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# Time-Dependent Viscoelastic Functions for Cis-1,4-Polybutadiene Melts

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## Summary

Transient linear and nonlinear viscoelastic functions were measured on cis-1,4-polybutadiene melts and compared to the ROUSE theory and a nonlinear modification of the network theory. The latter was found to overestimate material nonlinearity, especially of the first normal stress coefficient at cessation of steady shear flow. Steady-state functions were recovered from the time dependent measurements. Single step strain experiments in the linear region were recorded by computer, up to 7 milliseconds after the sudden shear jump; a paradox arised in the interpretation of shear versus normal stress after a sudden shear strain.

## Introduction

Recently, we have published comprehensive data of dynamic modulus and oscillatory first normal stress coefficients for cis-1,4-polybutadiene melts (ALVAREZ 1982a). It was concluded that all data at low strains, i.e. linear viscoelasticity, could be satisfactorily reproduced by the ROUSE theory modified for entanglements (ALVAREZ 1981) and corrected to take into account the molecular weight distribution (ALVAREZ 1982b).

However, linear viscoelastic data do not provide a rigorous test for theory. The next step in complexity may be the transient behaviour, while the most severe tests known are most certainly strain histories with changes of sign in the strain, namely large amplitude oscillations and/or multiple step strain experiments with positive and negative steps in succession.

In the present paper, we report measurements of single step strains in the linear region, and linear and nonlinear transient measurements up to, and from steady state, and the fit of an empirical nonlinear modification of the network theory to these data. The network theory is known to be identical to the ROUSE theory, but the nonlinear modification of the former was found to overestimate the nonlinearity of the present data. We do not proceed with further empirical modifications here.

## Theory

According to LODGE (1971), the ROUSE theory, the network theory and the generalized MAXWELL model are identical representations of the linear viscoelastic fluid. The network theory is a special case of a class of equations represented by:

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$$\underset{\approx}{\tau}(t) = \int_{-\infty}^{t} m(t - t')\underset{\approx}{\gamma}_{[0]}(t - t')dt' \qquad (1)$$

where $\underset{\approx}{\tau}$ is the stress tensor and $\underset{\approx}{\gamma}_{[0]}$ is the contravariant finite strain tensor (BIRD 1977); the material memory function m(t - t') can be obtained from a balance equation:

$$\frac{\partial}{\partial t} n_{tt'p} + \lambda_p^{-1} n_{tt'p} = 0 \qquad (2)$$

where $n_{tt'p}$ is the number of segments of complexity p per unit volume, created at time interval t' to t' + dt'. On integration of (2) and summing over p, it is found:

$$m(t - t') = n_{tt'}kT = kT\sum_{p=1}^{\infty} \frac{\eta_p}{\lambda_p^2} e^{-(t - t')/\lambda_p} \qquad (3)$$

with the initial condition

$$n_{t't'p} = \frac{\eta_p}{\lambda_p^2} \qquad (4)$$

When $\eta_p$ and $\lambda_p$ are interpreted as the viscosity and relaxation time of the pth mode, (2) becomes identical to the result of the ROUSE theory. In the network terminology, $1/\lambda_p$ is the pth segment loss probability and the number of segments of type p created per unit volume is $\eta_p \lambda_p^{-2}$. The modification by CARREAU (1972) consisted of the introduction of empirical functions $g_p$ and $f_p$ to correct the segment loss probability and the number of segments created per unit volume respectively. $g_p$ and $f_p$ were made to be functions of the second invariant of the rate-of-strain tensor $II = \sqrt{\underset{\approx}{\dot{\gamma}}:\underset{\approx}{\dot{\gamma}}/2}$ and must obey $f_p = 1$, $g_p = 1$ as $II \rightarrow 0$, otherwise they were left unspecified. Equation (3) becomes:

$$n_{tt'II(t')} = \sum \frac{\eta_p f_p(II(t'))}{\lambda_p^2} \exp\left[-\int_{t'}^{t} \frac{dt''}{\lambda_p g_p(II(t''))}\right] \qquad (5)$$

Setting $g_p = 1$ yielded an older model named the BIRD-CARREAU model (1968). Additionally, second normal stress coefficients could be obtained provided the strain measure in (1) were replaced by $(1 - \varepsilon)\underset{\approx}{\gamma}_{[0]} - \varepsilon\underset{\approx}{\gamma}^{[0]}$ where $\varepsilon$ is the ratio of the second to the first normal stress coefficient.

