Broadband Dielectric Spectroscopy as a Tool for Polymer Analysis

September 13, 2011

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INTRODUCTION

- **Dielectric behavior of a polymer**

various kinetic motions

displacement, oscillation, and orientation

of all the species like electrons, ions, atoms, and molecules in the polymer

Measurements of dielectric spectra can be a very powerful tool to analyze their motions.

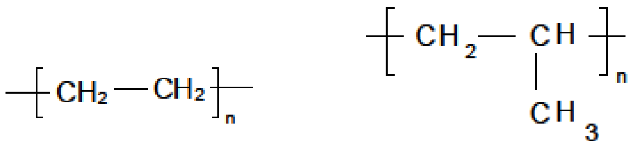
Frequency and temperature dependencies of the real part (ε_r’) and imaginary part (ε_r”) of relative complex permittivity were measured at frequencies from 10^{-2} to 10^5 Hz, from 0.4 to 4.5 THz, and from 3.6 to 30 THz.

EXPERIMENTAL PROCEDURES

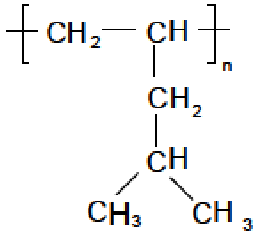
A. Samples

Polymer	Polarity	Thickness (μm)	T_g (°C)
Low density polyethylene (PE)	N	30	-110
Polypropylene (PP)	N	140	-20
Poly(methyl pentene) (PMP)	N	50	150
Polystyrene (PS)	N	150	100
Poly(phenylene sulfide) (PPS)	(P)	25	88
Polyamide-6 (PA)	P	200	50
Poly(L-lactide) (PLLA)	P	100, 180	60
Polyethylene terephthalate (PET)	P	25	80
Bisphenol A epoxy resin (EP)	P	200	151

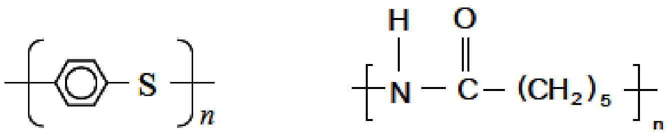
P: polar, (P): slightly polar, N: nonpolar, T_g: glass transition temperature



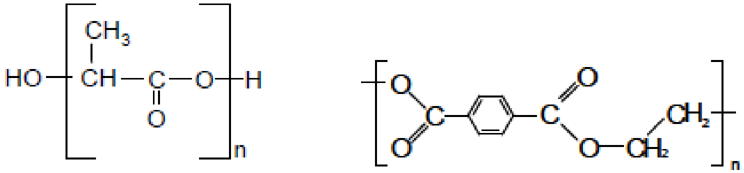
(a) PE (b) PP



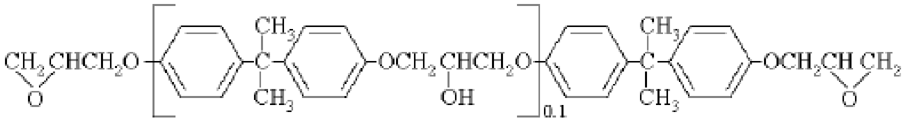
(c) PMP (d) PS



(e) PPS (f) PA



(g) PLLA (h) PET



(i) EP

Chemical structures of samples

EXPERIMENTAL PROCEDURES

- PA
  - The base PA **PA-0 or B (in THz Spectra)**
  - Its nanocomposites (synthetic mica nanoparticles)
    - 2 wt% **PA-2 or N2 (in THz Spectra)**
    - 4 wt% **PA-4 or N4 (in THz Spectra)**
    - 5 wt% **PA-5 or N5 (in THz Spectra)**

EXPERIMENTAL PROCEDURES

B. Experimental Methods

- **Complex permittivity: Solartron impedance analyzer**
  - Temperatures: -80 - 200 ^{o}C
  - Frequency: 10^{-2} - 10^{5} Hz
  - Atmosphere: in vacuum or in N_2 at 1 atm
  - Voltage: ac 3 V_{rms}
- **THz-TD spectra (dichroic): Tochigi Nikon Rayfact SpecTera**
  - Temperature: 30 ^{o}C
  - Frequency: 0.9 - 4.0 THz in the transmission mode with a resolution of 0.049 THz.
- **FT-IR measurements: Nicolet 6700**
  - Frequency: 4 - 30 THz
- **FT-IR dichroic measurements: Jasco VIR-F**
  - Frequency: 12 - 30 THz

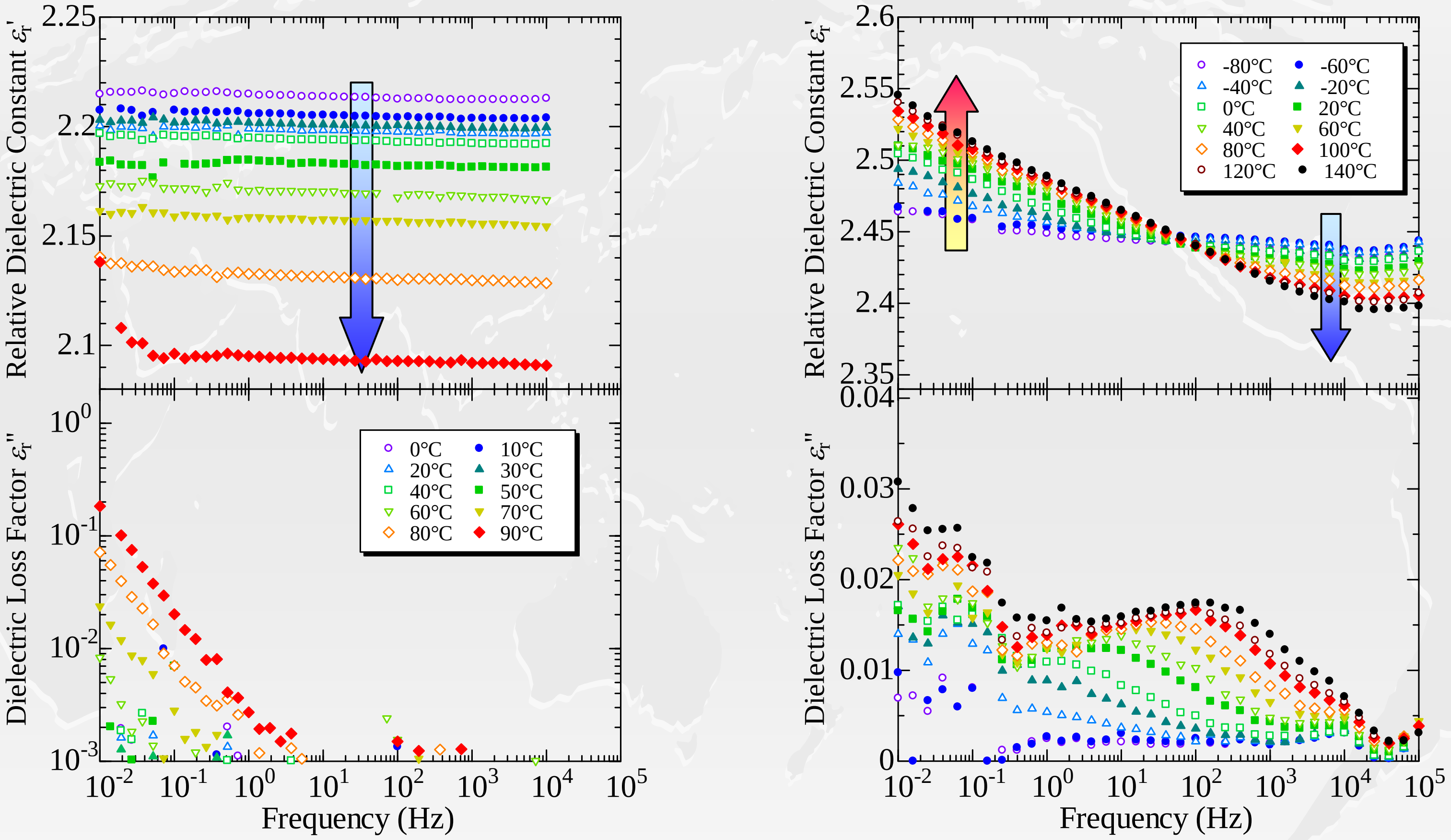
Chapter 1

SPECTRA OBSERVED AT ELECTRICAL FREQUENCIES IN VARIOUS POLYMERS

RESULTS & DISCUSSION

Complex Permittivity at Electrical Frequencies

- *Nonpolar polymers* -



(a) PE

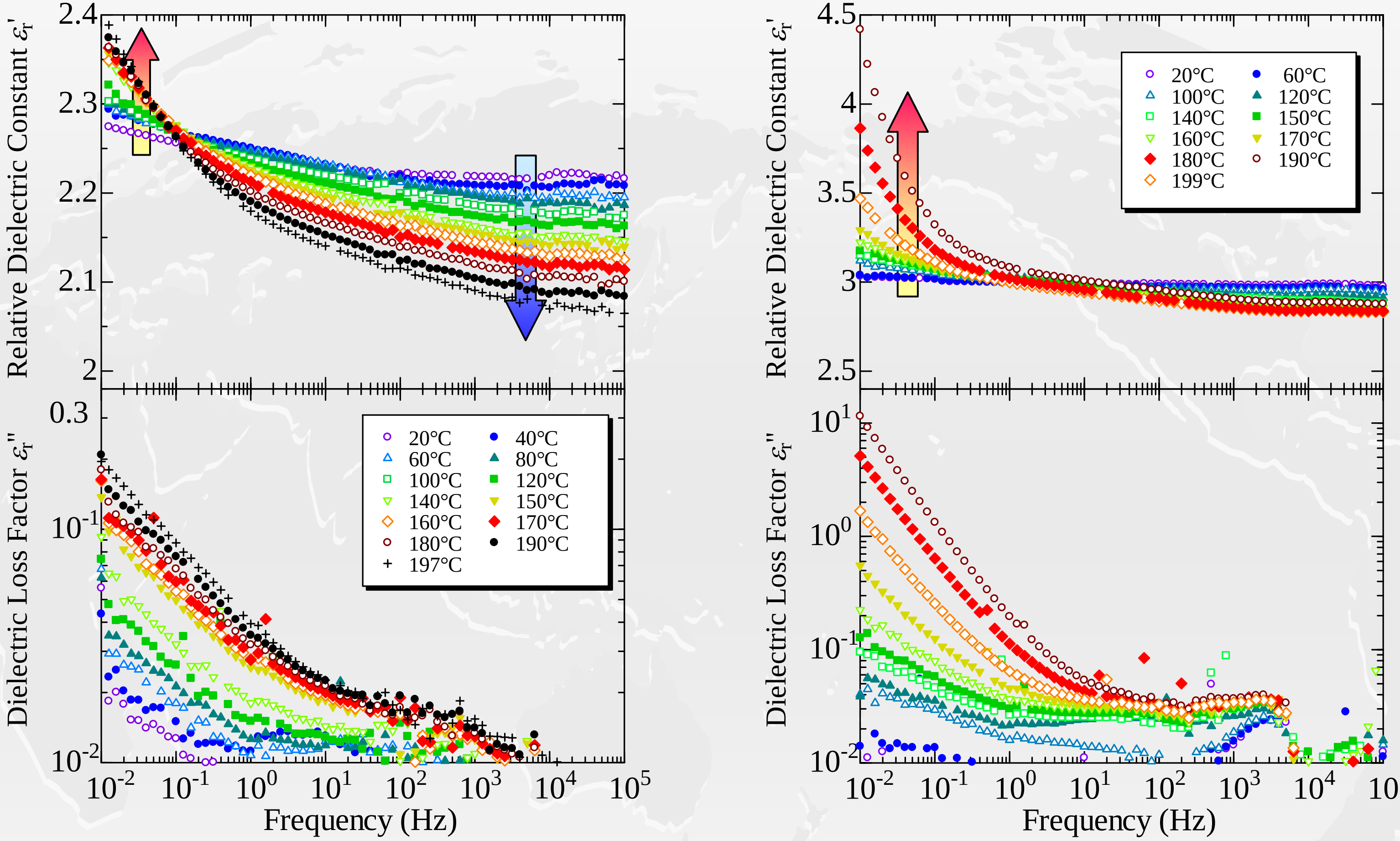
(b) PP

Nonpolar

Nonpolar

Comparison of complex permittivity at electrical frequencies among various polymers.

Complex Permittivity at Electrical Frequencies



(c) PMP

(d) PS

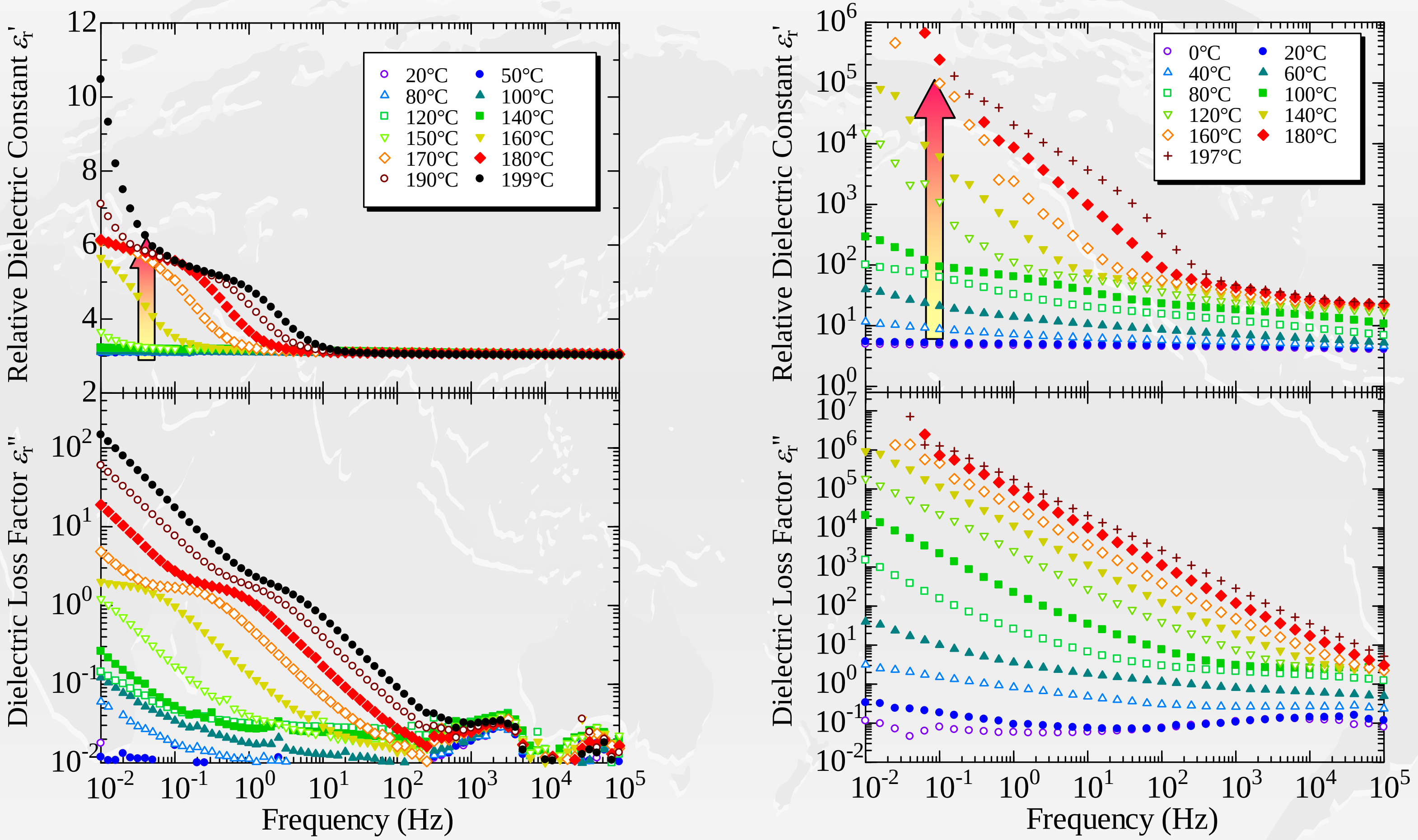
Nonpolar

Nonpolar

Comparison of complex permittivity at electrical frequencies among various polymers.

