COMPLEX DYNAMICS IN PMMA/CARBON COMPOSITES

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Dr. Antonio Faraone	NCNR & Materials Sciences and Engineering Dept., UMD

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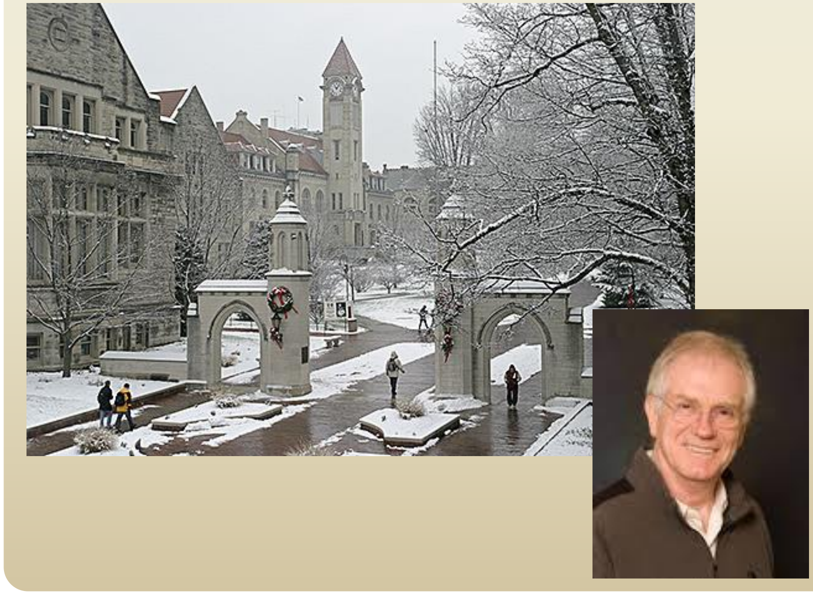
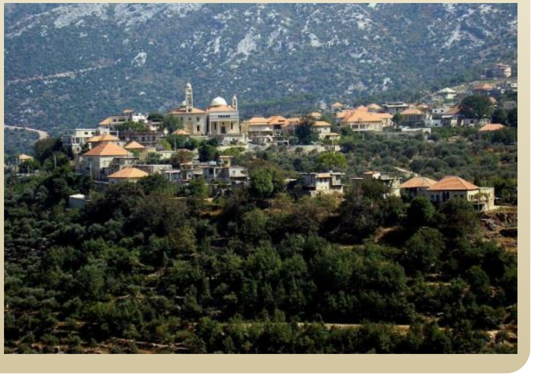
American University of Beirut

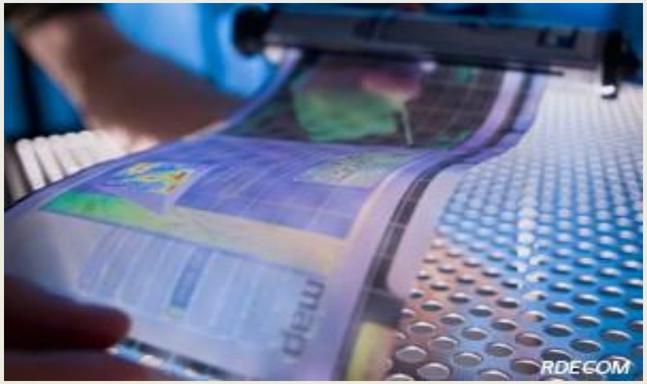
Indiana University Bloomington



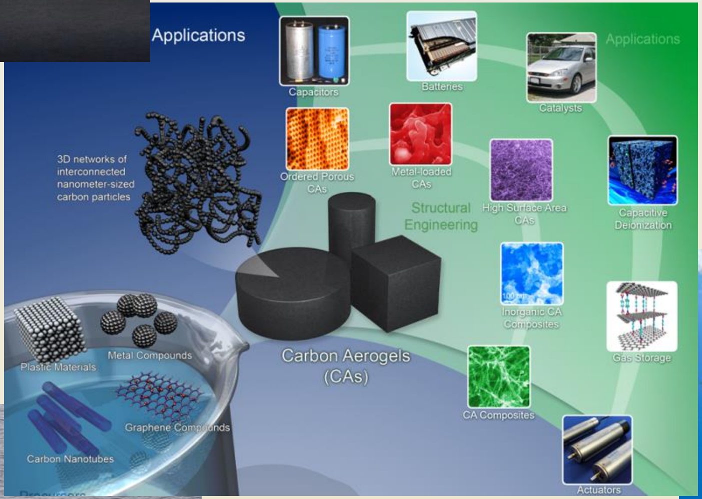


Carbon nanocomposite applications

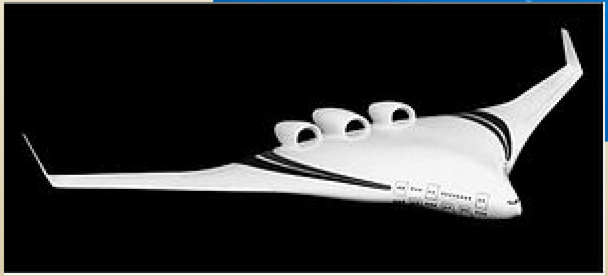
http://plasancarbon.com/



http://www.research.a-star.edu.sg/feature-and-innovation/6383



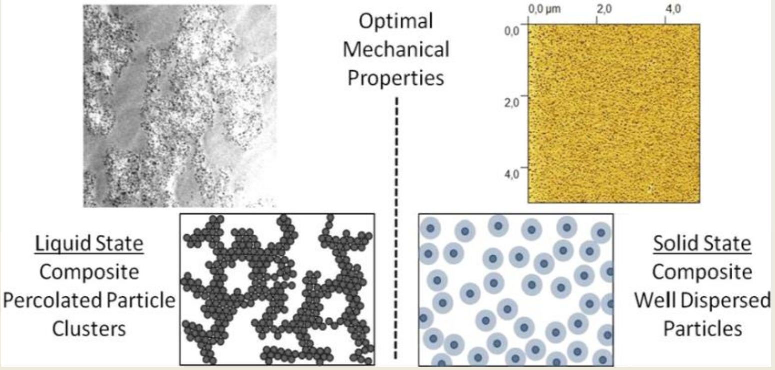
http://en.wikipedia.org/wiki/M80_Stiletto



http://en.wikipedia.org/wiki/Blended_wing_body

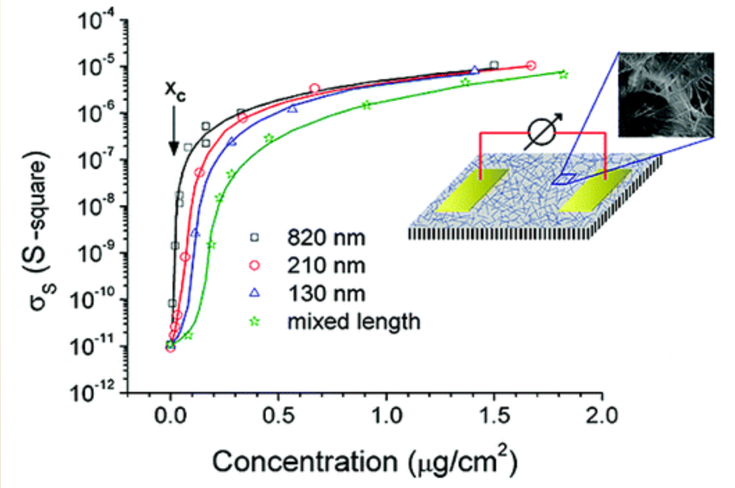
Nanocomposites with Percolated Filler Networks

Material optimization requires control over dispersion and filler network

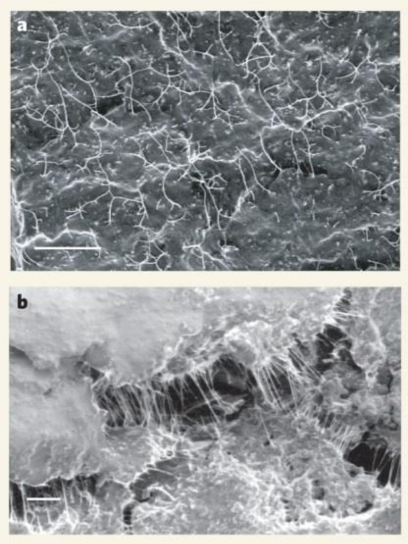


Maillard, Kumar et al. *Nano Letters* **12** (2012)
Ackora. Kumar et al. Macromolecules **43** (2010)

SWNT networks serve as conduction and stress-propagation pathways within the composite



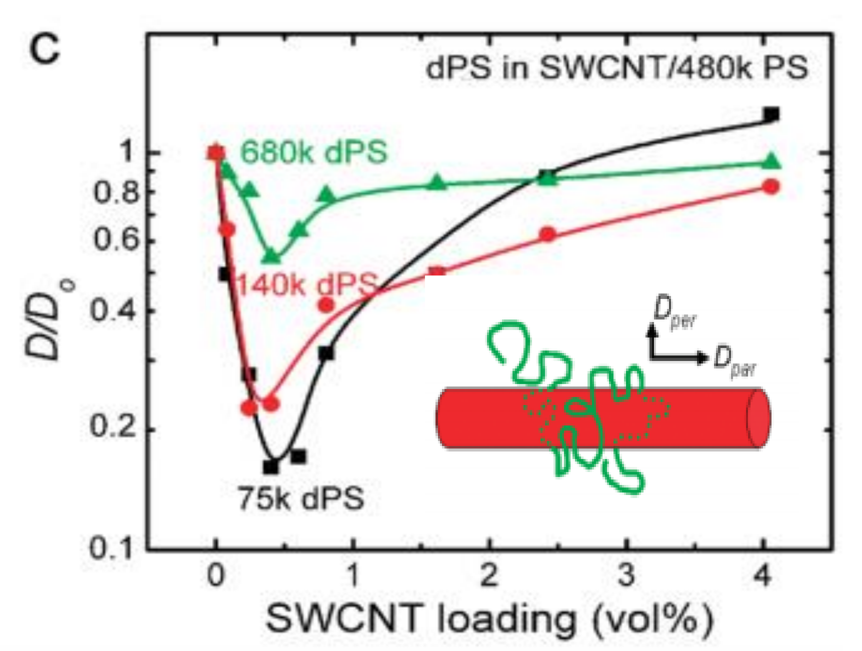
Simien et al. *ACS Nano* **2** (2008)



Ajayan & Tour, *Nature* **447** (2007)

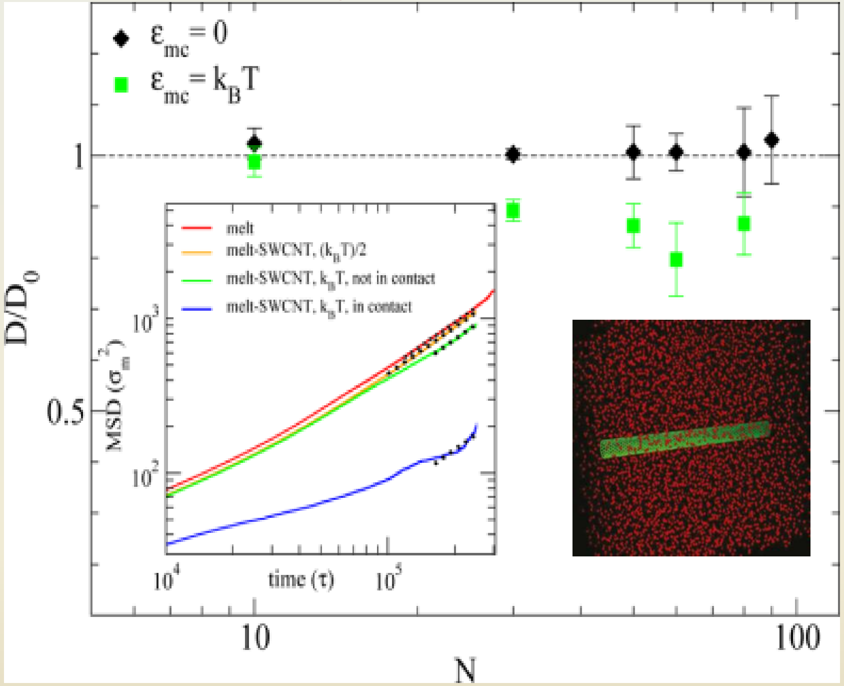
Polymer Diffusion in Percolated SWNT Networks

