

Differences in the molecular weight and the temperature dependences of self-diffusion and zero shear viscosity in linear polyethylene and hydrogenated polybutadiene

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Within the context of a generalized coupling model we can support the hypothesis that, while the mode of relaxation for self diffusion (D) and shear flow (η) are the same, the entanglement interactions are different. We assume that there are two distinct coupling parameters n_D and n_η for self diffusion and shear flow respectively. The model predicts the molecular weight and temperature dependences to be scaled by the relevant coupling parameters as:

$$\eta \propto [M^2 \exp(E_a/kT)]^{1/(1-n_\eta)} \quad \text{and} \quad D \propto M [M^2 \exp(E_a/kT)]^{-1/(1-n_D)}$$

for melts with Arrhenius temperature dependences. We have found that $n_\eta = 0.43$ and 0.42 for polyethylene (PE) and hydrogenated polybutadiene (HPB) which scale η as $M^{3.5}$ and $M^{3.4}$. Also the apparent flow activation energies E_a^* of $6.35 \text{ kcal mole}^{-1}$ for PE and $7.2 \text{ kcal mol}^{-1}$ for HPB scale to primitive activation energies E_a of 3.6 and $4.2 \text{ kcal mole}^{-1}$ for PE and HPB respectively. On the other hand the M^{-2} dependence of D results in $n_D = 1/3$. Then the reported activation energies for self-diffusion in PE and HPB of 5.49 and $6.2 \text{ kcal mole}^{-1}$ scale to primitive activation energies of 3.7 and $4.1 \text{ kcal mole}^{-1}$, respectively.

(Keywords: self-diffusion; zero shear viscosity; polyethylene; hydrogenated polybutadiene; molecular weight differences)

INTRODUCTION

The shining successes of the reptation model¹⁻³ of the motion of polymer chains has been somewhat tarnished by the fact that, while the molecular weight dependence of the self diffusion coefficient, D , is correctly predicted, the molecular weight dependence of the zero shear viscosity, η_0 , is predicted to follow a $M_w^{3.0}$ law when the experimentally observed dependence is approximately $M_w^{3.4}$. There have now been several attempts to modify the Doi-Edwards tube model to account for the observed differences by providing for tube leakage⁴, tube renewal⁵, constraint release⁶ or other such mechanisms as methods of increasing the 'entanglement drag' contributions⁶ during shearing flow relative to self-diffusion.

In this paper, we will use a generalized coupling model^{7,8} to support the underlying assumption essential to the modified Doi-Edwards models, i.e. that while the fundamental modes of molecular relaxation for self-diffusion and shear flow are the same, the molecular interactions via entanglement coupling are different. We will show that the difference in coupling parameters for self diffusion and zero shear viscosity accounts not only for the observed $D \propto M^{-2}$ and $\eta_0 \propto M^{3.4}$ dependence but

also for the observed differences in apparent activation energies, E_a^* for melts that have Arrhenius temperature dependence.

THE GENERALIZED COUPLING MODEL

General development

The coupling model proposed by Ngai^{7,8} has been found to be applicable to a large range of relaxation phenomena^{7,9}, including polymers¹⁰⁻¹³. The model assumes the existence of a 'primitive' relaxation mode which is coupled, through an unspecified mechanism, with its surroundings. As described below, the coupling parameter, n , which specifies the strength of the coupling also scales the viscoelastic functions with for example, molecular weight.

Two related predictions which result from the model^{7,8} are that a relaxing quantity obeys, for $0 \leq n < 1$,

$$H(t) = H_0 \exp(-t/\tau_e)^{1-n} \quad (1)$$

for sufficiently long times and that the effective relaxation time, τ_e , is related to the 'primitive' relaxation time, τ_0 , by

$$\tau_e = [(1-n)\exp(-n\gamma)\exp(-S_\gamma/R)\omega_c^n \tau_0]^{1/(1-n)} \quad (2)$$

Here n is the parameter specifying the strength of the coupling of the mode to its surroundings, $\gamma = 0.5772$ is the Euler's constant, ω_c is a cut-off frequency and $-S_\gamma$ is an entropy change.

