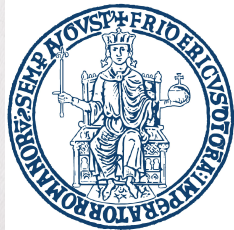


Modeling the Linear and Nonlinear Rheology of Unentangled Associating Polymers

Hongwei Liu

Supervisor: Giovanni Ianniruberto

September 10, 2020



UNIVERSITÀ DEGLI STUDI DI NAPOLI
FEDERICO II



Outline

- 1 Linear Rheology of Polydisperse Associating and non-Associating Polymers
 - Sticky-Rouse Model
 - Polydisperse Sticky-Rouse Model
 - Polydispersity: GEX Distribution
- 2 Future Work on Unentangled Associating Polymers
 - Linear Rheology of Polydisperse Systems
 - Nonlinear Rheology
- 3 Conclusions

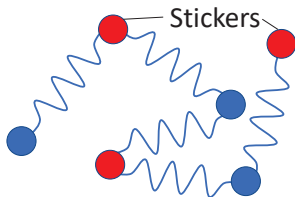


Section 1

Linear Rheology of Polydisperse Associating and non-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.

- $N = 6(\text{blue and red}), S = 3(\text{red})$

Polydisperse Sticky-Rouse Model

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

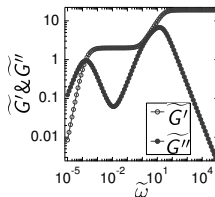
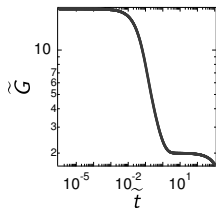
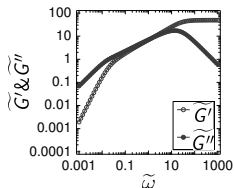
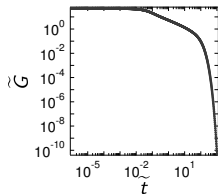
$$G(t) = \sum_{i=1} w_i \frac{\rho RT}{M_i} \left[\sum_{p=1}^{S_i} \text{EXP}\left(\frac{-tp^2}{\tau_s S_i^2}\right) + \sum_{p=S_i+1}^{N_i} \text{EXP}\left(\frac{-tp^2}{\tau_0 N_i^2}\right) \right] \quad (1)$$

where w_i and M_i are weight fraction and molecular weight of the i th component. $N_i = M_i/M_0$ is the number of elementary Rouse segments per chain, S_i is the number of the stickers of the i th chain, and $\tau_0 N_i^2$ is the Rouse relaxation time of the i th chain, where M_0 and τ_0 are the molecular weight and characteristic time of the elementary Rouse segment, respectively. The Rouse stress relaxation modulus is expressed as a sum of contributions from fractions of different M_i , and the contribution of each fraction is expressed in terms of the Rouse modes for that chain of N_i segments.

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

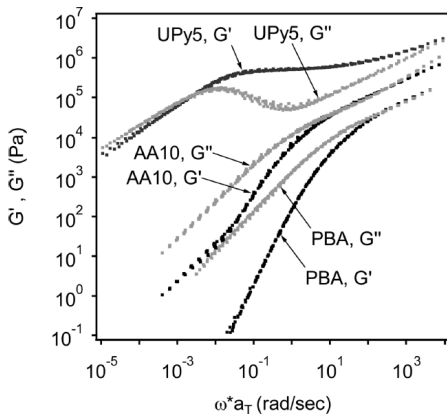
Playing with Eqn. (1)

Monodisperse case. UP: $N = 50, S = 0$, DOWN: $N = 20, S = 2$. (\tilde{x} means non dimensional.)



