Chain Entanglements in Homopolymer Melts and Binary Blends

Jun-ichi Takimoto, Yuta Suzuki, Atsushi Higuchi, Seiji Imai,

Sathish K. Sukumaran

sa.k.sukumaran@gmail.com; sathish@yz.yamagata-u.ac.jp

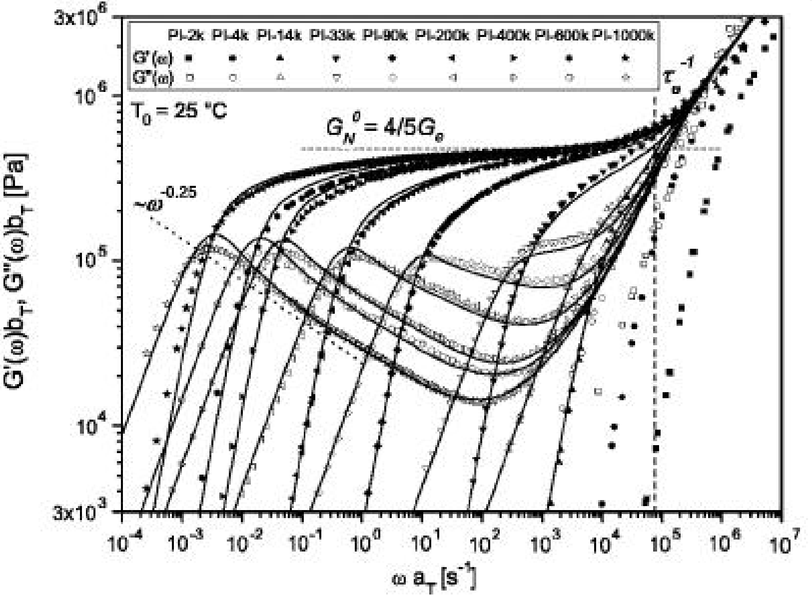
Graduate School of Organic Materials Science
Yamagata University, Yonezawa, Japan

Acknowledgements:
Discussions: Hiroshi Watanabe, Yumi Matsumiya
Funding: Japan Society for the Promotion of Science (Kakenhi)

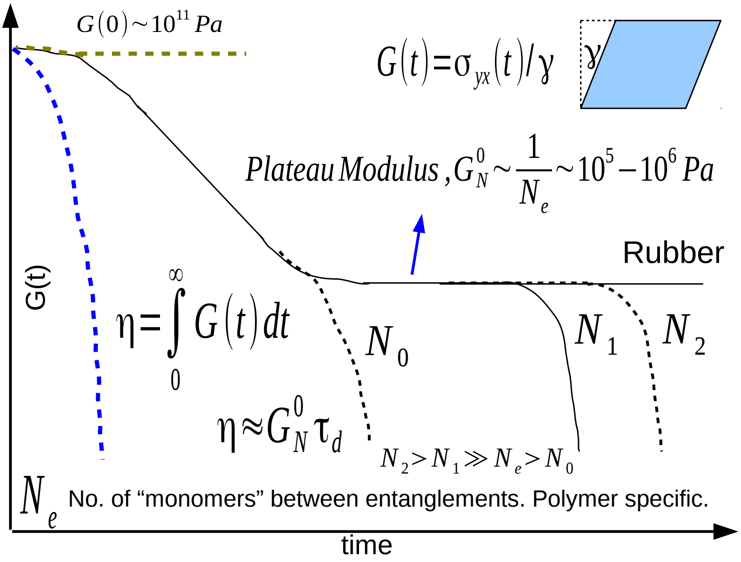
Outline

Outline

Rheology and Entanglements



Macroscopic property - Relaxation Modulus



Entanglement molecular weights of various polymer melts

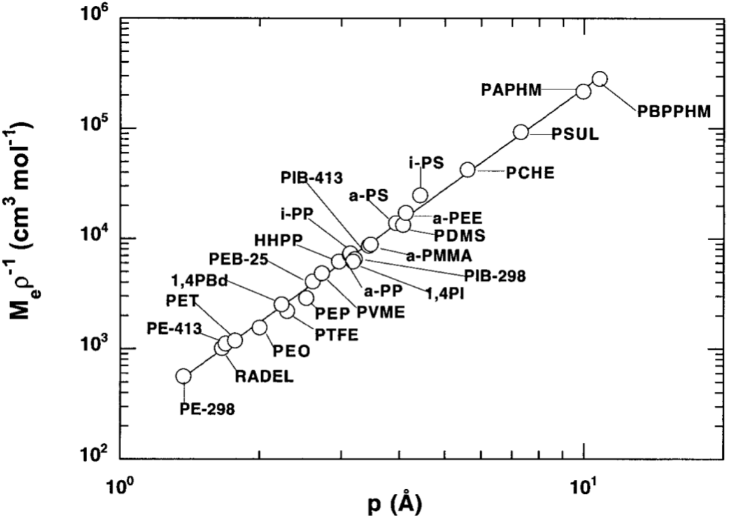
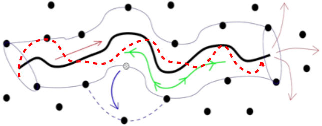


Figure 1. $M_e\rho^{-1}$ vs. p for assorted polymers.