Tracer diffusion exp. shows initial decrease in polymer diffusion that recovers beyond percolation



Mu, Winey et al. *Macromolecules* **42** (2009)

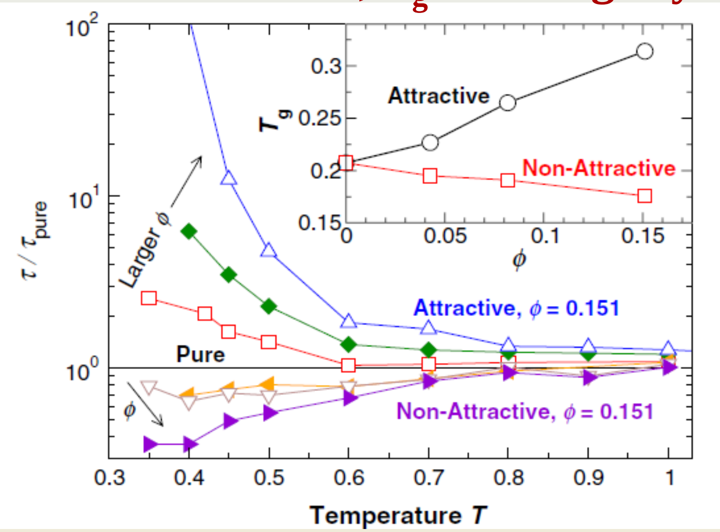
MD simulations attribute the diffusion behavior to polymer/SWNT interactions



Karatrantos et al. Macromolecules **45** (2012)

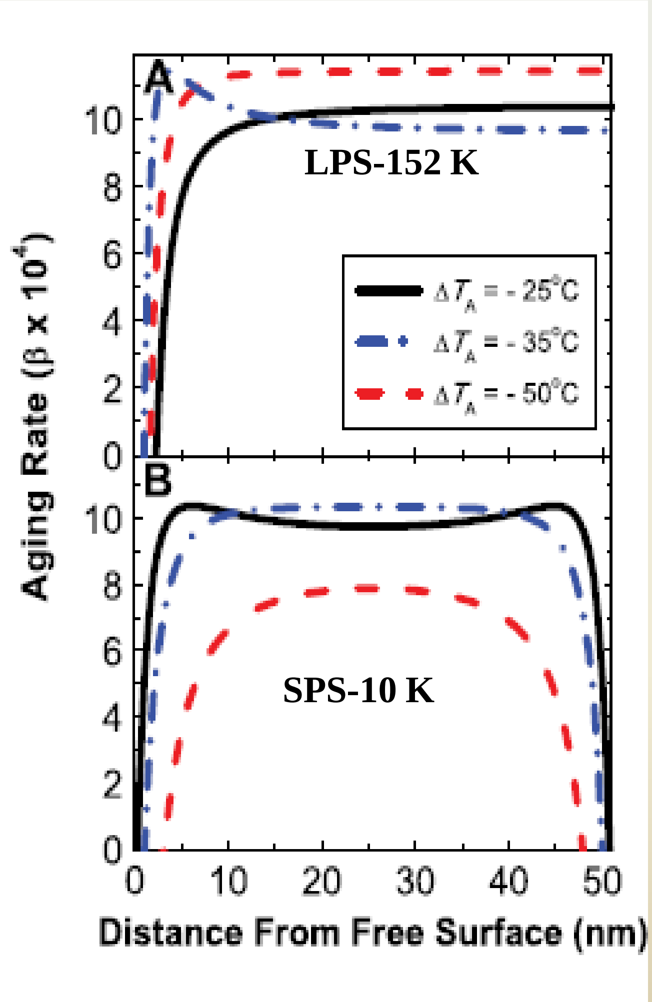
Local dynamics define ageing and fragility properties of polymers

Attractive interactions increase relaxation times, T_g and fragility



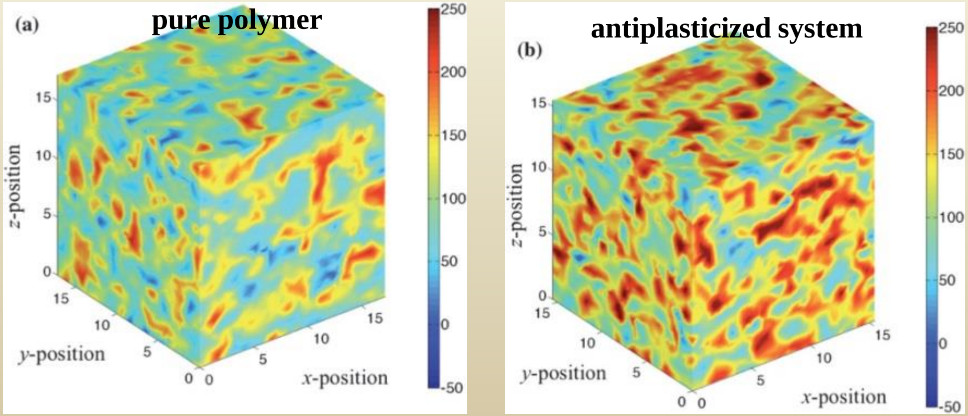
Francis Starr and Jack Douglas *PRL* **106** (2011)

Interfacial attractions modify the aging rate in thin polymer films



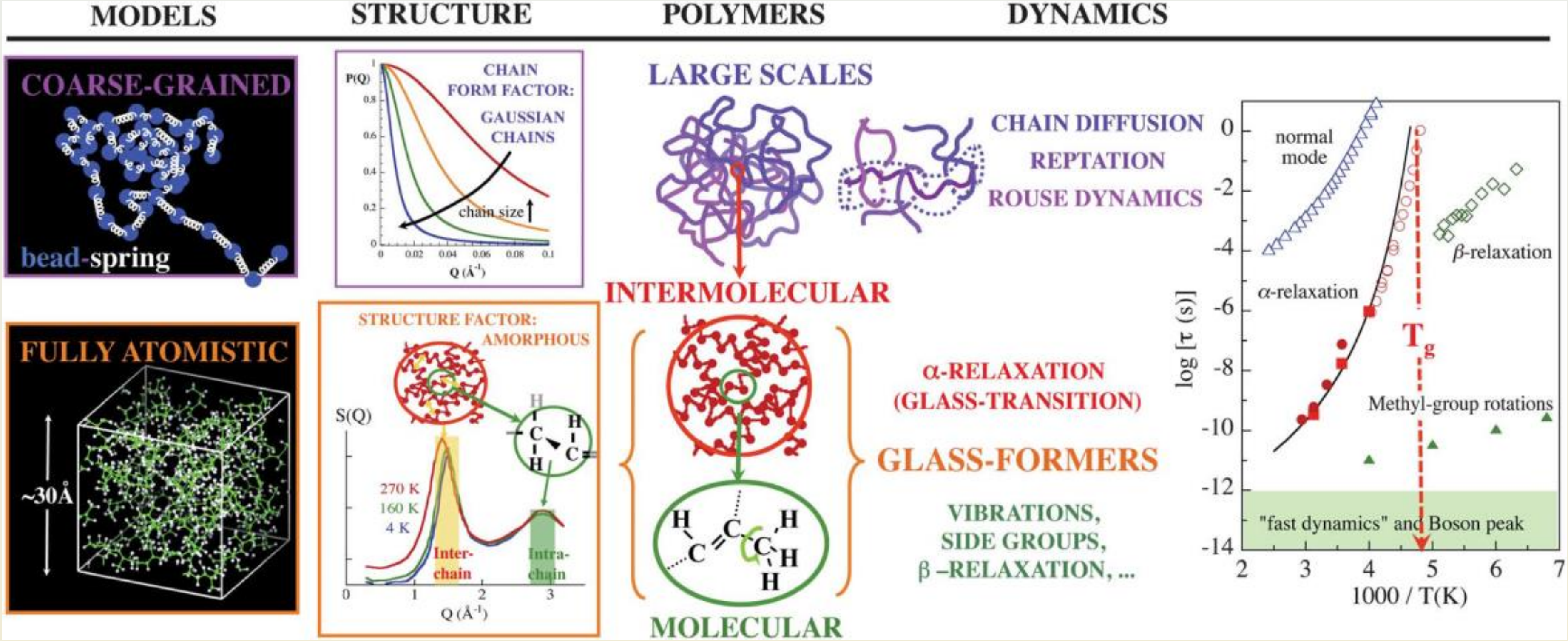
Friedberg, Glynos, and Peter Green, *PRL* **108** (2012)

Local mobility affects local molecular stiffness and elastic constants



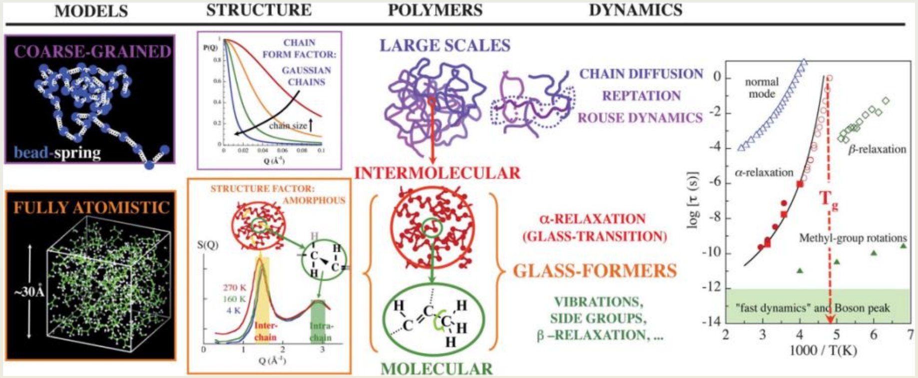
Robert Riggleman, Jack Douglasb and Juan J. de Pablo, *Soft Matter* **6** (2010)

Characterizing Polymer Dynamics

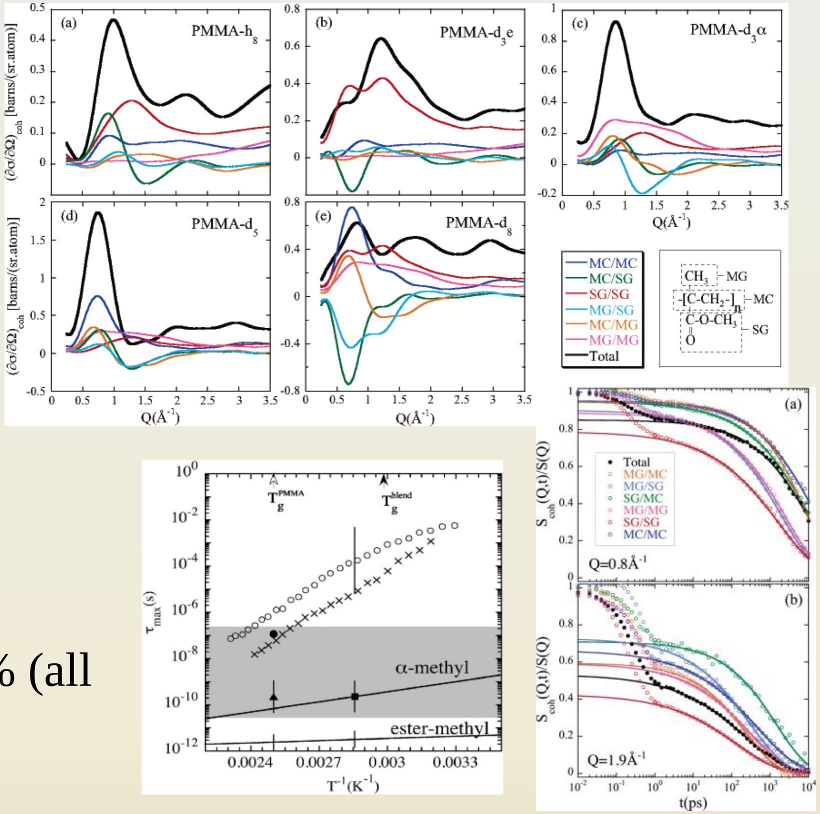


Arbe, Alvarez & Colmenero, *Soft Matter* **8** (2012)

