



Relaxation time of polypropylene glycol and polypropylene glycol dimethylether-like polymers in terms of fluid-phase temperature and pressure dependent hole fraction

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ABSTRACT

We present a model explaining relaxation time of PPG (polypropylene glycol) and PPGM (polypropylene glycol dimethylether) as representative compounds, with different molecular weights, PPG2 ($M_w = 2 \text{ kg mol}^{-1}$), PPG3 ($M_w = 3 \text{ kg mol}^{-1}$), PPGM1 ($M_w = 1 \text{ kg mol}^{-1}$), and PPGM2 ($M_w = 2 \text{ kg mol}^{-1}$), as a function of hole fraction at various fluid phase temperatures and high pressures. Proposed model based on the structural relaxation behavior of chain molecules given by “thermo-occupancy” function in terms of temperature and temperature–pressure dependent hole fraction is discussed and compared with the free volume model. The former is the most universal behavior than the latter in terms of temperature and pressure. We discuss activation energy parameter and transmission coefficient for the species in terms of chain length and end groups such as dimethylether. Scaling relaxation time parameter in the proposed model has similar trend with relaxation time parameter of Adam–Gibbs theory.

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1. Introduction

The relaxation behavior of polymers has been extensively studied in terms of temperature and pressure [1–7]. Similarly, the temperature dependency of dielectric relaxation of some polymers has been expressed with three parameters using Vogel–Fulcher (VF) form, viz. $\tau = \tau_0 \exp[B/(T - T_0)]$ [8,9]. The pressure dependence of τ as the phenomenological extension of the VF equation has been analyzed by a number of studies [10,11,5].

Dynamic lattice liquid (DLL) [12] can describe the molecular rearrangements [13] which are related to temperature and free volume [13]. Wand et al. [14] enhanced the Simha–Somcynsky equation of state (SS EOS) in order to represent the PVT behavior of polymers and gases at low pressure. Induced modification of the free volume contribution of the SS-EOS along with proposed universal constants have been founded to be guides for the actual work. On the other hand, Dlubek et al. [15] has applied the free volume theory of Cohen and Turnbull [16,17] to the structural relaxation processes in some liquid polymers, viz. $\tau = C^{-1} \exp(\gamma V_f^*/V_f)$ where V_f is the mean specific free volume and γV_f^* is the minimum specific free volume required for the occurrence of a structural relaxation process.

Extensive experimental efforts for explaining the relaxation phenomena have been studied thermodynamically in terms of temperature and pressure [10,14,18,19]. Alternatively, we have developed a theoretical model for interpreting the

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relaxation time of the polymers as a transport phenomenon relating the Eyring Significant Structure (ESS) transport theory and the Simha–Somcynsky (SS) hole theory [20,21]. In our model, we employed the poly(propylene glycol) (PPG) and poly(propylene glycol dimethylether) (PPGM) compounds using the temperature and pressure dependent specific volume and dielectric relaxation measurements given by Prevosto et al. [22].

2. Theories

2.1. The SS-EOS theory

Simha–Somcynsky (SS) developed an equation of state (EOS) based on the lattice–hole model [20] yielding the temperature and pressure dependent occupied site fraction, $y(P, T)$. The occupied site fraction, $y(P, T)$, and the complementary hole fraction, $h(P, T)$, are given by the following equation:

$$y = 1 - h = \frac{sN}{sN + N_h} \quad (1)$$

where s is the number of segments in a molecule, and N and N_h are the number of molecules and holes, respectively. The SS theory is formulated in terms of scaled volume, \tilde{V} , scaled temperature, \tilde{T} , and scaled pressure, \tilde{P} , viz.:

$$\tilde{V} = V/V^*; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \quad (2)$$

where the scaling parameters are defined as follows: V^* , T^* (by $q_z \varepsilon^* / ck$), and P^* are defined correspondingly as molar volume sv^* of the molecule, a balance between attraction and thermal energy contributed by the external degrees of freedom, and the ratio between molecular attraction energy $q_z \varepsilon^*$ and volume sv^* . The number of interchain nearest neighbors in a lattice of the coordination number, z , is given by $q_z = s(z - 2) + 2$. The SS-EOS equation, derived configurationally from the Helmholtz energy, is given by

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{1}{1-\zeta} + \frac{2y}{\tilde{T}} Q(1.011Q - 1.2045) \quad (3)$$

where $Q = (y\tilde{V})^{-2}$ and $\zeta = 2^{-1/6}y(y\tilde{V})^{-1/3}$. The minimization of the Helmholtz energy of an ensemble by $\partial F/\partial y|_{\tilde{V}, \tilde{T}, \tilde{P}} = 0$ gives the occupied site fraction, y :

$$\frac{s}{3c} \left(\frac{s-1}{s} + \frac{\ln(1-y)}{y} \right) = \frac{\zeta - \frac{1}{3}}{1-\zeta} + \frac{y}{6\tilde{T}} Q(2.409 - 3.303Q). \quad (4)$$

Here $3c$ that appears explicitly in the equilibrium condition is the molecule total freedom degree. Utilizing the ideal chain flexibility employing $3c = s + 3$ and using Eqs. (3) and (4), we can compute the hole fraction, $h = 1 - y$ as a measure of the free volume [23,24] and determine the scaling parameters, P^* , V^* , T^* and the structural parameter $3c/s$ by superimposing experimental P – V – T data on the theoretical \tilde{P} , \tilde{V} , \tilde{T} surface.

2.2. The relaxation time theory

Debye–Stokes–Einstein equation relates the relaxation time τ with viscosity, η [11]

$$\tau = \frac{4\pi\eta r^3}{3kT} \quad (5)$$

where k is the Boltzmann constant and r is the radius of a molecule. The Eyring shear viscosity can be expressed in terms of jumping frequency, k' [21,25,26] as

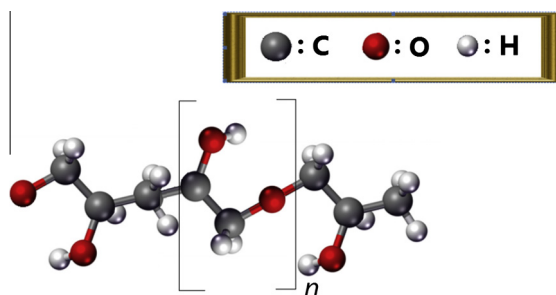


Fig. 1a. Molecular structure of the studied polymer.

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