Modelling the Linear Viscoelastic Response of Unentangled Associating Polymer Melts

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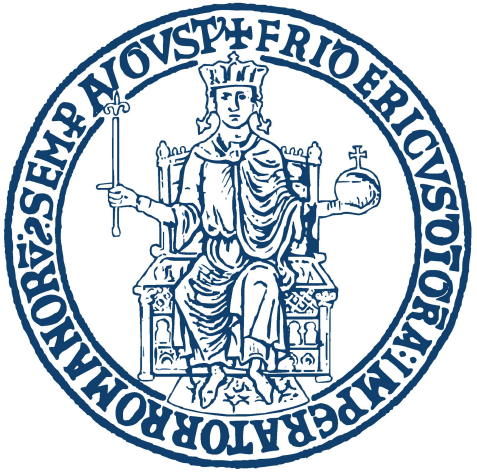


Università degli Studi di Napoli Federico II

Outline

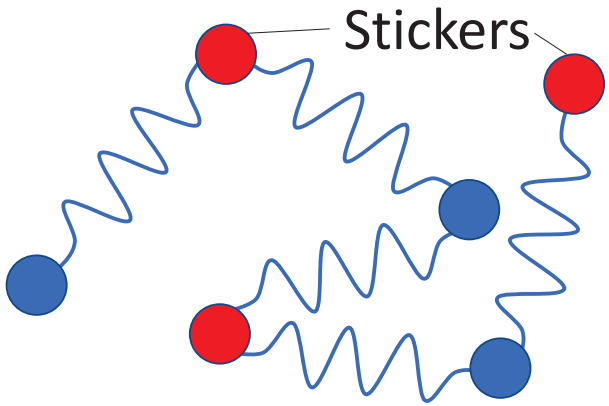
1. Background of Associating Polymers
2. Bead-dependent Friction (BDF) Model
3. Linear Viscoelastic Response
4. Conclusions

Section 1

Background of Associating Polymers

Sticky-Rouse Model

Sticky-Rouse model is based on the idea that stickers along the chain provide an additional effective drag, delaying the terminal relaxation time.



A significant stress relaxation only occurs when the stickers change partners, characterized by an average timescale τ_s, $\tau_s > \tau_0 (N/S)^2$ is required to have a delay of the terminal relaxation caused by stickers, where τ_0 is the elementary Rouse time.

- $N = 6$ (blue and red), $S = 3$ (red)

Relaxation Modulus

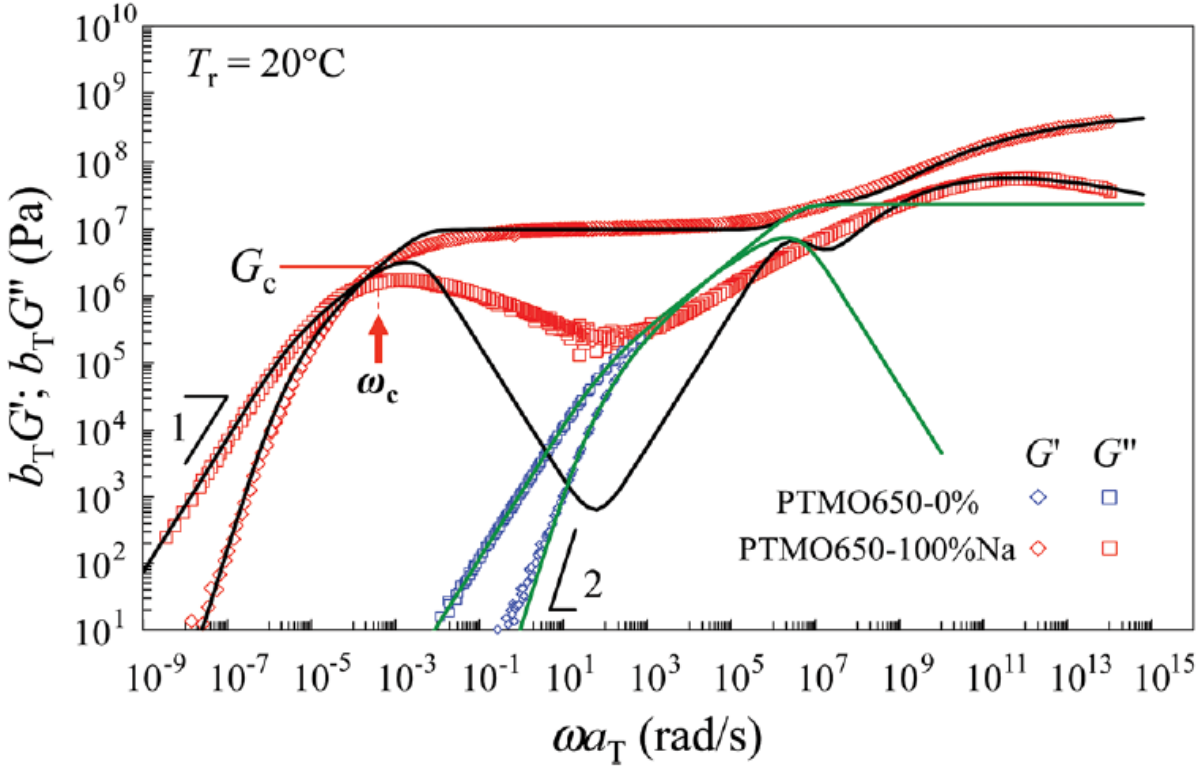
- *Chen et al.*[1] give the expression of shear relaxation modulus

$$G(t) = \frac{\rho R T}{M}\Big[\sum_{p=1}^{S} \mathrm{EXP}\Big(\frac{-tp^2}{\tau_s S^2}\Big) + \sum_{p=S+1}^{N} \mathrm{EXP}\Big(\frac{-tp^2}{\tau_0 N^2}\Big)\Big] \qquad (1)$$

where M is molecular weight. N is the number of elementary Rouse segments per chain, S is the number of the stickers per chain, and $\tau_0 N^2$ is the Rouse relaxation time of the chain.