Complex Permittivity at Electrical Frequencies

- Polar polymers -



(e) PPS

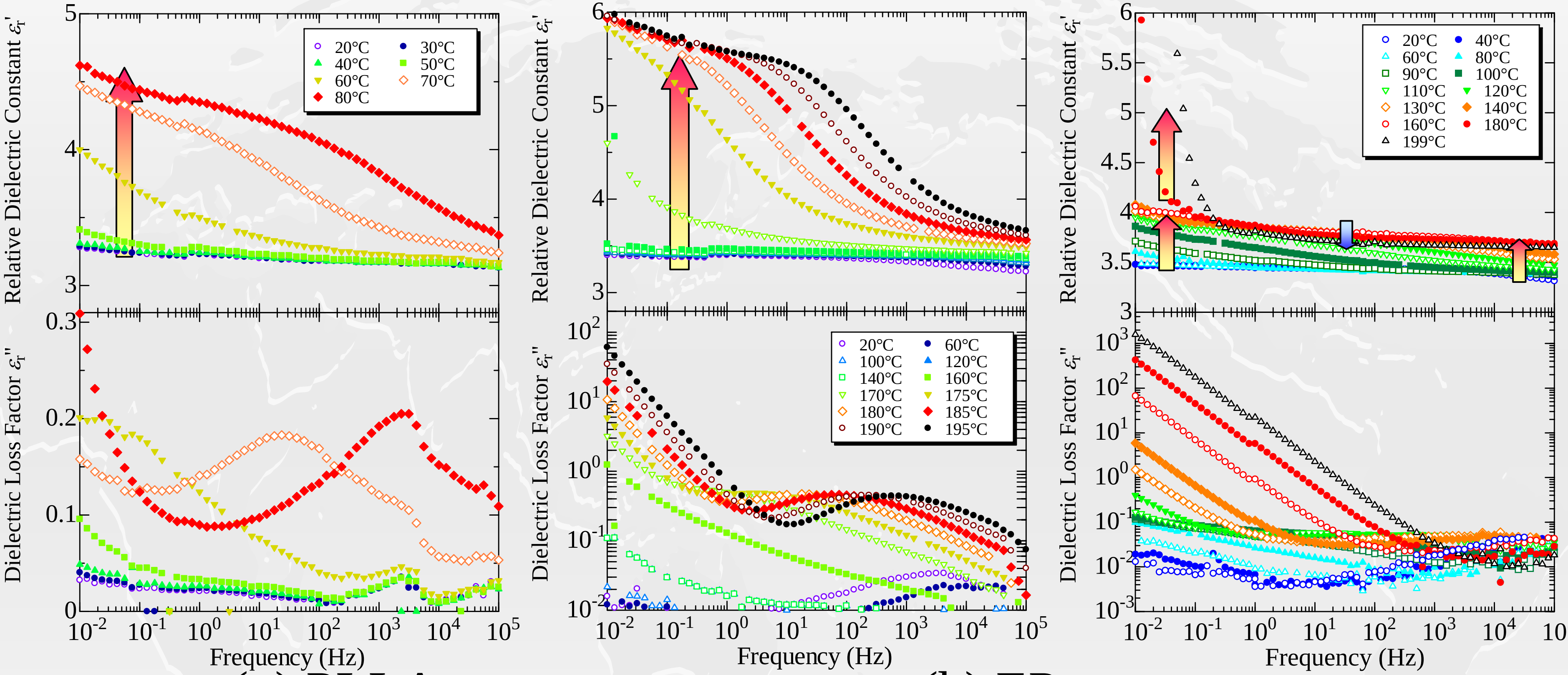
(f) PA

Slightly polar

Polar

Comparison of complex permittivity at electrical frequencies among various polymers.

Complex Permittivity at Electrical Frequencies



(g) PLLA

(h) EP

(i) PET

(crystallinity χ_c = 39%)

Polar

Polar

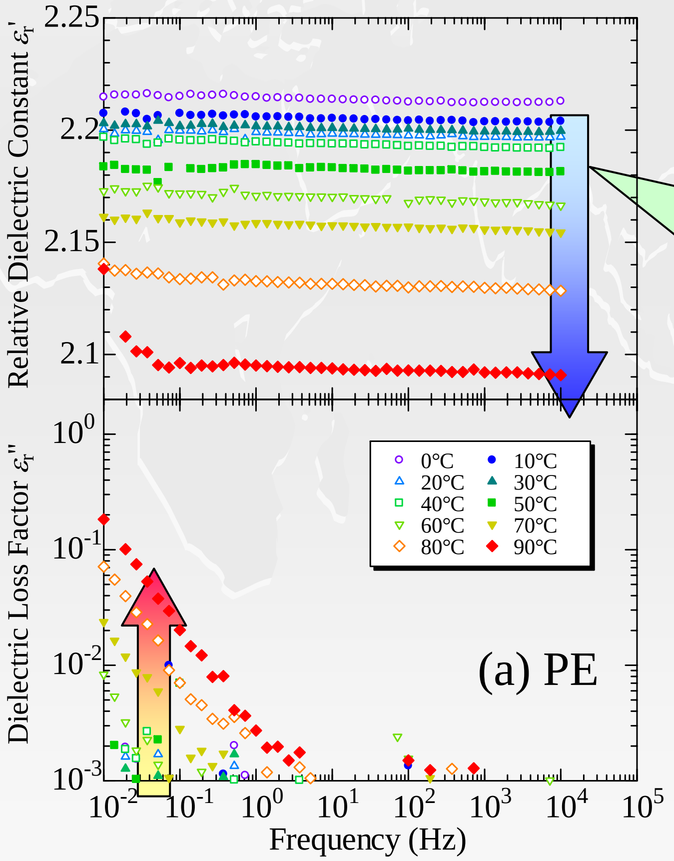
Polar

Comparison of complex permittivity at electrical frequencies among various polymers.

Complex Permittivity at Electrical Frequencies

◆ *Nonpolar polymers*

- ε_r’ shows - a clear negative temperature dependence
  (at frequencies higher than around 1 Hz for PP, PMP, and PS)



The increase in temperature inherently obstructs the formation of ordered structures.

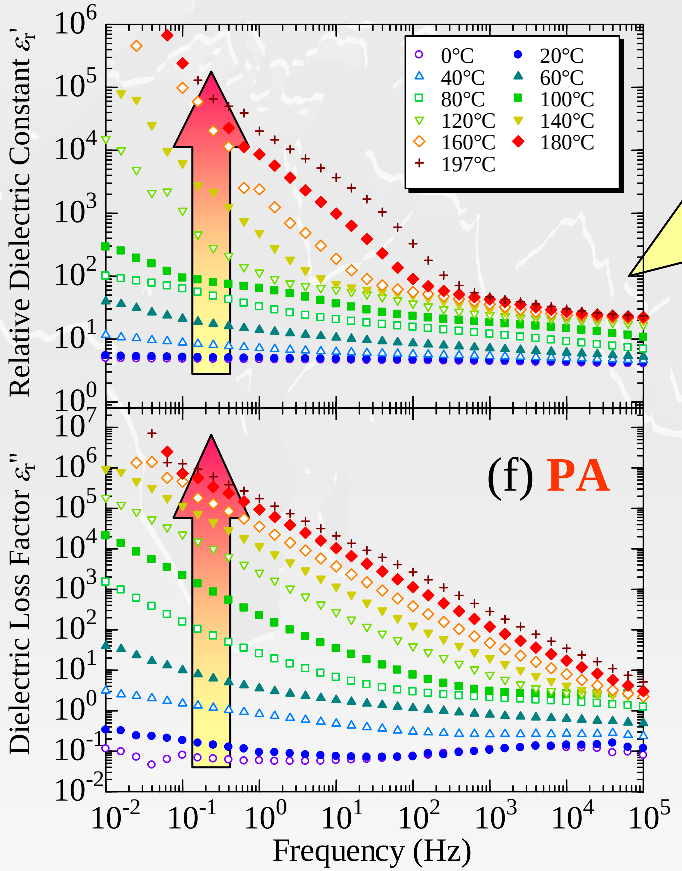
ε_r”: no clear peaks

- increases very slightly at low frequencies only when the temperature is high.

Complex Permittivity at Electrical Frequencies

◆ ***Polar polymers***

- ε_r' shows - a clear and sharp positive temperature dependence
  - a sharp negative frequency dependence



The increase in temperature softens the polymer structure.

↓

The molecular motion is enhanced to make polarization easier.

Example: **PA**

More than 10^4 of ε_r' observed at low frequencies at high temperatures like 120 ^{o}C and above.

- ε_r" increases at low frequencies at high temperatures.

Mechanism of the increase in ε_r’ and ε_r”

The increase in ε_r’ and ε_r” at low frequencies at high temperatures

⇒ Motion of mobile carriers

- Mobile carriers such as electrons, holes, or ions are present in the sample

→

Conduction current would flow upon the application of a voltage in the same phase of the applied voltage.

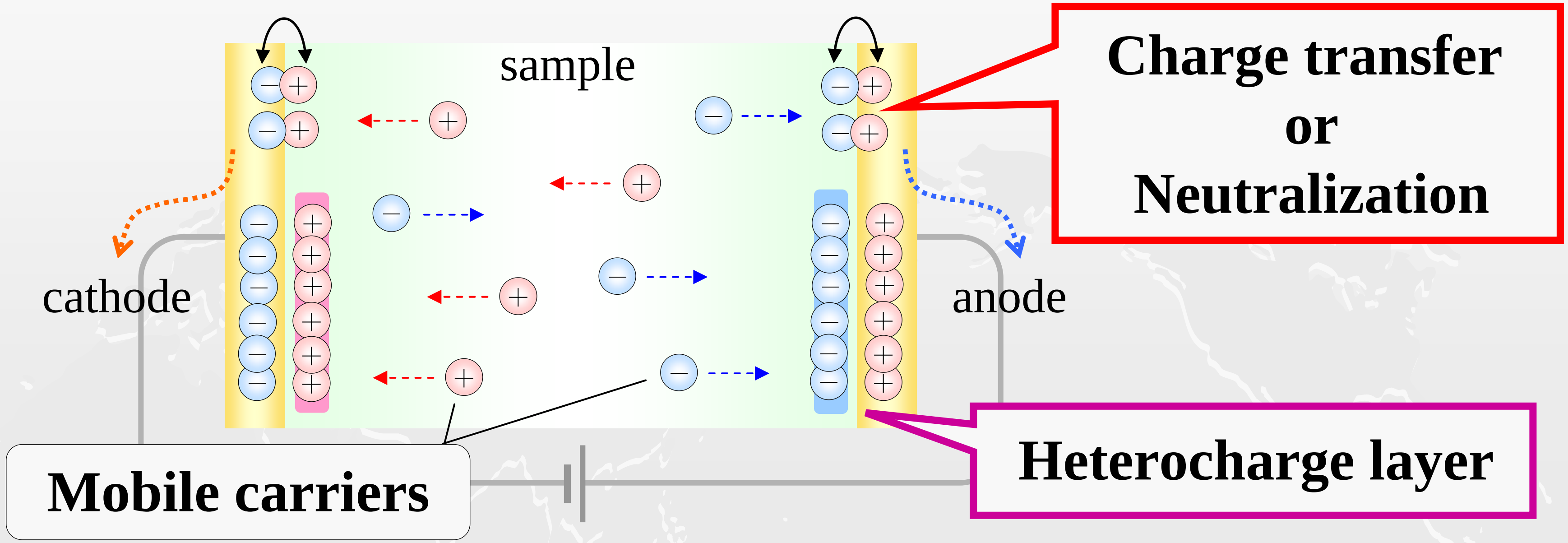
→ **Joule heating**

$$\varepsilon_r'' = \frac{\sigma}{2\pi f \varepsilon_0}$$

σ : conductivity
f : frequency of the applied voltage
ε_0 : permittivity of vacuum

→ **Increase in ε_r”**

Carrier Transport Process



Charge transfer or Neutralization

Heterocharge layer

Mobile carriers

a) If the mobile carriers exchange charge on the electrodes…

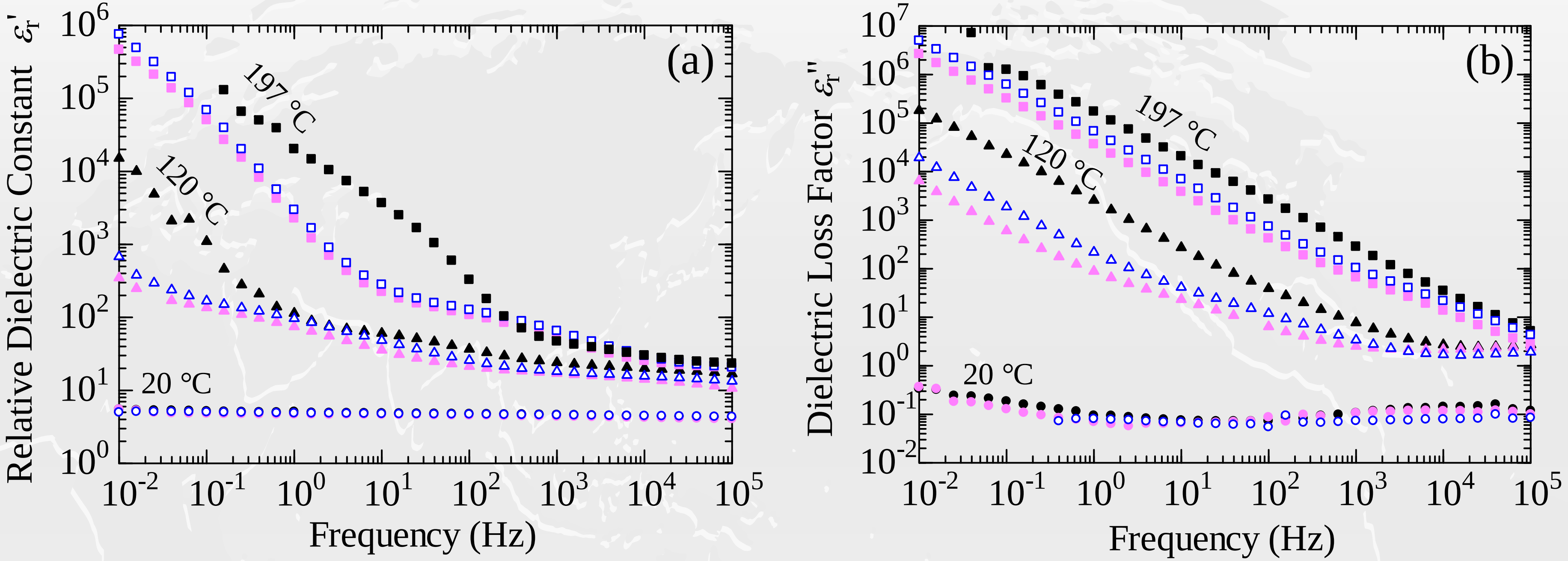
- ✓ Electrical neutrality is maintained throughout the sample.
- ✓ No image charge is induced, and ε_r’ should not increase.

b) If carriers accumulate in the vicinity of the electrodes…

- ✓ Image charge is induced (space charge polarization).
- ✓ ***Contribute to ε_r’.***

Complex Permittivity at Electrical Frequencies

PA and its NCs



Comparison of relative dielectric constant (a) and loss factor (b) at 20 °C (circles), 120 °C (triangles), and 197 °C (squares). The solid black, solid pink, and open blue symbols represent PA-0, PA-2, and PA-5, respectively [5].

[5] N. Fuse et al., *IEEE Trans. Dielectr. Electr. Insul.*, Vol. 16, No. 2, pp. 524-530, 2009.

Effects of Nanofillers on Complex Permittivity in PA

- **Carrier transport is restricted in NCs**

Strong interaction between the resin and nanofillers induced by their enormously large total surface area [5].

- Polyamide is known to have **relaxation peaks** called α and β
  - alignment of dipoles in the amorphous phase
  - rotation of amide groups bonded by hydrogen bonds with water molecules

- It was confirmed that the average relaxation time becomes longer by the nanofiller addition for both α and β peaks.

The suppression of molecular motion by the nanofillers [5].

