

COMPARISON OF VISCOELASTIC AND DIELECTRIC PROPERTIES OF TYPE-A CHAIN: EXPERIMENTAL ATTEMPT FOR DEEPER UNDERSTANDING OF POLYMER RHEOLOGY

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ABSTRACT

Viscoelastic and dielectric properties of type-A chains differently average the same chain dynamics, so that comparison of those properties resolves some details of this dynamics in a purely experimental way. Some examples of this comparison are presented in the talk.

INTRODUCTION

Molecular understanding of polymer rheology has been one of the central targets in the community of rheology, and extensive studies have been made from both experimental and theoretical aspects.^{1,2} Comparing viscoelastic and dielectric properties of so-called *type-A chains* in long time scales, we may find some details of the molecular dynamics underlying the rheological behavior of those polymers, as explained below.

The type-A chain has the electrical dipoles \mathbf{p} parallel along the chain backbone (cf. **Fig.1**) and its viscoelastic and dielectric properties in long time scales commonly reflect the large-scale chain motion over the end-to-end distance R . Nevertheless, this motion is differently averaged in the viscoelastic and dielectric properties. For example, the relaxation modulus $G(t)$ under a step strain γ and the dielectric relaxation function $F(t)$ under a step electric field E are expressed in terms of the bond vector of n -th subchain (or coarse-grained segment) at time t , $\mathbf{u}(n,t)$, as³⁻⁵

$$G(t) = \frac{\nu k_B T}{\gamma} \int_0^N \left\{ 3 / \langle \mathbf{u}^2 \rangle_{\text{eq}} \right\} \langle u_x(n,t) u_y(n,t) \rangle_\gamma dn \quad (1)$$

$$F(t) = \frac{\nu}{E} \int_0^N m_d \left\{ \langle u_E(n, \infty) \rangle_E - \langle u_E(n, t) \rangle_E \right\} dn \quad (2)$$

Here, ν is the number density of the chain, $k_B T$ is the thermal energy, $\langle \mathbf{u}^2 \rangle_{\text{eq}}$ is the mean-square end-to-end distance of the subchain at equilibrium, and m_d is the dipole moment per unit length of the backbone of the type-A chain (with no dipole-inversion being considered in Eq.2). In Eq.1, u_x and u_y stand for the components of $\mathbf{u}(n,t)$ in the shear (x) and shear gradient (y) directions, respectively, and $\langle \dots \rangle_\gamma$ denotes the ensemble average under the step strain. In Eq.2, u_E is a component of $\mathbf{u}(n,t)$ in the direction of the electric field, and $\langle \dots \rangle_E$ indicates the ensemble

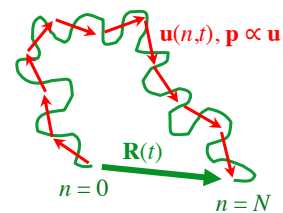


Fig.1. Schematic illustration of type-A chain without dipole inversion.

average under the step electric field E . For sufficiently small γ and E (in the linear response regime), the chain dynamics determining $\langle u_x u_y \rangle_\gamma$ and $\langle u_E \rangle_E$ coincides with the equilibrium dynamics. However, $G(t)$ and $F(t)$ are determined by the second- and first moment averages of $\mathbf{u}(n,t)$, respectively. Namely, the same dynamics is differently averaged in the viscoelastic $G(t)$ and dielectric $F(t)$. This difference enables us to experimentally resolve some details of the chain dynamics through comparison of viscoelastic and dielectric properties of type-A chains. Some examples of this comparison are presented below.

