

## Workshop on “Soft Matter: from Fundamentals to Functionality”

	<b>Session Chair: Sathish K. Sukumaran</b>
13:30 – 14:10	<b>Unentangled Polymers under Fast Sear Flow: a Simulation Study</b> Jun-ichi Takimoto Yamagata University, Yonezawa, Japan
14:10 – 14:50	<b>Nonlinear modification of the Rouse model: chain volume conservation &amp; anisotropic friction reduction</b> Youngdon Kwon Sungkyunkwan University, Suwon, Republic of Korea
14:50 – 15:30	<b>Nonlinear Stress Relaxation of End-Associative Star Chain</b> Hiroshi Watanabe Changchun Institute of Applied Chemistry, Changchun, China Kyoto University, Kyoto, Japan
15:30 – 15:50	<i>Short Break</i>
	<b>Session Chair: Jun-ichi Takimoto</b>
15:50 – 16:30	<b>Stable Photo-active Layer of Organic Solar Cell Prepared by Sequential Solution Deposition</b> Kyungkon Kim Ewha Womans University, Seoul, Republic of Korea
16:30 – 17:10	<b>Using swelling of polymer thin films to investigate the tightly bound layer at a polymer/substrate interface</b> Sathish K. Sukumaran Yamagata University, Yonezawa, Japan

Date: 2024, February 19 (Monday)

Venue: Room 406, Research Center for Green Materials and Advanced Processing (GMAP)  
Yamagata University, Yonezawa

Organizers:

Sathish K. Sukumaran

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# Unentangled Polymers under Fast Shear Flow: a Simulation Study

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Although the linear viscoelasticity of unentangled polymeric liquids can be described very well by the Rouse model, unentangled polymers do show various nonlinear behaviors. For example, the steady elongational viscosity shows thickening and then thinning at higher strain rate [1]. This thinning is successfully described by the “friction-reduction” model. On the other hand, the steady shear viscosity  $\eta(\dot{\gamma})$  decreases as  $\dot{\gamma}^{-1/2}$  at high shear rate  $\dot{\gamma}$  [2]. To understand the origin of this shear thinning, we are now studying various properties of unentangled polymer chains under fast shear flow. The main results obtained so far are:

(1) If there is no excluded volume interaction among the “monomers” (or “beads”) of the chains (for example DPD model), then there is only very weak shear thinning. (2) The Kremer-Grest (KG) model with short chain length does show the shear thinning  $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-1/2}$  (but within rather limited shear rate range). (3) If we allow chain crossing (by replacing the bond potential in the KG model by a simple harmonic spring) then we can study very long but unentangled chains. This model also shows the thinning behavior  $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-1/2}$  in a wider shear rate range. (4) The chain length  $R$  under fast shear flow behaves as  $R \propto \dot{\gamma}^{1/4}$ . (5) The 1st normal stress coefficient  $\Psi_1$  satisfies the relation  $\Psi_1(\dot{\gamma})/\Psi_1(0) = (\eta(\dot{\gamma})/\eta(0))^2$ .

According to the generalized Rouse model [3], the result (5) indicates that the fluctuation-dissipation theorem holds even under shear flow. But to reproduce all the simulation results for  $\eta$ ,  $\Psi_1$  and  $R$  by the model, we need to assume that the friction constant does not change by the shear flow but the spring constant must grow as  $\dot{\gamma}^{1/2}$ . This indicates that the shear thinning cannot be described simply by friction reduction alone. Another possible model for the shear thinning is the “blob” model [2]. A simple application of the shear blob model can reproduce  $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-1/2}$  and  $R \propto \dot{\gamma}^{1/4}$ , but it is very difficult to explain the relation  $\Psi_1(\dot{\gamma})/\Psi_1(0) = (\eta(\dot{\gamma})/\eta(0))^2$  by blob models. We hope we get better understanding through the discussion in this Workshop.

