# *Polymer- Based Nanocomposite Materials*

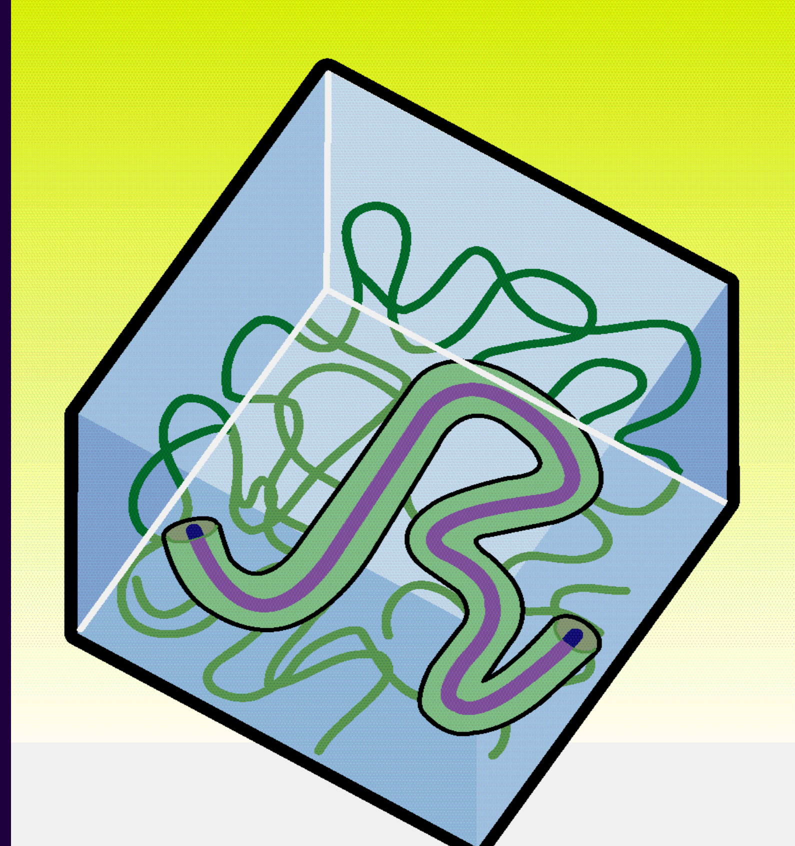
*Dr. Mircea Chipara*
*The University of Texas Pan American*
*Department of Physics and Geology*

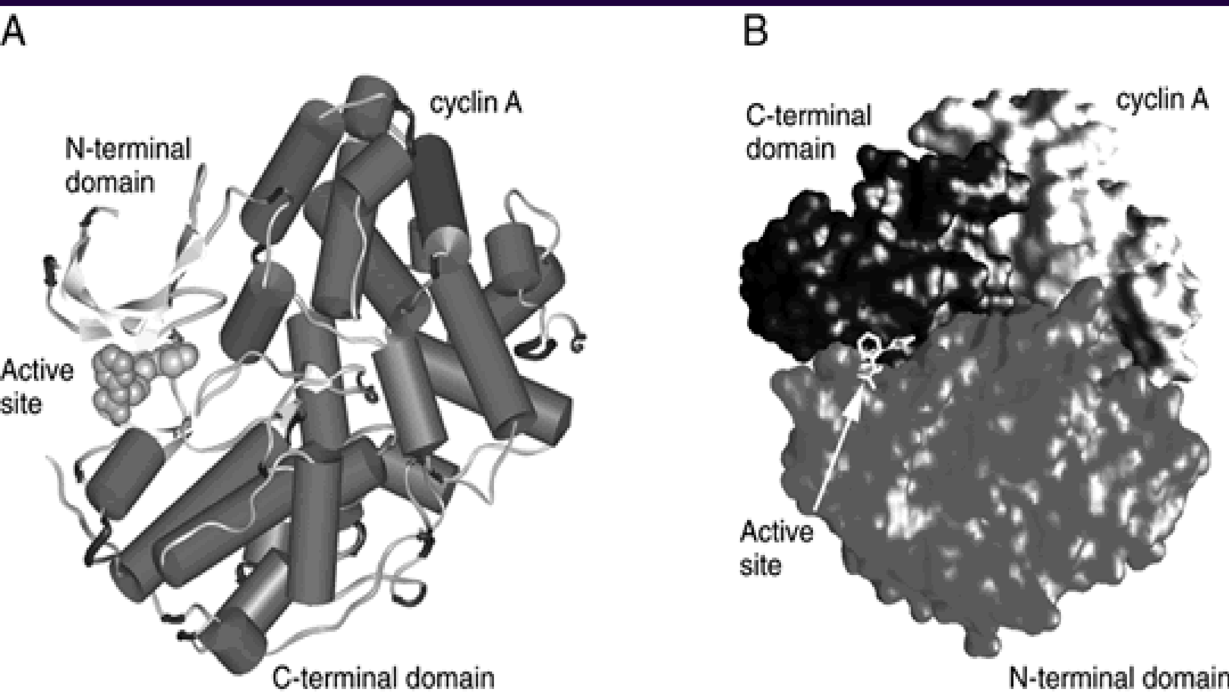
# *Polymer- Based Nanocomposite Materials*

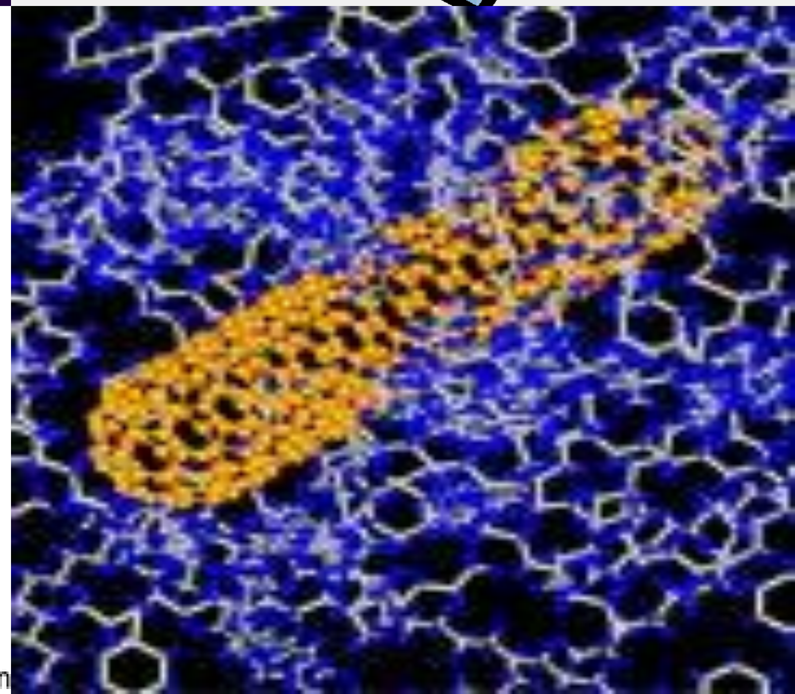
- *Polymer – Based Nanocomposites for Structural Applications*
- *Polymer – Based Nanocomposites for Thermal Applications*
- *Polymer-Based Nanocomposites for Electrical Applications*
- *Polymer-Based Nanocomposites for Magnetic Applications*
- *Polymer-Based Nanocomposites for Special Applications (thermoelectric, optical, photonic, ferroelectric, piezoelectric, and pyroelectric)*
- *Ferroic Polymer-Based Nanocomposites*

# Polymer

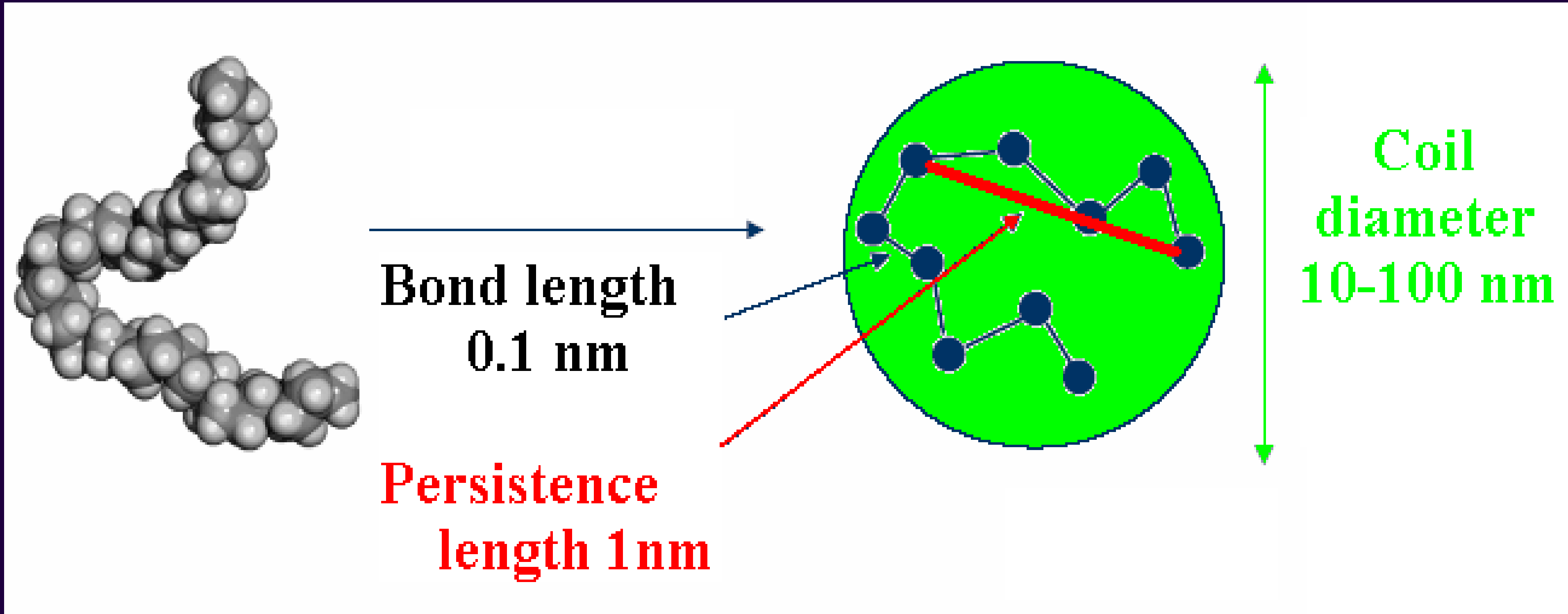
***Polymer (from Greek πολύ-ς /po΄li-s/ much, many and μέρος /΄meros/ part) is a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds.***

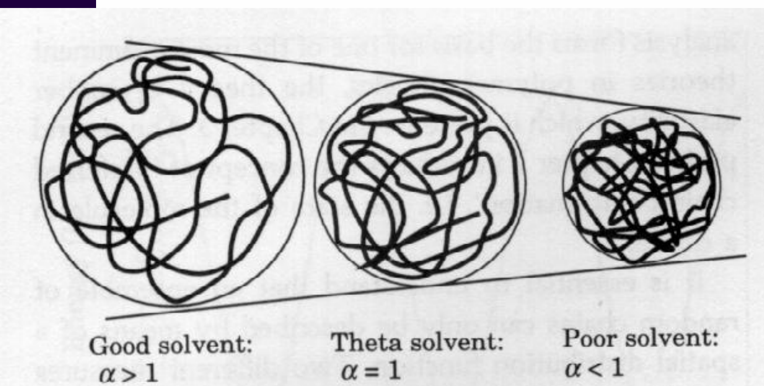




# Most Important Scales in Polymers




Angstrom = 1Å = 1/10,000,000,000 meter = $10^{-10}$ m

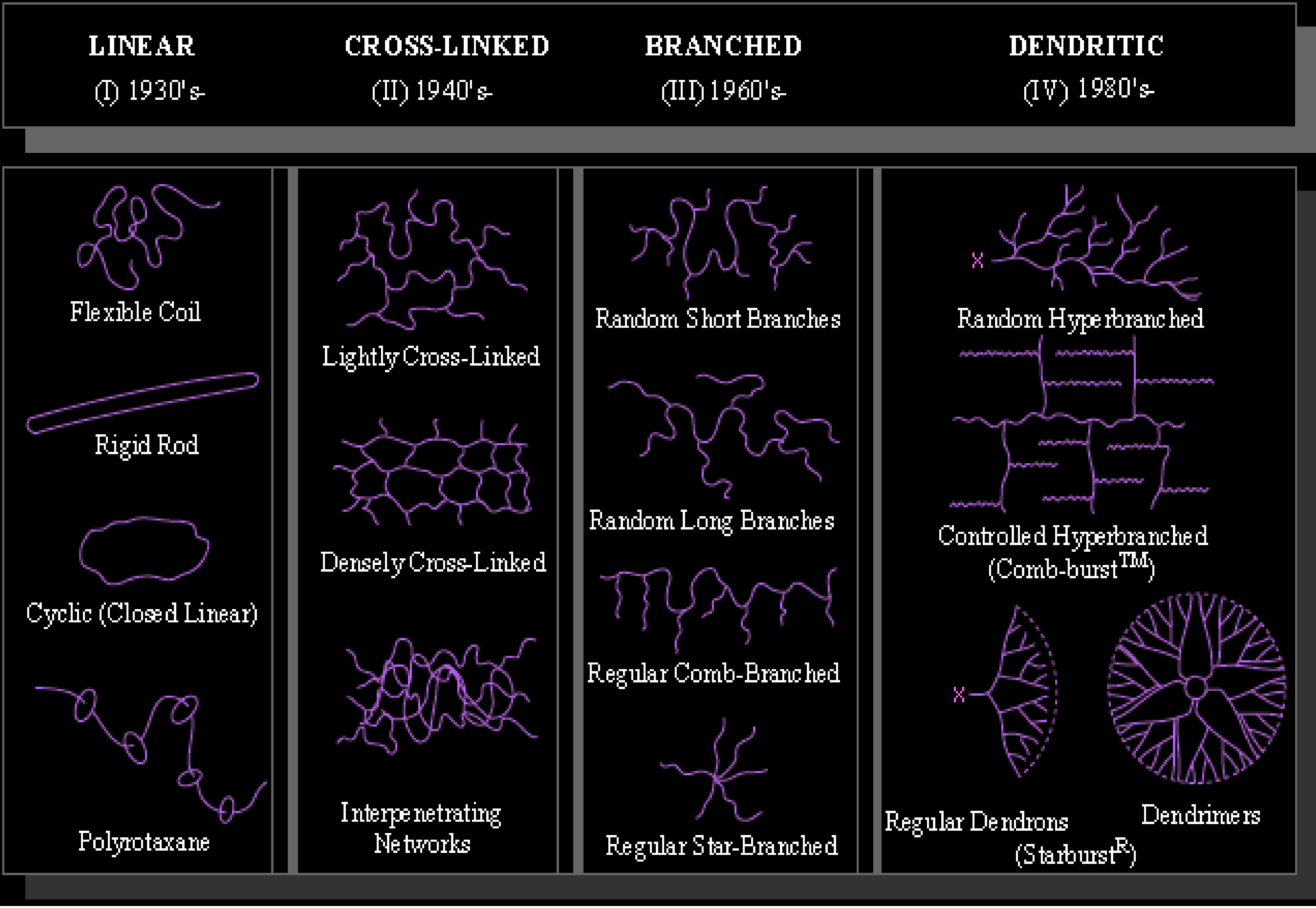
Nanometer = 10 nm = 1/1,000,000,000 meter = $10^{-9}$ m

Micrometer = 1µm = 1/1,000,000 meter = $10^{-6}$ m

Millimeter = 1mm = 1/1,000 meter = $10^{-3}$ m

**This figure shows the most important scales in polymers. The typical bond length of polymers is of the order of 0.1 nm. The persistence length defined as the average length of the macromolecular chain that behaves like a rigid unit (rod) is about 1 nm and The coil diameter of the polymer is frequently ranging between 10 and 100 nm.**

# Most Important Scales in Polymers

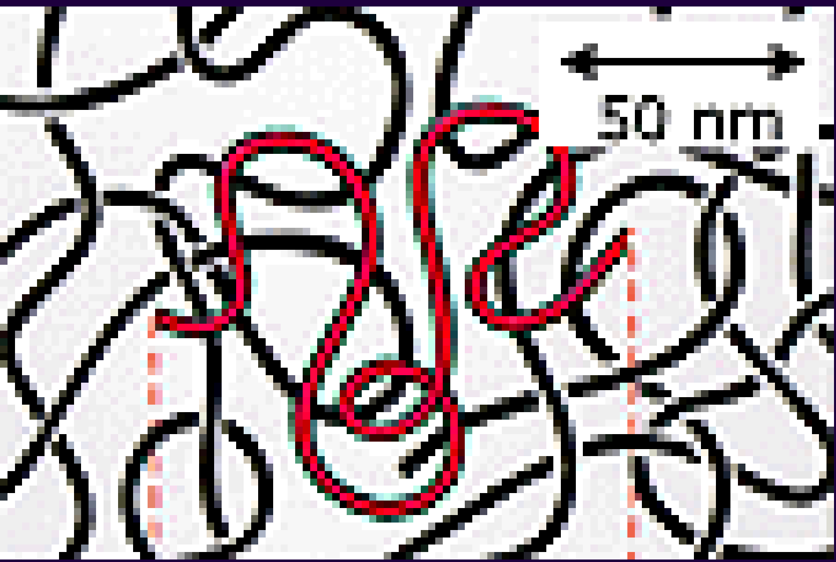


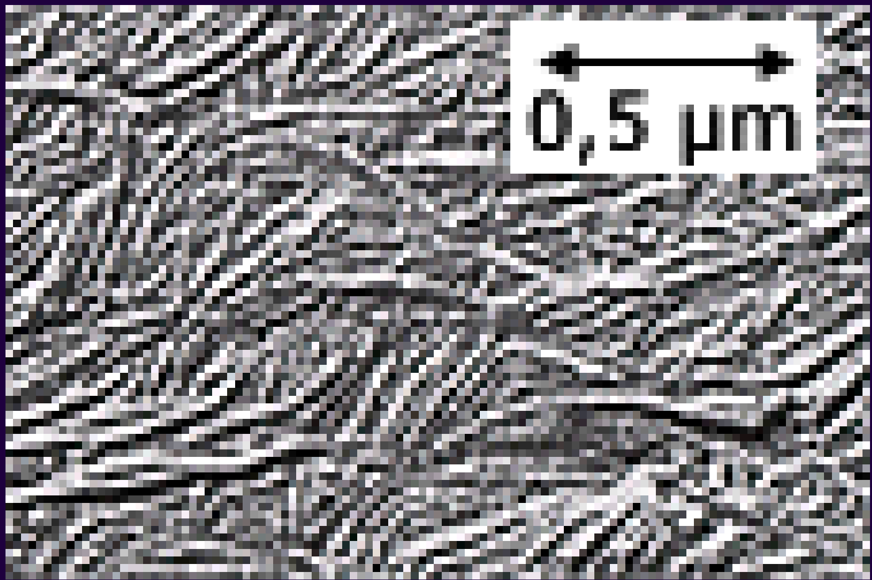
# *What is a Polymer ?*

•Each polymer molecule consists of linked basic units called monomers.

•The number of monomers in a chain can be very large, from thousands to several millions.

•The chains may be entangled like spaghetti (as above) or be ordered in crystalline formations.

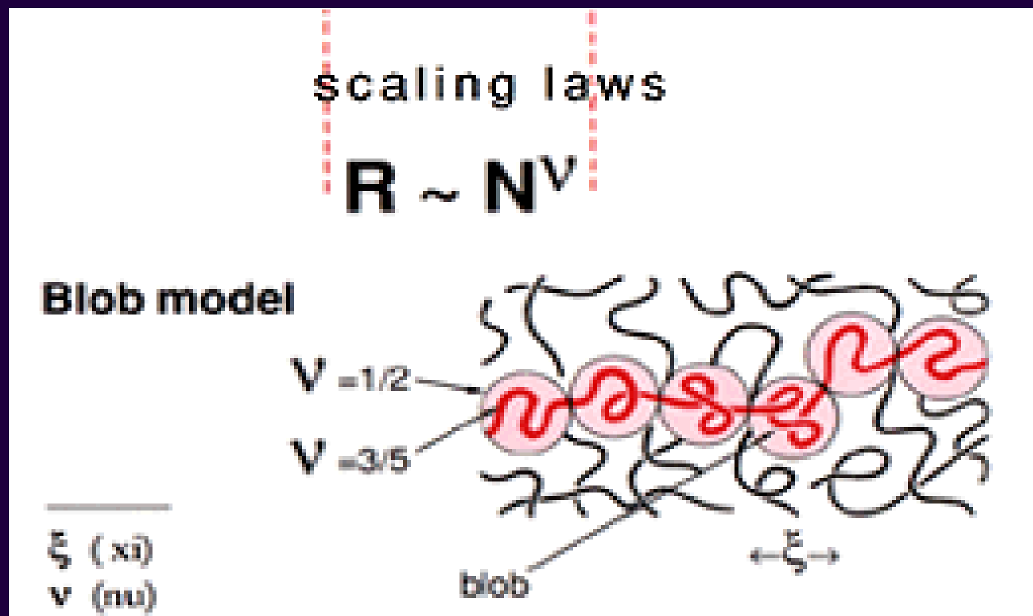



•A Frisbee is a mixture of crystalline (ordered) and amorphous (disordered) polymer structures. This makes the material both strong and flexible

# *What is a Polymer ?*

**•Long polymeric chains: Size can be described by simple proportion ratios called scaling laws:**
**When the number of monomers N is doubled, the size is increased by the scaling factor 2*v*.**
**The exponent *v* is universal in the sense that it is the same for all polymer chains although it depends on the polymer concentration.**
**The blob model is used to describe polymer solutions, crosslinked polymers (gels), polymer welds, interfaces, polymers at surfaces etc.**




*v=1/2 for ideal random coil*

*v=3/5 for self avoiding random coil*

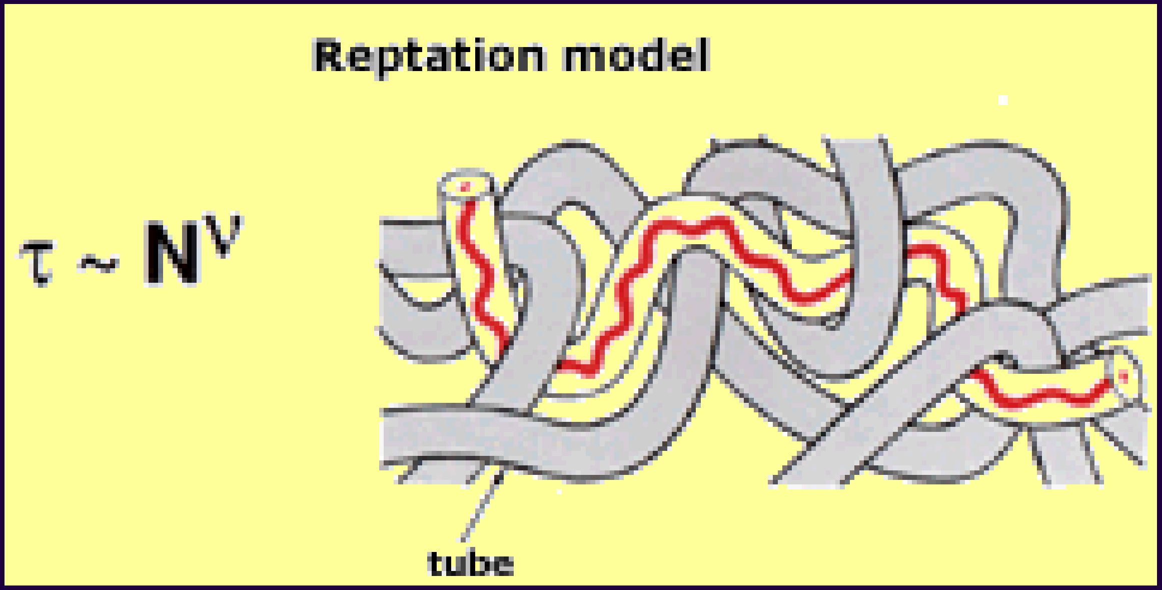
*v=1/3 for globules (chain collapse) like DNA*

# *What is a Polymer ?*

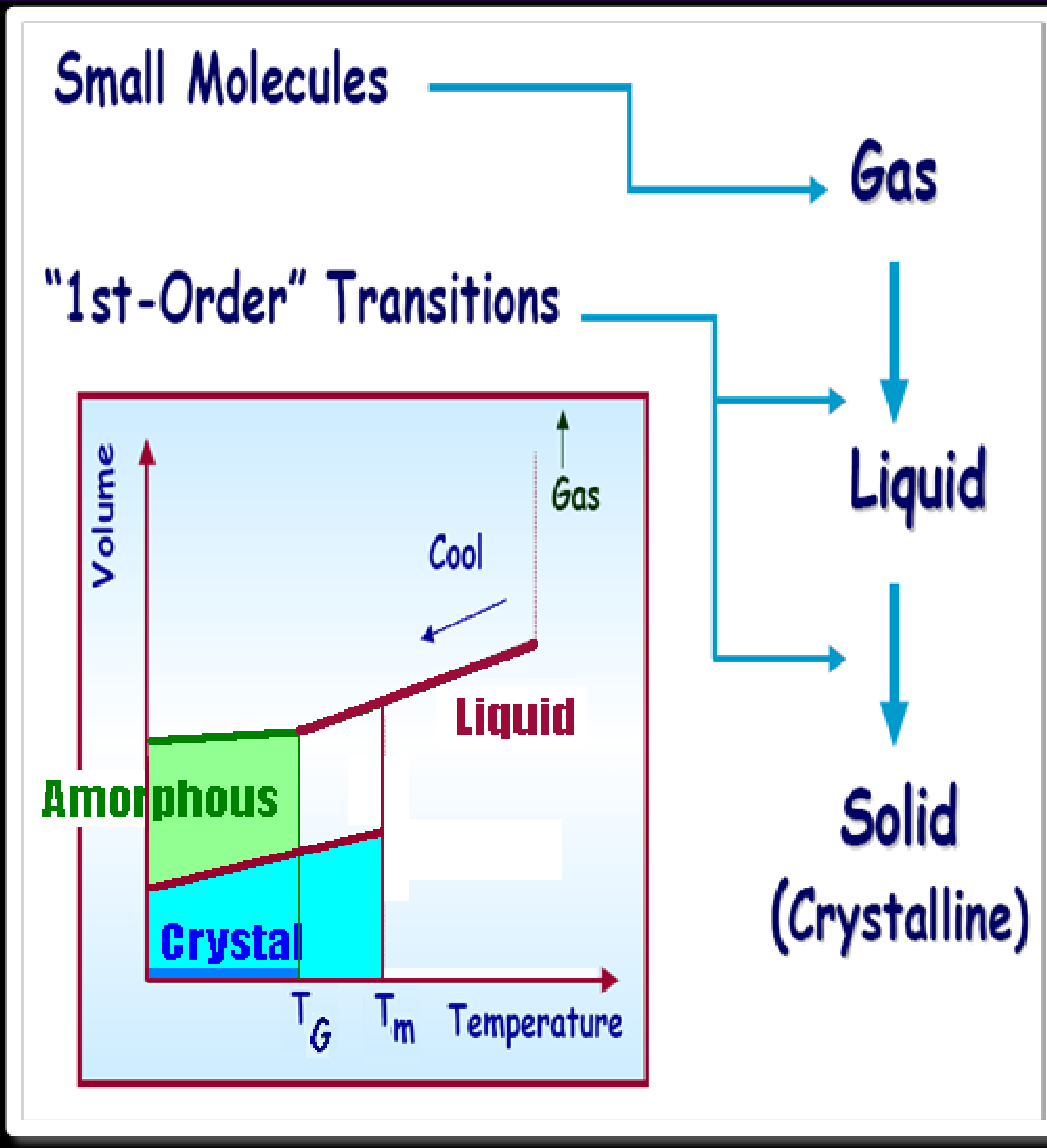
The snake-like (reptile-like) motion of an entangled polymer chain is explained by imaging that it is confined to a "tube" formed by adjacent chains.

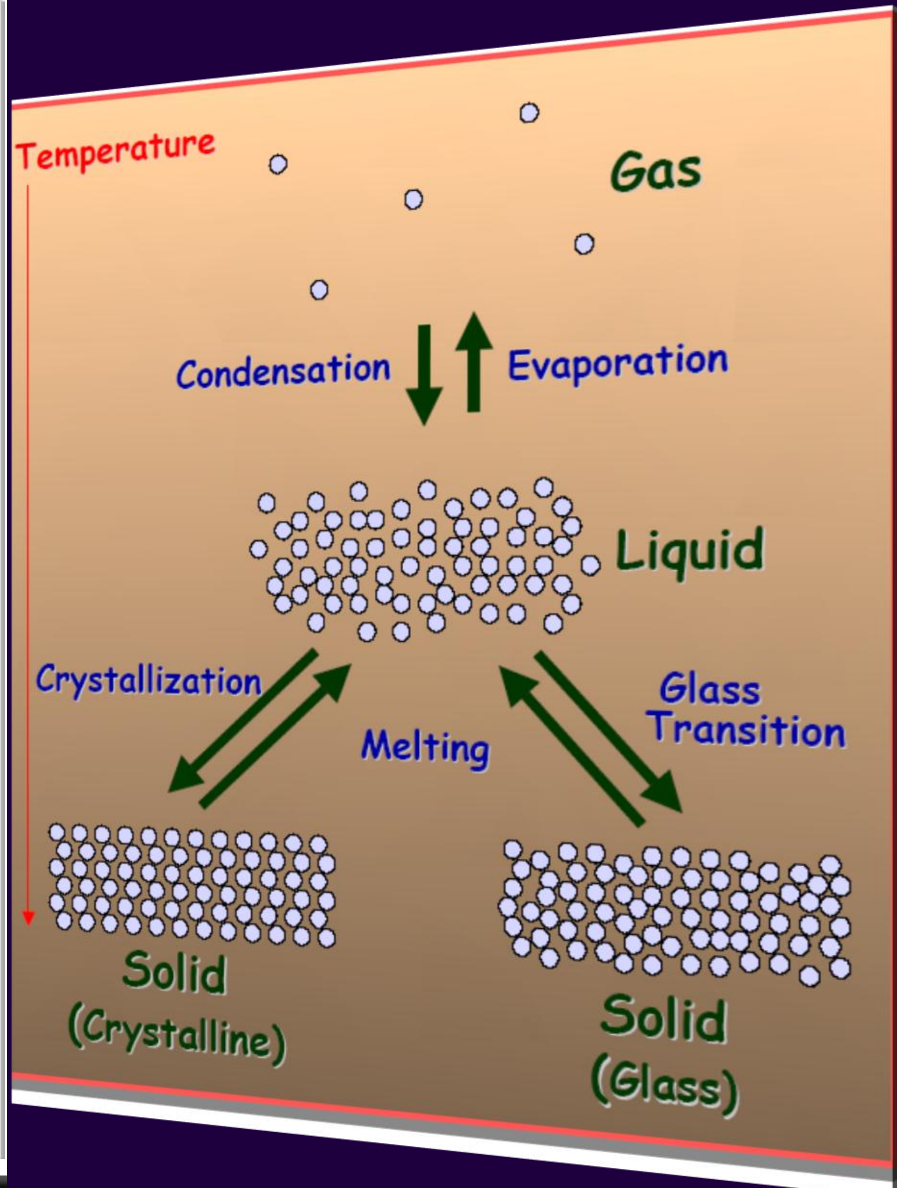
The **reptation time t**, the time needed for the chain to completely move out of the tube, can be obtained from simple scaling arguments.

The reptation model leads to a smaller exponent (*v*= 3) than the measured one (*v*= 3.3) but it can nevertheless explain a number of phenomena and is very powerful in its simplicity.