TEST OF TUBE DILATION PICTURE FOR ENTANGLED POLYMERS

For entangled chains, tube models consider that the chain relaxes through several different mechanisms, reptation (for linear chains) and/or arm retraction (for star chains), contour length fluctuation (CLF), and constraint release (CR).^{1,2} Among these mechanisms, the CR mechanism considers the relaxation of a given chain (probe) activated by the motion of surrounding chains, thereby introducing a flavor of multiple chain dynamics into the tube model. Some models further assume that the relaxed portion of chains serves as a solvent for the probe chain to *fully* dilate the tube (to a level in the corresponding solution), thereby successfully describing $G(t)$ of linear and star chains.^{4,5} However, comparison of dielectric and viscoelastic data of a typical type-A polymer, high-*cis* polyisoprene (PI), resolved a limitation of this *full-DTD* molecular picture, as explained below.^{4,5}

For this comparison, it is convenient to rewrite Eq.2 with the aid of the Green-Kubo theorem (valid at equilibrium) as^{4,5}

$$\Phi(t) \equiv \frac{F(t)}{F(0)} = \frac{1}{N} \int_0^N dn \int_0^N dn' C(n,t;n') \quad \text{with } C(n,t;n') = \left\langle \mathbf{u}^2 \right\rangle_{\text{eq}}^{-1} \left\langle \mathbf{u}(n,t) \cdot \mathbf{u}(n',0) \right\rangle_{\text{eq}} \quad (3)$$

A conformational analysis shows that $\Phi(t)$ is essentially identical to the survival fraction $\varphi'(t)$ of the dilated tube.^{4,5} Thus, the $\Phi(t)$ data (obtained from dielectric experiments for PI) allow us to formulate the reduced relaxation modulus $\mu(t) = G(t)/G(0)$. Specifically, the full-DTD molecular picture assumes that the relaxed portion of the chains always behaves as a solvent to dilate the tube diameter to $a_{f\text{-DTD}}(t) = a_{\text{eq}} \{\varphi'(t)\}^{-d/2}$, with a_{eq} = equilibrium tube diameter and $d \cong 1.3$ (tube dilation exponent). This full-DTD assumption leads to a relationship, $\mu_{f\text{-DTD}}(t) = \{a_{\text{eq}}/a_{f\text{-DTD}}(t)\}^2 \varphi'(t) = \{\varphi'(t)\}^{1+d}$.

For binary blends of linear PI with molecular weights $M_2 = 308\text{k}$ and $M_1 = 21\text{k}$, $\mu_{f\text{-DTD}}(t)$ thus obtained dielectrically (green curves) is compared with the viscoelastically measured $\mu(t)$ data (black circles) in **Fig.2**. At $t = 0.5\text{-}500$ ms where the low- M chain has fully relaxed but the high- M chain has not, $\mu_{f\text{-DTD}}(t)$ is smaller than the $\mu(t)$ data of the blends having a small fraction of the high- M chain, $\nu_2 = 0.2$ and 0.1 . This failure of the full-DTD picture results from the assumption that the relaxed portion of the chain (the whole backbone of the low- M chain at those t) always behaves as the solvent to fully dilute the tube for the high- M chain. In reality, the high- M chain moving through the CR motion cannot always explore the whole part of this diluted tube and thus the effective tube diameter for that chain $a^*(t)$ is smaller than $a_{f\text{-DTD}}(t)$ at those t . This problem of the full-DTD picture can be removed if we evaluate the maximum possible lateral displacement $a_{\text{CR}}(t)$ allowed by the CR motion and express the reduced relaxation modulus as $\mu_{f\text{-DTD}}(t) = \{a_{\text{eq}}/a^*(t)\}^2 \varphi'(t)$ with $a^*(t) = \min\{a_{\text{CR}}(t), a_{f\text{-DTD}}(t)\}$.

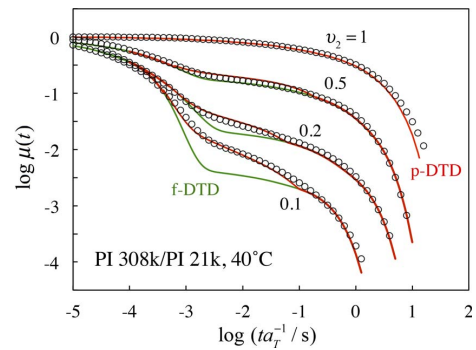


Fig.2. Comparison of $\mu_{f\text{-DTD}}(t)$ and $\mu_{p\text{-DTD}}(t)$ deduced within the tube model with $\mu(t)$ data of PI/PI blends with various ν_2 .

