

# Relaxation Behavior of Network Polymers with Random Connectivity

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## 1 Introduction

- Adhesive Bonding Technology as a Key to Multi-Materialization
- Theoretical Models for Rubber
- Objectives

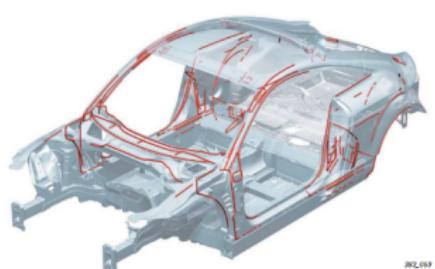
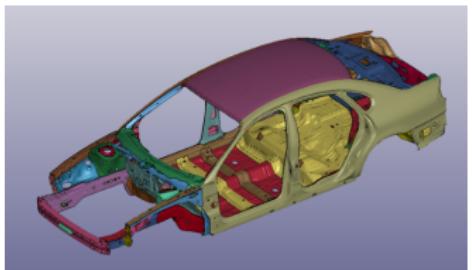
## 2 Simulation

- Generation Recipe of Random Networks
- Phantom and KG Chains as Strands
- Simulation Conditions

## 3 Results

- Networks with Phantom Chains
- KG Chain Networks
- Relaxation in KG Networks

# Adhesive Bonding Technology



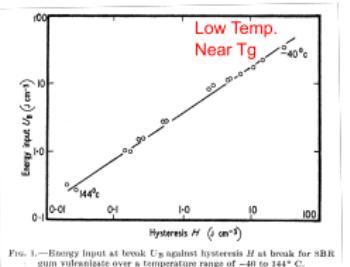
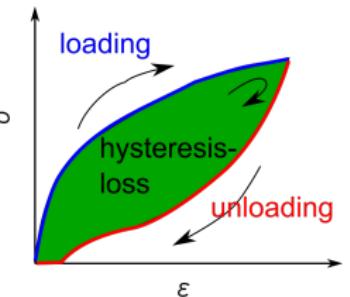
- For Energy conservation
  - weight reduction of cars
  - multi-materialization
  - adhesive bonding technology is a key
- durability in long-term use is important
  - Especially for fatigue tests
  - reliability of polymer materials is still ambiguous

Let me start with this slide as background.

1. focusing on Energy conservation
  - weight reduction of cars is a big issue.
  - for that purpose, multi-materialization, using Aluminum, Magnesium, CFR(T)Ps is discussed.
  - (POINT) these different colors
  - in the process, adhesive bonding technology is a big key.
  - these red lines are the adhesive are used for bonding.
2. requirements for network polymers used as adhesives are
  - not only high primary mechanical properties
  - but also the ability to withstand fatigue tests

# Mechanical Hysteresis Loss and Fracture Energy

- Mechanical Hysteresis Loss
  - Reduced stress on unloading
  - Energy dissipation during cycle
  - Positive correlation with fracture energy<sup>a</sup>
- The origin of Hysteresis Loss<sup>b</sup>
  - Viscoelastics
  - Crystallization
  - Derived by added filler



<sup>a</sup>K.A.Grosch, J.A.C.Harwood, A.R.Payne,  
Rub. Chem. Tech., 41, 1157(1968)

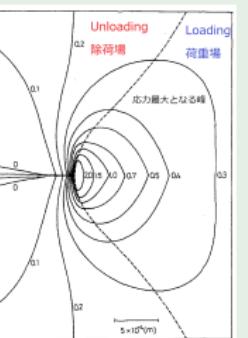
<sup>b</sup>A.R.Payne, J.Poly.Sci.:Sympo., 48, 169(1974)

- Mechanical Hysteresis is illustrated in this figure.
- (POINT)
- this green area is equivalent to Energy dissipation during cycle
- Positive correlation with fracture energy had been reported by Payne.
- The origin of hysteresis loss is also categorized by Payne
- We focus on this Viscoelasticity based one

# Andrews Theory for Rubber Toughness

## Andrews Theory

- Focused on stress field around the crack<sup>a</sup>
  - Stress Loading zone
  - Unloading one
  - divided by stress maximum line
- On the progress of the crack,
  - stress field is transit
  - Hysteresis Loss  $\Rightarrow$  Energy Dissipation
  - The progress of Crack is Suppressed
- Bigger Hysteresis Loss results in Higher Toughness.



