Polymer Bulletin 7, 137–144 (1982)

**Polymer Bulletin**

# Effect of Molecular Weight Heterodispersity on Linear Viscoelastic Properties of Entangled Polymers

**G.A. Alvarez and H.-J. Cantow**

Institut für Makromolekulare Chemie der Universität Freiburg, Hermann-Staudinger-Haus,
Stefan-Meier-Straße 31, D-7800 Freiburg i.Br., Federal Republic of Germany

## Summary

The nonlinear, binary blending law of BOGUE has been generalized to include a finite number of entangled species. Good agreement has been observed between the ROUSE theory modified according to this law and linear viscoelastic experiments on cis-1,4-polybutadiene melts and concentrated solutions. The more difficult case of heterogeneity due to simultaneous degradation and crosslinking can only be qualitatively accounted for.

## Introduction

The ROUSE theory excells as a physical theory because it correlates in molecular terms a single type of experiment: linear viscoelastic response. This is an important result, since nonlinear theories necessarily converge to the linear limit for small strains.

Recently, a modification of the ROUSE theory for entangled polymers was proposed (ALVAREZ 1981), consisting of the introduction of two regimes of relaxation times to account for motions of segments below and above the critical entanglement length. The molecular-weight-dependence of each regime was scaled to agree with known phenomenological relations. A smooth transition between the two regimes was found to improve the fit of theory and experiment for cis-1,4-polybutadiene (PB).

The question concerning the effect of molecular weight heterodispersity on the linear response of entangled polymers remained unanswered. Formal results from the ROUSE theory for a continuous distribution of molecular weights below the critical entanglement molecular weight $M_c$ are well known (PETICOLAS 1963). No such study has been made for entangled polymers.

In this paper we simulate the effect of polydispersity in the ROUSE theory by means of the nonlinear, binary blending law of BOGUE (1970), which we have extended for a finite number of species. The ROUSE theory modified according to this law exhibits the following features, in agreement with experimental results: 1) the terminal region of the storage modulus is shifted to lower frequency as suggested in the past (GRAESSLEY 1974), 2) the loss modulus is relatively insensitive to molecular weight heterodispersity, 3) oscillatory first normal stress coefficients are extremely sensitive to polydispersity, and 4) the weight-average appears acceptable as the correlating molecular weight parameter for the zero-shear viscosity.

0170-0839/82/0007/0137/$01.60

## The general nonlinear blending law

Discrete molecular weight averages can be calculated according to the general formula:

$$M_a = \frac{\sum_i w_i M_i^{\,a}}{\sum_i w_i M_i^{\,(a-1)}} \tag{1}$$

and the normalization condition:

$$1 = \sum_i w_i \tag{2}$$

where $w_i$ is the weight fraction of the ith species and $M_o \equiv M_n$, $M_1 \equiv M_w$, etc. Knowledge of the averages up to $a = i + 1$, together with the normalization condition (2) will fix the distribution of i species and their weight fractions, without need of a distribution function.

The generalized MAXWELL model (BIRD 1977) gives for oscillatory shear flow with $\omega$ as the angular frequency:

$$\eta'(\omega) = \frac{G''(\omega)}{\omega} = \int_o^\infty \frac{1}{1 + (\omega\tau)^2} H(\tau)\,d\tau \tag{3}$$

$$\eta''(\omega) = \frac{G'(\omega)}{\omega} = \int_o^\infty \frac{\omega\tau}{1 + (\omega\tau)^2} H(\tau)\,d\tau \tag{4}$$

where $\eta'$ is the real part and $\eta''$ the imaginary part of the complex viscosity, $\tau$ is the time constant of each MAXWELL element, and $H(\tau)$ is the distribution function of $\tau$'s. Additionally, the following limits can be defined:

$$\eta_o = \lim_{\omega \to o} \eta'(\omega) = \int_o^\infty H(\tau)\,d\tau \tag{5}$$

$$\Psi^d_{1_o} = \lim_{\omega \to o} \frac{\eta''(\omega)}{\omega} = \int_o^\infty H(\tau)\,\tau\,d\tau \tag{6}$$

where $\eta_o$ is referred to as the zero-shear viscosity and $\Psi^d_{1_o}$ is the zero-shear first normal displacement stress coefficient.

