Polymer Bulletin 7, 51–58 (1982)

Polymer Bulletin

Oscillatory Normal Stresses in Melts and Concentrated Solutions of cis-1,4-Polybutadiene

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

Oscillatory normal stresses were measured in melts and concentrated solutions of cis-1,4-polybutadiene (PB), and compared to the Rouse theory, including polydispersity and molecular weight dependence. Good agreement was obtained in all but one sample consisting of low molecular weight PB oil, where the first normal complex stress coefficient was abnormal.

Introduction

Small-amplitude oscillatory shear flow is the simplest way to introduce time-dependent stresses in rheological equations of state. In addition to strain, material functions are thus expected to depend on time or frequency.

The molecular theory of Rouse successfully predicts frequency dependence of material functions, at small strains, for polymer melts and concentrated solutions. Important modifications of the theory have been the extension (FERRY 1955) to entangled polymers, the derivation of oscillatory normal stress coefficients (WILLIAMS 1969), and the formulation of the constitutive equation (LODGE 1971). Recently, we have improved the accuracy of the predictions by postulating a smooth transition between entangled and nonentangled submolecules (ALVAREZ 1981). Additionally, we are able to include molecular weight heterodispersity in the model by blending a finite number of components together with a nonlinear law (ALVAREZ 1982). It will be shown below that the molecular weight heterogeneity of the polymer has a strong influence on the normal stresses, at low frequency.

In this paper we exploit the unique opportunity given by small-amplitude oscillatory shear flow, to be able to correlate normal stresses with molecular theory. To our knowledge, no work on oscillatory normal stresses for melts has been published up to now, apart from early work on rubber vulcanizates (WARD 1958). Measurements on dilute solutions have been made (WILLIAMS 1969), and on concentrated solutions (CHRISTIANSEN 1981).

OSCILLATORY SHEAR MATERIAL FUNCTIONS

The unsteady response of cis-1,4-polybutadiene (PB) melt (M_w = 488 kgmol^{-1}, M_w/M_n = 2.3), contained between a plate and a small-angle cone undergoing small-amplitude, transverse oscillations, is shown in Figure 1. Measurement reveals that shear stress oscillates with frequency ω, and phase shift with respect to strain (or strain rate); normal stress

0170-0839/82/0007/0051/$01.60

oscillates with frequency 2ω about a nonzero mean value, also with phase shift to strain.

The sinusoidally-varying shear stress may be represented as:

$$\tau_{yx} = \mathrm{Re}\left\{\tau_{yx}^{o} e^{i\omega t}\right\} \tag{1}$$

where τ_{yx}^{o} is complex. Within the framework of linear viscoelasticity, the complex viscosity function is defined by:

$$\tau_{yx}^{o} = -\eta^{*}\dot{\gamma}_{yx}^{o} \tag{2}$$

where

$$\eta^{*} = \eta' - i\eta'' \tag{3}$$

The real part η', the dynamic viscosity may be associated with energy losses, while the imaginary part η'' may be associated with energy storage.

The normal stress response can be written

$$\tau_{jj} = d_j + \mathrm{Re}\left\{\tau_{jj}^{o} e^{2i\omega t}\right\} \tag{4}$$

and then, functions analogous to the complex viscosity can be defined:

$$\tau_{xx}^{o} - \tau_{yy}^{o} = -\Psi_1^{*}(\dot{\gamma}_{yx}^{o})^2 \tag{5}$$

$$d_x - d_y = -\Psi_1^{d}\left|\dot{\gamma}_{yx}^{o}\right|^2 \tag{6}$$

$$\Psi_1^{*} = \Psi_1' - i\Psi_1'' \tag{7}$$

The same treatment is valid for other combinations of normal stresses, but in the present experiment only the above defined functions can be measured.

Next, we summarize the results of the molecular theory which allows prediction of the above defined functions.