Characterizing Polymer Dynamics



Arbe, Alvarez & Colmenero, *Soft Matter* **8** (2012)



Genix, Colmenero et al., *Macromolecules* **39** 6260 (2006)
Genix, Colmenero et al., *Macromolecules* **39** 3947 (2006)
Genix, Colmenero et al., *Phys. Rev. E* **72** (2005)
Colmenero, Moreno & Alegria *Prog. Pol. Sci.* **30** (2005)
Moreno, Alegria & Colmenero, *Macromolecules* **34** (2001)

Sample Preparation

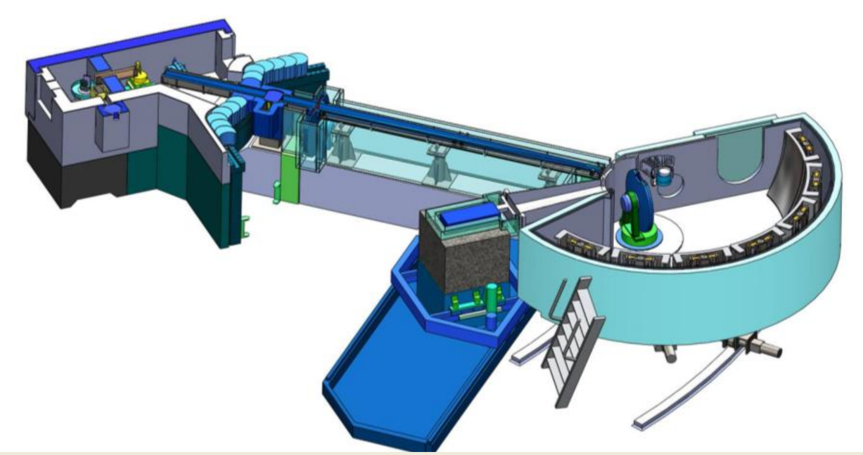
PMMA/SWNT composites with 1v%, 8v% and 15v% (all above percolation threshold ~ 0.3v%)

- Proper sonication of SWNT/DMF to ensure good dispersion
- Polymer mixed with the suspension
- Composites obtained by precipitation

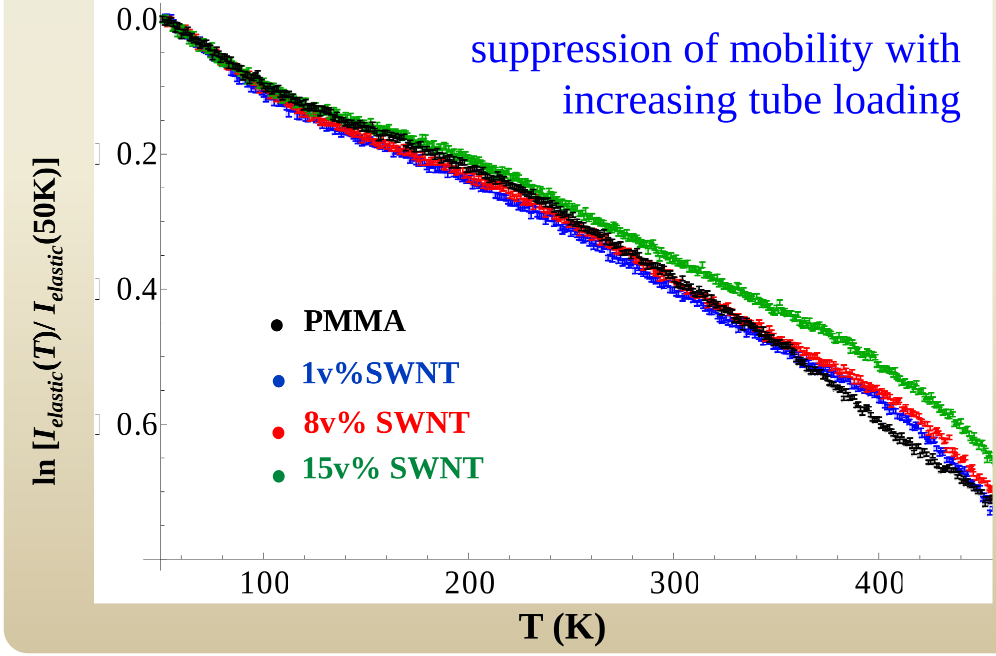
Samples were prepared with PMMA with $M_w > M_e$ (12.5kg/mol)

SWNT/PMMA Composites: Suppressed Polymer Mobility

Neutron Backscattering incoherent elastic scans



Elastic scans pick up motions faster than 2ns



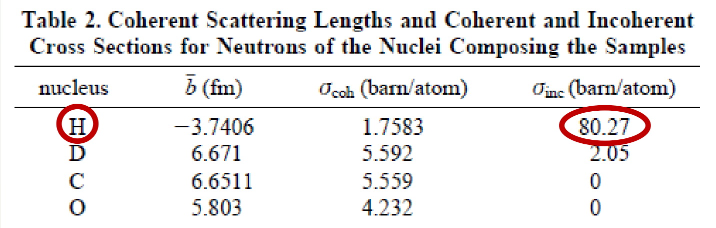
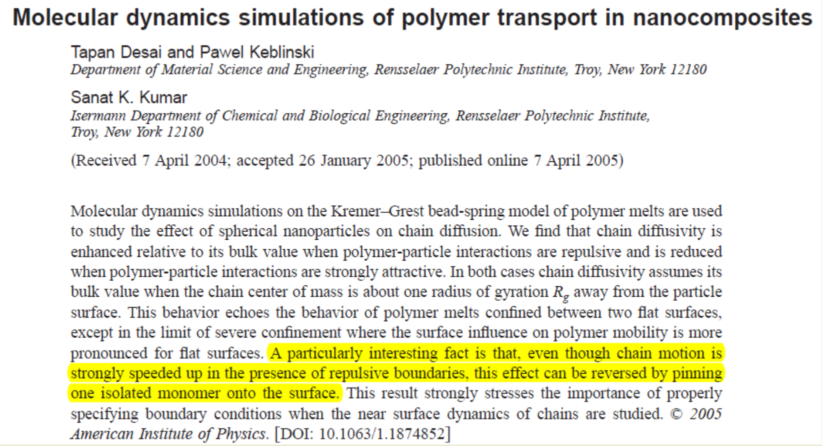


Table 2. Coherent Scattering Lengths and Coherent and Incoherent Cross Sections for Neutrons of the Nuclei Composing the Samples

nucleus	$\bar{b}$ (fm)	σ_{coh} (barn/atom)	σ_{inc} (barn/atom)
H	−3.7406	1.7583	80.27
D	6.671	5.592	2.05
C	6.6511	5.559	0
O	5.803	4.232	0



Molecular dynamics simulations of polymer transport in nanocomposites

Tapan Desai and Pawel Keblinski
Department of Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180

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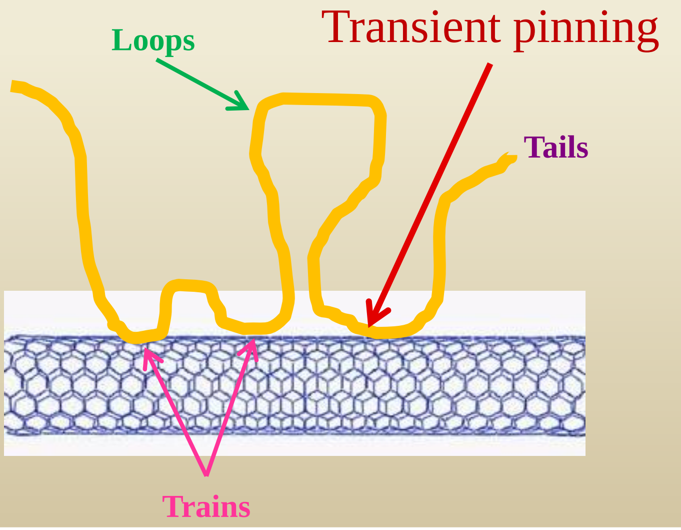
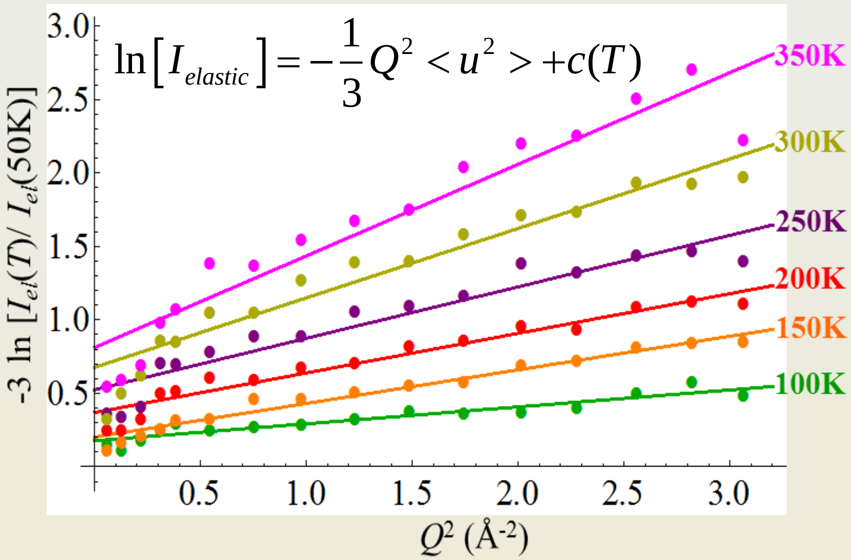
(Received 7 April 2004; accepted 26 January 2005; published online 7 April 2005)

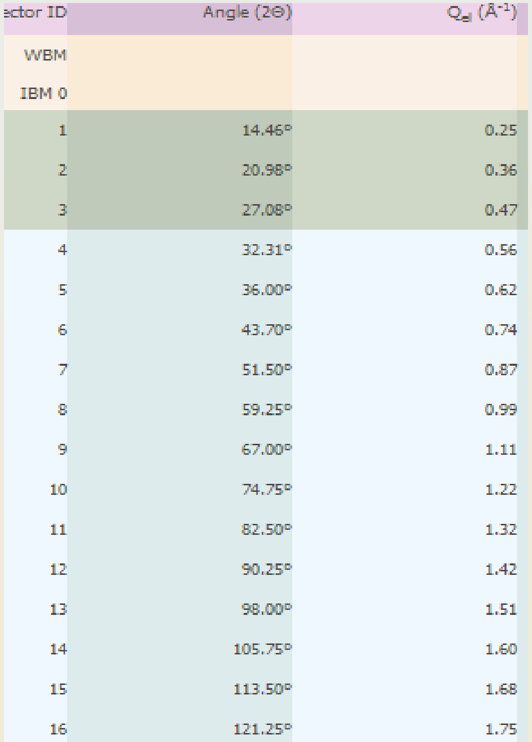
Molecular dynamics simulations on the Kremer–Grest bead-spring model of polymer melts are used to study the effect of spherical nanoparticles on chain diffusion. We find that chain diffusivity is enhanced relative to its bulk value when polymer-particle interactions are repulsive and is reduced when polymer-particle interactions are strongly attractive. In both cases chain diffusivity assumes its bulk value when the chain center of mass is about one radius of gyration R_g away from the particle surface. This behavior echoes the behavior of polymer melts confined between two flat surfaces, except in the limit of severe confinement where the surface influence on polymer mobility is more pronounced for flat surfaces. A particularly interesting fact is that, even though chain motion is strongly speeded up in the presence of repulsive boundaries, this effect can be reversed by pinning one isolated monomer onto the surface. This result strongly stresses the importance of properly specifying boundary conditions when the near surface dynamics of chains are studied. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1874852]