[1] Chen, Q.; Tudryn, G. J.; Colby, R. H. Ionomer dynamics and the sticky Rouse model. Journal of Rheology. 2013.

Comparison of Chen's Model with Data



Discrepancies appeared in the frequency regime around $1/\tau_R$

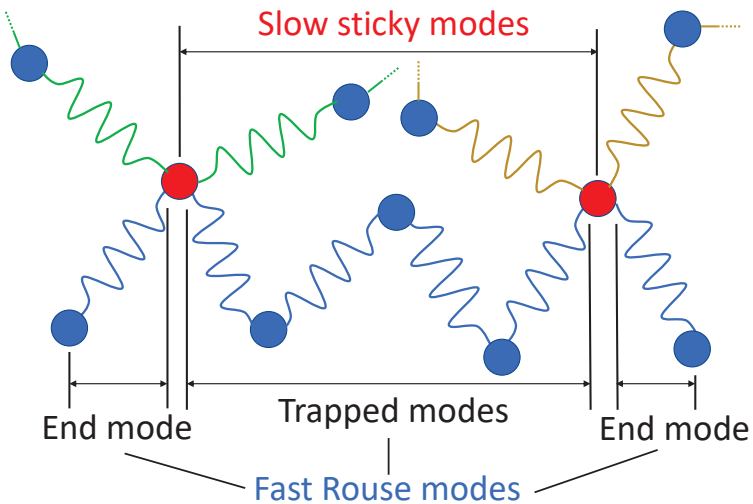
Stochastic Model

Cui improved the model by proposing the stochastic model[2]

$$G_{stocha}(t) = G_{fast}(t) + G_{sticky}(t) \tag{2}$$

where $G_{fast}(t)$ has the following two parts:

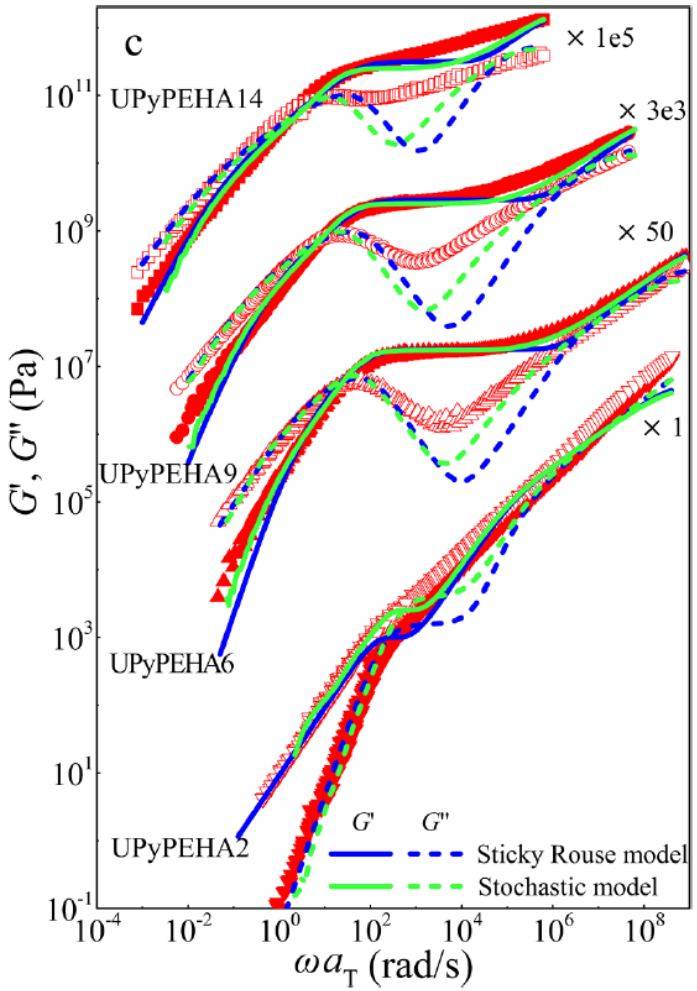
$$G_{fast}(t) = \rho RT/M(G_{trapped}(t) + G_{ends}(t)) \tag{3}$$



[2] Cui, Guanghui, et al. "Linear shear and nonlinear extensional rheology of unentangled supramolecular side-chain polymers." Journal of Rheology 62.5 (2018): 1155-1174.

Comparison of Cui's Model with Data

- Cui's stochastic model reduced the discrepancies (compare the green and blue curves).



Comparison of Cui's Model with Data

- The parameters applied in both models were somewhat different from those indicated by NMR.

TABLE III. Parameters used in the stochastic and "classic" sticky-Rouse models.

