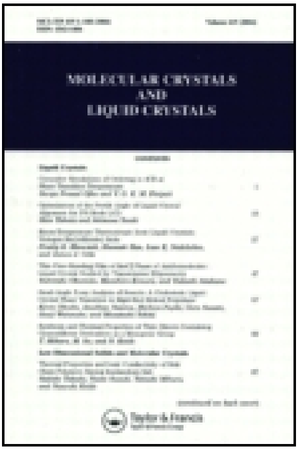

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Order Parameter and Temperature Dependence of the Viscosities of Nematic Semi-Flexible Polymers

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ORDER PARAMETER AND TEMPERATURE DEPENDENCE OF THE VISCOSITIES OF NEMATIC SEMI-FLEXIBLE POLYMERS

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Abstract The order parameter and temperature dependence for a complete set of nematic viscosities is computed in the framework of free volume theory for semi-flexible nematic polymers. The effect of the flexibility of the macromolecular chains as well as the effect of the molar mass is also discussed.

INTRODUCTION

For nematic materials constituted by low molecular weight molecules, the hydrodynamic viscosities present generally a strong temperature dependence[1] as a consequence of two main effects. First, this viscosities depend on the order parameter S(T), itself temperature dependent. Second, the relaxation times associated to viscous dissipation also show a strong temperature dependence. For all known low molecular weight nematics, the thermal behaviour of a complete set of independente viscosities can be written as[2-4]:

$$\gamma_1 = g_1 . S^2 . \tau_1(S,T) \qquad (1)$$

$$\gamma_2 = g_2 . S . \tau_2(S,T) \qquad (2)$$

$$\gamma_3 = \alpha_6 + \alpha_5 = bS.\tau_3(S,T) \tag{3}$$

$$\alpha_4 = (a - \frac{b}{3}S).\tau_3(S,T) \tag{4}$$

$$\alpha_1 = c_1.S^2.\tau_3(S,T) \tag{5}$$

where g_1, g_2, a, b, and c_1 are coefficients (nearly) temperature independent, and τ_1, τ_3, τ_2 are, respectively, the relaxation times for orientation stresses, shear stresses, and for the coupling between orientation and flow. Also for simple nematics, the temperature dependence of the relaxation times τ_i follows a Vogel-like behaviour[2-4]

$$\tau_i \sim \exp(\frac{u_i S^2}{T-T_o}) \tag{6}$$

to a reasonable approximation (u_i and T_o are ≈ constants).

Eqs. (1-5) are essentially based on the possibility to decompose the "viscosity tensor" relating thermodynamic forces and fluxes into the product of two tensors, one describing the dynamics, and the other describing the symmetry of the nematic phase. As long as this hypothesis remains valid for nematic polymers, eqs. (1-5) also do so. On the contrary, eq. (6) is a high-temperature approximation valid for $T >> T_o$, which is the most common situation for simple nematics. For nematic polymers, the nematic range may extend up to the glass transition temperature so eq. (6) should not be valid over the full nematic range. On the other hand, eqs. (4) and (6) predict a constant viscosity above the clearing point T_{NI}, which is not consistent with the experimental data.

The aim of this paper is to present a computation of the temperature dependence of the relaxation times τ_i in the framework of free volume theory, by a suitable generalization of the Cohen-Grest model[5]. As a result, it is shown that the relaxation times $\tau_i(T)$ can be written as

$$\tau_i = \exp\left(\frac{v_i}{V_a} \cdot \frac{2(T_o-T_1)}{T-T_o + \sqrt{(T-T_o)^2 + 4T(T_o-T_1)}}\right) \qquad (7)$$

where (T_o-T_1) depend on S^2 in a way which will be explicitely given below. For $T >> T_o$, eq. (7) reduces to the previously proposed eq. (6). For $T > T_o$ only, eq. (7) can be written as a W.L.F. like expression. Therefore, by use of only <u>ten</u> parameters $g_1, g_2, a, b, c_1, v_1/v_a, v_2/v_a, v_3/v_a, T_o, T_1$, it is possible to describe the thermal behaviour of the <u>five</u> independent viscosities given by eqs. (1-5) <u>plus</u> that of the isotropic viscosity over the full "liquid" range up to the glass transition. Unfortunately, the scarce experimental data reported up to now on the viscosities of nematic polymers does not allow us to contrast it with our predictions. Such comparison has only been done for low molecular weight nematics[6]: the agreement shown is fairly good.