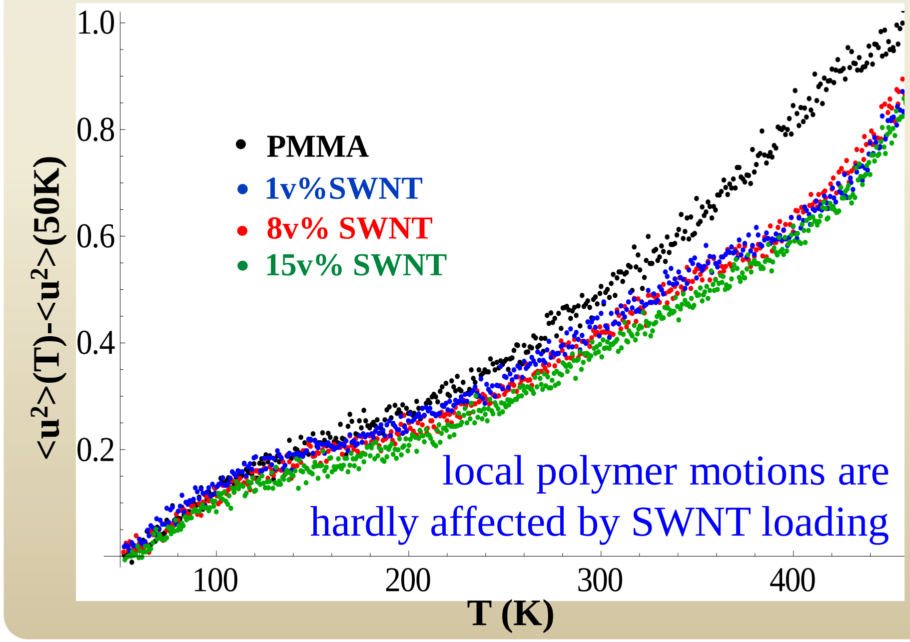
Atomic Mean Square Displacements

Q-dependence of the incoherent elastic intensity

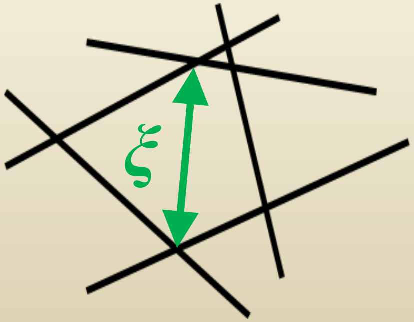


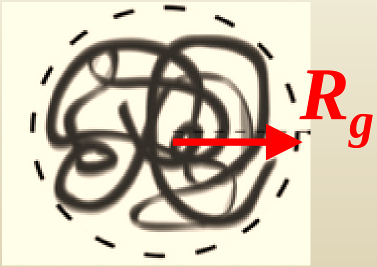


ector ID	Angle (2Θ)	Q_{el} (Å^{-1})
WBM		
IBM 0		
1	14.46°	0.25
2	20.98°	0.36
3	27.08°	0.47
4	32.31°	0.56
5	36.00°	0.62
6	43.70°	0.74
7	51.50°	0.87
8	59.25°	0.99
9	67.00°	1.11
10	74.75°	1.22
11	82.50°	1.32
12	90.25°	1.42
13	98.00°	1.51
14	105.75°	1.60
15	113.50°	1.68
16	121.25°	1.75



local polymer motions are hardly affected by SWNT loading

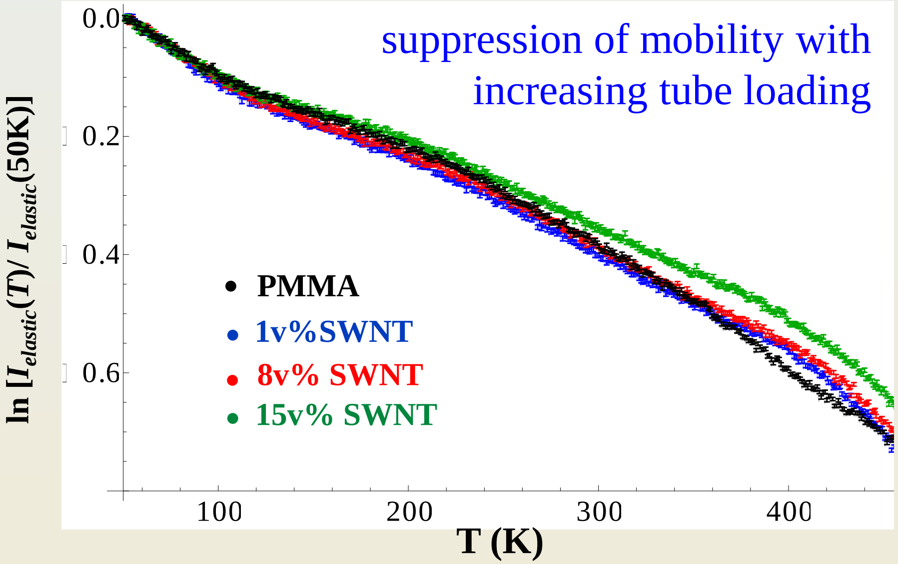




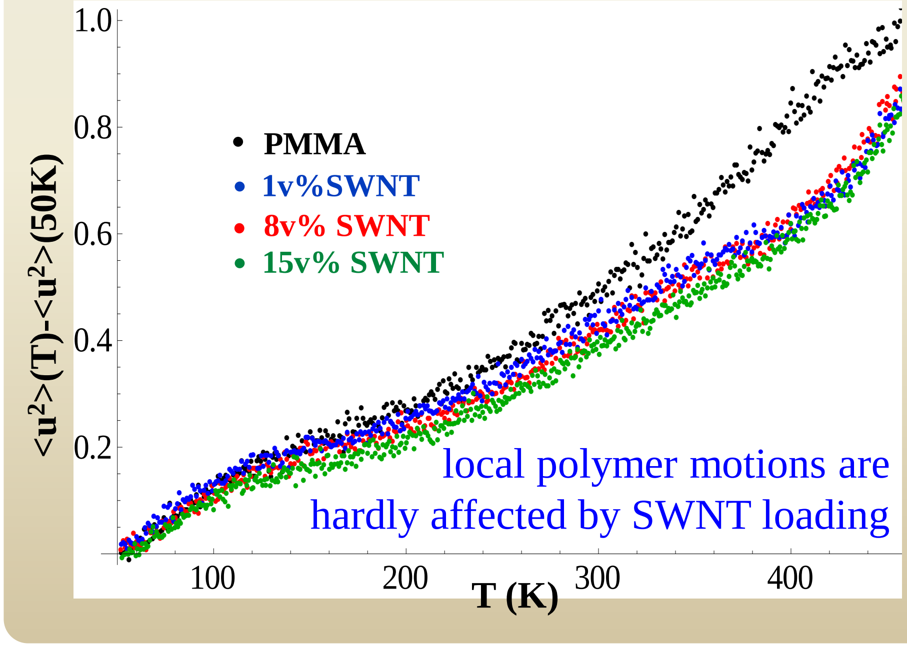
average mesh size ξ: 7–28 nm

coil diameter $2R_g$ ~ 29nm

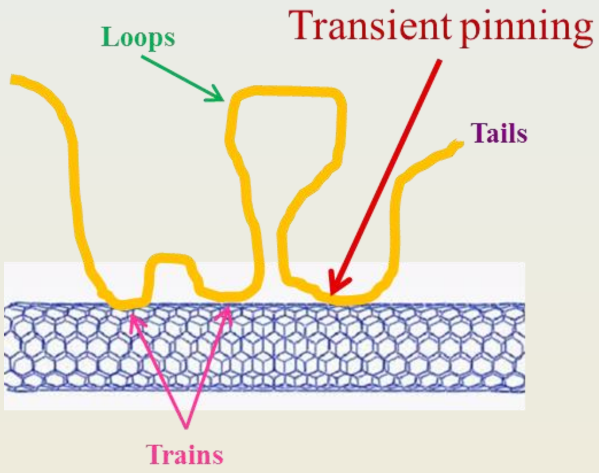
Dynamical arrest of non-interfacial segments

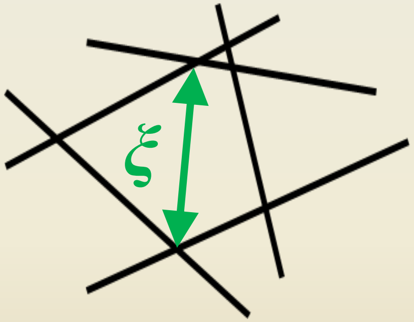


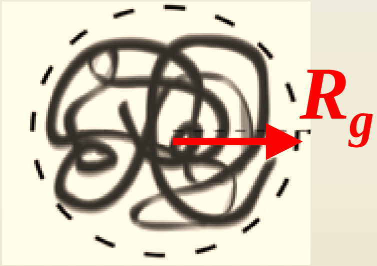
suppression of mobility with increasing tube loading

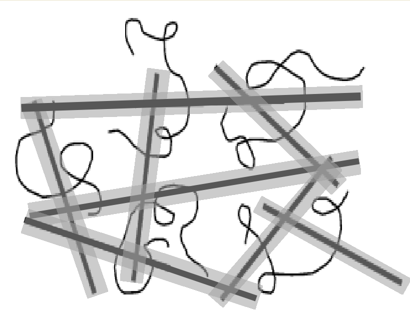


local polymer motions are hardly affected by SWNT loading





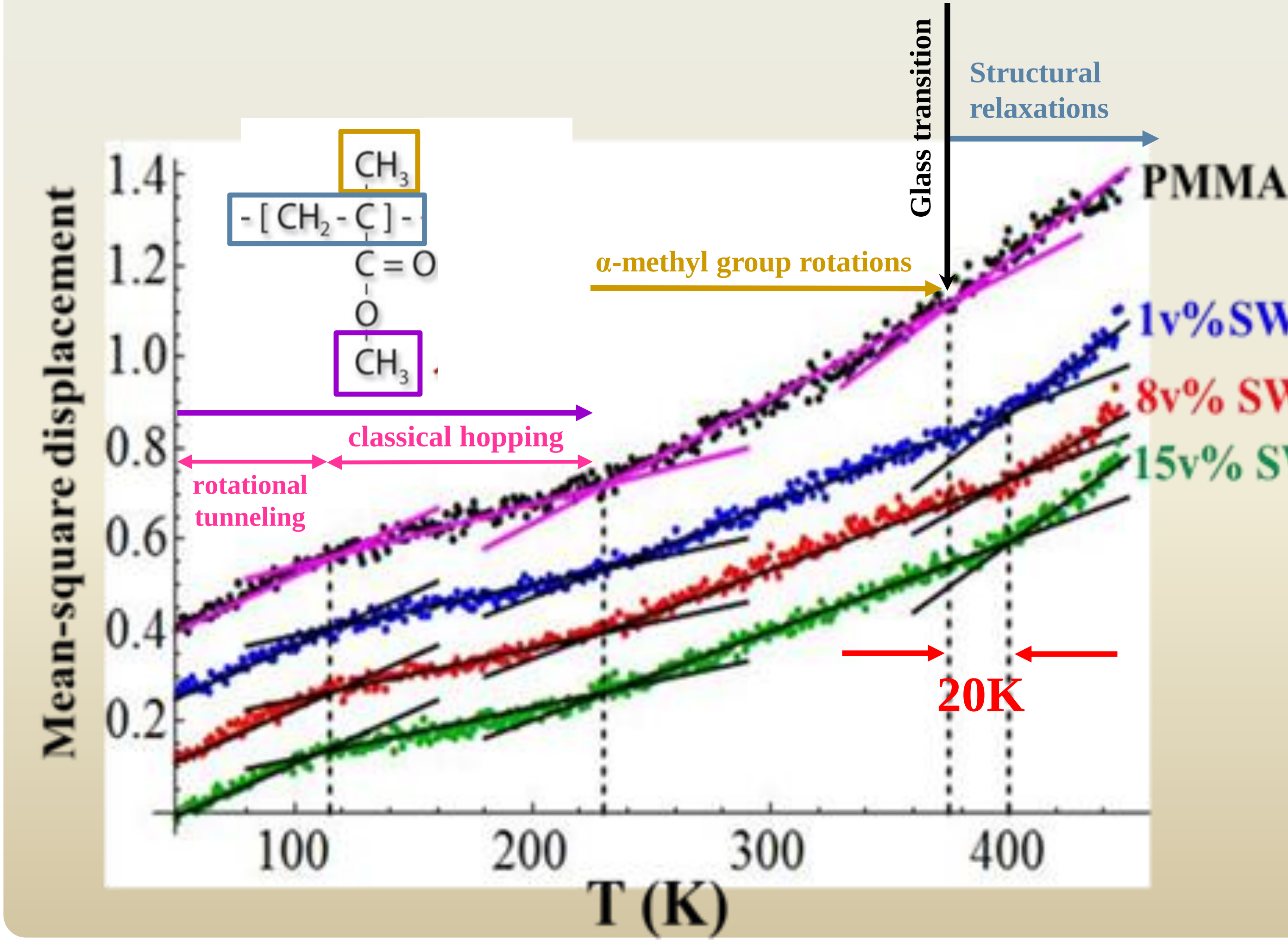


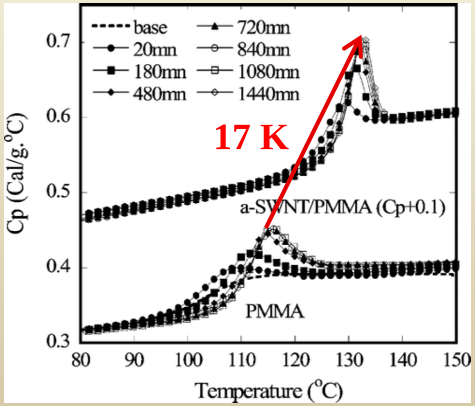


MSD patterns: Thermally induced dynamic phases

$$f.du = dU - TdS \Rightarrow \kappa u.du = dU - TdS$$ ⟶ Helmholtz equation

- At low temperatures: $\frac{1}{2}\kappa\langle u^2\rangle = \Delta U = \frac{3}{2}k_B T \Rightarrow \langle u^2\rangle = 3k_B T/\kappa$ Harmonic model

