Nonlinear Rheology of Concentrated Poly(vinyl alcohol)/Borax Aqueous Solution

Yanjie Zhang[1,2] Quan Chen,[1,2]* and Hiroshi Watanabe[1,3]*

[1]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China
[2]University of Science and Technology of China, Hefei, China
[3]Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan

ABSTRACT

Nonlinear rheological behavior was examined for an aqueous solution of poly(vinyl alcohol) (PVA; $M_w = 101$ kg mol^{-1} and $M_n = 67$ kg mol^{-1}) mixed with sodium tetraborate decahydrate (borax). In a neat solution with the PVA concentration of $w_{PVA} = 15$ wt% but without borax, the PVA chains were in a concentrated but barely entangled state. On addition of borax to this solution at a molar concentration of $C_{borax} = 15$ mM, a well percolated transient network of the PVA chains was formed because of dynamic crosslinks between the chains formed through complexation with the borate ions dissociated from borax. Consequently, this PVA/borax solution showed sticky-Rouse type linear viscoelastic (LVE) relaxation much slower than the relaxation of the neat PVA solution. The PVA/borax solution also exhibited time-flow rate separable damping of the viscosity decay function $\eta_-(t,\dot{\gamma})$ on cessation of fast flow as well as time-strain separable damping of the nonlinear relaxation modulus $G(t,\gamma)$ under large step strain. The electrical conductivity measured together with the stress was found to be very close to that in the quiescent state, which unequivocally indicated that the concentration of the free borate and sodium ions determining the conductivity was hardly affected by the strain/flow. The flow/strain undoubtedly disrupted the percolated PVA network, and the conductivity would have increased if this disruption were to release free borate ions. Thus, the observed flow/strain-insensitive conductivity strongly suggested that the disrupted network was rapidly reformed under flow/strain through the intrinsic Rouse motion of the PVA chains in the disrupted portions of the network. The sticky Rouse model[1-4] applicable to the PVA/borax solution at equilibrium was modified for this flow/strain-induced disruption followed by rapid reformation. This modification simply considered that the fast intrinsic Rouse motion in the disrupted portions averages the orientational anisotropy within those portions; the slow sticky Rouse dynamics itself was not modified in the model. This simple model well captured the features of the PVA/borax solution seen for $\eta_-(t,\dot{\gamma})$ and $G(t,\gamma)$. This success of the modified model in turn demonstrates an importance of a simple but unexplored mechanism of the nonlinearity of associative chains, the conformational averaging of the chain on the network disruption followed by rapid reformation.

ACKNOWLEDGEMENTS

REFERENCES

1. L. G. Baxandall, Dynamics of Reversibly Cross-Linked Chains, *Macromolecules*, **22 (4)**, 1982-1988, 1989. https://doi.org/10.1021/ma00194a076.

2. H. Watanabe, Y. Matsumiya, Y. Masubuchi, O. Urakawa, T. Inoue, Viscoelastic Relaxation of Rouse Chains undergoing Head-to-Head Association and Dissociation: Motional Coupling through Chemical Equilibrium, *Macromolecules*, **48 (9)**, 3014-3030, 2015. https://doi.org/10.1021/acs.macromol.5b00409.

3. Q. Chen, G. J. Tudryn, R. H. Colby, Ionomer Dynamics and the Sticky Rouse Model, *J. Rheol.*, **57 (5)**, 1441-1462, 2013. https://doi.org/10.1122/1.4818868.

4. Y. Zhang, Q. Chen, Creep Dynamics of Non-entangled Symmetric Associative Polymers, *Acta Polymerica Sinica*, **52 (7)**, 796-805, 2021. https://doi.org/10.11777/j.issn1000-3304.2021.21014.