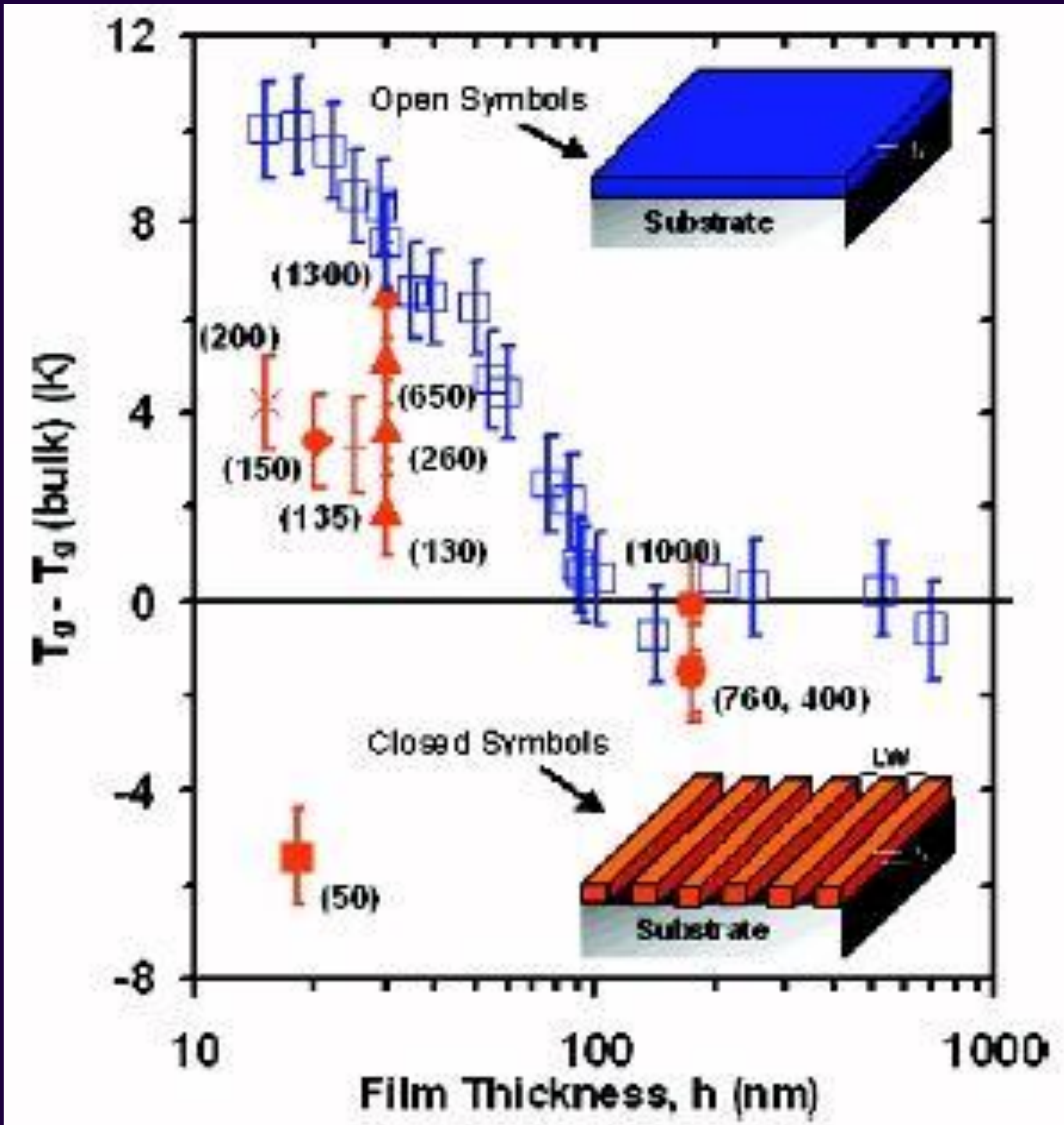


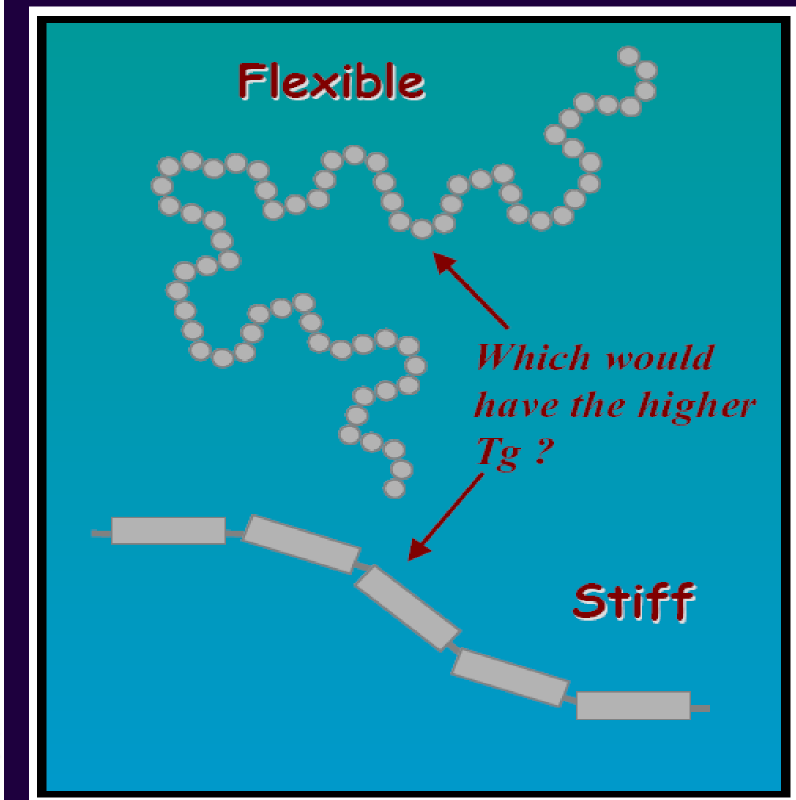
# Phase Transitions in Polymers



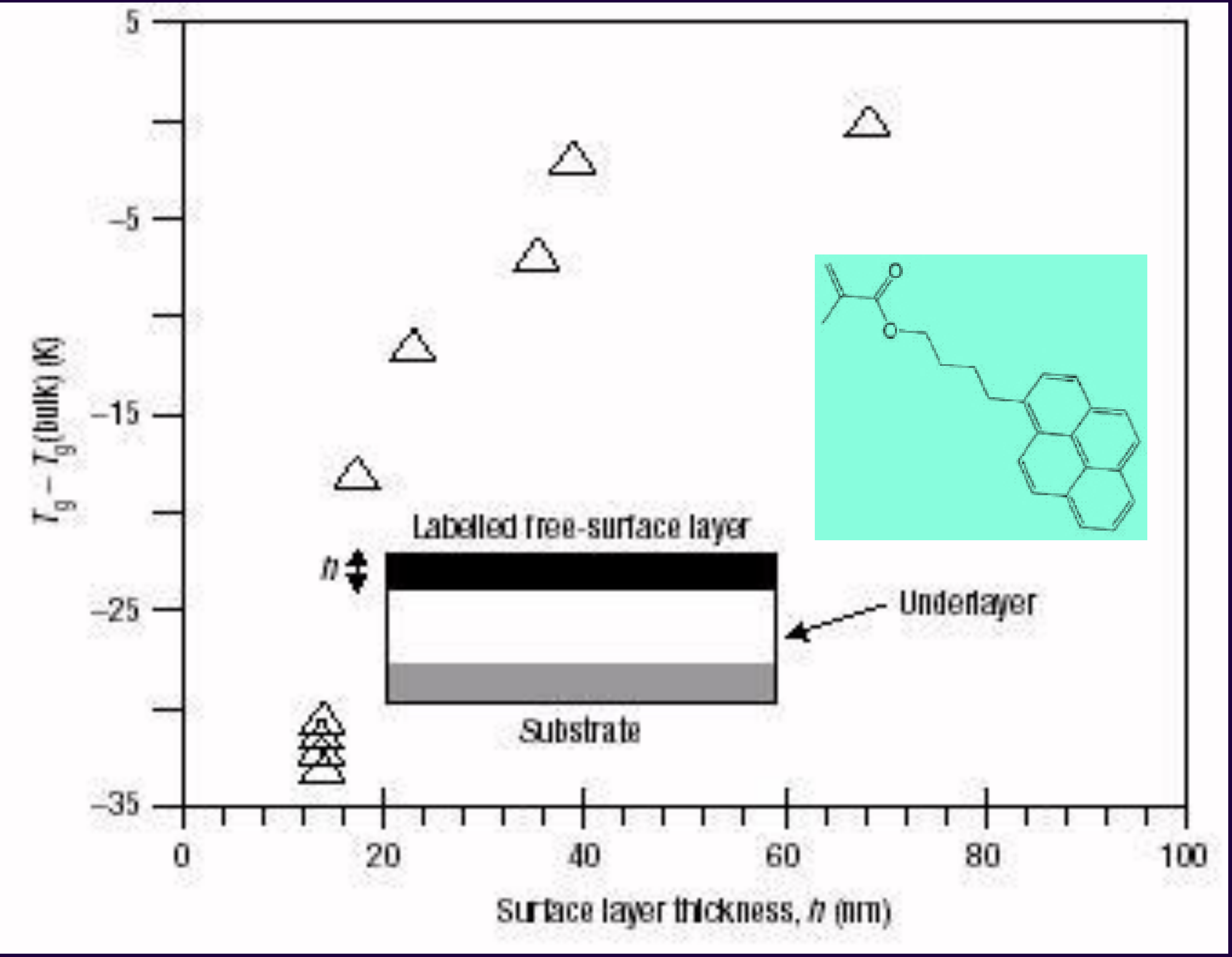



# *Phase Transitions in Polymers*



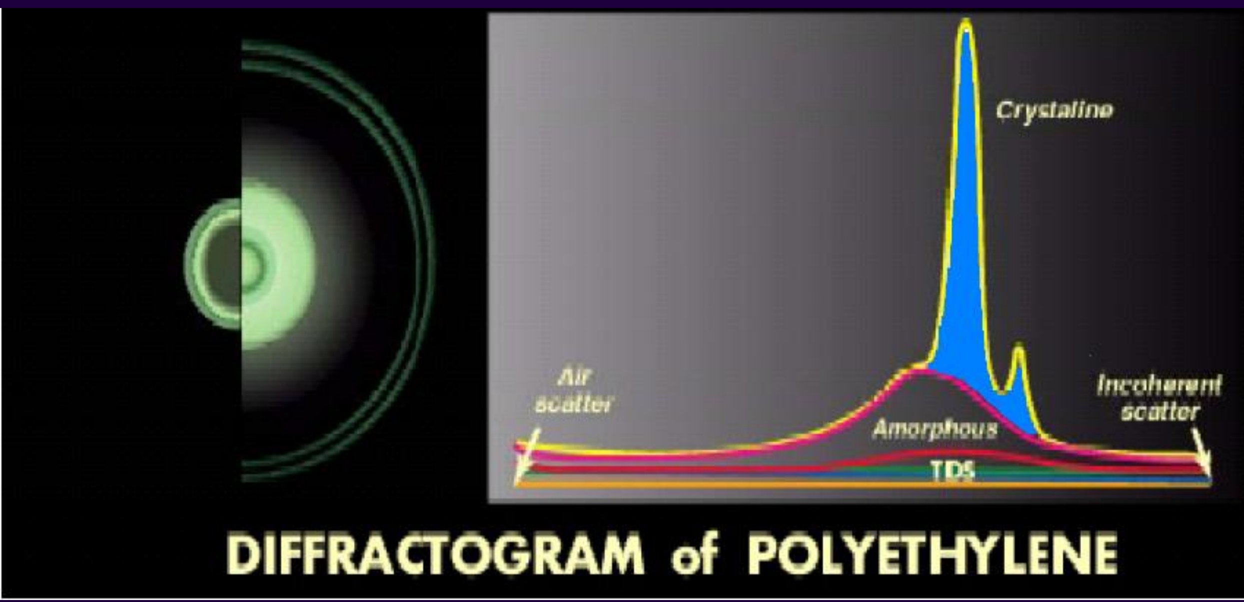



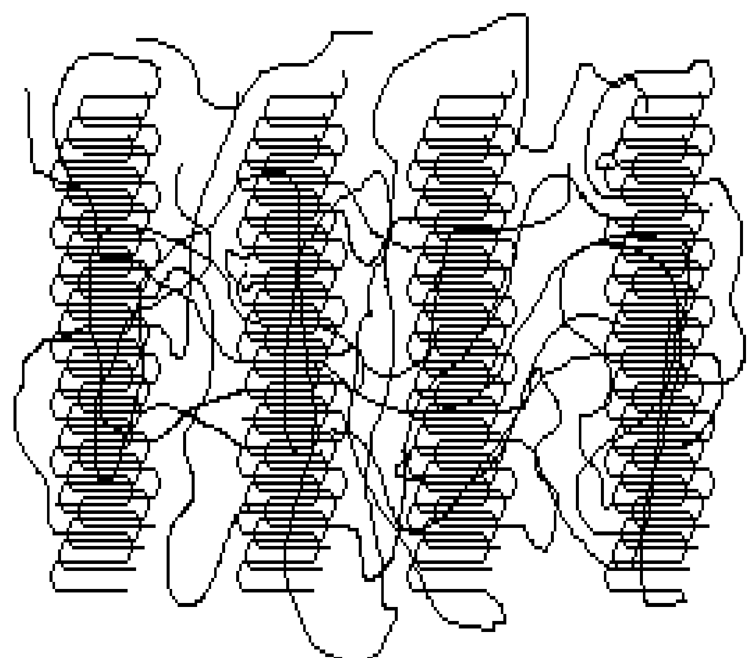
# Phase Transitions in Polymers



# Semi-Crystalline Polymers

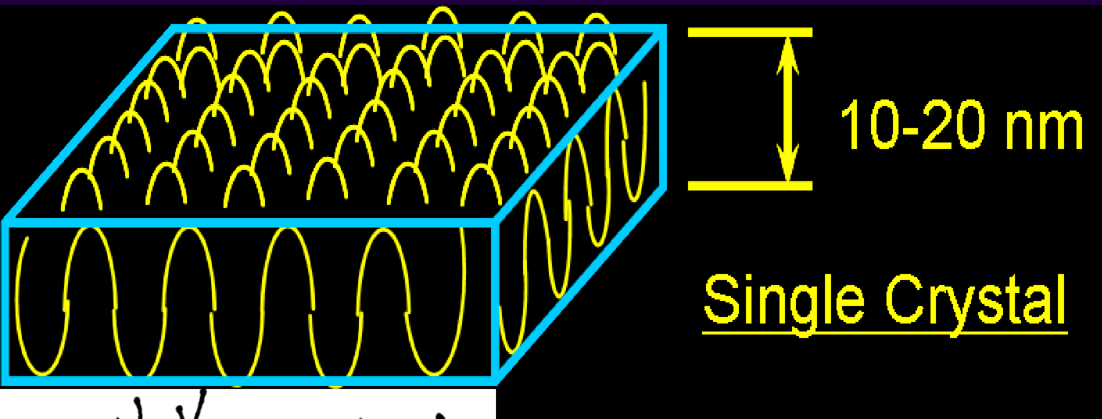
*Semi-crystalline polymers have both crystalline and amorphous regions. Semicrystallinity is a desirable property for most plastics because they combine the strength of crystalline polymers with the flexibility of amorphous. Semi-crystalline polymers can be tough with an ability to bend without breaking.*

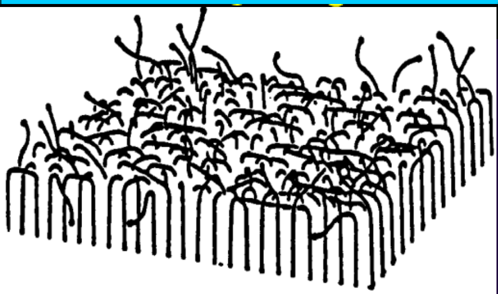


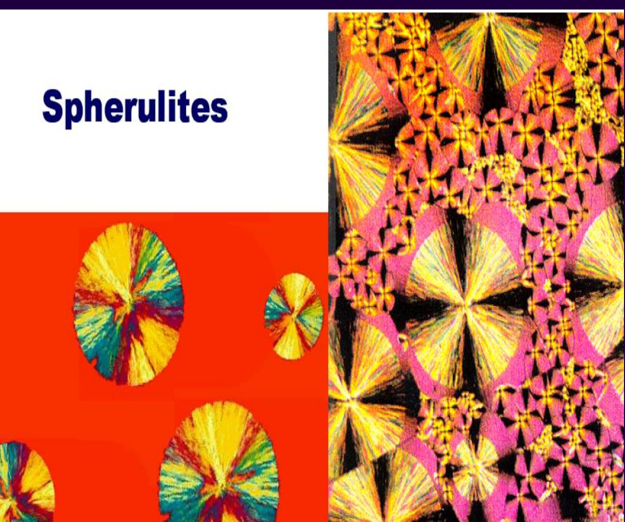
# *Semi-Crystalline Polymers*

***Folded Chain Model of PE***



***Switchboard Model***

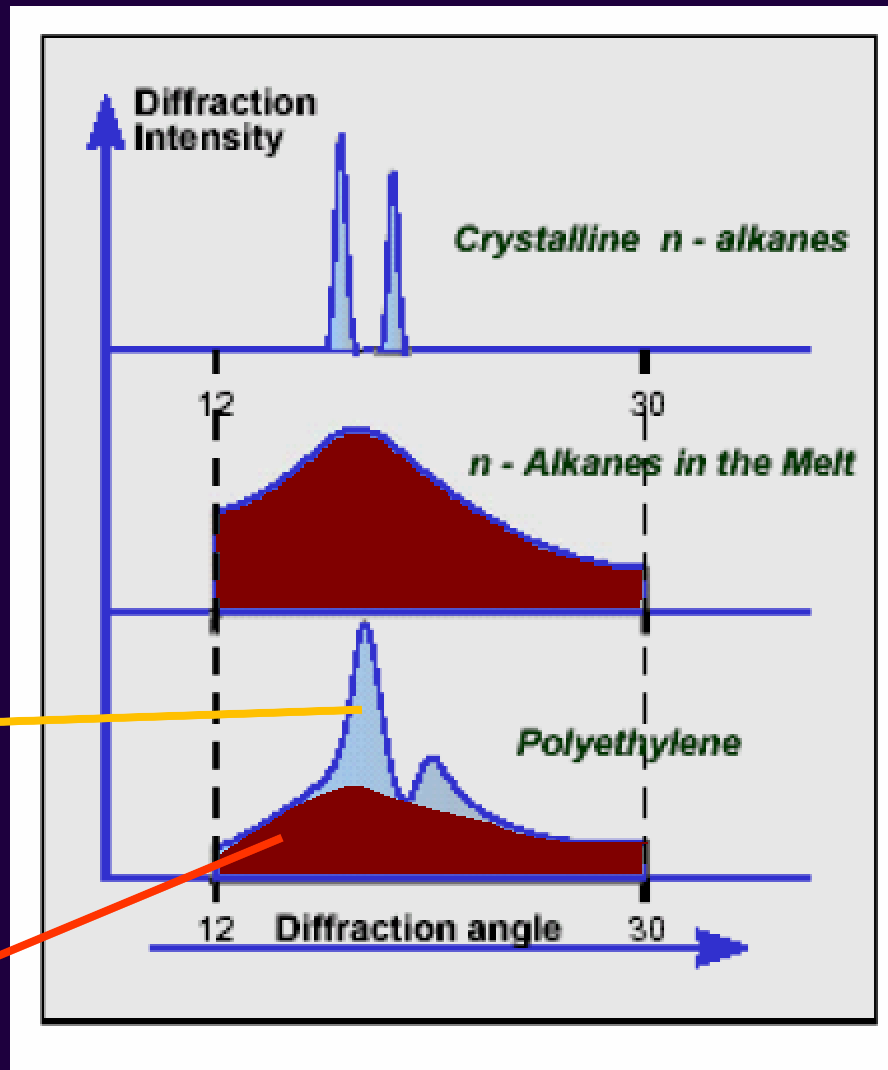



***Crystalline***

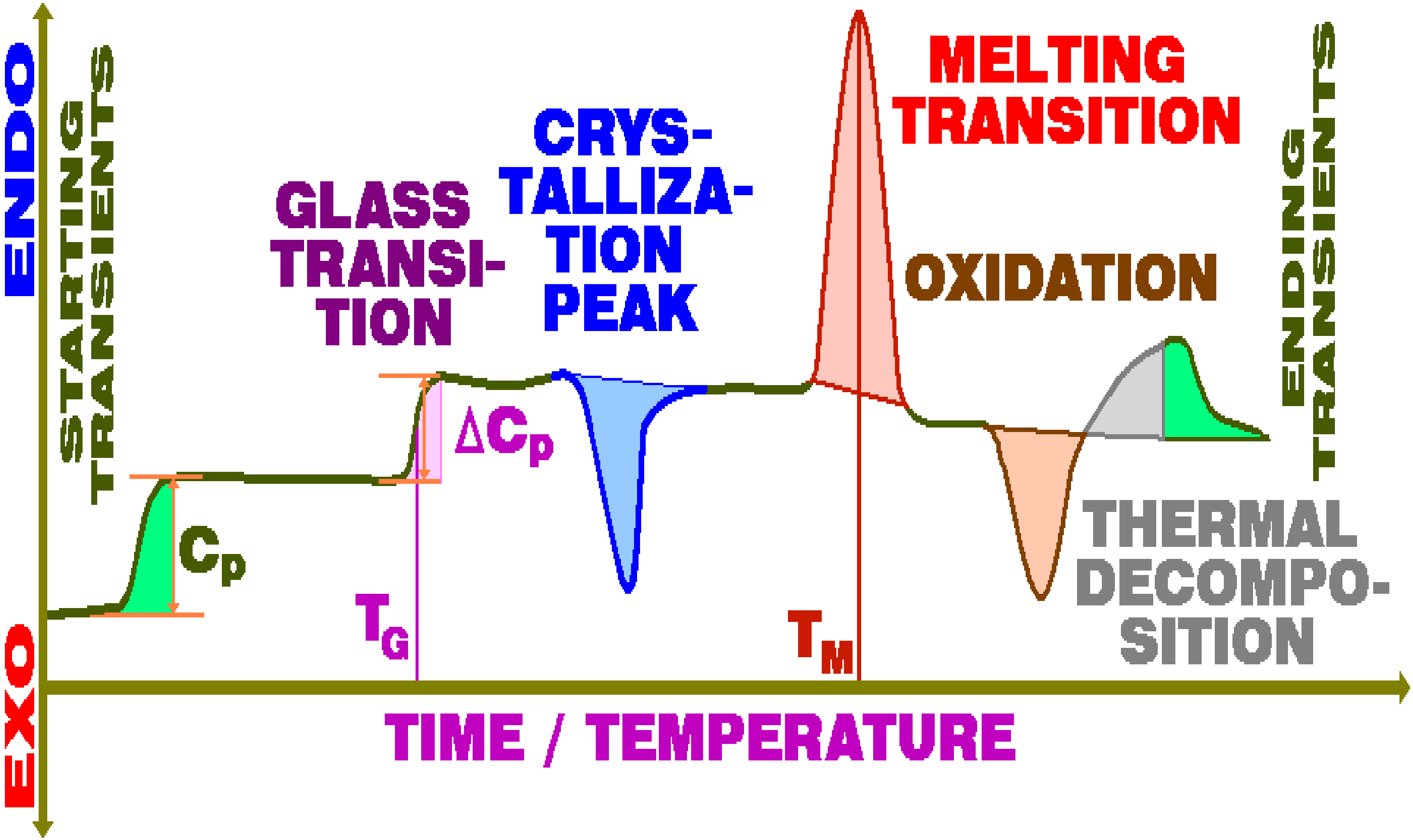
***Domains***

***Amorphous***

***Domains***



# Phase Transitions in Polymers



# *Polymer- Based Nanocomposite Materials*

## *Structural Nanomaterials*

- *Strong/Flexible/Light Films and Fabrics*

## *Conducting Nanomaterials*

- *Strong/Flexible/Light/Transparent Conducting Nnaomaterials*
- *Antistatic Coatings (Charging Effects)*
- *Electromagnetic/Radiation Shielding (Interference/Damage)*

## *Magnetic Nanomaterials*

- *Detectors*
- *Drug delivery*

# *Polymer- Based Nanocomposite Materials*

***Add nanometer - sized nanoparticles to a polymeric matrix:***

- ***1-dimensional nanofillers (platelets such as nanoclays)***

- ***2-dimensional nanofillers (nanowires such as carbon nanotubes)***

- ***3-dimensional nanoparticles (spherical or cubic nanoparticles such as perovskites, magnetite, barium ferrite)***

# Polymer- Based Nanocomposite Materials

## How to disperse the nanoparticles within the polymeric matrix?

- Thermo-mechanical methods (extrusion)
- Melt processing
- Sonication in solution followed by solvent evaporation.
- Stirring/mixing components in solution followed by solvent evaporation.
- In situ polymerization

# Polymer-Carbon Nanostructure Composites

***Carbon Nanotubes, Carbon Nanofibers, and Graphene have the tendency to agglomerate.***

***Difficult dispersion of carbon nanostructures in polymers***

***Solutions:***

- ***Surface modification via chemical or physical functionalization***
- ***Sonication***

# *The Polymer Composite Cube*

***Most frequently used systems:***

- ***Polymer - carbon nanotubes/nanofibers***
- ***Polymer - nanoclay***

# The Polymer Composite Cube

## ASSUMPTIONS

- ***A cube of polymer of side $L_P$ and density $\rho_P$***
- ***A cube of filler of side $L_F$ and density $\rho_F$***
- ***A concentration $C_F$ of the filler within the polymeric matrix.***

$$m_P = \rho_P L_P^3$$

$$m_F = \rho_F L_F^3$$

$$C_F(\%) = \frac{m_F}{m_F + m_P} x100$$

$$C_F(\%) = \frac{\rho_F L_F^3}{\rho_F L_F^3 + \rho_P L_P^3} x100$$

$$\rho_P C_F L_P^3 = \rho_F L_F^3 (100 - C_F)$$

# *The Polymer Composite Cube*

## *ASSUMPTIONS*

- ***Accordingly:***
- ***Simplified model:***
  - *Density of polymer and filler almost equal*
  - *Very low concentration regime: $C_F$*
  - *A single cubic particle*

$$\rho_P C_F L_P^3 = \rho_F L_F^3 (100 - C_F)$$

$$\frac{L_F}{L_P} = \left[\frac{\rho_P C_F}{\rho_F (100 - C_F)}\right]^{1/3}$$

$$\frac{L_F}{L_P} = \left[\frac{\rho_P C_F}{\rho_F (100 - C_F)}\right]^{1/3}$$

$$L_F \approx L_P \left[\frac{C_F}{(100 - C_F)}\right]^{1/3}$$

# *The Polymer Composite Cube*

## *ASSUMPTIONS*

- ***Very low filler concentration***
  - $C_F$=0.1 %
  - POLYMER SIDE 1 m
  - A single cube of filler with a side of 0.1 m

$$L_F \approx L_P \left[ \frac{C_F}{(100 - C_F)} \right]^{1/3}$$

$$L_F \approx L_P \left[ \frac{0.1}{99.9} \right]^{1/3} \cong \frac{L_P}{10}$$

# The Polymer Composite Cube

## ASSUMPTIONS

- ***Filler consists of N identical cubes of side $x_F$***
- ***Total mass of filler is $m_F$***

$$m_F = N\rho_F x_F^3$$

$$C_F = \frac{N\rho_F x_F^3}{N\rho_F x_F^3 + \rho_P L_P^3} x100$$

$$C_F \rho_P L_P^3 = N\rho_F x_F^3 (100 - C_F)$$

$$x_F = L_P \left[ \frac{C_F \rho_P}{N\rho_F (100 - C_F)} \right]^{1/3}$$

# The Polymer Composite Cube

## ASSUMPTIONS

- Filler consists of N identical cubes of side $x_F$
- Simplified model:
  - Density of polymer and filler almost equal.
  - $C_F$=0.1 %

$$x_F = L_P \left[ \frac{C_F \rho_P}{N \rho_F (100 - C_F)} \right]^{1/3}$$

$$x_F = L_P \left[ \frac{C_F}{N (100 - C_F)} \right]^{1/3}$$

$$x_F = L_P \left[ \frac{.1}{99.9 N} \right]^{1/3}$$

$$x_F = \frac{L_P}{10} \left[ \frac{1}{N} \right]^{1/3}$$

# The Polymer Composite Cube

$$x_F = \frac{L_P}{10}\left[\frac{1}{N}\right]^{1/3}$$

**ASSUMPTIONS**

- **POLYMER SIDE 1 m**
- ***Filler side 1mm →N=10$^{6}$***
- ***Filler side 1micron →N=10$^{15}$***
- ***Filler side 1 nm →N=10$^{24}$***

$$N = \frac{L_P^3}{1000\,x_F^3}$$

# *The Polymer Composite Cube*

## *Interface thickness $\xi$*

$$m_I = \rho_P[(x_F + \xi)^3 - x_F{}^3] = 3\rho_P x_F \xi (x_F + \xi)$$

- *Interface mass $m_I$*

$$m_I = 3\rho_P x_F^2 \xi$$

- *Assumption $x >> \xi$*
- *Mass fraction of the polymer in the interface*

$$f_I = \frac{m_I}{m_P} = \frac{m_I m_F (m_P + m_F)}{m_P m_F (m_P + m_F)} = \frac{m_I C_F (m_P + m_F)}{100 m_P m_F}$$

# The Polymer Composite Cube

**Mass of the filler very small**

$$f_I = \frac{m_I C_F (m_P + m_F)}{100 m_P m_F} \approx \frac{m_I C_F}{100 m_F}$$

$$m_I = 3\rho_P x_F^2 \xi$$

**Mass fraction of the polymer in the interface**

$$f_I \approx \frac{m_I C_F}{100 m_F} = \frac{3\rho_P x_F^2 \xi C_F}{100 \rho_F x_F^3}$$

$$f_I = \frac{3\rho_P \xi C_F}{100 \rho_F x_F}$$

# The Polymer Composite Cube

$$f_I = \frac{3\rho_P \xi C_F}{100\rho_F x_F} = 1$$

*Maxim value of f is 1.*

*At f=1 is obtained*

$$C_F = \frac{100}{3}\frac{\rho_F}{\rho_P}\frac{x_F}{\xi}$$

*Density of filler and polymer almost equal*

$$C_F = \frac{100}{3}\frac{x_F}{\xi}$$

# The Polymer Composite Cube

$$C_F = \frac{100}{3}\frac{x_F}{\xi}$$

For $x_F$=1nm and $C_F$=0.33 %

For $x_F$=3nm and $C_F$=1.00 %

For $x_F$=30nm and $C_F$=10 %

For $x_F$=300 nm and $C_F$=100 %

# The Polymer Composite Cube

- Attractive Interactions
  - Specific volume decreases
  - Overall density increases
  - Packing density increases
  - Glass transition temperature shifted upwards
  - Degree of crystallization increased
- Repulsve Interactions
  - Specific volume increases
  - Overall density decreases
  - Packing density decreases
  - Glass transition temperature shifted downwards
  - Degree of crystallization decreased