A restatement of the basic physics of the Ngai model is that in complex systems the primitive relaxation mode is not only modified from an exponential to a fractional exponential, but also the primitive τ_0 is no longer directly observed, but is shifted to a longer time, τ_e , according to equation (2).

In the case of polymer melts (and concentrated solutions) equations (1) and (2) are found to be relevant in the entanglement regime. Through entanglements, each polymer chain couples to its surroundings. Here we assume that the polymer chain is a Rouse chain¹⁴, then the Rouse modes of relaxation of each chain, indexed by i , have primitive relaxation times τ_{0i} given by the familiar expression¹⁵

$$\tau_{0i} = \frac{M^2}{i^2} \left(\frac{a^2 \zeta_0(T)}{6\pi^2 M_0^2 kT} \right) \quad i = 1, 2, 3 \dots \quad (3)$$

The relaxation mechanism given by equation (3) now works through the entanglement coupling by shifting each of the primitive τ_{0i} to its effective τ_{ei} . Since the zero shear viscosity and the self diffusion coefficients are determined primarily by the longest Rouse relaxation times, in the developments which follow we will consider only τ_{01} . Substitution of equation (3) into equation (2) shows immediately that the Ngai model demands that the molecular weight dependence of the relaxation mechanism is scaled by n as

$$\tau_{e1} \propto M^{2/(1-n)} \quad (4)$$

Furthermore, if the local friction coefficient, ζ_0 , has an Arrhenius temperature dependence

$$\zeta_0 \propto \exp(E_a/RT) \quad (5)$$

Then the primitive relaxation energy, E_a , is also scaled by the same n as

$$\tau_{e1} \propto \exp(E_a/[(1-n)RT]) \quad (6)$$

and the apparent activation energy observed in the laboratory is given by

$$E_a^* = E_a/(1-n)$$

Zero shear viscosity

The coupling model^{10-12,16} predicts that the contribution of the terminal Rouse relaxation time, τ_{01} , to the relaxation modulus is expressed as:

$$G(t) = G_N^0 \exp - (t/\tau_{e1})^{(1-n)} \quad (7)$$

where τ_{e1} is determined from equations (2) and (3) and G_N^0 is the plateau modulus. Then the zero shear viscosity is given as

$$\eta_0 = \int_{-\infty}^{\infty} tG(t) d \ln t = G_N^0 \tau_{e1} \Gamma[1/(1-n)]/(1-n) \quad (8)$$

where Γ denotes the gamma function. Then combining

equations (8), (6), (5), (3) and (2) we readily see that in the regime where the viscosity follows an Arrhenius temperature dependence

$$\eta_0 \propto M^{2/(1-n)} \exp(E_a/[(1-n)RT]) \quad (9)$$

and we introduce the notation that n_η is the coupling parameter in shearing flows.

Self-diffusion coefficient

For self diffusion the basic mechanism of chain motion is still the Rouse terminal mode, τ_{01} . Then during a time τ_{e1} given as

$$\tau_{e1} = \left[(1-n_D) \omega_c^{n_D} \exp(-S_\gamma/R) \left(\frac{M^2 a^2 \zeta_0(T)}{6\pi^2 M_0^2 kT} \right) \right]^{1/(1-n_D)} \quad (10)$$

the centre of mass of the chain will have moved a distance approximately equal to the radius of gyration of the chain, R_g . (Here we introduce n_D as the coupling parameter relevant to self-diffusion). Then following an argument similar to that of DeGennes³ and Tirrell¹⁷, the self diffusion coefficient, D_S is

$$D_S \propto \frac{R_g^2}{\tau_{e1}} \quad (11)$$

and combining with equation (10)

$$D_S \propto \frac{M}{[M^2 \zeta_0(T)]^{1/(1-n_D)}} \quad (12)$$

and when the temperature dependence of $\zeta_0(T)$ follows that of the Arrhenius equation we can write

$$D_S \propto M^{1-2/(1-n_D)} \exp\left(-\frac{E_a}{(1-n_D)kT} \right) \quad (13)$$