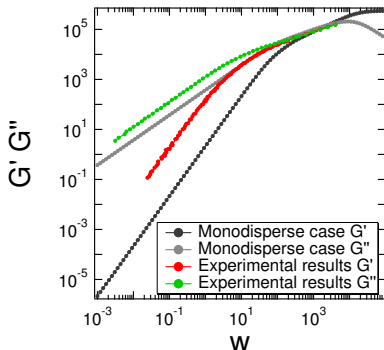
Experimental data

Lewis et al, 2014 reported the viscoelastic response of unentangled melts, both with and without stickers. For poly(butyl acrylate) (PBA), the polydispersity index is 2.5.



Effects of Polydispersity on Moduli

When the PBA is modeled as a monodisperse polymer, i.e. $M = M_w$, some discrepancies appear.



Moduli and frequencies are made dimensional by using $\rho RT/M_w$ and the experimental value of the average relaxation time, respectively.

Molecular Weight Distribution (MWD): GEX

Predictions can improve by accounting for polydispersity. A three-parameter generalised exponential (GEX) function is usually used to describe accurately a wide class of monomodal distributions.

$$W_{GEX}(M) = \frac{b}{M^* \Gamma(\frac{a+1}{b})} \left(\frac{M}{M^*}\right)^a \text{EXP} \left[- \left(\frac{M}{M^*}\right)^b \right], \quad (2)$$

where M^* , a , b are parameters and M is molar mass. The corresponding weight-average and number-average molecular weights, respectively M_w and M_n , are given by

$$M_w = \int M \cdot W_{GEX}(M) dM = M^* \cdot \Gamma(\frac{a+2}{b}) / \Gamma(\frac{a+1}{b}), \quad (3)$$

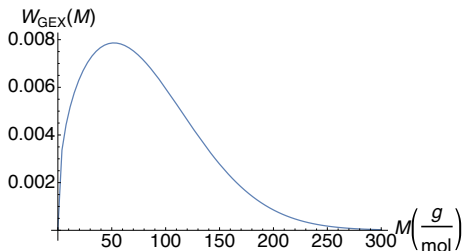
Molecular Weight Distribution (MWD): GEX

and

$$M_n^{-1} = \int M^{-1} W_{GEX}(M) dM = M^* \cdot \Gamma\left(\frac{a}{b}\right) / \Gamma\left(\frac{a+1}{b}\right). \quad (4)$$

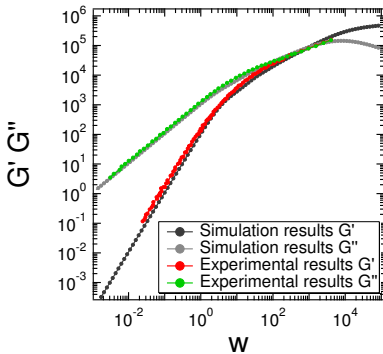
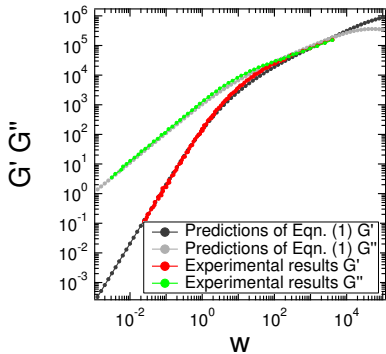
Following *van Ruymbeke et al., 2002*, we set $b = 2$, while M^* and a are determined from M_w and M_n .

- The result is:



Comparison with Data

GEX was used to determine the MWD of poly(butyl acrylate) (PBA). The prediction of Eqn. 1 ($S_i = 0$) is found in good agreement with the experimental data. Similarly, Langevin approach can be used to simulate the data, which paves a path to predict the moduli of associating polymers.