Fetters, L. J.; Lohse, D. J.; Graessley, W. W. J. Polym. Sci., Part B, 37, 1023 (1999)

Reptation and the Tube model



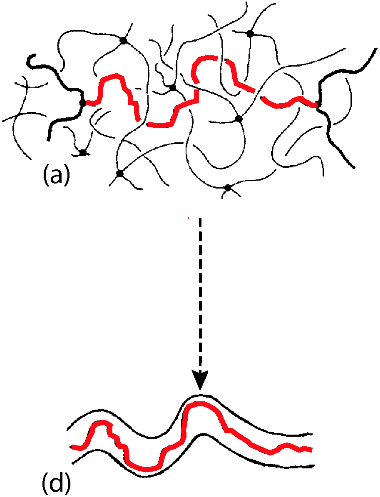
Other chains constrain motion perpendicular to the backbone. Assume the chain moves within a tube.

Motion along the tube axis (primitive path) is not hindered. The chain executes a 1-d RW along the tube axis (Reptation).

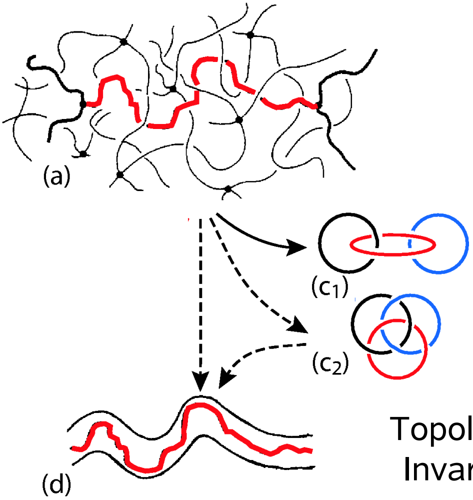
RW on a RW gives $\tau_d \sim N^3$ (N monomer units) and high viscosity ($\eta \sim N^3$)

Tube model needs one extra input. **Diameter of the tube (d_T)** - related to the length of the primitive path.

Melt → Tube: Different Approaches

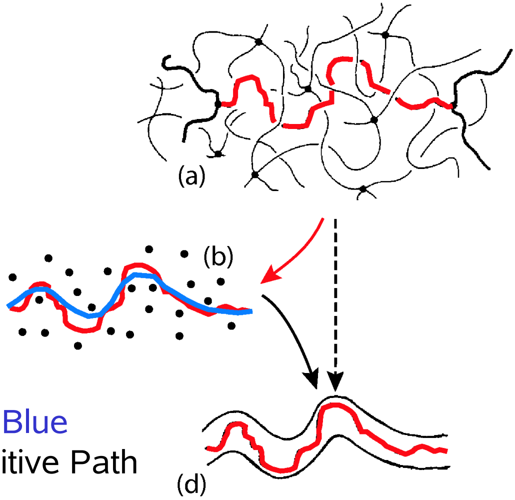


Different Approaches: Knot theory



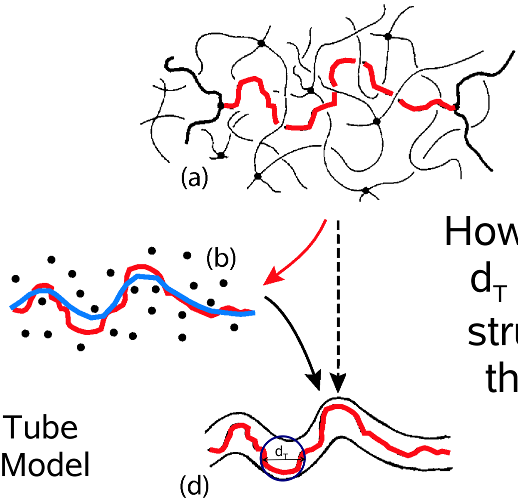
Topological Invariants

Different Approaches: Primitive Path



Blue
Primitive Path

So what's missing?



How to obtain d_T from the structure of the melt?