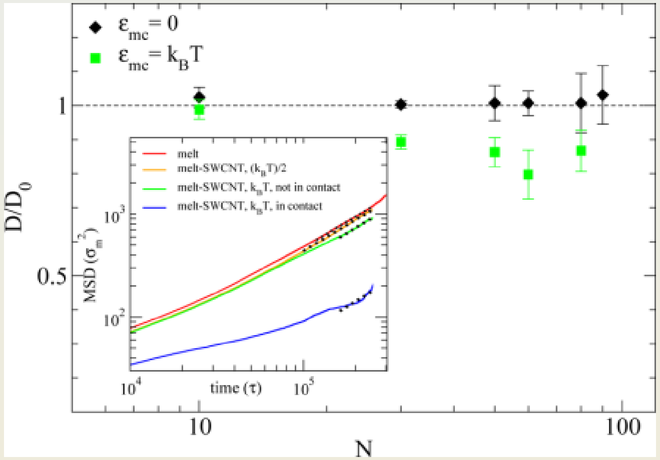




Flory et al., Macromolecules 2010

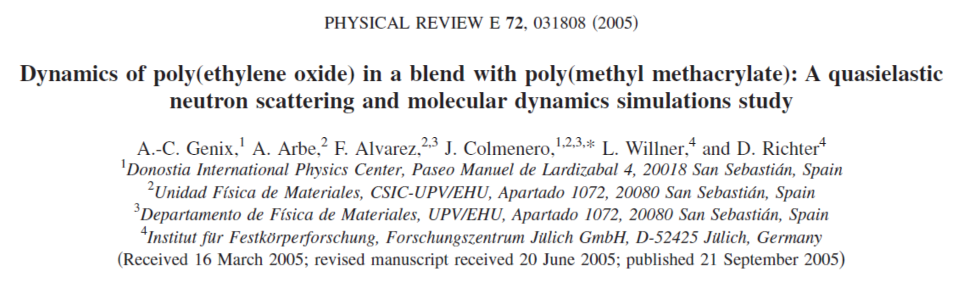
Comparison with related literature

Attractive polymer/filler potential reduces the MSD of chains in the proximity of the filler



Karatrantos, Clarke et al, Macromolecules **4** (2012)

PEO/PMMA blends exhibit a similar phenomenon: dynamics of the fast component are effectively restricted by the slower one


PHYSICAL REVIEW E **72**, 031808 (2005)

Dynamics of poly(ethylene oxide) in a blend with poly(methyl methacrylate): A quasielastic neutron scattering and molecular dynamics simulations study

A.-C. Genix,[1] A. Arbe,[2] F. Alvarez,[2,3] J. Colmenero,[1,2,3,*] L. Willner,[4] and D. Richter[4]
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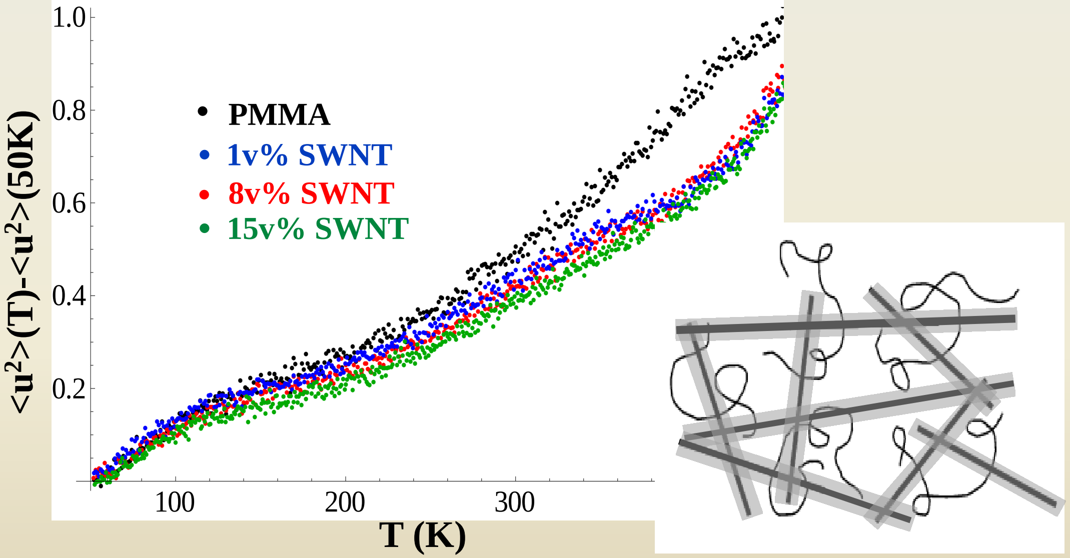
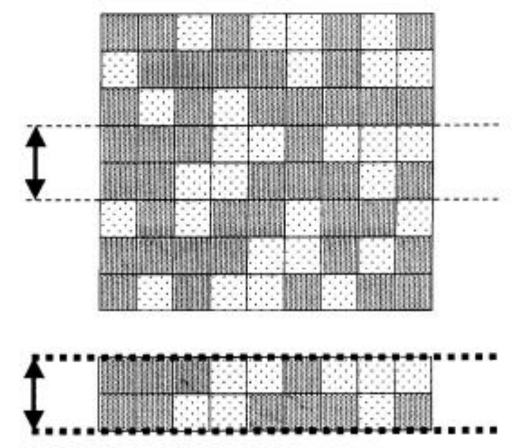
[2]*Unidad Física de Materiales, CSIC-UPV/EHU, Apartado 1072, 20080 San Sebastián, Spain*
[3]*Departamento de Física de Materiales, UPV/EHU, Apartado 1072, 20080 San Sebastián, Spain*
[4]*Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*
(Received 16 March 2005; revised manuscript received 20 June 2005; published 21 September 2005)



Increase in T_g results from the percolation of slow domains

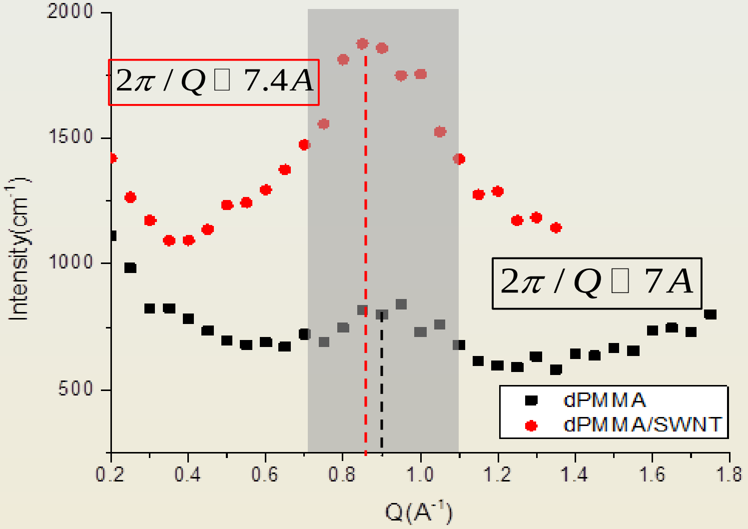


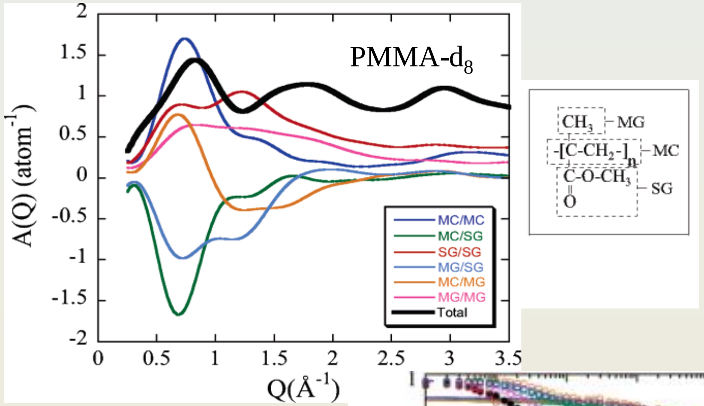
Long & Lequeux, Eur. Phys. J. E **4** (2001)

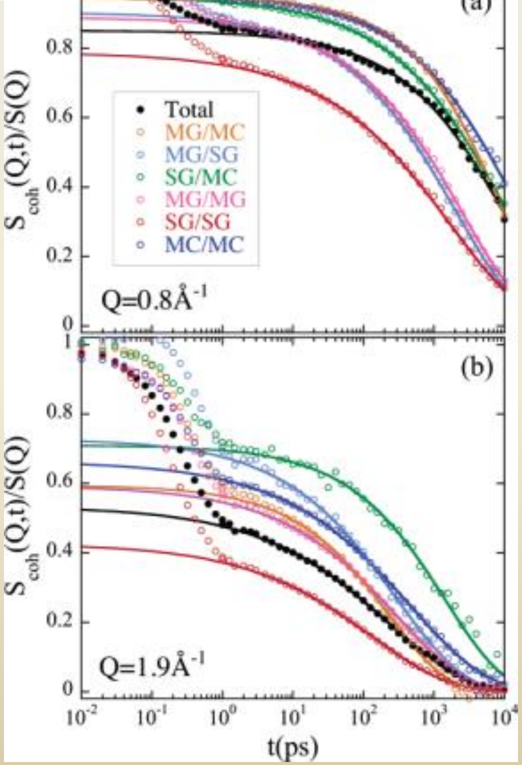
- Transient pinning of polymer segments close to the attractive SWNT interfaces promote the existence of slow domains in their proximity
- The percolation of the nanotubes causes connectedness of the slow domains, which dynamically arrests the fast bulk chains and constrain the extent of their motions