TEMPERATURE DEPENDENCE OF THE RELAXATION TIMES τ_i

Let us consider a nematic melt composed by semi-flexible chains. Each chain is divided into "segments" which may be considered as rigid ones, whose characteristic lenght is of the order of the Kuhn segment length. To each segment we associate a cell volume v, which is the sum of the volume occupied by the segment (v_o) plus the excess volume $v-v_o$; the free volume is defined as $v_f = v-v_c$; the exchange of free volume among contiguous liquid like cells ($v_f > 0$), is assumed to be free.

The distribution function of the segments gives the probability that one particular segment has orientation Ω, and that the cell associated to it has a volume v. We will assume that this function can be factorized as $\phi(\Omega).\rho(v)$. Therefore the free energy per segment is given by the sum of the following terms: a) a local term, $f_1(v)$, which is the sum of minus the work to remove the segment from the interior of the cell plus the work to expand the cell from its average value $\bar{v}$ to its actual volume v[5]; b) another local term, $f_2(\Omega,v)$, corresponding to the Maier-Saupe[7] mean field orientation potential; c) a non-local term giving the free energy corresponding to the steric interaction among different segments[8]; d) the entropy associated to $\rho(v)$; e) the orientational entropy, associated to $\Phi(\Omega)$; f) the communal entropy $(-T\Sigma_c)$. For a semi flexible freely jointed chain, we have (for $v > v_c$):

$$F = \int \frac{d\Omega}{4\pi} \int dv.f(\Omega,v).\rho(v).\Phi(\Omega) - T\Sigma_c \tag{8}$$

where

$$\begin{aligned} f(\Omega,v) &= f_o + \frac{1}{2}\chi(v_c - v_o)^2 + \zeta(S).(v - v_c) - \frac{1}{2}u(v).S.P_2(\theta) \\ &+ kT.J(v). \int \frac{d\Omega'}{4\pi}.\phi(\Omega').|\sin(\Omega,\Omega')| \\ &+ kT.\ell n\ \rho(v) + kT.\ell n\ \phi(\Omega) \end{aligned} \tag{9}$$

The $\zeta(S)$ factor is assumed to be given by

$$\zeta(S) = \zeta_o + \frac{kT_1}{v_a + \bar{v}_f} + \mathcal{O}(S^2) \tag{10}$$

The distribution function $\phi(\Omega)$ is normalized to one, and the normalization of $\rho(v)$ is such that

$$\int_{v_c}^{\infty} dv.\rho(v) = \int_{0}^{\infty} dv_f.\rho(v_f) = p \tag{11}$$

where p is the fraction of liquid-like cells. For $p > p_c$, an infinite liquid cluster is presented and the system behaves like a liquid: $p = p_c$ defines the glass transition.

Minimization of F with the constraints of normalization of $\phi(\Omega)$ and $\rho(v)$ yields a couple of autoconsistent equations for $\phi(\Omega)$ and $\rho(v)$. We will not present the details of calculation here, but only the main results relevant for the computation of the relaxation times τ_i. The average free volume is given by

$$\frac{1}{\bar{v}_f} = \frac{\zeta^*}{kT} - R_1^* \tag{12}$$

where

$$\zeta^* = \frac{\zeta_o}{2} + \frac{uS^2}{2v_c^2} + \frac{kT_1}{v_a+\bar{v}_f} \tag{13}$$

$$R_1^* \simeq R_1^o \left(1 + S^2.(R_1^o - 1).\frac{v''_s}{v'_s} + \ldots\right) \tag{14}$$

$$R_1^o \simeq \frac{1}{v_f + \frac{v_s(v_c)}{v'_s}} \tag{15}$$

Eq. (12) is formally analogous to the equation for $\bar{v}_f$ reported on Ref. 5, but with different coefficients. The interesting point is that ζ^* includes both the effect of the Maier-Saupe mean field potential and the effect of the steric interaction free energy through T_1. By defining

$$T_o = T_1 + \frac{v_a}{k_B}\left(\zeta^* - kT.\ R_1^*\right) \tag{16}$$

and solving eq. (12) for $\bar{v}_f$, we get an expression which is formally the same as that of Cohen-Grest[5]

$$\bar{v}_f = \frac{v_a}{2(T_o - T_1)}\{T-T_o + \sqrt{(T-T_o)^2 + 4T(T_o - T_1)}\} \tag{17}$$

As $\tau_i \sim \exp(v_i/\bar{v}_f)$ where v_i is the minimum characteristic volume for, respectively, relaxation of orientation stresses (i = 1), shear stresses (i = 3) or the coupling orientation-flow (i = 2), eq. (7) is therefore proved.