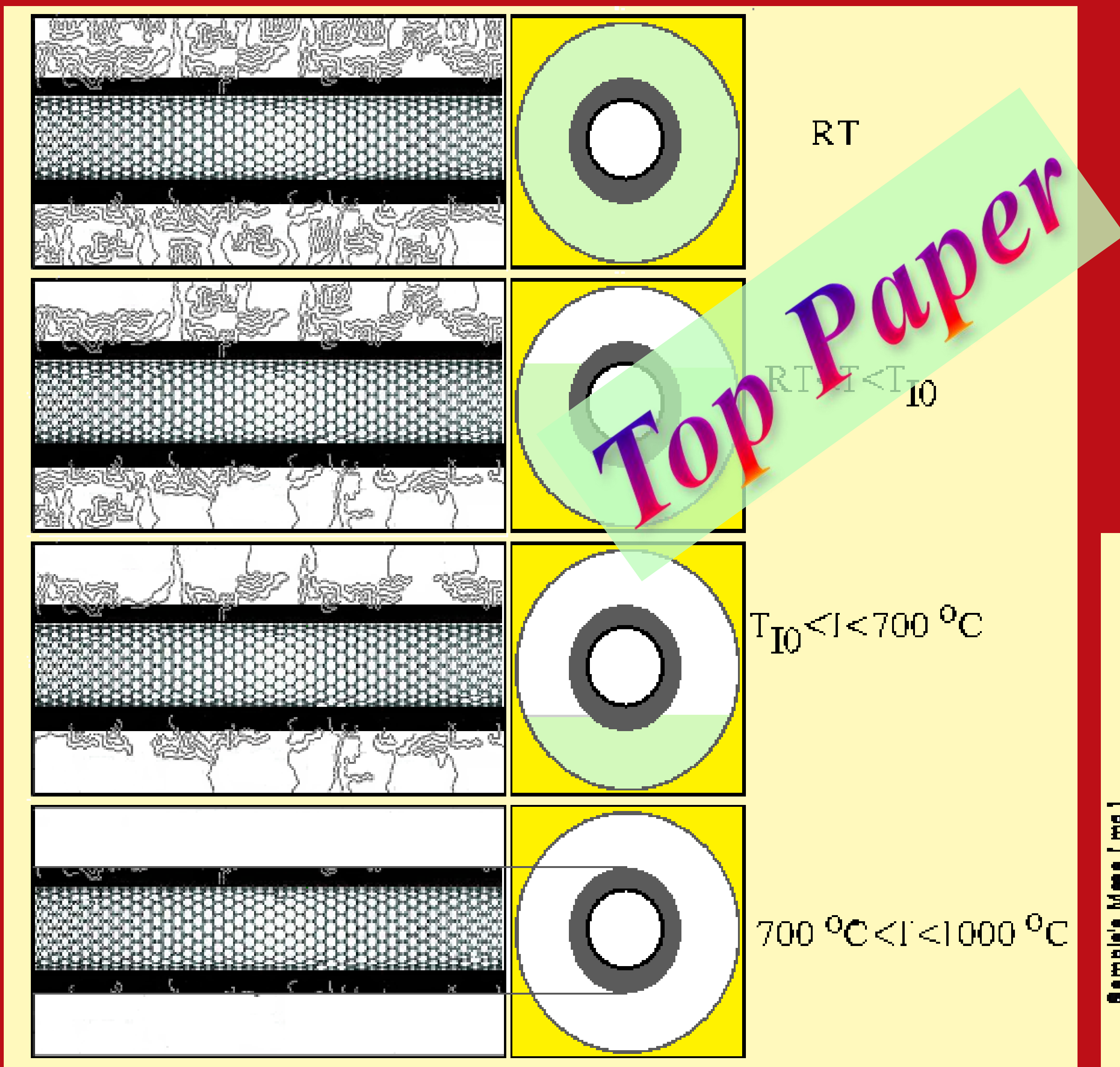
# *Polymer – Based Nanocomposites for Structural Applications*

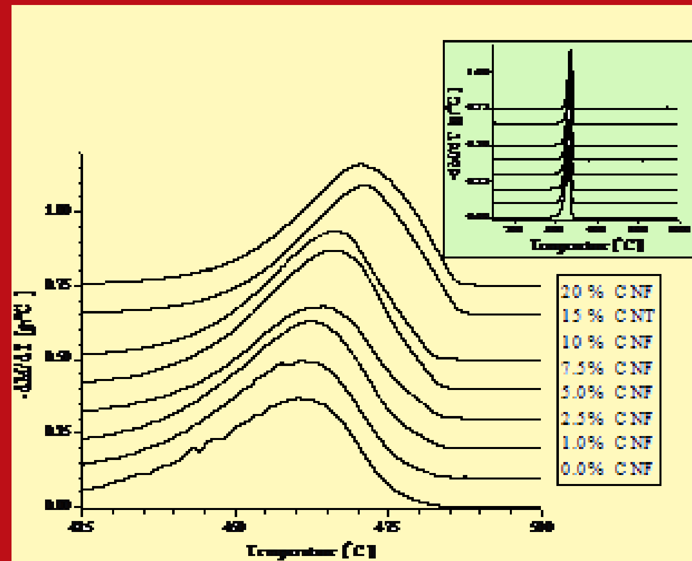
*Most frequently used systems:*

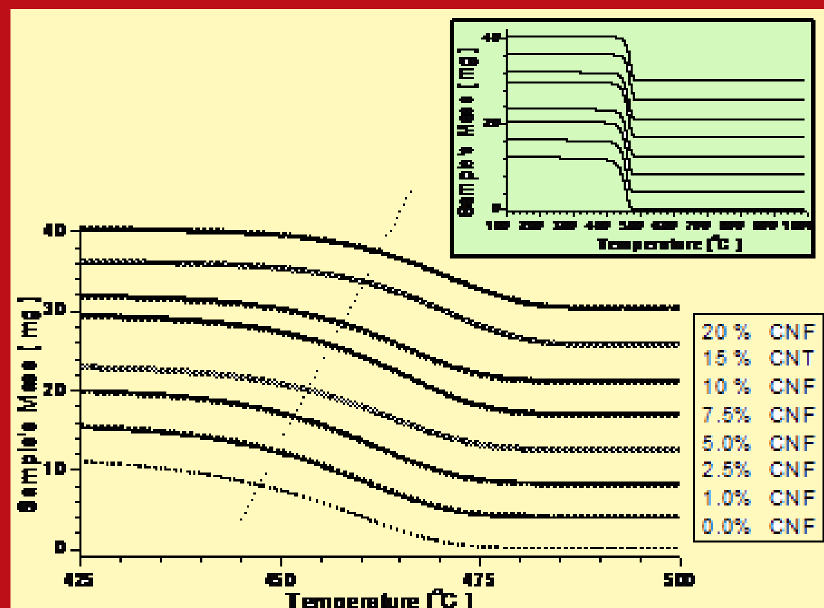
*•Polymer - carbon nanotubes/nanofibers*

*•Polymer - nanoclay*

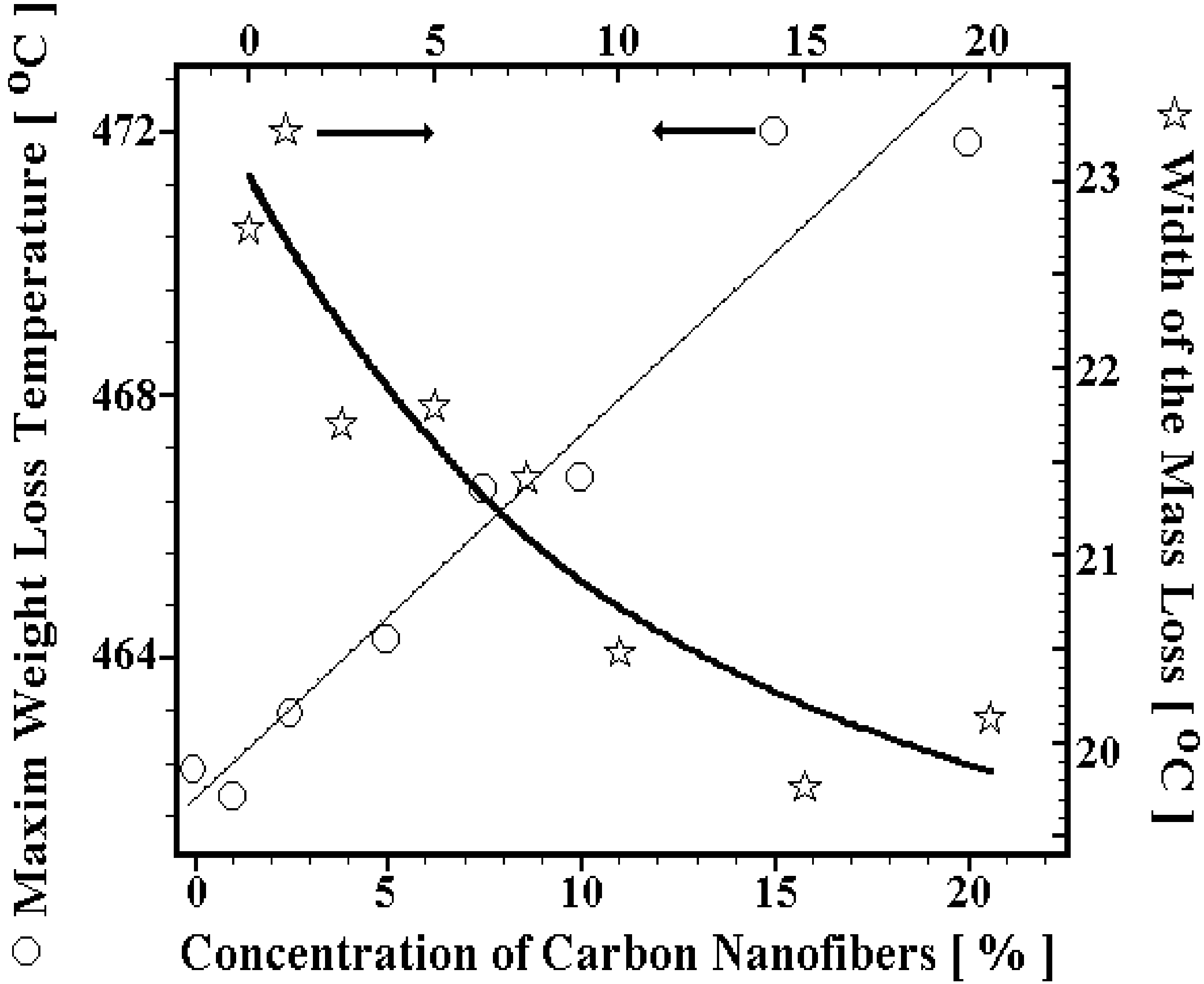
# *Polymer – Based Nanocomposites for Thermal Applications*

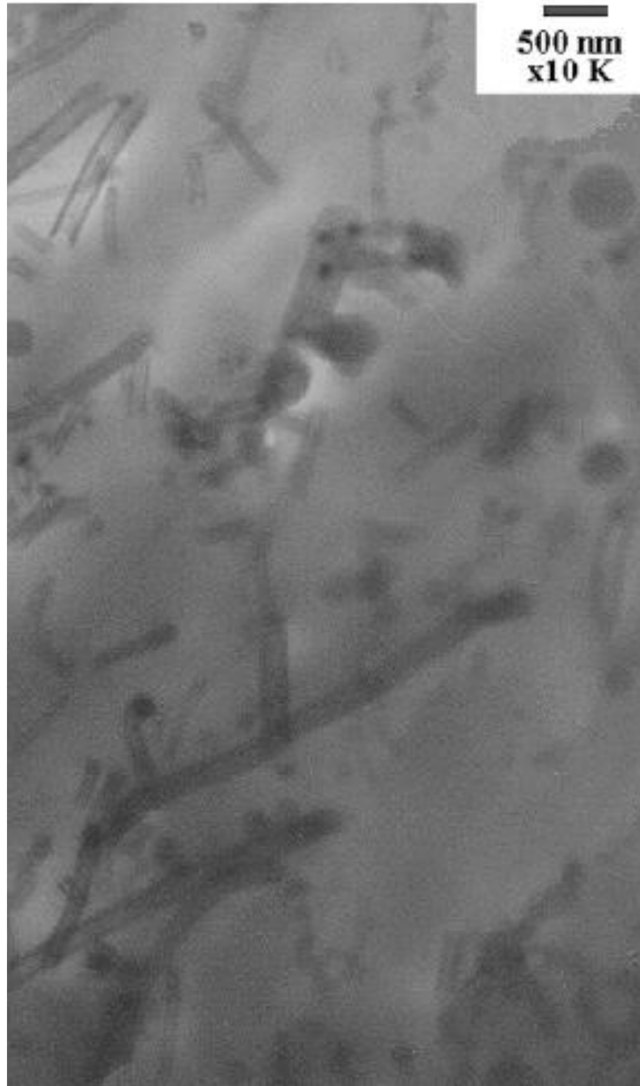


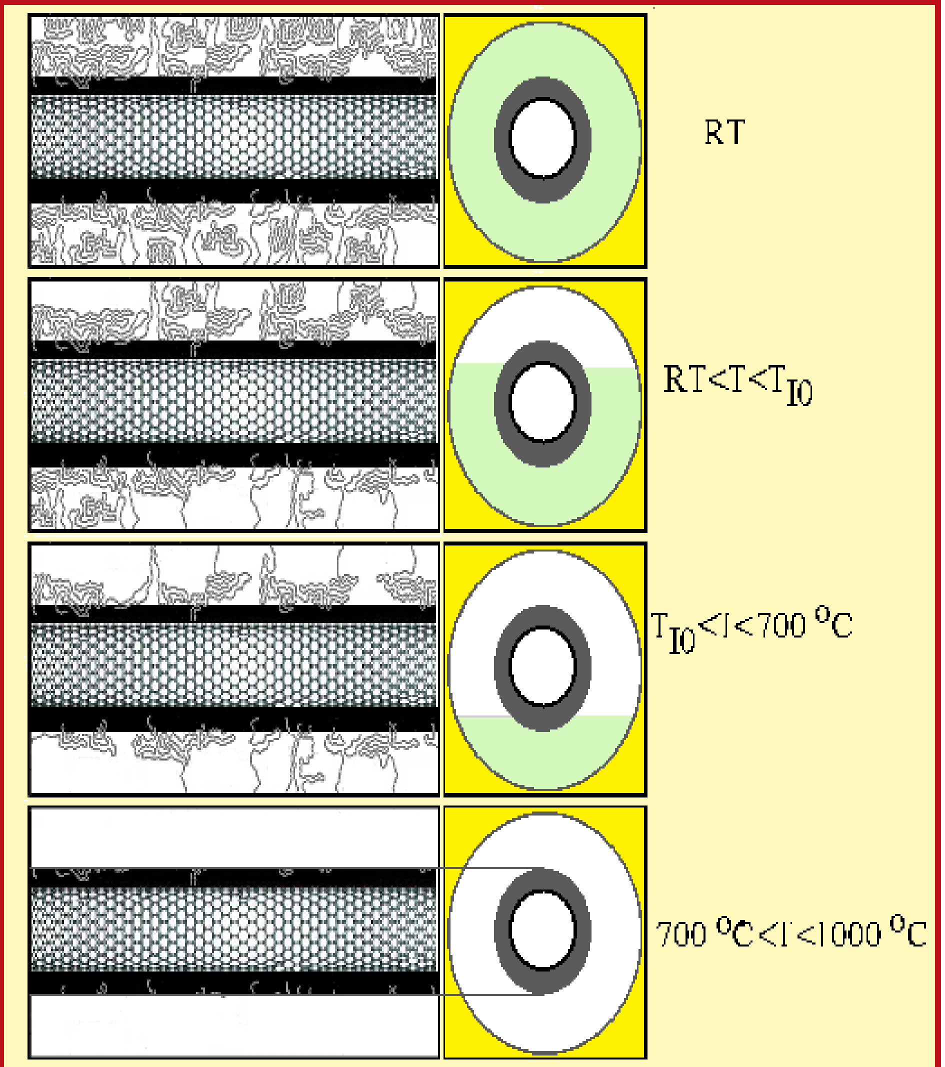
# Thermal Degradation in Nitrogen: PP-CNF

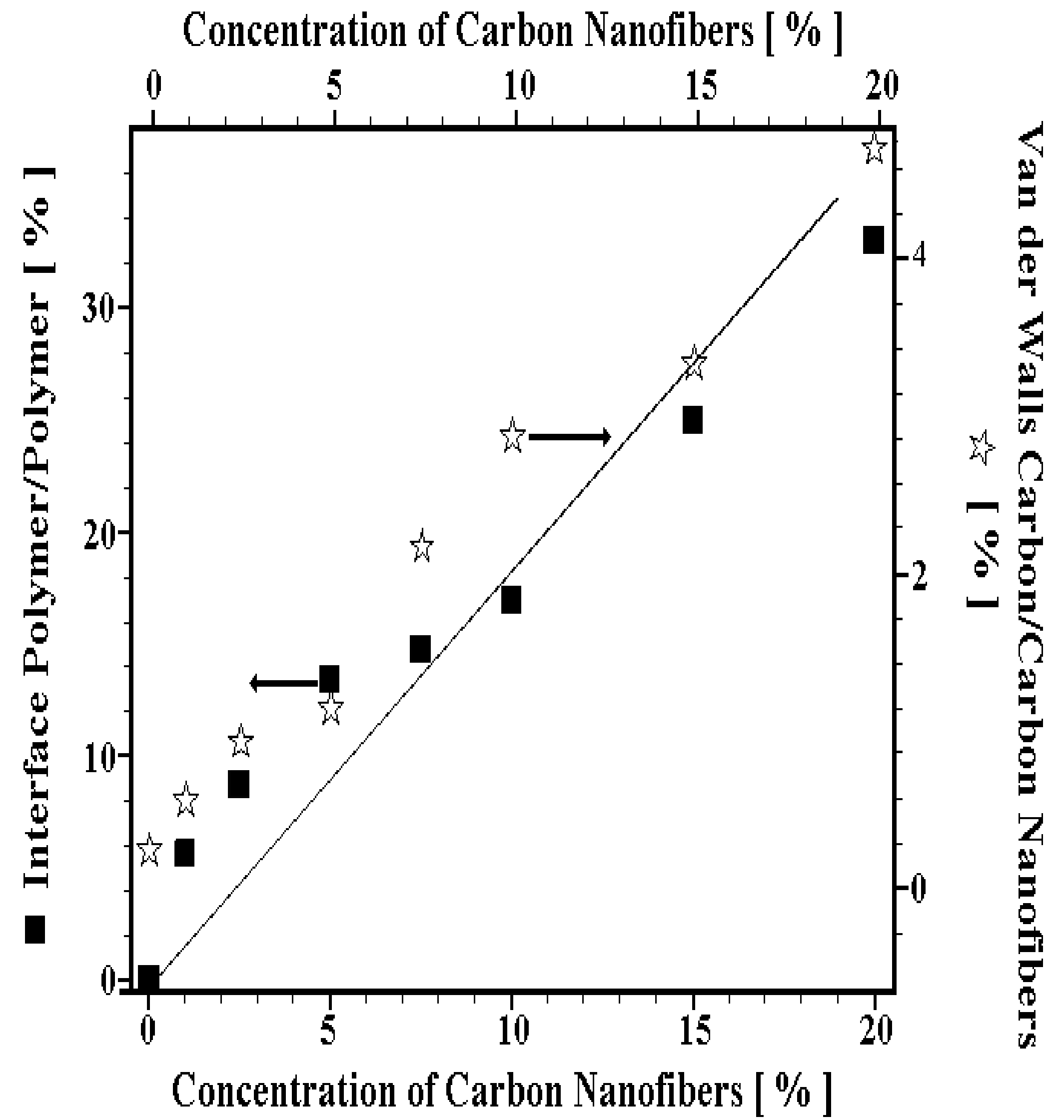



*M. D. Chipara, K. Lozano, A. Hernandez, M. Chipara,*
*TGA analysis of polypropylene-carbon nanofibers composites,*
*Polymer Degradation and Stability, 93(4):871-876, 2008.*

# Thermal Degradation in Nitrogen: PP-CNF

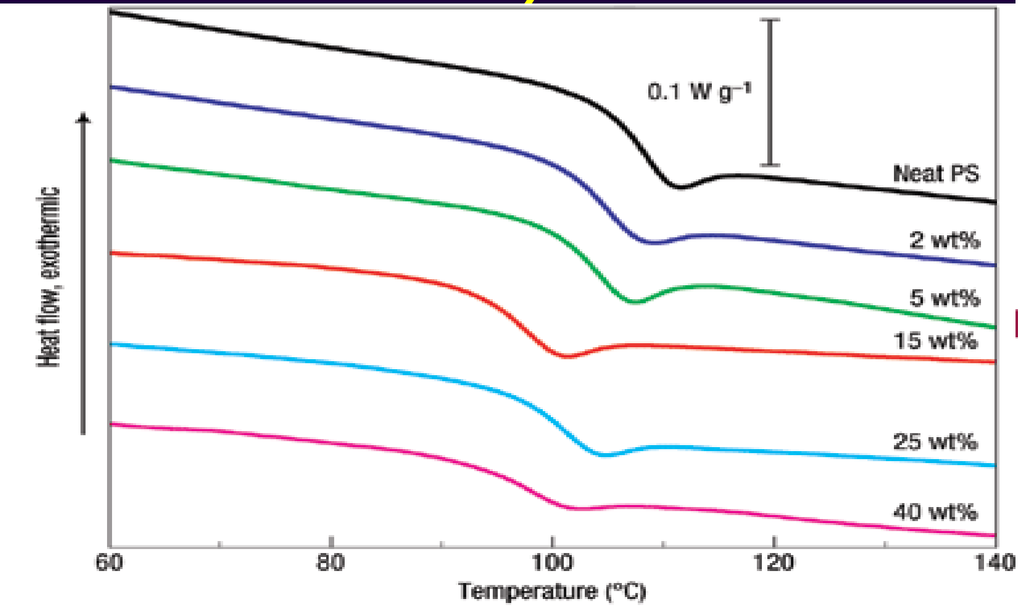


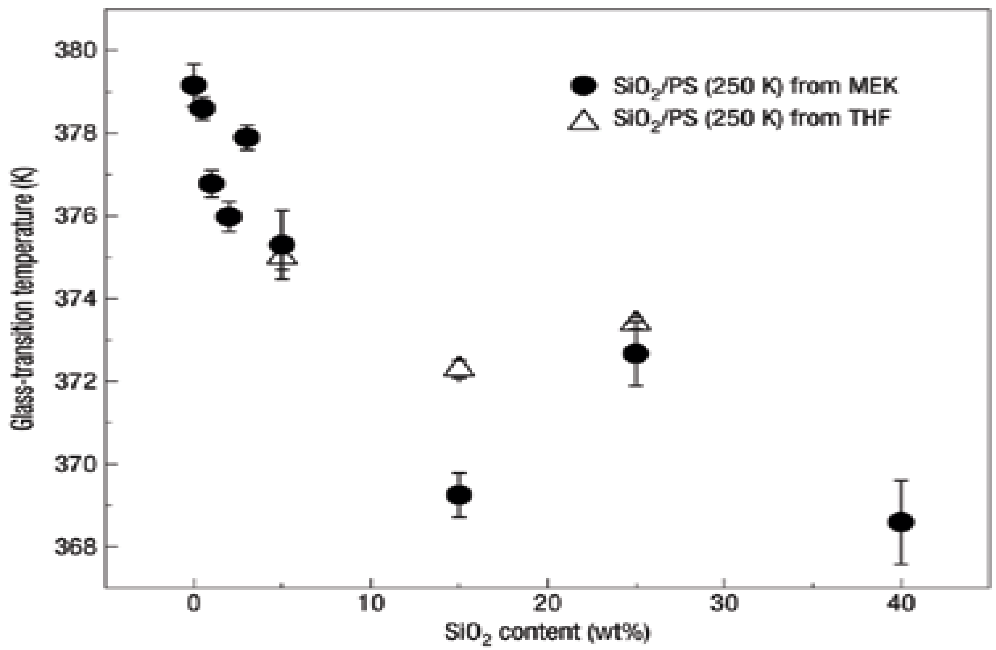

*M. D. Chipara, K. Lozano, A. Hernandez, M. Chipara,*
*TGA analysis of polypropylene-carbon nanofibers composites,*
*Polymer Degradation and Stability, 93(4):871-876, 2008.*

