

Nonlinear Viscoelasticity of Amorphous Polymers in the Vicinity of the Glass Transition Temperature.

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Nonlinear viscoelasticity of atactic polystyrene around the glass transition was studied by means of constant rate elongation. The strain-induced birefringence and the stress were simultaneously measured and then the stress was separated into two components (Rubbery and Glassy components) by using the modified stress-optical rule. Behavior of the R component, having the molecular origin of chain orientation, was essentially linearly viscoelastic. On the other hand, the G component, originated by rotational orientation of chain units, showed remarkable thinning phenomena, which is commonly observed for glassy materials. Thus, the separation of stress for polymeric material simplifies phenomenological interpretation of nonlinear viscoelasticity of polymers near the glass transition zone.

Keywords : Glass transition/ Stress-optical Rule/ Viscoelasticity/ Amorphous polymer/ Rheo-optics/ Rheology/ Polystyrene

The glass transition phenomena are widely observed in various polymeric systems. In the vicinity of the glass transition temperature, the modulus typically varies from the glassy modulus (ca. 10^9 Pa) to the rubbery modulus (ca. 10^6 Pa). Most widely accepted interpretation for the glass transition is "freezing of molecular motions", that is, competition between molecular relaxation time scale and experimental time scale. However, the molecular motion responsible to the glass transition is not fully specified.

We have previously found a new method [1] for decomposing the stress (modulus) into two components having different molecular origins. This method is based on the modified stress-optical rule: The rule says that the stress, $\sigma(t)$ and birefringence, $\Delta n(t)$, are composed of two

components (denoted by subscripts R and G) and that proportionality holds valid for each component.

$$\sigma(t) = \sigma_R(t) + \sigma_G(t) \quad (1)$$

$$\Delta n(t) = C_R \sigma_R(t) + C_G \sigma_G(t) \quad (2)$$

Here C_i is the proportionality coefficient called the stress-optical ratio for the component i . Eqs. 1 and 2 can be solved for $\sigma_R(t)$ and $\sigma_G(t)$. Systematic studies on various polymers revealed that the R component is related with the chain orientation and the G component is with rotational orientation of a structural unit around main chain axis. In the rubbery state the contribution of $\sigma_G(t)$ can be ignored.

Recently, we applied this method to constant elongation experiments of polystyrene around the glass transition temperature. [2] Figure 1 shows representative data

FUNDAMENTAL MATERIAL PROPERTIES — Molecular Rheology —

Scope of research

The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.

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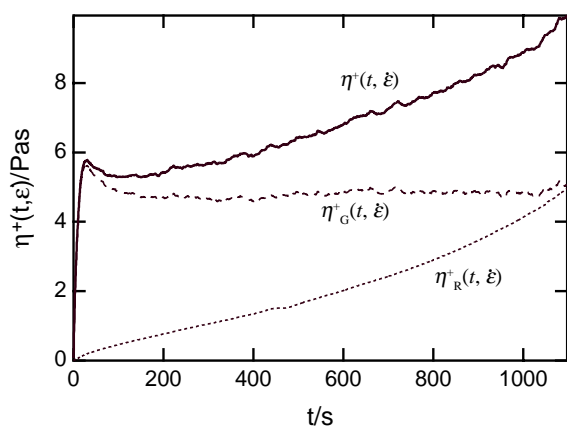


Figure 1. Stress growth during constant rate elongation of polystyrene at 100°C with $\dot{\epsilon}=0.001\text{s}^{-1}$

for stress growth at 100°C with rate of strain, $\dot{\epsilon}=0.001\text{s}^{-1}$. Here the tensile stress is reduced by rate of strain, $\eta^+(t, \dot{\epsilon})=\sigma(t)/\dot{\epsilon}$. The stress increases vary rapidly on start-up of deformation, shows a maximum, and then increases again with time. This type of stress growth cannot be described with linear viscoelastic theory for the small strain regime.

Dotted and broken lines in Figure 1 shows the result of decomposition of the stress into the two components. The R component, $\eta_R^+(t, \dot{\epsilon})=\sigma(t)_R/\dot{\epsilon}$, increased monotonically with time. We found that $\eta_R^+(t, \dot{\epsilon})$ was in accord with linear viscoelastic theory. This means that the response of R component does not change in a wide range of strain examined.

On the hand, $\eta_G^+(t, \dot{\epsilon})$ increases vary rapidly and then decreases and apparently reaches a steady state at long times. We may define the steady state viscosity, $\eta_{EG}(\dot{\epsilon})$. The result quite resembles the features of the ordinary entangled polymer systems under shear flow, although the two phenomena have different molecular origins.

Similar results were obtained at different rates of strain and different temperatures. Figure 2 shows $\dot{\epsilon}$ dependence of $\eta_{EG}(\dot{\epsilon})$. Here, in order to compare the data at different temperatures, the data are reduced to 115°C with the method of reduced variables: $\eta_{EG}a_{TG}^{-1}$ is plotted against $a_{TG}\dot{\epsilon}$, where a_{TG} is the shift factor for the G component determined by dynamic measurement. The data at different temperatures lie on a single curve. This result in turn suggests that the method of reduced variables works well for the G component even in the nonlinear viscoelastic region around the glass transition zone.

For the shear viscosity of polymer melts in the terminal flow zone, the non-Newtonian thinning is observed at rates $\dot{\gamma}>\tau^{-1}$ where τ is the longest relaxation time. In addition, viscosity is close to $|\eta^*(\omega)|_{\omega=0}$, measured in the linear regime(Cox-Melz rule). In contrast, Figure 2 demonstrates that η_{EG} has much stronger rate dependence than

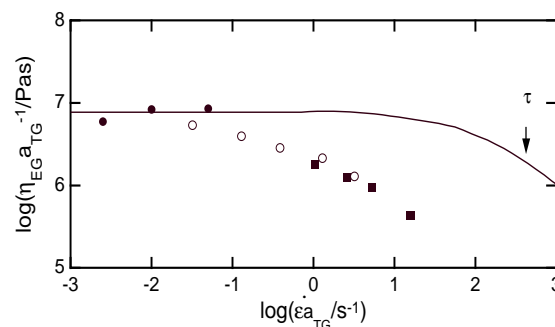


Figure 2. Rate dependence of viscosity for the G component. Line in the figure indicates $|\eta_{EG}^*(\omega)|_{\omega=0}$.

$|\eta_{EG}^*(\omega)|_{\omega=0}$. The rate where thinning starts is about 300 times smaller than that for $|\eta_{EG}^*(\omega)|_{\omega=0}$. It is well-known that the shear thinning of viscosity of polymer melts is associated with the strong strain dependence of the shear relaxation modulus. The very strong rate dependence of η_{EG} may be related to the very strong strain dependence of the Young's relaxation modulus.

As demonstrated in Figure 1, the separation of stress into the two components simplifies the phenomenological interpretation of viscoelasticity around the glass transition zone. The remarkable nonlinear viscoelasticity around the glass transition zone can be related with the strong rate dependence of the G component. We also emphasize that σ_G is a well-behaving viscoelastic quantity, for which the viscosity exhibits strong but smooth thinning and the method of reduced variables works well; see Figure 2.

Finally, we point out that viscoelastic behavior of the G component quite resembles that of inorganic glasses. η_E of these materials show a very similar shear thinning phenomenon when $\dot{\epsilon}$ exceeds a certain $\dot{\epsilon}$, a few hundredth of τ^{-1} . [3] Such a similarity strongly suggests a universal relaxation mechanism for glass forming materials, a cooperative relaxation mechanism which is insensitive to details of molecular structures.

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