## Experimental

97 % cis-1,4-polybutadiene (PB) of $M_n = 218$ kg mol$^{-1}$ and $M_w = 488$ kg mol$^{-1}$ (Courtesy of CHEMISCHE WERKE HÜLS AG) identical to that used in previous studies was moulded under pressure at 40 °C and then transferred to the

cone-plate gap of an INSTRON 3250 Rheometer with thermostated strain gauges. An additional film of material around the cone truncation insured absence of voids in this region, and then the gap was brought to the final setting slowly ($\eta_o \simeq 10$ MPa s) in steps of 5 µm. This procedure ensured good adhesion of the material to the walls. After a minimum time of 12 hours the experiment was ready for start. The instrument was operated manually and the input strain and output torque and thrust amplifier signals were digitized and stored permanently.

## Results

### a) Single linear step strain

From the generalized MAXWELL model, the relaxation modulus G(t - t') and the memory function m(t - t') are related by m(t - t') = ∂G(t - t')/∂t'. Thus, from (3):

$$G(t - t') = \sum \frac{\eta_p}{\lambda_p} e^{-(t - t')/\lambda_p} \tag{6}$$

For the ROUSE theory

$$\eta_p = ckT\lambda_p \tag{7}$$

$$\lambda_p = \frac{f_o b^2 N^2}{6\pi^2 p^2 kT} \tag{8}$$

$f_o$ is the bead friction coefficient, b is the root-mean-square end-to-end distance for two adjacent beads at equilibrium and c is the number of molecules per unit volume.

The modified ROUSE distribution accounts for a smooth transition between entangled and nonentangled submolecules, thus

$$\lambda_{p_{mod}} = \lambda_p p_e^{2.4\exp(-p/p_e)} \quad , \quad p_e = M/M_c \tag{9}$$

where $M_c$ is the critical molecular weight for entanglements in the zero-shear viscosity.

There are no normal stresses in the ROUSE theory, but the following argument can be used to extract them. For simple shear in the 1,2 plane a simple relationship exists between three components of $\underset{\approx}{\gamma}_{[0]}$ referred to a Cartesian coordinate system, namely

$$\gamma_{[0]11} - \gamma_{[0]22} = \gamma\gamma_{[0]12} \tag{10}$$

where γ is the amount of shear. Assuming that during the time of shear the network connectivity does not change, then, according to (1):

$$\tau_{11} - \tau_{22} = \gamma\tau_{12} \tag{11}$$

at any instant along the time axis. The two sides of (11) are the material functions plotted in Figure 1 for the PB melt at 298 K. The cone angle was

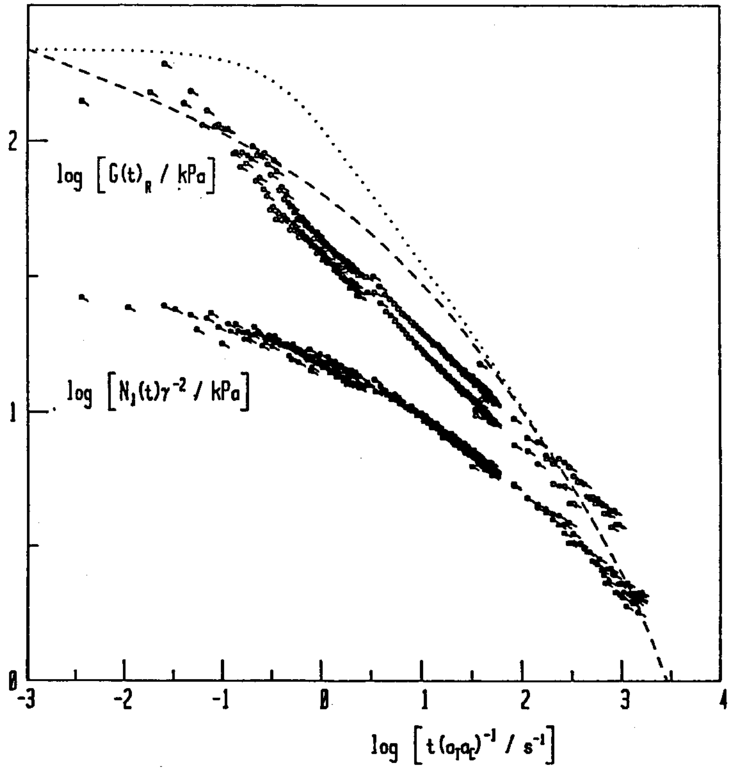

Figure 1. Stress relaxation versus time in step strain, $\gamma \approx 1$, PB melt, 298 K. - - - Rouse theory with smooth transition into plateau and . . . with sharp transition. Two experiments separated by $t = \infty$