# Phase Transitions in Polymers

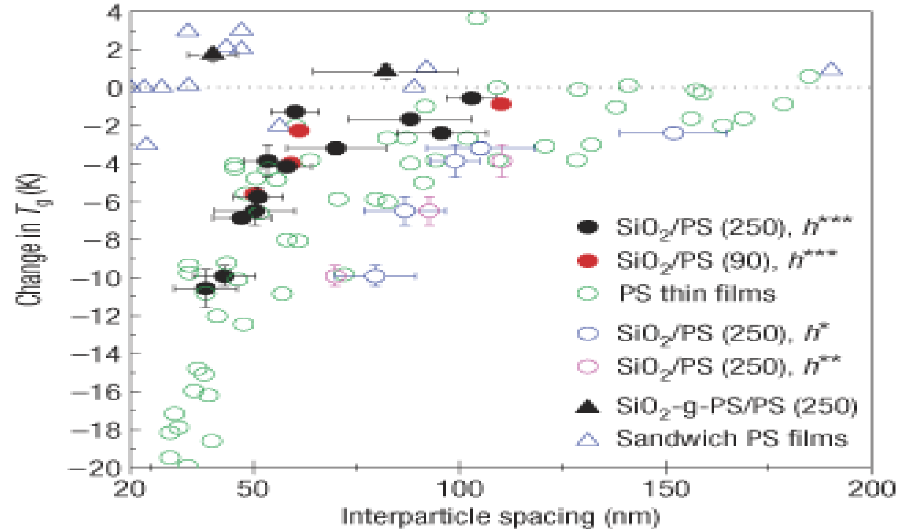
a



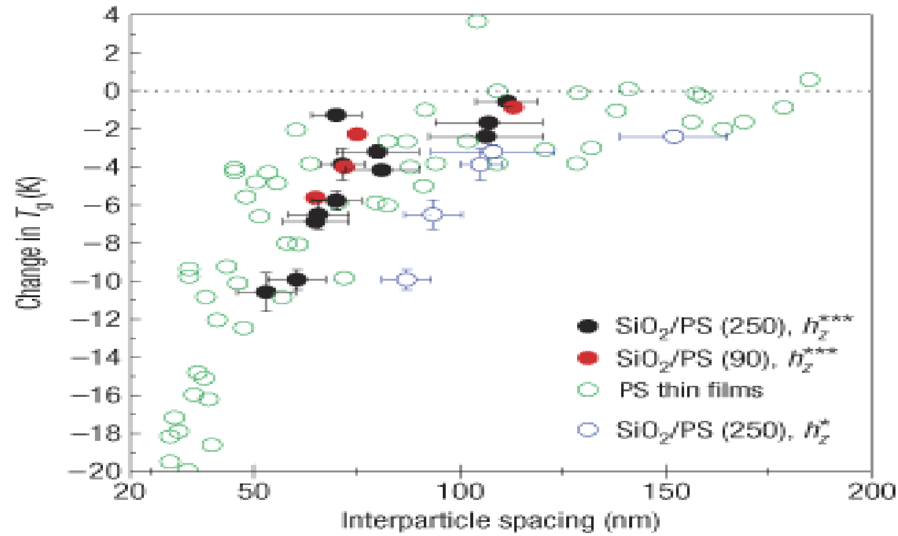

b



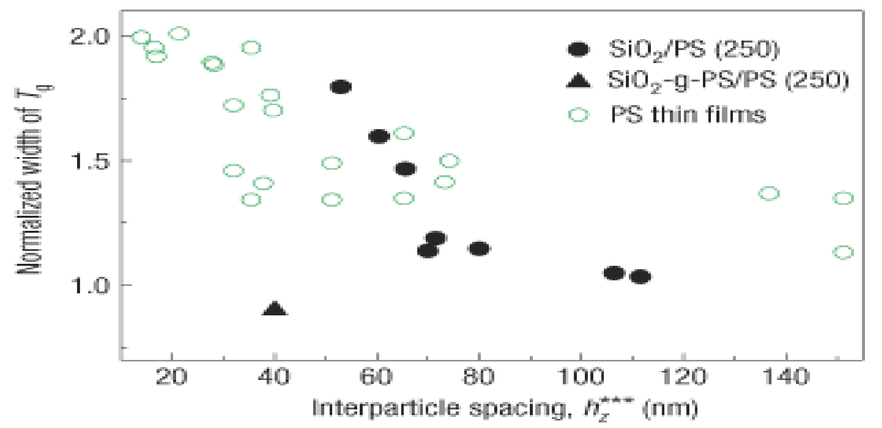

a



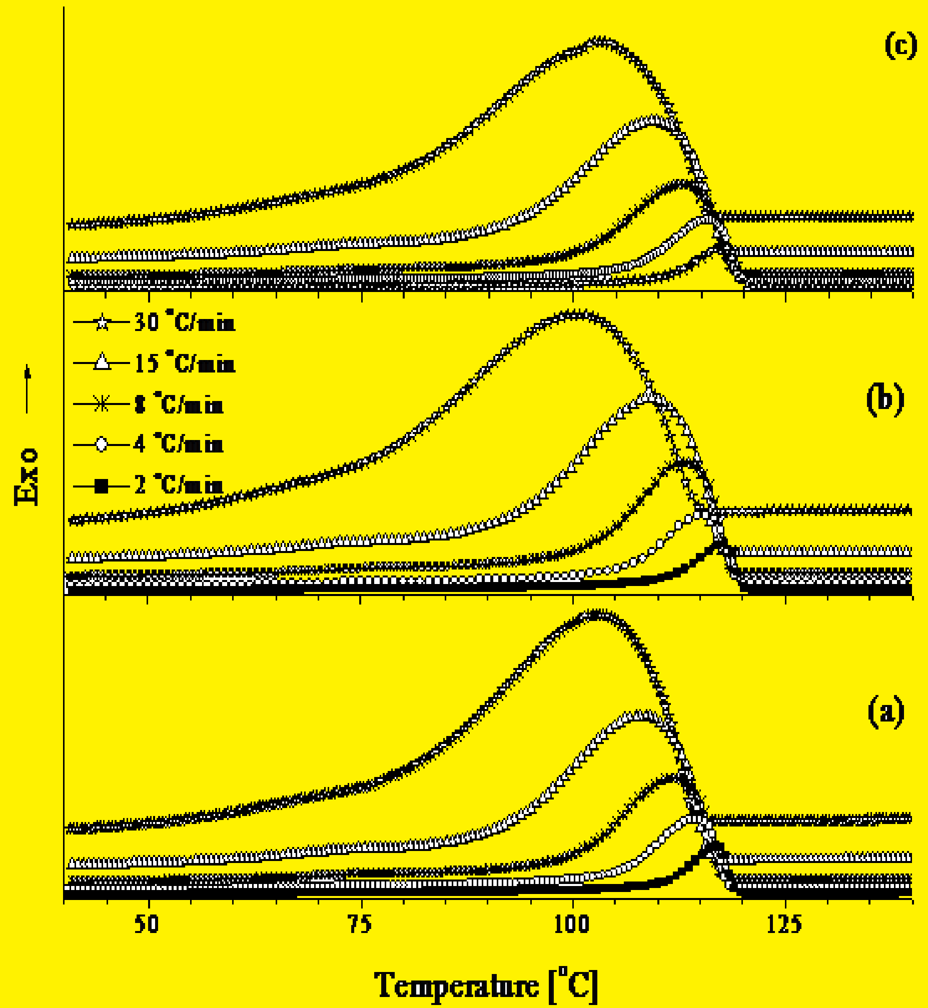

b



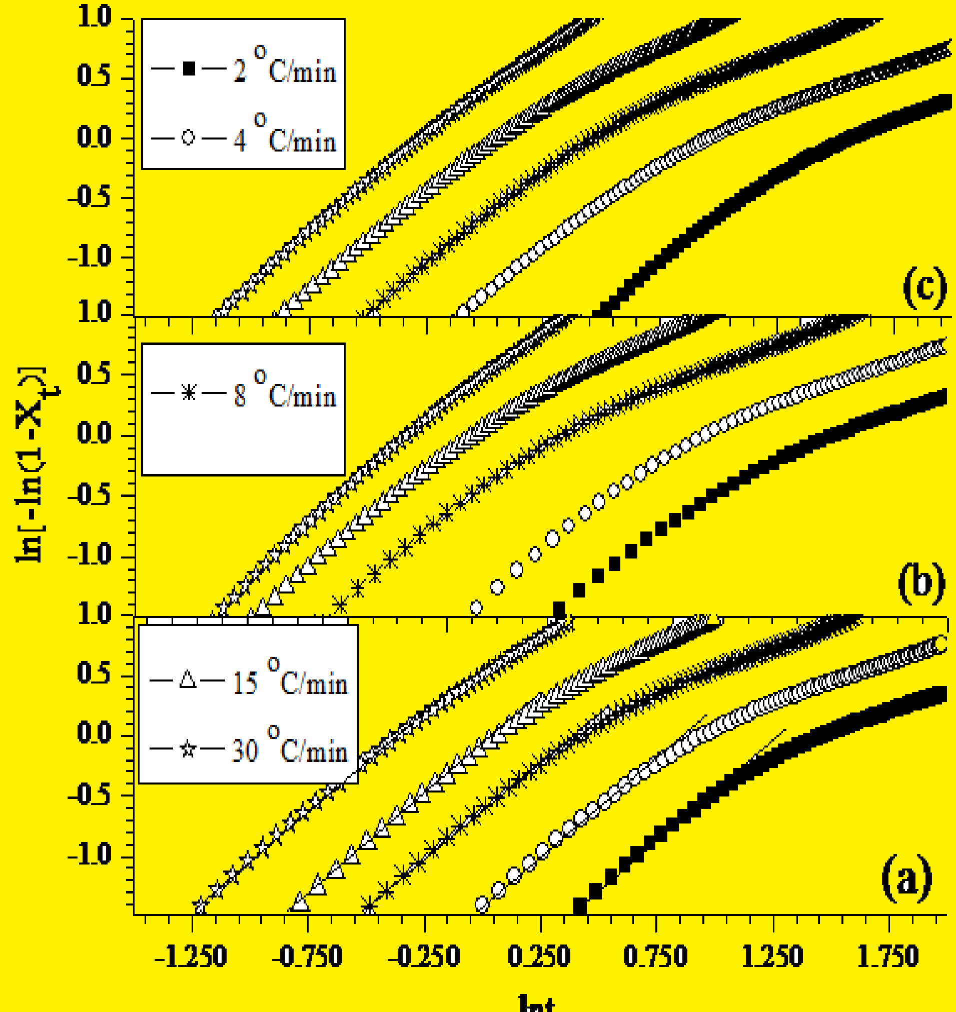

c



# Crystallization Kinetics: PE-MWNTs




**Avrami Plot**

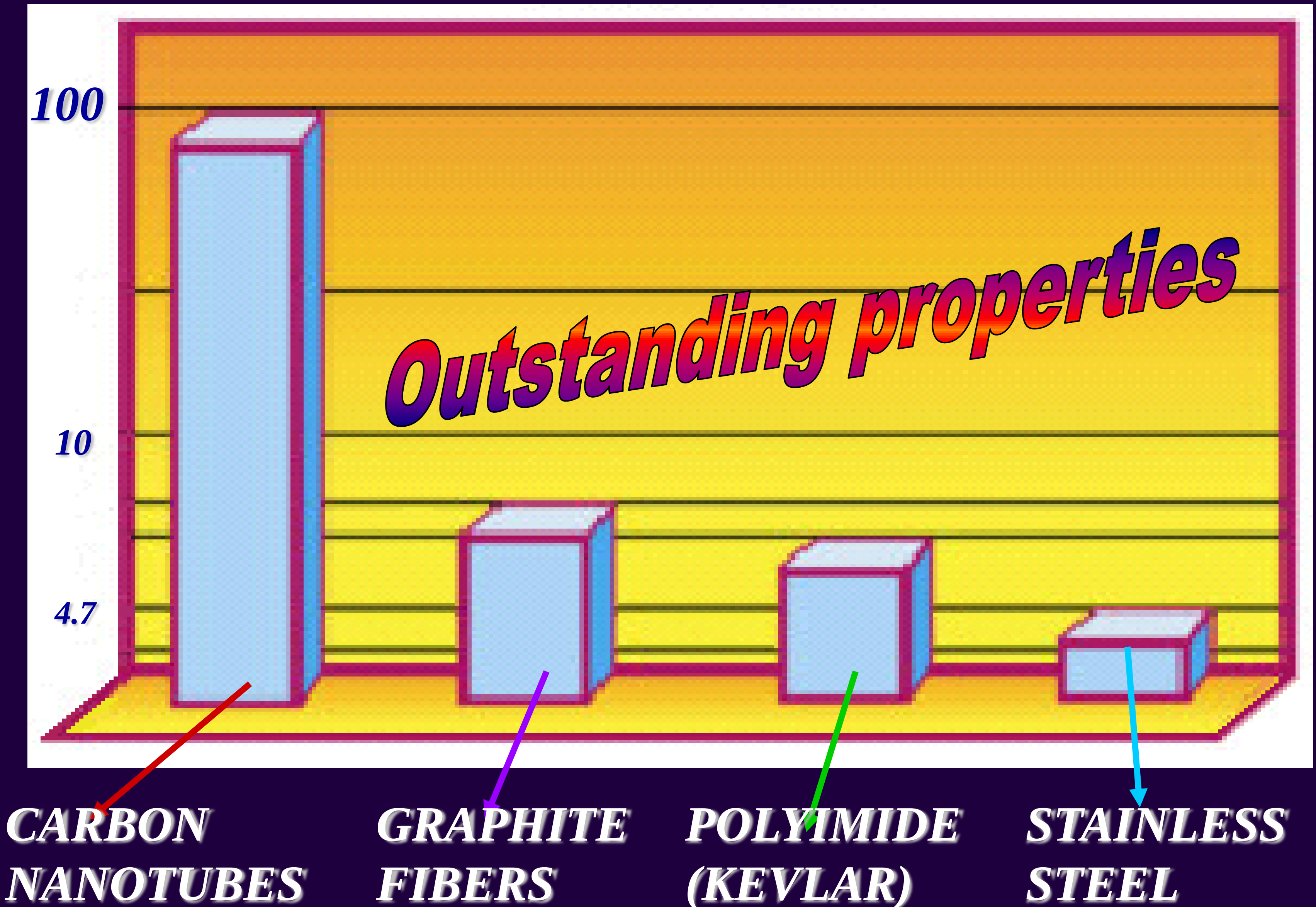



*A. R. Adhikari, K. Lozano, M. Chipara, Nonisothermal crystallization kinetics of polyethylene-/carbon nanofiber composites*

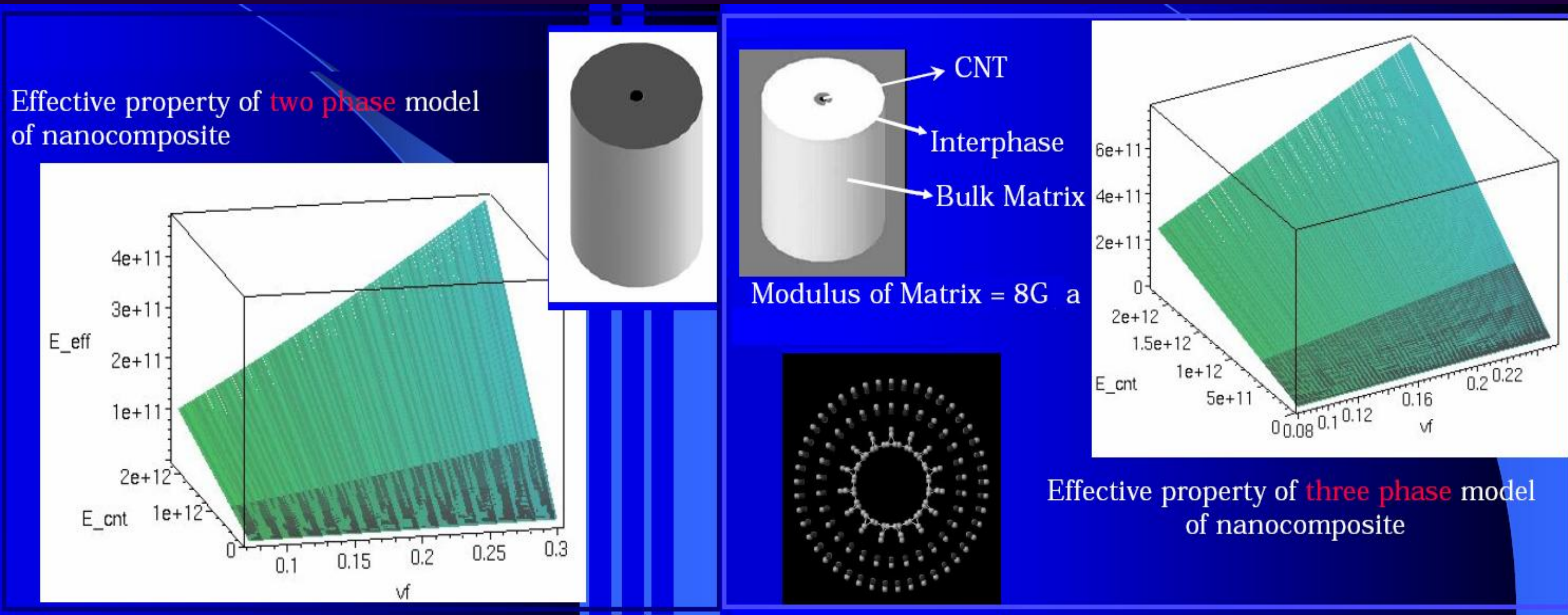
*Submitted to e-polymer*

# *Carbon Nanotubes: Mechanical Strength*

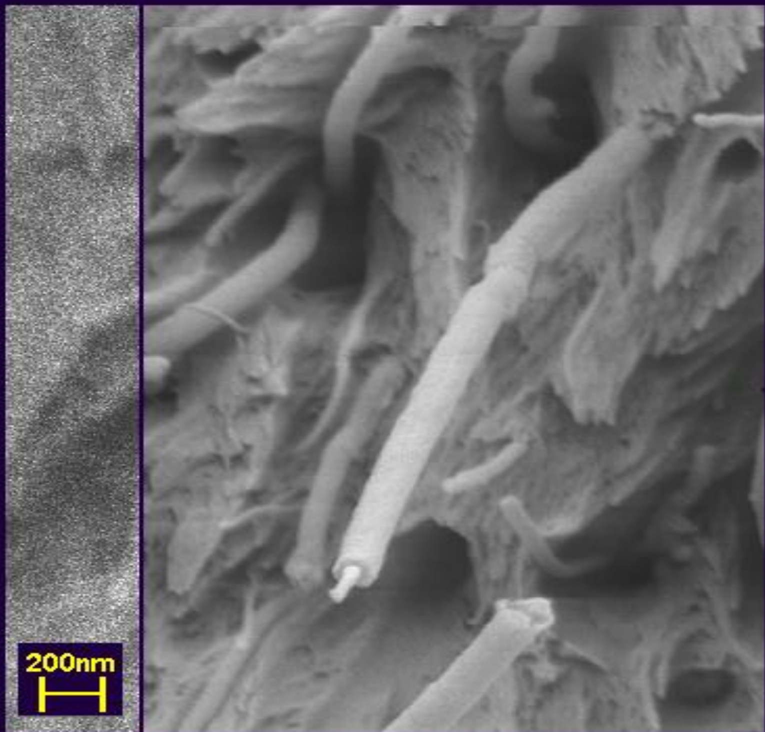
## *Tensile Strength*

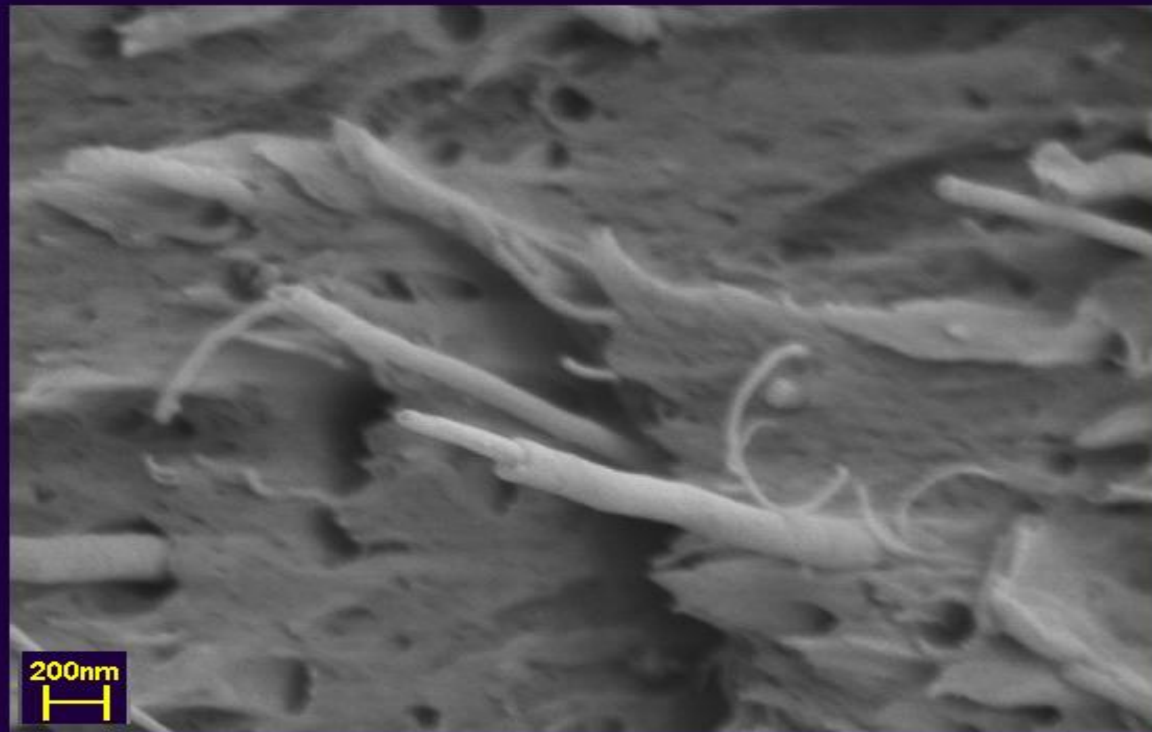


# *Modeling the Mechanical Properties*



# *Modeling the Mechanical Properties*




*Phys Rev Lett* ***2000***, *84*, 5552-5555

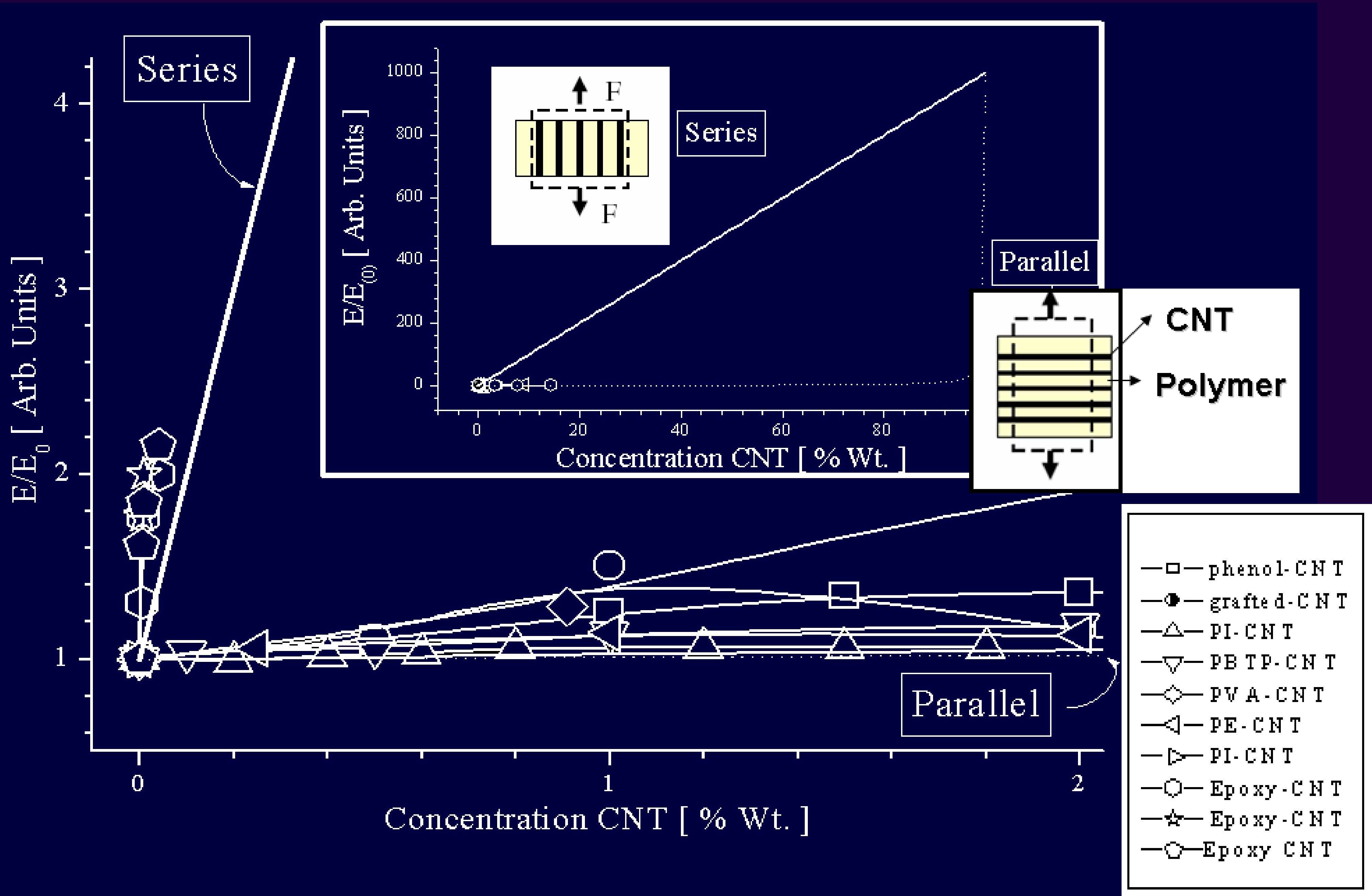
F = U -TS

$$f = \left[\frac{\partial F}{\partial l}\right]_{V,T} = \left[\frac{\partial U}{\partial l}\right]_{V,T} - T\left[\frac{\partial S}{\partial l}\right]_{V,T}$$

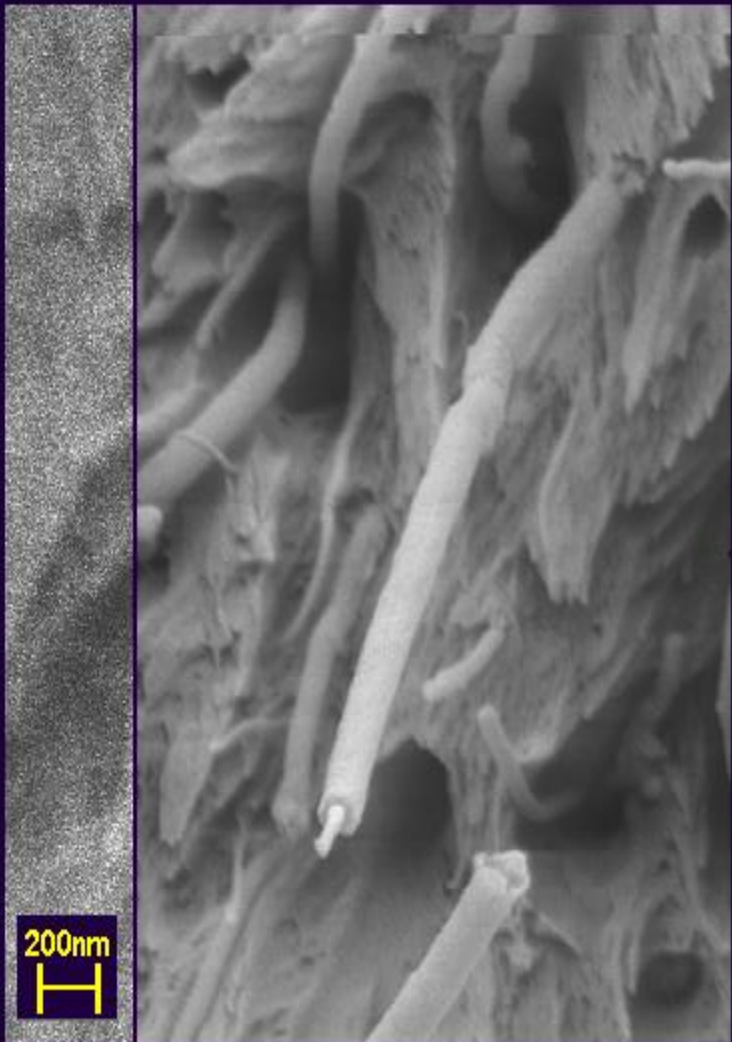
**Carbon Nanotubes** ↔ **Internal Energy Change**

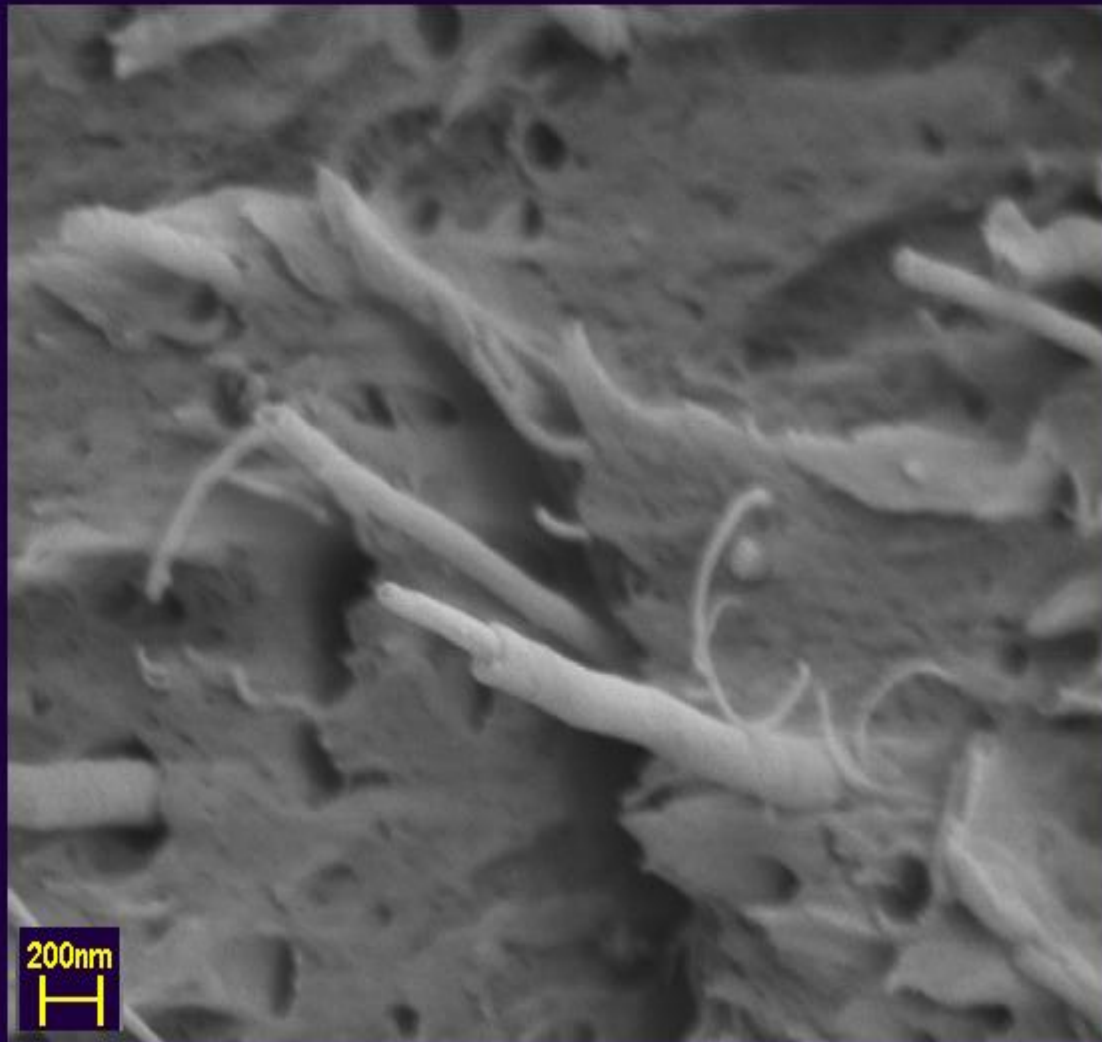
**Entropy Change** ↔ **Polymer (Rubber)**