Langevin Approach

- Langevin equations

$$\left\{ \begin{array}{l} \zeta \frac{d\mathbf{R}_1}{dt} = -H(\mathbf{R}_1 - \mathbf{R}_2) + \zeta \mathbb{K} \cdot \mathbf{R}_1 + \mathbf{f}_1, \text{ if } n = 1 \\ \zeta \frac{d\mathbf{R}_n}{dt} = -H(2\mathbf{R}_n - \mathbf{R}_{n+1} - \mathbf{R}_{n-1}) + \zeta \mathbb{K} \cdot \mathbf{R}_n + \mathbf{f}_n, \\ \quad \text{if } n = 2, \dots, N-1 \\ \zeta \frac{d\mathbf{R}_N}{dt} = -H(\mathbf{R}_N - \mathbf{R}_{N-1}) + \zeta \mathbb{K} \cdot \mathbf{R}_N + \mathbf{f}_N, \text{ if } n = N \end{array} \right. \quad (5)$$

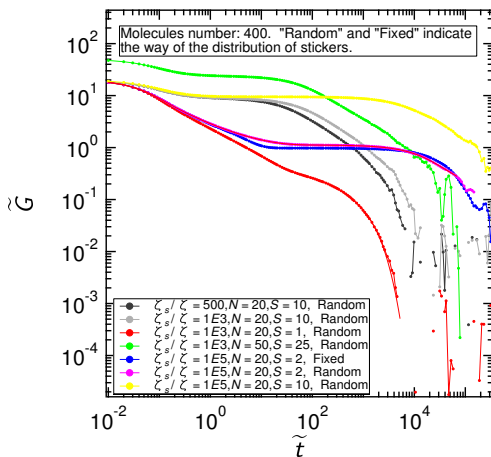
where $H = 3k_B T/R_0^2$ and R_0 is the end-to-end distance for a subchain at the equilibrium state, \mathbf{f}_n is the random force characterized by

$$\begin{aligned} \langle \mathbf{f}_n(t) \rangle &= 0, \\ \langle f_{n\alpha}(t) f_{m\beta}(t') \rangle &= 2\zeta k_B T \delta_{nm} \delta_{\alpha\beta} \delta(t-t'). \end{aligned} \quad (6)$$

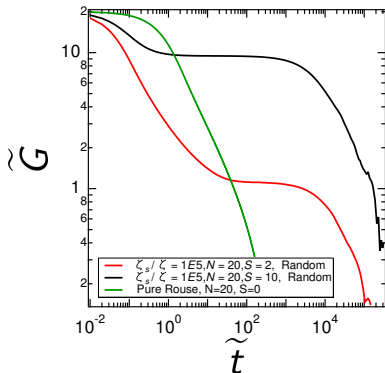
The ζ in Eqn. (5) can be ζ or ζ_s depending on if the bead is ordinary or sticky.

Simulation Results: $G(t)$

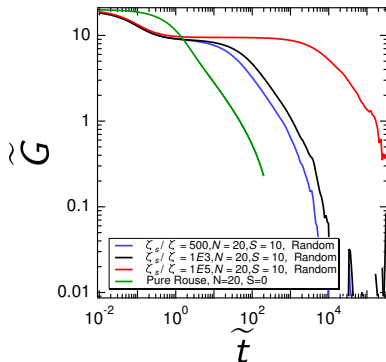
- Larger density of stickers leads to higher second plateau.