Sample codes	M_n[a] (kg/mol)	PDI[a]	S		τ_s (μs)		τ_0
			NMR[a]	Models[b]	Stochastic	Classic[c]	(ns)
UPyPEHA2	16.6	1.24	2	0.2	5	25	0.70
UPyPEHA6	22.0	1.38	7	3	29	65	1.0
UPyPEHA9	23.7	1.71	11	8	56	100	2.5
UPyPEHA14	24.6	2.38	17	21	83	200	500

Section 2

Bead-dependent Friction (BDF) Model

Langevin Approach

- Langevin equations

$$\begin{cases} \zeta \frac{\mathrm{d}\mathbf{R}_1}{\mathrm{d}t} = -H(\mathbf{R}_1 - \mathbf{R}_2) + \zeta \mathbb{K} \cdot \mathbf{R}_1 + \mathbf{f}_1, \text{if } n = 1 \\ \zeta \frac{\mathrm{d}\mathbf{R}_n}{\mathrm{d}t} = -H(2\mathbf{R}_n - \mathbf{R}_{n+1} - \mathbf{R}_{n-1}) + \zeta \mathbb{K} \cdot \mathbf{R}_n + \mathbf{f}_n, \\ \quad \text{if } n = 2, ..., N-1 \\ \zeta \frac{\mathrm{d}\mathbf{R}_N}{\mathrm{d}t} = -H(\mathbf{R}_N - \mathbf{R}_{N-1}) + \zeta \mathbb{K} \cdot \mathbf{R}_N + \mathbf{f}_N, \text{if } n = N \end{cases} \tag{4}$$

where $H = 3k_B T / R_0^2$ and R_0 is the end-to-end distance for a subchain at the equilibrium state, $\mathbf{f}_n$ is the random force characterized by

$$\begin{aligned} &\langle \mathbf{f}_n(t) \rangle = 0, \\ &\langle f_{n\alpha}(t) f_{m\beta}(t') \rangle = 2\zeta k_B T \delta_{nm} \delta_{\alpha\beta} \delta(t - t'). \end{aligned} \tag{5}$$

The ζ in Eqn. (2) can be ζ or ζ_s depending on if the bead is ordinary or sticky.

Normal Coordinates

To find the normal coordinates, we consider the linear transformation of $\boldsymbol{R}_n(t)$

$$\boldsymbol{X}_p(t) = \int_0^N \phi_{pn} \boldsymbol{R}_n(t) dn \tag{4}$$

and choose ϕ_{pn} so that the equation of motion for $\boldsymbol{X}_p$ has the following form,

$$\zeta_p \frac{\partial \boldsymbol{X}_p}{\partial t} = -k_p \boldsymbol{X}_p + \boldsymbol{f}_p. \tag{5}$$

From eqn. $\zeta_n \frac{\partial \boldsymbol{R}_n}{\partial t} = k \frac{\partial^2 \boldsymbol{R}_n}{\partial n^2} + \boldsymbol{f}_n$ and eqn. (4)

$$\zeta_p \frac{\partial \boldsymbol{X}_p}{\partial t} = \zeta_p \int_0^N \phi_{pn} \frac{\partial \boldsymbol{R}_n}{\partial t} dn = \zeta_p \int_0^N \psi_{pn} \left(k \frac{\partial^2 \boldsymbol{R}_n}{\partial n^2} + \boldsymbol{f}_n \right) dn. \tag{6}$$

where $\psi_{pn} = \frac{\phi_{pn}}{\zeta_n}$.

Normal Modes

Finally, we arrive at

$$\zeta_p k \frac{\partial^2 \psi_{pn}}{\partial n^2} = -k_p \phi_{pn}. \tag{7}$$

i.e.,

$$\zeta_p k \frac{\partial^2 \psi_{pn}}{\partial n^2} = -k_p \zeta_n \psi_{pn}. \tag{7'}$$

with

$$\frac{\partial \psi_{pn}}{\partial n} = 0 \text{ at } n = 0 \text{ and } n = N \tag{8}$$

and

$$\boldsymbol{f}_p = \zeta_p \int_0^N \psi_{pn} \boldsymbol{f}_n \, dn. \tag{9}$$

Relaxation Spectrum

For an arbitrary ζ_n, Eq. (7') can only be solved numerically as an eigenvalue problem. In other words, we go back to the discrete representation of the chain, with $N+1 \gg 1$ the bead number per chain, and $n = \{0,1,2,\dots,N-1,N\}$ the generic bead. By calling $\frac{k_p}{\zeta_p k} = a_p$, the finite difference version of Eq. (7') is

$$\left(\frac{1}{\zeta_0} - a_p\right)\psi_{p0} - \frac{1}{\zeta_0}\psi_{p1} = 0 \tag{10}$$

$$n = 1,\dots,N-1 \qquad -\frac{1}{\zeta_n}\psi_{p,n-1} + \left(\frac{2}{\zeta_n} - a_p\right)\psi_{pn} - \frac{1}{\zeta_n}\psi_{p,n+1} = 0 \tag{11}$$

$$-\frac{1}{\zeta_N}\psi_{p,N-1} + \left(\frac{1}{\zeta_N} - a_p\right)\psi_{pN} = 0 \tag{12}$$

where

$$a_p = \frac{k_p}{\zeta_p k} = \frac{k_p b^2}{\zeta_p 3 k_B T} \tag{13}$$

From each a_p, we can compute the corresponding relaxation time τ_p as:

$$\tau_p = \frac{\zeta_p}{k_p} = \frac{1}{a_p k} = \frac{b^2}{a_p 3 k_B T} \tag{14}$$

Sticker Chain Matrix and Modulus

By writing (10-12) in discrete form,

$$\begin{matrix}
\frac{1}{\zeta_0} & -\frac{1}{\zeta_0} & 0 & \dots & \dots & \dots & \dots & \dots & 0 \\
-\frac{1}{\zeta_1} & \frac{2}{\zeta_1} & -\frac{1}{\zeta_1} & 0 & \dots & \dots & \dots & \dots & 0 \\
0 & \dots & \dots & \dots & \dots & \dots & \dots & \dots & 0 \\
0 & \dots & 0 & -\frac{1}{\zeta_n} & \frac{2}{\zeta_n} & -\frac{1}{\zeta_n} & 0 & \dots & 0 \\
0 & \dots & \dots & \dots & \dots & \dots & \dots & \dots & 0 \\
0 & \dots & \dots & \dots & \dots & \dots & \dots & -\frac{1}{\zeta_N} & \frac{1}{\zeta_N}
\end{matrix} \qquad (15)$$