# Polymer-Carbon Nanotubes Composites



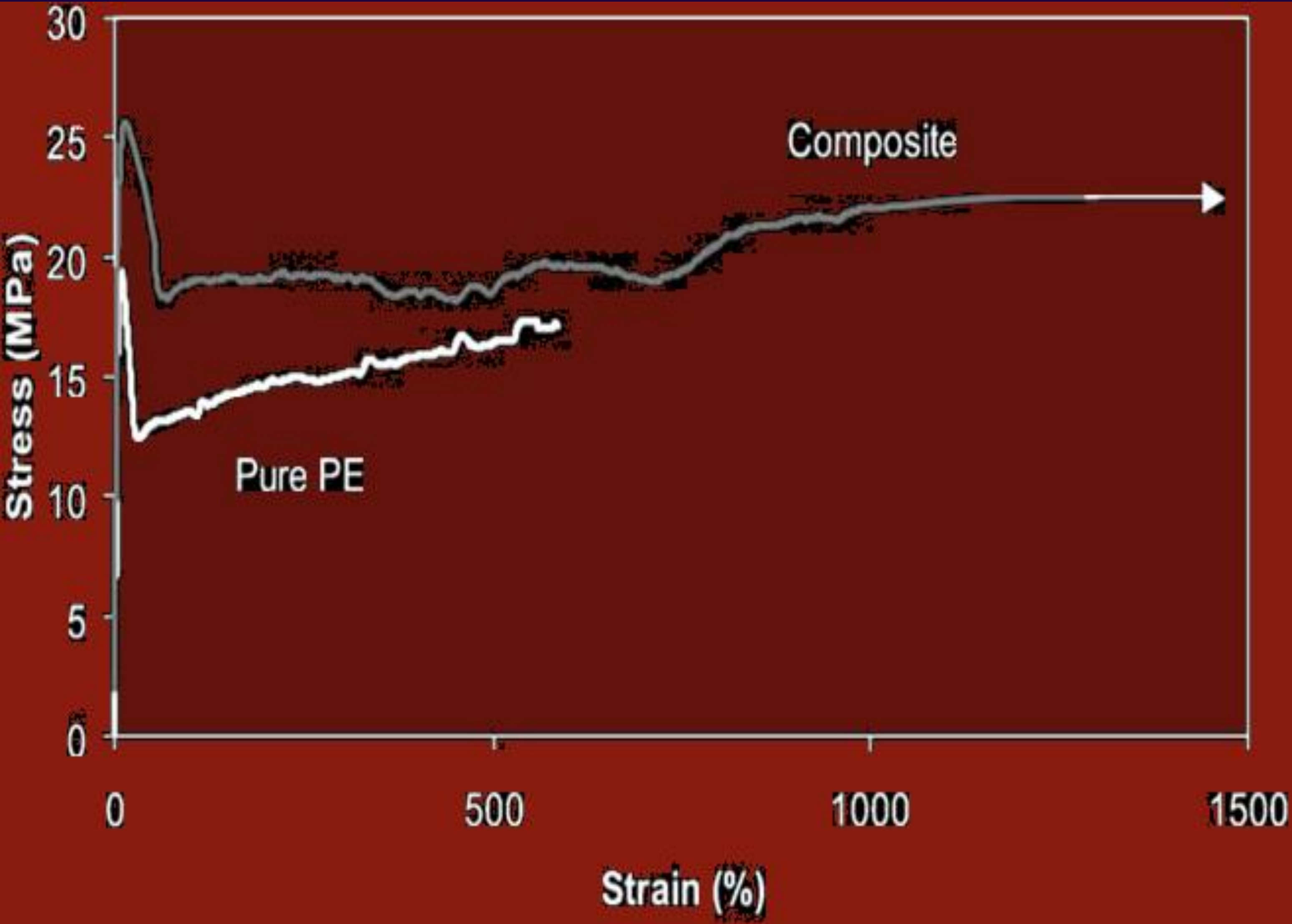
# Nanotube/Polymer Interface



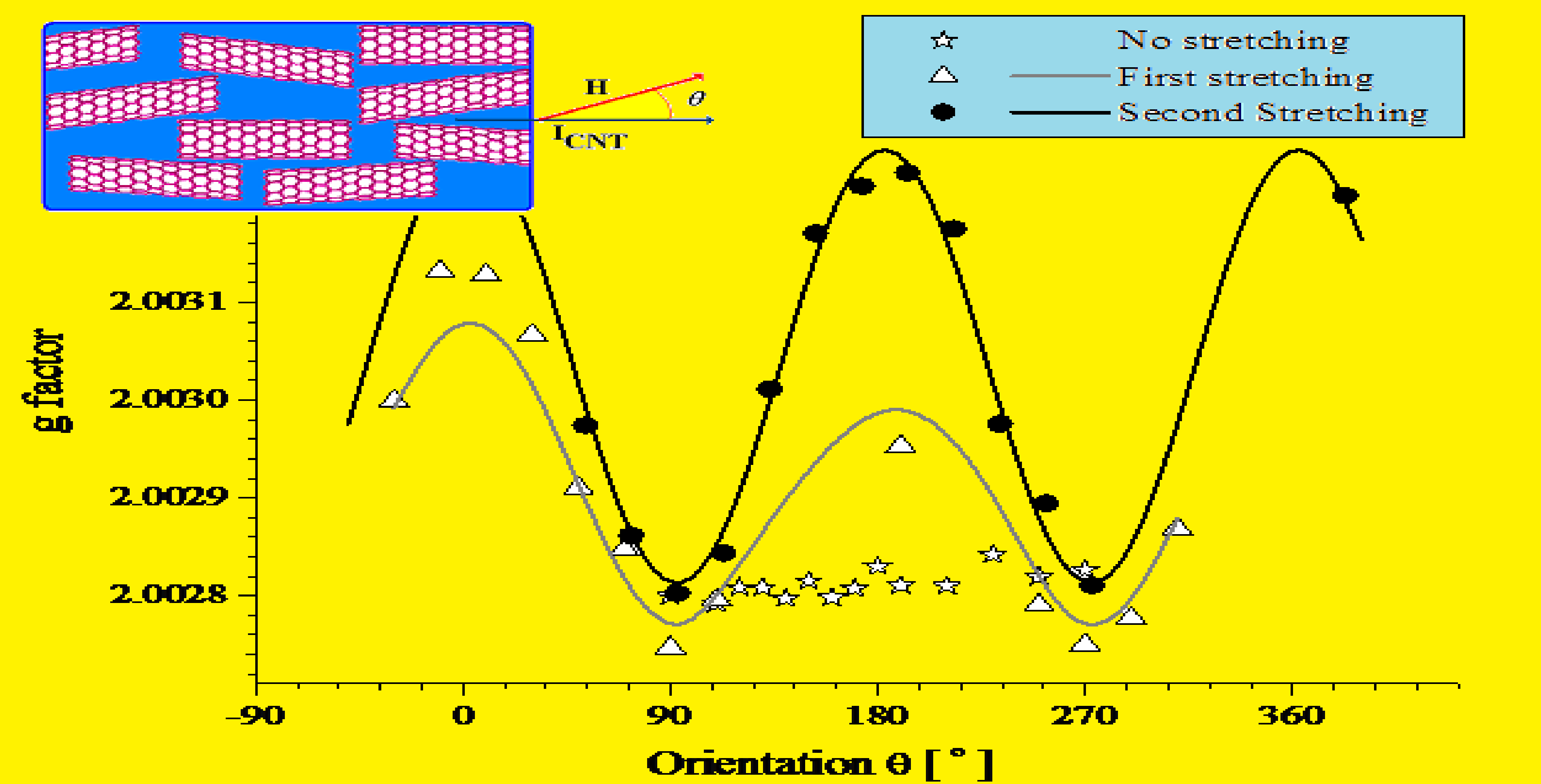




*Phys Rev Lett* ***2000****, 84,* 5552-5555

# *Mechanical Properties :HDPE- VGCNF*

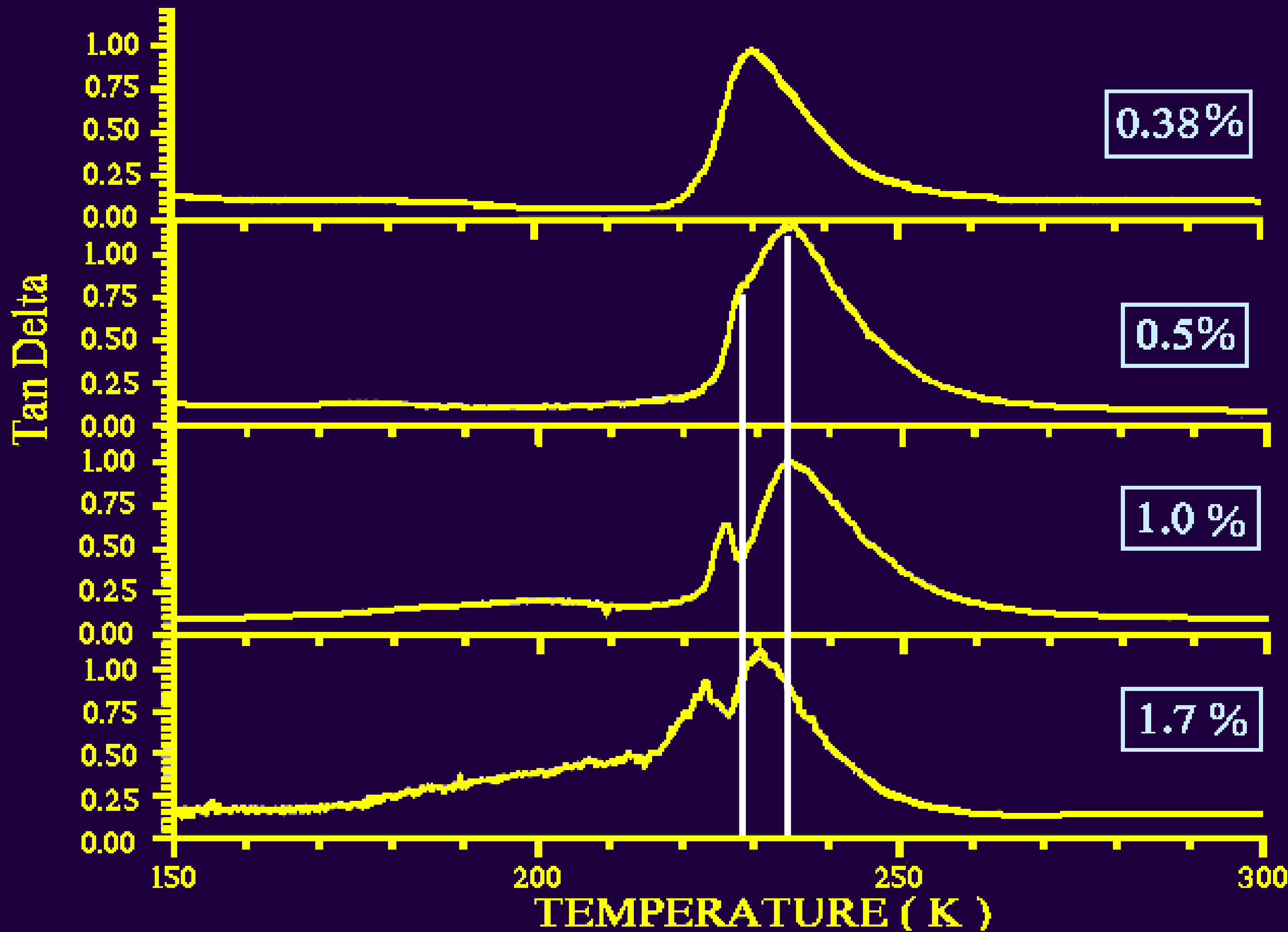



# VGCNF Orientation in HDPE- VGCNF



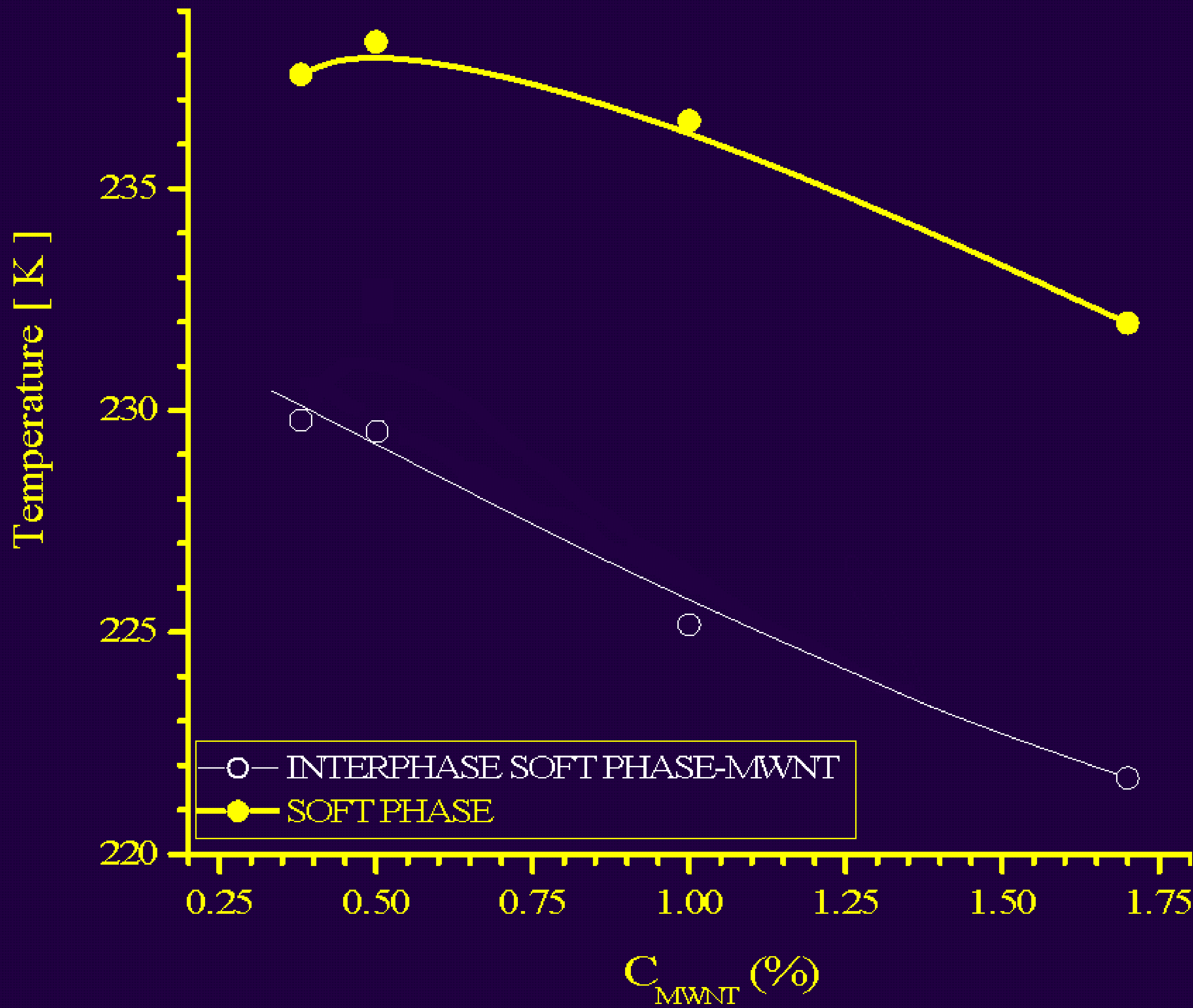

*M. Chipara, K. Lozano, M. D. Chipara, On the assessment of the orientation of carbon nanofibers dispersed within polyethylene by electron spin resonance spectroscopy, Carbon, 45(13): 2698-2701, 2007.*

# *SIS – MWNT: Effect of MWNT on $T_G^{PI}$*



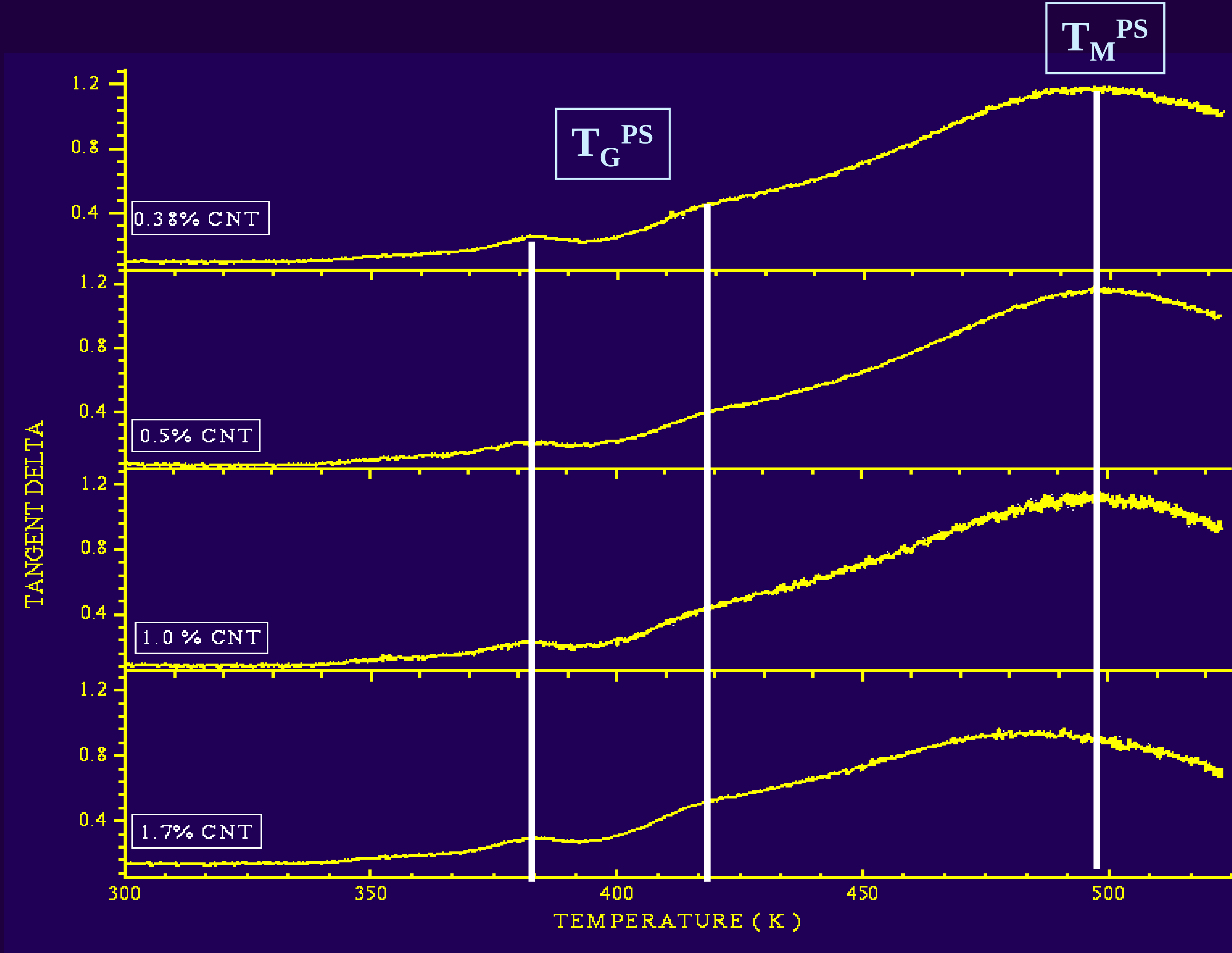

- *Doping splits and shifts the $T_G$ of the soft phase (isoprene)*

# *SIS – MWNT: SIS/MWNT Interactions*




- ***Doping affects the $T_G$ of the soft phase (isoprene)***

# *SIS – MWNT: Effect of MWNT on $T_G^{PS}$*




- *Doping affects the $T_G$ of the hard phase (styrene)*

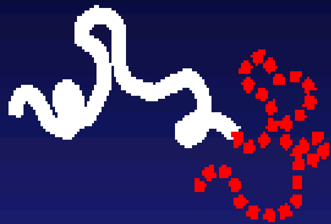
# *Mechanical Properties :HDPE- VGCNF*

- ***Montmorillonite is hydrophilic***
- ***Most polymers are organophilic and water immiscible***

***Difficult dispersion of nanoclays in polymers***

***Solutions: Surface modification.***
***In situ polymerization.***
***(exfoliation and intercalation)***

# Microphase Separation

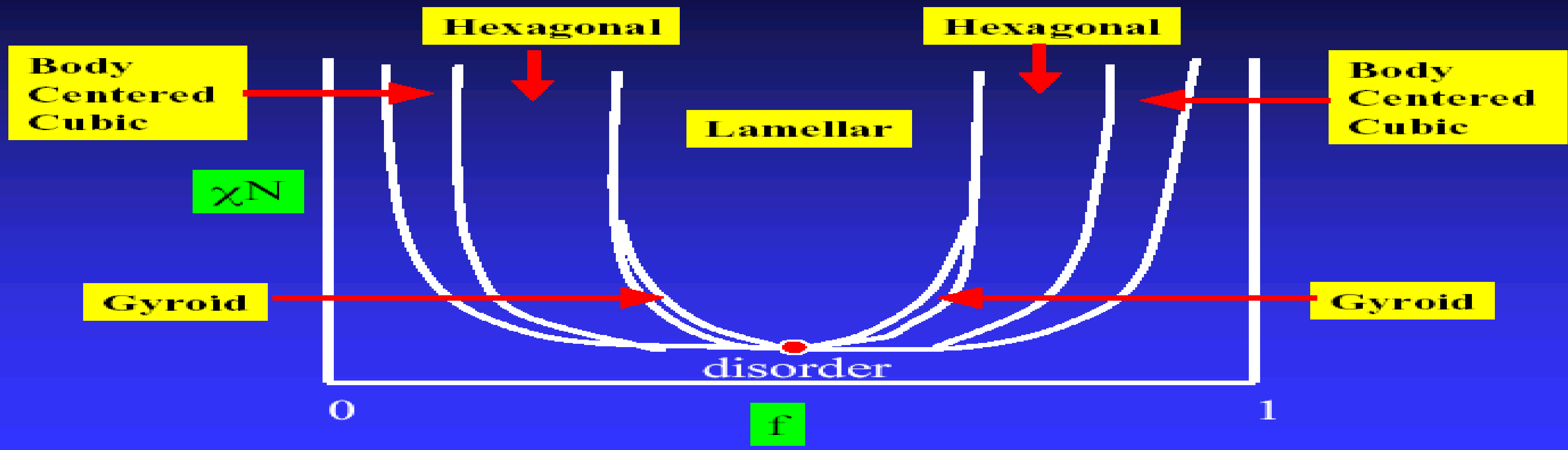


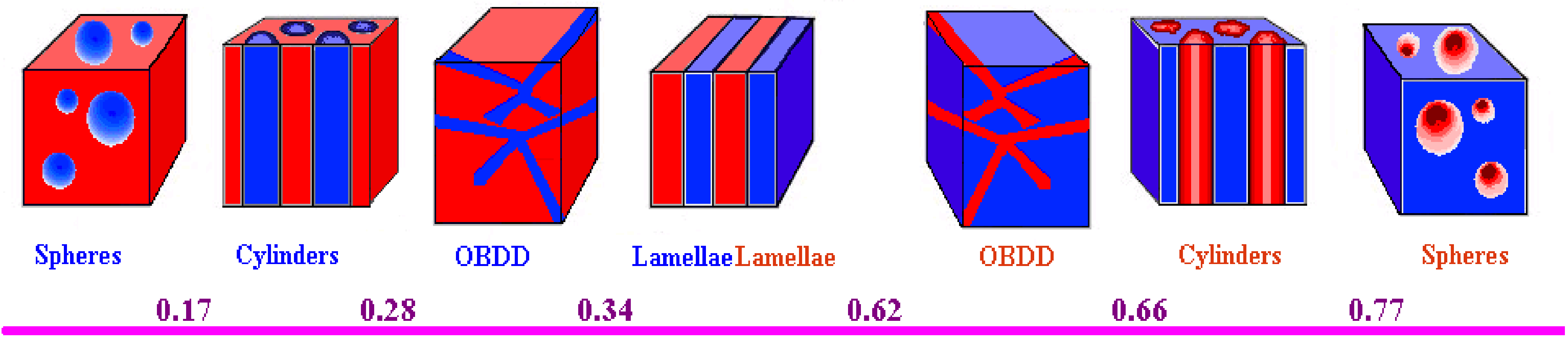
Macroscopic phase separation is prevented by the covalent bond between the blocks.

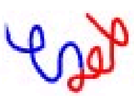

Creation of an interphase boundary region

Microphase separation takes place on the nanometer scale.

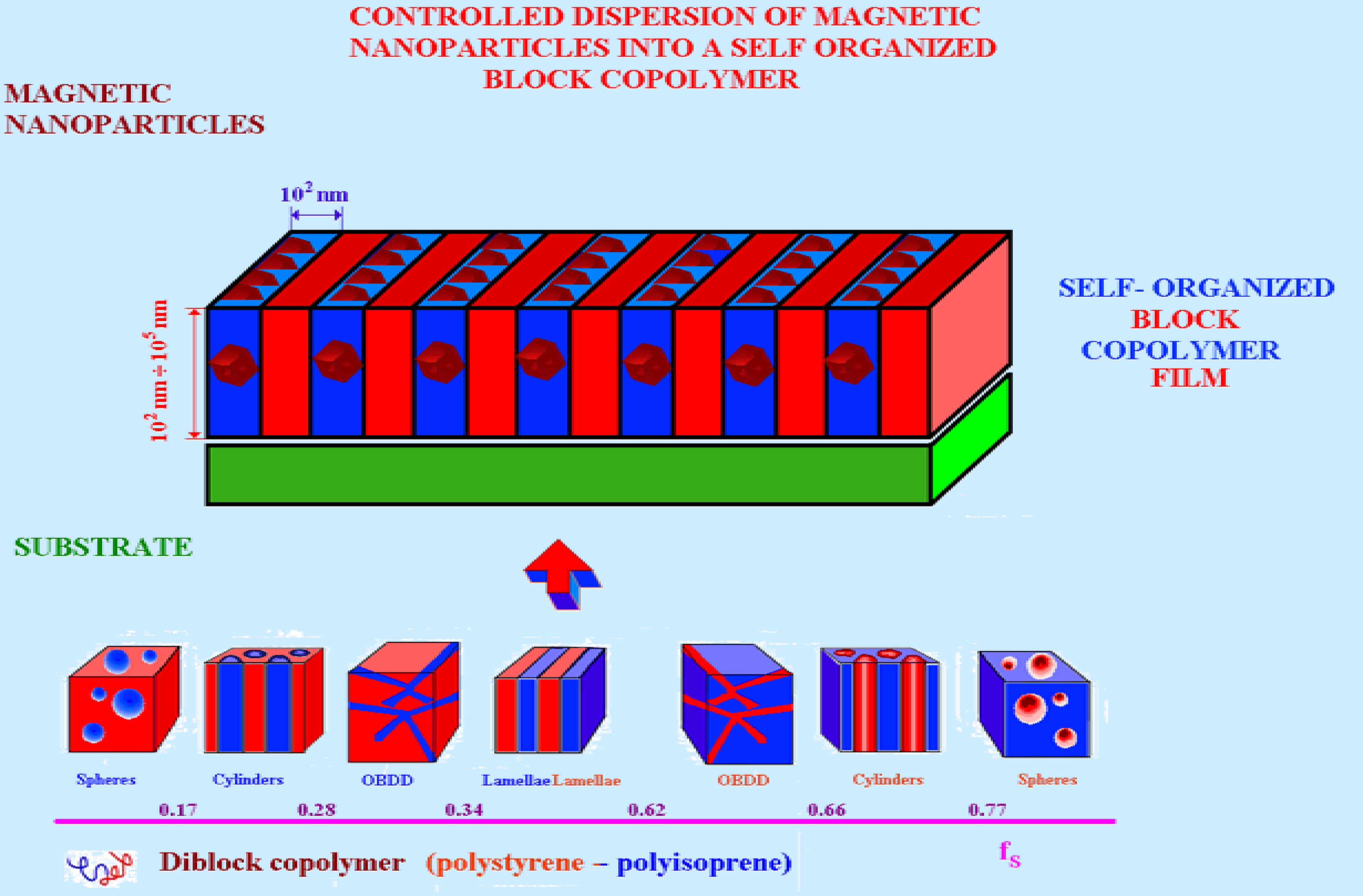
# Phase Diagram



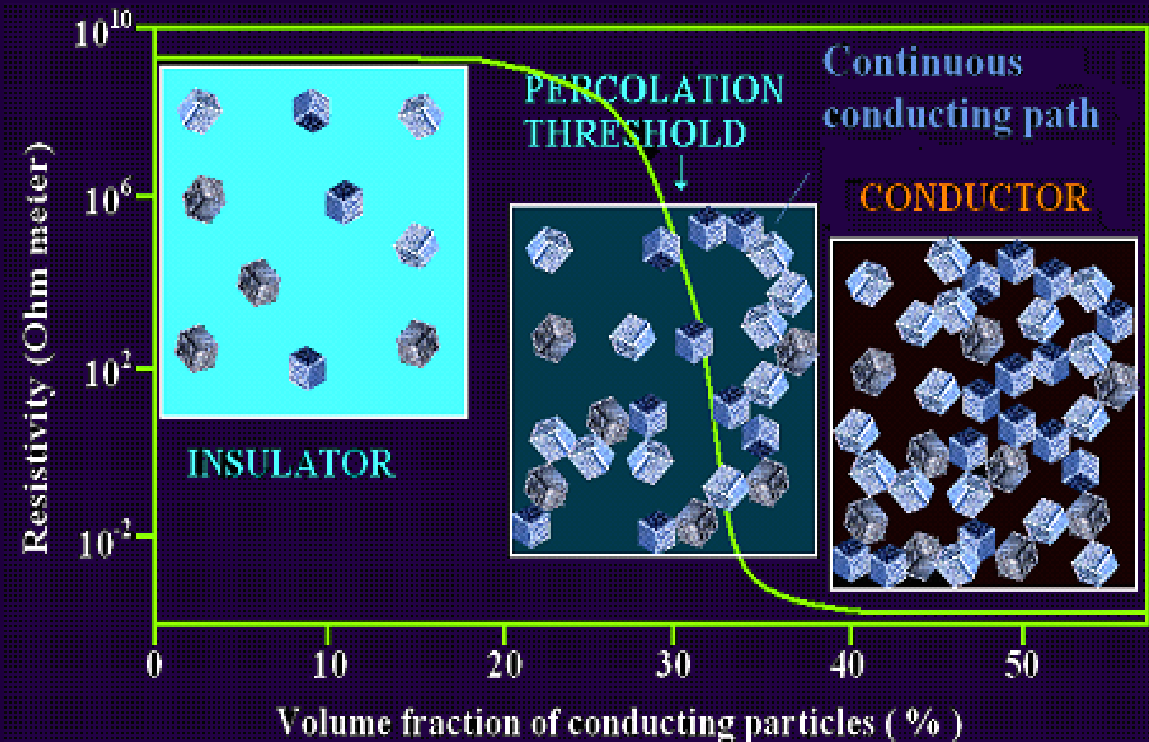





**Diblock copolymer (polystyrene – polyisoprene)**

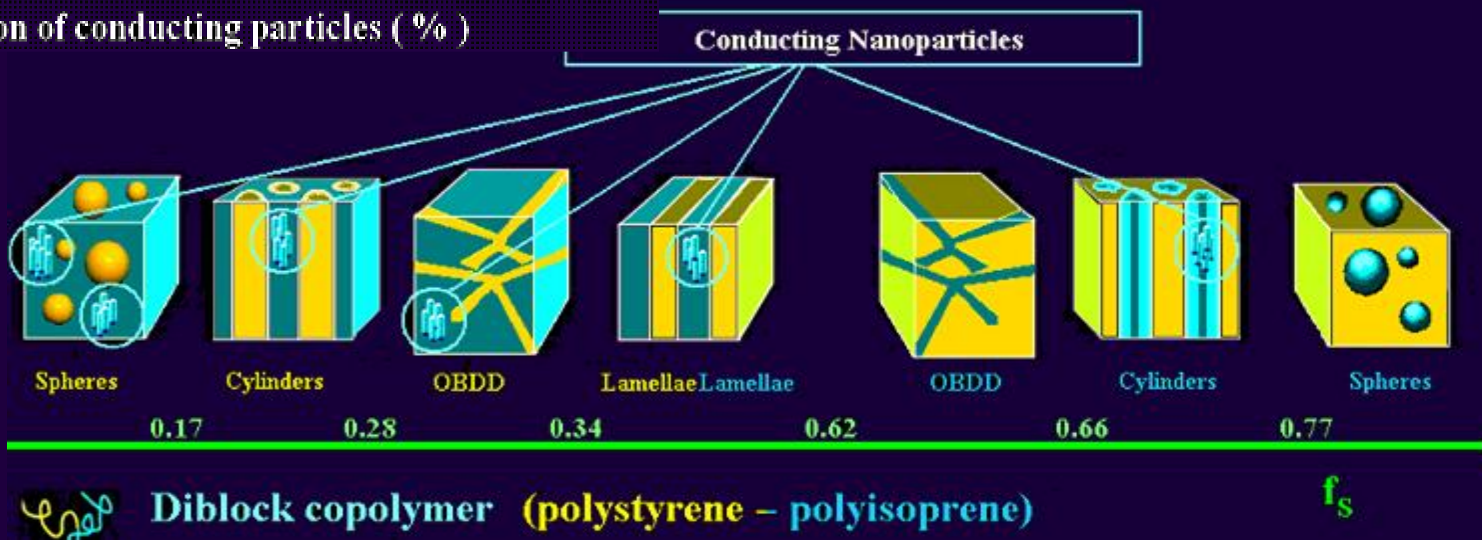
# Schematic of the future technology for ultra high magnetic data media, based on self-assembly capabilities



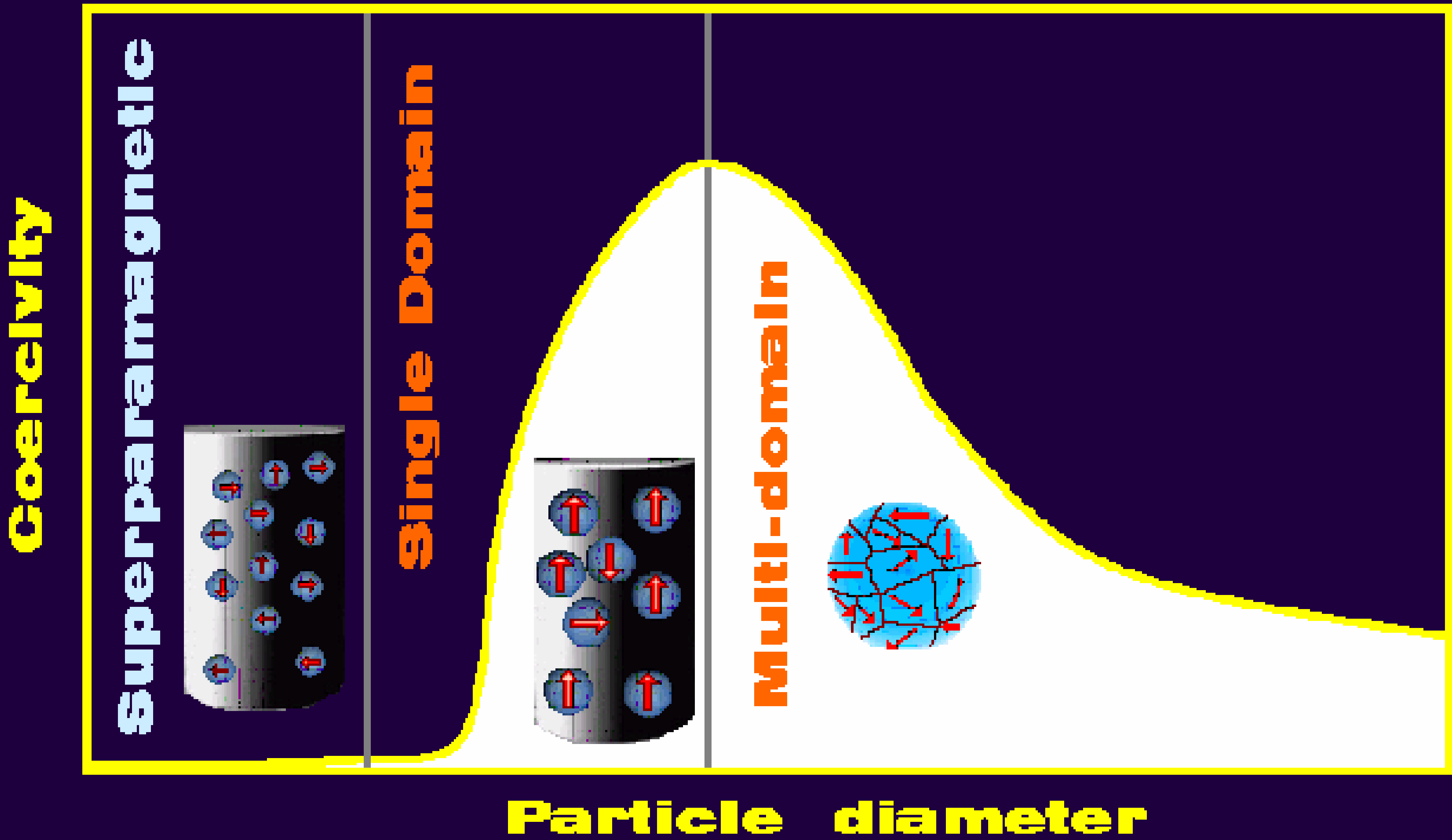
# *Polymer-Based Nanocomposites for Electrical Applications*



