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Micro- and Macroconformation of Macromolecules
5. A Scale-up Rule of Rouse Theory to Entangled Homopolymers and Random Copolymers

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SUMMARY

A semiempirical modification of FERRY's extension of the
ROUSE spectrum in the entanglement region is proposed,
with a smooth transition in the relaxation behaviour. Con-
sequently the zero shear viscosity-molecular weight relat-
ionship is modelled. With the molecular weight between the
entanglements as the only parameter measurements on cis-
1,4-polybutadiene could be reproduced accurately, compar-
ing favourably with the recent multiparameter theory by
SHEN.
A simple linear weighting scheme for the average friction
coefficient of chemical and configurational copolymers, e.
g. cis-trans-polybutadienes, is proposed.

INTRODUCTION

The foundations of viscoelastic theory date back to 1874
when BOLTZMANN proposed an alternative to classical elast-
icity theory in order to describe the time-dependent eff-
ects named by him elastische Nachwirkung (retarded elastic
recovery). Formally, molecular theories of the dynamic
response of amorphous polymers should take into account
intermolecular potential energies of interaction as well
as intramolecular interactions. This is the role of phase-
space theories of polymers. A first approximation is made
in so-called "dilute solution" theories where the system
is composed of a single molecule without concentration
gradients, i. e. a system configuration space is used.

The ROUSE [1], BUECHE [2] and ZIMM [3] kinetic theory repres-
ents the first substantial advance towards the unsolved
problem of the exact description of the allowable motions
of a polymer chain. They suggested that the polymer molec-
ule could be broken into N submolecules or non-bendable
"springs" with N+1 frictional centres or spherical "beads".
The following assumptions are made: 1. Inertial forces can
be neglected for the small masses and low frequencies con-
sidered. 2. The beads experience in their motion a hydro-
dynamic drag given by STOKES' law, i. e. the drag force on
the bead is proportional to the relative velocity of the
bead and solvent with the friction coefficient the proport-
ionality constant. 3. The beads are small enough to exper-

ience "Brownian motion" forces. 4. The submolecules retain the Gaussian nature of end-to-end fluctuations and, then, the force law for the spring is HOOKE's law with a spring constant given by $3kT/<\sigma^2>_O$ where $<\sigma^2>_O$ is the mean-root-square average of the end-to-end distance of the sub-molecule composed of q monomer units.

The start of the application of ROUSE theory to undiluted polymers was made by BUECHE [4]. He proposed to replace solvent-polymer friction coefficients by, normally, much higher polymer-polymer friction coefficients, other things left unchanged. Assuming that $f = q\zeta_O$, where ζ_O is the monomeric friction coefficient, and replacing $<h^2>_O = N<\sigma^2>_O$ the relaxation time τ_p is given by

$$\tau_p = <h^2>_O P\zeta_O \,/\, 6\pi^2 p^2 kT \qquad\qquad (1)$$

with p the motional mode index, P the degree of polymerization, $\zeta_O = kT/D$ and D the diffusion coefficient.

Modern theories [5] [6] as well as early modification of the ROUSE theory by FERRY [7] ascribe a basic characteristic of entangled polymer systems: the presence of two sets of relaxation times relating short range, fast rearrangements for segments with molecular length below M_C and long range, slow motions above M_C. In the tube model the two sets of retardation or relaxation times are manifested in the rapid motions allowed inside the tube of width d and the much slower conformational rearrangements necessary for escape along the tube of length l. In the older terminology the tube width corresponds to $M_e \simeq M_C/2$ and the ratio $1/d$ to M/M_e. FERRY et al. [7] considered the phenomenological viscosity-molecular weight law in connection with the two relaxation mechanisms to replace the ROUSE spectrum of relaxation times, leaving the theory, so to say, intact. Their modification of Equation 1 may be written, with n the number of molecules per unit volume

$$\tau_p = <h^2>_O PQ\zeta_O \,/\, 6\pi^2 p^2 kT \qquad\qquad (2)$$

where $\qquad Q = p_e^{2.4}$, $p \leq p_e \qquad Q = 1$, $p > p_e \qquad (3)$

and $\qquad p_e = M/M_C \simeq M/2M_e \simeq 0.5\nu_e M \qquad\qquad (4)$

with ν_e the entanglement density.