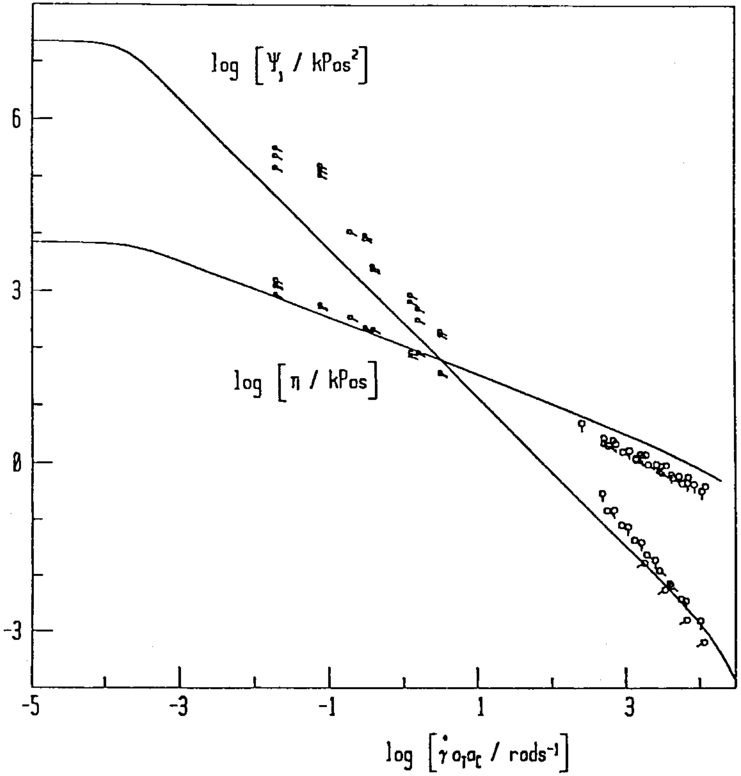

Figure 2. Steady-state viscosity and first normal stress coefficient vs. shear rate, PB melt, 298 K. Data from start of shear ○ , cessation of shear ● ,and from slit die rheometer □. Lines are predictions of Carreau model

6 degrees and the plate diameter was 20 mm. $\gamma \simeq 1$. The broken lines are results of the ROUSE theory with smooth transition, equations (6) - (9), and the dotted lines are results of the ROUSE theory with a sharp transition between entangled and nonentangled submolecules.

The discrepancy between the two material functions in Figure 1 could be due to instrumental axial compliance. Alternatively, the material could fail to obey equation (1). Other types of constitutive equations are given by LODGE (1974).

b) Steady-state functions from the ROUSE theory

Steady-shear viscosity and first normal stress coefficient for the PB melt at 298 K are given in Figure 2. The high shear rate viscosities were obtained on a slit die rheometer. The solid lines are predictions of CARREAU model; these are equivalent to postulating a type of COX-MERZ relationship:

$$\eta(\dot{\gamma}) = \eta'(c\omega) \tag{12}$$

where c is a time shift factor of the order of 1. $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ can, thus, be obtained from the ROUSE theory in this manner.

c) Transient measurements

Figures 3 - 6 present results of viscosity and first normal stress coefficients at start and cessation of steady shear flow respectively. The shear rate range was .01 - 1.6 rad $s^{-1}$, from basically linear behaviour to a limiting shear rate given by expulsion of the material from the cone-and-plate gap. The two highest shear rates in each plot were gained with a cone angle of 1.2 degrees. All other data were obtained with a cone angle of 6 degrees. The plate diameter was 20 mm. This allowed some preliminary conclusions on the effect of cone angle on the measurements. Thus, torque measurements, Figures 3 and 5, are likely to be independent of cone angle, but thrust measurements reveal a definite deviation in the linear region for a cone angle of 1.2 degrees, although all linear measurements for a cone angle of 6 degrees coincide, Figure 4. It could be concluded that torque measurements are reliable at all cone angles, while normal stress measurements are reliable only at cone angles $\geq 6$ degrees.

The solid lines in Figures 3 - 6 are results of CARREAU model with parameters obtained from the ROUSE theory and Figure 2. The theoretical material functions as well as the functions $f_p$ and $g_p$ are given elsewhere (ALVAREZ 1982c). The quality of the fit between theory and experiment is seen to decrease as we proceed from Figure 3 to Figure 6. No overshoots are observed experimentally up to the highest shear rates. Less overshoot is known to be predicted by the BIRD-CARREAU theory mentioned above, and no overshoot at all would be predicted for $f_p g_p > 1$.