Thus, by specifying $H(\tau)$, which is equivalent to specifying the relaxation modulus $G(t)$ of each MAXWELL element, the complete linear viscoelastic response according to this model can be derived. Only frequency dependent functions are considered in this paper; time dependent functions will be given elsewhere.

A general nth-order law for the blending of q species, each with weight fraction $w_i$, can be written

$$H\binom{n}{q} = \left\{ \sum_{i=1}^{q} w_i \left[ H_i\left(\frac{\tau}{\lambda_i}\right) \right]^{\frac{1}{n}} \right\}^n \tag{7}$$

where

$$H_i = h(\xi), \ \xi = \frac{\tau}{\left(\prod_{i=1}^{q} \tau_{m_i}\right)^{1/q}} \tag{8}$$

and

$$\lambda_i = \frac{\zeta_{o_b}}{\zeta_{o_i}} \tag{9}$$

$\zeta_{o_b}$ and $\zeta_{o_i}$ are monomeric friction coefficients for the blend and for component i respectively. $\tau_{m_i}$ is the maximum (or any convenient reference) relaxation time for component i.

The requirement that the zero-shear viscosity of the blend $\eta_{o_b}$ depends only on the weight-average molecular weight $M_w$ according to the law:

$$\eta_{o_b} = AM_w^{3.4} \tag{10}$$

where A is a constant independent of molecular weight, places a restriction on equation (9) as follows:

$$\lambda_i = \frac{M_w^{3.4 - n}}{M_i} \tag{11}$$

The cubic blending law (n = 3) has the advantage of reproducing the experimentally observed concentration and molecular weight dependence of the limits (5) and (6) (KURATA 1974), while the fourth order law would imply, according to (11), that the longest relaxation time of the blend would be larger than the longest relaxation time of the highest molecular weight component, which would be unreasonable. A ternary blend was found to improve the agreement between theory and experiment, over the binary blend.

## Results

Measurements of storage G' and loss G" modulus in the eccentric rotating disc instrument INSTRON 3250, for cis-1,4-polybutadiene (PB) melts and 24 % w/w solutions of PB in n-tetradecane, reduced to 298 K and to the melt density, are presented in Figures 1 and 2. The dynamic viscosity, the loss factor and the first normal displacement stress coefficient obtained by the exact equivalences:

$$\eta' = \frac{G''}{\omega}, \ \tan\delta = \frac{G''}{G'}, \ \Psi_1^d = \frac{\eta''}{\omega} \tag{12}$$

are shown in Figures 3 and 4. The dashed lines in these figures are results from the ROUSE theory modified for entanglements (ALVAREZ 1981) with a single molecular weight equal to $M_w$ of the PB melt ($M_w$ = 488 kgmol$^{-1}$). The solid lines were calculated according to equation (7) with n = q = 3, where the q molecular weights and weight fractions were obtained by matching the first q + 2 molecular weight averages, calculated by