The procedure of extending "dilute solution" theories to the concentrated regime has received strong criticism from ZIABICKI [8] by mathematical arguments. SHEN et al. [9] recently have proposed a multiparameter theory based on in-creased-toward-the-centre friction coefficients and inter- and intra-molecular "slipping" elastic couplings. Results obtained by SHEN for various polymers are in excellent agreement with experiment; he also obtained the expected behaviour of the equilibrium modulus vs. molecular weight.

SEMIEMPIRICAL MODIFICATION OF THE ROUSE SPECTRUM IN THE ENTANGLEMENT REGION

The abrupt transition in the FERRY approach at a critical value of the index p_e gives semiquantitative agreement for the storage modulus $G'(\omega)$ and rather poor agreement for the loss modulus $G''(\omega)$

$$G'(\omega) = \frac{J'(\omega)}{J'(\omega)^2 + J''(\omega)^2} = nkT \sum_{p=1}^{N} \frac{\omega^2 \tau_p^2}{1 + \omega^2 \tau_p^2} \qquad (5)$$

$$G''(\omega) = \eta'(\omega)\omega = \frac{J''(\omega)}{J'(\omega)^2 + J''(\omega)^2} = nkT \sum_{p=1}^{N} \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2} \qquad (6)$$

with $J'(\omega)$ and $J''(\omega)$ the corresponding compliances and $\eta'(\omega)$ the dynamic viscosity.

We have found that a modification of Equation 3, of the type

$$Q = p_e^{2.4} e^{-p/p_e} \qquad (7)$$

provides remarkably good fit of both the storage and loss functions, as shown in Figures 1 - 4, for high molecular weight cis-1,4-polybutadiene in bulk. For comparison the fits according to FERRY's extension of the ROUSE spectrum are given for all the functions above in the Figures, where a_T in the abscissa is the usual frequency-temperature shift factor, with 298 K the reference temperature. Only the loss factor or tangent δ worsens considerably applying our modification (Figure 5). Temperature dependence of $<h^2>_0$ has been taken into account [10]. An additional factor of 1.5, and replacing P by $\bar{P}_w$ throughout, takes into account a normal distribution of molecular weights.

A smooth transition in the relaxation behaviour of the entangled samples will imply a corresponding smooth transition in the viscosity-molecular weight relationship around M_c.

By setting $\omega = 0$ in Equation 6, it is found that the zero shear melt viscosity in the non-entanglement region is [11]

