330
PSbPMMA 50-130k	1.99e-1	3584	257