<sup>a</sup>E.H.Andrews, Y.Fukahori, J. of Mat. Sci. 12, 1307 (1977)

- On the fracture of rubber,
- Andrews proposed a model focused on Stress fields around the Crack top area
- stress fields can be divided in two regions, stress loading zone and unloading one.
- (POINT)
- On the progress of the crack,
  - stress field is transit
  - During this transition, Hysteresis Loss is occur and dissipate energy
  - through this process, the progress of Crack is suppressed
- So Bigger Hysteresis Loss results in Higher Toughness.

# Classical Theory of Rubber Elasticity

## Neo-Hookean Model

$$W = C_1(I_1 - 3)$$

against Uniaxial elongation

$$\sigma_{nom} = 2C_1 \left( \lambda - \frac{1}{\lambda^2} \right) = G \left( \lambda - \frac{1}{\lambda^2} \right)$$

## Mooney-Rivlin Model

$$W = C_1(I_1 - 3) + C_2(I_2 - 3)$$

against Uniaxial elongation

$$\sigma_{nom} = 2 \left( C_1 + C_2 \frac{1}{\lambda} \right) \left( \lambda - \frac{1}{\lambda^2} \right)$$

## With or without Junction Points fluctuation

### Affine Network Model <sup>a</sup>

$$G_{affine} = \nu k_B T$$

$\nu$ : Number density of strands in the system

### Phantom Network Model <sup>a</sup>

$$G_{phantom} = \nu k_B T \left( 1 - \frac{2}{f} \right)$$

$f$ : Functionality of Junction Points

<sup>a</sup>P.J. Flory, Principles of Polymer Chemistry, (1953)

<sup>a</sup>H.M. James, E.J. Guth, Chem. Phys., 21, 6, 1039 (1953)

Here, the classical theories of rubber Elasticity are summarized.

- Considering junction points fluctuation, Phantom Network Model is proposed.
- in this model, Modulus is reduced depending on the functionality of junctions.
- (POINT)
- as this factor, one minus 2 over f: functionality

# Constraint Factors for Junction Points and Strands

## Vicinity of Junction Point

- Junction points are surrounded by many of adjacent strands(x in fig.).
- Fluctuation of junctions are suppressed.



## Effect of other strands (Combination of $G_c$ and $G_e$ )

- Suppress the fluctuation of Junction Point
  - Deviate from Phantom Network Model and higher  $G_c$
- Strands Entangles each other
  - Works as a Junction Point
  - Generate additional  $G_e$

Storage modulus  $G$  is combination of  $G_c$  and  $G_e$

- In the vicinity of Junction Point
  - Junction points are surrounded by adjacent strands.
  - So, Fluctuation of junctions are suppressed.
- Effect is mainly two.
  - One is Suppression of fluctuation of Junction Points
    - Deviation from PNM and higher  $G_c$
  - Other effect is that Strands Entangles each other
    - Entanglements works as a Junction Point
    - Generate additional  $G_e$
  - So, Storage modulus  $G$  is combination of  $G_c$  and  $G_e$
- (CLICK)
- Concerning these effect, two approaches were proposed
  - One is Constrained Junction model, on the uniaxial deformation, constraints are released and  $G$  approaches to  $G_c$
  - Other is topological effect, such as trapped entanglements
    - those were counted as  $G_e$

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## Vicinity of Junction Point

- Junction points are surrounded by many of adjacent strands(x in fig.).
- Fluctuation of junctions are suppressed.