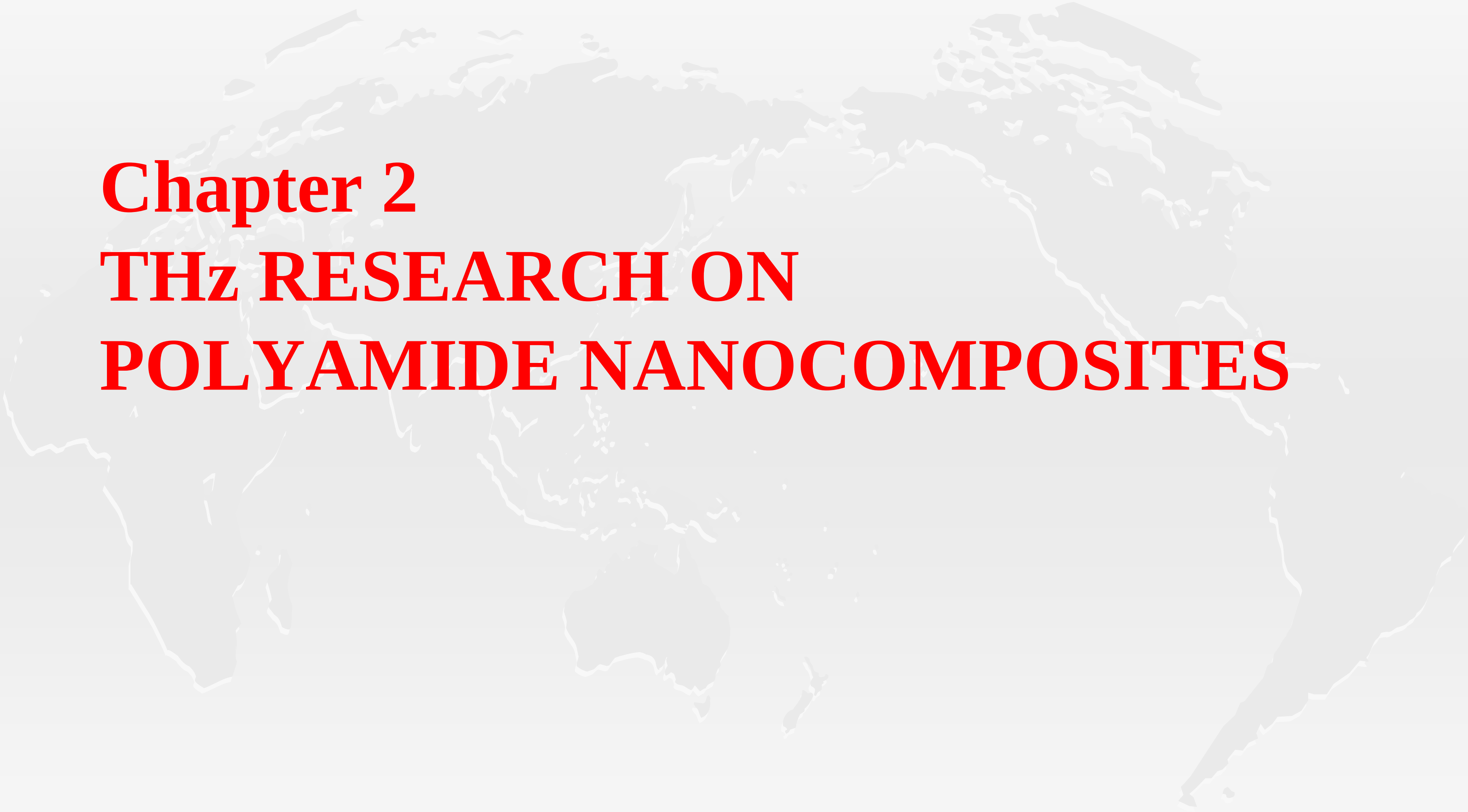
[5] N. Fuse et al., *IEEE Trans. Dielectr. Electr. Insul.*, Vol. 16, No. 2, pp. 524-530, 2009.

V. Conclusion of Chapter 1

- Measurements of complex permittivity spectra reflect a wide-aspect nature of polymers.
- Carrier transport in polymers and charge exchange on electrodes

  → affect both real and imaginary parts of permittivity, especially at low frequencies.
- Dipoles in a polymer or those due to impurities

  → also play an important role in determining temperature and frequency dependencies of ε_r'.

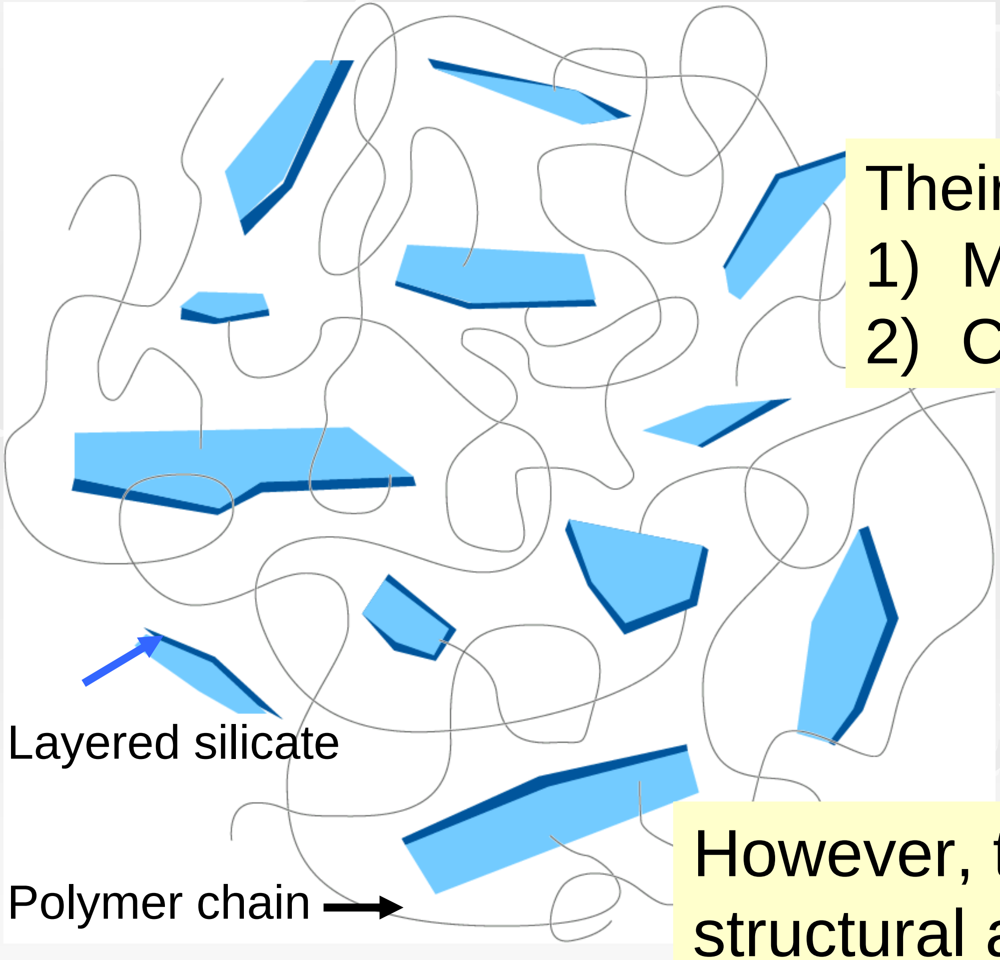


Chapter 2

THz RESEARCH ON POLYAMIDE NANOCOMPOSITES

Polymer nanocomposites

Polymer nanocomposites (NCs) are known to have good mechanical, thermal, and dielectric properties.



Their mechanism:

1) Molecular motion is restricted.
2) Crystalline regions are formed.

However, the details of these structural and morphological changes have not been clarified.

Samples investigated

Base polyamide-6: B

Nanocomposites: N2, N4, N5

Nanofiller: layered silicate

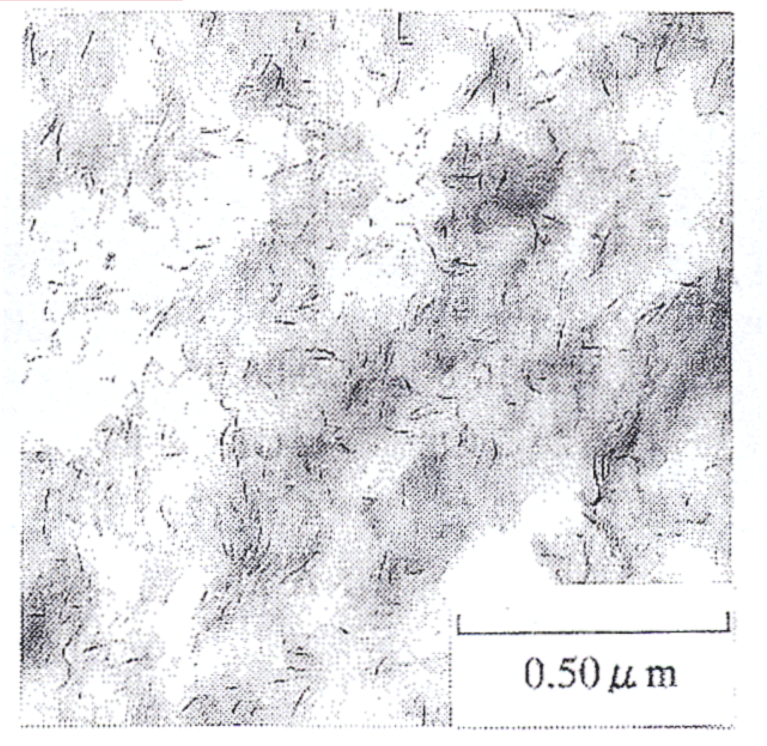
Synthetic mica: $NaMg_{2.5}Si_4O_{10}F_2$
thickness: ~1 nm, width: ~100 nm

Contents: 2, 4, and 5 wt%

Microcomposite: M

Filler: talc

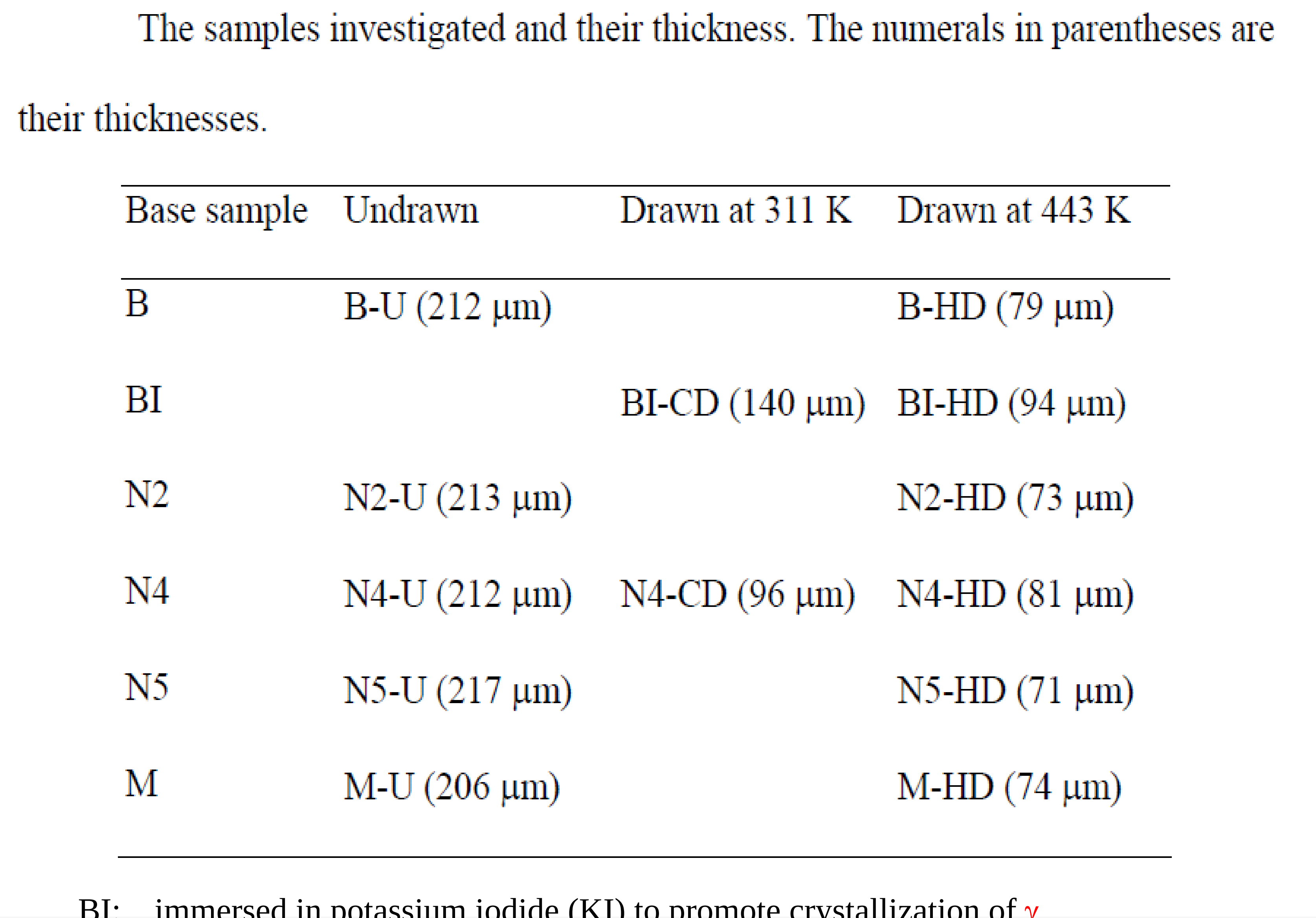
Content: 35 wt%



TEM image of nanocomposite*

*S. Katahira et al., Kobunshi Ronbunshu, vol. 55, No. 2, pp. 90-95 (1998) [in Japanese]

NC samples investigated

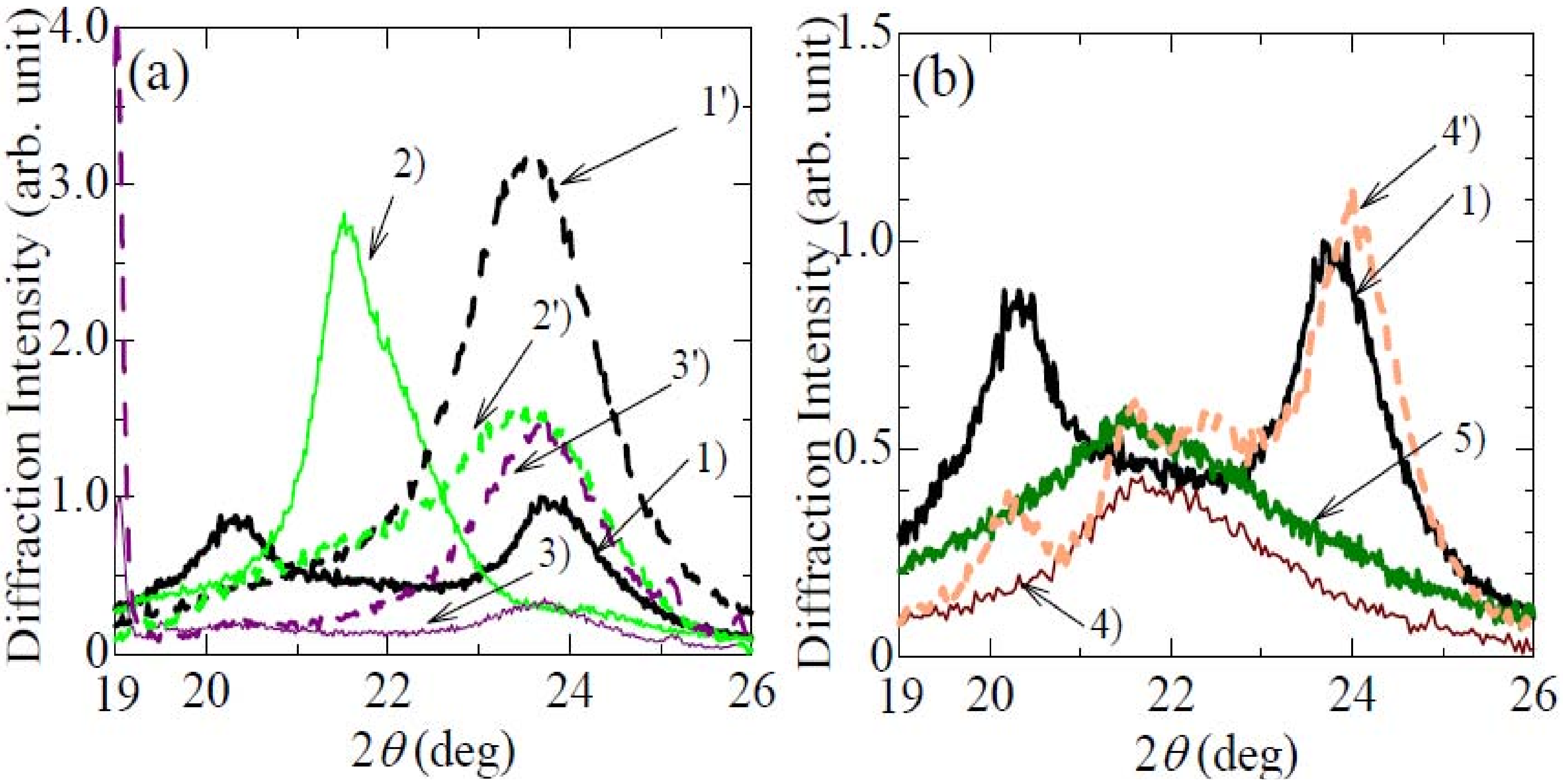


The samples investigated and their thickness. The numerals in parentheses are their thicknesses.