Molecular theory

In its modern form (LODGE 1971), the constitutive equation for the ROUSE/ZIMM model is identical with the generalized MAXWELL model:

$$\tau_{ij} = \sum_{p=1}^{\infty}\tau_{ij}^{(p)} \;;\; \tau_{ij}^{(p)} + \tau_p\frac{\partial\tau_{ij}^{(p)}}{\partial t} = -\eta_p\dot{\gamma}_{ij} \tag{8}$$

$$\eta_p = ckT\tau_p \text{ and } \tau_p = \frac{f_o b^2}{6kT\lambda_p} \tag{9}$$

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

$$\lambda_p = 4\sin^2\left[\frac{p\pi}{2(N+1)}\right] \simeq \left(\frac{p\pi}{N}\right)^2 \text{ for } N>>1 \tag{10}$$

The decoupled first-order linear differential equation (8) can be integrated and solved to give the required material functions. The complex viscosity is given by:

$$\eta^* = \eta_S + ckT\sum_{p=1}^{N}\frac{\tau_p}{1+i\omega\tau_p} \tag{11}$$

where η_S is the solvent viscosity.

In the calculations below we use a modification of (9):

$$\tau_{p_{mod}} = \tau_p Q$$

$$Q = p_e^{\,2.4e^{-p/p_e}}, \quad p_e = \frac{M}{M_C} \tag{12}$$

to account for a smooth transition between entangled and nonentangled submolecules (ALVAREZ 1981). M_C is the critical entanglement molecular weight.

The following relations have been derived for the generalized Maxwell model:

$$\omega\Psi_1^{\,d}(\omega) = \eta''(\omega) \tag{13}$$

$$i\omega\Psi_1^{\,*}(\omega) = \eta^*(\omega) - \eta^*(2\omega) \tag{14}$$

$$\Psi_2^{\,d} = 0, \ \Psi_2^{\,*} = 0 \tag{15}$$

This completes the treatment for homodisperse samples. In the presence of molecular weight heterogeneity the τ_p's are mixed according to a nonlinear law given elsewhere (ALVAREZ 1982).

Results

The first-normal stress coefficients defined by equations (5)-(7), were calculated, with inclusion of inertia, by means of equations given (BIRD 1964) for the cone-and-plate system. At each frequency, amplitude and phase shift values are extracted by computer from data as presented in Figure 1. In the Figure, the points are on-line digitized values of amplifier signals, and the lines are synthetic sine functions from the optimized amplitudes and phase shifts.

The measurement of normal stresses is, generally, not very accurate. It should be pointed out that the normal forces in Figure 1 are of the order of .1 gramm, and the same levels of force could be generated by axial displacement of the rheometer frame as low as 1μm. At present, the measurements are plagued by thermal instability of the room and a base line correction must be applied to the data, giving rise to large uncertainty in the displacement force, especially as normal forces relax slower than shear forces. An interesting hypothesis about the "lag" in the normal oscillations is that it is due to instrumental compliance ("yawning") of the type reported (MEISSNER 1972, GRAESSLEY 1977), especially as the "lag" increases with frequency.

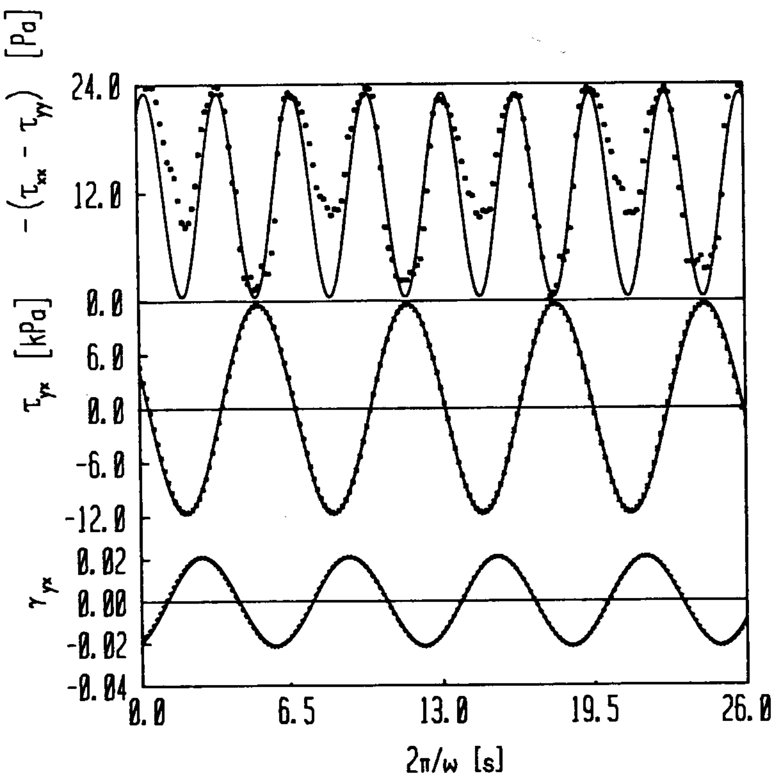

Figure 1. Response to oscillatory shear flow for PB melt. Points indicate shear strain, shear and normal stresses from bottom to top channels. Lines are synthetic sine functions with amplitude and phase shift optimized to fit the data