$$\eta_0 = \eta'(\omega)_{\omega \to 0} = n<h^2>_0 P\zeta_0/6\pi^2 \qquad (8)$$

This formula may be written including our modification as

$$\eta_0 = n<h^2>_0 P\zeta_0 p_e^{2.4} e^{-p/p_e} / 6\pi^2 \qquad (9)$$

The plot of η_0 - in units of Pas - vs. p_e in Figure 6 shows a smooth transition, whereas FERRY's modification exhibits the traditional sharp one.
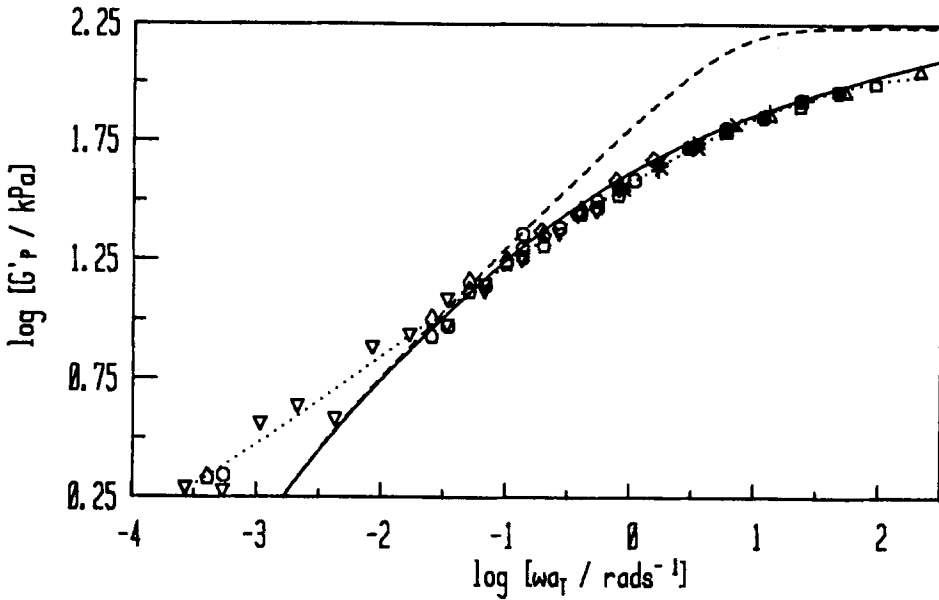
Figure 1: log G'(ω) cis-1,4-polybutadiene (M_W = 488.000) versus log(ωa$_T$) ——————— Equ. 7, — — — — — Equ. 3 .... best fit