Tube Model

Experiment: suggests "Universality"

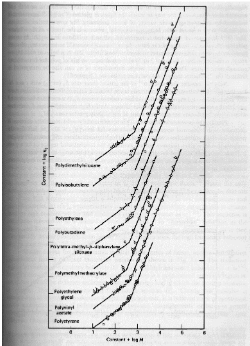
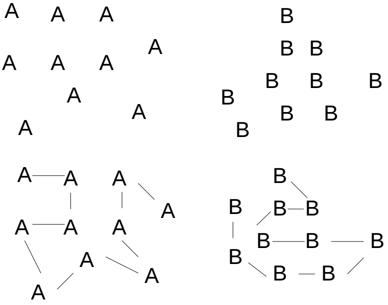


FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, 5, 261–357 (1968).]

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids Vol. 1"

for $N < N_c$, $\eta \sim N$

for $N > N_c$, $\eta \sim N^{3.4}$



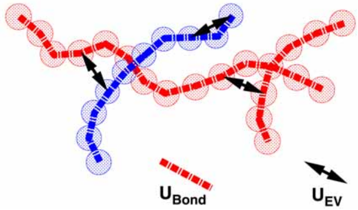
Relevant Features

Connectivity (polymer!), flexibility, liquid-like local structure, mutual uncrossability of chain backbones.

Bead-spring Models

Bead-spring model
(K.Kremer & G.S. Grest)

- Dense monomeric liquid
- Flexible chains

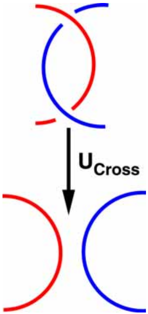


$$\left\langle r_N^2 \right\rangle \approx c_\infty b^2 (N-1)$$

$$c_\infty = 1.86$$

$$b = 0.97\sigma$$

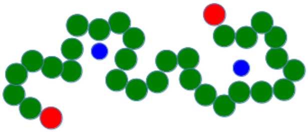
- Topology conservation



$$U_{Cross} \approx 75 k_B T$$

Finding the Primitive Paths

Fix the ends of the chain in space

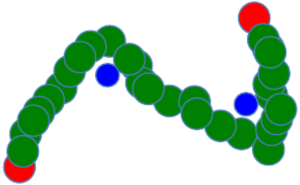


⇓ ⇓

Remove the slack in the chain contour
Do not allow the chains to cross each other

⇓ ⇓

Obtain the primitive path mesh



Everaers et al., Science 303, 823 – 826 (2004)
Kröger, Computer Physics Communications 168, 209 – 232 (2005)

Chain in MD box

Figure: Stiff Chain

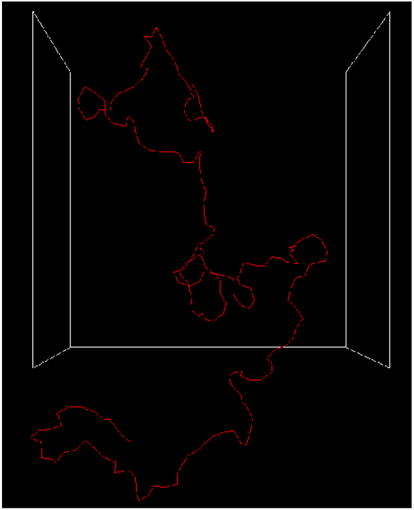
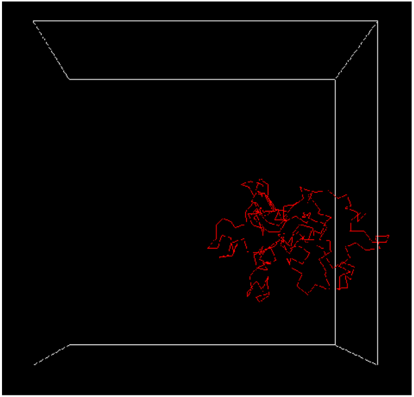
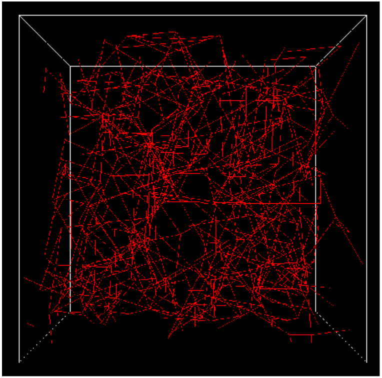
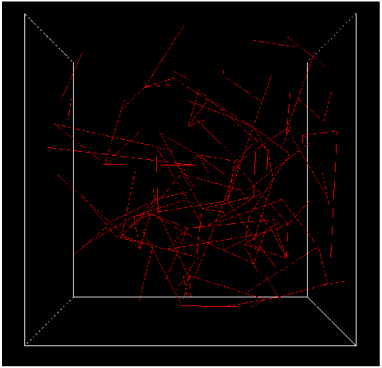