## Effect of other strands (Combination of $G_c$ and $G_e$ )

- Constrained Junction Model
  - $G$  approaches to  $G_c$ .<sup>a</sup>
- Topological relationships
  - Contribution of entanglement.<sup>b</sup>

$$G_e = T_e G_N^0$$

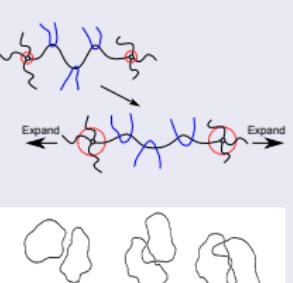


Figure 4. Three topological relationships between two closed loops.  
(a) not entwined, (b) once entwined, (c) twice entwined.

- In the vicinity of Junction Point
  - Junction points are surrounded by adjacent strands.
  - So, Fluctuation of junctions are suppressed.
- Effect is mainly two.
  - One is Suppression of fluctuation of Junction Points
    - Deviation from PNM and higher  $G_c$
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<sup>a</sup>P.J.Flory, J.Chem.Phys., 66, 12, 5720 (1977)

<sup>b</sup>D.S.Pearson and W.Graessley, Macromol., 11, 3, 528 (1978)

# Recent approach for Constraints (Entanglements)

- Diffused-Constraint Model
  - Confining potential affect all points along the chain.<sup>a</sup>
- Nonaffine Tube Model
  - Improved model of "Edwards' Tube Model".<sup>b</sup>
- Slip-tube Model
  - A pairwise interaction of chains is introduced.<sup>c</sup>

- These three models are the major recent approach for a evaluation of constraints.
- All recent models are based on Phantom Network Model.
- The latest Rubinstein's Slip-tube model" seems proper.
- (Point and CLICK)
- In that model,  $G_c$  and  $G_e$  is separated simply.
- Contribution of  $G_e$  will be reduced depending on deformation

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<sup>a</sup> A. Kloczkowski, J.E. Mark, B. Erman, Macromol., 28, 5089 (1995)

<sup>b</sup> M. Rubinstein, S. Panyukov, Macromol., 30, 25, 8036 (1997)

<sup>c</sup> M. Rubinstein, S. Panyukov, Macromol., 35, 6670 (2002)

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- Slip-tube Model
  - A pairwise interaction of chains is introduced.<sup>c</sup>

$$f^*(\lambda^{-1}) = G_c + \frac{G_e}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35}$$
$$G_c = \nu k_B T \left(1 - \frac{2}{\phi}\right), \quad G_e = \frac{4}{7} \nu k_B T L$$

where  $\nu$  is the number density of network chains,  
 $L$  is the number of slip-links per network chain

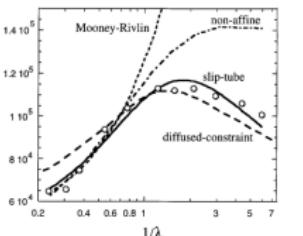


Figure 5. Fit of the data by Pak and Flory<sup>20</sup> on cross-linked polydimethylsiloxane (open circles) by the diffused-constrained model (dashed line), Mooney-Rivlin expression (dotted line), nonaffine tube model (dash-dotted line), and the slip-tube model (solid line).

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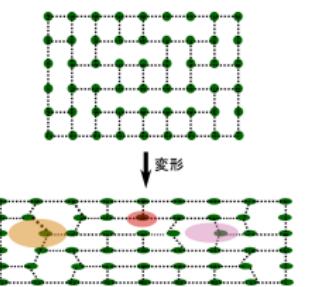
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<sup>b</sup>M. Rubinstein, S. Panyukov, *Macromol.*, 30, 25, 8036 (1997)

<sup>c</sup>M. Rubinstein, S. Panyukov, *Macromol.*, 35, 6670 (2002)

# Random Networks as a key for PNM

- Introduction of Random Connectivity.
- Criteria for PNM is fulfilled<sup>a</sup>.
  - the mean values  $\bar{r}$  of strands are fluctuate
  - fluctuations  $\Delta r = r - \bar{r}$  are Gaussian
  - the mean-square fluctuations depend only on structure
- Previous Work for Random Network
  - Random endcrosslink for telechelics<sup>b</sup>
  - Primitive Chain Network Simulation<sup>c</sup>



- Introduction of Random Connectivity is known to a key for Phantom Network model.
- As a result, Criteria for PNM is fulfilled
- (POINT)
- these two previous works deal random network
- the networks treated in these work is not so simple, and discussion is complicated.