Base sample	Undrawn	Drawn at 311 K	Drawn at 443 K
B	B-U (212 μm)		B-HD (79 μm)
BI		BI-CD (140 μm)	BI-HD (94 μm)
N2	N2-U (213 μm)		N2-HD (73 μm)
N4	N4-U (212 μm)	N4-CD (96 μm)	N4-HD (81 μm)
N5	N5-U (217 μm)		N5-HD (71 μm)
M	M-U (206 μm)		M-HD (74 μm)

BI: immersed in potassium iodide (KI) to promote crystallization of γ crystals

XRD spectra



Effects of the drawing (a) and the KI treatment (b) on XRD spectra. 1): B-U, 1'): B-HD, 2): N4-U, 2'): N4-HD, 3): M-U, 3'): M-HD, 4): BI-CD, 4'): BI-HD, 5): N4-CD. Note that the sharp peak at around 19° is due to talc in sample M.

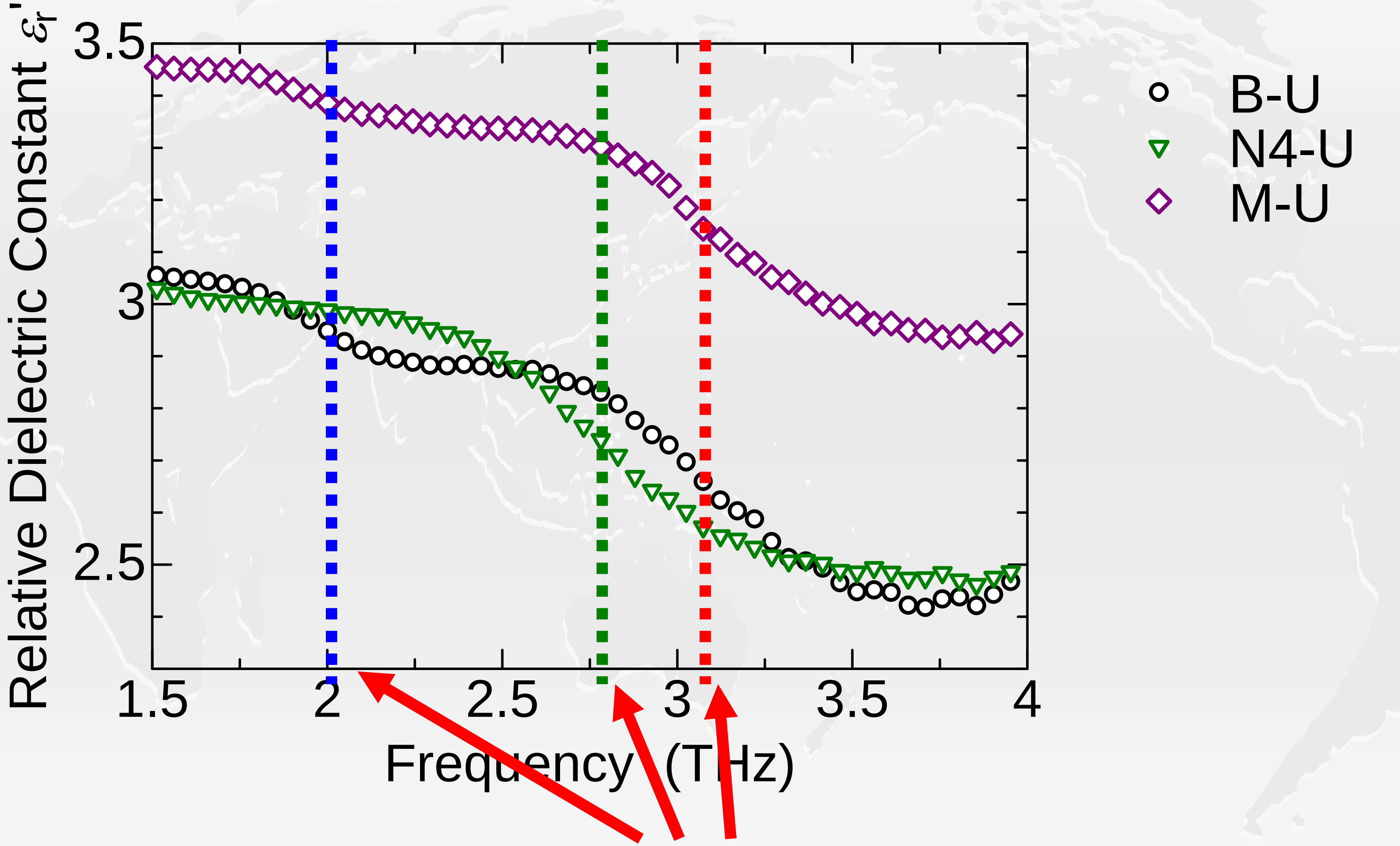
XRD spectra

- Origin of XRD peaks:
  Peaks at 20.1° and 23.7°: due to α crystals in polyamide.
  Peak at 21.6°: due to γ crystals in polyamide.

- Important points:
  1) The 21.6° peak is stronger in N4-U than in B-U and M-U.
  -> Nanofillers promote crystallization of γ crystals.

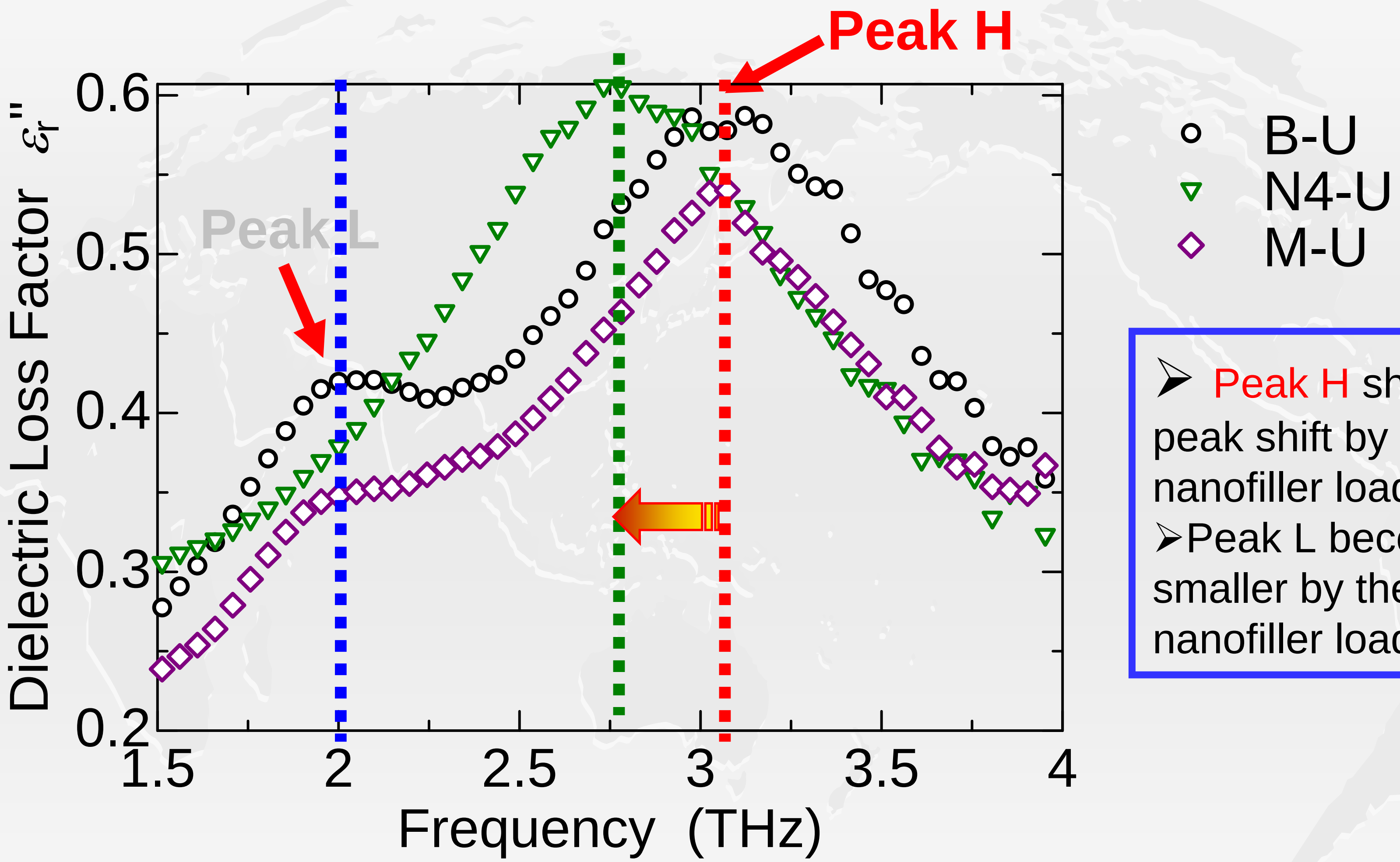
  2) Drawing increases the 23.7° peak.
  -> Drawing promotes formation of α crystals and converts the dominant crystal form in N4-U from γ to α.

Dielectric constant spectra (undrawn samples)



Medium frequency of each step

Dielectric loss spectra (undrawn samples)



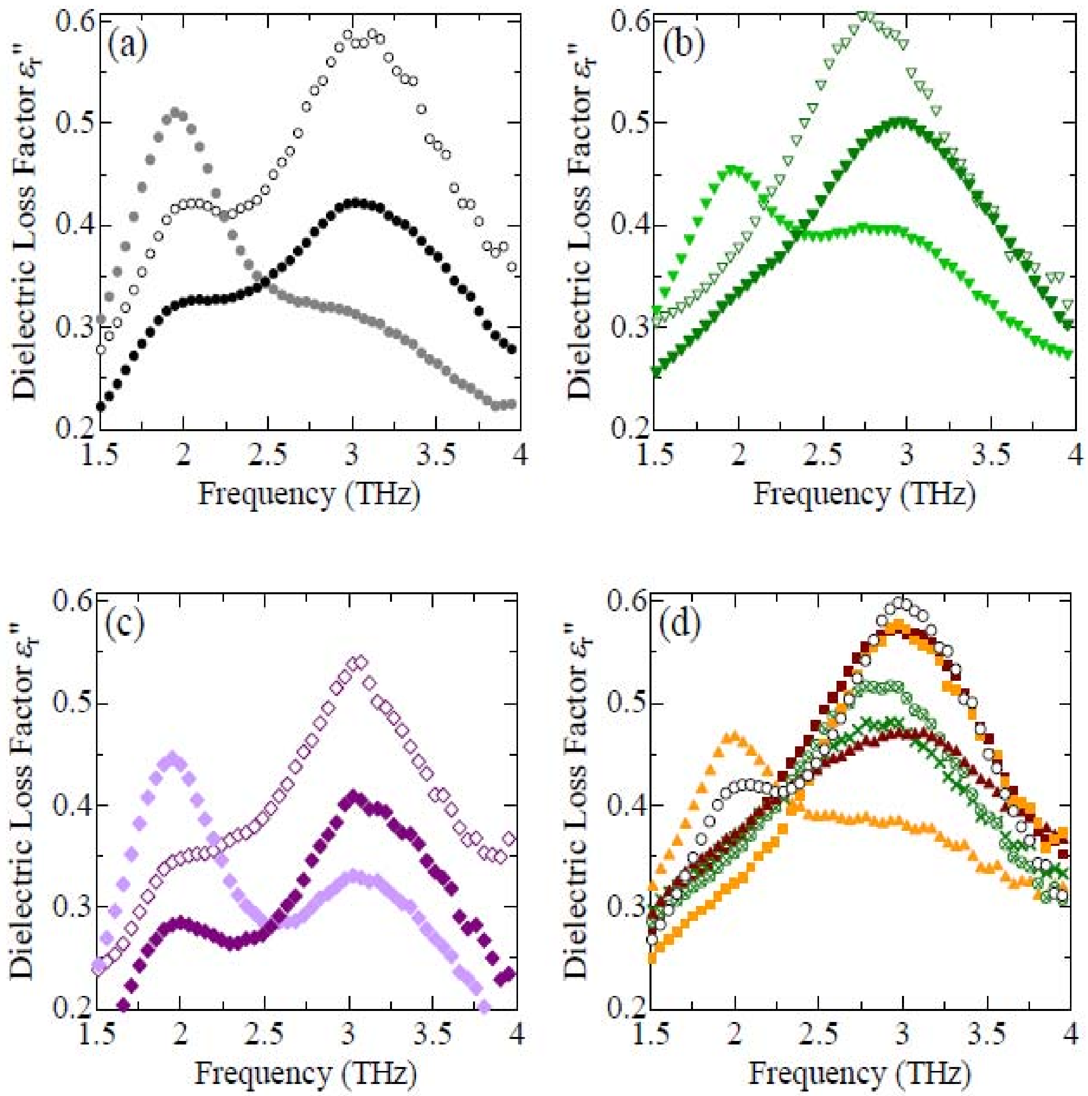
- ➢ Peak H shows a peak shift by the nanofiller loading.
- ➢Peak L becomes smaller by the nanofiller loading.

➢Peak frequency of…

Peak L: almost the same in all the samples.

Peak H: lower in N4-U.

Dielectric loss spectra (all samples)



Effects of the drawing on the dielectric loss spectra measured for B (a), N4 (b), M (c), and KI treated samples (d).

(a) ○: B-U, ●: B-HD (0°), ●: B-HD (90°)

(b) ▽: N4-U, ▼: N4-HD (0°), ▼: N4-HD (90°)

(c) ◊: M-U, ♦: M-HD (0°), ♦: M-HD (90°)

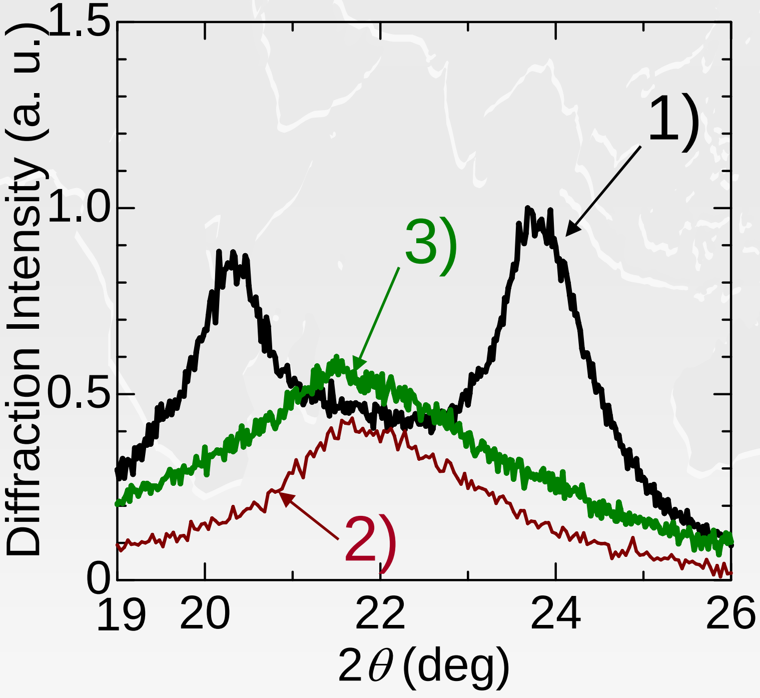
(d) ○: B-U, ×: N4-CD (0°), ⊗: N4-CD (90°), ▲: BI-CD (0°), ■: BI-CD (90°), ▲: BI-HD (0°), ■: BI-HD (90°).

The numerals in parentheses are the angles between the incident THz electric field and the drawing direction. Note that the undrawn samples have no angular dependencies.