Figure: Flexible Chain



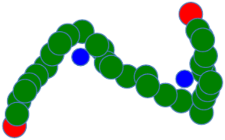
Configuration after Topological Analysis



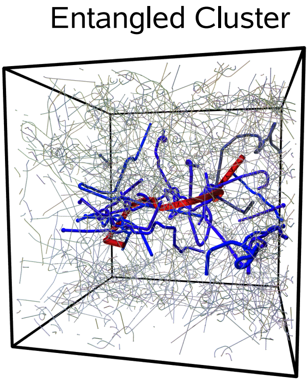


Chains: Straight segments + sharp kinks

Kinks = Entanglements (?)



From Primitive Paths to Physical Properties



Tube diameter

$$d_T = a_{pp} = \langle R^2 \rangle / L_{pp}$$

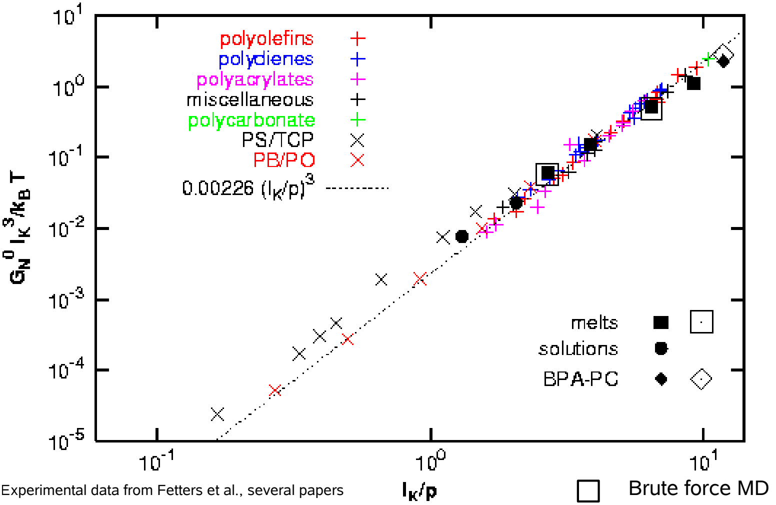
Measure L_{pp}. Calculate d_T.

$$G_N^0 = \frac{4}{5} \frac{k_B T}{p a_{pp}^2} = \frac{4}{5} \frac{\rho k_B T}{N_e}.$$

Can calculate G_N^0 and N_e.

Melt Configuration to Plateau Modulus using MD

Experiments/Simulation Comparison



Experimental data from Fetters et al., several papers

SKS, Grest, Kremer, Everaers, *J. Polym. Sci. B* (2005)
Everaers, SKS, Grest, Svaneborg, Sivasubramanian, Kremer, *Science* 303, 823 (2004)

Outline

Entanglements in Melts & θ Solutions: Conjectures

Melts: Packing Ansatz Fixed number of segments in entanglement volume

Y. H. Lin, *Macromolecules*, 20, 3080 (1987)

T. A. Kavassalis and J. Noolandi, *Phys. Rev. Lett.* 59, 2674 (1987)

θ Solutions: Fixed number of pairwise contacts in entanglement volume

R. H. Colby and M. Rubinstein, *Macromolecules*, 23, 2753 (1990)

Melts: Equivalence of Packing Ansatz and Pairwise Contacts

S. T. Milner, *Macromolecules*, 38, 4929 (2005)

Pairwise Entanglements (Sliplink-like)

S. F. Edwards, *Proc. Phys. Soc.* 92, 9, (1967)
P.-G. de Gennes, *J. Phys. Lett. (Lee Ulis, Fr.)* 35, L-133 (1974)

F. Brochard and P.-G. de Gennes, *Macromolecules* 10, 1157 (1977)

Packing Ansatz 1: Lin-Kavassalis/Noolandi

n_{seg}: Number of segments in a cube of side l

$=$ (Number density of segments with N_K steps)(volume of cube of side l)

$$n_{seg} = \frac{\rho_K}{N_K}\, l^3$$

ρ_K: Number density of Kuhn steps
N_K: Number of Kuhn steps in one segment
l: end-to-end distance of the segment

Lin-Kavassalis/Noolandi Conjecture: Entanglement happens when

$$n_{seg} = n^* = \frac{\rho_K}{N_{e,K}}\, a^3$$

n^*: independent of polymer species!
$N_{e,K}$: number of Kuhn steps in one entanglement segment
a: End-to-end distance of the entanglement segment (Tube Diameter)

