

PREDICTION OF THE RHEOLOGICAL PROPERTIES OF STAR—TYPE BRANCHED POLYMER SOLUTIONS BY MEANS OF THE FIXED SPECTRUM MODEL

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ABSTRACT

The Rouse-Zimm model with slippage was improved and the basic parameters of model were modified to explain the rheological properties of star-type branched polymer solutions. The theoretical results show good agreement with experimental data.

In improving the quasilinear viscoelastic model, the memory function in the integral equation was kept unchanged and the measure of deformation was reinvestigated, thus resulting in a new constitutive equation which is called the fixed spectrum model. A typical example is that in which Johnson, Segalman^[1], Hso,^[2] Schummer^[3] and others employed the concept of "non-affine deformation" to replace the supposition^[4] of "affine deformation" introduced when the constitutive equation of the Rouse-Zimm model was deduced. The Rouse-Zimm model with slippage was thus obtained and had the model equation as follows^[5].

$$\underline{\underline{T}} = \sum_{p=1}^N \underline{\underline{T}}_p \quad (1)$$

$$\underline{\underline{T}}_p + \tau_p \left[\frac{D}{Dt} \underline{\underline{T}}_p - (\underline{\underline{V}}_v \cdot)^T \cdot \underline{\underline{T}}_p - \underline{\underline{T}}_p \cdot \underline{\underline{V}}_v \cdot \right] = nkT \underline{\underline{1}} \quad (2)$$

Where $\underline{\underline{T}}$ is the extra stress tensor due to polymer molecules added into the solvent. $\underline{\underline{T}}_p$ is the contribution to $\underline{\underline{T}}$ by p-th motion mode of the Rouse molecular chain; the τ_p are the relaxation times, which are given by a material

time τ_0 , a measure of hydrodynamic interaction and the number of modes (segments) N ; V_v^* is the micro velocity gradient of solvent, n is the number concentration, k is the Boltzmann constant, T is absolute temperature. I is the unit tensor, and D/D_t is the material derivative. It was proved in Ref. [5] that this new model is of a more general ability to expound the rheological properties of polymers than the original equation. In [5], the Cox-Merz equation was used to determine the specific form of the slippage function for the linear polymer solutions with moderate concentration, and the variation law of the slippage function in a wide shear rate range was thus obtained.

It is worth while to point out that the fixed spectrum model can be employed to explain the rheological properties of star-type branched polymer solutions apart from those of linear polymer solutions. The point is the investigation of the effect of branching on the basic parameters of the model.

The model requires to determine three basic parameters: the average segment number of the chain molecule N (equivalent to the molecular weight), the time constant of the relaxation spectrum of material τ_0 and the limit value of the slippage function $a < 0 >$ within the linear flow range. The formulas are as follows.

$$N = f N_0 = f \frac{\bar{M}_w}{1280} \quad (3)$$

where $\bar{M}_w$ is the weight average molecular weight and f is the modified factor of the chain segment number. For a solution with moderate concentration, $f \approx 1$.

$$\tau_0 = \tau_p \cdot \lambda_p = \frac{6\eta_0 \bar{M}_w}{cRTN^2} \quad (4)$$

where τ_p and λ_p are the relaxation time and its eigenvalue, respectively, η_0 the zero viscosity and c the concentration.

$$a < 0 > \approx 1 \text{ (for the solution with moderate concentration)} \quad (5)$$

From an analysis it is known that the star-type branching makes little difference to the average segment number of the chain molecule N , that the slippage function limit value $a < 0 >$ depends on concentration rather than on structure, and that the parameter most affected by branching is the time constant of the relaxation spectrum τ_0 .

The experiment in Ref. [6] indicates: the existence of branches causes the intensity of the relaxation spectrum of the original linear polymer to reduce in the long time range but increase in the short-time range, that is,

the relaxation spectrum of the branched polymer moves in the direction of the short time range, as compared with that of the linear polymer with equivalent molecular weight, and therefore the parameter $(\tau_0)_b$ of the star-type branching sample can be no longer worked out by Eq. (4) and must be modified. The inference is that when the molecular weights are equivalent to each other, $(\tau_0)_b < (\tau_0)_l$ the latter represents the time constant of the linear sample.

