

Molecular Picture of Dynamic Tube Dilatation for Entangled Polymers –Coarse-Graining of Length Scale Consistent with Time Scale –

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要旨：絡み合い緩和に対する現在の管モデルでは、ある鎖に対するトポロジ的拘束を表す管の直径が、周囲の鎖の運動によって時間とともに膨張すると考えられている。この管膨張の描像は絡み合いセグメントの粗視化に対応する。セグメントの運動性を考慮して時間スケールと整合する形で粗視化を行えば、管膨張描像が実際の絡み合い系に適用できることが実験的に示された。

1. Introduction.

The "segment" of flexible polymer chains is the fundamental concept for description of the polymer conformation/dynamics. Typically, a given number of monomers is coarse-grained into the segment and all structural/dynamic properties of polymers are described in terms of the position of the segments. However, in most of the cases, no careful consideration is made for the choice of this number. In this talk, the author focuses on the relaxation of entangled polymers and attempts to explain how the coarse-graining of the length scale is to be made consistently with the time scale.

2. Molecular Picture of Full-DTD.

For well-entangled flexible polymer chains, the viscoelastic relaxation function $G(t)$ exhibits a well-defined plateau corresponding to the so-called entanglement length, a . In the tube model, this a is regarded as a characteristic length for the topological constraint and the corresponding *entanglement segment* (of the molecular weight M_e and size a) is utilized as the fundamental motional unit for the slow dynamics. The current model considers that the entanglement segments of a given chain are confined in a tube-like region formed by the surrounding chains (matrix chains) and the tube diameter dynamically dilates from a to $a'(t)$ with time because of the motion of the matrix chains. With this molecular picture of dynamic tube dilatation (DTD), successive $\beta(t)$ ($= \{a'(t)/a\}^2$) entanglement segments are mutually equilibrated over the length scale of $a'(t)$ through their motion to behave as a coarse-grained motional unit, and the normalized viscoelastic relaxation function is expressed in terms of this $\beta(t)$ and the survival fraction of the tube $\varphi'(t)$ ($=$ fraction of the segments trapped in the initial tube at time 0) as

$$\mu(t) \equiv G(t)/G_N = \varphi'(t)/\beta(t) \text{ with } G_N = \text{entanglement plateau modulus} \quad (1)$$

In most of the models,¹⁻³ the portions of the chains having escaped from the initial tube are assumed to give no topological constraint and behave as a simple solvent. Then, the tube is fully dilated to that in a polymer solution of a concentration $\varphi'(t)$. In this molecular picture of full-DTD, the equilibrated segment number is given by $\beta_{f\text{-DTD}}(t) = \{\varphi'(t)\}^{-d}$ with the dilation exponent $d = 1 - 1.3$, and the relaxation function is expressed as

$$\mu(t) = \{\varphi'(t)\}^{1+d} \text{ for full-DTD process} \quad (2)$$

3. Test of Full-DTD/partial-DTD Pictures.

For polymers having type-A dipoles parallel along the chain backbone, the tube survival fraction $\varphi'(t)$ can be determined from their dielectric data. ($\varphi'(t)$ essentially coincides with the dielectric relaxation function.) Thus, the full-DTD expression of $\mu(t)$ (eq 2) can be tested in a purely empirical way by comparing the dielectrically evaluated $\mu_{f\text{-DTD}}(t) = \{\varphi'(t)\}^{1+d}$ and viscoelastically measured $\mu(t)$.

For *cis*-polyisoprene (PI) having the type-A dipoles, the results of this comparison (with $d = 1.3$) are shown in Figures 1 and 2. For blends of linear PI (Figure 1), $\mu_{f\text{-DTD}}$ (dotted curves) agrees well with the μ data (circles) at long and short t but a significant difference is noted at intermediate t . For monodisperse star PI (Figure 2), $\mu_{f\text{-DTD}}$ is considerably smaller than the μ data in the dominant part of the terminal relaxation regime.

This failure of the full-DTD picture is related to an inconsistency in the coarse-graining of the length scale made in this picture: In a given time scale t , the mutual equilibration can occur through the so-called constraint release (CR) motion only up to a certain number $\beta_{\text{CR}}(t)$ because of the limited CR mobility of the segment. Correspondingly, the spatial coarse-graining is allowed only within a length scale of $a\{\beta_{\text{CR}}(t)\}^{1/2}$. However, the full-DTD picture makes the coarse-graining over a length scale of $a\{\beta_{f\text{-DTD}}(t)\}^{1/2} = a\{\varphi'(t)\}^{-d/2}$ irrespective of the $\beta_{\text{CR}}(t)$ value. Thus, this molecular picture naturally fails in a range of time where $\beta_{\text{CR}}(t) < \beta_{f\text{-DTD}}(t)$.

The CR equilibration number $\beta_{\text{CR}}(t)$ can be estimated from the Rouse-like CR relaxation time data of dilute probe chains entangled with much shorter matrix. The failure of the full-DTD picture seen in Figures 1 and 2 was confirmed to occur when $\beta_{\text{CR}}(t) < \beta_{f\text{-DTD}}(t)$. On the basis of this result, we may consider a partial-DTD (p-DTD) picture in which the spatial coarse-graining is made to the maximum level consistent with the values of $\beta_{\text{CR}}(t)$ and the tube survival fraction $\varphi'(t)$: The equilibration number in this picture is given by

$$\beta_{p\text{-DTD}}(t) = \min[\beta_{\text{CR}}(t), \{\varphi'(t)\}^{-d}] \quad (3)$$

The relaxation function for the p-DTD picture, $\mu_{p\text{-DTD}}(t) = \varphi'(t)/\beta_{p\text{-DTD}}(t)$ (cf. eq 1), is shown with the solid curves in Figures 1 and 2. This $\mu_{p\text{-DTD}}(t)$ agrees considerably well with the $\mu(t)$ data (circles), indicating the validity of the simple p-DTD picture.

This result in turn suggests that the spatial coarse-graining beyond the entanglement length a works for linear and star polymers if it is made consistently with the time scale (that determines the CR equilibration number). This type of consistent coarse-graining would offer a route for describing the dynamics of polymers having more complicated topology such as pom-poms and combs.

References

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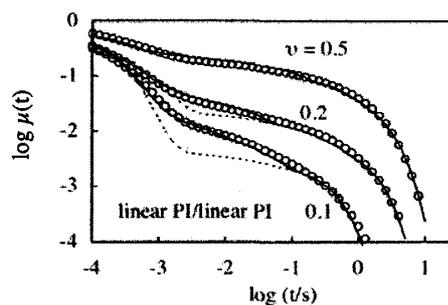


Fig.1 Comparison of the normalized relaxation function of blends of linear PI at 40°C (circles) with those deduced from the molecular pictures of full-DTD (dotted curves) and partial-DTD (solid curves). The number of entanglement segments per long and short chain components are $N_2 = 60$ and $N_1 = 4$, and the volume fraction of the long chain components v varies from 0.5 to 0.2.

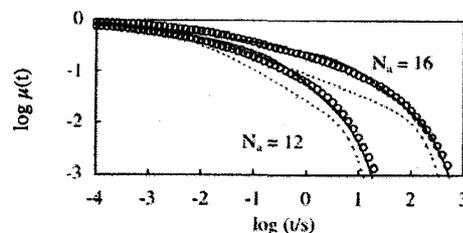


Fig.2 Comparison of the normalized relaxation function of monodisperse 6-arm star PI (circles) with those deduced from the molecular pictures of full-DTD (dotted curves) and partial-DTD (solid curves). The number of entanglement segments per arm is $N_a = 12$ and 16.