SWNT/PMMA Composites: Structural characterization

Diffraction on deuterated samples





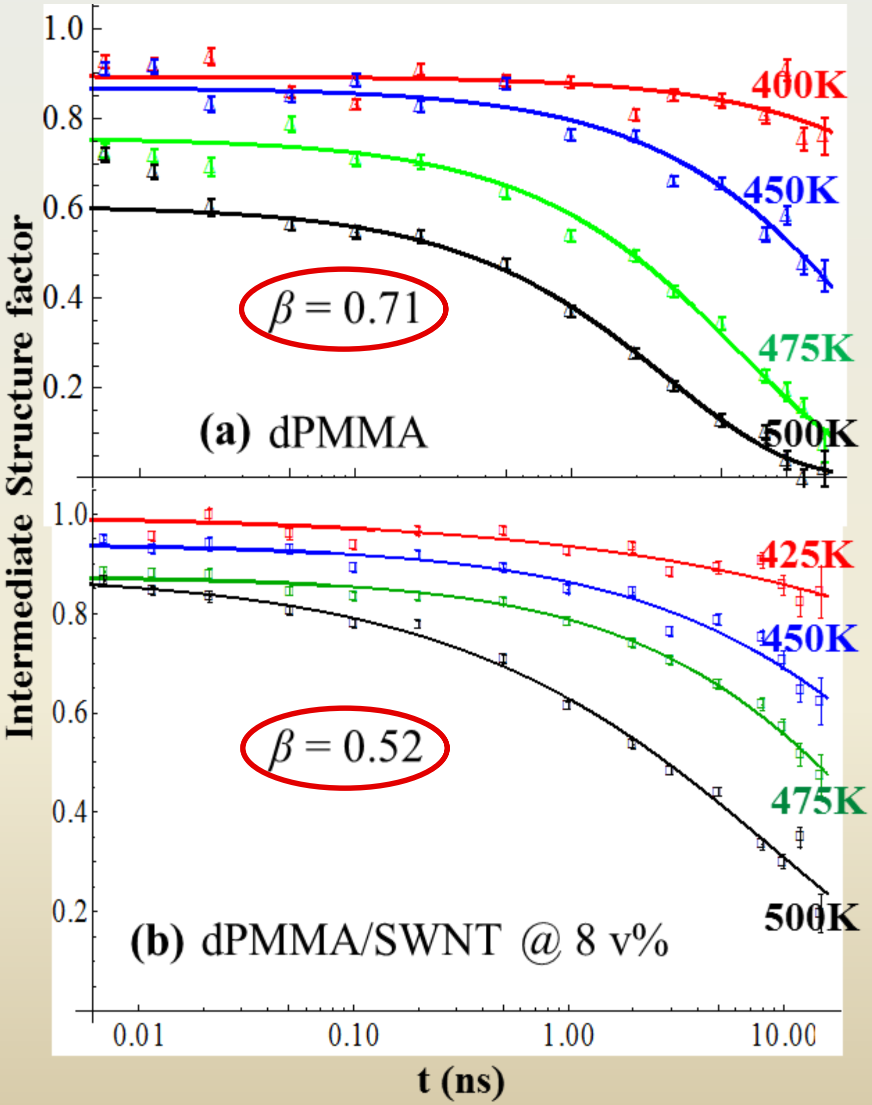


Slight perturbation of the local structure of the polymer chains

Genix, Colmenero et al., *Macromolecules* **39** 6260 (2006)
Colmenero, Moreno & Alegria *Prog. Pol. Sci.* **30** (2005)
Moreno, Alegria & Colmenero, *Macromolecules* **34** (2001)

SWNT/PMMA Composites: Slowdown of Inter-Chain Relaxations

Neutron Spin Echo measurements



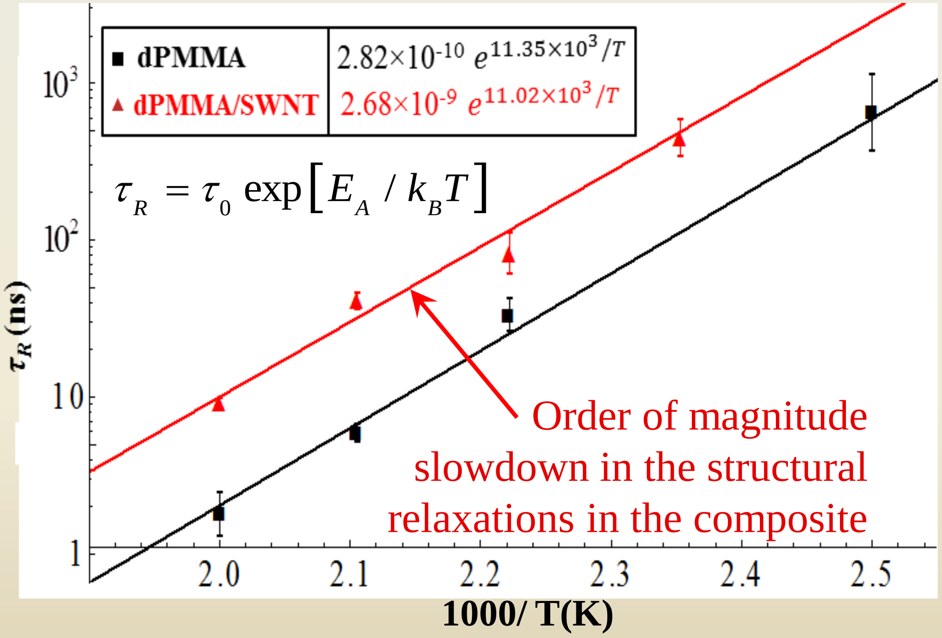
KWW stretched exponential:

$$\frac{S(Q,t)}{S(Q,0)} = DWF \exp\left[-\left(\frac{t}{\tau_R}\right)^{\beta}\right]$$

Debye Waller Factor

Relaxation time

Stretching exponent

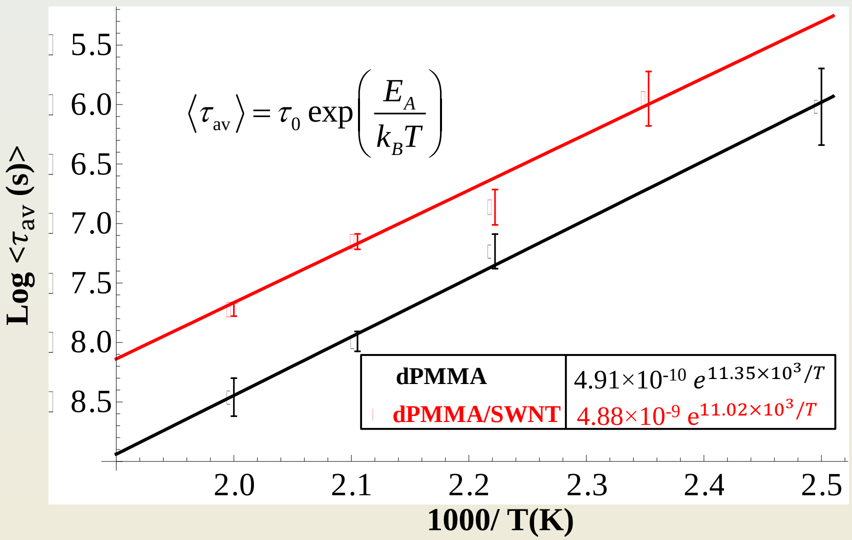


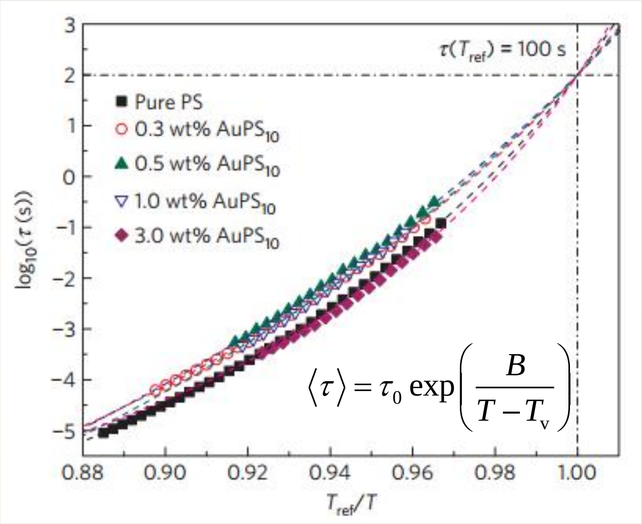
$$\tau_R = \tau_0 \exp\left[E_A / k_B T\right]$$

Order of magnitude slowdown in the structural relaxations in the composite

$$\boxed{E_A \approx 38.5 k_B T}$$

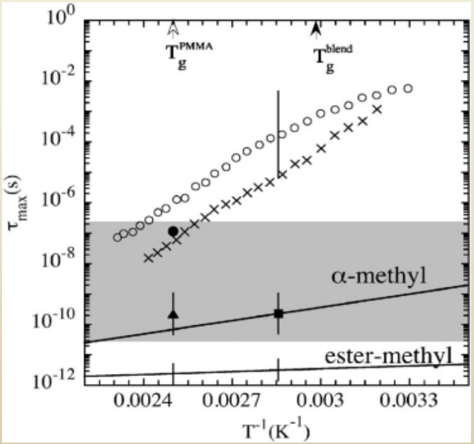
Deviation of the relaxations from the Vogel-Fulcher function





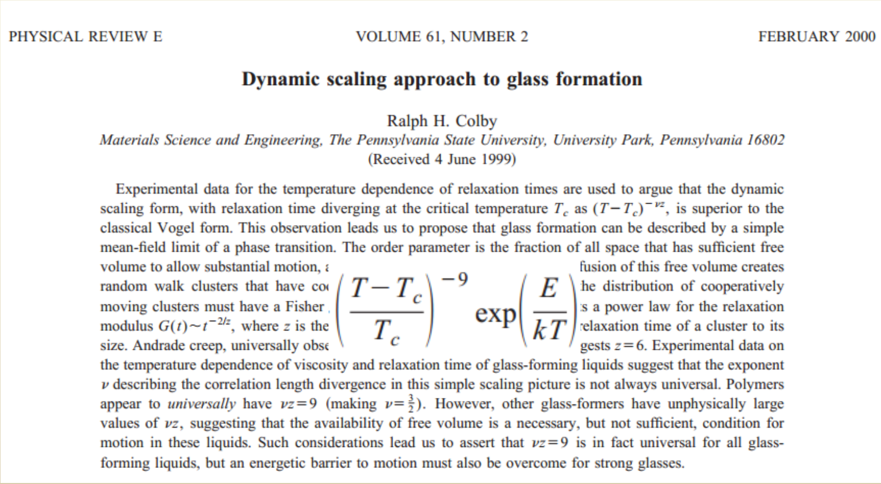
Oh & Green, Nature Materials **8** (2009)

Significant contribution from activated rotational side groups



Moreno, Alegria & Colmenero, *Macromolecules* **34** (2001)

Fundamental divergences from the theoretical hypothesis behind VF function



PHYSICAL REVIEW E VOLUME 61, NUMBER 2 FEBRUARY 2000

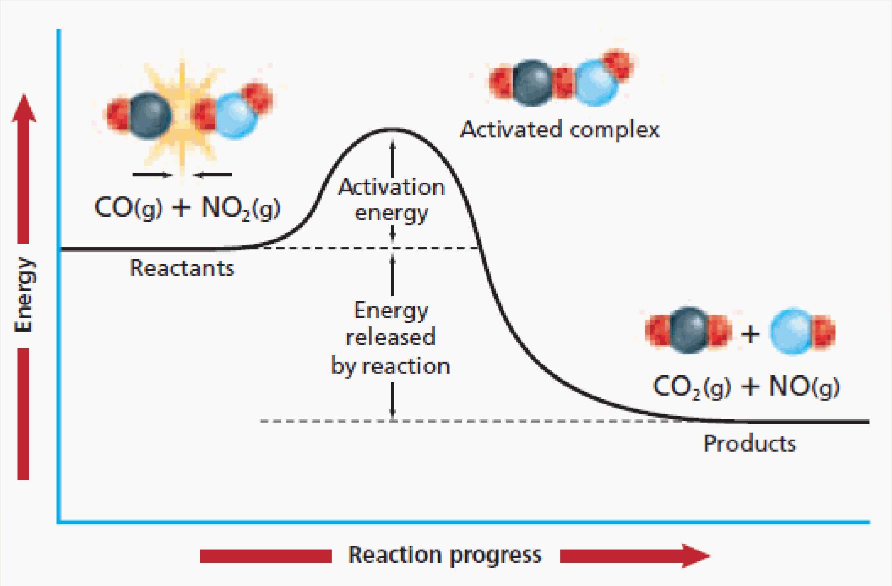
Dynamic scaling approach to glass formation

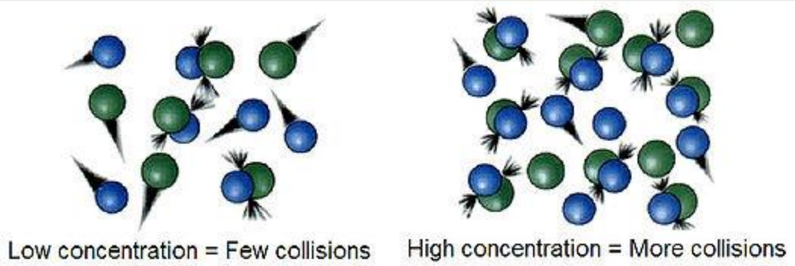
Ralph H. Colby
Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802
(Received 4 June 1999)