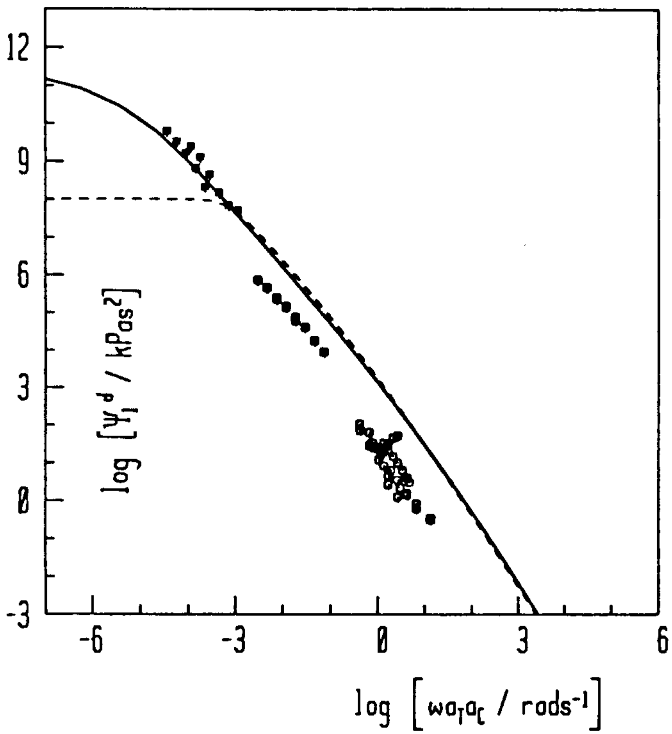

Figure 2. Dependence of first normal displacement stress coefficient on frequency for PB melts ○, 24 % solutions of PB in n-tetradecane □, and in low molecular weight PB oil (M_n = 1.5 $kgmol^{-1}$) ●. Lines represent heterodisperse —— and monodisperse --- Rouse theory. T_{ref} = 298 K, reference density: melt

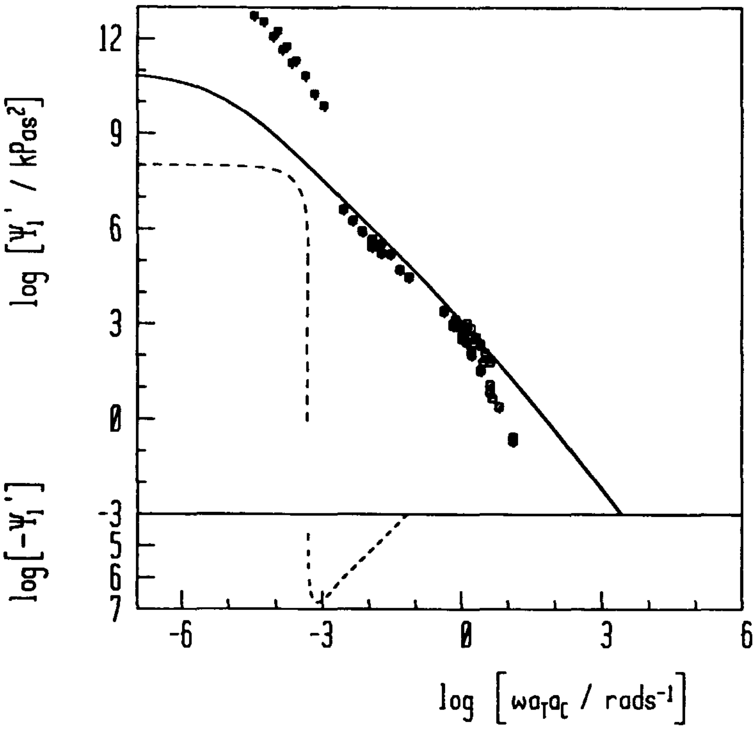

Figure 3. Dependence of first normal in phase stress coefficient on frequency. Symbols as in Figure 2. The monodisperse Rouse theory exhibits a change of sign