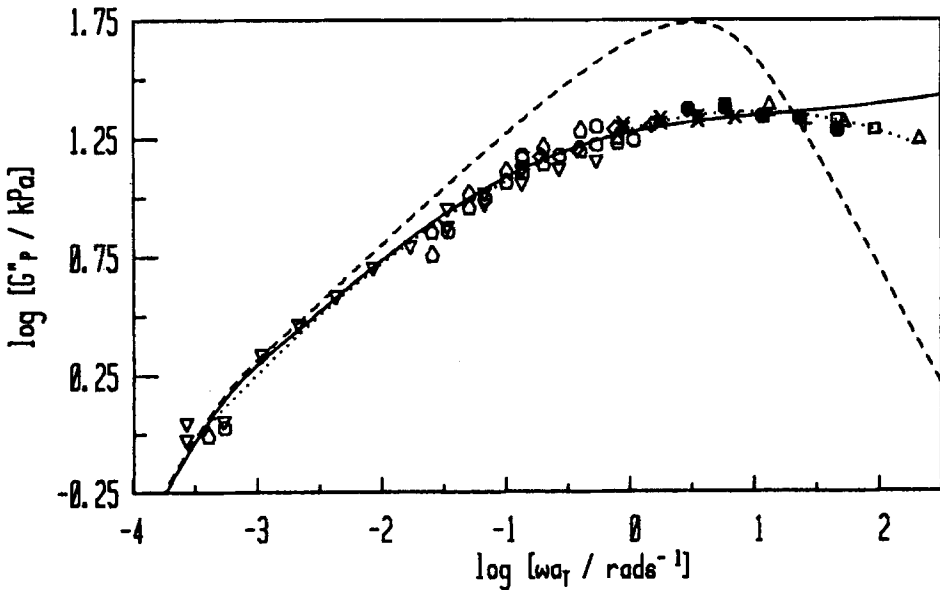
Figure 2: log G''(ω) cis-1,4-polybutadiene (M_W = 488.000) versus log(ωa$_T$) ——————— Equ. 7, — — — — — Equ. 3 .... best fit
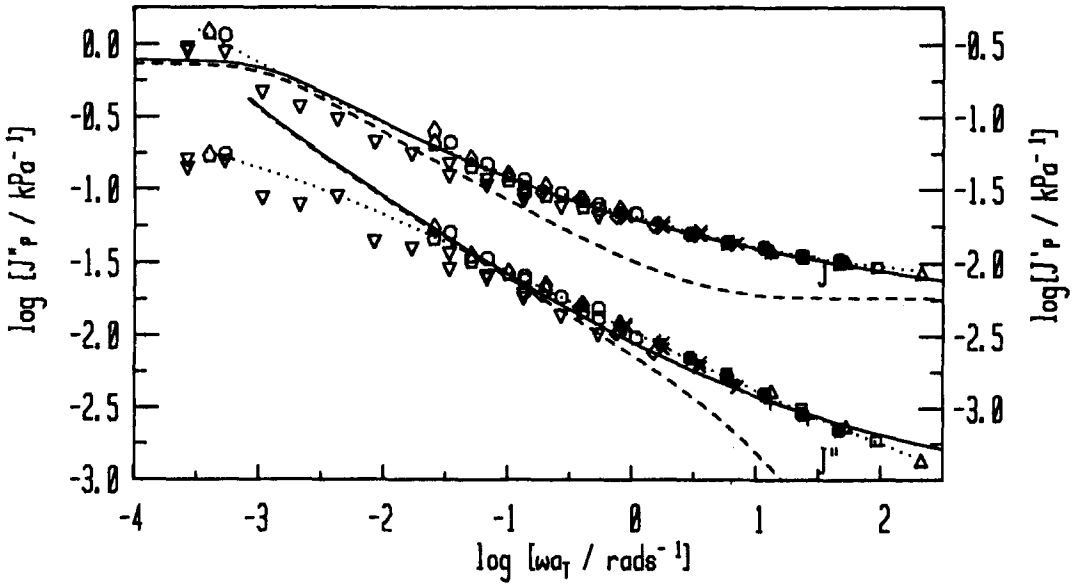
Figure 3: log J′(ω) and log J′′(ω) cis-1,4-polybutadiene
$\overline{M_W}$ = 488.000) vs. log(ωa$_T$) ———— Equ. 7, – – – – Equ. 3
·········best fit
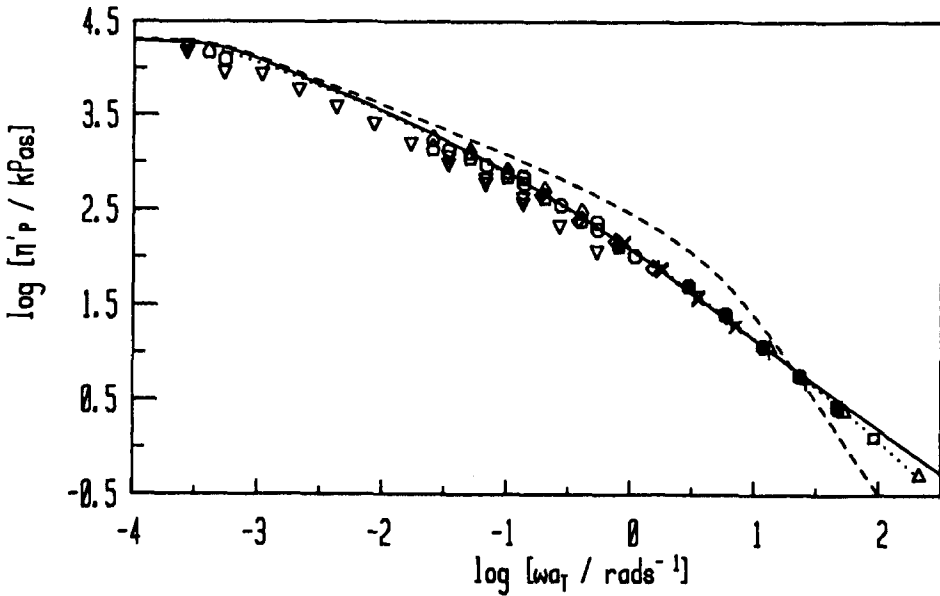
Figure 4: log η′(ω) cis-1,4-polybutadiene (M$_W$ = 488.000)
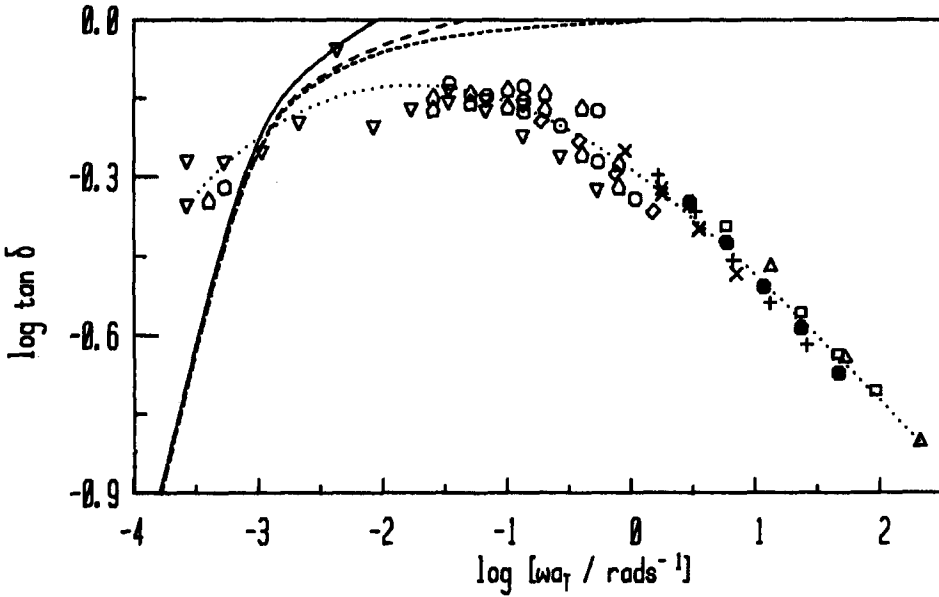versus log(ωa$_T$) ———— Equ. 7, – – – – – Equ. 3
········· best fit