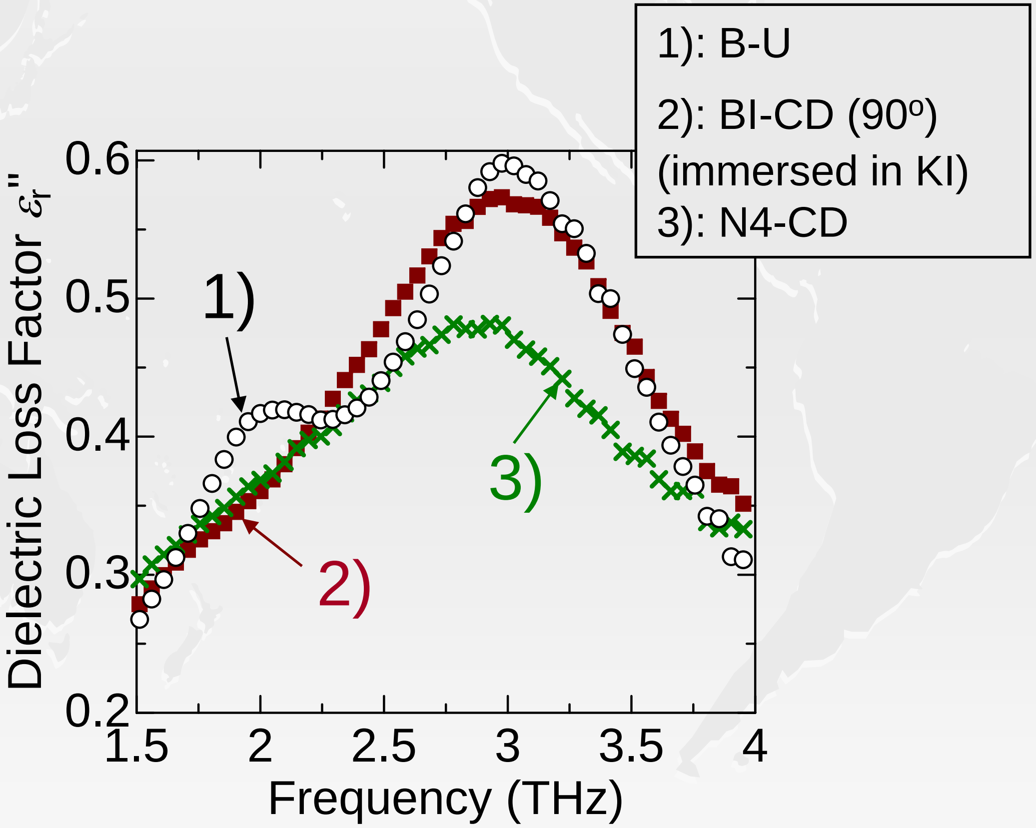
Mechanism of the peak shift in Nanocomposites (1)

- Two candidates:
  i) Polymer/nanofiller interaction   ii) Formation of γ crystals

Sample B was immersed in a potassium iodide (KI) solution.



XRD spectra



1): B-U

2): BI-CD (90°)
(immersed in KI)
3): N4-CD

Dielectric loss spectra

Mechanism of the peak shift in Nanocomposites (2)

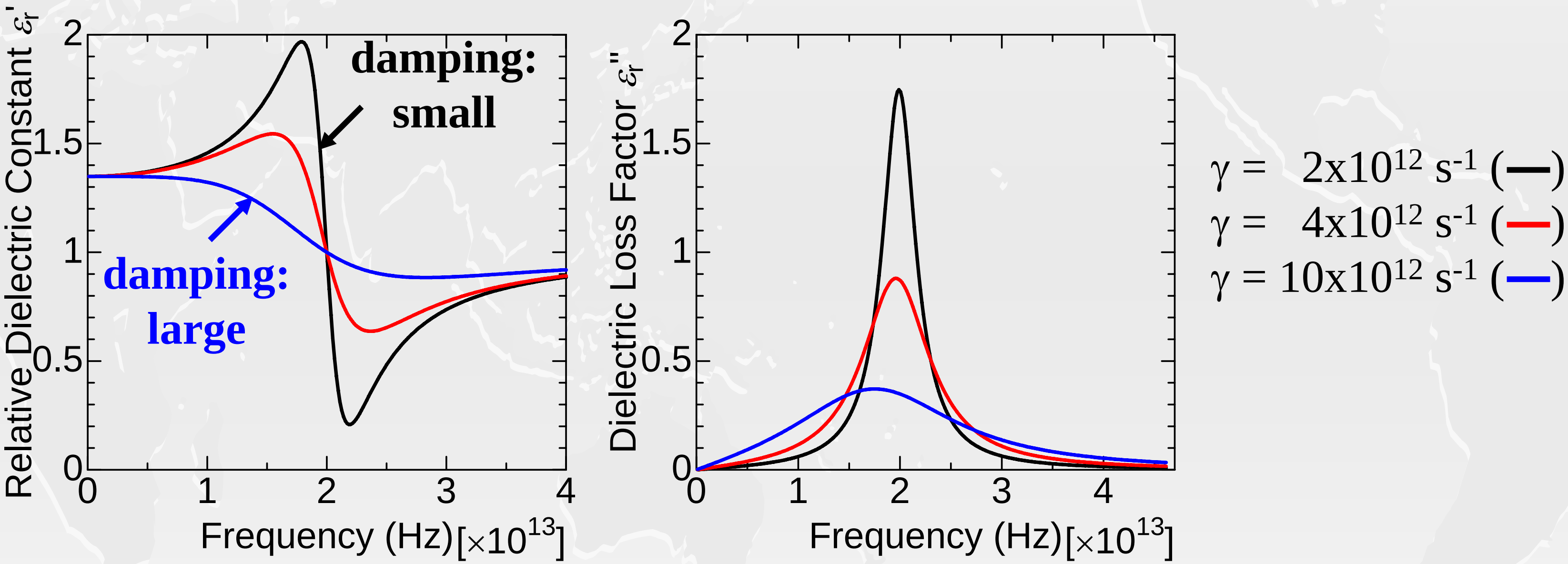
- Important points obtained from sample BI-CD (immersed in KI):

1) The sample BI-CD immersed in KI has γ crystals.
2) However, the peak frequency of peak H is exactly the same as that observed in sample B-U.

The peak shift:
Not ascribable to the presence of γ crystals
Due to the interaction between the polymer matrix and nanofillers

THz Peaks due to Resonance Phenomena

- There are polarization processes due to resonance such as atomic polarization at THz frequencies.
- The spectral shape of a resonance type approaches a relaxation type if damping is large.



There is a possibility that the two THz peaks are due to certain atomic polarization processes.

ε_r” at THz Frequencies (PA)

- The ε_r” peak at around 1.9 THz does not appear in the undrawn PA-4 film and that its intensity becomes largest and smallest when the THz electric field is parallel and perpendicular to the drawing direction.
- Polarization angular dependence is opposite to that observed for the ε_r” peak seen around 2.5 to 3.0 THz.
- A similar opposite relation was confirmed about the appearance and disappearance of X-ray diffraction peaks associated with α and γ crystals in PA [9].

[14] N. Nagai et al., *Appl. Phys. Lett.*, 85, 4010, 2004.

The ε_r” absorption around 1.9 THz

polarization aligned parallel to the molecular chains in α crystals

The other absorption around 2.5 to 3.0 THz

motion of polar groups perpendicular to the molecular chains

The assignments of this absorption → amide groups [14].

V. Conclusion of Chapter 2

1) The XRD intensity due to γ crystals is larger in NCs

->The nanofiller loading promotes the formation of γ crystals.

2) The drawing of the sample promotes formation of α crystals

3) Peak H is largest when the THz electric field is perpendicular to the drawing direction.

->Peak H is due to the motion of polar groups perpendicular to the molecular chains

4) Peak frequency of peak H shifts to a lower frequency by the nanofiller loading

-> Strong interaction is formed between the nanofiller and resin.

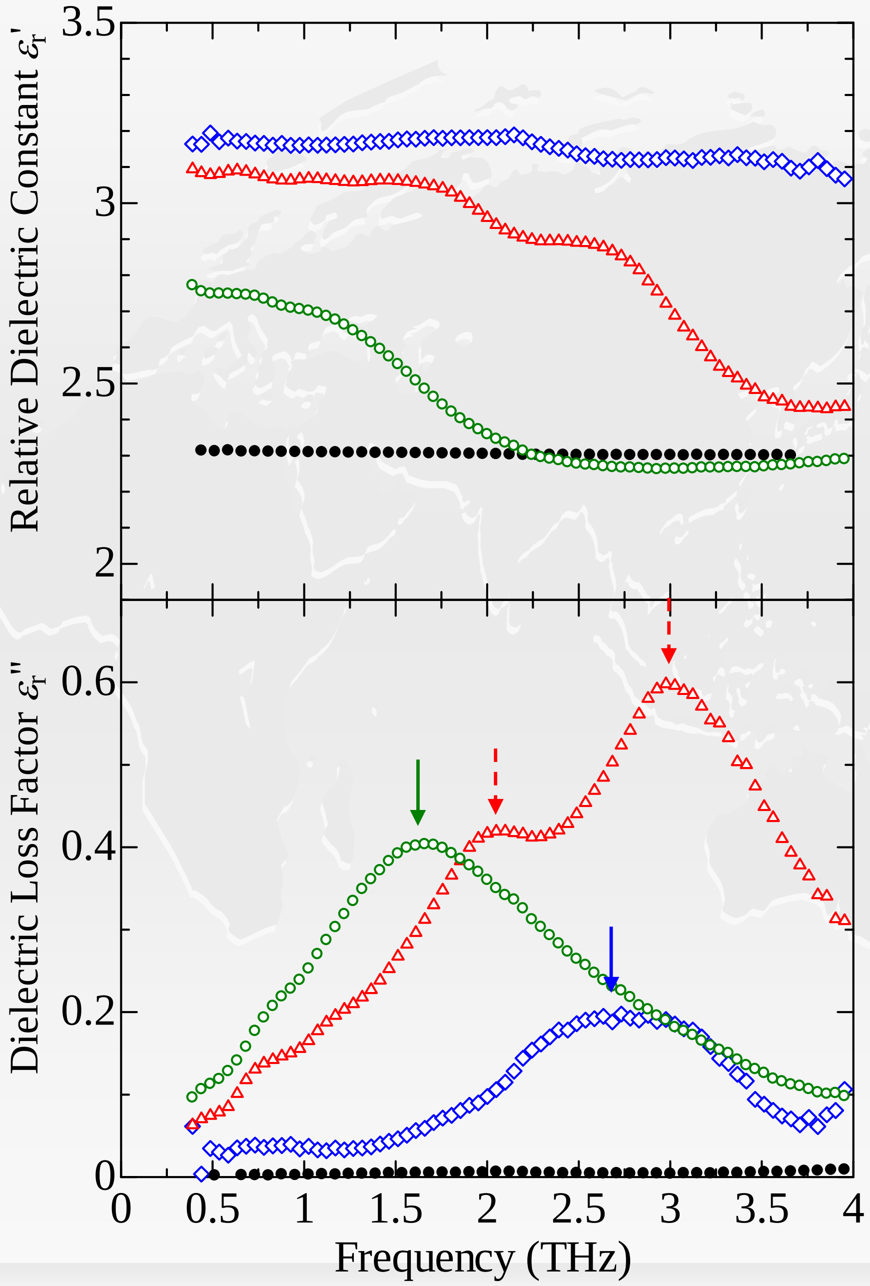
5) Peak L shows a good agreement between its intensity and the XRD intensity due to a crystals.

-> Peak L is due to α crystals.

Chapter 3

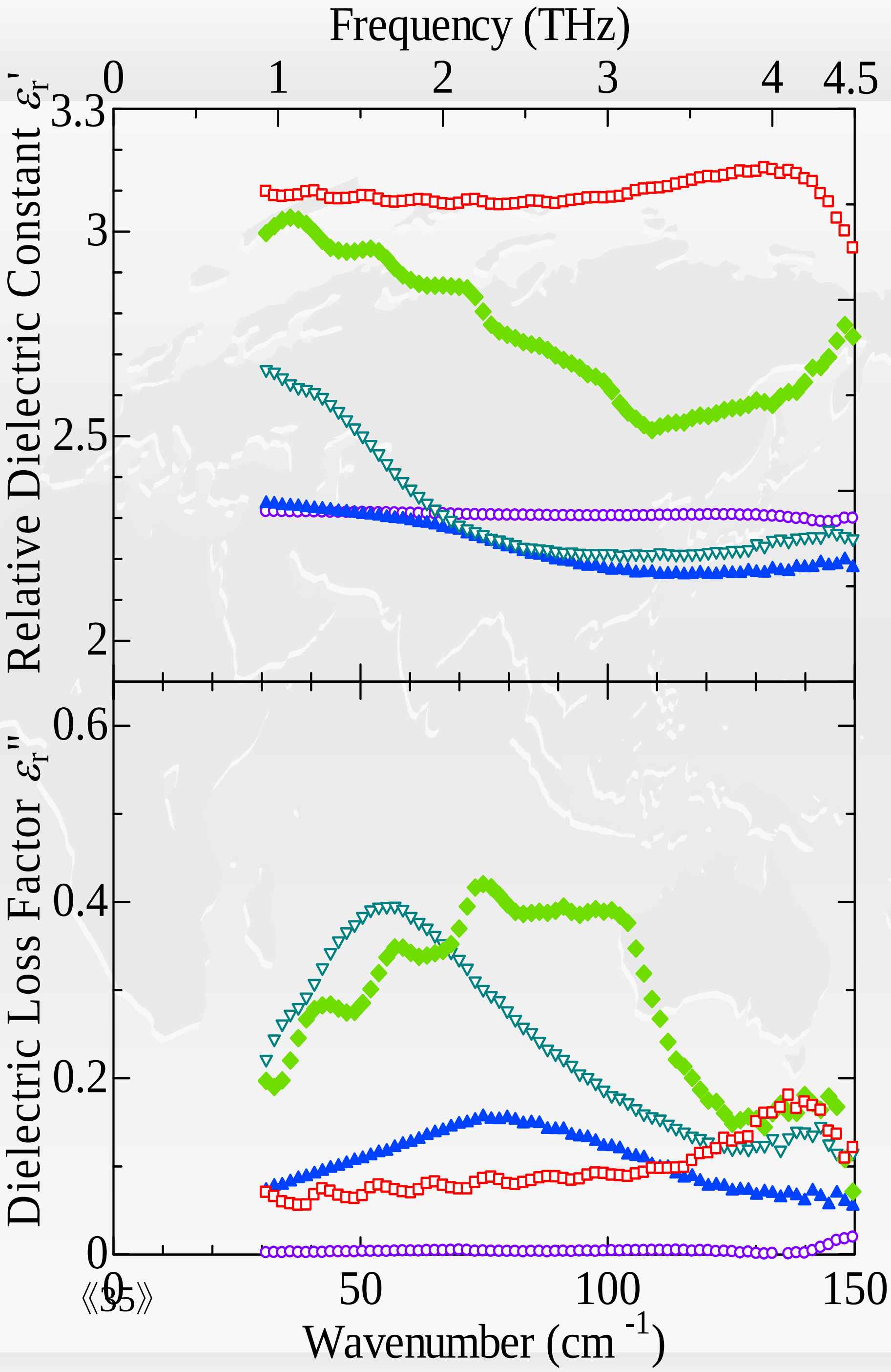
THz RESEARCH ON VARIOUS POLYMERS

Complex Permittivity at THz Frequencies at 30 ºC

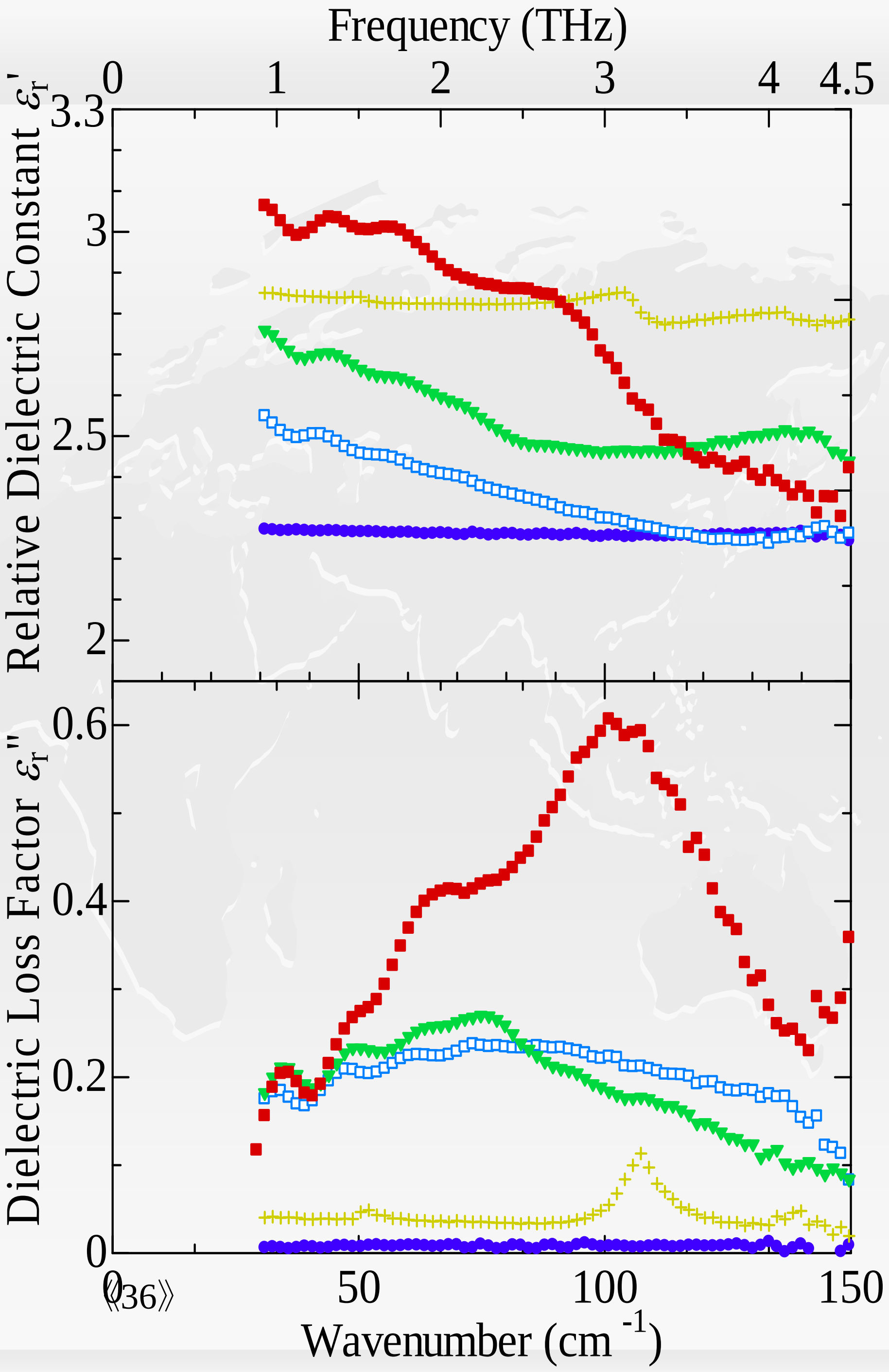


Comparison of complex permittivity at THz frequencies among PE (●), PA (△), PLLA (○), and PET (◇) [8].