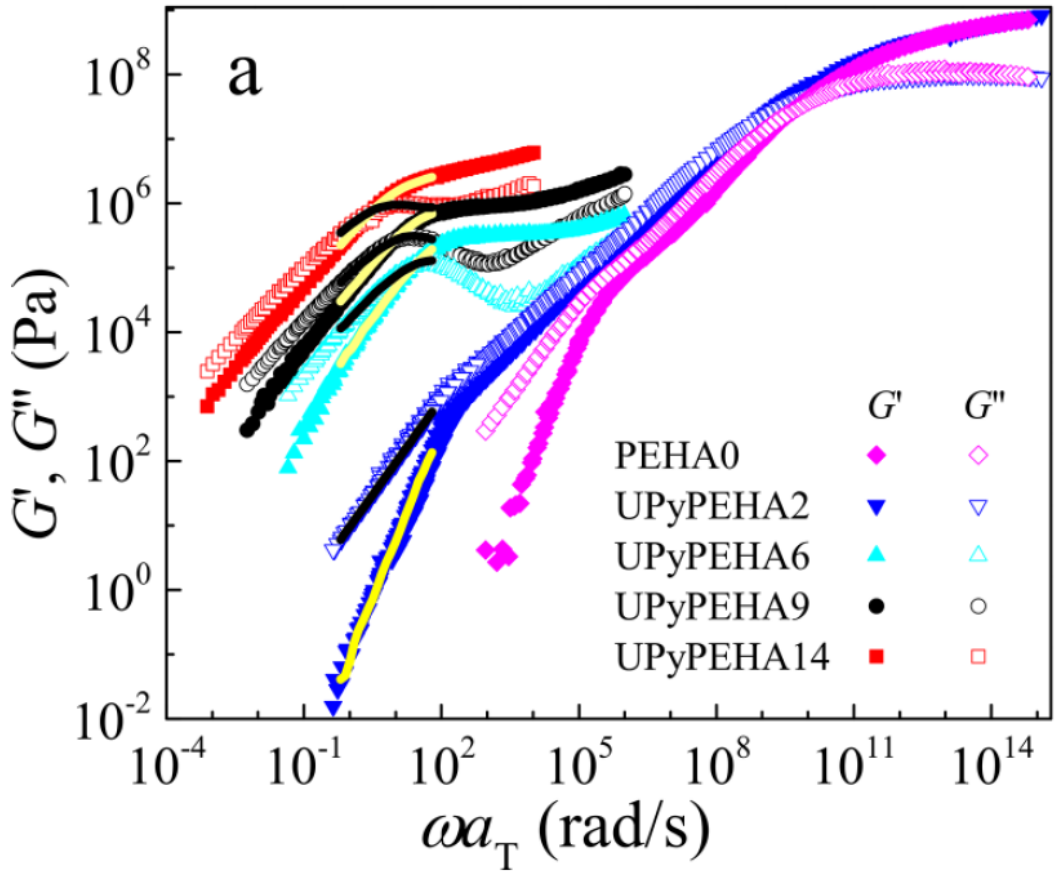
The relaxation modulus can be written as

$$G(t) = \nu k_B T \sum_{p=1}^{N} exp\left(-\frac{2t}{\tau_p}\right) \qquad (16)$$