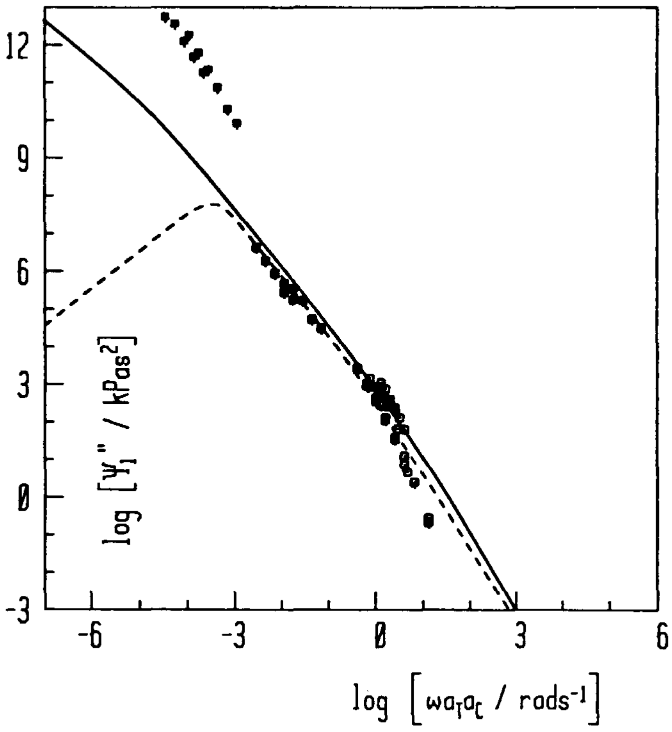

Figure 4. First normal out of phase stress coefficient versus frequency. Symbols as in Figure 2

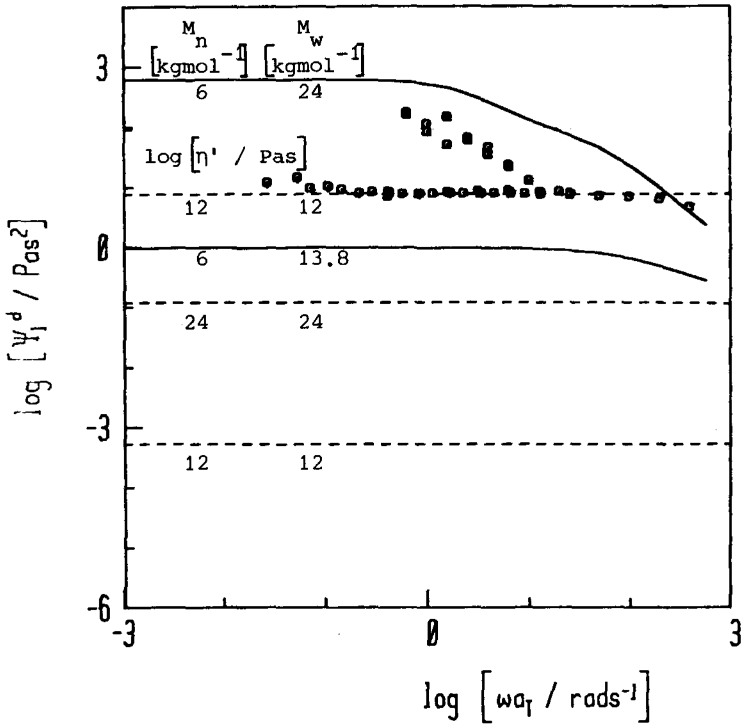

Figure 5. First normal displacement stress coefficient and dynamic viscosity versus frequency for low molecular PB oil (M_n = 6 kgmol^{-1}). Solid lines are theoretical curves with M_w/M_n = 2.3 below, and M_w/M_n = 4 above. The dashed lines are given by monodisperse theory with same M_w as solid lines. T_{ref} = 298 K