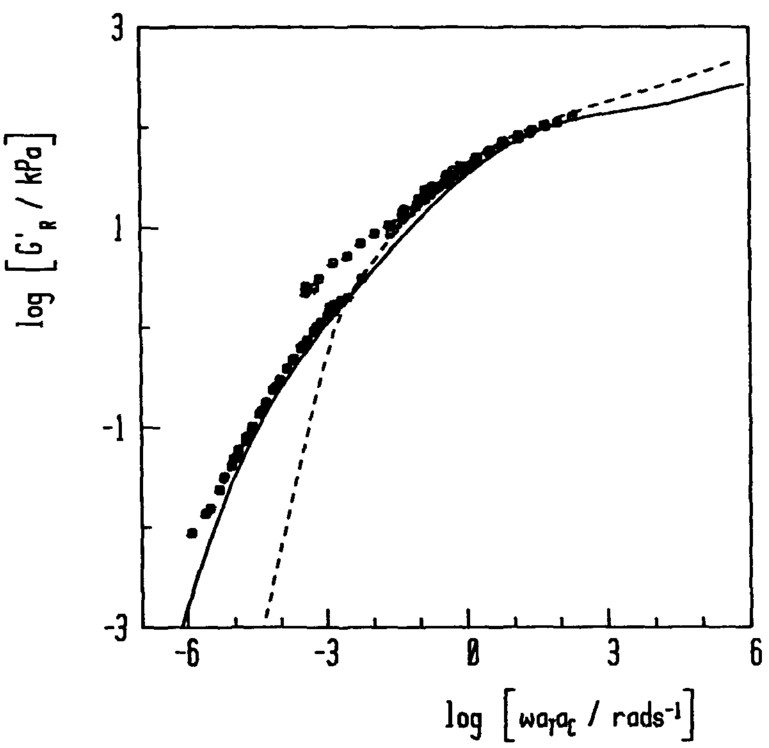

Figure 1. Storage modulus versus frequency for PB melt ○ and 24 % w/w solution of PB in n-tetradecane ● Dashed lines are calculated from the monodisperse ROUSE theory and solid lines according to heterogeneity correction. $T_{ref}$ = 298 K, reference density: melt

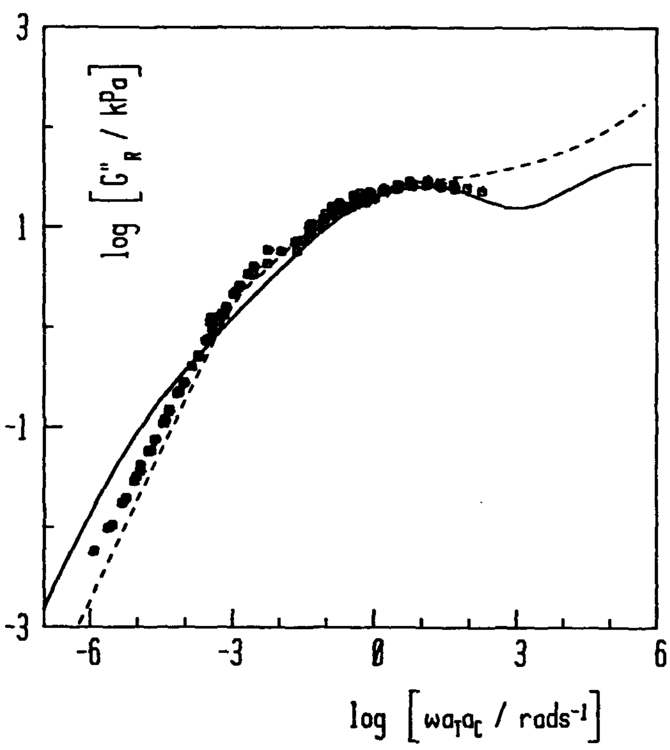

Figure 2. Loss modulus versus frequency for PB melt ○ and 24 % w/w solution of PB in n-tetradecane ● . Lines have the same meaning as in Fig. 1

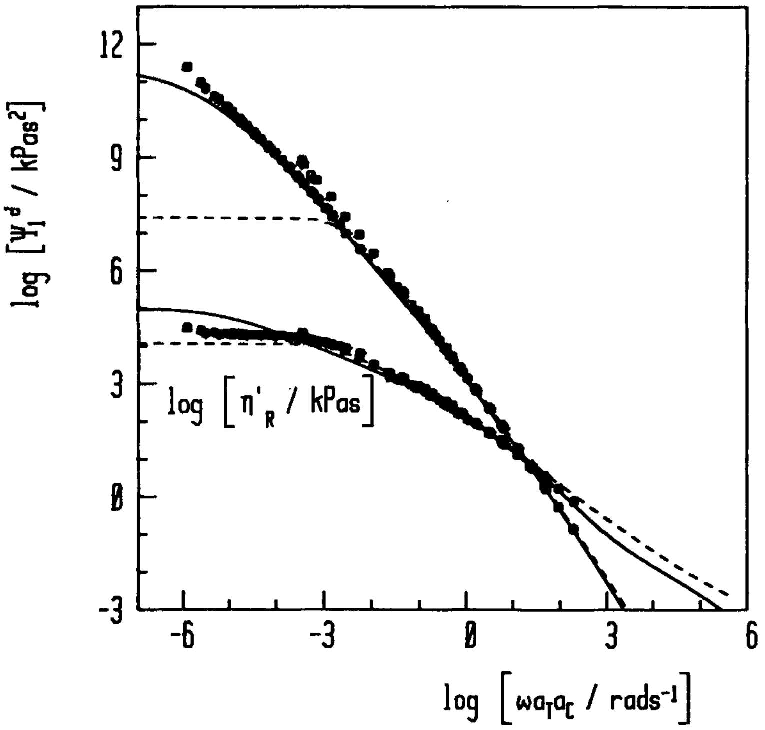

Figure 3. First normal displacement stress coefficient and dynamic viscosity calculated from experimental data given in Figures 1 and 2 resp. Lines are calculations for monodisperse - - - and polydisperse ——— ROUSE theory