Ferry^[7] points out that the property of the star-type branched polymer is related to that of the linear polymer through the dimension contraction factor g ascribed to branching, g is defined as the ratio between the quadratic means of rotational radius of the two kinds of molecules

$$g = \langle \rho_0^2 \rangle_b / \langle \rho_0^2 \rangle_l < 1 \quad (6)$$

According to Ham^[8], if the star-type polymer has Ψ arms whose molecular weights are equivalent, then the value of g is

$$g = (3\Psi - 2) / \Psi^2 \quad (7)$$

Bueche^[9] states that when there are equivalent molecular weights the ratio between viscosities of the branched and the linear polymers is

$$\eta_b / \eta_l = g \cdot E(g) \quad (8)$$

where $E(g)$ is the factor when the interaction and entanglement between the molecules are under consideration. For a dilute solution, $E(g) = 1$ and in the case of the entanglement $E(g) = g^{5/2}$

After they considered the hydrodynamic interaction, Zimm and Kilb^[10] discovered that when the distributions of the molecular weight are the same the ratio between the intrinsic viscosities of the branched and the linear polymers is

$$[\eta]_b / [\eta]_l = \sqrt{g} \quad (9)$$

By referring to the above formulae, we have calculated the values of g and $\sqrt{g}$ about the solutions of three kinds of star-type branched polystyrene (the solvent is 1-chloronaphthalene)^[11], and tried to calculate their time constants by the formulae below. The calculations as well as the primary parameters of the three samples are tabulated.

$$(\tau_0)_{b1} = (\tau_0)_l \quad (10a)$$

$$(\tau_0)_{b2} = (\tau_0)_l \cdot g \quad (10b)$$

$$(\tau_0)_{b3} = (\tau_0)_l \cdot g \quad (10c)$$

where $(\tau_0)_i$ is the time constant in terms of the linear molecule (see Eq. (4)).

Table 1 The primary parameters of the solutions of three kinds of star-type branched PS

Samples	H_1	J_1	G_1
$\bar{M}_w(\text{g/mol})$	2.06×10^5	1.25×10^5	6.05×10^5
$c(\text{g/ml})$	0.45	0.45	0.45
$T(\text{K})$	298	298	298
$\eta_0(\text{dyn} \cdot \text{s/cm}^2)$	6.7×10^2	1.4×10^2	1.05×10^4
N	161	98	473
Ψ	6.4	8	7
g	0.420	0.344	0.388
$\sqrt{g}$	0.65	0.59	0.62
$(\tau_0)_{b1} \text{ (s)}$	2.88×10^{-6}	0.995×10^{-6}	1.52×10^{-5}
$(\tau_0)_{b2} \text{ (s)}$	1.21×10^{-6}	0.34×10^{-6}	5.89×10^{-6}
$(\tau_0)_{b3} \text{ (s)}$	1.86×10^{-6}	0.58×10^{-6}	9.50×10^{-6}

Substitute the obtained parameters respectively into the constitutive model (the Rouse-Zimm model with slippage function) given by [5], compare the theoretical curves of the material function (shear viscosity and the first normal stress difference function) with the experimental results given by [11], and you will find that there is a rather big difference between the theoretical curves and the experimental data if the calculations by (10a) or (10b) are used. Instead, when the calculations by (10c) are taken the theoretical predictions are in quite good agreement with practical measurements for all the three samples (see Figs. 1 and 2). This means that with suitable modification the new model indeed accounts for the non-linear viscoelasticity of the star-type branched polymer solution.

It is to be explained why the above (10c) should be employed to calculate the time constant of the relaxation spectrum of the star-type branched polymer. Here the only thing we can say is that the validity of (10c) is assured if the molecular weight is replaced by the apparent hydrodynamic volume $[\eta]M$ when the calculation of τ_0 is made by using Eq (4) and the Zimm and Kilb's formula is referred to. In spite of this, so far

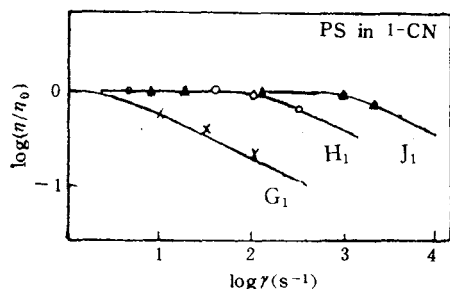


Fig. 1 Comparison between theoretical curves and the measurements of (η/η_0) of samples H_1, J_1, G_1

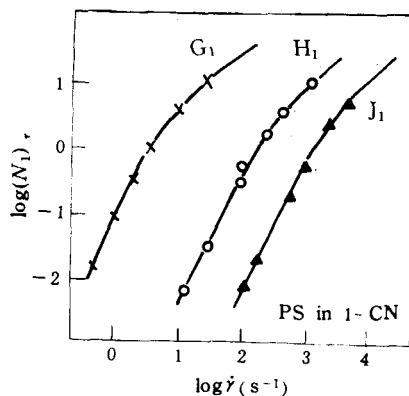


Fig. 2 Comparison between theoretical curves and the measurements of $(N_1)r$ of samples H_1, J_1 and G_1

there is no perfect constitutive equation theory to deal with the rheological properties of the star-type branched polymers owing to the complexity of the influence on them. It is therefore thought that the success of (10c) is a promising advance in theory. This does not only support the theoretical conception of Ferry, Zimm and others, but also proves that the concept of “non-affine deformation” and the Rouse-Zimm model with slippage have a fairly good capability to expound the rheological properties of polymers.

Keywords:

Rheological properties; Fixed spectrum model; Star-type branched polymer solutions

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