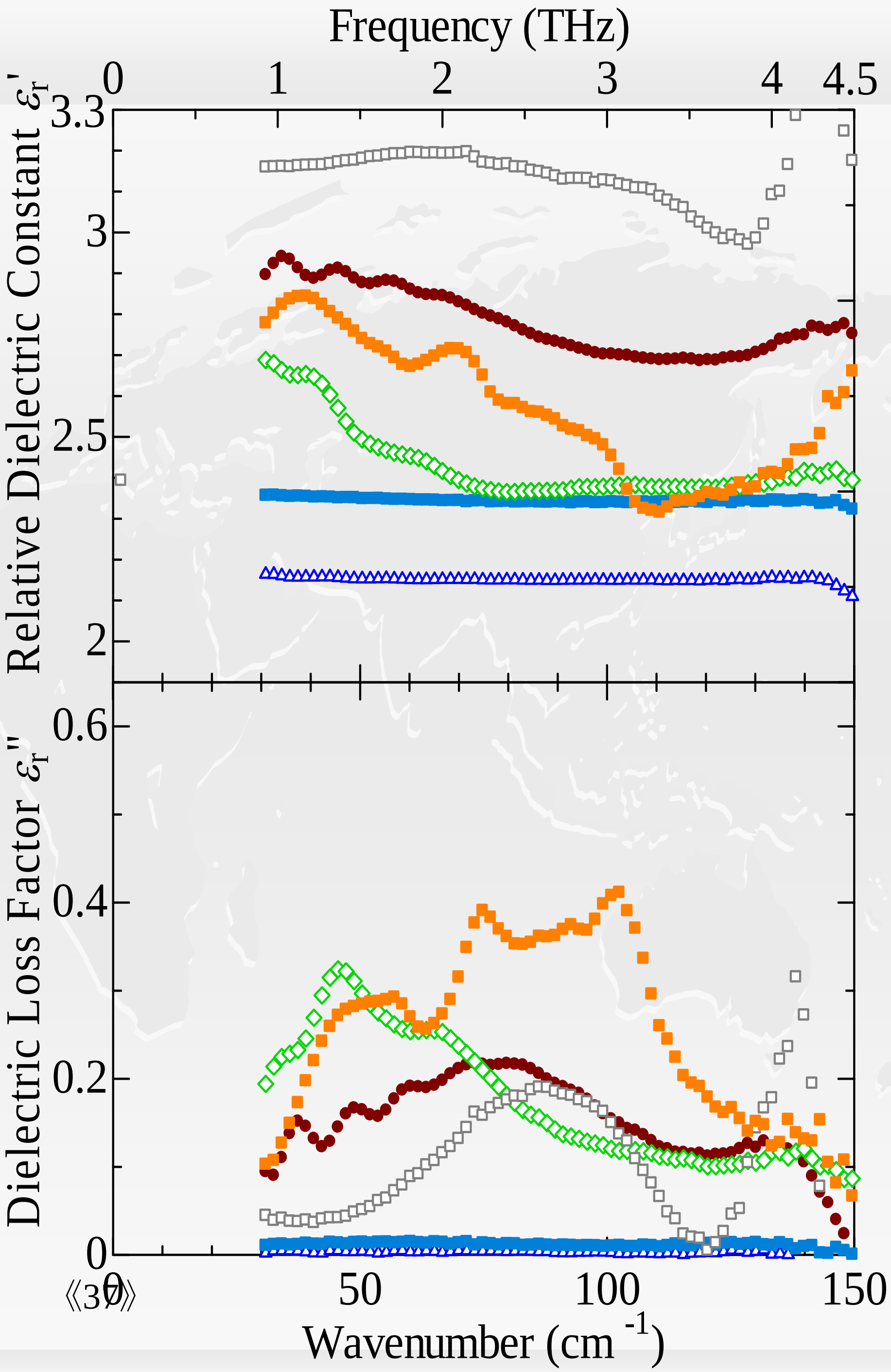
[8] Y. Ohki et al., *IEEE Conf. Electr. Insul. Dielectr. Phenom.*, 1-1, 2009.



Complex permittivity at THz frequencies. Polyethylene (○), poly(methyl methacrylate) (▲), polylactide (▽), polybutylene succinate adipate (◆), and polyimide (□).



Complex permittivity at THz frequencies. Polypropylene (●), starch ester (□), polyphenylene sulfide (+), polybutylene adipate terephthalate (▼), and polyamide (■).



Complex permittivity at THz frequencies. Polystyrene (■), polymethylpentene (△), polyethylene naphthalate (●), polycaprolactone (◇), polyethylene terephthalate (□), and polybutylene succinate (■).

THz-TDS Spectra

Nonpolar polymer PE

- The frequency dependence of ε_r' of PE is very flat.

→ a constant value around 2.2 to 2.3

- No dielectric loss peaks

THz-TDS Spectra

Polar polymers

- One or two downward stepped changes in ε_r'

- At frequencies higher than 3.0 THz, ε_r' monotonically decreases and approaches a value close to the value of PE.

THz Peaks due to Resonance Phenomena

- ε_r’ approaches a similar value close to 2.3, the value of PE, in most polymers when the frequency increases to a very high value around 3.8 THz

Only electronic and atomic polarization associated with chemical bonds of light atoms can follow such a high frequency electric field.

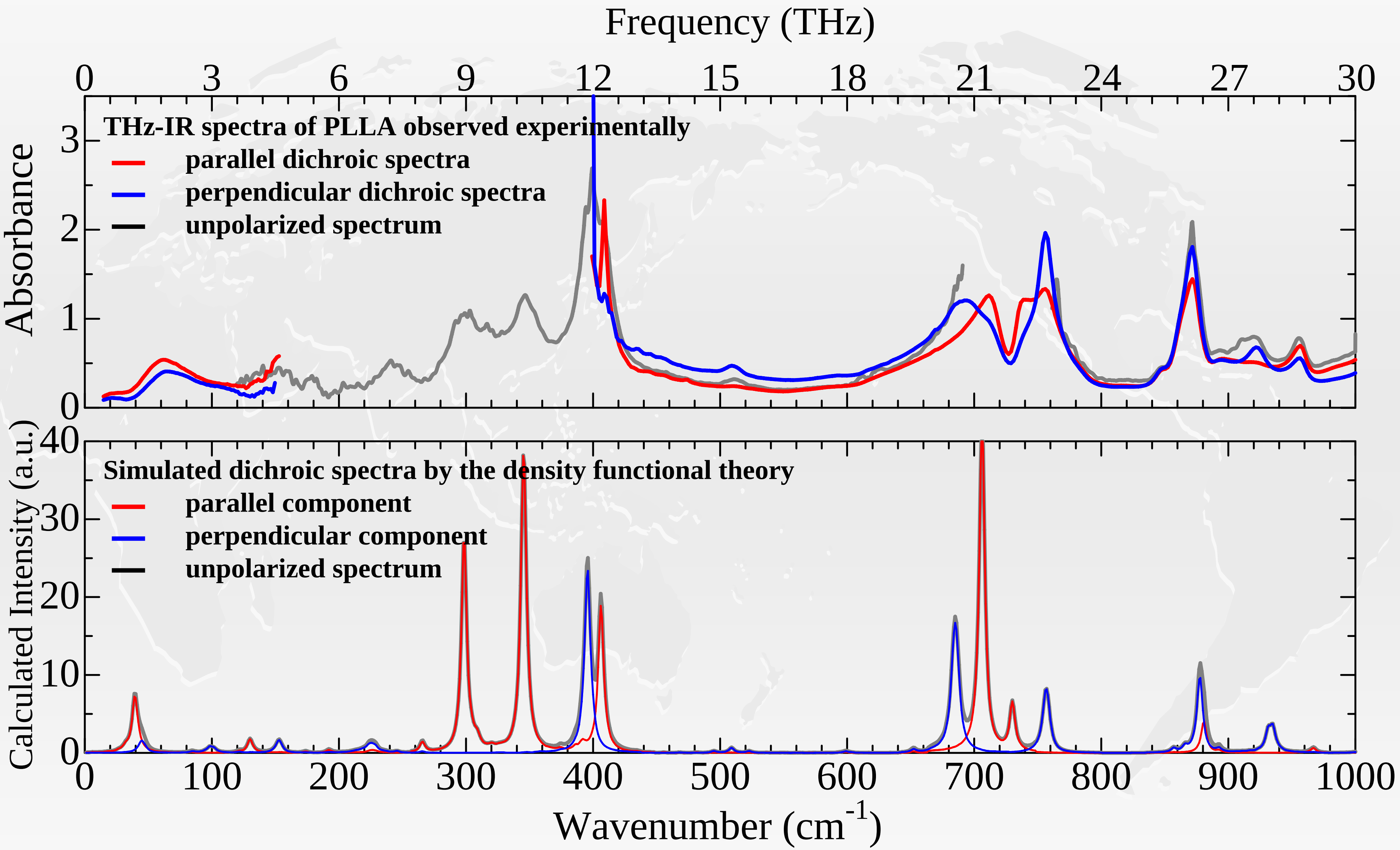
Considering ε_r’ values of gases (e.g. 1.00053 for dry air) and the density differences between gases and solids, ε_r’ = 2.3 is reasonable for the sum of electronic and atomic polarization.

THz-TDS Spectra

Polar polymers

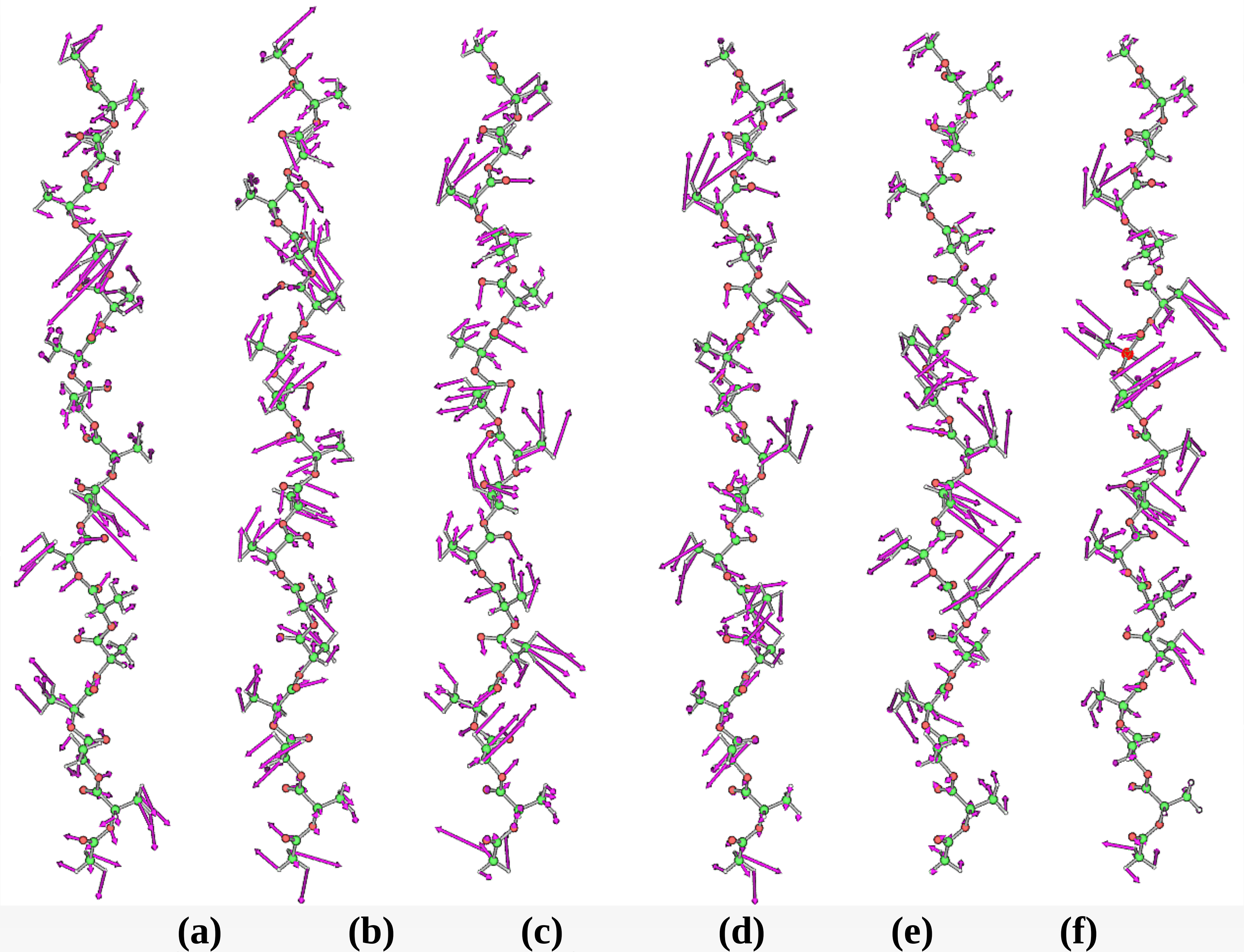
- Dielectric loss peaks around 2.0 and 3.0 THz
  - Only PA has two peaks
  - PLLA and PET have one peak
  - These peaks seem to be due to some relaxation phenomena if we see only their spectral shapes.

Simulation of THz spectra (PLLA)*



***1P-31**

***Analysis of terahertz spectra of amorphous polylactide using density functional theory*, N. Fuse et al.**



Vector components of six typical molecular vibrations simulated for the oligomer model with 16 lactide units, at 39.2 (a), 39.7 (b), 40.6 (c), 43.5 (d), 44.1 (e), and 45.1 cm^{-1} (f), constituting the 40 cm^{-1} band. (a), (b) and (c) are components parallel to the molecular helical axis, (d), (e) and (f) are components perpendicular to the molecular helical axis. 🟢: carbon, 🟠: oxygen, ○: hydrogen, ➔: vibrational direction

Simulation of THz spectra (PLLA)

Absorption spectra observed for PLLA and those calculated for an oligomer model optimally structured with 28 lactide units are compared.

- The numerical simulation successfully reproduces
  - the absorption spectra observed in the whole frequency range
  - dichroic spectra observed at frequencies above 395 cm^{-1}
- The simulation also shows
  - the peak at around 40 cm^{-1} is due to molecular vibrations along the molecular helical axis
  - it becomes larger with an increase in molecular length.
- The mutual intensities of dichroic spectra around 40 cm^{-1} obtained numerically agree with those observed experimentally around 55 cm^{-1}.

The peak observed at 55 cm^{-1} can be assigned to vibration modes at 40 cm^{-1} in the oligomer model, although the peak frequency is different.

V. Conclusion of Chapter 3

- Measurements of complex permittivity spectra reflect a wide-aspect nature of polymers.
- Spectra at THz frequencies

  → a powerful clue to clarify the nature of a polymer.

Thank you!