Experimental data for the temperature dependence of relaxation times are used to argue that the dynamic scaling form, with relaxation time diverging at the critical temperature T_c as $(T-T_c)^{-\nu z}$, is superior to the classical Vogel form. This observation leads us to propose that glass formation can be described by a simple mean-field limit of a phase transition. The order parameter is the fraction of all space that has sufficient free
volume to allow substantial motion, a … fusion of this free volume creates
random walk clusters that have co… he distribution of cooperatively
moving clusters must have a Fisher … s a power law for the relaxation
modulus $G(t) \sim t^{-2/z}$, where z is the … relaxation time of a cluster to its
size. Andrade creep, universally obse… gests $z=6$. Experimental data on
the temperature dependence of viscosity and relaxation time of glass-forming liquids suggest that the exponent ν describing the correlation length divergence in this simple scaling picture is not always universal. Polymers appear to *universally* have $\nu z=9$ (making $\nu=\frac{3}{2}$). However, other glass-formers have unphysically large values of νz, suggesting that the availability of free volume is a necessary, but not sufficient, condition for motion in these liquids. Such considerations lead us to assert that $\nu z=9$ is in fact universal for all glass-forming liquids, but an energetic barrier to motion must also be overcome for strong glasses.

$$\left(\frac{T - T_c}{T_c}\right)^{-9} \exp\left(\frac{E}{kT}\right)$$

Collision Theory

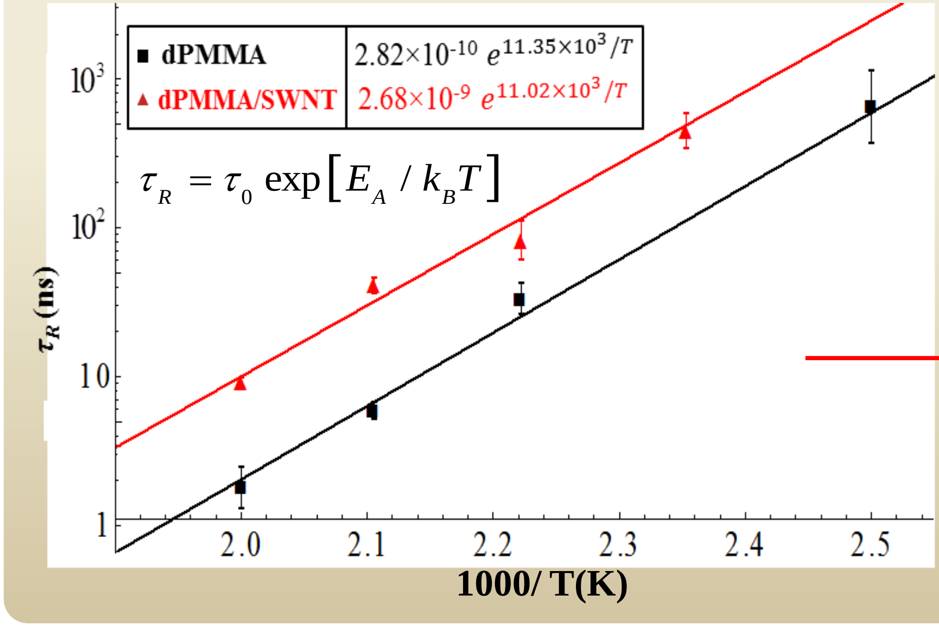




$$k(T) \propto \rho \exp\left[E_A / k_B T\right]$$

Rate constant

Frequency factor



decrease in the number of polymer segments that can collectively relax at a given temperature in the composite

Effect of polymer adsorption in intercalated silicates

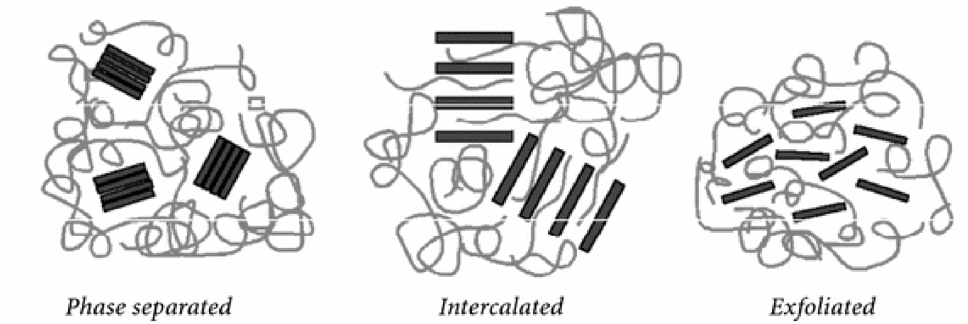
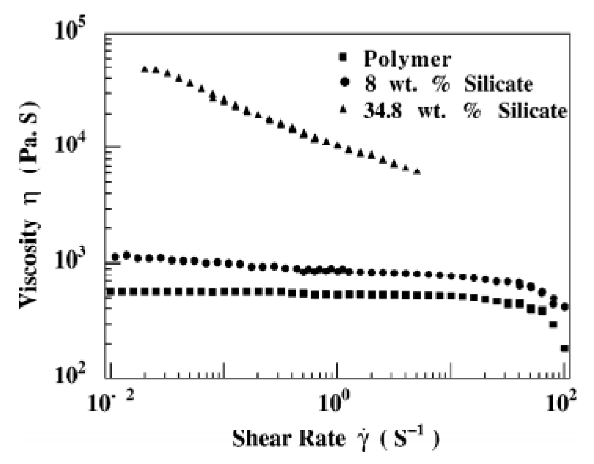
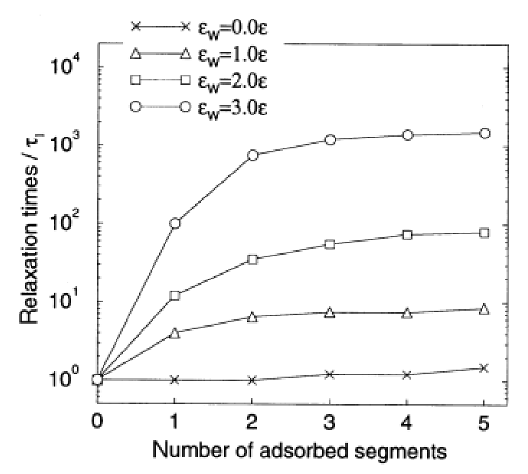
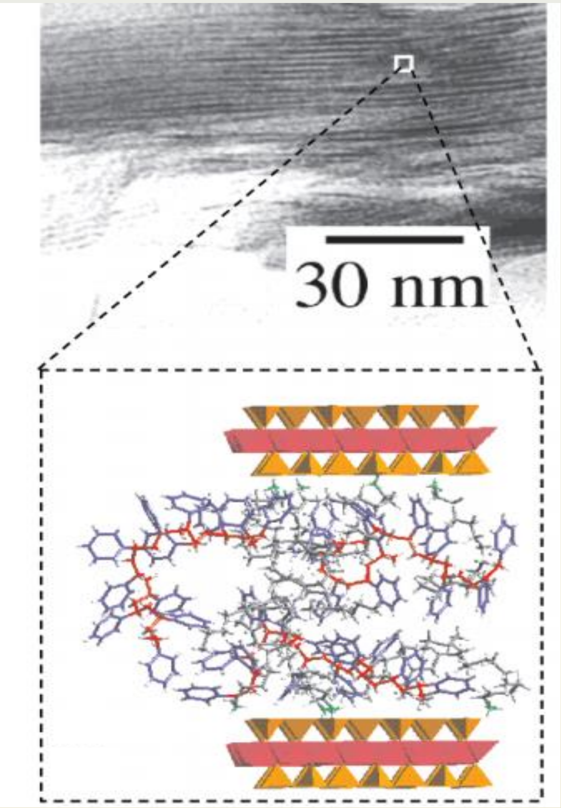

Phase separated *Intercalated* *Exfoliated*

Fig. 1. Schematic representation of different polymer/silicate hybrid structures.

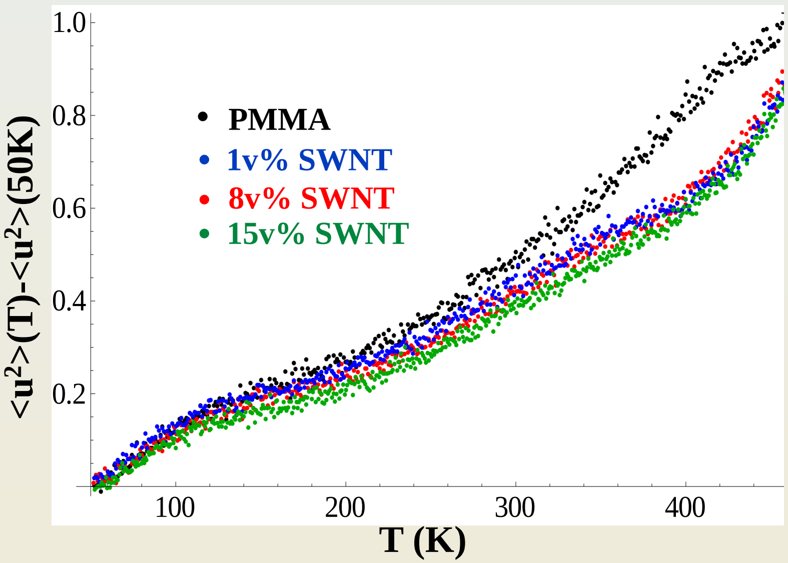


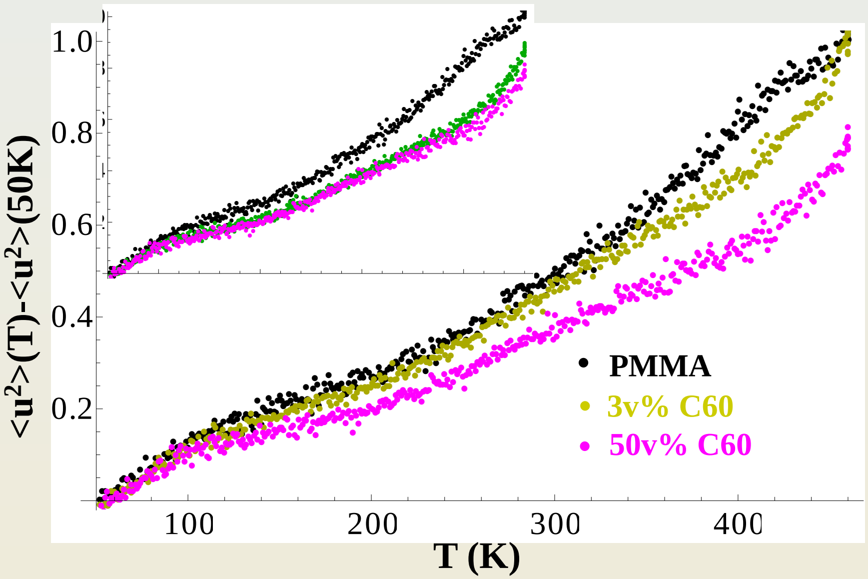




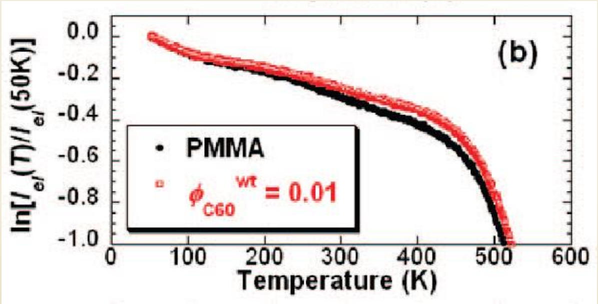
Giannelis, Krishnamoorti & Manias (1999), Polymer-Silicate Nanocomposites: Model Systems for Confined Polymers and Polymer Brushes

