Phenomenological Model for Linear Viscoelasticity of Monodisperse Polymer

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There have been a number of researches on the calculation of molecular weight distribution (MWD) from linear viscoelastic data[1,3]. Most algorithms adopted quadratic mixing rule which was derived from double reptation theory[4,5]. Although recent molecular theories provide simulation results which predict the linear viscoelasticity of polydisperse polymer for a given MWD, calculation of MWD is the inverse problem. Hence, the success of the inverse calculation needs accurate models for the linear viscoelasticity of monodisperse polymer and effective numerical algorithm such as regularization method. Accurate molecular theories cannot be used for this goal because use of these models implies that we have to solve nonlinear partial differential equation with nonlinear fitting. Hence, we need analytical model for monodisperse polymers. To the authors' knowledge, analytical equations based on molecular theories are not as accurate as phenomenological model. Well-known phenomenological model is BSW spectrum[6]. However, this model does not provide analytical equation for dynamic and relaxation moduli, which makes model identification unnecessarily difficult. In this talk, we suggest a simple phenomenological model for loss modulus which allows us to identify its parameters easily. We will convert the loss modulus to relaxation and storage moduli by use of the continuous spectrum which can be obtained by the Fuoss-Kirkwood relation[7,8]. We expect that the simple model will be used effectively for the calculation of MWD.

Marin and Graessley[9] reported that the following phenomenological model is capable of fitting linear viscoelasticity of monodisperse polymer:

$$s\tilde{J}(s) = J_g + \frac{1}{\eta_o s} + \sum_{k=1}^{2} \frac{J_k}{1+(\tau_k s)^{\alpha_k}} \tag{1}$$

where $\tilde{J}(s)$ is the Laplace transform of creep compliance. It is usual that J_g is so small that it can be neglected. The two parameters η_o and τ_1 have strong depen-

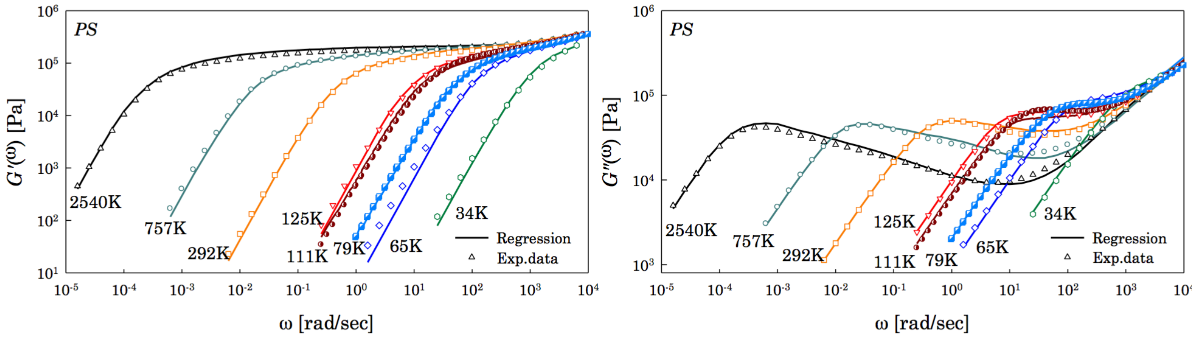

Figure 1. Validity of modified Cole-Cole model.

Table 1. Specific information of monodisperse polystyrene.

samples	M_w [kg/mol]	PDI
*PS6	2540	1.13
PS5	757	1.09
PS4	292	1.09
PS3	125	1.05
PS2	65	1.02
PS1	34	1.05
**mPS179K	179	1.09
mPS111K	111	1.07
mPS79K	79	1.04

Table 2. The list of the values of the parameters.

	$k = 1$	$k = 2$
J_k^∞ [Pa^{-1}]	2.1998×10^{-5}	5.2988×10^{-6}
α_k	0.3481	0.5786
τ_2 [s]	2.4691×10^{-4}	
ν	3.4634	
η_0^e [Pa·s]	40.5956	
r	4.1306	
M_e [kg/mol]	12.9412	

* Schausberger *et al.*, Rheol. Acta (1985)[10]

** Jeon, thesis (2010)[11]

dence on molecular weight while α_1, α_2 and τ_2 should be independent of molecular weight. For the polymers with wide range of molecular weight, J_1 and J_2 seem to have weak dependence of molecular weight. However, they did not investigate systematically molecular weight dependence of the parameters because conventional regression with respect to Eq. (1) usually results in non-systematic dependence of parameters on molecular weight. Hence, we modified Eq. (1) relying on molecular theories and observed molecular weight dependence of zero-shear viscosity and steady state compliance. We modeled

$$\eta_o(M) = \eta_o^e\left(\frac{M}{2M_e}\right)\left[1+\left(\frac{M}{2M_e}\right)^{\nu-1}\right];$$

$$J_k(M) = J_k^\infty \frac{M/(rM_e)}{1+M/(rM_e)}; \qquad (2)$$

$$\tau_1(M) = \tau_2\left(\frac{M}{M_e}\right)^{\nu}$$

where M_e is the entanglement molecular weight. Since this model has 9 parameters to be determined by regression and some of parameters vary in logarithmic scale, conventional regression such as Levenberg-Marquardt algorithm is apt to fail robust results. Hence, we adopted Monte Carlo algorithm.

Figure 1 shows the validity of the model. The experimental data are those of monodisperse polystyrenes measured by two research groups. Table 1 is the specification of materials and Table 2 is the list of the values of the parameters.

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