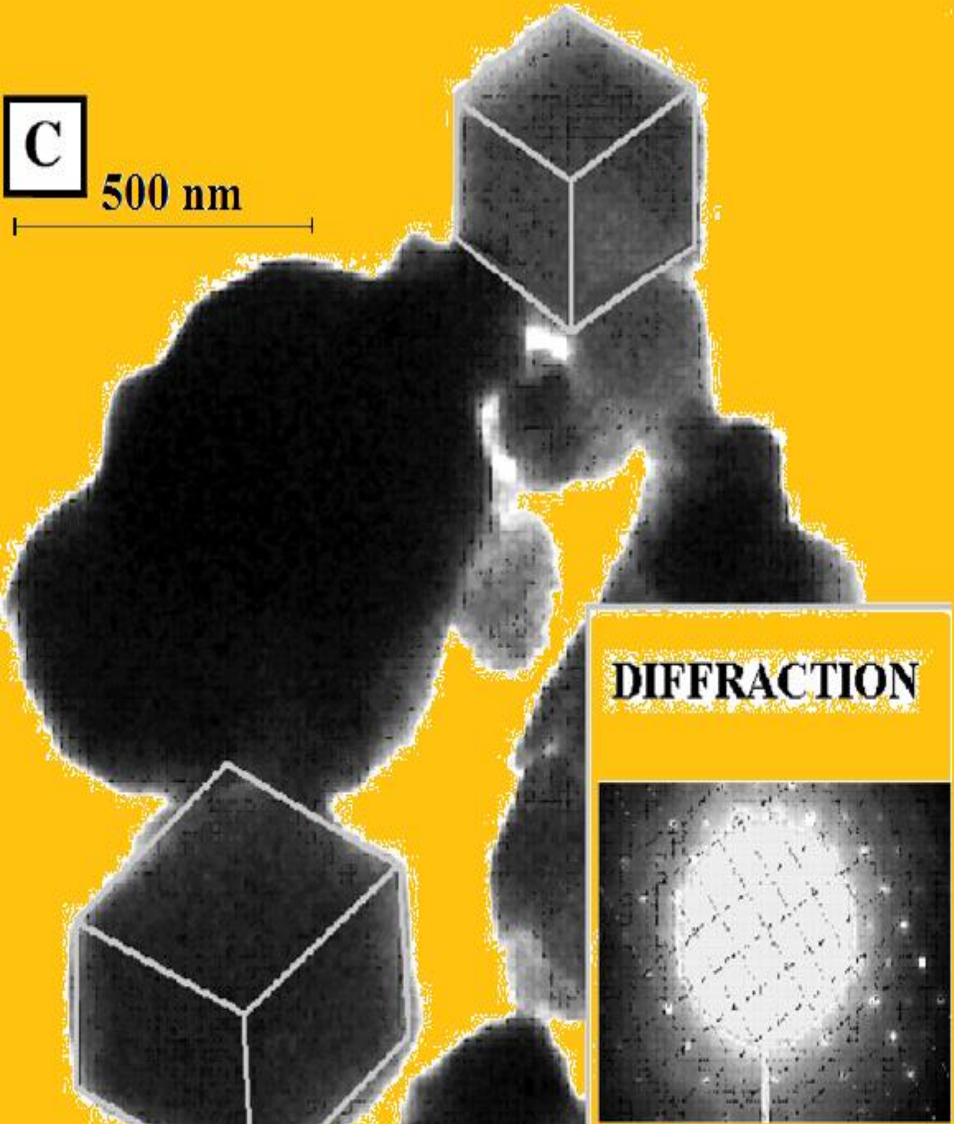

## *Percolation in Composite Materials*

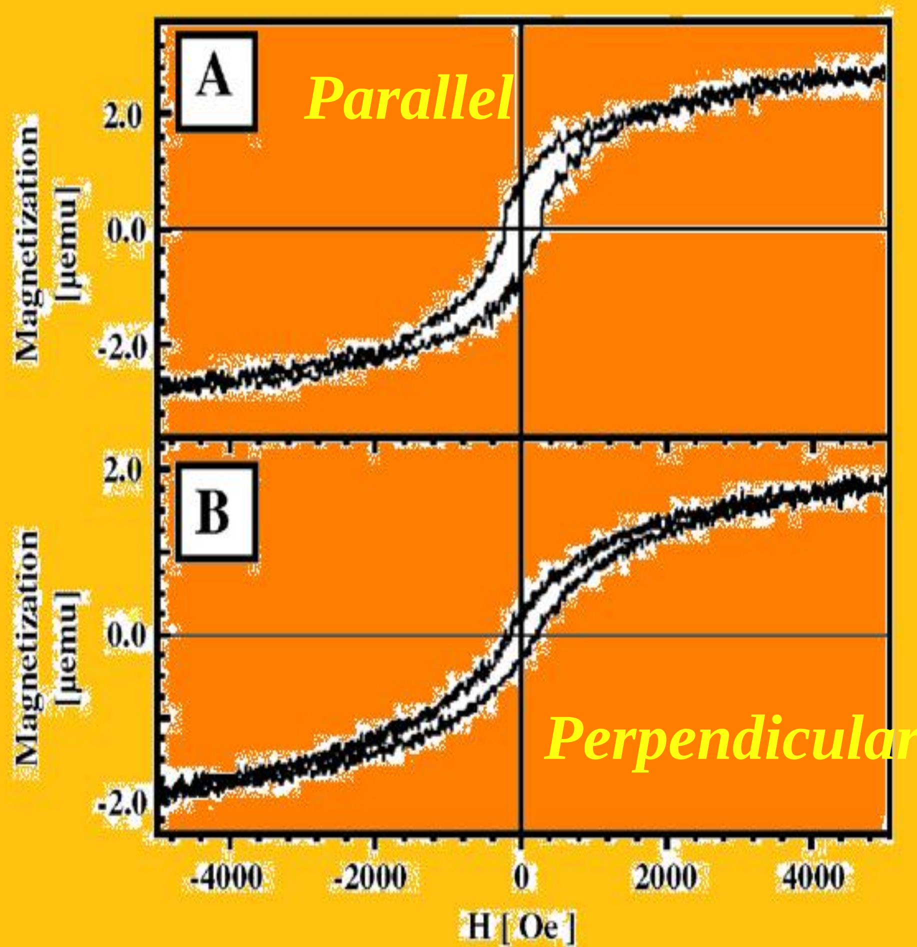


# *Magnetic Properties of Nanoparticles*



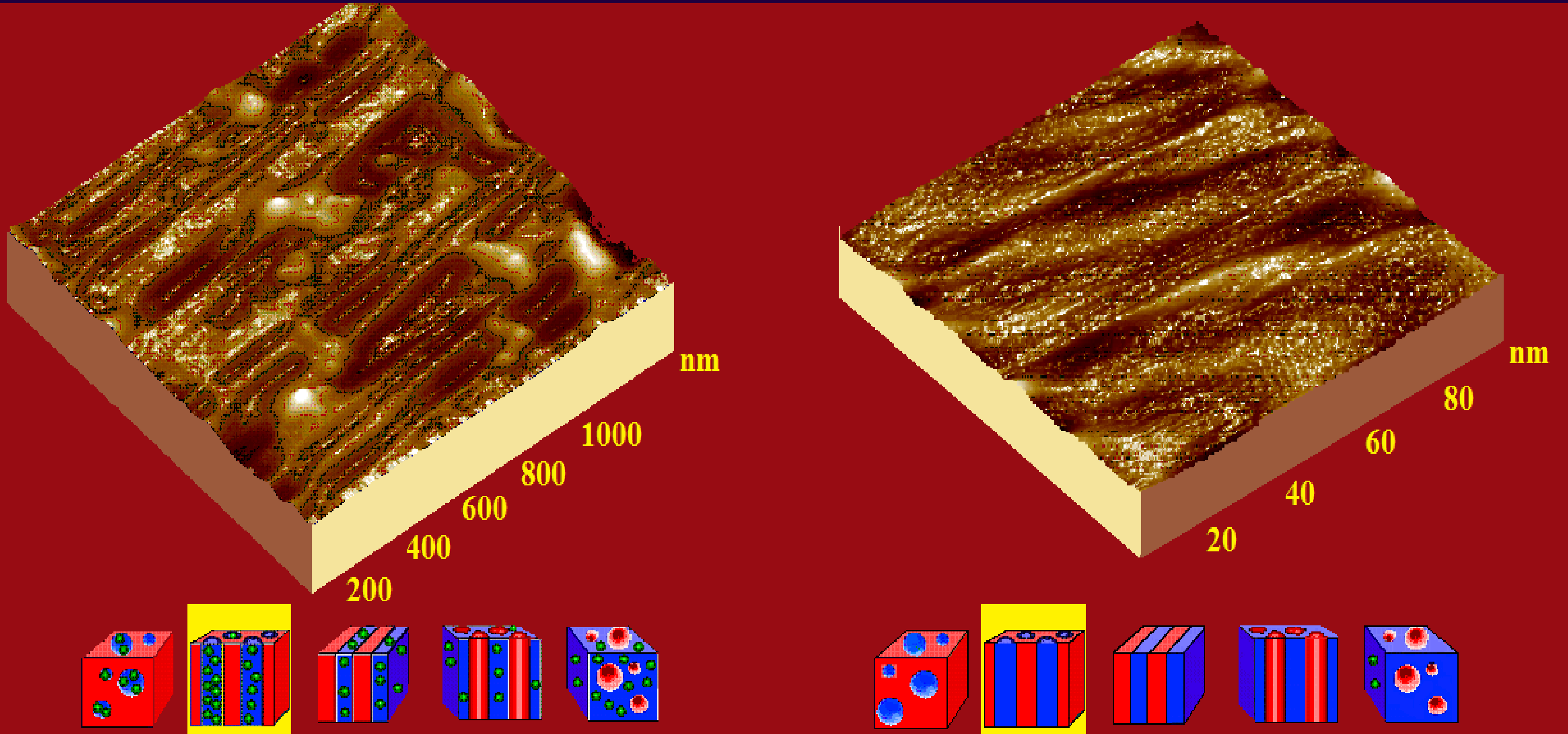
# PPY-Fe Nanocomposites




*M. Chipara M, R. Skomski, D. J. Sellmyer, Electrodeposition and Magnetic Properties of Polypyrrole – Fe Nanocomposites, Materials Letters, 61 (11-12): 2412-2415, 2007.*

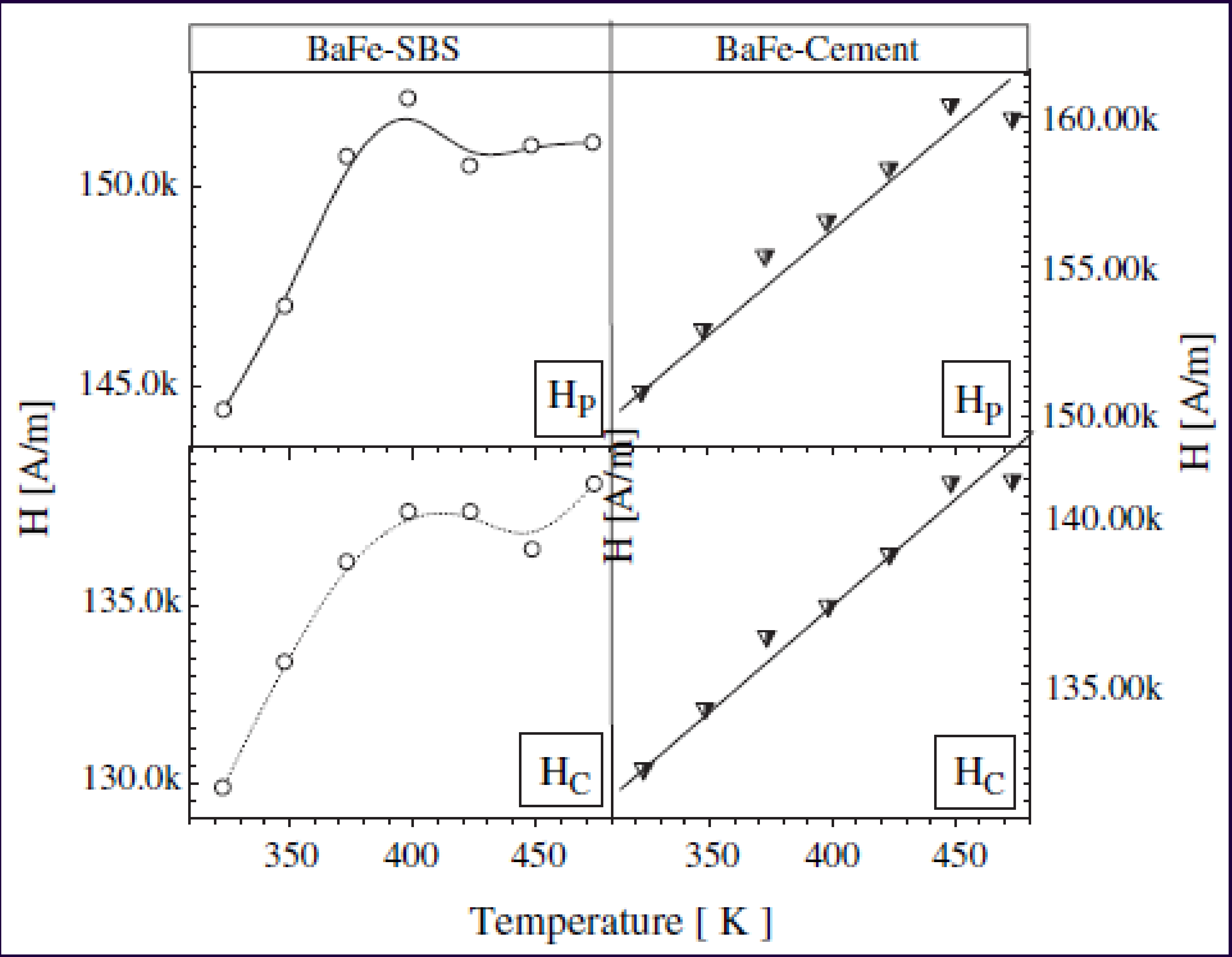
# BaFe-SBS: Self-Healing Features




*M. Chipara, D. Hui, J. Sankar, D. Leslie-Pelecky, A. Bender, L. Yue, R. Skomski, D. J. Sellmyer, On styrene–butadiene–styrene–barium ferrite nanocomposites, Composites B, 35, 3, 235-243, 2004.*

*N. Ali, M. Chipara, S. Balascuta, R. Skomski, D. J. Sellmyer, Magnetic Properties of Barium Ferrite Dispersed Within Polystyrene-Butadiene-Styrene Block Copolymers, JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY , 9 , 6, 3678-3683 (2009)*

# Barium Ferrite SBS

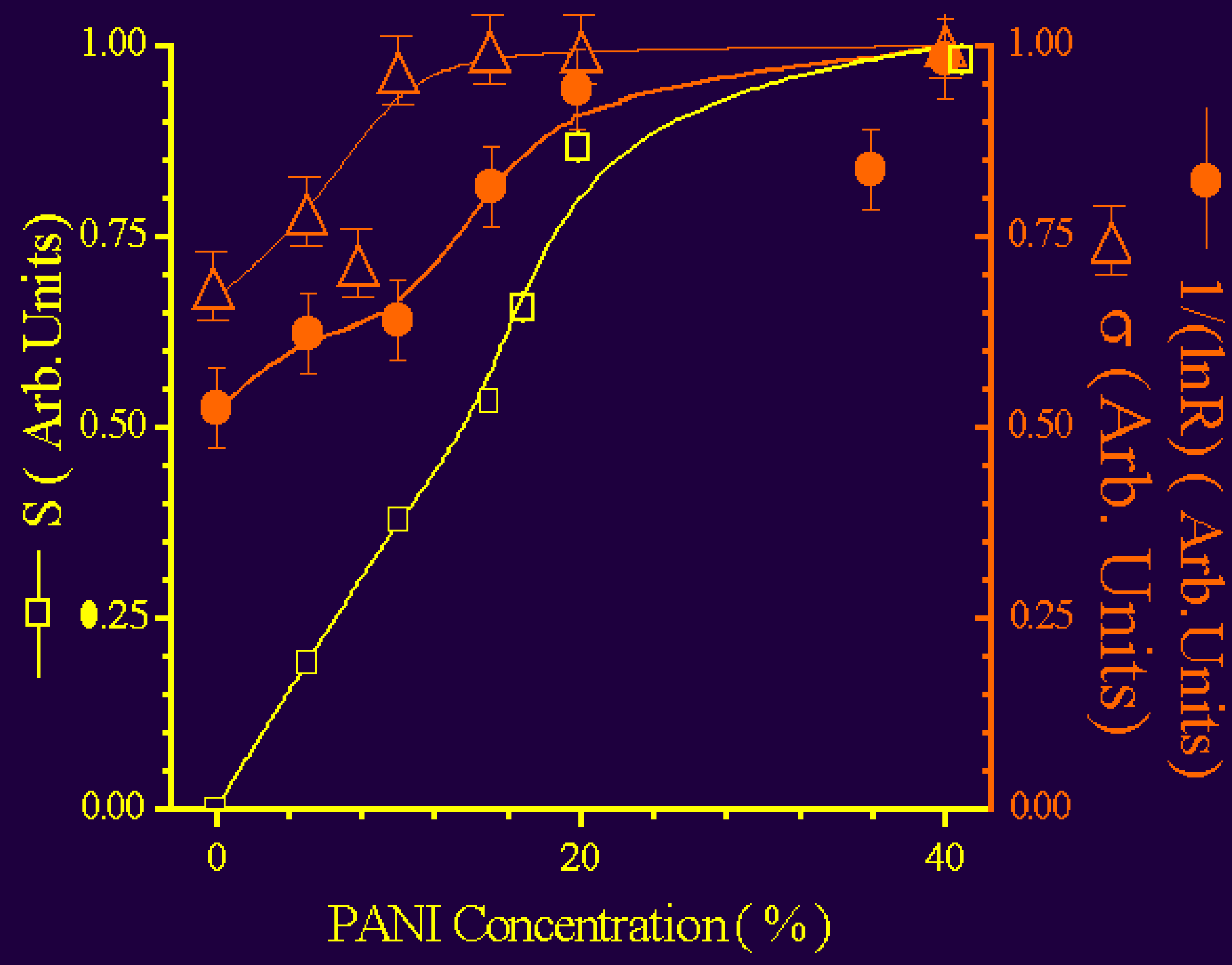



***The temperature dependence of the coercive field and of the resonance linewidth are different in a cement and in a block copolymer.***

*N. Ali, M. Chipara, S. Balascuta, R. Skomski, D. J. Sellmyer, Magnetic Properties of Barium Ferrite Dispersed Within Polystyrene-Butadiene-Styrene Block Copolymers, JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY , 9 , 6, 3678-3683 (2009)*

# PANI-PE Composite for NIR Behavior

- *Correlation of S, Electrical Conductivity, and Tensile Strength*



# *Polymer- Based Nanocomposite Materials*

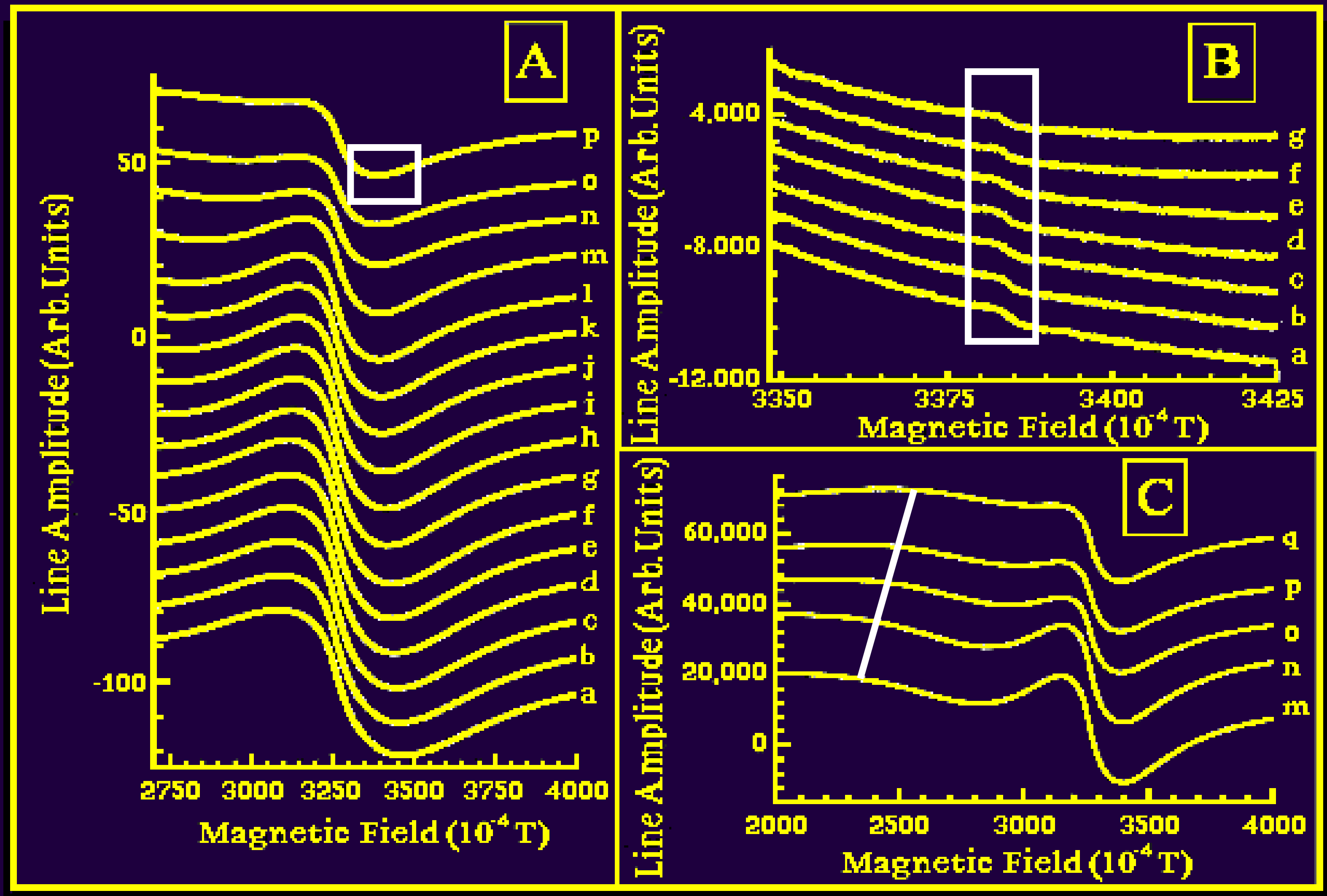

*Acknowledgements:*

- *UNL MRSEC*
  - *Prof. D. J. Sellmyer* — *Prof. R. Kirby*
  - *Dr. R. Skomski*

- *UTPA*
  - *Prof. Karen Lozano* — *Prof. M. D. Chipara*

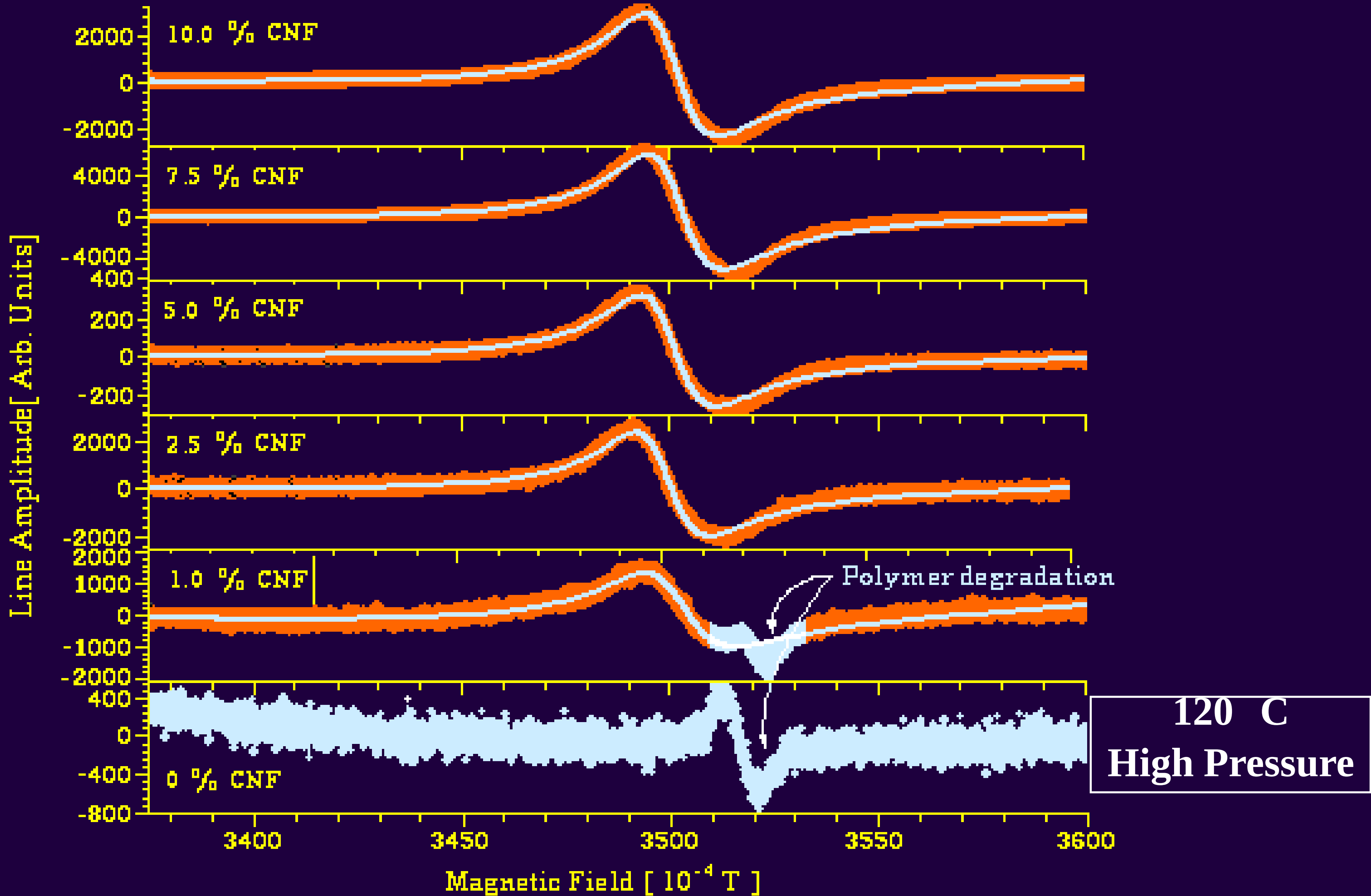
- *Romania*
  - *Dr. Popescu Mihai* — *Dr., S. V. Nistor*
  - *Dr. N. Grecu* — *Dr. I. Morjan*
  - *Dr. Mihai Secu* — *Dr. S. Aldica*
  - *Dr. R. Alexandrescu*

# *UHMWPE-SWNT: ESR Spectra*




- *ESR signals from catalyst and carbon nanotubes*

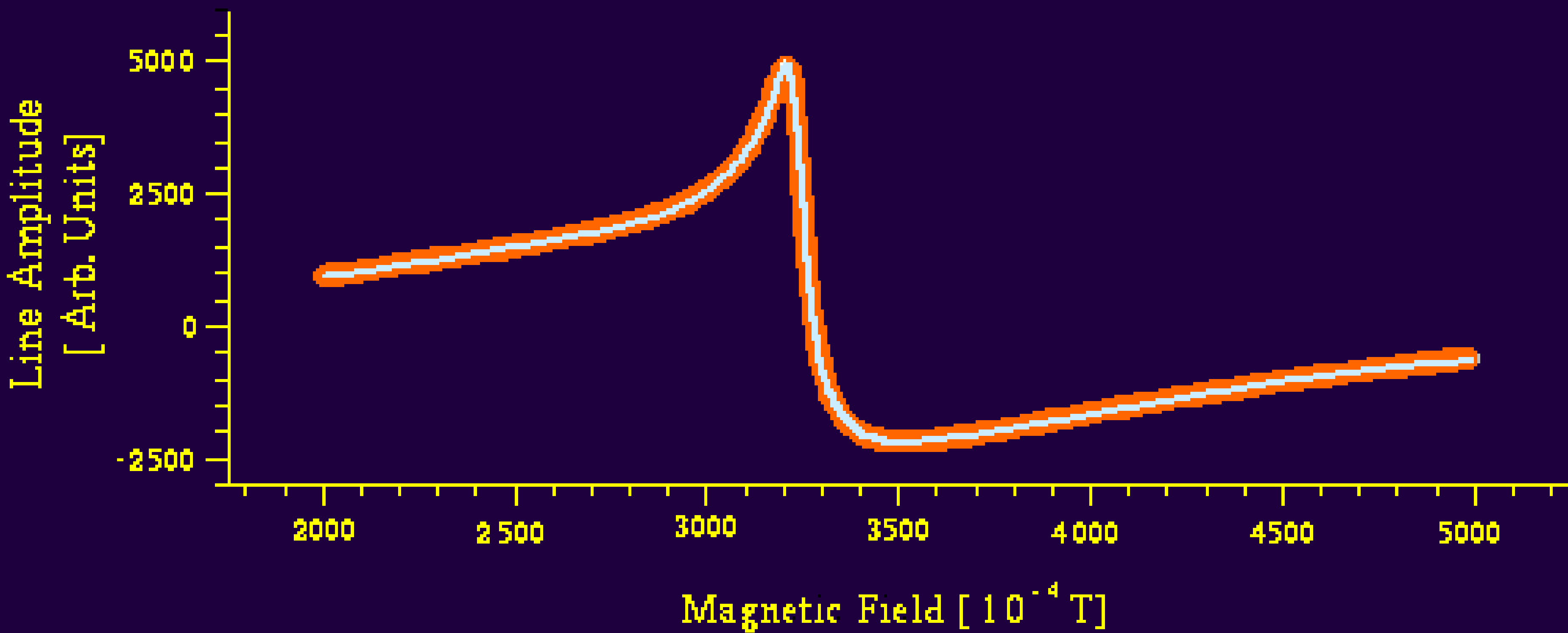
# *PC-CNF: ESR Spectra*




- ***Thermo-oxidative degradation of polymer during sample***

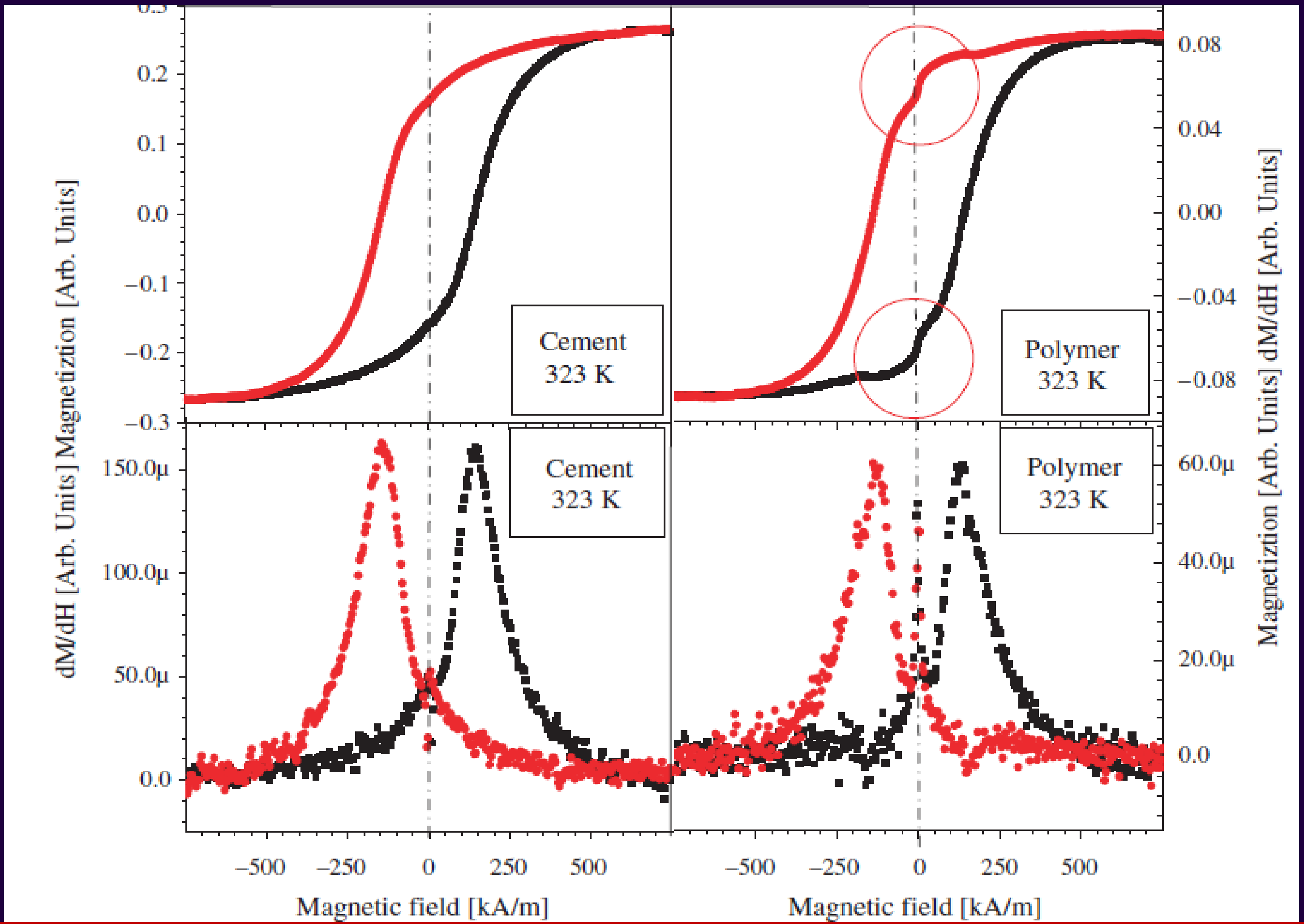
# *CNF: ESR Spectrum*

✵ ***ESR Signal (orange) and simulated spectrum (light blue) of CNF***




❖ ***Reconvolution with single Dysonian and Lorentzian components***

# Barium ferrite – SBS Magnetic and Superparamagnetic Features

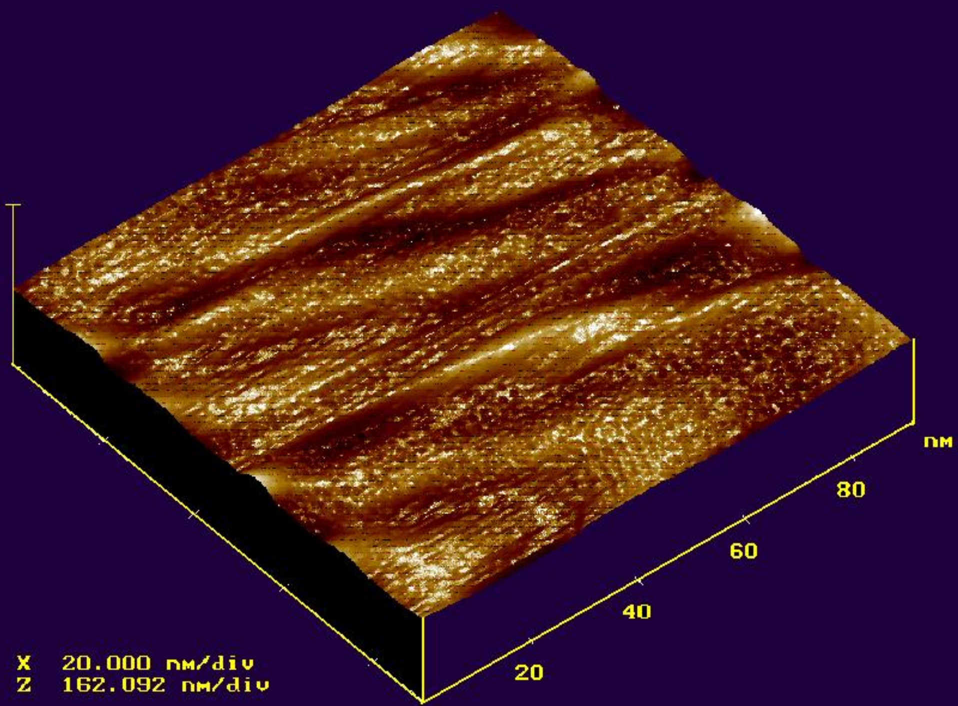



*N. Ali, M. Chipara, S. Balascuta, R. Skomski, D. J. Sellmyer, Magnetic Properties of Barium Ferrite Dispersed Within Polystyrene-Butadiene-Styrene Block Copolymers, JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY , 9 , 6, 3678-3683 (2009)*