<sup>a</sup>P. J. Flory, Proc. R. Soc. London. A, 351, 351 (1976)

<sup>b</sup>G.S. Grest, et.al., Non-Cryst. Solids, 274, 139 (2000)

<sup>c</sup>Y. Masubuchi, Nihon Reoroji Gakkaishi, 49, 2, 73 (2021)

# Objectives

- Recent approach for rubber elasticity models are based on Phantom Network Model.
- Introducing random connectivity, MD simulation studies were carried out.
- To investigate the criteria for Phantom Network Model, Two model chains are used.
  - ① Employing phantom chain, basics for PNM is examined.
  - ② Changing the chain to KG Chain, constraints effects are investigated.
    - Excluded Volume Effect
    - No mutual crossing of Strands

This is an objective of this work.

- Recent approach for rubber elasticity models are based on Phantom Network Model.
- Introducing random connectivity, MD simulation studies were carried out.
- To investigate the criteria for Phantom Network Model, Two model chains are used.
  1. Employing phantom chain, basics for PNM is examined.
  2. Changing the chain to KG Chain, constraints effects are investigated.
    - for KG Chain:
    - Excluded Volume Effect is exist
    - and No mutual crossing of Strands
    - Phantom chain has nothing, just connection.

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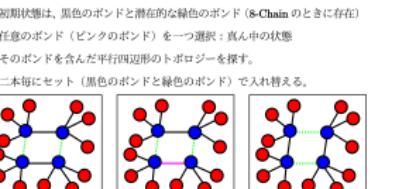
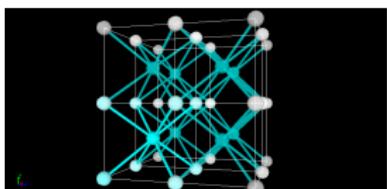
- Generation Recipe of Random Networks
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- Relaxation in KG Networks

# Generation of Initial Structure of Random Networks

- ① 8-Chain Model is used as starting structure in **Real space**.
  - Randomly selected edge is removed until desired functionality.
  - Topological model is generated.
- ② Randomness is introduced in **topological space**.
  - By **edge exchange**, random connectivity is introduced for each node.
- ③ Corresponding real space structure is generated.
- ④ According to e2e distance of strand, system size and multiplicity are set.



- 8-Chain Model is used as starting structure in **Real space**.
  - Randomly selected edge is removed until desired functionality.
  - Topological model is generated.
- Randomness is introduced in **topological space**, by **edge exchange**, random connectivity is introduced for each node.
- Corresponding real space structure is generated from this.
- According to e2e distance of strand, system size and multiplicity are varied to keep  $\rho = 0.85$ .

# Phantom and KG Chains as Strands

- Phantom Chain:
  - No Excluded Volume is set (no segmental interaction).
  - "Force Cap LJ" is set as Angle Potential to enumerate e2e length of KG Chains.
  - Harmonic bond ( $k=1000$ )
- KG Chain:
  - Excluded Volume is set by Repulsive LJ Potential.
  - Bond Potential is set to FENE.
  - Because of above two potentials, No Chain crossing will occur.

- Conditions for Phantom and KG Chains are shown here.
- Important point is,
- for phantom chain,
- Employing "Force Cap LJ" for 1, 3 interaction of inner chain segments,
- the angle is almost the same as KG chain
- and e2e length of KG Chains is emulated in phantom chain.
- the conditions for KG Chain is very popular repulsive one.