Section 3

Linear Viscoelastic Response

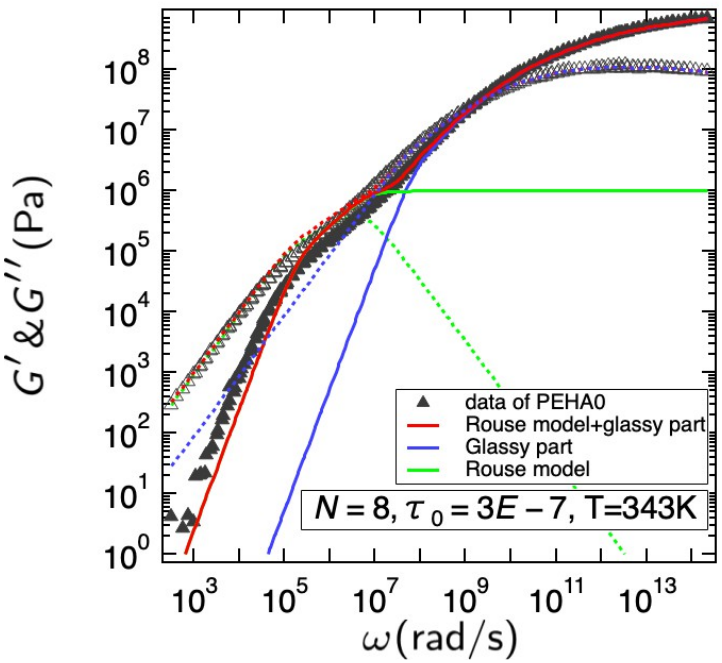
Unentangled Polymer Melt Data



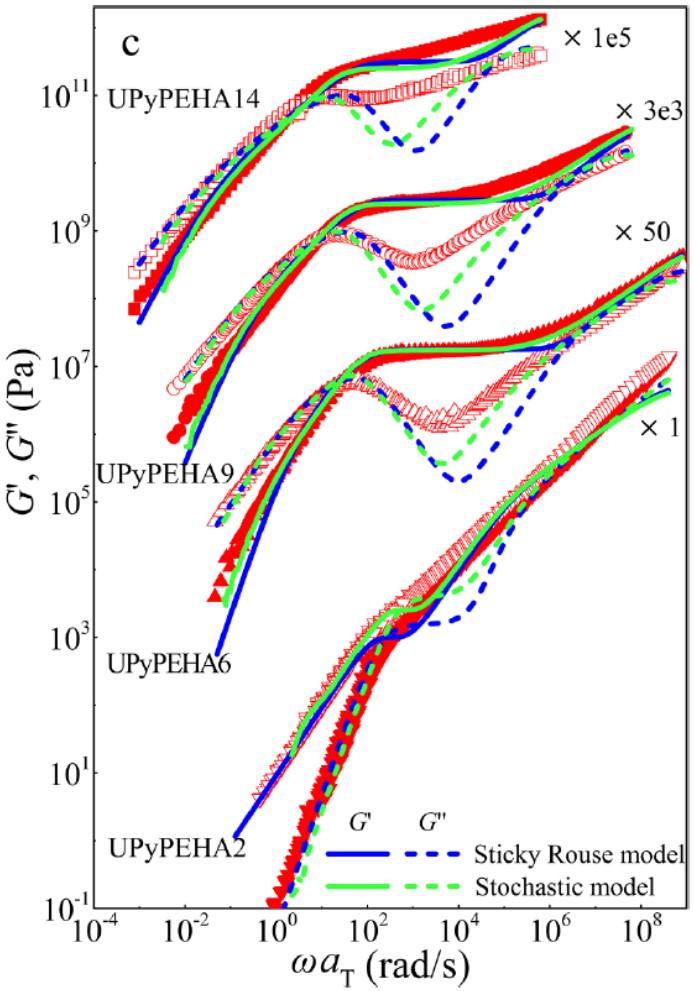
- The data collapsed in the high frequency regime, suggesting the samples have the same T_g.

Non-sticker System

- The glassy spectrum was extracted from the data in the high frequency regime.
- τ_0 was determined from the zero-shear viscosity.
- The Kuhn number N was estimated by the chemical properties of PEHA0 (13 monomers per Kuhn segments).



Two Percent System



There was no plateau for the two percent system.

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NMR indicates two stickers per chains in the 2% system (i.e. $S = 2$).

No Network Formed in UPyPEHA2

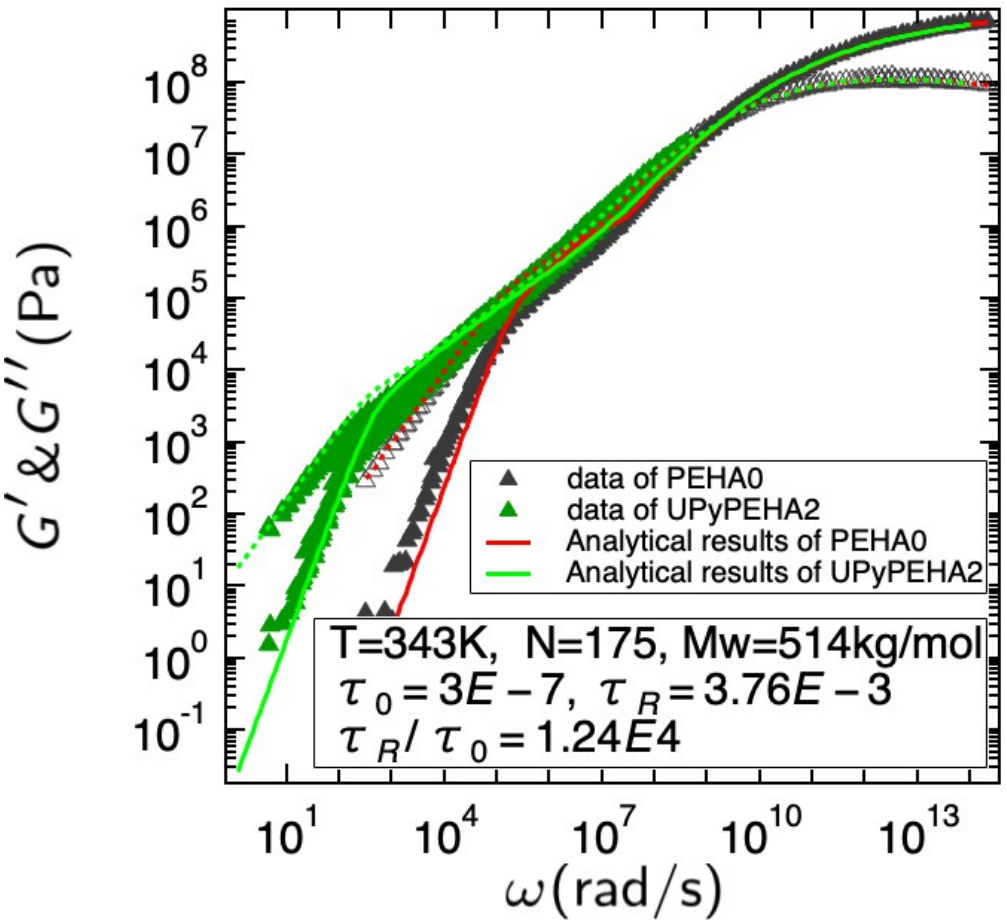
- Polymers with sticky points are usually modelled by assuming that the polymer dynamics occurs with the sticky points being endowed with a sufficiently large friction coefficient. However, this concept only applies if chains form a temporary network, from which they must detach to relax. Such condition is obtained only if chains contain at least 3 stickers.
- In the 2% sample, the number S of stickers per chain is $S = 2$, and hence chains can only combine to create indefinitely long chains, but no network can form.