## Conclusions

Further experiment is required to elucidate the sources of failure of equation (11) in the present work. Definite results about the effect of instrument compliance on melt transient experiments could be obtained by measuring successive dilutions of the melt, provided concentration shift

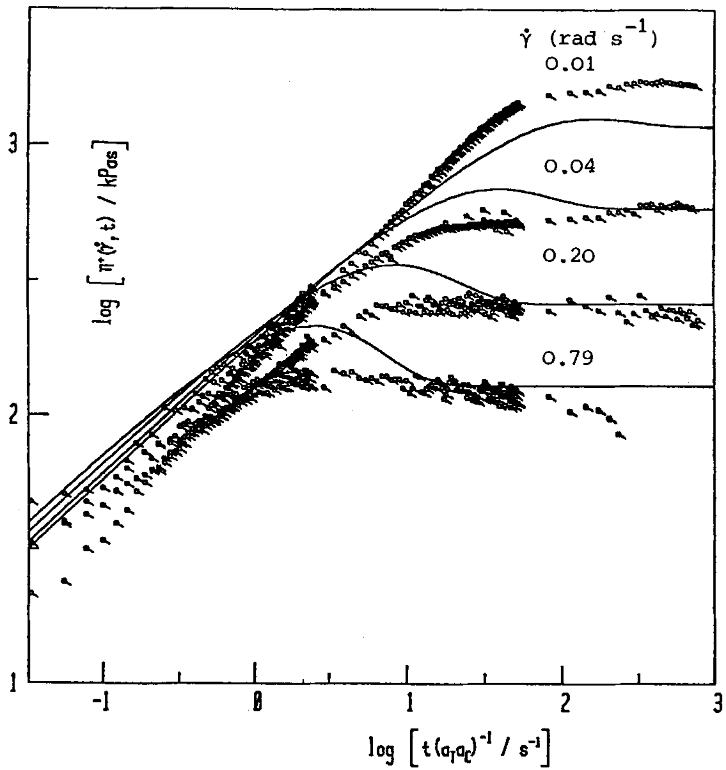

Figure 3. Viscosity at start of steady shear flow vs. time, PB melt, 298 K. Shear rate: .01 - .8 rad/s. Lines are predictions of Carreau model

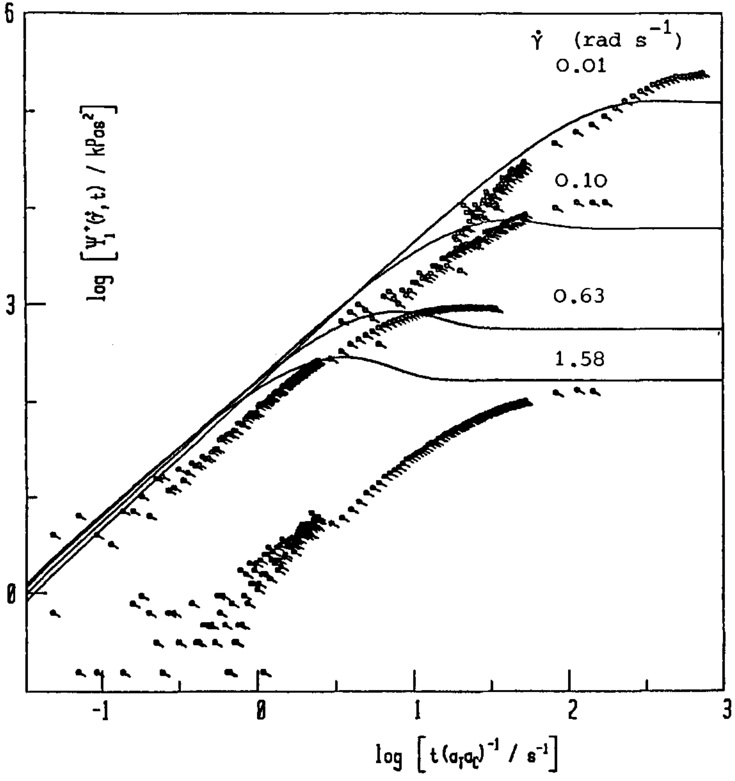

Figure 4. First normal stress coefficient at start of steady flow vs. time. Cone angle: 6 degrees, except data at 1.6 rad/s where cone angle: 1.2 deg. Lines are predictions of Carreau