Now some remarks are in order. (1) For other kinds of semi-flexible chains the orientational entropy term in eq. (9) is different, according to the kind of semiflexible chains considered; explicit expressions are given e.g. on Ref. 8. Nevertheless, eqs. (16), (17) and by consequence eq. (7) remain formally valid. (2) As already remarked on Ref. 5, eq. (17) shows that $\bar{v}_f = 0$ only at 0^oK.(3) A W.L.F. like equation can be derived from eqs. (7, 17):

$$\ell n\ a_T = -c_{1i} + \frac{c_{1i}c_{2i}}{T-T_\infty+c_2} \tag{18}$$

where

$$c_{1i} \simeq \frac{v_i}{v_a}\cdot\frac{T_o-T_1}{T_\infty-T_o}\ ;\ c_{2i} \cong T_\infty - T_o \tag{19}$$

DISCUSSION

It is interesting to remark that eqs. (1-5) agree to those ones derived by Kuzuu and Doi[9] for rigid rod solutions by solving a kinetic equation, with the exception of eq. (5);

according to Ref. 9, α_1 depends only on $P_4(\theta)$. We believe that this discrepancy is due to the approximations done in Ref. 9 because the number of viscosities of a nematic material must not depend on the value of $\langle P_4 \rangle$.

The molar mass dependence of the nematic viscosities cannot be computed without a detailed theory for the coefficients $g_1, g_2, \dots, c_1$. In the infinite semi-rigid chain limit, we may consider the situation analogous to that of the nematic-columnar phase transition. A computation of the enhanancement of the nematic viscosities based on a N.A.C. type hamiltonian[10] or on a Landau-Ginzburg hamiltonian[11] gives essentially the same results: by assuming that $\tau \sim \xi^2$, one gets $\delta\gamma_1 = - \delta\gamma_2 = - \delta\alpha_2 \sim \xi$, $\delta\alpha_4 \sim \xi$, $\delta\alpha_1 \sim - \xi$, and $\delta\gamma_3 \sim \xi$. The Miesowicz viscosities η_a and η_c are also $\sim \xi$ while η_b remains finite. On the other hand, Meyer's analysis[12] yields $(\gamma_1, -\gamma_2, \alpha_1, \gamma_3, \eta_c) \sim L^2$ and $\eta_b, \eta_a \sim L^o$ for semiflexible chains. The difference between the two conjectures is probably due to the fact that, for semi-rigid chains correlations in a direction perpendicular to the director are taken into account; for semi-flexible chains correlations must not extend beyond the persistence length (much smaller than the chain length).

Let us now discuss the effect of molecular flexibility and molar mass on the apparent activation energy given by

$$\frac{E^{(i)}_{app}}{R} \simeq \frac{v_i}{v_a} \cdot \frac{T^2(T_o - T_1)}{(T-T_o)^2} \tag{20}$$

The persistence length ℓ_p is included in eq. (9) through the orientational entropy and the steric interaction term; both are proportional to ℓ_p,[8] so $T_1 \sim \ell_p$. On the other hand, the average free volume will depend on the molecular mass; to a first approximation we take $\overline{v}_f \sim M$. As a consequence, eq. (16) yields a relation between T_o and M of the form

$$T_o \simeq A - \frac{B}{M} \qquad (21)$$

At constant M, A is proportional to ℓ_p. This result agrees with the expectation that the asymptotic temperature T_o will increase as flexibility decreases. The preceding arguments lead to

$$\frac{d\,E_{app}}{dM} \sim \frac{1}{M^2} \qquad (22)$$

thus predicting that the apparent activation energy tends to a constant value at high molecular mass.

The generalization of eq. (7) to include the effect of pressure is straightforward[5]. The result is

$$T_o(P) = T_o + \frac{v_a}{k_B} P \qquad (23)$$

The value of v_a/k_B can be estimated as[4] $(\beta_N-\beta_k)/(\alpha_N-\alpha_k)$ where the subscripts N and K refer respectively to the nematic and crystal phases, α is the thermal expansion coefficient and β is the compressibility.

CONCLUSION

We have proposed here a generalization of the free volume theory in order to the computation of the order parameter and temperature dependence of all the five independent nematic viscosities for a polymer melt of semi-flexible macromolecules. It is shown that with a few number of parameter (ten) the five nematic viscosities plus the isotropic viscosity can be computed over their full temperature range down to the glass transition temperature. These results are compatible to those ones relative to simple nematics[2,3,4,6] and nematic mixtures[13], previously reported.

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