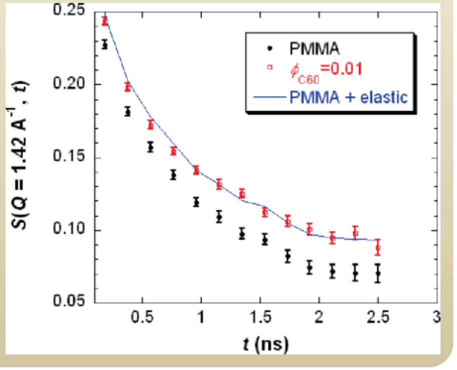
Comparison with C60 and related literature





- gradual decrease in mean-square displacements below percolation
- Upon percolation, the local motions of the non-interfacial units are dynamically arrested
- the resistance to displacements in polymeric systems is known as plasticization

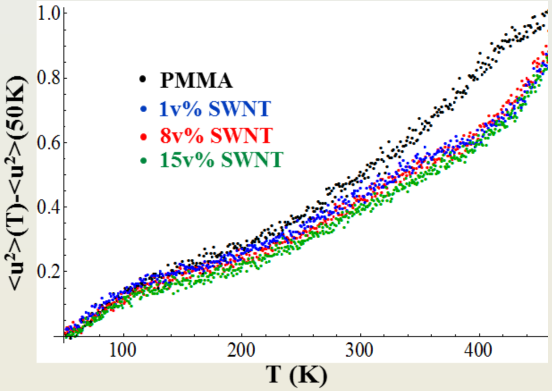


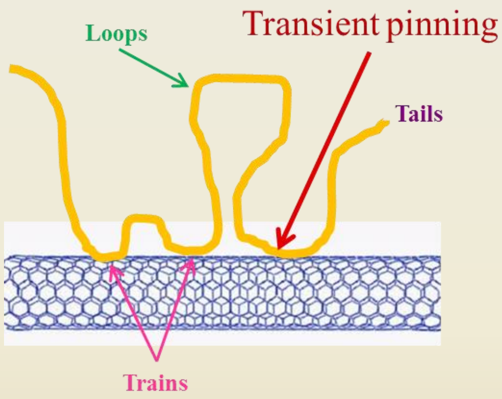


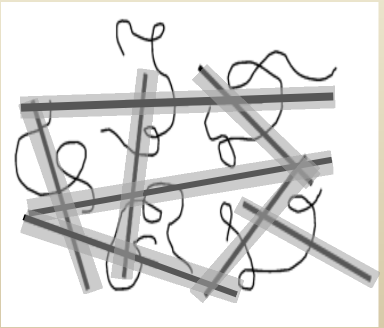
Kropka, P. Green et al. *Nano Lett.*, Vol. 8, **2008**

Concluding Remarks

- Favorable interactions between PMMA and carbon fillers cause remarkable shifts in Tg of their composites and pin the polymer segments at the filler surface
- Our data supports a picture of two dynamic populations: interfacial segments experiencing a transient pinning and non-interfacial segments that are mobile
- In a percolated network the range of motion of the non-interfacial segments is remarkably suppressed relative to the pure polymer but is hardly affected by the compactness of the network. This is known as **kinetic arrest**.
- The transient pinning of polymer segments affects not only the local polymer mobility but also the longer-range structural relaxations due to the connectivity of the chains
- Our results suggest that interfacial PMMA/carbon attraction would result in a slowdown of physical ageing of such composites, which gets further enhanced with percolation

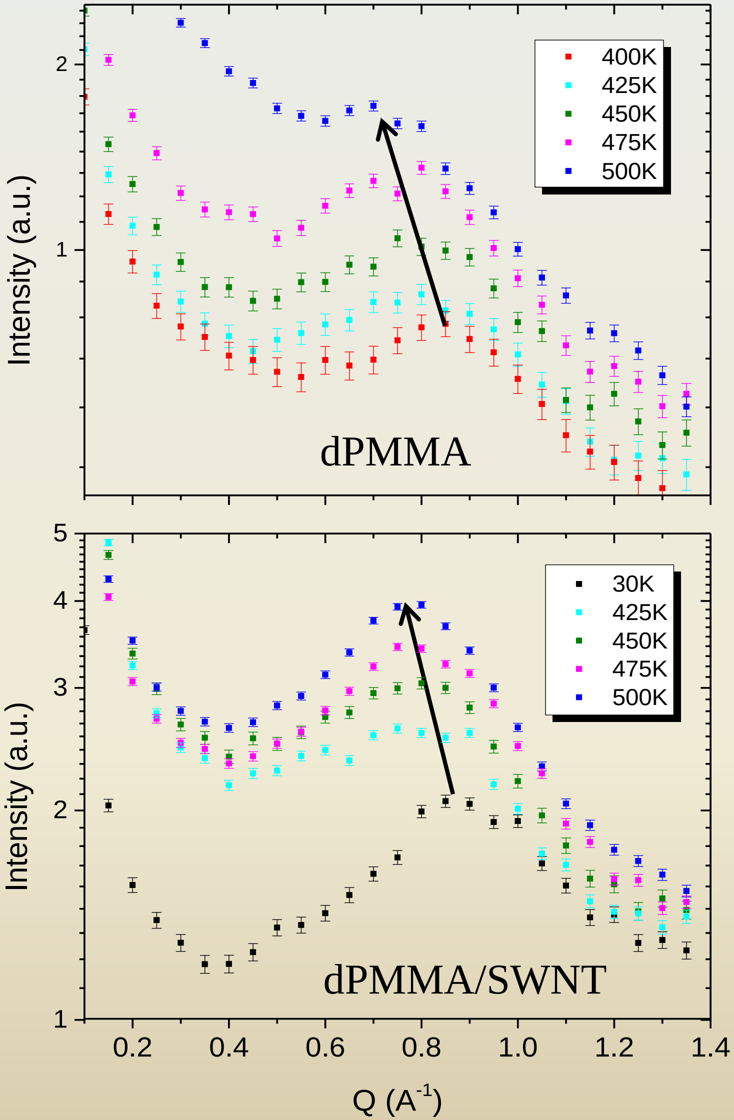


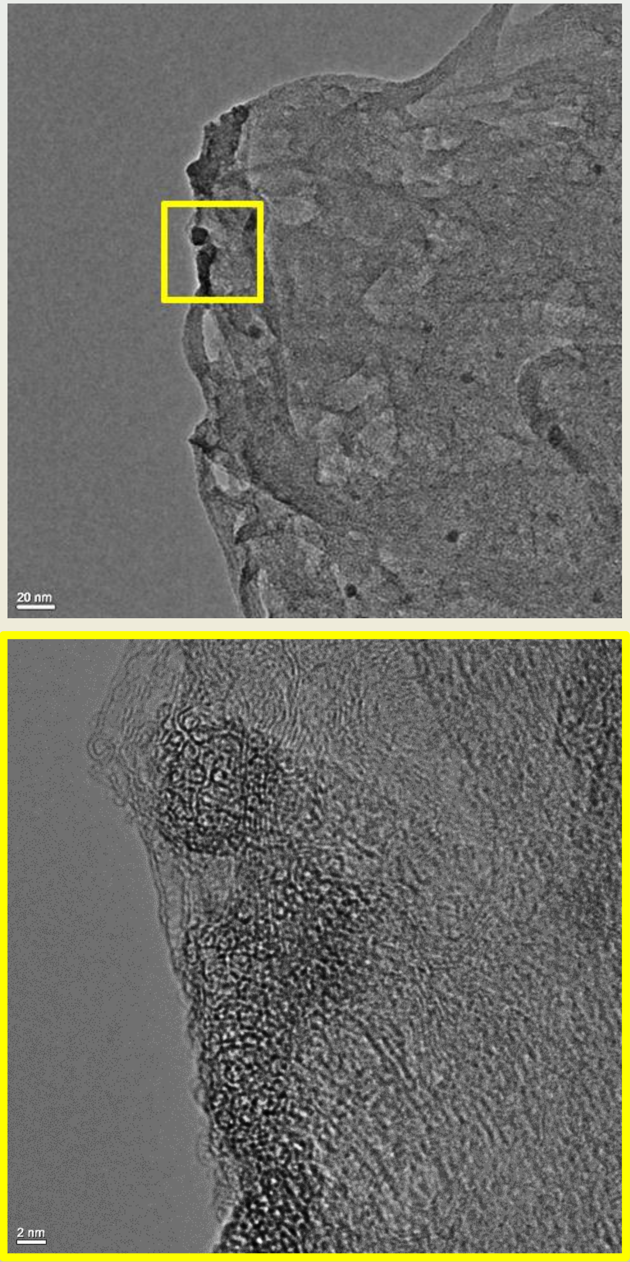


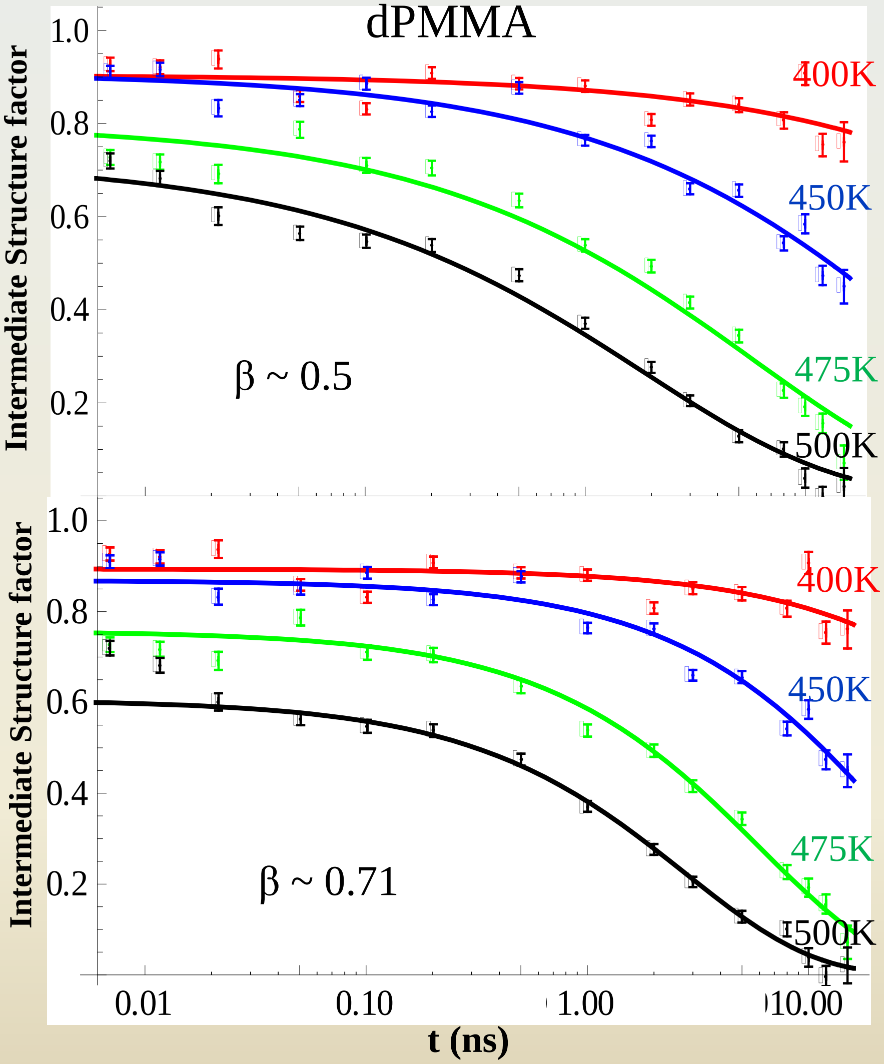


Thank you!

Questions?


Intensity (a.u.)
2
1
400K
425K
450K
475K
500K
dPMMA
Intensity (a.u.)
5
4
3
2
1
30K
425K
450K
475K
500K
dPMMA/SWNT
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Q (A^{-1})


20 nm
2 nm


dPMMA
Intermediate Structure factor
1.0
0.8
0.6
0.4
0.2
400K
450K
475K
500K
β ~ 0.5
Intermediate Structure factor
1.0
0.8
0.6
0.4
0.2
400K
450K
475K
500K
β ~ 0.71
0.01
0.10
1.00
10.00
t (ns)