No Network Formed in UPyPEHA2

- According to the above concept, the $S = 2$ situation is one of a Rouse chain with (nearly) the same monomeric friction coefficient of the non-sticky sample. Relaxation is then described as that of a Rouse chain with a pseudo-Rouse-time coinciding with the lifetime of the stickers. Indeed, these indefinitely long chains will break up (i.e., relax completely) at that time.
- The $S = 2$ chain thus provides a good estimate of the characteristic breaking time of the sticky points.
- Needless to say, at high frequencies the Rouse relaxation is superseded by the glassy one.

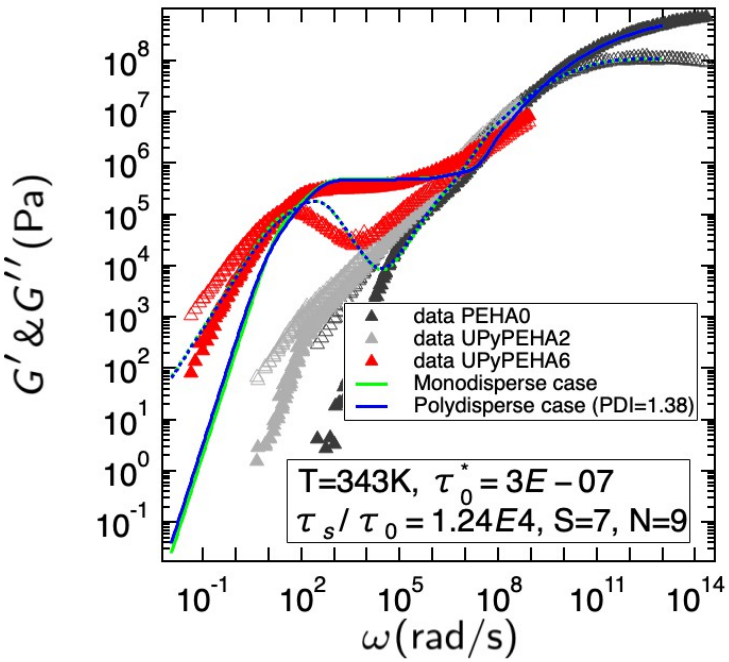
Results of Two Percent System

- τ_s is the longest time (i.e. the Rouse time) of the 2% system.



Six Percent System

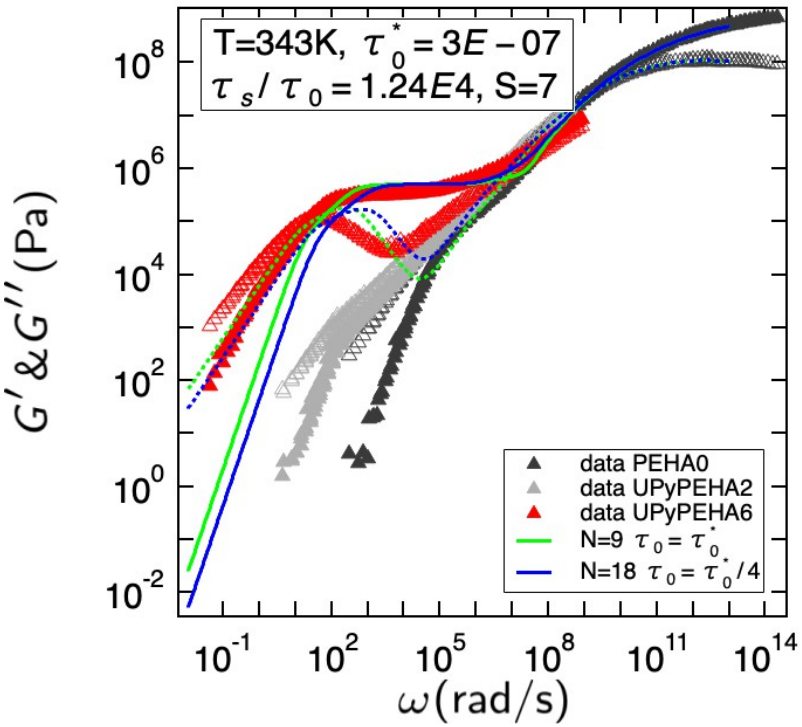
- To deal with the 6% system (having $S = 7$ stickers per chain) we can use the sticker time determined by the 2% system, together with τ_0 determined by the non-sticker system.



- Discrepancies in the intermediate regime remain even when accounting for polydispersity.