The coupling model applied to hydrogenated polybutadiene and polyethylene viscosity and diffusion data

In comparing the coupling parameters n_η and n_D , there must be a point of commonality or the mere observation that n_η and n_D are different is not particularly informative. However, in the preceding development of equations (9) and (13) we have an important underlying assumption which is that the primitive relaxation mechanism of the molecule is the same for both shear flow and self diffusion, i.e., the terminal Rouse mode. Therefore, there exists not only a primitive time, τ_{01} , but also a primitive activation energy, E_a . If the hypothesis that the mechanism of motion in self diffusion and in shear flow is the same, but the coupling to the environment via entanglements is different, then E_a should be the same in self diffusion and in shear. In what follows we show that this is indeed the case.

The coupling parameter for shear flow, n_η , has been determined for polyethylene (PE) and hydrogenated polybutadiene (HPB) by Ngai and Plazek¹² from analyses of the terminal relaxations. For polyethylene it is found that $n_\eta = 0.43$ and for the hydrogenated polybutadiene $n_\eta = 0.42$. These values scale the molecular weight dependence of the zero shear viscosity as $M^{3.5}$ and $M^{3.4}$ respectively (see equation (9)), which is in good agreement with experimentally reported values. Both PE and HPB exhibit Arrhenius temperature dependences of viscosity

Table 1 Summary of results for the shear behaviour of polyethylene and hydrogenated polybutadiene

	Polyethylene	Hydrogenated Polybutadiene
Coupling parameter	0.43	0.42
Viscosity–Molecular weight relation		
Observed	$\eta_0 \propto M_w^{3.5}$	$\eta_0 \propto M_w^{3.6}$
Predicted	$\eta_0 \propto M_w^{3.5}$	$\eta_0 \propto M_w^{3.4}$
Apparent activation energy, E_a^* , kcal mole ⁻¹	6.35	7.2
Primitive activation energy, E_a , kcal mole ⁻¹	3.6	4.2

Table 2 Summary of results for the self-diffusion behaviour of polyethylene and hydrogenated polybutadiene

	Polyethylene	Hydrogenated Polybutadiene
Coupling parameter	1/3	1/3
Self diffusions coefficient—molecular weight relation		
Observed and predicted	$D_s \propto M^{-2}$	$D_s \propto M^{-2}$
Apparent activation energy, E_a^* , kcal mole ⁻¹	5.47	6.19
Primitive activation energy, E_a , kcal mole ⁻¹	3.7	4.1

($T \gg T_g$). The reported apparent flow activation energies, E_a^* are 6.35 and 7.2 kcal mole⁻¹ for PE¹⁸ and HPB¹⁹, respectively. From equation (9) the primitive activation energies, E_a are determined to be 3.6 and 4.2 kcal mole⁻¹ for PE and HPB, respectively. These results are summarized in Table 1.

For the self-diffusion behaviour, the observed molecular weight dependence¹⁷ is $D \propto M^{-2}$ for both PE^{20–22} and HPB^{23,24}. Then from equation (13) the coupling parameter is $n_D = 1/3$ for both materials. For both PE and HPB the apparent activation energy E_a^* for self diffusion is lower than that observed in shear flow. For PE: $E_a^* = 5.47$ kcal mole⁻¹^{17,25} and for HPB: $E_a^* = 6.2$ kcal mole⁻¹²⁴ in diffusion. From $n_D = 1/3$ and equation (13) we find immediately that the primitive activation energies, E_a , for self diffusion are 3.7 kcal mole⁻¹ for PE and 4.1 kcal mole⁻¹ for HPB. These values of E_a are the same as found for the viscosity and are summarized in Table 2. This similarity of the primitive activation energies for shear flow and diffusion supports the hypothesis that while the modes of molecular relaxation in shear flow and self-diffusion are the same, the molecular interactions (or coupling) via entanglements are different.

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