Dynamic Tube Dilation in Branched Polymers

H. Watanabe

Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan

1. INTRODUCTION

The entanglement segment is utilized as the motional unit for describing the global dynamics of flexible polymer chains. This unit can be coarse-grained with time according to the loosening of entanglements due to constraint release (CR). The tube model often incorporates this coarse-graining as a simplified molecular picture of dynamic tube dilation (DTD) [1]. Validity of this DTD picture is discussed in this talk.

2. RESULTS AND DISCUSSION

If the relaxed portions of the chains behave as a simple solvent, the system having the tube survival fraction $\varphi'(t)$ in the time scale of t is equivalent to an entangled polymer solution of a concentration $\varphi'(t)$. For this case, the tube diameter is *fully* dilated to that in the solution, $a'(t) = a\{\varphi'(t)\}^{-d/2}$ with a and d (= 1-1.3) being the entanglement segment size and the dilation exponent, respectively. Then, the normalized viscoelastic relaxation function is expressed as

$$\mu_{\text{f-DTD}}(t) = \{\varphi'(t)\}^{1+d} \text{ for full-DTD} \qquad (1)$$

For *cis*-polyisoprene (PI) having the type-A dipole, $\varphi'(t)$ can be dielectrically determined to make an experimental test of eq 1. The full-DTD picture was found to be valid for monodisperse *linear* PI [1,2]. However, this picture fails for monodisperse *star* PI [2] as well as *Cayley-tree* type PI [3]; compare $\mu_{\text{f-DTD}}$ (dotted curves) and μ data (circles) in Figure 1.

This failure is related to inconsistent coarse-graining in the full-DTD picture. The CR process activating DTD is associated with the maximum possible number $\beta_{\text{CR}}(t)$ of the entanglement segments that can be coarse-grained in the given time scale t. Then, the tube diameter can be only *partially* dilated to $a^*(t) = \{\beta^*(t)\}^{1/2}a$ with $\beta^*(t) = \min[\beta_{\text{CR}}(t), \{\varphi'(t)\}^{-d}]$, and the corresponding expression of μ is given by

$$\mu_{\text{p-DTD}}(t) = \varphi'(t)/\beta^*(t) \text{ for partial-DTD} \qquad (2)$$

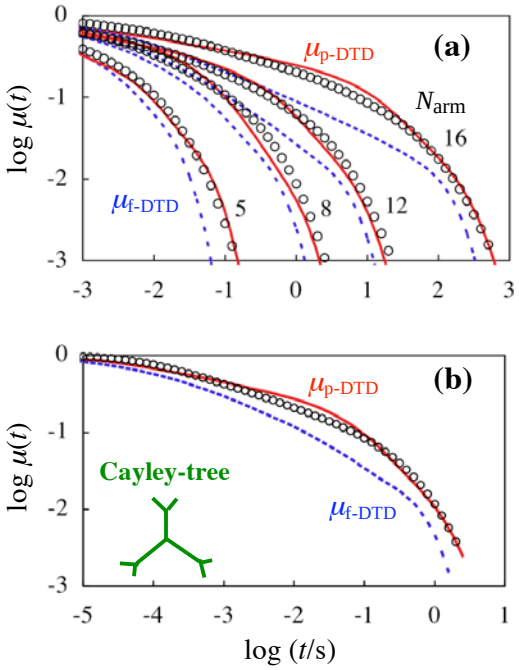

Fig.1 Comparison of $\mu_{\text{f-DTD}}$ and $\mu_{\text{p-DTD}}$ with μ data for **(a)** 6-arm star PI having $N_{\text{arm}} = M_{\text{arm}}/M_{\text{e}}$ as indicated and **(b)** Cayley-tree PI having inner and outer arms of $10^{-3}N = 6$ and 3, respectively.

$\beta_{\text{CR}}(t)$ was evaluated from the known data of CR time and eq 2 was tested experimentally [2,3]. As shown in Figure 1, $\mu_{\text{p-DTD}}$ (solid curves) are satisfactorily close to the μ data (circles), demonstrating the validity of the partial DTD picture based on the consistent coarse-graining of the length and time scales on the basis of the Rouse-CR mechanism [2,3].

REFERENCES [1] Watanabe, *Prog. Polym. Sci.* **1999**, *24*, 1253.
[2] Watanabe et al, *Macromolecules* **2006**, *39*, 2553.
[3] Watanabe et al, *Macromolecules*, submitted.