Effect of Number of Beads

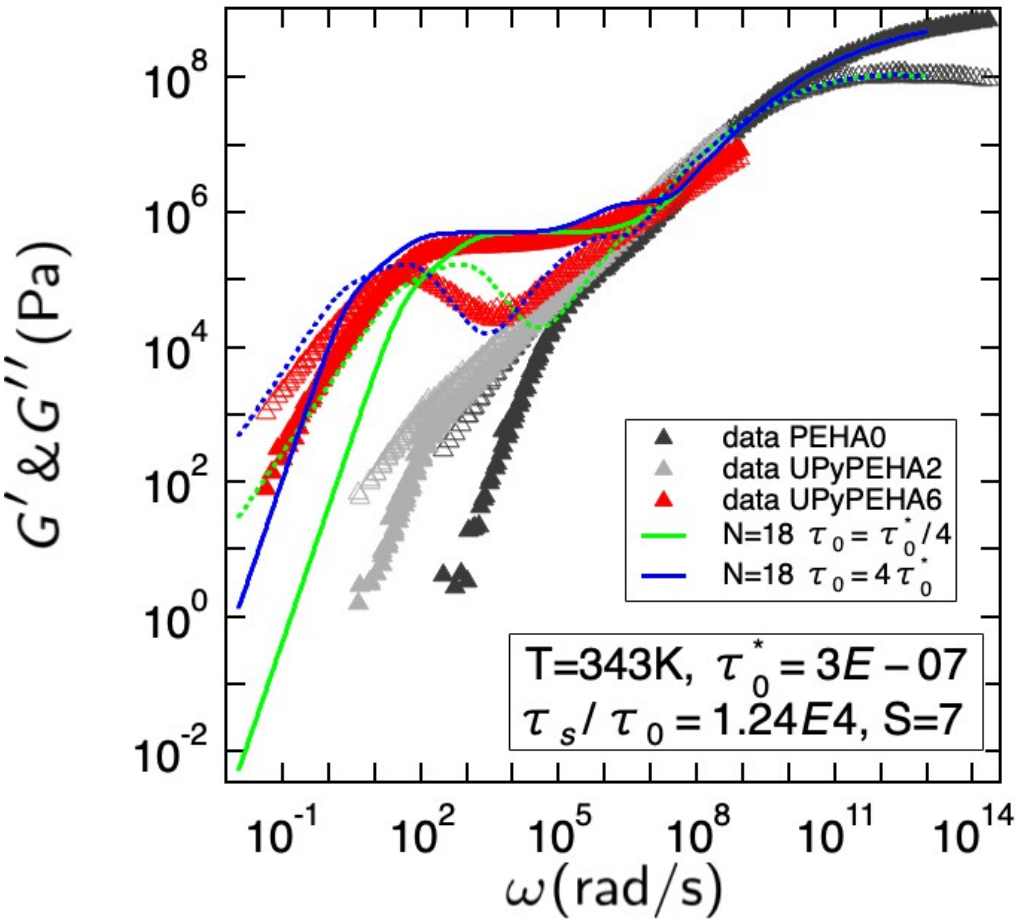
- The prediction in the intermediate frequency regime can slightly be improved by artificially increasing the number N of beads.



- Perhaps the τ_0 value determined from the non-sticker case may not be suitable in the sticky one.

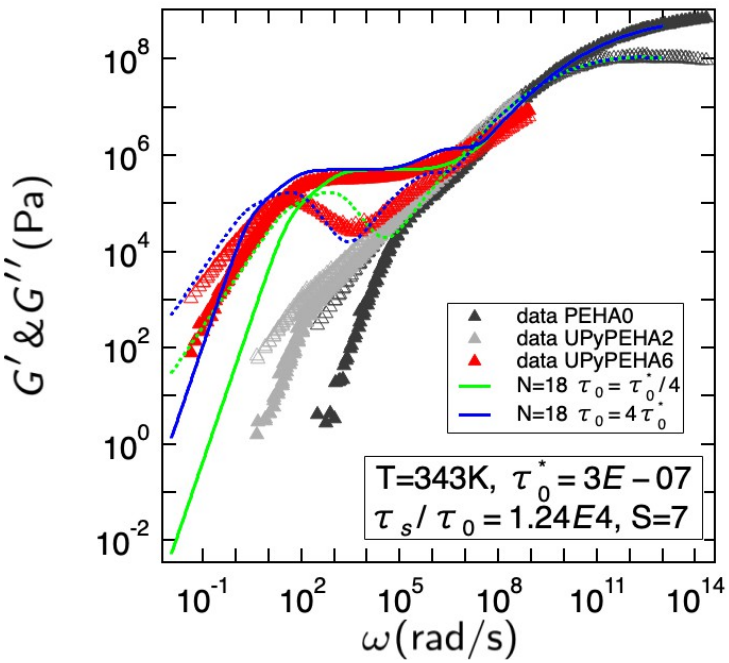
Effect of τ_0

- The elementary relaxation time τ_0 may become larger due to trapped entanglements, i.e., entanglements that become long lived because of stickers.