## References

- [1] Matsumiya *et al.*, *Macromolecules* **51** 9710 (2018). [2] Colby *et al.*, *Rheol. Acta* **46** 569-575 (2007). [3] Watanabe *et al.*, *Macromolecules*, **54**, 3700 (2021)

# Nonlinear modification of the Rouse model: chain volume conservation & anisotropic friction reduction

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Constitutive modification of the Rouse model has been performed employing the variation of Brownian force intensity constraining the incompressibility of molecular chains in addition to the effects of time dependent spring constant and friction coefficient. Assuming the normal mode-independence of stochastic forces (delta-correlation between the eigen-modes) yields the following simple constitutive equation for the conformation tensor  $\mathbf{c}_p$  (the case of isotropic friction):

$$\mathbf{c}_{p(1)}(\tilde{t}) = -\frac{\theta_p r_\kappa(\tilde{t})}{\theta_1 r_\zeta(\tilde{t})} \left[ \mathbf{c}_p(\tilde{t}) - \frac{1}{I_{p,2}(\tilde{t})} \mathbf{I} \right] \quad (p = 1, 2, \dots, N).$$

Here  $\tilde{t}$  is dimensionless time,  $\theta_p$  is the  $p$ -th eigenvalue of the Rouse matrix,  $I_{p,2}(\tilde{t})$  is the second invariant of  $\mathbf{c}_p$ ,  $\mathbf{c}_{p(1)}(\tilde{t})$  is its upper convected time derivative and  $\mathbf{I}$  is the identity tensor.  $\kappa(t) = \kappa_{eq} r_\kappa(t)$  and  $\zeta(t) = \zeta_{eq} r_\zeta(t)$  are time-dependent spring and bead friction coefficients, respectively, with  $\kappa_{eq}$  and  $\zeta_{eq}$  defined as their equilibrium values.  $N$  is the total number of springs in one chain molecule.

Setting the number of beads per chain  $N = 20$  and the Weissenberg number  $Wi = 20$  in simple shear and uniaxial extensional flows we have obtained the computational results and compared them with those of the previous results<sup>1</sup>. The current modeling together with FENE and friction reduction closely describes the previous outcome<sup>1</sup> with all three effects (however, B-variation instead) into account. Therefore, this method of Brownian force variation constraining the chain volume may play as a useful alternative, since it does not introduce any additional parameter to be determined. Also, the close coincidence of the method of chain incompressibility with the previous idea of random force variation<sup>1</sup> suggests that the B-variation suggested in the past study<sup>1</sup> may automatically enforce volume conservation of unentangled chains.

The anisotropy in friction reduction regarded as an indispensable complexity for the nonlinear modification of the Rouse model is in addition considered under the constraint of chain volume conservation, and then possible way of modeling is suggested.

## References

- [1] T. Sato, *et al.*, *Phys. Fluids*. **33**, 063106 (2021).

# Nonlinear Stress Relaxation of End-Associative Star Chain

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Associative polymers exhibit rich rheological behavior that reflects competition between the intrinsic chain dynamics and the association/dissociation kinetics. For those polymers having long-lived associative groups (often referred to as stickers), the slow rheological features are governed by the sticker dissociation. Under small strains, models treating the effect of thermal dissociation of the stickers just as an enhancement of local friction (so-called sticky chain models [1,2]) have been successfully applied to various associative polymers. In contrast, large strains mechanically disrupt the sticker to activate nonlinear rheological behavior. Recently, we have incorporated the effect of this sticker disruption in the sticky bead-spring dynamics to describe nonlinear damping behavior of linear associative chains under single-step strain [3].

The current work extends this concept of strain-induced sticker disruption (followed by rapid thermal reformation) to associative star chains having the stickers at the arm ends to examine their nonlinear behavior under single- and double-step strain. The star chains forming a transient network at those stickers were modelled as a simple bead-spring chain shown in Fig.1, and the bead-spring analysis was conducted for a fast intrinsic relaxation process activated on the sticker disruption and a slow sticky relaxation process governed by the reformed (and intact) stickers. This analysis, combined with a free energy consideration, successfully described the nonlinear damping function  $h(\gamma)$  of model associative chains (tetra-PEG chains) subjected to the single-step strain; see Fig.2. The analysis for those chains under the double-step strain revealed that a cascaded memory and an isochronal cross-correlation of the arm conformations, both activated on the sticker disruption by the first strain, govern the relaxation under the second step strain. Details of these results will be presented on site.