Packing Ansatz 2: Packing Length

One Gaussian "segment": end-to-end distance, a

$$a^2 = N_{e,K} l_K^2$$

N_K: Number of Kuhn steps in one segment; l_K: Kuhn length

$N_{e,K}$: number of Kuhn steps in one entanglement segment

Using $n^* = \frac{\rho_K}{N_{e,K}} a^3$, we get $\boxed{\frac{N_{e,K}}{\rho_K} = \frac{(n^*)^2}{\rho_K^3 l_K^6}}$ & $\boxed{a = \frac{n^*}{\rho_K l_K^2}}$

$N_{e,K}$, a and packing length, l_p

$$\boxed{l_p \equiv \frac{1}{\rho_K l_K^2}} \Rightarrow \boxed{\frac{N_{e,K}}{\rho_K} = (n^*)^2 l_p^3} \ \& \ \boxed{a = n^* l_p}$$

Binary Blends: Mixing rule for the Tube Diameter

Segment number density

$$\text{Melt}: \rho_{seg} = \frac{\rho_K}{N_{e,K}} \Rightarrow \text{Blend}: \rho_{seg,b} = \phi_1 \frac{\rho_{K1}}{N_{e,K1}} + \phi_2 \frac{\rho_{K2}}{N_{e,K2}}$$

ϕ_j: volume fraction of component j

Packing ansatz: Lin-Kavassalis/Noolandi

Number of entanglement segments in the entanglement volume $= n^*$

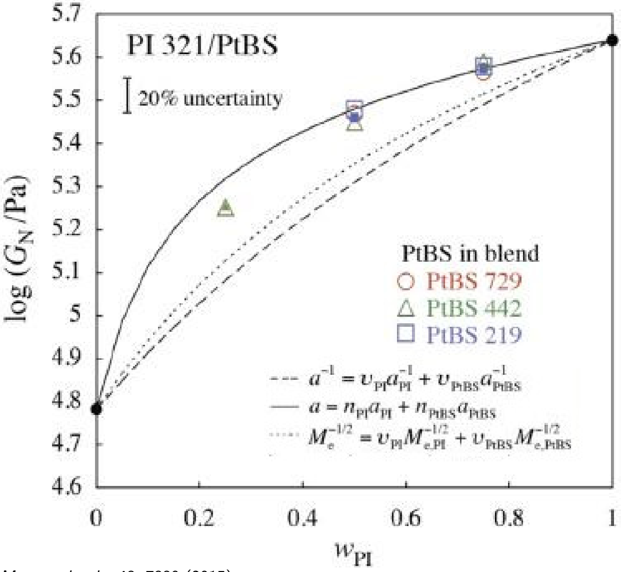
$$\rho_{seg,b}\, a_{b,1}^3 = \rho_{seg,b}\, a_{b,2}^3 = n^* \Rightarrow a_{b,1} = a_{b,2} \equiv a_b$$

Harmonic average (Lin-Kavassalis/Noolandi)

$$\frac{1}{a_b} = \frac{\phi_1}{a_1} + \frac{\phi_2}{a_2}$$

a_j: tube diameter of component j homopolymer melt

Binary Blends: Experiments – Plateau Modulus



Y. Matsumiya et al., *Macromolecules* 48, 7889 (2015)

Binary Blends: Mixing rules

Harmonic average (Lin-Kavassalis/Noolandi)

$$\frac{1}{a_b} = \frac{\phi_1}{a_1} + \frac{\phi_2}{a_2}$$

ϕ_j: volume fraction of component j

a_j: tube diameter of component j homopolymer melt

Kuhn number fraction

$$a_b = f_{K,1}\, a_1 + f_{K,2}\, a_2$$

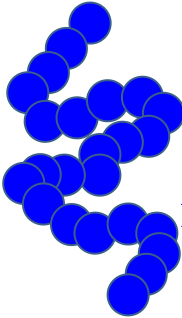
$f_{K,j}$: number fraction of Kuhn segments of component j

How to understand the experiments?

Q. Chen et al. *Macromolecules* 41, 8694 (2008); H. Watanabe et al. *Macromolecules* 44, 1585 (2011)
Y. Matsumiya et al., *Macromolecules* 48, 7889 (2015)

Outline

cis-Poly(isoprene) (PI) & Poly(p-tert-butyl styrene) (PtBS)