Effects of Stickers and Friction



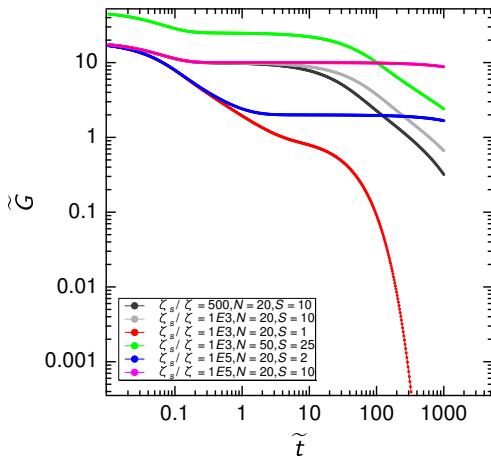
Effects of stickers



Effects of friction

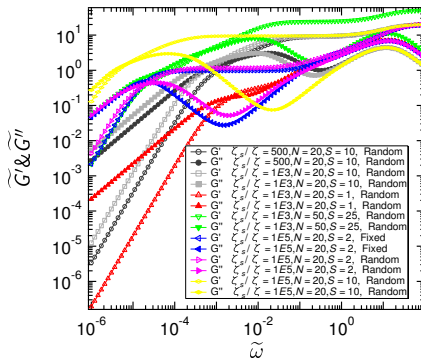
Chen et al predictions: $G(t)$

- We suppose $\tau_s = \tau_0 \cdot \zeta_s / \zeta$



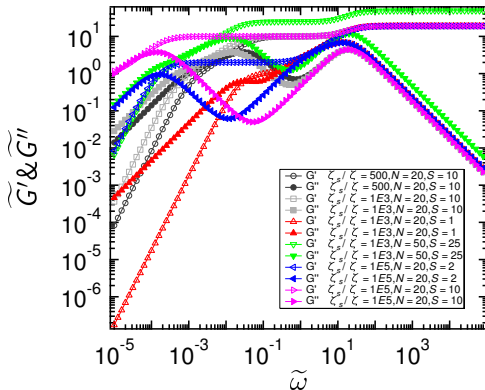
Simulation Results: G' & G''

- Fixed distribution makes sharper peak in the lower frequency regime (see blue and pink curves).
- Sticker density fixes the plateau level (see pink and yellow).
- Friction of sticky beads affects both the terminal and intermediate regions.



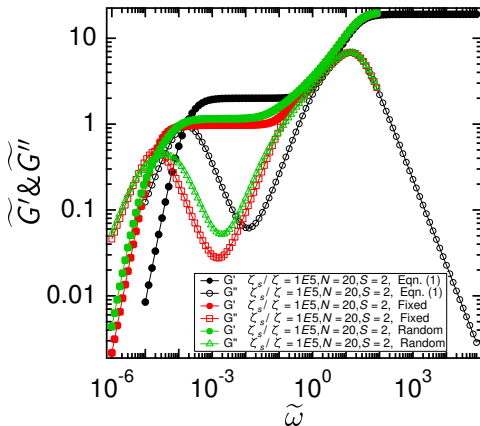
Chen et al Results: G' & G''

- We can see a similar trend as the simulation predictions.



Eqn. (1) vs Simulations

- Eqn. (1) amplifies the number of stickers (higher plateau modulus) possibly because it ignores dangling ends.





Section 2

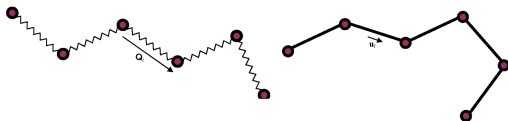
Future Work on Unentangled Associating Polymers

Future Work

- We simply replace Rouse chains with Fraenkel chains to account for the finite extensibility (FENE).
- FENE effects are expected to be particularly relevant when we have a small number of Kuhn segments between stickers.
- Nonlinear rheological data of unentangled associating polymers would be welcome.

Fraenkel Model

Rouse vs. bead-rod chains



Virtually no difference in LVE, while in NLVE bead-rod chains automatically account for FENE effects

We mimic rods as stiff Fraenkel springs

$$\mathbf{F} = H(\ell - \ell_K)\mathbf{u} \quad \mathbf{Q} = \ell\mathbf{u} \approx \ell_K\mathbf{u}$$



Section 3

Conclusions

Conclusions

- We have successfully simulated the polydisperse PBA, which will be a good start for simulating polydisperse sticky chains.
- Chen's formula is reasonably consistent with our simulations. However, there are some drawbacks. For example, we can not have a clear idea from Eqn. (1) about the distribution of stickers. Yet, Eqn. (1) is not able to tell the difference between the end modes and the trapped modes. The Langevin approach can overcome these defects.
- The nonlinear rheology will be studied very soon.