Figure 5: log tan δ cis-1,4-polybutadiene (M_W = 488.000) versus log(ωa_T) ————— Equ. 7, — — — — Equ. 3 ———————— Rouse theory without transition ······· best fit
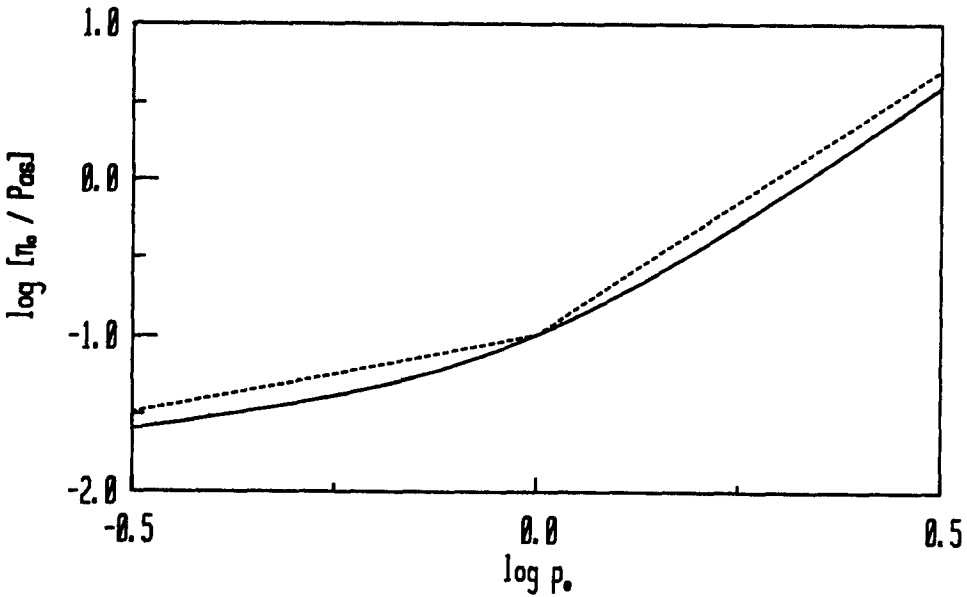