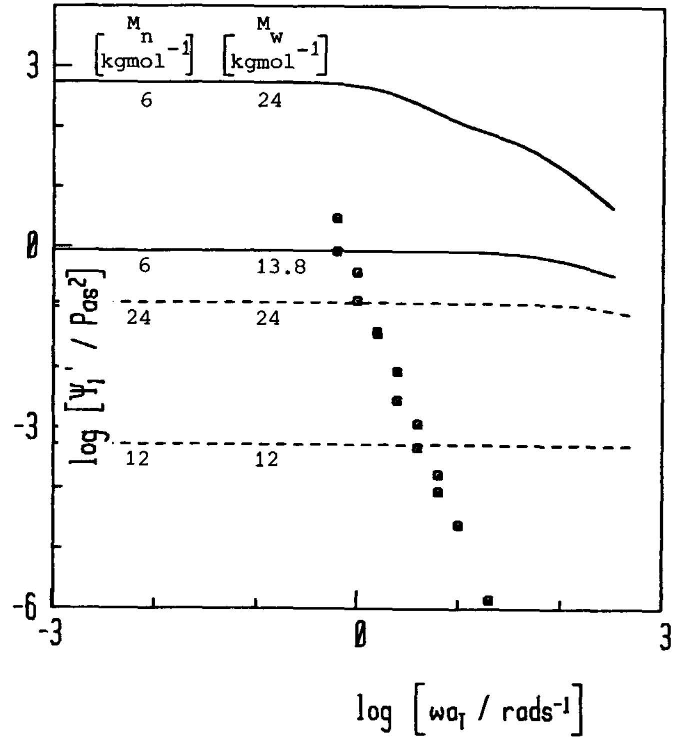

Figure 6. First normal in phase stress coefficient and theoretical curves versus frequency for sample and parameters as in Figure 5

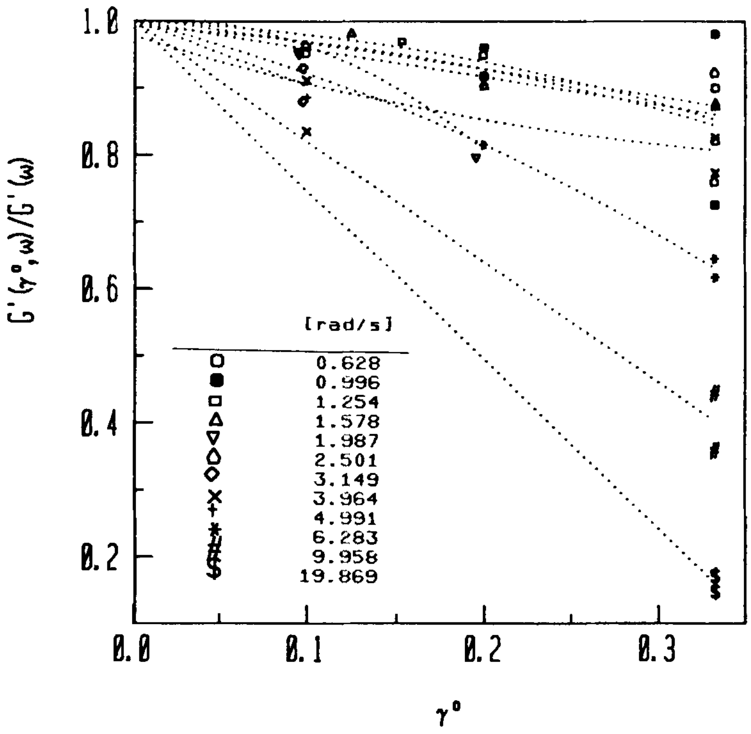

Figure 7. Dependence of finite-amplitude storage modulus on strain in frequency range .628 to 19.9 rads^{-1} for the PB melt