PI

a ≈ 5.8 nm

Tg ≈ – 70°C

Stiffness

Flexible Stiff

Monomer size

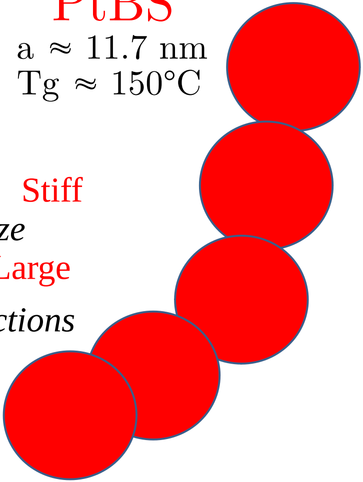
Small Large

Specific Interactions

PtBS

a ≈ 11.7 nm

Tg ≈ 150°C



H. Watanabe, O. Urakawa, "Component Dynamics in Miscible Polymer Blends", Functional Polymer Blends: Synthesis, Properties, and Performance ed. Mittal (2012)

Outline

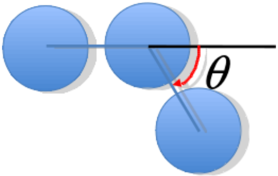
Molecular Dynamics Simulations

Simulation Model

Kremer-Grest model + bond angle potential

Vary the stiffness of the chain

$$U(\theta) = k_\theta \left(cos\theta - cos\theta_0\right)^2$$



$k_\theta = 2.0$

Blend 1

$\theta_0 = 0^\circ$ – "stiff"

$\theta_0 = 90^\circ$ – "flexible"

Blend 2

$\theta_0 = 20^\circ$ – "stiff"

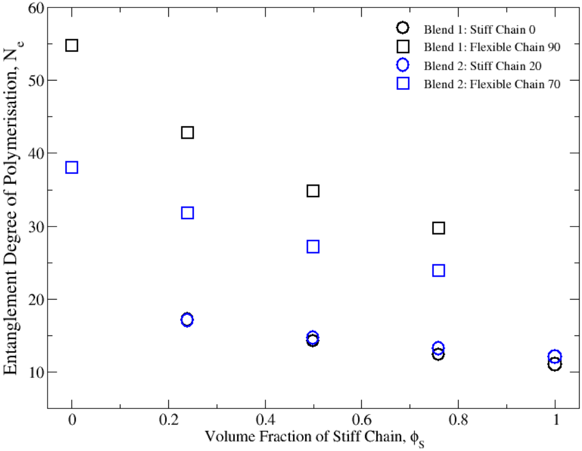
$\theta_0 = 70^\circ$ – "flexible"

Number of beads per chain, N = 200

Number of chains = 50

Simulations using LAMMPS and Cognac

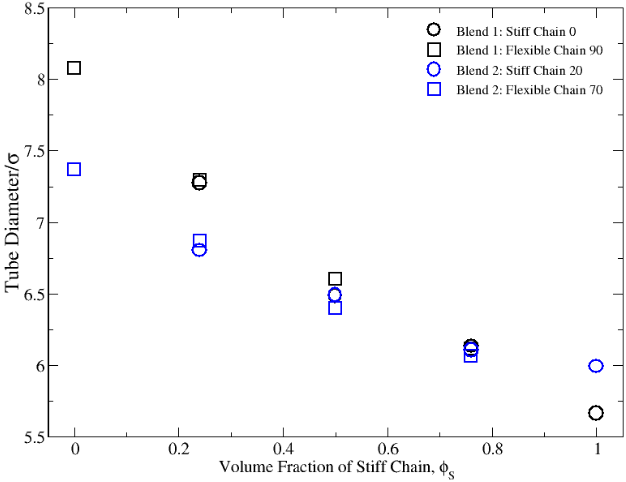
Binary Blends: Entanglement length (from Z1)



N_e of flexible chain **decreases** upon blending with a stiff chain

N_e of stiff chain **increases** upon blending with a flexible chain

Binary Blends: Tube Diameter



Tube diameters of both components are approximately equal !

Binary Blends: Mixing Rules

Harmonic average (Lin-Kavassalis/Noolandi)

$$\frac{1}{a_b} = \frac{\phi_1}{a_1} + \frac{\phi_2}{a_2}$$

ϕ_j: volume fraction of component j

a_j: tube diameter of component j homopolymer melt

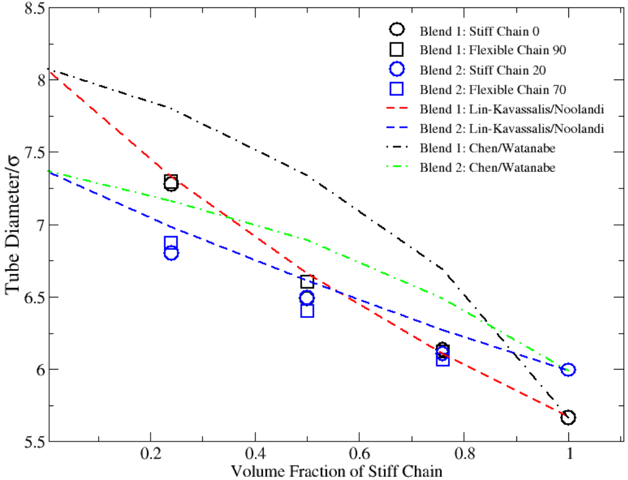
Kuhn number fraction

$$a_b = f_{K,1}\, a_1 + f_{K,2}\, a_2$$

$f_{K,j}$: number fraction of the Kuhn segments of component j

Q. Chen et al. *Macromolecules* 41, 8694 (2008); H. Watanabe et al. *Macromolecules* 44, 1585 (2011)
Y. Matsumiya et al., *Macromolecules* 48, 7889 (2015)