Temperature Dependency of Polarization

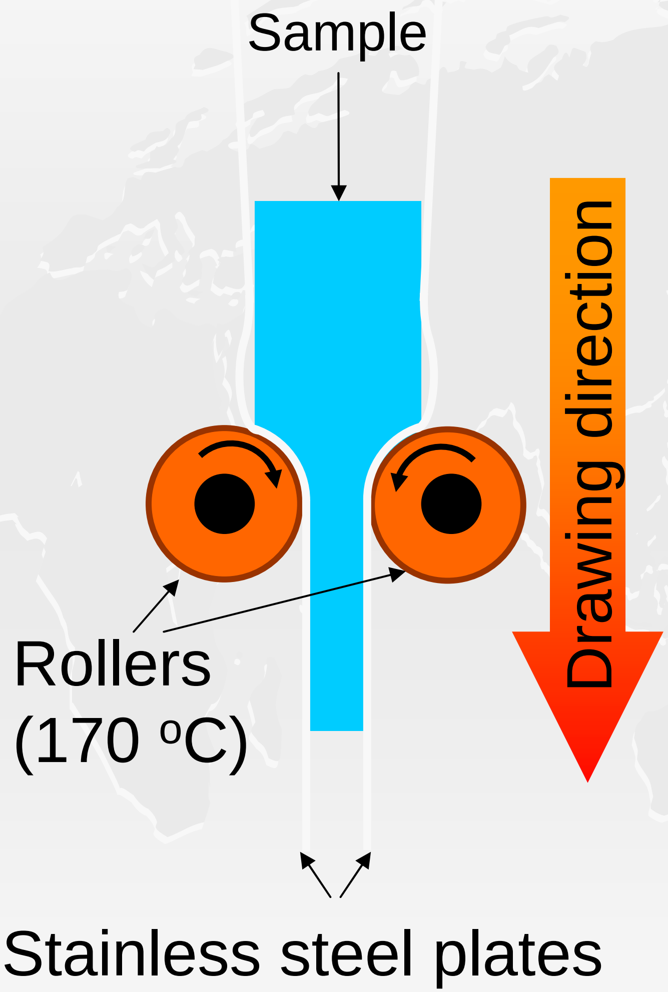
- Among various kinds of polarization processes,
  - **Electronic polarization** should be independent of temperature.
  - **Atomic polarization** would be scarcely dependent on temperature.

▪▪▪▪▶ The polarization that depends on temperature should be related to dipoles and/or mobile charge carriers, regardless of the dependency being positive or negative.

Since PE, PP, PMP, and PS are nonpolar,

the dipoles responsible for ε_r' at low frequencies should be due to impurities such as residues of catalyst used for polymer synthesis or reaction byproducts.

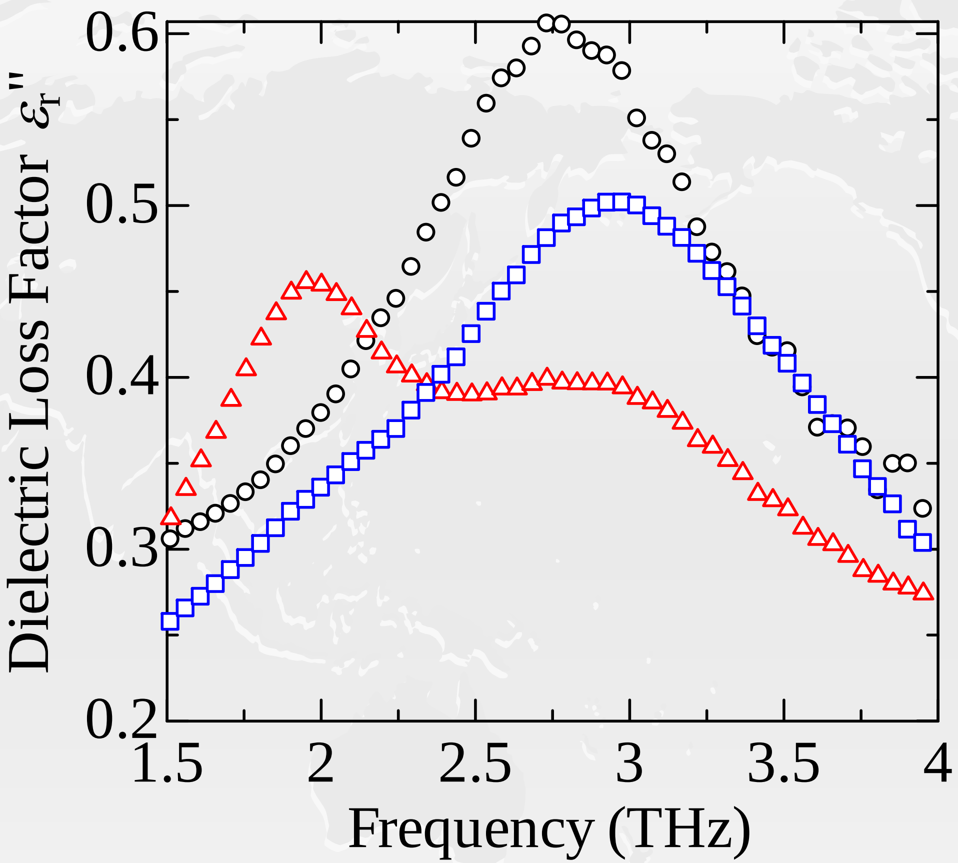
Sample drawing



Drawing condition
Temperature: 170 °C
Rate: 2.5 times the original length

The samples undrawn and drawn are distinguished by adding letters U and HD on the sample names.
e.g.) B-U, N4-HD

ε_r" at THz Frequencies (PA)



Effects of drawing on the dielectric loss spectra measured for PA-4 (○), PA-4-HD (0°, △), and PA-4-HD (90°,□). 'HD' indicates that the films were drawn at 170 °C [9].

[9] Y. Ohki et al., Appl. Phys. Express, Vol. 1, No. 12, 122401, 2008.

Experimental procedures

X-ray diffraction (XRD)

✓ Meas. mode: Cu-Kα radiation, 2θ/θ scanning mode
✓ Equipment: Rigaku Rint Ultima III
✓ Temperature: room temperature

Dielectric spectra in THz region

✓ Meas. Mode: THz time domain meas.
✓ Equipment: Tochigi-Nikon Rayfact Spectera spectrometer
✓ Light property: linearly polarized light, 0.5 - 4 THz
✓ Temperature: room temperature

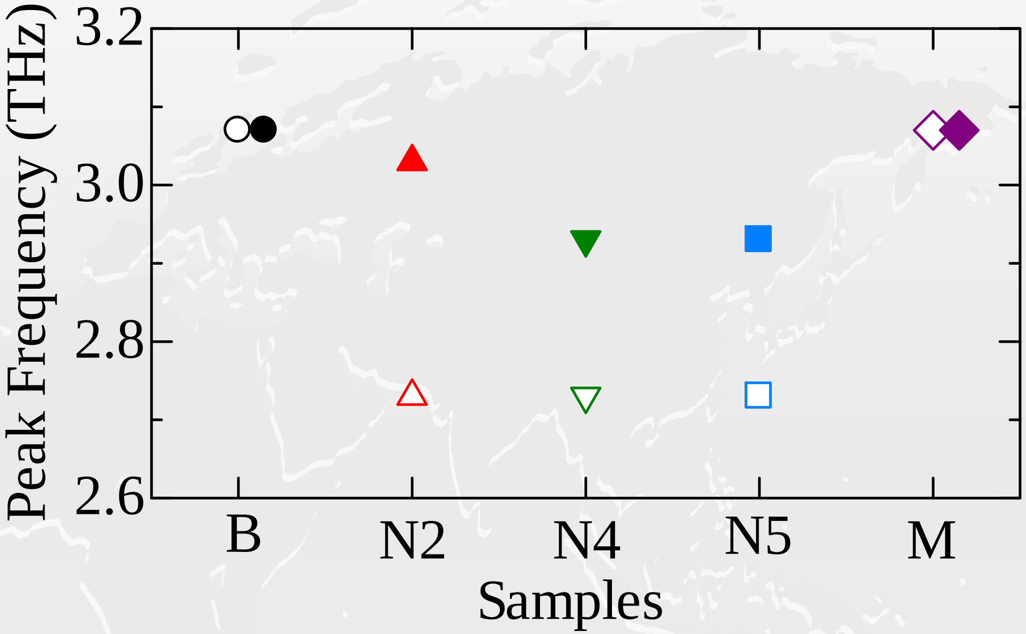
KI Treatment

Sample BI

The film B was immersed in a 0.1 mol/L potassium iodide (KI) aqueous solution for 168 h at room temperature.
It was drawn to a length about twice the original length by a two-roller press at 38 ^{o}C in order to erase surface wrinkles.

→ BI-CD

Meaning of the peak shift (1)



The peak frequencies of peak H.

Open symbols:
undrawn samples
Solid symbols:
drawn samples

- ➢ The peak shift becomes smaller when the NC samples are drawn.

The drawing seems to weaken the restriction of molecular motion.

Meaning of the peak shift (2)

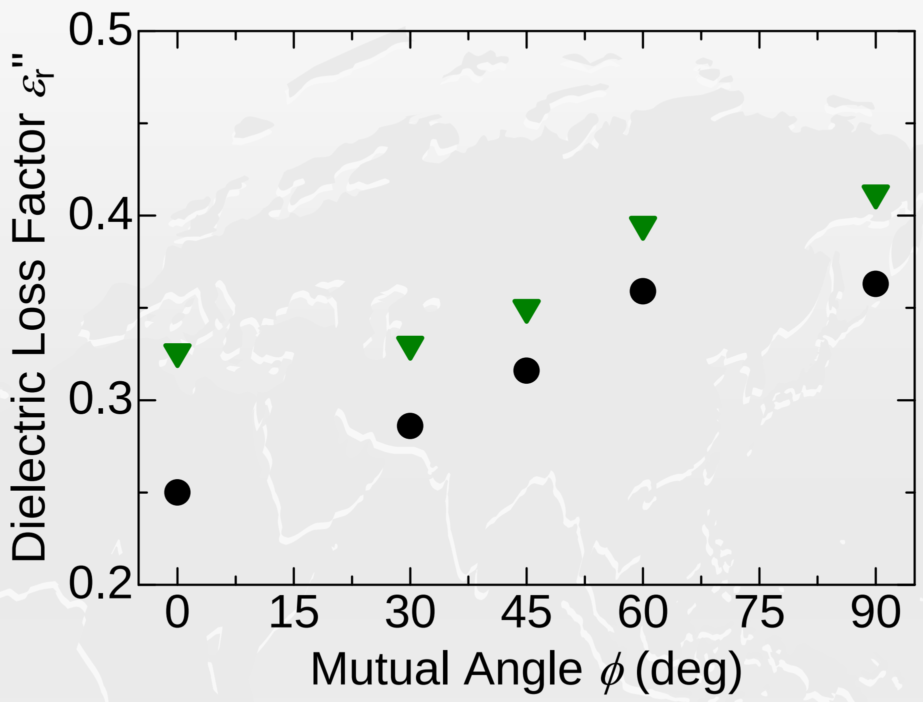
- The dielectric relaxation responsible for peak H is due to a Debye-type process. ➔ ε_r'' should satisfy
  $2\pi f = 1/\tau$.   (f: frequency, τ: the relaxation time)

The shift to a lower frequency means a longer τ.

- The relaxation time τ becomes longer by the nanofiller loading, and not by the microfiller loading.

Ionic interaction acts between polymer and nanofillers in NCs. Such interaction is assumed to restrict molecular motion, resulting in a longer τ.
The polymer/nanofiller interaction is so strong due to a very large total interfacial area.

Angle dependencies of ε_r” at peak H

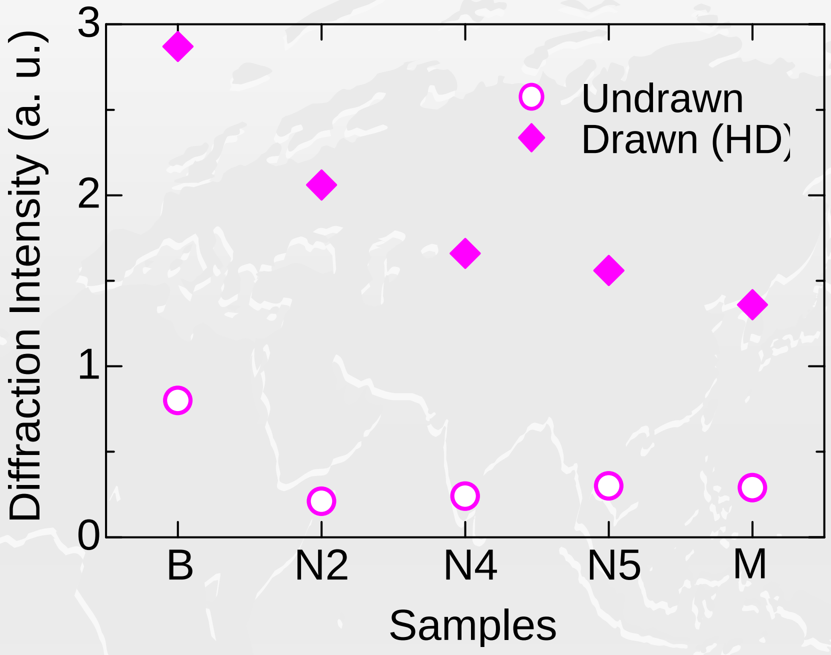


Mutual angle (ϕ): between the THz polarization and the drawing direction.

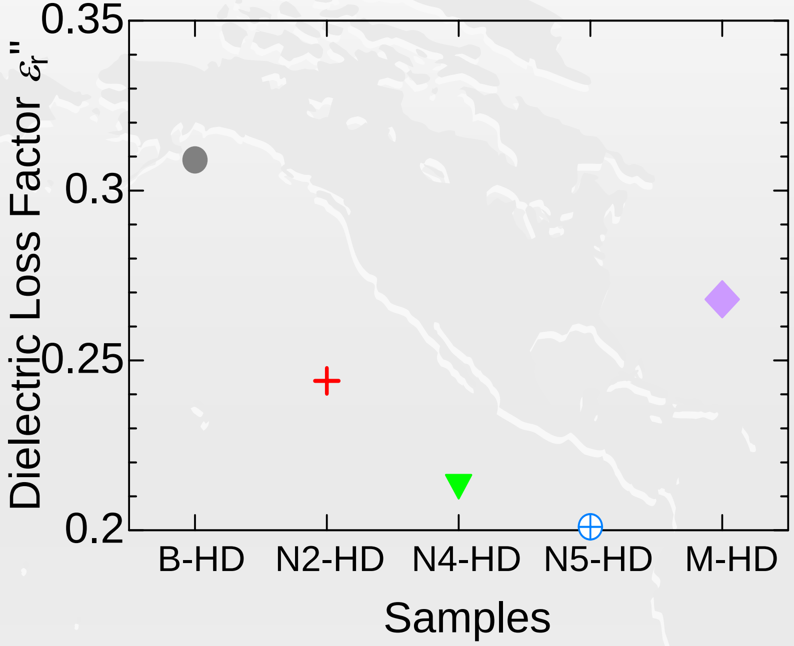
- ➢ Peak H is largest when the THz electric field is perpendicular to the drawing direction

Peak H is due to the motion of polar groups perpendicular to the molecular chains.