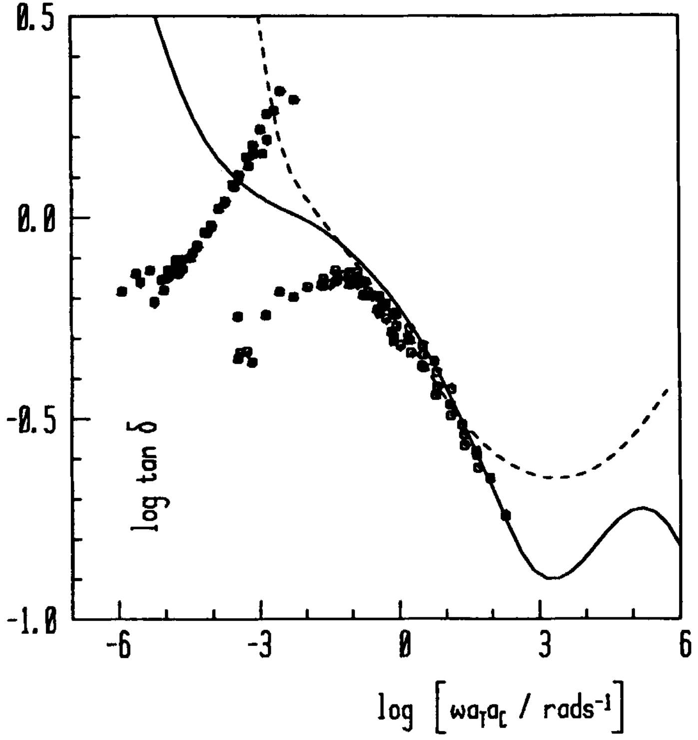

Figure 4. Loss factor calculated from experimental data in Figures 1 and 2. Lines show calculations according to monodisperse - - - and polydisperse ——— ROUSE theory

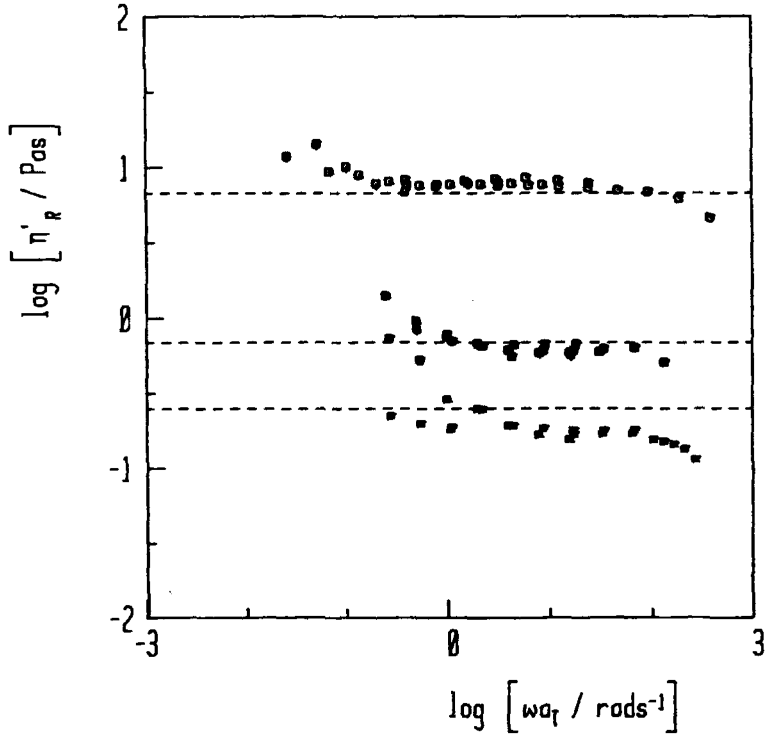

Figure 5. Dynamic viscosity versus frequency for PB oils with $M_n$ = 1.5, 3 and 6 resp., from bottom to top. Dashed lines are calculated according to monodisperse theory modified for entanglements. $T_{ref}$ = 298 K