# Reluxation of Initial Structure in KG Network

## KG Network: KG chain as strand

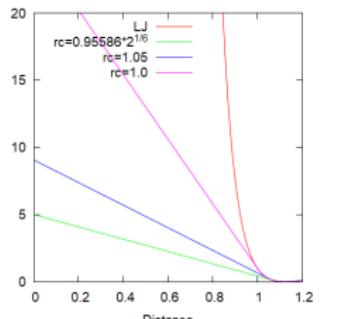
- Relaxation of initial structure is important.

$$U_{KG}(r) = \begin{cases} U_{nonbond} = U_{LJ} \text{ where } r_c = 2^{(1/6)}\sigma \\ U_{bond} = U_{LJ} + U_{FENE} \end{cases}$$

## Initial Structure Relaxation

- According method of Auhl<sup>a</sup>
  - Using force-capped-LJ pot.
  - relaxed by Slow Push Off

$$U_{FCLJ}(r) = \begin{cases} (r - r_{fc}) * U'_{LJ}(r_{fc}) + U_{LJ}(r_{fc}) & r < r_{fc} \\ U_{LJ} & r \geq r_{fc} \end{cases}$$



- force-capped-LJ Pot.
- gradually entangled

<sup>a</sup>R. Auhl et al. J. of Chem. Phys., 119, 12718 (2003)

- For KG model without mutual chain crossing,
- Relaxation of initial structure is important.

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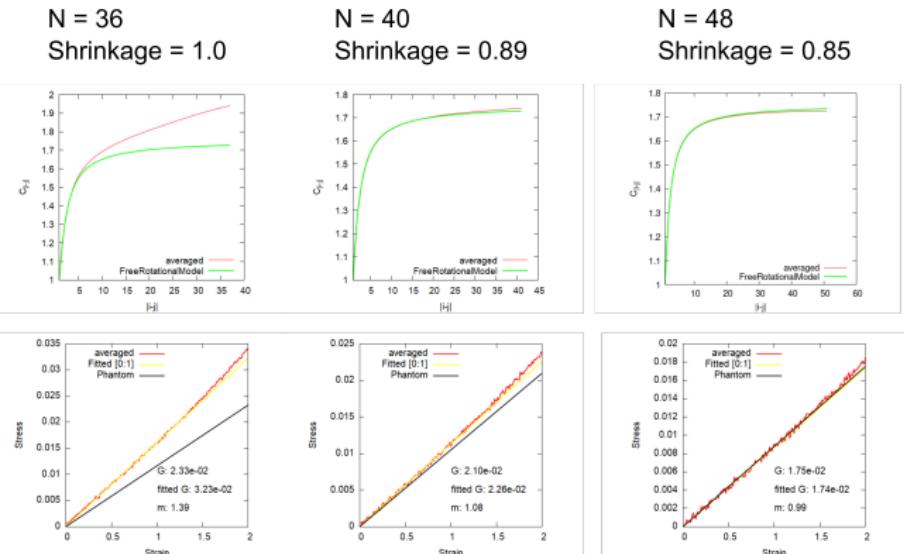
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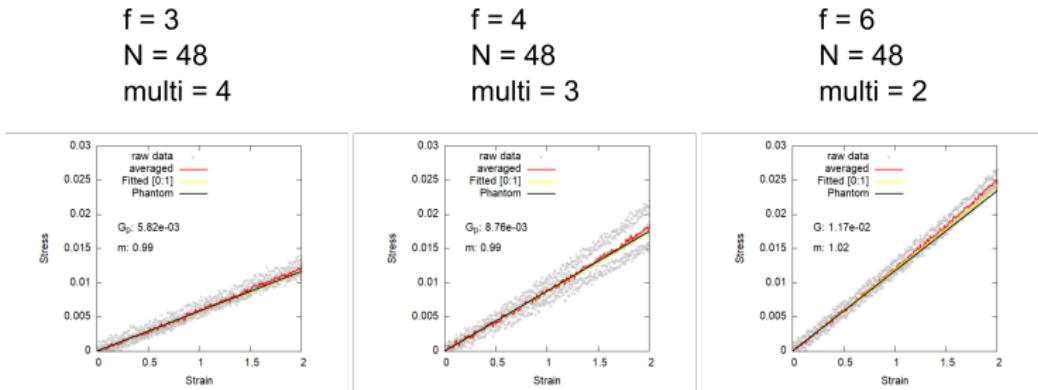
# Strand length Effect for Phantom Chain NW( $f=4$ )

- Strand-length is varied from 36 to 48
- System size is reduced to keep  $\rho = 0.85$



- Keeping the density, Strand length were varied by shrinking the system.
- Shorter chain length resulted in higher modulus.
- (POINT left two)
- With proper chain length,  $N=48$ , nice fit to PNM nature is found.
- These results shows that
- shorter chain reduced fluctuation mobility of junction point and resulted in deviation from PNM.