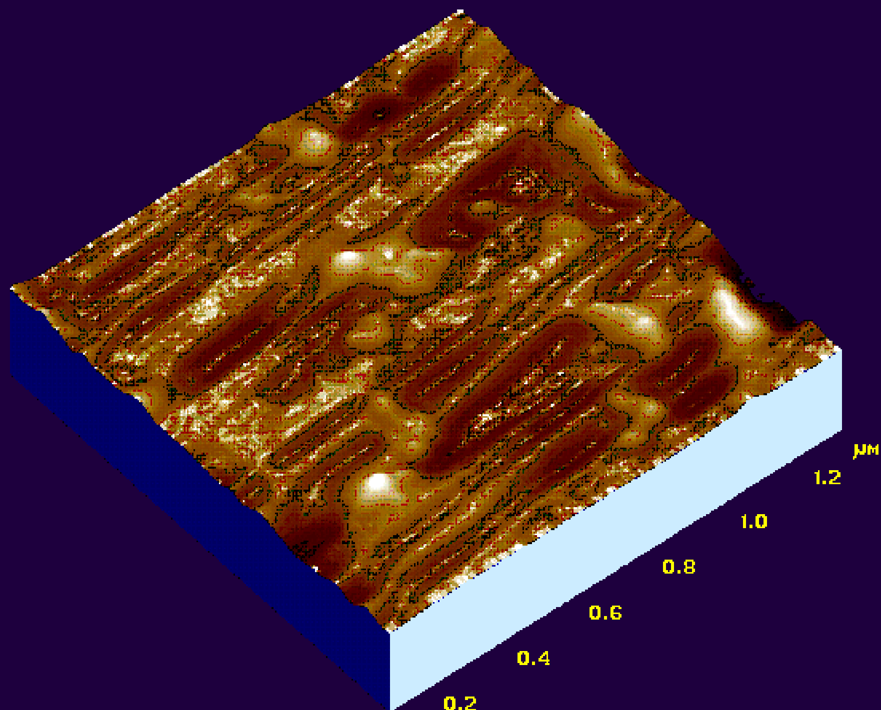
# Barium ferrite – SIS Morphology

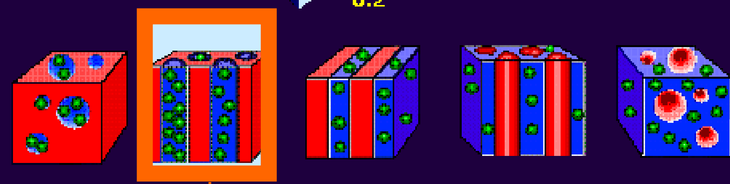
- ***AFM Images of Polymer and Nanocomposite***

SIS Block Copolymer




Ba-Ferrite (10%) – SIS Composite



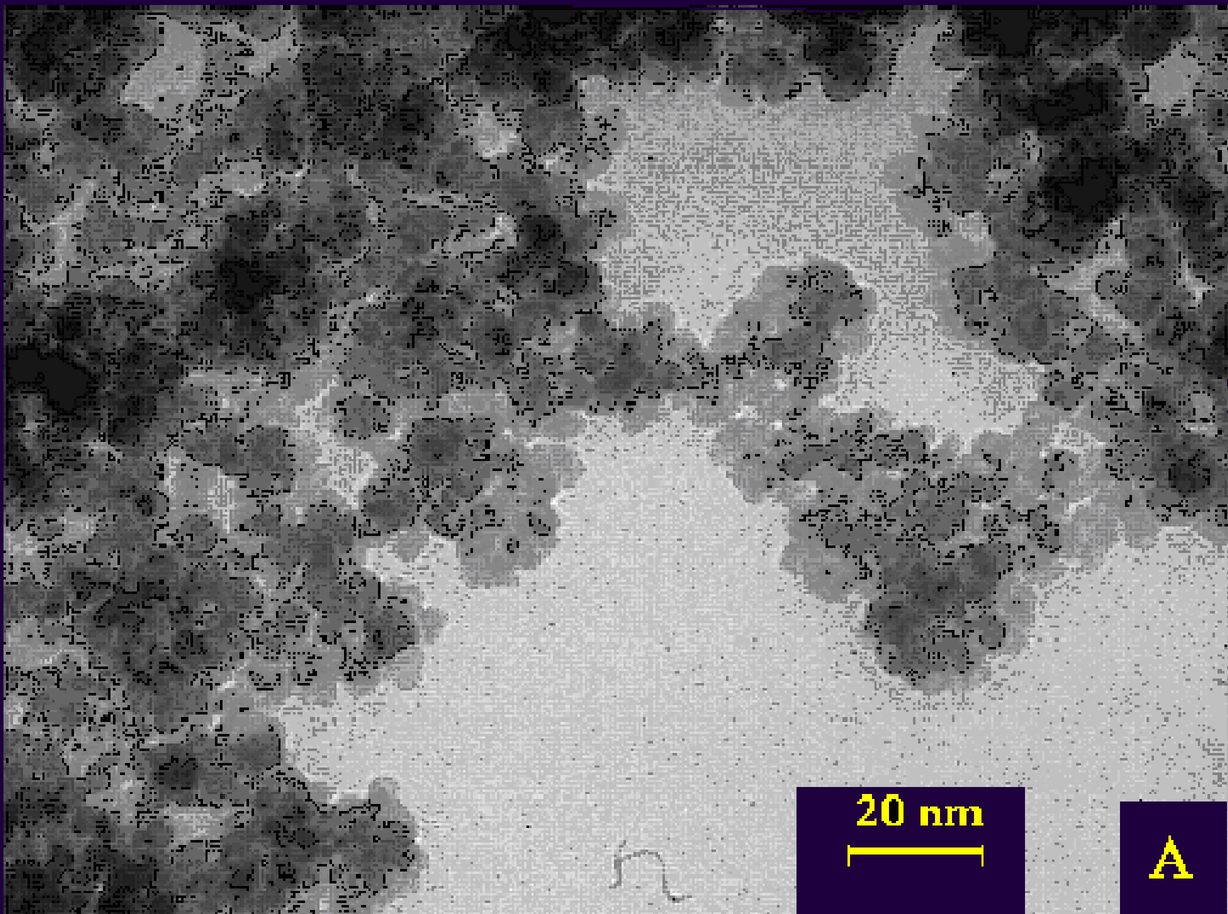



cylinder morphology

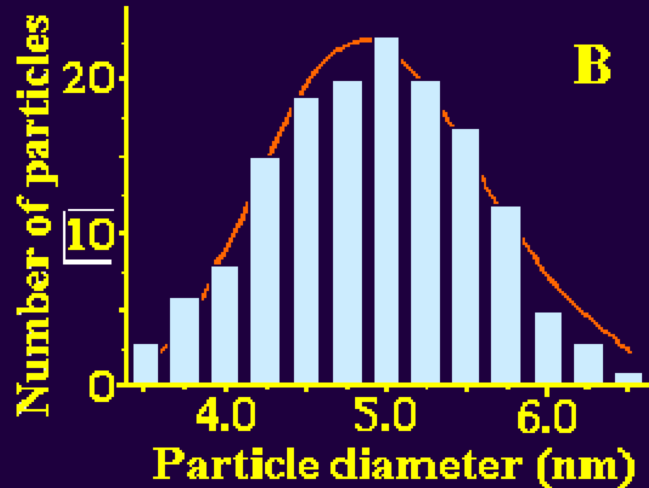
- ***Potential magnetic storage assembly***

# *SIS - Titanium Doped Gamma Iron Oxides*

TEM of titanium doped iron nanoparticles




Particle Size



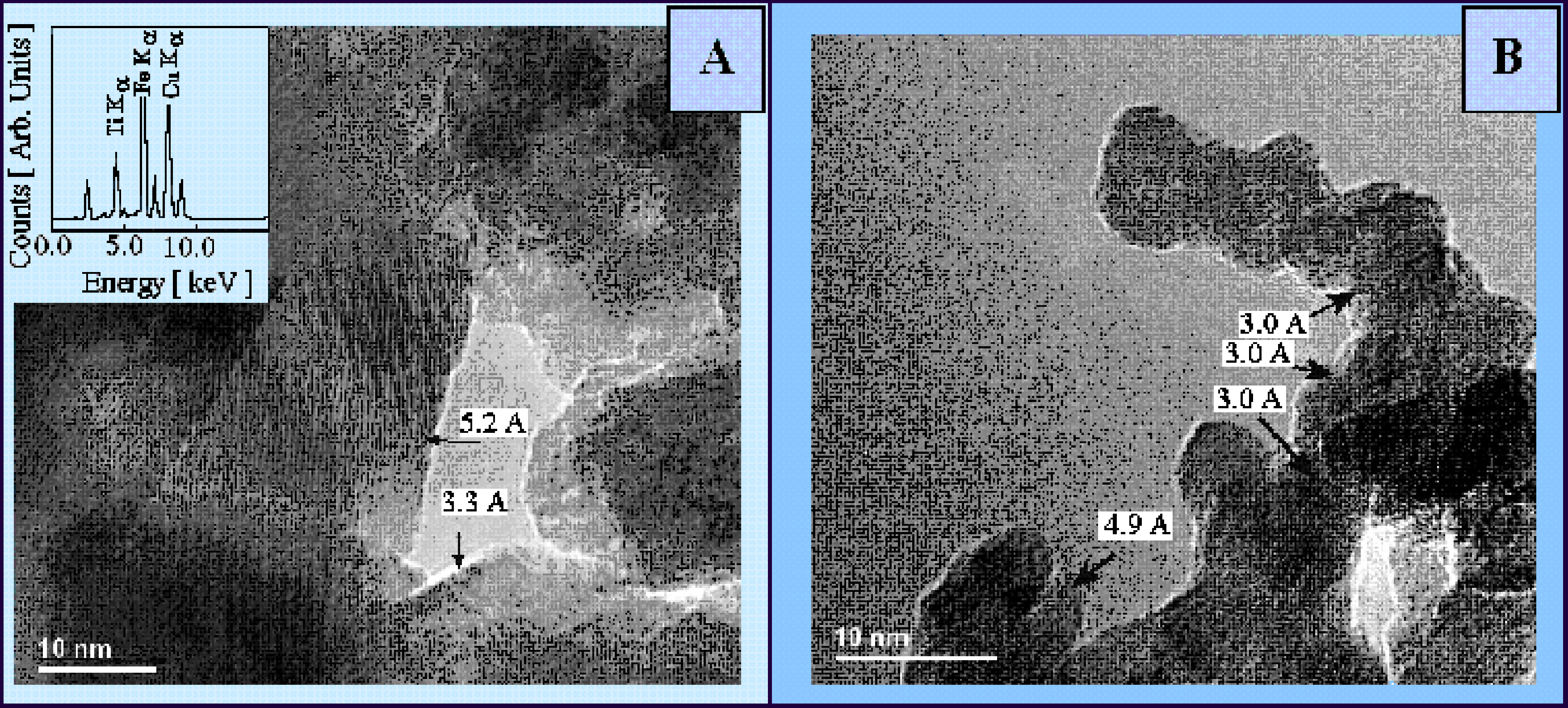


Small Angle
Electron Diffraction

# *SIS - Ti doped Iron Oxides: HR-TEM*

$\gamma Fe_2O_3$ (5.2 Å) Ti-$\gamma Fe_2O_3$ (4.9 Å)

X-Ray [$\beta FeO(OH)$] (3.3 Å) Ti[$\beta FeO(OH)$] (3.3 Å)

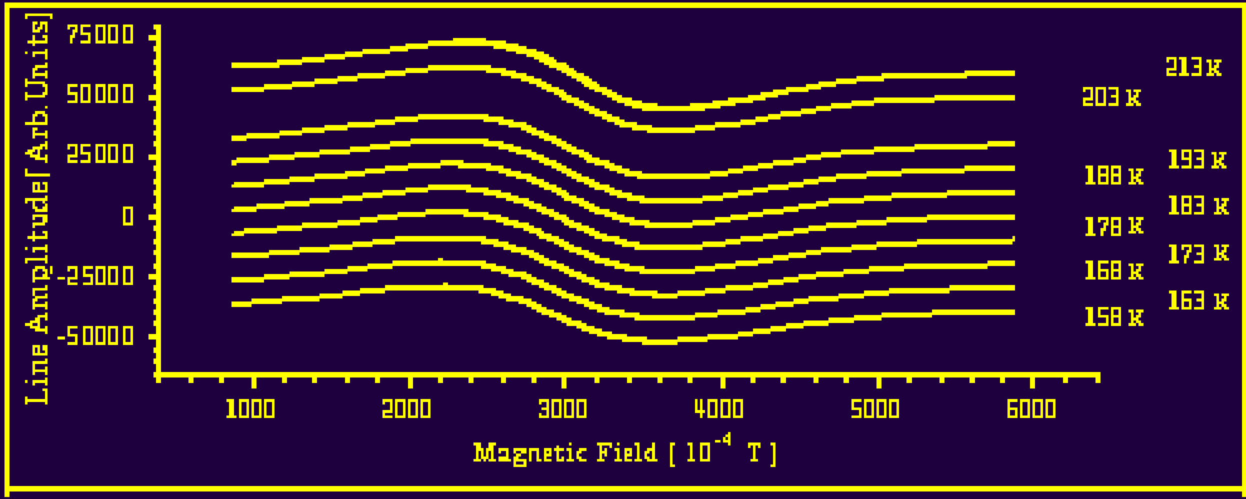



❖ ***HR-TEM confirms doping and crystalline iron oxide formation***

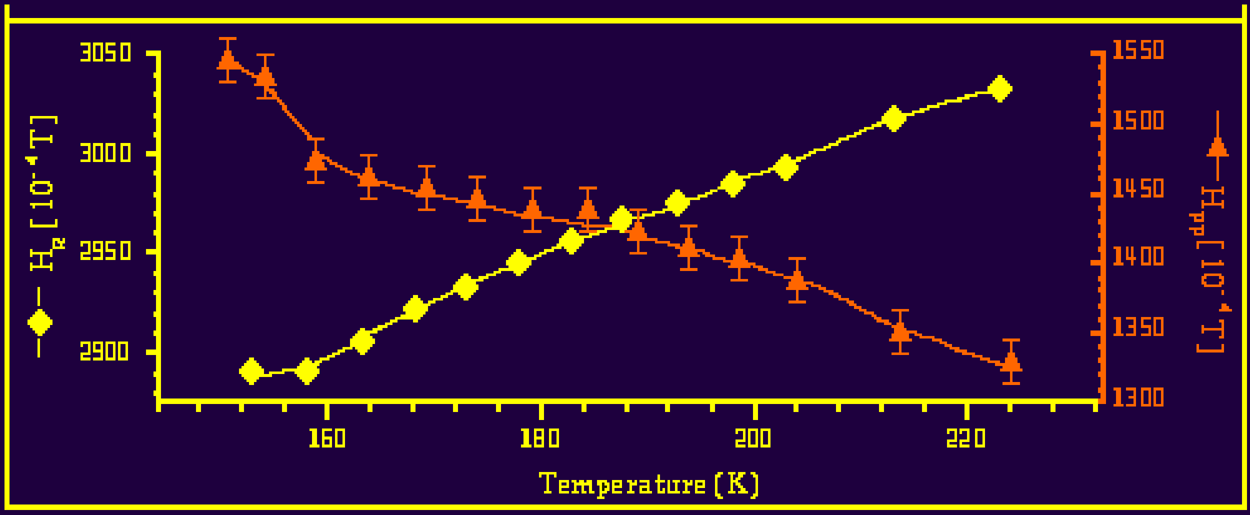
*J. Poly. Sci., B: Poly. Phys.* **2005, *43*,** 3432-3437

# FMR of SIS – Ti Doped Iron Oxides

- ***FMR Spectra at Various Temperatures***

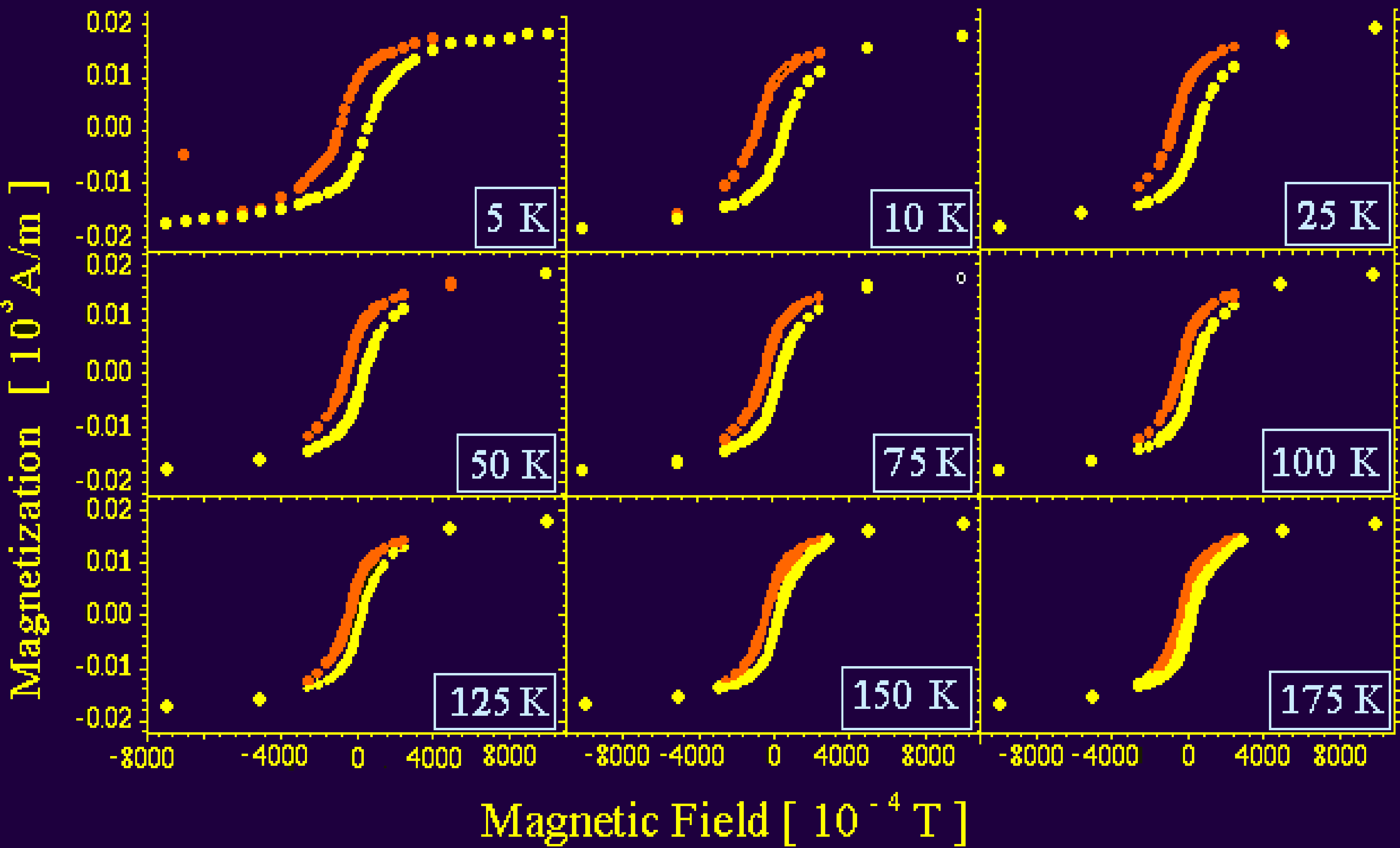



- ***Dependence of $H_R$ and $H_{PP}$ on Temperature (Thermal Activation)***



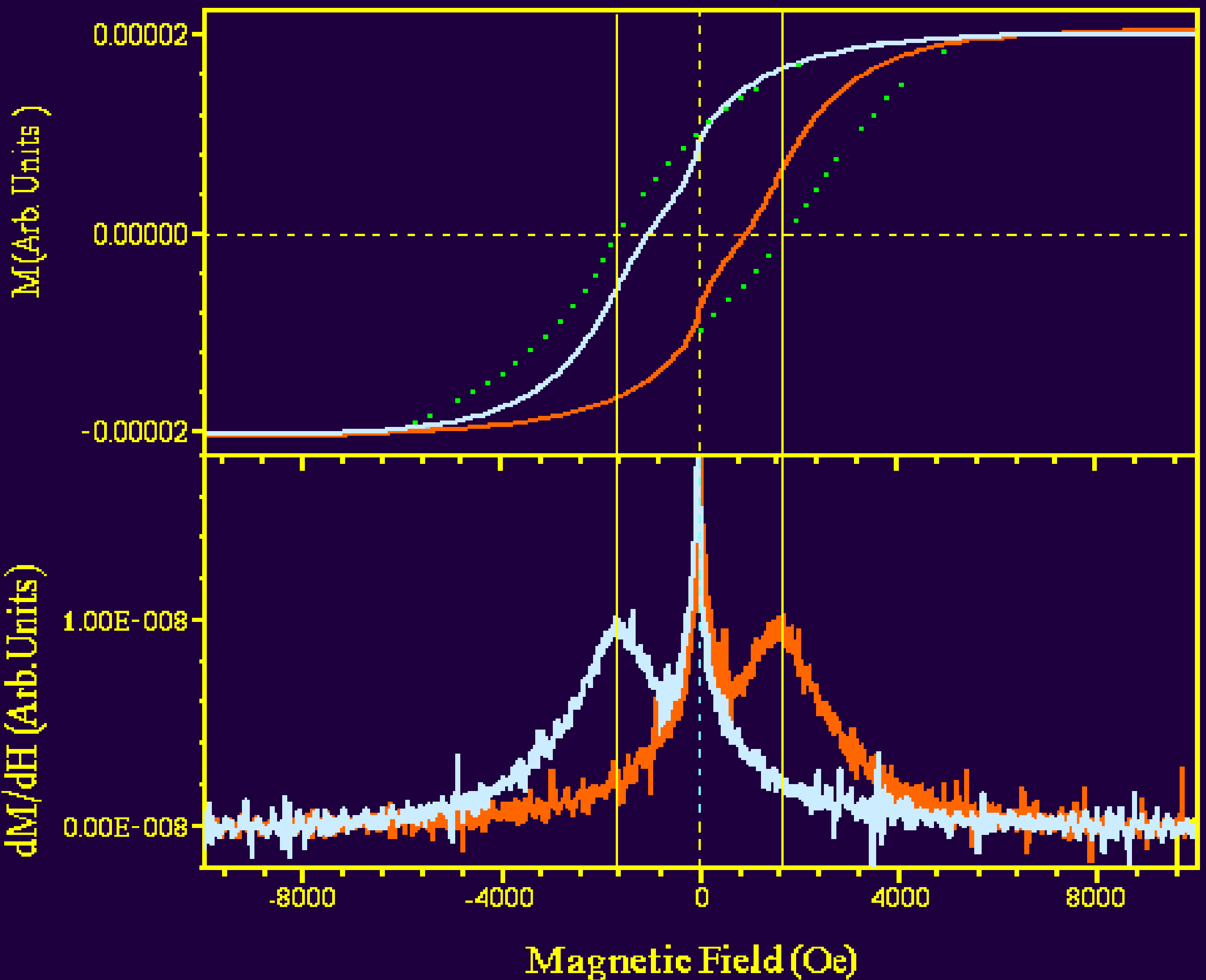
# *Magnetism of SIS – Ti Doped Iron Oxides*

- ***Hysteresis Loops at Various Temperatures (Ferromagnetic)***



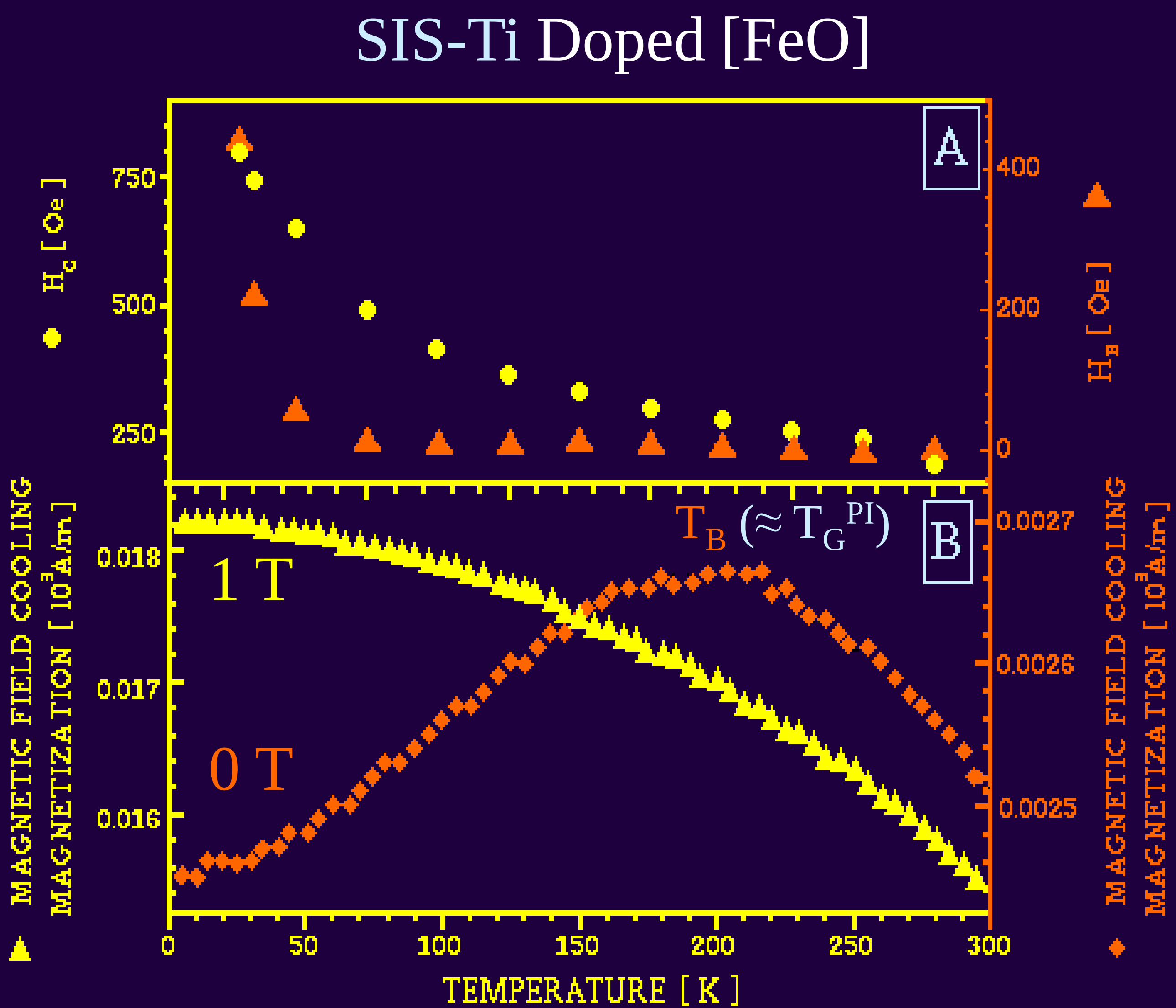
# Magnetism of SIS – Ti Doped Iron Oxides

- *5 K Hysteresis Loop and dM/dH*



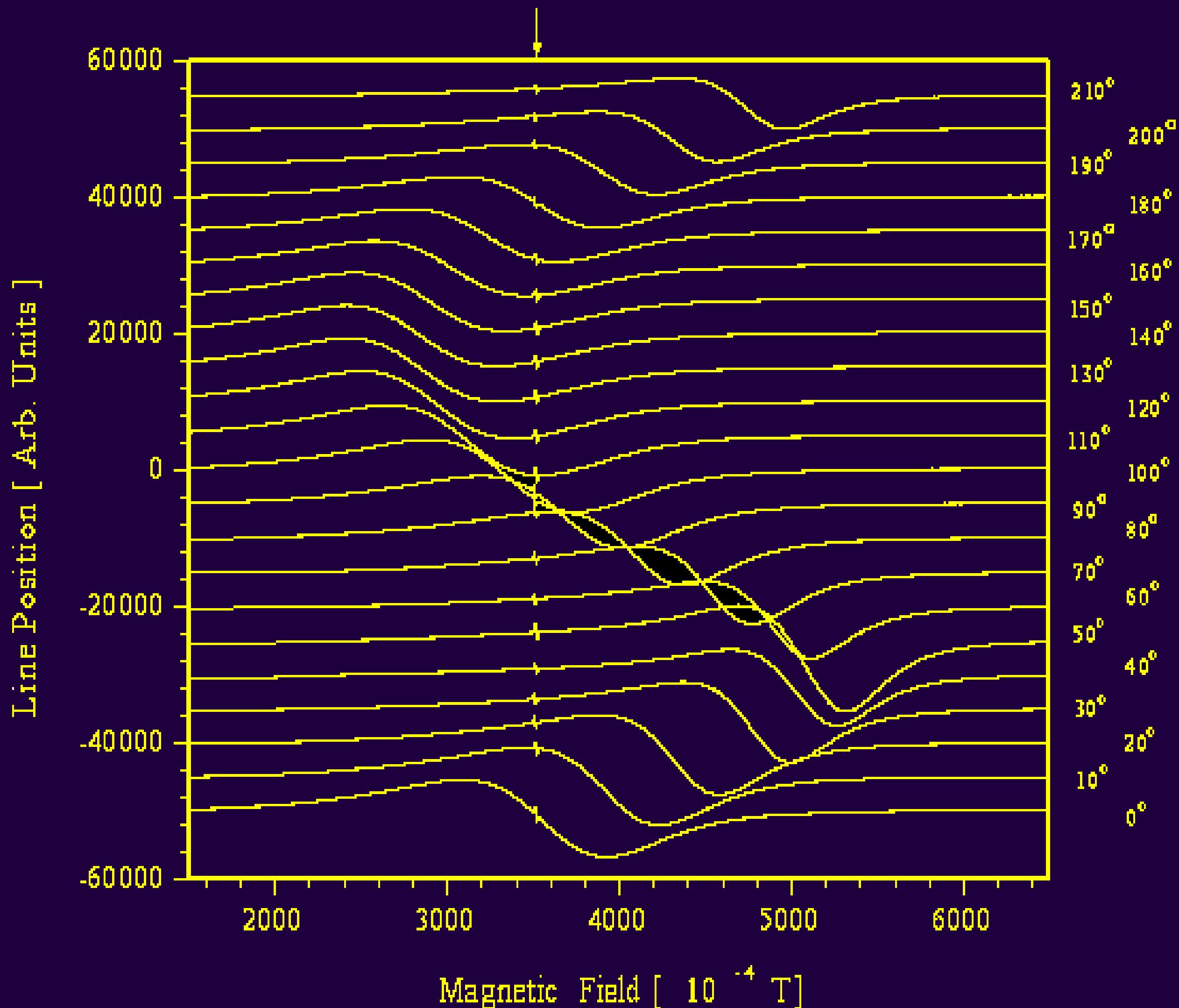
# *Temperature Dependence of Magnetization*