Viscoelastic measurements for reference binary blends (containing *self-unentangled* high- M components) allow us to evaluate $a_{CR}(t)$ and thus $\mu_{f-DTD}(t)$ for the partial-DTD picture.^{4,5} This $\mu_{f-DTD}(t)$, shown with the red curve in Fig.2, is in excellent agreement with the $\mu(t)$ data in the entire ranges of t and ν_2 . This result in turn demonstrates an importance of the comparison between dielectric and viscoelastic data.

EIGENFUNCTION OF LOCAL CORRELATION FUNCTION

Chemical coupling of living anionic PI chains of different M allows us to prepare homo-PI chains with inversion of type-A dipoles at a given (n^* -th) segment. For those dipole-inverted PI, the dielectric relaxation function is expressed in terms of C defined in Eq.3 as⁴

$$\Phi(t; n^*) = \frac{1}{N} \left\{ \int_0^{n^*} dn - \int_{n^*}^N dn \right\} \left\{ \int_0^{n^*} dn' - \int_{n^*}^N dn' \right\} C(n, t; n') \quad (4)$$

The local correlation function C can be expanded with respect to its eigenfunctions $f_p(n)$ as $C(n, t; n') = \sum_p f_p(n) f_p(n') \exp(-t/\tau_p)$ (with τ_p being p -th relaxation time). Thus, the dielectric data of a series of dipole inverted PI having the same M but different n^* allow us to experimentally resolve $f_p(n)$ for a few low-order modes. An example is shown in Fig.3 for PI being entangled with polybutadiene and exhibiting CR relaxation.⁴ The standard tube model assumes the Rouse-type CR associated with sinusoidal $f_p^{[R]}(n) = \sin(p\pi n/N)$ (black curves). However, experimental $f_p(n)$ moderately deviate from $f_p^{[R]}(n)$. From mathematical coincidence of the Rouse eigenfunction equation and the Schrödinger equation for a quantum particle in a well potential, this deviation can be related to an extra relaxation enhanced at around the chain end⁴ (where the motional constraint is weaker compared to the middle of the chain).

If the chain moves coherently along its backbone (as in the case of reptation), the eigenfunction is common for $C(n, t; n')$ and the orientation function governing the viscoelastic relaxation, $S(n, t) = \{3/\langle \mathbf{u}^2 \rangle_{eq}\} \langle u_x(n, t) u_y(n, t) \rangle_\gamma$ shown in Eq.1. In contrast, if the chain motion is incoherent, $f_p(n)^2$ determines $S(n, t)$. Thus, comparison of dielectrically determined $f_p(n)$ and viscoelastic data allows us to test this motional coherence. It turned out that the chains in unentangled solutions exhibit the incoherent motion whereas some magnitude of coherence emerges for entangled chains in concentrated solutions/bulk.⁴ An importance of the comparison between dielectric and viscoelastic data is demonstrated also from this experimental finding.

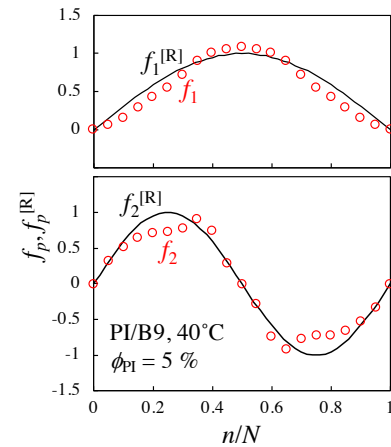


Fig.3. Eigenfunction of PI relaxing through CR mechanism.

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