# Comparison of Functionality ( $f = 3, 4, 6$ )



- With proper chain length,  $N=48$
- functionality effect on modulus were examined and all fit to PNM.
- (POINT all)

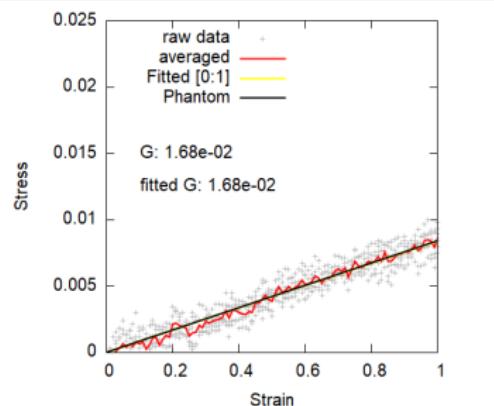
Figure: Comparison of Functionality ( $f = 3, 4, 6$ )

# Mechanical Response for KG Chains( $f=4$ , $N=48$ )

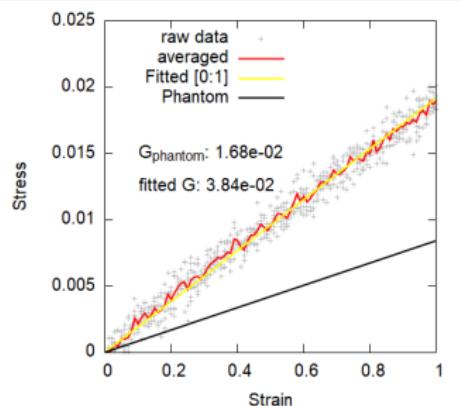
## 4-Chain Random Network with KG Chain

- Excluded Volume Effect by non-bonding LJ Potential.
- No strands mutual crossing by FENE bond.

## Phantom Chain

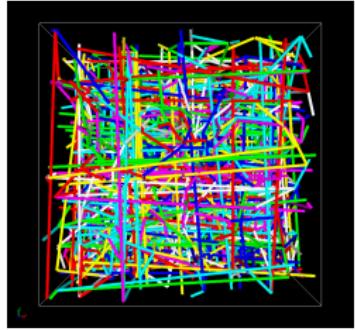


## KG Chain



- based on the results of networks consist of phantom chain.
- KG Network was examined with same strand length( $f=4$  and  $N=48$ ).
- For KG NW, Modulus is much higher than PNM Predict.
- (POINT)

# Analysis of Entanglements in Network: Z1-code



## Comparison with Homopolymer Melt

- Z is number of entanglements per chain

	Homo	4 Chain NW
Segments	50	48
Chains	200	768
Entanglements	204	800
Entangled Chains	134	557
$\langle Z \rangle_{z1}$	1.02	1.04

## Z1-code?

- Z1-code is an algorithm to visualize and count entanglements<sup>a</sup>

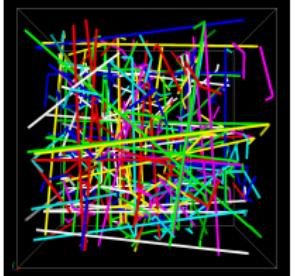
<sup>a</sup>M. Kröger, Comput. Phys. Commun. 168, 209 (2005)

- to investigate for higher modulus,
- Employing Z1-code, number of entanglements per chain Z was calculated.
- the number is almost the same as homo-polymer melts.
- (POINT left two)
- 1.02 and 1.04