Figure 6: log zero shear viscosity η_0 [Pas] versus log p_e ——————— Equ. 9, — — — — FERRY
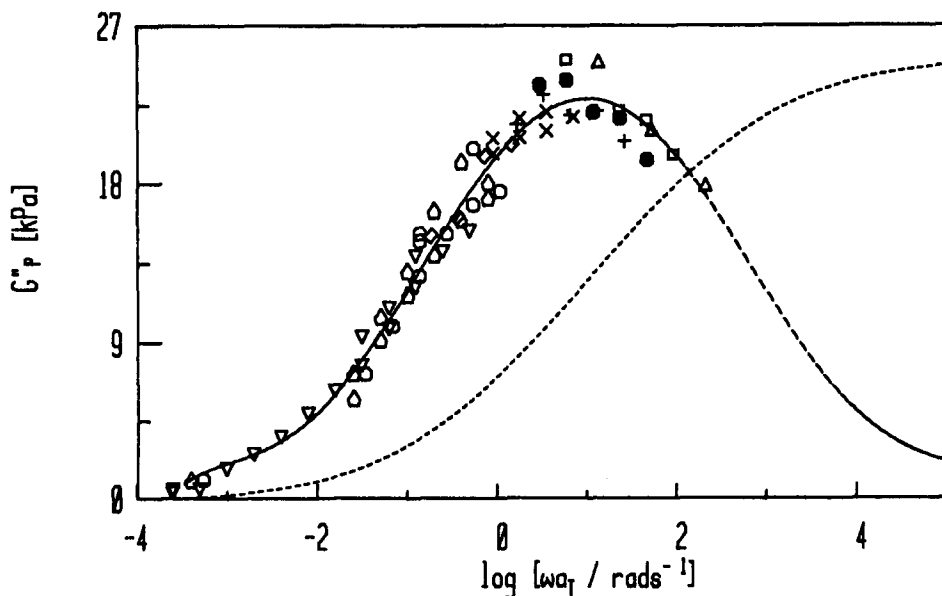
Figure 7: $G''(\omega)$ cis-1,4-PB (M_W = 488.000) versus $\log(\omega a_T)$

DIAD FRICTION COEFFICIENT FOR COPOLYMERS

From a molecular view the dynamic parameters are influenced by the chemical as well as by the configurational individuality of the macromolecules, by the unperturbed dimensions, $<h^2>_0$, the Q-parameter within the entanglement region and ζ_0 , the monomer friction coefficient. Structure and temperature dependence of $<h^2>_0$ may be determined by thermoelastic measurements under equilibrium conditions, in the swollen state, as performed, i. e., for the isomeric cis-trans-1,4-polybutadienes [10]. M_c for the Q-parameter may be derived from the maximum of the loss modulus vs. $\log(\omega a_T)$ (Figure 7). M_e = 2460 has been found for cis-1,4-polybutadiene in this manner. ζ_0 may be obtained, additionally, from dynamic measurements.

This monomer friction coefficient is composed, however, in a polymer melt, by intra- as well as by inter-molecular contributions. In particular, the question seems to be crucial, how ζ_0 adds up for chemical and configurational copolymers. Cis-1,4-polybutadiene and polyethylene, e. g., effectively are homopolymers, whereas cis-trans-1,4-polybutadienes and all non-stereoregular macromolecules based on asymmetrically substituted vinyl monomers are configurational copolymers. Like chemical copolymers, which consist of subunits being different concerning their chemical structure, the configurational copolymers are built up by sequences of differing isomerism.

A simple linear weighting scheme may be proposed to take into account the complexity of the sequence structure. To this purpose the monomer friction coefficient, ζ_O , may be substituted by diad friction coefficients, ζ_{i-j} , i and j being the diad subunit under question. For a binary copolymer, of the constitutional or of the configurational type, consisting of A and B units, the homopolymer diad friction coefficients, ζ_{AA} and ζ_{BB} , and the interstep diad friction coefficient, $\zeta_{\overline{AB}}$, have to be taken into account within the relevant equations, e. g. Equ. 9

$$f_{A-B}/q_{A-B} = \zeta_{A-B} = (q_{AA} + q_{BB} + q_{\overline{AB}})^{-1} \cdot$$
$$(q_{AA}\zeta_{AA} + q_{BB}\zeta_{BB} + q_{\overline{AB}}\zeta_{\overline{AB}}) \qquad . \qquad (\ 10 \ )$$

This scheme may be tested experimentally and additionally the universality of the entanglement "slipping" parameters as proposed. The weighting scheme according to Equation 10 may be applicable on diluted systems also when introducing the corresponding diad friction coefficients for polymer-solvent. The approach may describe the pronounced effect of stereoregular sequences on friction often found.

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