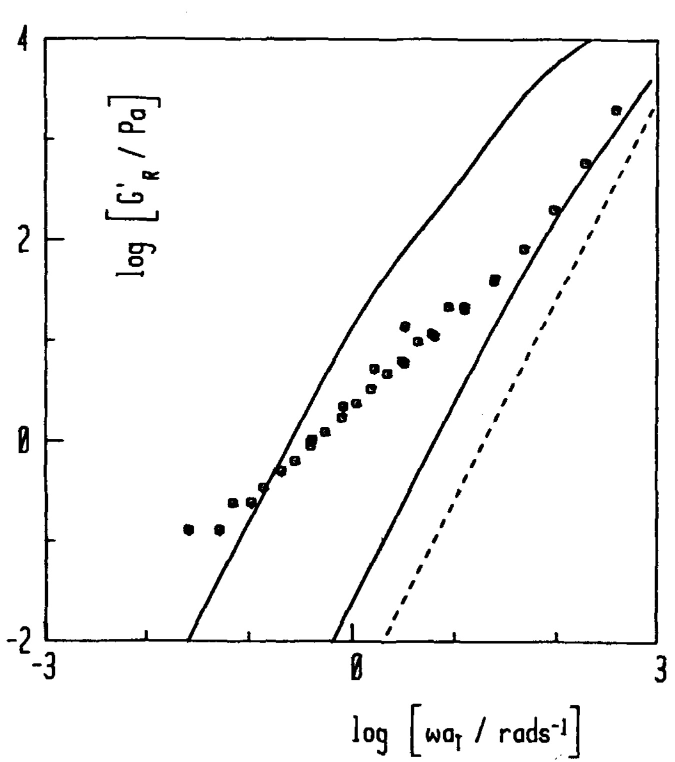

Figure 6. Storage modulus versus frequency for PB oil ($M_n$ = 6). Dashed line indicates monodisperse ROUSE theory with M = 12 and solid lines indicate blends calculated for $M_n$ = 6, $M_w$ = 13.8,... and $M_n$ = 6, $M_w$ = 24,..., resp., from bottom to top

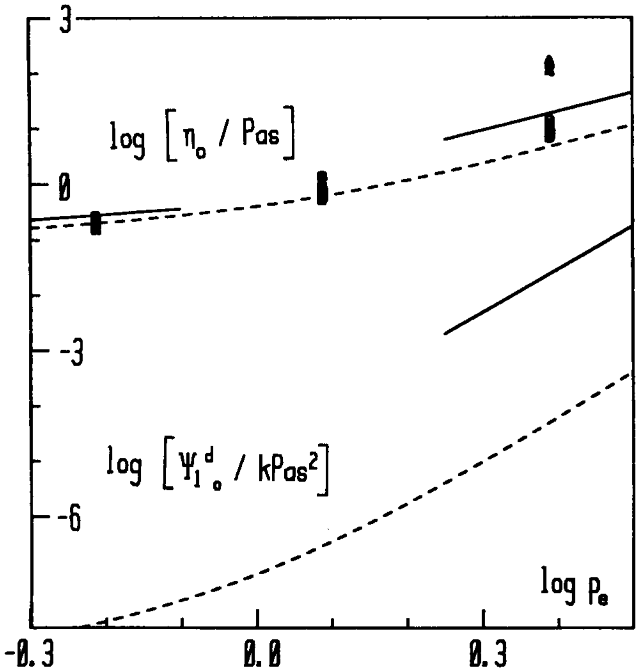

Figure 7. Zero-shear viscosity □, ●, ○ and zero-shear first normal displacement stress coefficient Δ versus weight-average molecular weight for PB oils as in Fig. 5. Dashed lines from equations (13)-(15), solid lines according to linear and cubic blending law, below and above $M_C$, resp

means of equations (1) and (2), with values obtained by gel permeation chromatography for the PB melt ($M_w/M_n = 2.3$).