# Reduced Entanglements by NPT Model

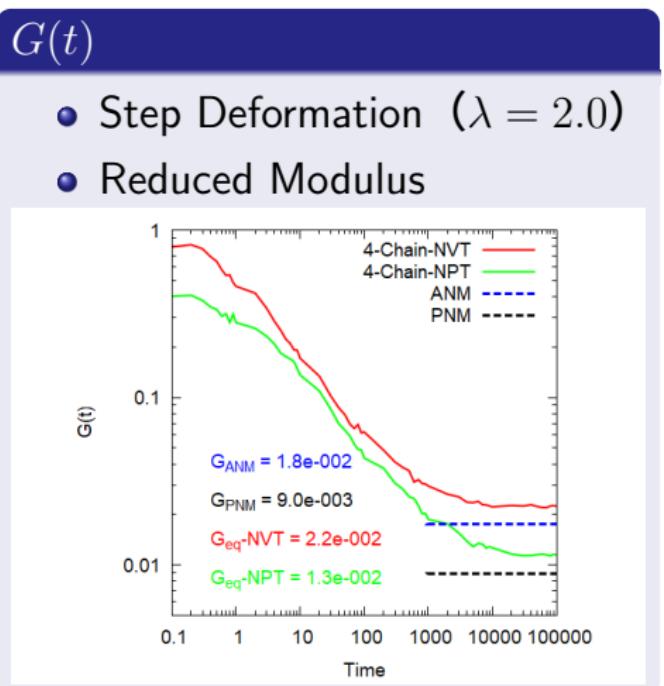
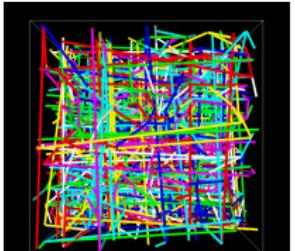
- 4-Chain-NPT

$$\langle Z \rangle_{Z1} = 0.36$$



- 4-Chain-NVT

$$\langle Z \rangle_{Z1} = 1.04$$



- Employing NPT relaxation, number of entanglements are reduced.
- calculated  $\langle Z \rangle_{Z1} = 0.36$
- equilibrated modulus on stress relaxation is much reduced.

# Entanglement effect in Slip-tube Model

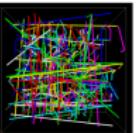
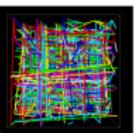
## Entanglement in Slip-tube Model

Theoretical model by Rubinstein<sup>a</sup>

$$G_c = \nu k_B T \left(1 - \frac{2}{\phi}\right), \quad G_e = \frac{4}{7} \nu k_B T L$$

and L is the number of slip-links per network chain

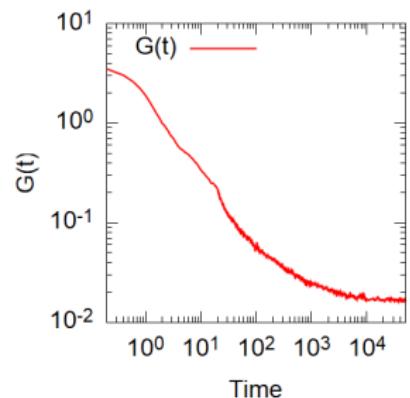
<sup>a</sup>M. Rubinstein, S. Panyukov, Macromolecules, 35, 6670 (2002)

	Ensemble	NPT	NVT
	<i>Chains, <math>\nu</math></i>	<b>768, 0.018</b>	
	$G_c = \nu \times (1 - 2/4)$	0.009	
	Entanglements	278	800
	Entangled Chains	249	557
	$L$	$278/768=0.36$	$800/768=1.04$
	$G_e = 4/7 \times \nu \times L$	0.004	0.011
	$G_{calcd.} = G_c + G_e$	<b>0.013</b>	<b>0.020</b>
	$G_{measd.}$	<b>0.013</b>	<b>0.022</b>