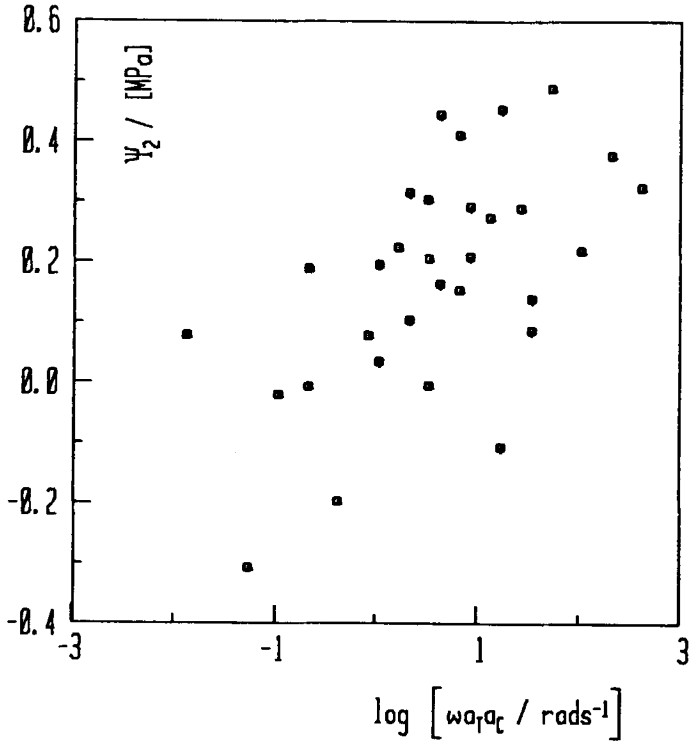

Figure 8. Second normal stress coefficient versus frequency for PB melt in eccentric rotating disk experiment

The measured normal stress coefficients and the fits of these to molecular theory are shown in Figures 2-6, for the PB melt, two 24 % w/w solutions of PB in n-tetradecane and in low molecular weight PB oil (M_n = 1.5 kgmol^{-1}), as well as a low molecular weight PB oil (M_n = 6 kgmol^{-1}). Both the absissa and the ordinate are shifted in temperature and concentration according to the latest theoretical results (GRAESSLEY and EDWARDS 1981). Only for the sample of low molecular weight PB (M_n = 6 kgmol^{-1}, Figure 6) serious disagreement is found between theory and experiment, in stress as well as shear dependence. There is no explanation, at present, for this discrepancy.

Finite-amplitude oscillatory shear

The validity of the linear constitutive assumption embedded in (1) is well justified by the agreement of the measured functions with the results of the molecular theory. The deviations from linearity are nevertheless strong, for melts, as shown in Figure 7. The simplest finite-amplitude strain model is the corotational JEFFREYS model, which yields (1) as a first and second term in an expansion over strain.

Second normal stress difference

According to theoretical analysis (YAMAMOTO 1969), the total normal force acting on the discs in the Eccentric Rotating Disc rheometer gives the second normal stress difference $\tau_{yy} - \tau_{zz}$. A second normal stress coefficient is defined by:

$$\tau_{yy} - \tau_{zz} = \frac{F_z}{\pi R^2} = \left(-\Psi_2 + \frac{\rho\omega^2 R^2}{4}\right)\gamma^2 \qquad (16)$$

where the second term is the sample inertia, is plotted in Figure 8. A change of sign in $\Psi_2(\omega)$ is observed. For the Rouse theory $\Psi_2(\omega) = 0$.

Acknowledgements

Continued financial support from the DEUTSCHE FORSCHUNGSGEMEINSCHAFT is greatly appreciated. CHEMISCHE WERKE HÜLS AG we thank for the PB samples.

References

L.C. ACKERS AND M.C. WILLIAMS, J. Chem. Phys. 51, 3834 (1969)
G.A. ALVAREZ AND H.-J. CANTOW, Polym. Bull. 4, 383 (1981)
G.A. ALVAREZ AND H.-J. CANTOW, Polym. Bull. 7, No.2/3 (1982)
R.L. CRAWLEY AND W.W. GRAESSLEY, Trans. Soc. Rheol. 21, 19 (1977)
J.D. FERRY ET AL., J. Appl. Phys. 26, 359 (1955)
H.W. GAO, S. RAMACHANDRAN AND E.B. CHRISTIANSEN, J. Rheol. 25, 213 (1981)
W.W. GRAESSLEY AND S.F. EDWARDS, Polymer 22, 1329 (1981)
A.S. LODGE AND Y. WU, Rheol. Acta 10, 539 (1971)
J. MEIßNER, J. Appl. Polym. Sci. 16, 2877 (1972)
A.F.H. WARD AND G.M. JENKINS, Rheol. Acta 1, 110 (1958)
M.C. WILLIAMS AND R.B. BIRD, I&EC. Fundamentals 3, 42 (1964)
M. YAMAMOTO, Japan. J. Appl. Phys. 8, 1252 (1969)

Accepted March 2, 1982
C

Responsible for the text: The Editors (see inside title page of this issue).
For advertisements: E. Lückermann, Kurfürstendamm 237, D-1000 Berlin 15,
Tel. (030) 882 1031, Telex 01-85411, Springer-Verlag Berlin Heidelberg New York
Printed in Germany by Beltz Offsetdruck, Hemsbach/Bergstraße