## References

- [1] L. Leibler et al., *Macromolecules*, **24**, 4701 (1991).
- [2] M. Rubinstein and A. N. Semenov, *Macromolecules*, **31**, 1386 (1998).
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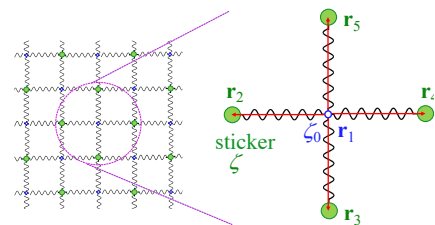


Fig.1 Bead-spring star chain

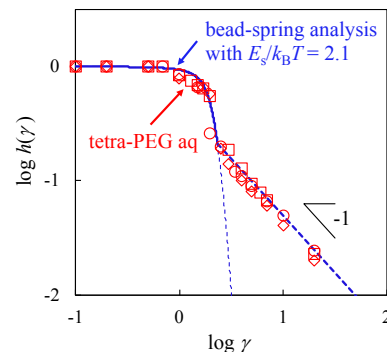


Fig.2 Comparison of damping function of tetra-PEG transient gel with bead-spring analysis.

# Stable Photo-active Layer of Organic Solar Cell Prepared by Sequential Solution Deposition

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In order to commercialize organic solar cells (OSCs), it is essential to address changes in the optimized morphology of the photoactive layer caused by external stimuli, which can lead to degradation. This study presents a method to enhance OSC stability by employing the crosslinking additive 1,8-dibromooctane (DBO) and a sequential deposition (SqD) process to construct the photoactive layer. The crosslinking additive incorporated in the donor polymer (PTB7-Th) secures the crystalline morphology through partial photo-crosslinking. Ellipsometry experiments verify the increase in the glass transition temperature of the crosslinked PTB7-Th. Following the removal of the non-crosslinked polymer and residual additive by chlorobenzene, the polymer crystallinity is further improved. The crosslinked polymer layer establishes an efficient and stable heterojunction with a non-fullerene acceptor (IEICO-4F) layer through the SqD process. The OSC, which is based on the immobilized PTB7-Th, demonstrates outstanding stability against both light soaking and thermal aging. [1,2]

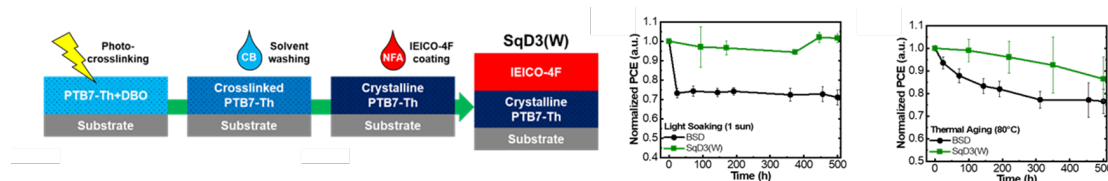


Figure 1. Sequential deposition process of cross-linked polymer donor and non-fullerene acceptor layer

## References

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# Using swelling of polymer thin films to investigate the tightly bound layer at a polymer/substrate interface

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As polymer chains can strongly adsorb to an attractive surface, a tightly bound polymer layer can exist in supported polymer thin films and polymer nanocomposites [1]. The tightly bound layer can be up to a few tens of nanometres thick and strongly influence the physical properties. Therefore, in situ techniques that can shed light on the characteristics of the tightly bound layer without unduly disturbing it are desirable. Recently, we introduced an approach to estimate the thickness of the tightly bound layer at a polymer/substrate interface using the swelling of polymer thin films when exposed to solvent vapour. The approach was tested on two hydrophilic polymers chitosan [2] and poly(vinyl alcohol) (PVA) [3] using thin films of thickness several tens to several hundred nanometres spin coated onto carefully prepared hydrophilic silicon wafers. For the two polymers, the time dependence of the thin film thickness during swelling was studied using variable angle spectroscopic ellipsometry. Assuming that the tightly bound layer cannot swell when exposed to solvent vapour, we found that a single time-dependent swelling ratio could describe the swelling of *all* of the thin films investigated. We also deduced that the tightly bound layer was approximately 18 nm for chitosan and 15 nm for PVA. To corroborate the aforementioned approach, the swelling of the PVA thin films was also investigated using X-ray reflectivity. Electron density profiles determined by modelling the X-ray reflectivity data clearly indicated that at the polymer/substrate interface there existed a polymer layer of a slightly higher density than the rest of the film. The thickness of this polymer layer was found to be approximately 15 nm, consistent with the thickness of the tightly bound layer determined using spectroscopic ellipsometry. If time permits, I will briefly comment on the implications of the aforementioned findings for other systems where one can expect tightly bound polymer layers at the polymer/substrate interface to play a role.

## References

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[2] P. D. Lairenjam et al., *Macromolecules*, 54, 10931 (2021).

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