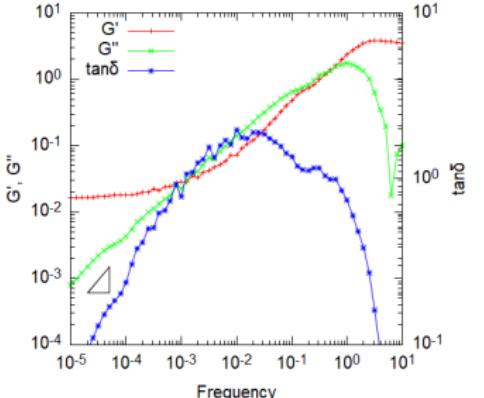
- Adapting Slip-tube model estimation, the measured modulus is fully explained.
- (POINT left two)

# G(t) for Step Shear and Dynamic Rheo-Spectrum

## G(t) for Step Stretch



## Dynamic Viscoelastics

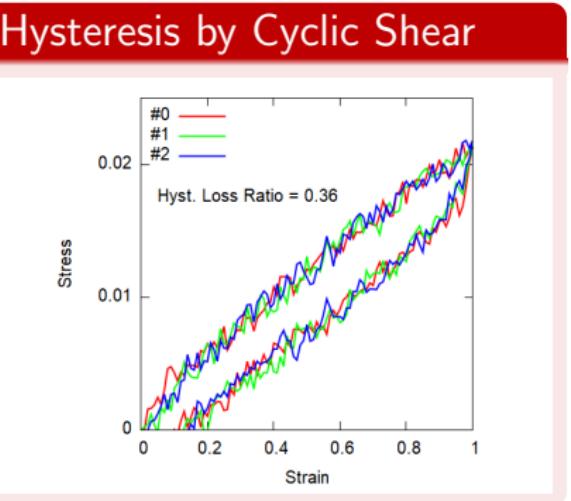
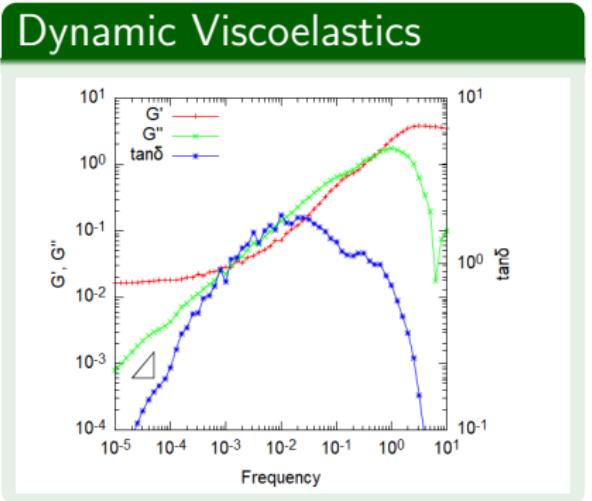


## Conditions

- 4-Chain KG-NW( $N=50$ )
- Step Stretch:  $\lambda = 2$
- $G(t)$  is transformed to Dynamic Viscoelastic Spectrum

- Let me move to the last item
- $G(t)$  and  $\tan\delta$  decayed on a time scale of this region
- (POINT)
  - it was longer than the longest relaxation time of homo-polymers of comparable length.
  - This prolonged relaxation time can be attributed to the reduced mobility of the cross-linking points due to the network structure

# Mechanical Hysteresis Loss



### Conditions

- 4-Chain KG-NW( $N=50$ )
- Cyclic Shear:  $\gamma = 1$ ,  $\dot{\gamma} = 5e^{-5}$

- Around this region
- (POINT) 10-5
- Hysteresis loss was checked using deformation rate of  $\dot{\gamma} = 5e^{-5}$
- rather high hysteresis loss was found 0.36
- this result should concern with the longer relaxation time
- Network connectivity should affect the nature of hysteresis loss.

# Conclusions

- Introducing random connectivity, MD simulation studies were carried out.
- To investigate the criteria for Phantom Network Model, Two model chains are used.
  - Employing phantom chain, basics for PNM is examined.
    - Proper strand length is the key for PNM.
    - Functionality effect was confirmed.
  - Changing the chain to KG Chain, constraints effects are investigated.
    - Trapped Entanglement was explained by Slip-tube Model
    - Hysteresis

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