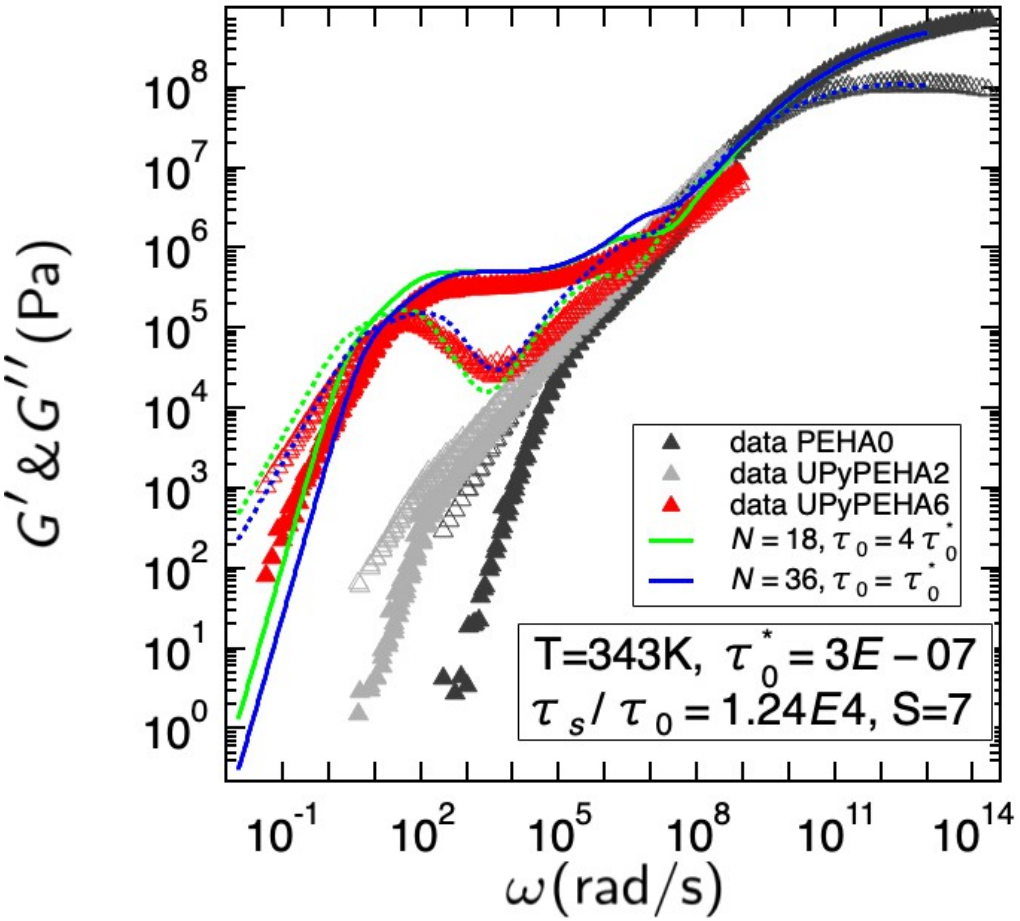
Effect of τ_0

- Furthermore, with increasing the number of stickers it is possible that two or more stickers belong to the same Kuhn segment. This can induce a cooperative behaviour of neighbouring stickers. In other words, stickers might have a characteristic time larger than that determined through the $S = 2$ system.



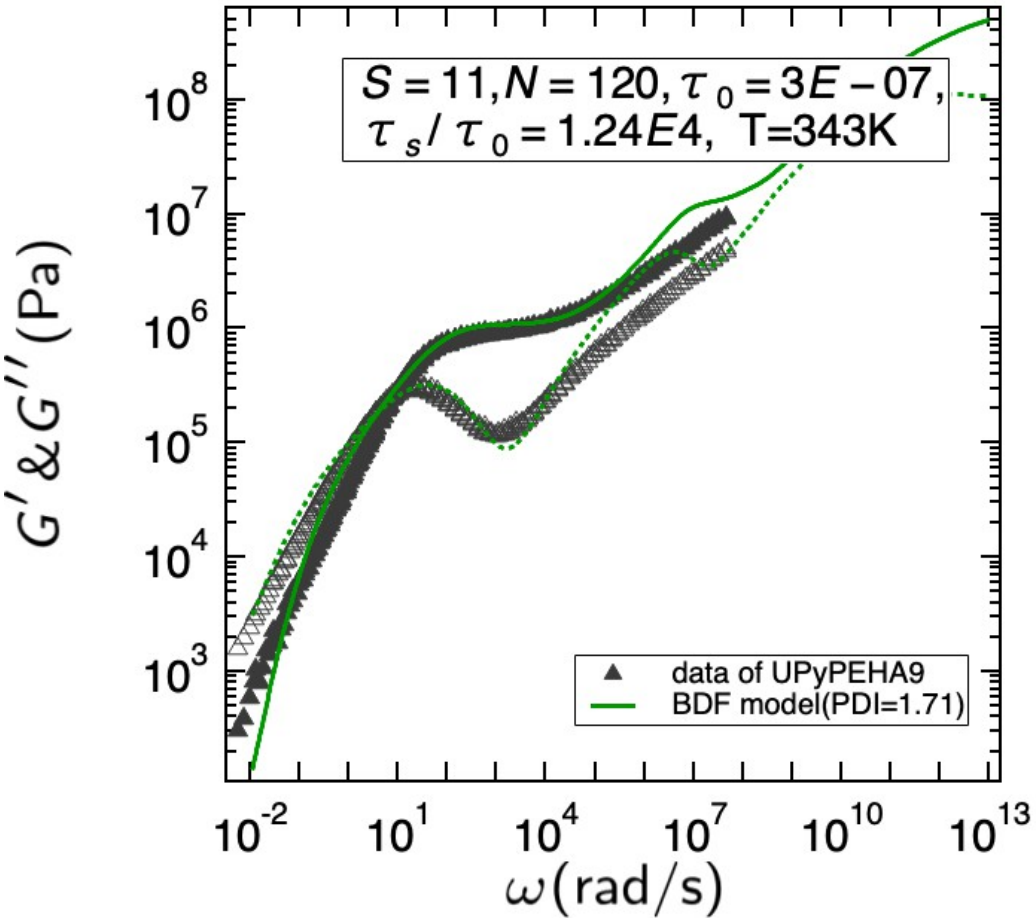
Larger Number of Beads

- The prediction has a better agreement with the data by using a larger number of beads.



Nine Percent System

- In the 9% system, an even larger number of beads and a longer τ_0 seem to be required to fit data.



Section 4

Conclusions

Conclusions

- We developed the bead-dependent friction model, which overcomes some weak points of Chen's model and Cui's model.
- We determine the basic sticker time from the 2% system. In that system no network is formed (no plateau), and chains effectivley stick by creating longer chains that relax when detachment occurs.
- With increasing sticker concentration, long-lived entanglements can be formed also in unentangled systems (trapped entanglements). We can mimic this effect by increasing the basic Kuhn segment time.
- When two or more stickers are in the same Kuhn segment, cooperative effects might come into play, effectively increasing the sticker time.
- Work is in progress to better understand/describe these phenomena.