- ***Temp dependence of coercive (left) and exchange bias fields (right)***
- ***Temp dependence for cooling in 1 T (left) and zero field (right)***



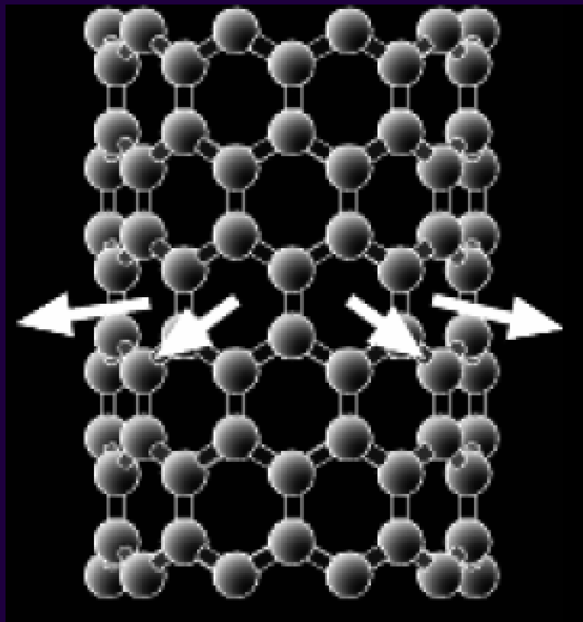

- ***Magnetization behavior controlled by $T_G^{PI}$***

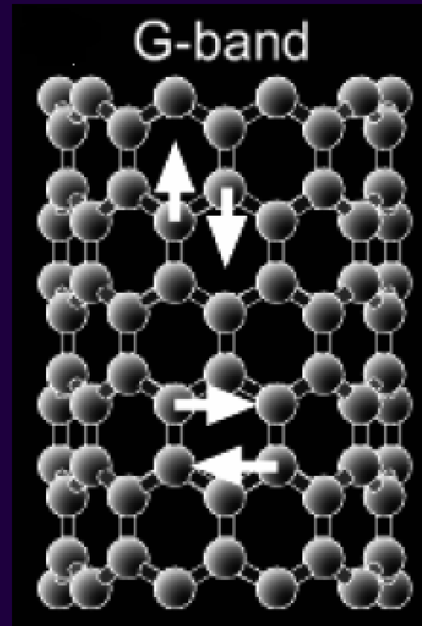
# *Oriented Nanoclusters: FMR FePt on PI*

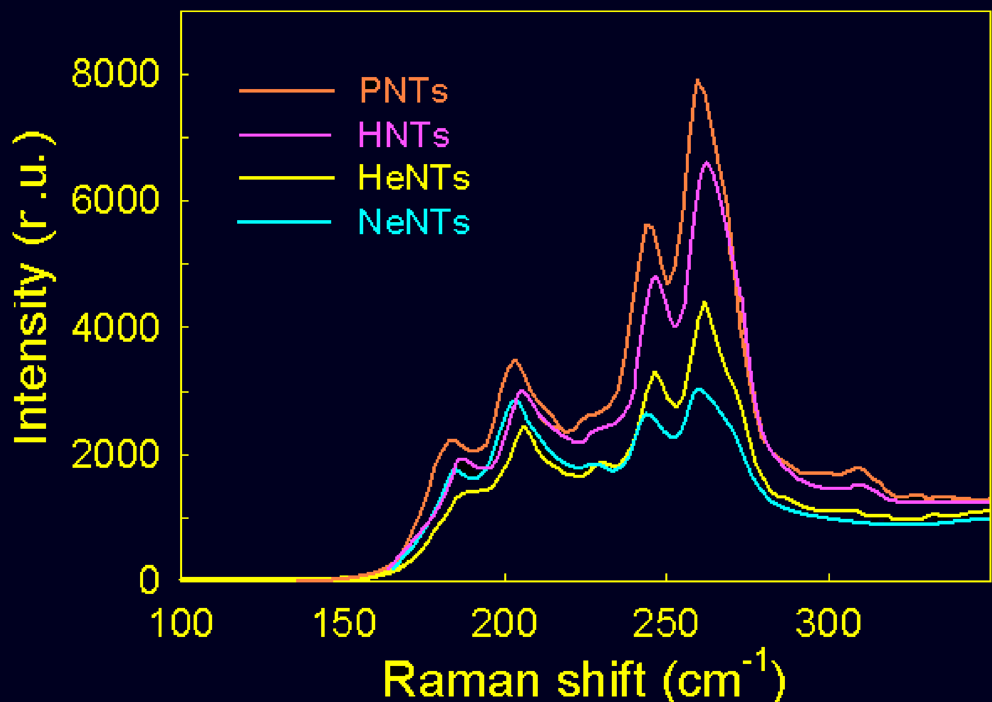


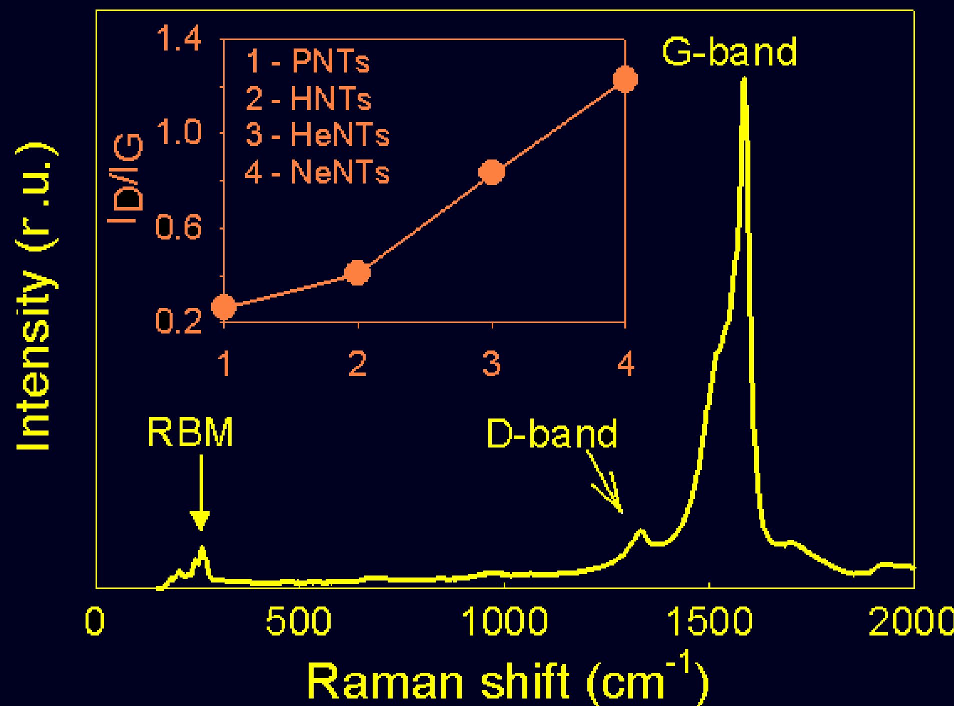

❖ ***Angular dependence of FMR reflects shape anisotropy***

# *Composite P3HT- Irradiated SWNT: Raman Data*

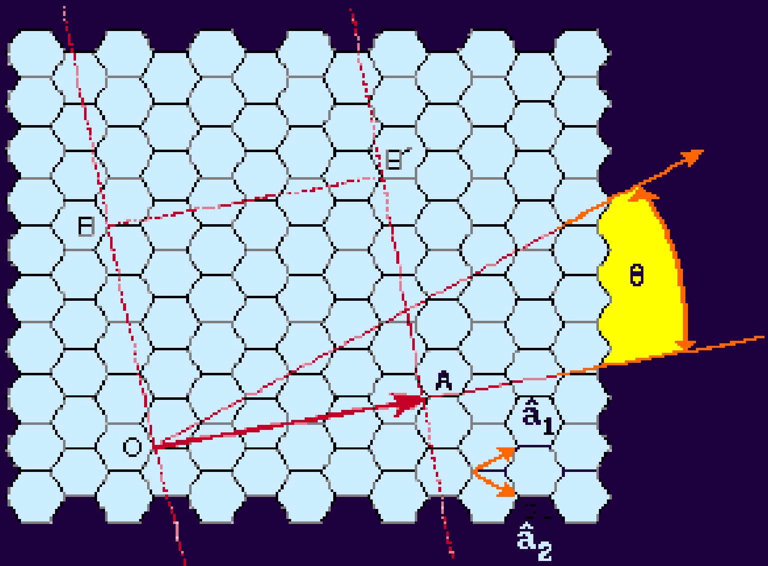


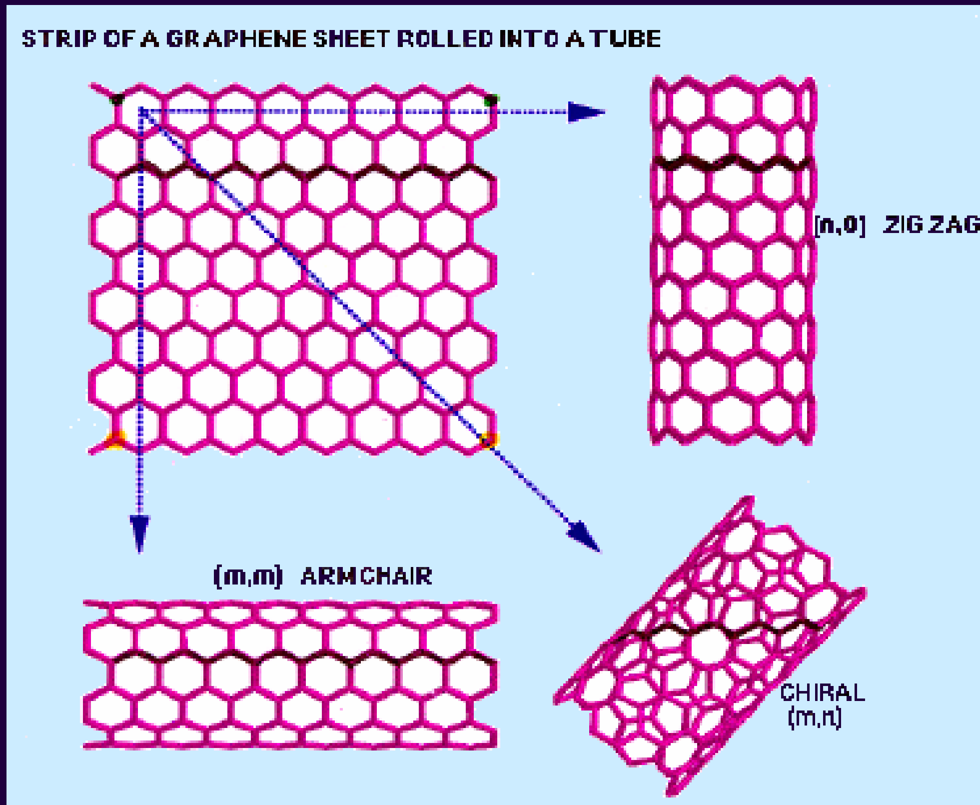


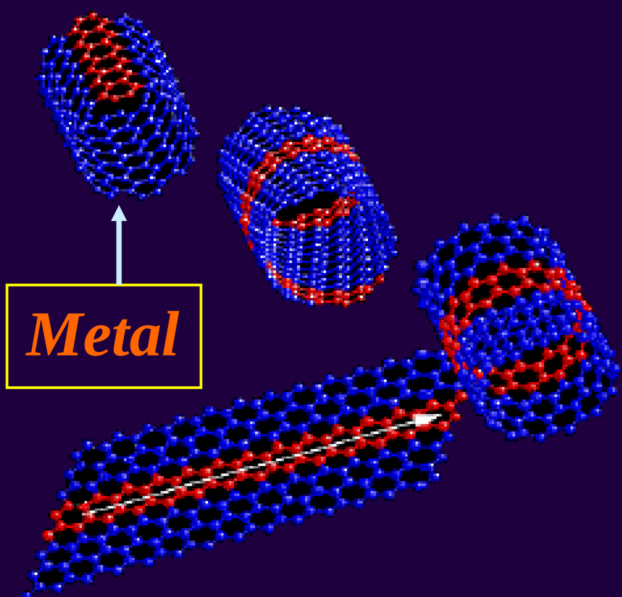



# *Carbon Nanotubes*




Chiral vector is defined on the hexagonal lattice as

$Ch = n\hat{a}_1 + m\hat{a}_2$,

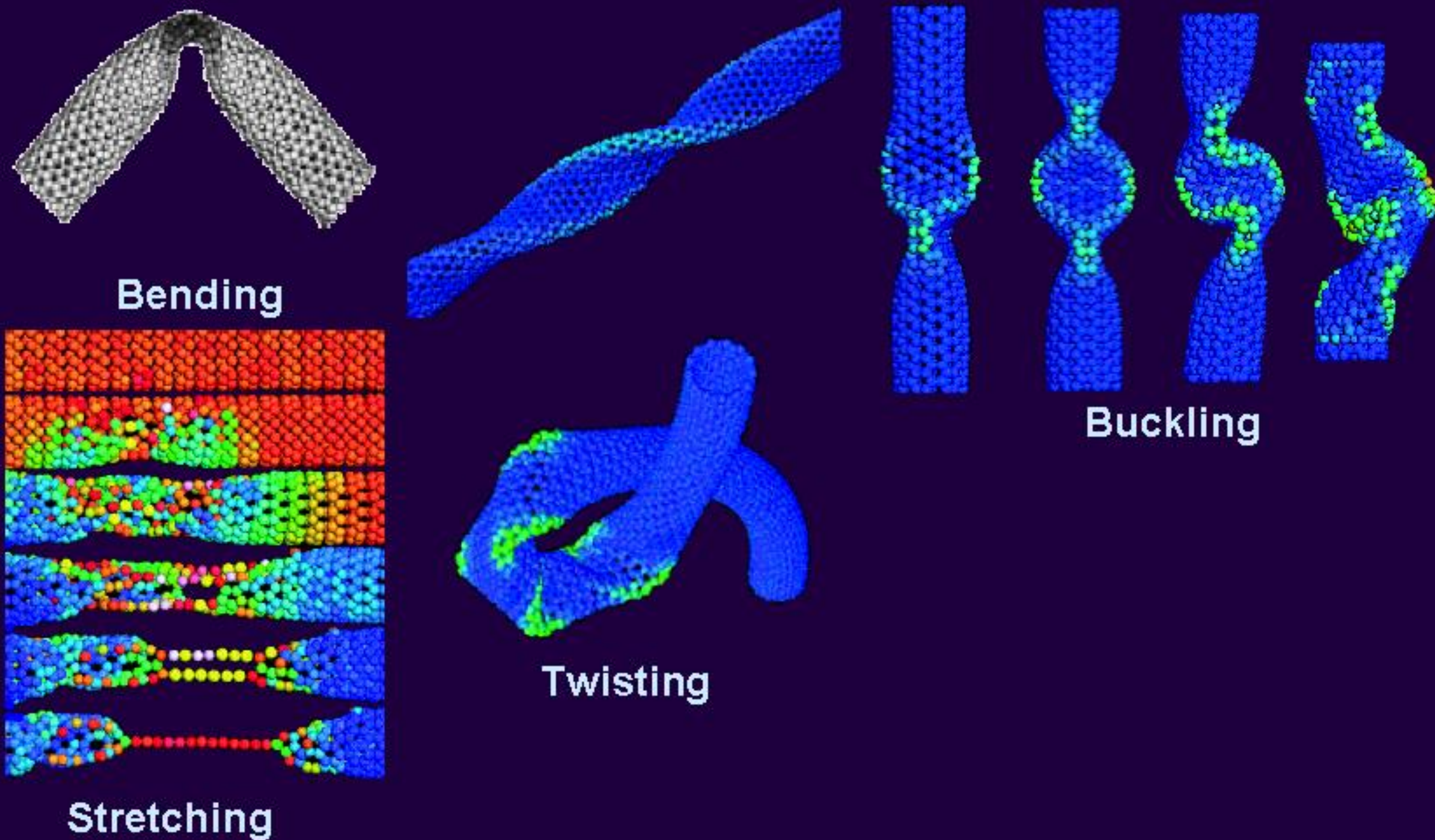
where $\hat{a}_1$ and $\hat{a}_2$ are unit vectors, $n$ and $m$ are integers.

# Carbon Nanotubes

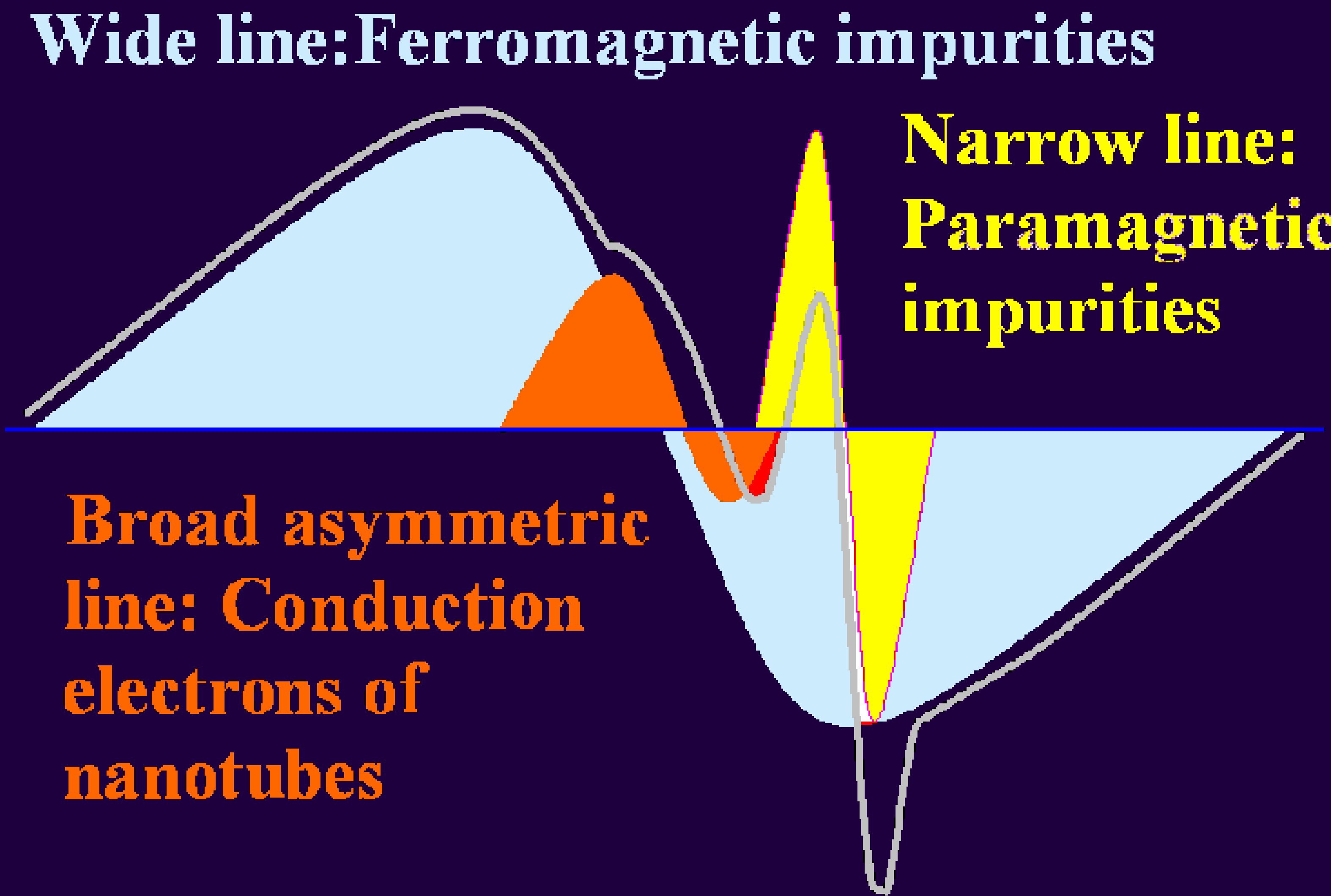
| | |
|---|---|
| Modulus | ~1000 GPa (SWCNT)<br>~1200 GPa (MWCNT) |
| Tensile Strength | ~ 100 GPa |
| Thermal Conductivity | 2000 W/m/K |
| Density | 1300 –1400 kg/cm$^3$ |
| Length | up to microns |

| Material | Young modulus [MPa] | Density [kgm$^{-3}$] | Specific stiffness [MPam$^3$kg$^{-1}$] |
|---|---|---|---|
| Single wall nanotube | 1,000,000 | 1,500,000 | 0.67 |
| 4340 Steel Q+T | 207,000 | 7,800,000 | 0.026 |
| 7075 Aluminium | 6,900 | 2,800,000 | 0.0025 |
| C fiber (from PAN) | 2,500 | 230,000 | 0.0109 |
| Spectra 1000 (UHMWPE) | 172,000 | 970,000 | 0.177 |
| Kevlar 149 | 186,000 | 1,440,000 | 0.13 |

# *Carbon Nanotubes: Mechanical Deformations*



# *ESR Profile of Non-Annealed CNT*



# ESR on Carbon Nanotubes: Line Position

- ***Spin-Orbit Coupling (Dependent Upon Fermi Level)***

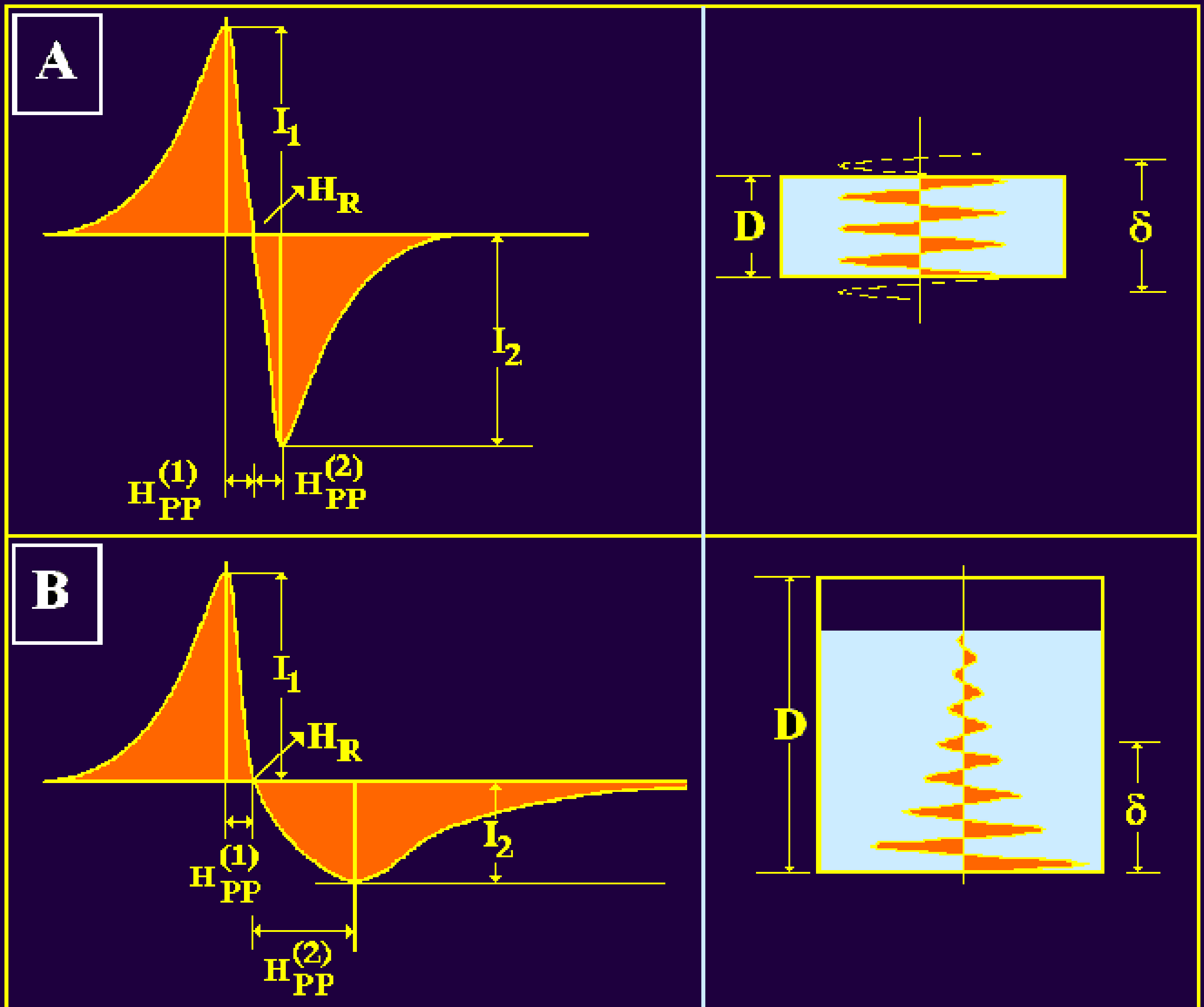
$$g = g_{th} + \frac{\lambda}{\Delta E}$$

- ***Orientation of CNT with $H_o$ (Anisotropy of g-Value)***

$$g_{av} = \sqrt{(g_{\|}\cos\theta)^2 + (g_{\perp}\sin\theta)^2} \approx g_{\|} + (g_{\perp} - g_{\|})\sin^2\theta$$

# ESR of Conducting Samples

- *Distortion of ESR spectra due to skin effect*



# *Nanotube Spin Temperature Dependence*

- ***Double integral (S) of EPR Line is related to the spin susceptibility***
- ***S for the resonance line should be temperature independent (Pauli)***
- ***Curie dependence associated with paramagnetic impurities***

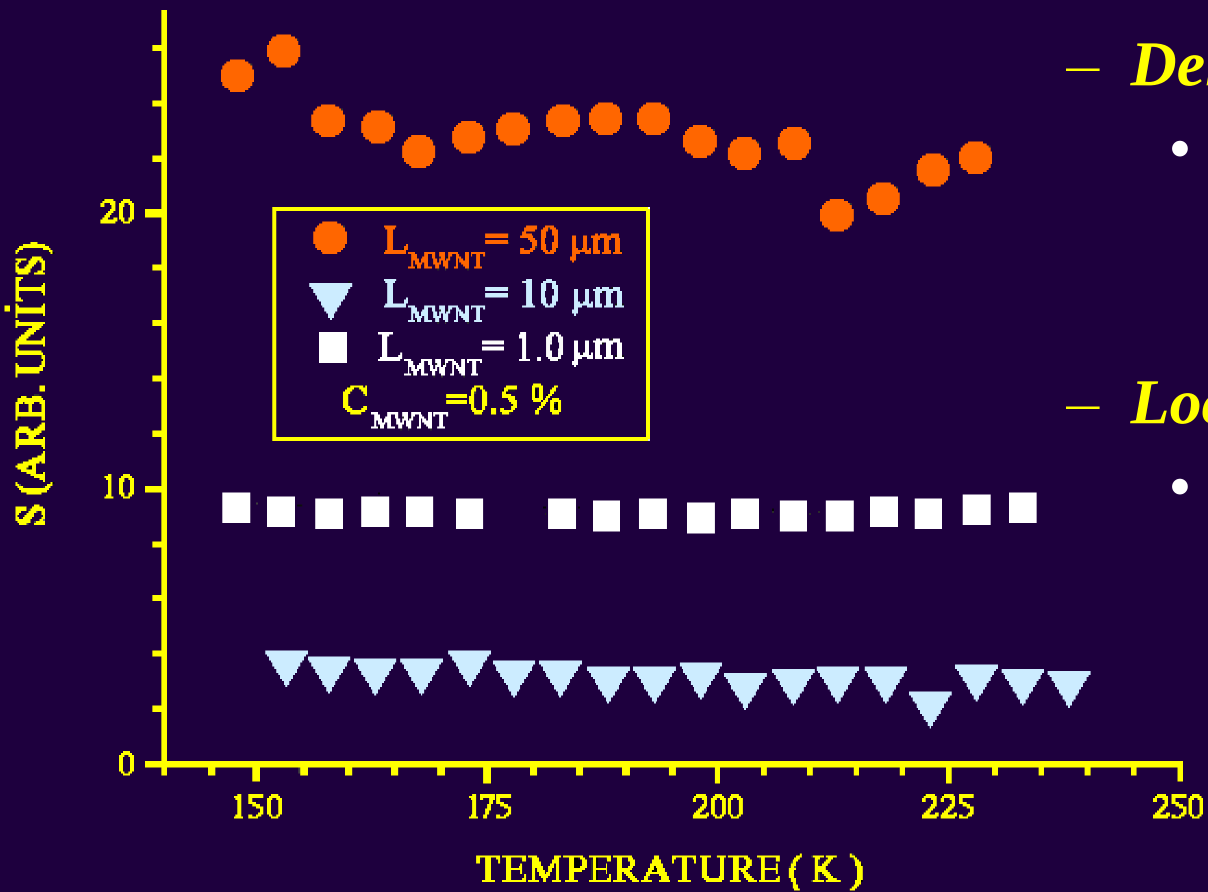
$$S \propto \chi = \chi_{Pauli} + \chi_{Curie}(T) \equiv \beta^2 N(E_F) + g\beta^2 \frac{J(J+1)}{3K_B T}$$

**where $N(E_F)$ is the density of states at the Fermi level, J is the total angular momentum and $K_B$ is the Boltzmann constant**

*Appl. Phys.* **1998** A 67, 23–27 *Phys*. Rev. B **2000** A 62, 17115–17119

# *Epoxy-MWNT: Temp Dependence of S*

✵ ***Temperature Dependence of S***




– ***Delocalized electrons***
  - ***Temperature independent S***

– ***Localized impurities***
  - ***Curie Weiss behavior***

❖ ***Temperature dependence of S controlled by conducting electrons***

# ESR on CNT: *Temp Dependence of $H_{pp}$*

✵ ***The Temperature Dependence of the Linewidth, $H_{PP}$***

$$H_{PP}(T) = H_{PP}^{0} + f(T) = \begin{cases} C_1 T^{m} & C < C_P \\ C_2 \sigma(T) & C \geq C_P \end{cases}$$

**"Localized Electrons"** (for $C < C_P$)

**"Delocalized Electrons"** (for $C \geq C_P$)

where $H_{PP}^{o}$, $C_1$, and $C_2$ are constants; σ is the electrical conductivity and $C_P$ is the percolation threshold for electrical conductivity

**Exponent Values of m (m=0, m=-1/2 , and m=3) have been reported**

*Phys. Rev. B* **1997**, *56*, 9275-9278 *Chem. Phys. Lett.* **1999**, *299*, 532-535


NASA
Pat Rawlings