Binary Blends: Tube diameter – compare mixing rules



Mixing rule

The harmonic average mixing rule (Lin-Kavassalis/Noolandi) works better

Summary: Blends of chains with different stiffness

Component tube diameters

Tube diameter of the two components are approximately $\boxed{\text{equal}}$
$a_{b,1}(\phi_1) = a_{b,2}(\phi_1)$

Mixing rule for the blend tube diameter

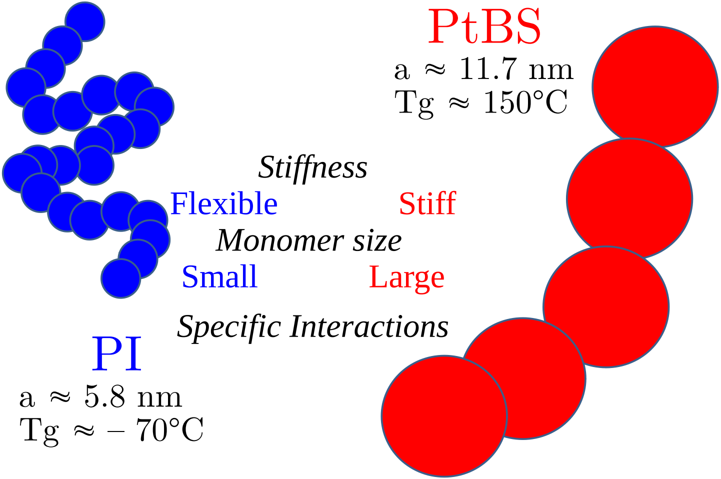
$\frac{1}{a_b} = \frac{\phi_1}{a_1} + \frac{\phi_2}{a_2}$
The harmonic average mixing rule works better

Origin of the harmonic average mixing rule

Straightforward extension of the Lin-Kavassalis/Noolandi conjecture for homopolymer melts

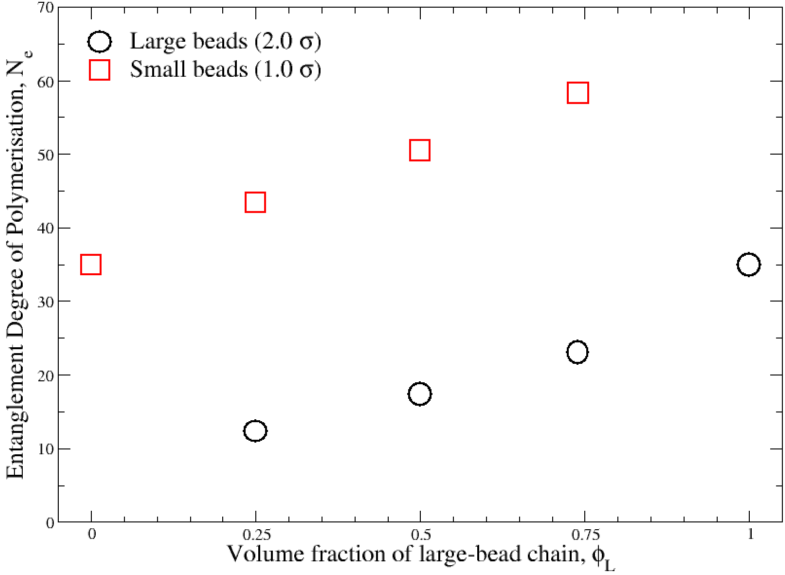
Outline

cis-Poly(isoprene) (PI) & Poly(p-tert-butyl styrene) (PtBS)