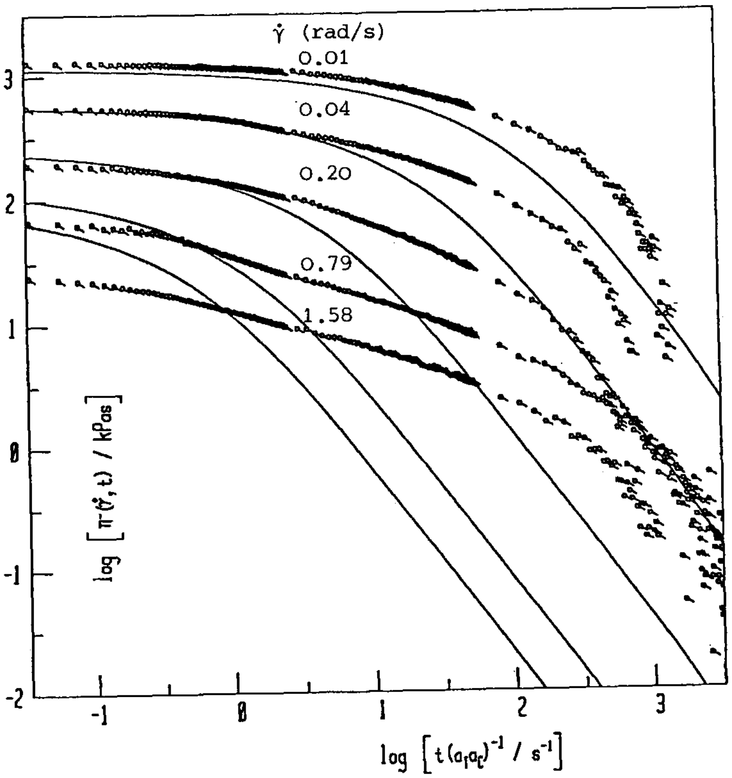

Figure 5. Viscosity at cessation of steady shear flow vs. time, PB melt, 298 K. Lines are predictions of Carreau model

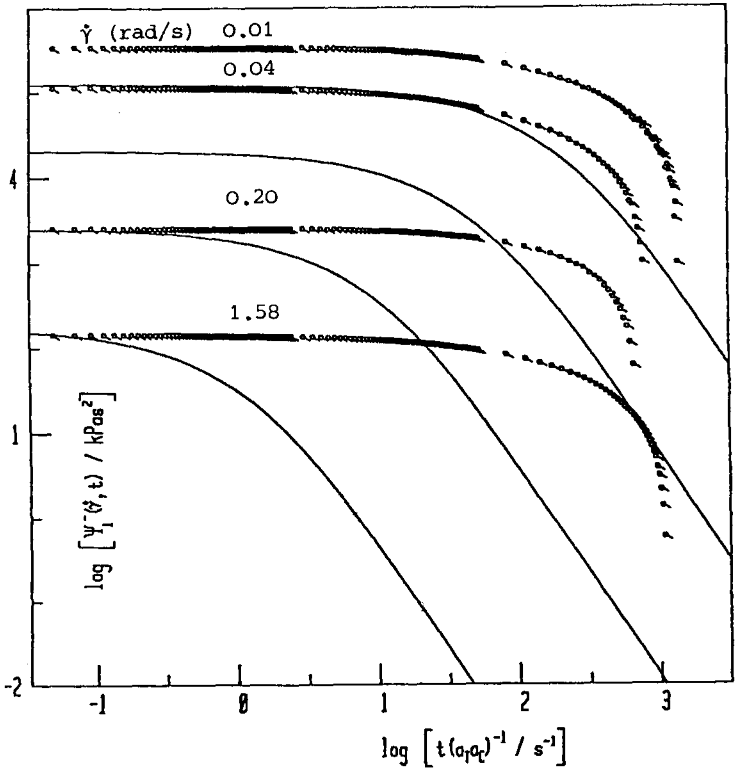

Figure 6. First normal stress coefficient at cessation of steady shear flow as in Figure 5

factors are well known for the reduction in concentration. cis-1,4-polybutadiene presents special advantage to this respect, since it is perhaps the most highly entangled polymer known.

On the theoretical side, it can be concluded that, although empirical modifications of the linear theory provide consistent results in qualitative agreement with experiment, it is the role of molecular theory to settle the appereance of parameters in the material functions, based on assumptions of molecular architecture. The best theory, at present, which satisfies these requirements, is the CURTISS-BIRD theory (1981).

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