Relation between α crystal and peak L (1)



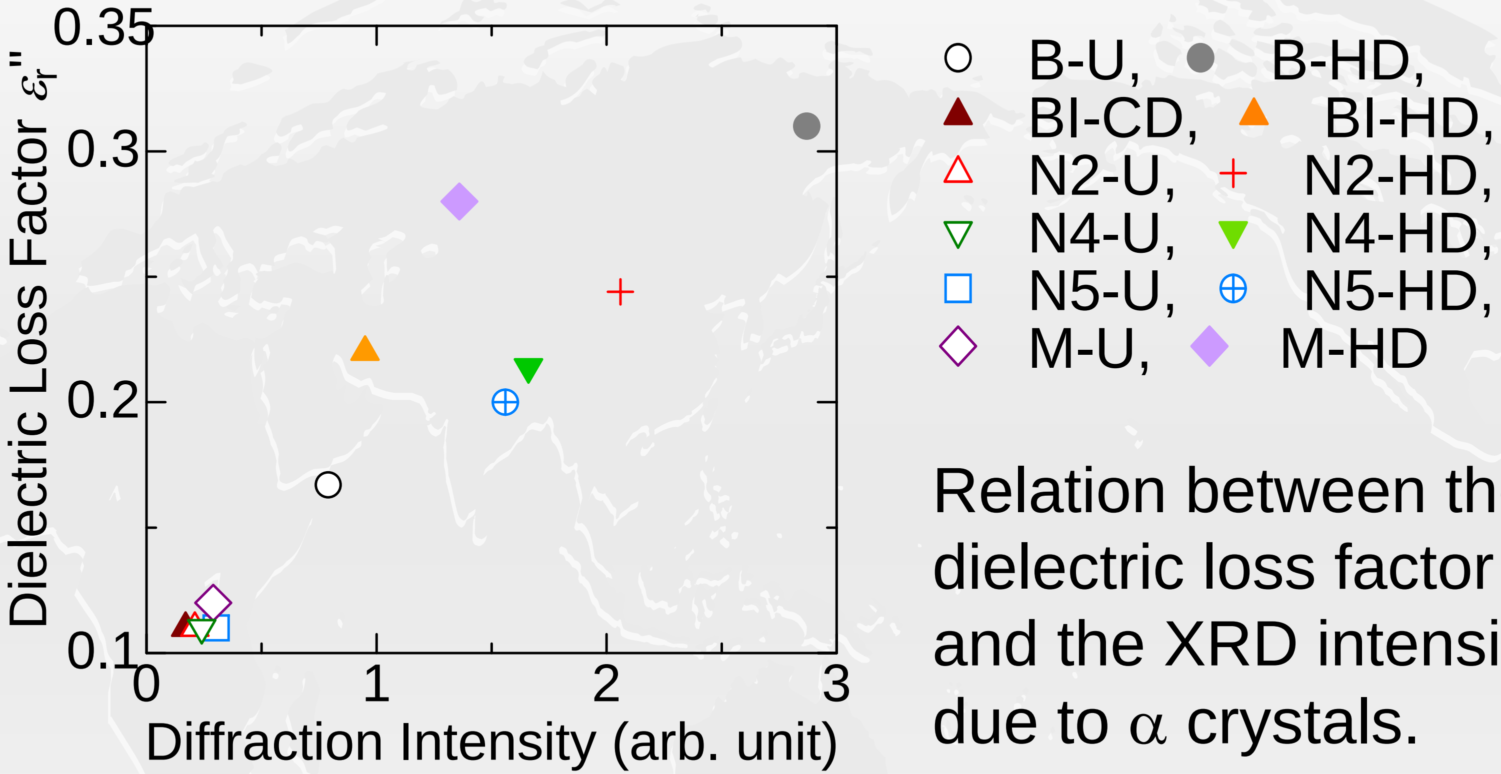
XRD intensity due to α crystals



Dielectric loss factor at peak L

1) Both the XRD intensity due to α crystals and ε_r'' are smaller in M and in three NCs than in B.
2) Dielectric loss factor ε_r'' decreases with an increase in the nanofiller content.

Relation between α crystal and peak L (2)



Relation between the dielectric loss factor at peak L and the XRD intensity at 23.7^{o} due to α crystals.

- ➢ A good correlation is observed.

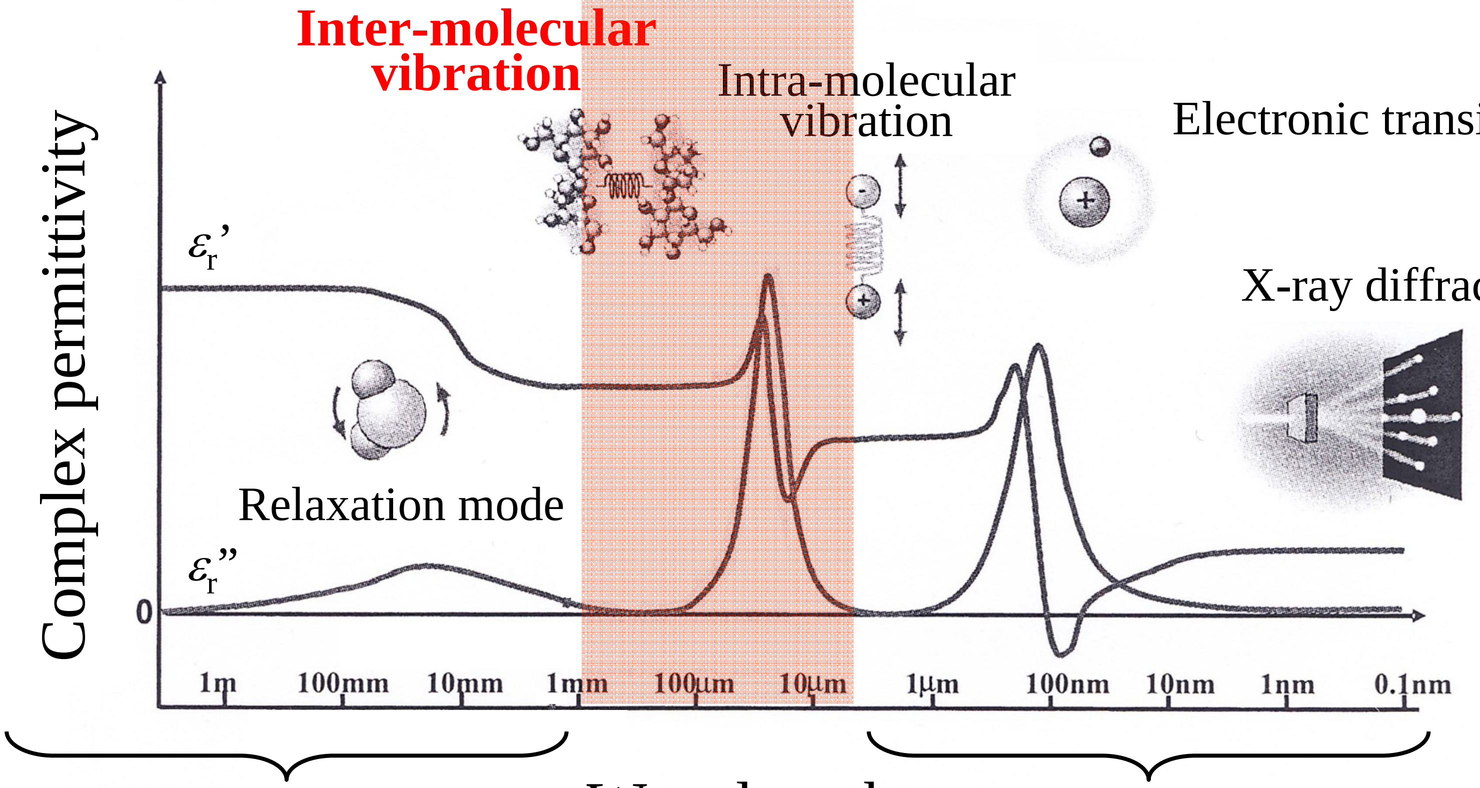
Peak L is due to α crystals.

Brief overview of spectroscopy

Electromagnetic wave ←

THz region

Light →



Wavelength

relaxation affected
by interactions between molecules

local resonant vibration

THz spectroscopy

- Recent development of a THz light source, THz time-domain spectroscopy (TDS), THz tomography, and other related devices and methods.

→

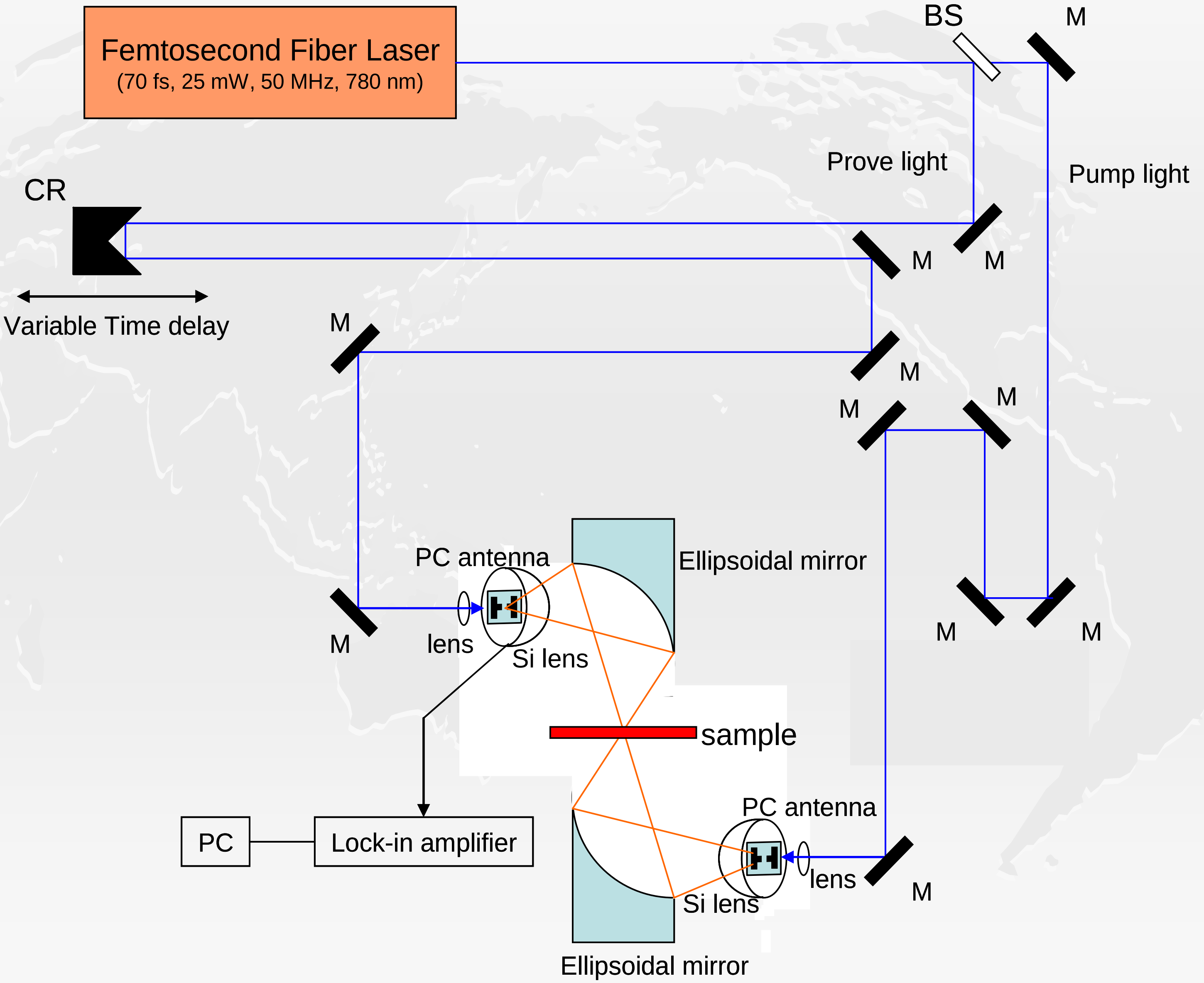
THz science and technology are growing rapidly.

- Many electrical insulating solids are translucent with a low loss at THz frequencies.

→

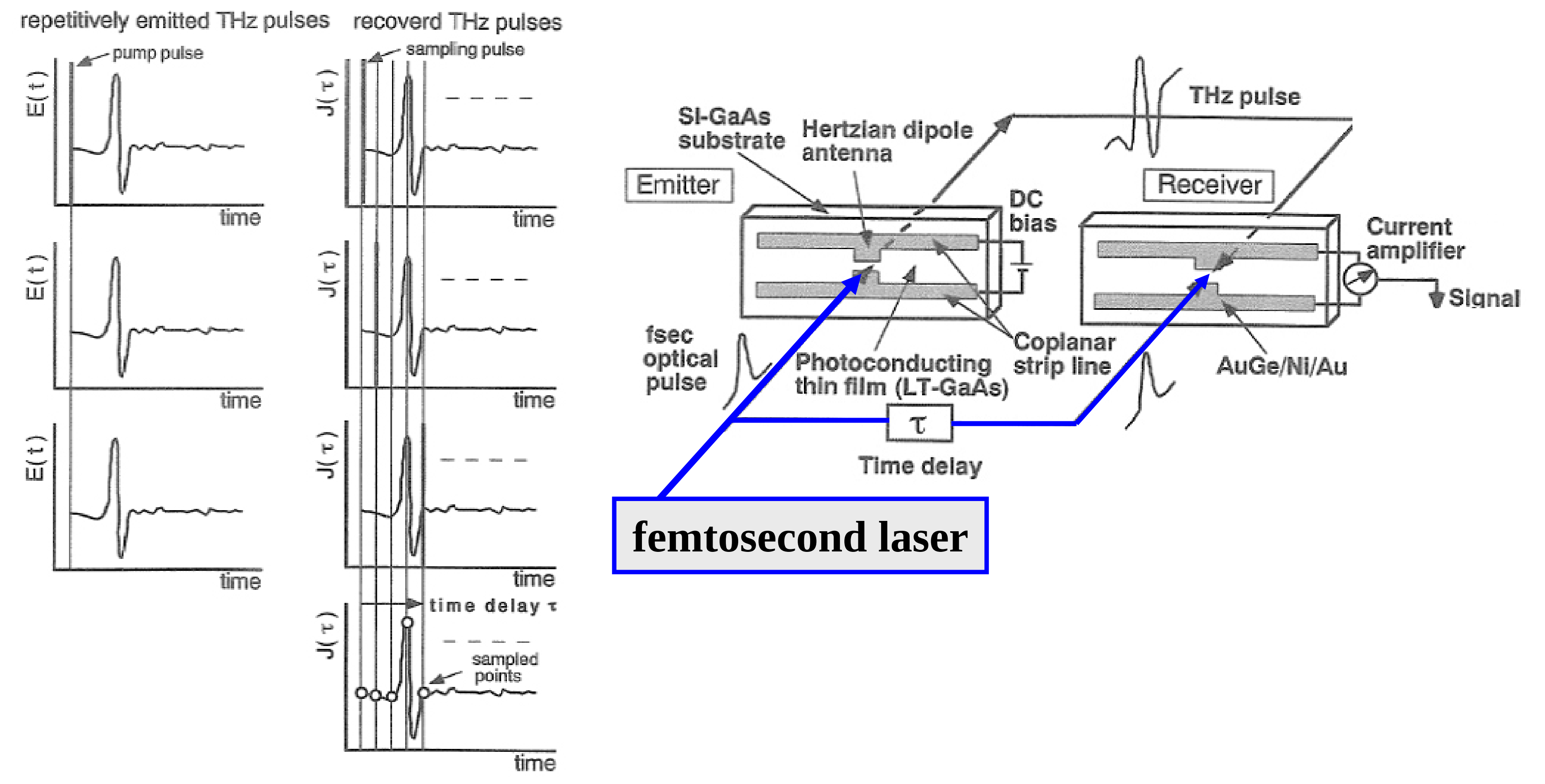
THz spectroscopy can be a good tool to analyze their nature.

THz device configuration



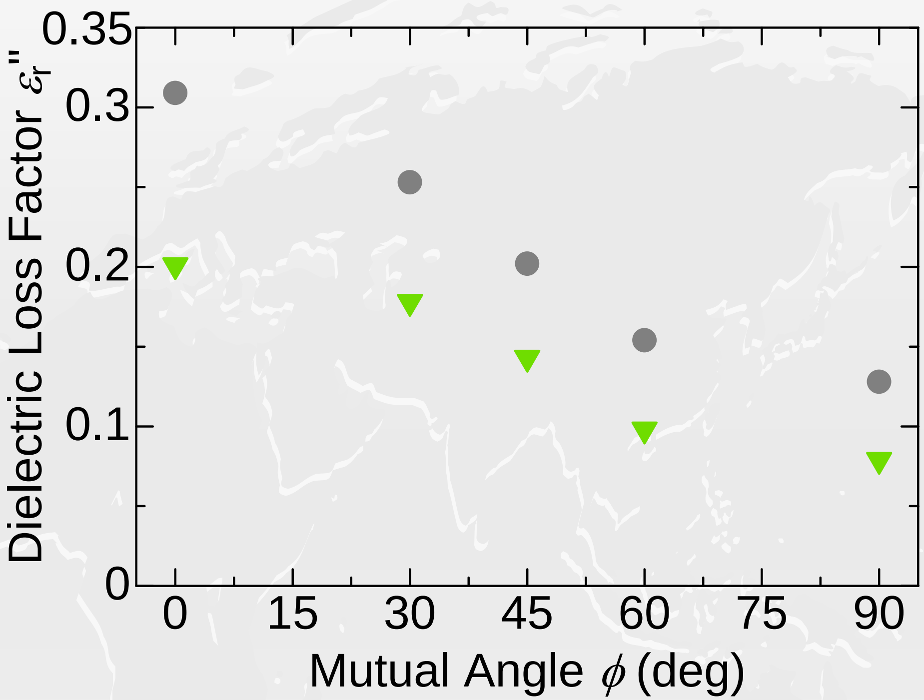
M: Mirror
BS: Beam splitter
CR: Corner reflector
PC antenna: Photo conductive antenna

Measurement principle of THz spectrum



Scanning a THz pulse wave by controlling a time delay mirror.

Angle dependencies of ε_r” at peak L



Mutual angle (ϕ):
Angle between the THz polarization and the drawing direction.

➢ Peak L is largest when the THz electric field is parallel to the drawing direction

Peak L is due to dipoles aligned parallel to the molecular chains in α crystals (?).