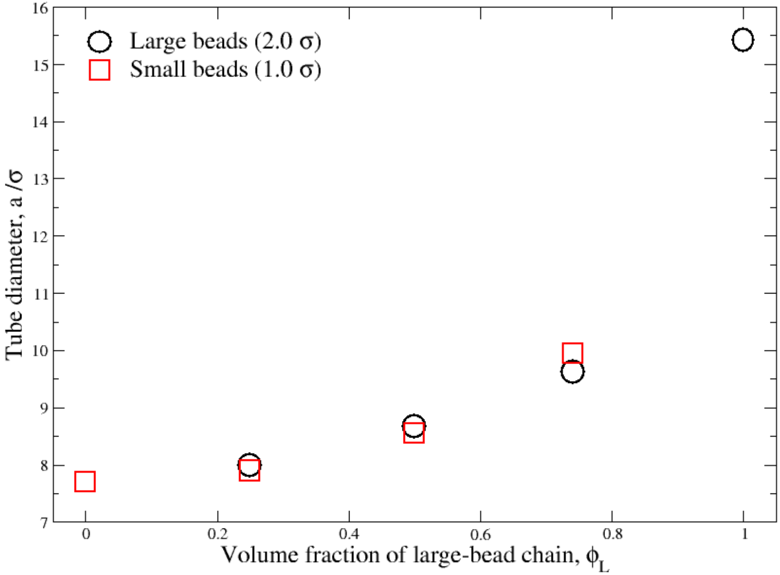


H. Watanabe, O. Urakawa, "Component Dynamics in Miscible Polymer Blends", Functional Polymer Blends: Synthesis, Properties, and Performance ed. Mittal (2012)

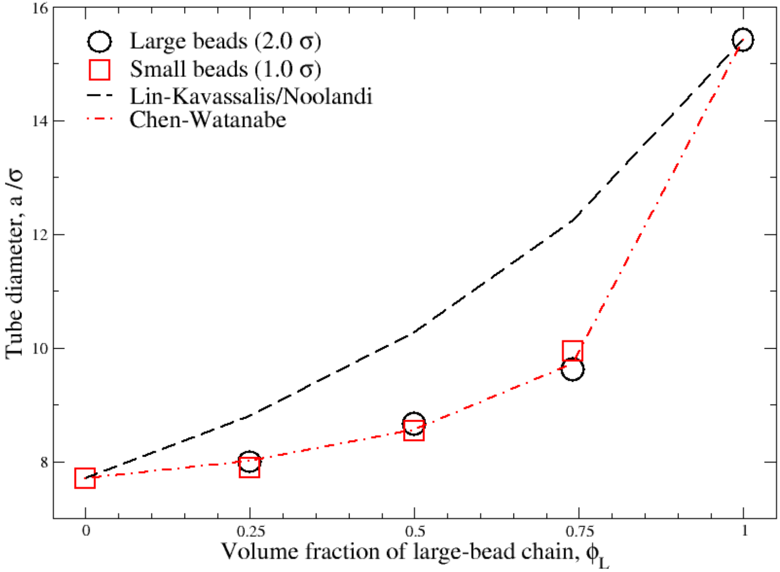
Large-small Blends: Entanglement Length (from Z1)



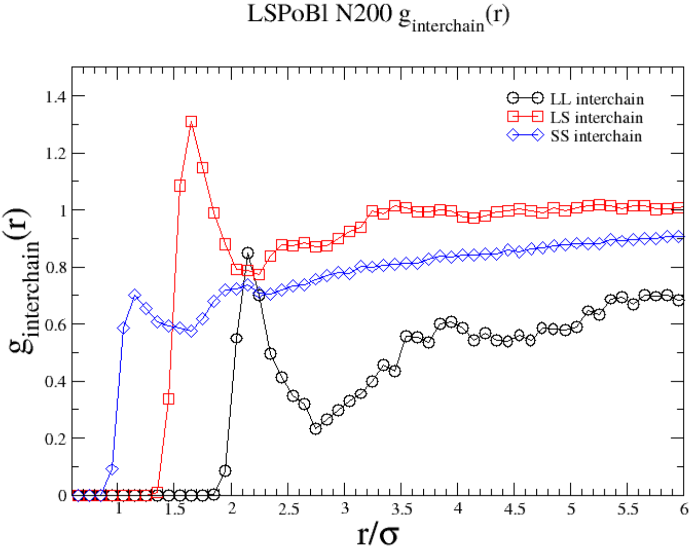
Large-small Blends: Tube Diameter



Large-small Blends: Mixing Rules



Mixing rule: Origin of the deviation? – Interchain g(r)



Summary: Blends with different monomer sizes

Component Tube Diameters

Tube diameter of the two components are approximately equal

$a_{b,1}(\phi_1) = a_{b,2}(\phi_1)$

Mixing rule

$a_b = f_{K,1}\ a_2 + f_{K,2}\ a_2$

Kuhn fraction average mixing rule (Chen-Watanabe) works better

Origin of the Kuhn fraction mixing rule (Chen-Watanabe)

Nonuniform mixing: Effect of local structure

Chain expansion in the blend (when compared to the melt)?

Other factors?