The master spectrum $h(\xi)$ was obtained for the storage modulus of the highest molecular weight component according to the modified ROUSE theory by means of the third order approximation of TSCHOEGL (1971) and then refined iteratively until the error between the value given by the ROUSE theory and the recalculated value according to equation (4), was negligible.

Good agreement between the polydisperse theory and experiment is observed in Figures 1-4, except for the loss factor, Figure 4, which is a very sensitive function, and includes experimental errors in both G' and G".

The dynamic viscosity of three Newtonian PB oils ($M_n$ = 1.5, 3 and 6 $\text{kgmol}^{-1}$ resp.) is shown in Figure 5. The dashed lines are results calculated from the monodisperse ROUSE theory, with M = 3, 6 and 12, resp. and a monomeric friction coefficient equal to one half of that employed for the PB melt ($\zeta_o = 4.0 \times 10^{-10}\ \text{Nsm}^{-1}$ for the PB melt). The modification of the ROUSE theory (ALVAREZ 1981), which implies that molecular segments below the critical entanglement molecular weight $M_C$ are unaffected by the presence of the network, predicts the observed smooth transition between the terminal and rubber region of the viscoelastic spectrum, and, at low molecular weight, Figure 5, it is also useful to explain the molecular weight dependence of viscoelastic functions. However, it is not possible with the present measurements to reach high enough frequency, so that viscoelastic functions become independent of molecular weight, as for the PB melt in Figures 1-4, where the monomeric friction coeffcient was obtained from the high frequency region, and the the molecular weight from low frequency measurements. The storage modulus of the PB oil ($M_n$ = 6) is given in Figure 6, and cannot be fitted either by linear distributions according to $M_n = 6$, $M_w = 13.8, \ldots$ or $M_n = 6$, $M_w = 24, \ldots$, although the dynamic viscosity correlates well with $M$-$\zeta_o$ as mentioned above. The molecular weight distribution of this oil is probably complex due to rapid, simultaneous degradation and crosslinking at room temperature.

Finally, the zero-shear viscosity and zero-shear first normal displacement stress coefficient measured in cone-and-plate geometry (ALVAREZ 1982) are plotted versus weight average molecular weight in Figure 7, for the PB oils mentioned above. The normal stress data are, however, not strictly Newtonian. The dashed lines were calculated according to the formulae (ALVAREZ 1981)

$$\eta_o = \frac{cf_o b^2 N^2}{6\pi^2} \sum_{p=1}^{N} p_e \frac{2.4e^{-p/p_e}}{p^2} \tag{13}$$

and

$$\Psi^d_{1_o} = \frac{cf_o^2 b^4 N^4}{36\pi^4 kT} \sum_{p=1}^{N} p_e \frac{4.8e^{-p/p_e}}{p^4} \tag{14}$$

with

$$p_e = \frac{M}{M_C} \tag{15}$$

where $f_o$ is the bead friction coefficient, b is the root-mean-square end-to-end distance between beads at equilibrium, N is the number of beads and c is the number of molecules per unit volume. The solid lines were calculated by equations (5) and (6) for M = 12 and $M_w/M_n = 2.3$, and equation (7) with $n = 1$ below and $n = 3$ above $M_C$.

It can be concluded that the heterogeneity correction presented here contributes a great deal to the accurate prediction of the linear viscoelastic properties of entangled polymers.

We thank the DEUTSCHE FORSCHUNGSGEMEINSCHAFT for generous financial support. CHEMISCHE WERKE HÜLS AG we thank for the polybutadiene samples.

## References

G.A. ALVAREZ AND H.-J. CANTOW, Polym. Bull. 4, 383 (1981); 7, 51 (1982)
R.B. BIRD, R.C. ARMSTRONG AND O. HASSAGER Dynamics of polymeric liquids. Vol. 1 New York, John Wiley & Sons, 1977
D.C. BOGUE ET AL., Polym. J. 1, 563 (1970)
W.W. GRAESSLEY, Adv. Polym. Sci. 16, 1 (1974)
M. KURATA ET AL., J. Polym. Sci.: Polym. Phys. Ed. 12, 849 (1974)
W.L. PETICOLAS, Rubber Chem. Technol. 36, 1422 (1963)
N.W. TSCHOEGL, Rheol. Acta 10, 582 (1971)

*Accepted March 16, 1982*